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AMPHIPHILIC COMPOUNDS IN ENHANCED OIL RECOVERY

Biennial Report for the Period
October 1, 1980—September 30, 1982

By
P. C. Ho
J. S. Johnson, Jr.

September 1984
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AMPHIPHILIC COMPOUNDS IN ENHANCED OIL RECOVERY

Biennial Report
October 1, 1980 — September 30, 1982

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ABSTRACT

Research in the final two years of the program "Amphiphilic Compounds in Enhanced Oil Recovery" (formerly "Ion Exchange Characteristics of Enhanced Oil Recovery") are reported here. The Summary following outlines the research during this period. Section 5, Program History, defines the context and describes the major themes and conclusions of the work since its initiation April, 1977.

In the early years, distributions of cations between minerals and solutions covering the salinity range of formation waters were measured. Clays and hydrous oxides were emphasized because of their high ion-exchange capacity. The objectives were to determine the equilibria between sodium and hardness ions (particularly Ca(II)) because of their importance in modeling the solids as a source of troublesome multivalent ions. A further purpose on a collateral program was to evaluate the conditions under which the adsorption of potential tracers is low enough so that retardation of their movement relative to ground water is not great enough to impair their usefulness. Ion exchange equations were adequate to represent the bulk of the observations, although with hydrous oxides, it is necessary to take into account variations in capacity with pH and ionic strength.

From the beginning to the present, the properties of aqueous-hydrocarbon systems containing amphiphiles has been the major interest, in common with most laboratories carrying out research supporting micellar flooding. The particular area we have emphasized is comparison of behavior when the organic-electrolyte amphiphile (protosurfactant) is of an equivalent weight lower than that necessary for formation of large micelles with that when it is in the surfactant range. In general, we have found surprisingly little qualitative difference between the two classes. Protosurfactants solubilize substantial amounts of hydrocarbons in aqueous medias, and cause the same types of phase behavior in compositions modeling micellar floods as surfactants.

More recently, an increasing fraction of our effort has been in applying small-angle neutron scattering (SANS) to micellar systems and in further development of the techniques for doing so. As a complement to other methods, SANS appears to have the potential to resolve many long-standing questions concerning the structure of micelles and microemulsions.

SUMMARY

This report covers the final biennium of "Amphiphilic Compounds in Enhanced Oil Recovery," formerly known as "Ion-Exchange Characteristics of Enhanced Oil Recovery Systems." Research results are reported in four categories.

PHASE STUDIES. A major theme of this program has been the study of amphiphilic properties of low-equivalent-weight organic salts (protosurfactants) and comparison of them with surfactants. Reported here are extensions of earlier observations of hydrotropic properties to other compounds. Another item presents concentration scans of phase behavior, analogous to those common in evaluation of oil-recovery surfactant systems. A third report presents analyses of phases coexisting in such scans.

FREE ENERGIES. Isopiestic measurements of water activities of solutions containing several sodium alkylbenzene sulfonates having from one to six alkyl groups are reported. One three-component water-NaCl-protosurfactant system is included. The results are consistent with formation of small complexes comprised of three or four protosurfactant anions, but a definitive choice of species cannot be made.

SMALL-ANGLE NEUTRON SCATTERING. Application of this technique to micellar systems was begun under "Chemicals for Enhanced Oil Recovery," and an increasing fraction of effort on this program has been devoted to this approach. Three topics are discussed. One is the question, still controversial, whether the large increases in intensity of radiation scattered by solutions of non-ionic surfactants as the phase separation temperature is approached arise primarily from particle growth or from approach to a critical point. Our results support approach to criticality of a dispersion of spherical particles whose size is only slightly, if at all, dependent on temperature. Another is a similar question with respect to oil-in-water microemulsions of an ionic surfactant. Our conclusion is the same, although because of the greater complexity of the system, we were not able at the time to infer as comprehensive an interpretation as for the non-ionic surfactant. The third applies the mean spherical approximation to scattering by a branched-tail ionic surfactant as a function of D_2O/H_2O ratio of the solvent. By this approach, we were able to interpret the peaks in scattering intensity as a function of angle arising from interaction between the charged micelles.

ADSORPTION OF INORGANIC IONS ON HYDROUS OXIDES. Measurements of cation and anion uptake by hydrous Al(III) oxide as a function of solution pH and electrolyte concentration, and of equilibria of trace ions between solution and solid, had been carried out under a collateral discontinued program "Multiple Tracers for Enhanced Oil Recovery" and under another program motivated by nuclear waste isolation "Systematic Study of Metal Ion Sorption on Select Geologic Media." In this report, some further discussion of the interpretation of these results by the ion exchange approach is presented.

INTRODUCTION

This document covers the last two years of a program known originally as "Ion-exchange Aspects of Enhanced Oil Recovery," now renamed "Amphiphilic Compounds in Enhanced Oil Recovery," to reflect its changing nature. Originally the topics included equilibria of Ca(II) and Mg(II) with Na(I) between solution phases and minerals common to oil-bearing formations. Also from the start, the chemistry of aqueous hydrocarbon systems containing amphiphilic compounds has been a strong interest. The term "ion-exchange" was perceived by us as also applicable to studies of these systems, by analogy with the similar media used in solvent extraction, frequently referred to as "liquid ion exchange." With our trend toward compositions more like those under investigation by others interested in micellar flooding and our extension to investigation of structures of surfactant solutions by small-angle neutron scattering, the new name seemed to convey better the recent emphasis of our work.

Our approach has perhaps been more fundamental than that of most of the surfactant research carried out by others motivated by enhanced oil recovery. We began with simpler systems, comprised of well-defined components, and worked toward overlap with the multicomponent systems of practical interest. We have also given much attention to low-equivalent-weight organic salts, which we refer to as proto-surfactants, in order to gain insight into the relative importance of the chemical nature of the surfactant component as opposed to the formation of micellar aggregates in the properties important in oil recovery. In this report, we describe phase behavior of protosurfactant-containing systems that is closely analogous to that of pure or of practical oil-recovery surfactant systems.

The structures of the microemulsion phases common in micellar-flood compositions are not well established in detail, and, particularly with respect to middle phases, there are differences of opinion with respect to gross aspects. Small-angle neutron scattering (SANS) has great promise of resolving some of these questions. The momentum-transfer region accessible is in the right range for the dimensions in these systems, from about ten to several hundred angstroms. The high scattering power of hydrogen isotopes, and the difference in nature of scattering by protons and by deuterons, give SANS strong advantages for this class of systems over small-angle x-ray scattering. We had anticipated for a long time the advent of the 20-meter sample-to-detector system being constructed by the National Center for Small-Angle Scattering Research at the Oak Ridge High Flux Isotope Reactor. Since its activation about three years ago, we have been applying the techniques on surfactant systems to the maximum extent feasible with our resources.

1. PHASE BEHAVIOR OF AQUEOUS-HYDROCARBON-PROTOSURFACTANT SYSTEMS

The motivation for our studies of low-equivalent-weight organic salts (protosurfactants) was outlined in the Introduction--to identify the extent which properties of micellar-flood systems depend on the properties of surfactants which result in the formation of micelles, as contrasted to other aspects of their amphiphilic nature. Earlier, solubilizations of hydrocarbons in aqueous media, with and without added alcohol, were reported. Miscibility behavior over the complete composition range of a four-component system, lacking only inorganic salt of the usual classes in flood systems, was determined. The effect of alkyl substitution from toluene sulfonate up into alkyl benzene sulfonates in the surfactant range was investigated. Compounds with carboxylate ionic groups were compared with sulfonates. Correlations of behavior with the molecular weight and chemical type of hydrocarbons were sought.

Without excessive oversimplification, we can summarize our results as indicating that there are no gross qualitative differences in patterns of behavior between surfactants and protosurfactants, certainly no sharp break in properties as alkyl content increased. A paper in press in the Journal of Colloid and Interface Science summarizes further evidence similar to that presented earlier. The analogies are extended in two other papers reprinted in this section, in which all five components are present, and phase behavior is determined as a function of variation of the composition of one of the components, organic salt, alcohol, or inorganic salt. Typical progressions from two- to three-phase to two phases are seen as a function of salt or alcohol content. The principal differences are that interfacial tensions, at least of the systems studied, although low, are not generally ultralow (millidyne/cm range), and the organic salt is found to a greater extent in more than one phase than in surfactant systems, in which it is usually highly concentrated in the microemulsion phase.

J. of Colloid & Interface Science (in press)

1.1 A COMPARISON OF AMPHIPHILIC PROPERTIES OF LOW-EQUIVALENT-WEIGHT ORGANIC SALT WITH SURFACTANT

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ABSTRACT

THE AMPHIPHILIC PROPERTIES OF LOW-EQUIVALENT-WEIGHT ORGANIC SALTS OF SODIUM BENZENE SULFONATES, CARBOXYLATES, AND SALICYLATES ARE UNDER STUDY. THESE ORGANIC SALTS, WHICH WE REFER TO AS "PROTOSURFACTANTS" RESEMBLE PETROLEUM SURFACTANTS WHICH POSSESS A POLAR HEAD GROUP AND HYDROPHOBIC NONPOLAR TAILS. THE DIFFERENCE BETWEEN PROTOSURFACTANTS AND SURFACTANTS IS THAT THE ALKYL CHAINS OF THE FORMER ARE SHORTER THAN USUALLY IS THOUGHT NECESSARY FOR FORMATION OF MICELLES IN AQUEOUS SOLUTIONS. THE AMPHIPHILIC PROPERTIES OF THESE PROTOSURFACTANTS RESEMBLE THOSE OF SURFACTANTS IN THAT THEY TEND TO INCREASE THE SOLUBILTY OF MATERIALS NORMALLY SLIGHTLY SOLUBLE IN WATER. IN MULTI-COMPONENT SYSTEMS CONTAINING PROTOSURFACTANTS ALONG WITH HYDROCARBONS, WATER, INORGANIC SALTS AND COSURFACTANTS, PHASE BEHAVIOR AND THERMODYNAMIC PROPERTIES ARE SIMILAR TO THOSE OF SURFACTANT SYSTEMS.

INTRODUCTION

WE REFER TO LOW EQUIVALENT-WEIGHT ORGANIC SALTS OF BENZENESULFONATES, -CARBOXYLATES, AND -SALICYLATES, ALSO KNOWN AS ORGANIC HYDROTROPIC AGENTS,[1] AS PROTOSURFACTANTS. THEIR AQUEOUS SOLUTIONS TEND TO INCREASE THE SOLUBILITY OF MATERIALS NORMALLY SLIGHTLY SOLUBLE IN WATER SUCH AS HYDROCARBONS IN WATER.

IN THE PAST FEW YEARS WE HAVE PUBLISHED SEVERAL PAPERS ON THE EFFECT OF ORGANIC HYDROTROPIC SALTS ON SOLUBILITY OF HYDROCARBON IN EITHER WATER, OR AQUEOUS/ALCOHOL SYSTEMS[2-7], AND ON PHASE BEHAVIORS OF THESE COMPOUNDS IN MULTI-COMPONENT SYSTEMS[8-10]. THESE ORGANIC SALTS OR PROTOSURFACTANTS ARE CHEMICALLY SIMILAR TO COMPONENTS OF ANIONIC SURFACTANTS USED IN ENHANCED OIL RECOVERY, WHICH POSSESSES A POLAR HEAD GROUP (EITHER $-SO_3Na$ OR $-COONa$) AND HYDROPROBIC TAILS, EXCEPT THAT THE NONPOLAR TAILS OF PROTOSURFACTANT ARE MUCH SHORTER THAN USUALLY IS THOUGHT NECESSARY FOR FORMATION OF MICELLES. WE BELIEVE THAT THE MISCIBILITIES AND PHASE BEHAVIOR OF SYSTEMS CONTAINING THESE COMPOUNDS ARE HELPFUL IN UNDERSTANDING THE MUCH MORE COMPLICATED HYDROCARBON/WATER/INORGANIC SALT/SURFACTANT/COSURFACTANT SYSTEMS OF MICELLAR FLOODING.

IN THIS PAPER WE PRESENT EXTENSIONS OF EARLIER RESULTS AND COMPARE PHASE BEHAVIOR OF PROTOSURFACTANTS TO SURFACTANTS IN CORRESPONDING SYSTEMS.

EXPERIMENTAL

MATERIALS. THE SOURCES OF HYDROCARBONS, ALCOHOL AND SOME OF THE PROTOSURFACTANTS USED IN THIS PAPER CAN BE FOUND IN REFERENCES 2 THROUGH 10. CYCLOHEXANECARBOXYLIC ACID (FLUKA AG) WAS CONVERTED TO THE SODIUM SALT BY TITRATION TO pH 7

with 10% NaOH. After the titration the solutions were filtered and washed several times with $CHCl_3$ to remove excess acid and the salt crystallized after volume reduction. Then the crude product was recrystallized two times from water. 1,3,5-Triisopropylbenzene (Fluka) was sulfonated with 15% oleum and the product 1,3,5-triisopropyl benzenesulfonic acid was converted to the sodium salt with 10% NaOH. Microanalysis of this salt was done by Galbraith Laboratories, Inc., Knoxville, Tennessee, and the results are: Calcd: C 58.82, H 7.52, S 10.46. Found C 58.63, H 7.84, S 10.27. Sodium dodecylsulfate (SDS; Fluka) and sodium dodecylbenzenesulfonate (hard type; SDBS; Tokyo Kasei Kogyo Co.) were used as received without further purification.

Methods. The solubility of hydrocarbon (toluene) in aqueous solutions was determined by gas chromatographic methods similar to those used previously.[2,3,7] The aqueous protosurfactant solutions were prepared with distilled water and concentration is expressed in terms of molality, moles/kg H_2O. The solubility was expressed as moles toluene/kg H_2O. Duplicates agreed to within about 5%, as expected from the innate precision of the method. The solubilities of protosurfactants in water and aqueous NaCl solutions were measured by using a Cary Model 11 UV-VIS or a Perkin Elmer Model 559 UV-VIS spectrophotometer in the wavelength range 250-270 nm. For surfactants, the solubility in water and NaCl solutions was determined by Epton two-phase titration[11]. The solubility was expressed as moles/kg H_2O.

The phase boundary curves with protosurfactants were obtained by the procedures of Ref. 7. In cases involving surfactants, because of their low solubilities in water, the phase boundary curves were obtained as follows: Weighed amounts of surfactant, water and either 1-butanol or toluene were placed in 8-ml test tubes with screw-on, teflon-lined caps, then titrated with either toluene or 1-butanol to cloud or clear end points.

The phase volume diagrams in the five-component systems were determined as in Ref. 9. All quantities were determined by weighing, and all compositions are presented as weight percentage. Sodium chloride is expressed as weight percent in water (g NaCl/(g NaCl + g H_2O)) and all the other components are weight percent of the total systems. The ratio of water to hydrocarbon (WOR), which is the ratio of weight of water to weight of hydrocarbon is one.

RESULTS

Comparison of hydrotropic effect of sodium cyclohexane carboxylate with sodium salts of aromatic carboxylate and sulfonate. We previously reported that in three-component systems of hydrocarbon (mostly toluene), water, and sodium alkylbenzenesulfonates[2] or -benzoates[3] or -salicylates[8], the solubility of the hydrocarbon in the aqueous phase increases sharply as the number of alkyl carbons (S_{AC}) substituted on the benzene ring of the organic hydrotropic salts (protosurfactants) increases and as the aqueous concentration of the organic salt increases.

Figure 1 compares the solubility of toluene as a function of the molality of aqueous salt solutions for a sodium salt of sulfonate, salicylate, and cyclohexane carboxylate with a corresponding number (six) of alkyl carbons. The solubility of toluene in aqueous sodium cyclohexanecarboxylate falls between that in diisopropylbenzenesulfonate

SOLUTION AND DIISOPROPYLSALICYLATE SOLUTION. THE RESULTS ARE CONSISTENT WITH THE EFFECT OF ORGANIC HYDROTROPIC SALT ON THE SOLUBILITY OF TOLUENE IN WATER - SALICYLATE IS THE HIGHEST, SULFONATE IS THE LEAST AND CARBOXYLATE IS IN BETWEEN[8]. THESE RESULTS PROVIDE FURTHER EVIDENCE THAT NOT ONLY THE ALKYL GROUP AFFECTS THE SOLUBILITY BUT THAT OTHER SUBSTITUENTS ARE IMPORTANT: THE CHARGED GROUP $-SO_3Na$ AND -COONa TO A MODEST EXTENT, BUT THE UNIONIZED ORTHOHYDROXYL GROUP TO A SURPRISINGLY LARGE EXTENT.

COMPARISON OF PHASE BOUNDARY CURVES OF SYSTEMS CONTAINING PROTOSURFACTANT AND SURFACTANT, TOLUENE, WATER AND 1-BUTANOL. THE MISCIBILITY RELATIONSHIPS IN FOUR-COMPONENT SYSTEMS OF TOLUENE/1-BUTANOL/AQUEOUS SOLUTIONS CONTAINING ONE MOLE OF SODIUM 2,4,6-TRIISOPROPYLBENZENESULFONATE AND A SULFONATE DEFINITELY IN THE SURFACTANT CLASS, SODIUM P-(1-HEPTYLNONYL)BENZENE SULFONATE, COMMONLY REFERRED TO AS TEXAS 1, SODIUM (P-ETHYL-(1-PENTYLHEPTYL)-BENZENESULFONATE, COMMONLY KNOWN AS TEXAS 2, HAVE BEEN STUDIED. AS BEFORE FOR CONVENIENCE, THESE SYSTEMS HAVE BEEN REPRESENTED IN TRIANGULAR COMPOSITIONAL DIAGRAMS WITH THE APICES HYDROCARBON, ALCOHOL, AND A FIXED RATIO OF ORGANIC SALT TO WATER.

FIGURE 2 PRESENTS THE CURVE SEPARATING SINGLE- AND MULTI-PHASE REGIONS OF THESE SYSTEMS; THE PHASE BOUNDARY CURVE REPORTED FOR THE SAME SYSTEM WITH TOLUENE AND SODIUM 2,5-DIISOPROPYLBENZENESULFONATE IN REFERENCE 7 IS PLOTTED FOR COMPARISON.

THE PATTERN OF ASYMMETRY EXHIBITED BY THE PHASE BOUNDARY CURVES FOR THE SYSTEM CONTAINING 1.0 MOLAL SODIUM 2,5-DIISOPROPYL-BENZENESULFONATE (S_{AC} = 6) IS ALSO SHOWN BY THE SYSTEM CONTAINING 2,4,6-TRIISOPROPYLBENZENESULFONATE (S_{AC} = 9). THE PATTERN IS ALSO FOUND IN SOME RESPECTS BY THE SYSTEM CONTAINING TEXAS 1 (S_{AC} = 16). THE MISCIBILITY BOUNDARY IS ASYMMETRIC, BUT THE PEAK IS MUCH BROADER IN EXTENSION TOWARD THE ALCOHOL-AQUEOUS SOLUTION SIDE OF THE DIAGRAM. THE PHASE BOUNDARIES OF SYSTEMS CONTAINING TEXAS 2 (S_{AC} = 14) BEAR SOME RESEMBLANCE TO THE PATTERN. IN CONTRAST TO THE LOWER-EQUIVALENT-WEIGHT SULFONATES, 1-BUTANOL IS NOT COMPLETELY MISCIBLE WITH ONE MOLAL TEXAS 1 OR TEXAS 2 IN THE ABSENCE OF TOLUENE. IN SPITE OF THE FACT THAT THE S_{AC} OF TEXAS 2 (14) IS INTERMEDIATE BETWEEN SODIUM TRIISOPROPYLBENZENESULFONATE (S_{AC} = 9) AND TEXAS 1 (S_{AC} = 16), THE BOUNDARIES FOR TEXAS 1 AND SODIUM TRIISOPROPYLBENZENESULFONATE ARE CLOSER THAN FOR TEXAS 2 AND SODIUM TRIISO-PROPYL-BENZESULFONATE; WITH TEXAS 2, MISCIBILITY WAS LESS THAN WITH TEXAS 1, I.E., THERE WAS A SMALLER AREA OF ONE-PHASE BEHAVIOR ADJACENT TO THE 1-BUTANOL APEX (TOP) ON A PSEUDO-THREE-COMPONENT REPRESENTATION.

WITH HIGH MOLALITIES OF BENZENESULFONATE SUBSTITUTED WITH UP TO SIX ALKYLCARBONS[2] OR WITH LOWER CONCENTRATIONS OF LOWER S_{AC}, SUCH AS BENZENESULFONATE (S_{AC} = 0), (SEE FIGURE 3) A SIMPLE PATTERN IS OBSERVED: MISCIBILITY BOUNDARIES APPROXIMATELY SYMMETRICAL WITH RESPECT TO THE ALCOHOL APEX AND INCREASES IN AREAS OF SINGLE-PHASE REGIONS WITH INCREASING ALKYL SUBSTITUTION OR AQUEOUS CONCENTRATION. THE PATTERN IS MORE COMPLEX AT LOWER MOLALITIES FOR HIGHER DEGREES OF ALKYL SUBSTITUTION; PRESUMABLY MORE THAN TWO PHASES COEXIST IN THE IMMISCIBLE AREA UNDER THE BOUNDARY. AS THE DEGREE OF ALKYL SUBSTITUTION INCREASES, THE VOLUME OF MULTI-PHASES (MORE THAN TWO) INCREASES. IN FIGURE 3, THE CONCENTRATION OF SODIUM BENZENESULFONATE (S_{AC} = 0) WAS REDUCED TO AS LOW AS 0.75 MOLAL (BELOW THIS CONCENTRATION, THE AQUEOUS BENZENESULFONATE SOLUTION AND 1-BUTANOL ARE NOT COMPLETE MISCIBLE).

No three-phase regions were observed, and the phase boundary curve is fairly symmetrical. From the results of systems containing Texas 1 and 2, it seems that the number of branches and position of the substituted groups are also influential factors on the miscibility; with low alkyl substitution, the effect of branching was small.[3]

Phase volume diagram of five-component systems - hydrocarbon scans. We have reported the scans of NaCl, alcohol and organic salt concentrations of systems containing n-octane, 1-butanol, water, NaCl and protosurfactants,[9] and the analysis of phase compositions of these systems[10]. Reported here are the scans of phase volume of five-component systems with all components and concentrations except that of the kind of hydrocarbon fixed. The hydrocarbons are aliphatic hydrocarbons with formula C_NH_{2N+2} where N equals to 5 to 16. The protosurfactants are Na 2,5-diisopropylbenzenesulfonate, Na p-tert-butylbenzoate and Na 3,5-diisopropylsalicylate.

Figure 4 gives the hydrocarbon scan of systems containing hydrocarbon, 1-butanol, water, NaCl and Na 2,5-diisopropylbenzenesulfonate (S_{AC} = 6). By preparation, the sodium diisopropylbenzenesulfonate is 4 wt.% and 1-butanol is 6 wt.% of the total system. The salinity is 5 wt.% of NaCl in water and the ratio of water to hydrocarbon (WOR) is one. Three-phase systems occur when n equals 5 to 8; n-pentane to n-octane, and the middle phase occupies a significant fraction of the total volume. With nonane, the middle phase merged with the bottom phase and showed opalscence in the bottom phase. From n-nonane up to n-hexadecane (n=16), only two-phase systems existed. The transition is 3 phases → 2 phases as the number of alkyl carbons (ACN) of the hydrocarbon increases.

Figure 5 gives the results of a scan of hydrocarbon with systems containing Na p-tert-butylbenzoate, and the other components are the same as in Figure 4. The concentration of benzonate is 4 wt.% and 1-butanol is 6 wt.% of the total system. The salinity is 8 wt.% of NaCl in water. The trend is found to be quite different from systems in Figure 4. From n-pentane up to n-hexadecane only three-phase systems existed. Even more surprisingly is the hydrocarbon scan in systems containing Na 3,5 diisopropylsalicylate (Figure 6). In Figure 6, the concentrations of salicylate is 2 wt.% and 1-butanol is 3.5 wt.% of the total system. The salinity is 4 wt.% NaCl in water. It can be seen that three phases are observed from n-pentane to n-octane, two from n-nonane to n-undecane, and three from n-dodecane up. With n-dodecane, the interface between middle and bottom phases at 28°C after 1 month showed opalescence and an indistinct meniscus. After shaking, the sample regains its distinct meniscus between middle and bottom phase. In order to confirm that the 3 phases to 2 phases then back to three phases transition is due to the presence of this particular protosurfactant, Na 3,5-diisopropylsalicylate, a scan of hydrocarbon of systems containing the components of interest in the absence of the protosurfactant was carried out. Only two phases are observed from n-pentane to n-hexadecane. The results in Figs. 4 to 6 show that with different type of protosurfactant the phase transition in hydrocarbon scans are different.

SOLUBILITIES OF PROTOSURFACTANTS AND SURFACTANTS IN WATER AND AQUEOUS SODIUM CHLORIDE SOLUTIONS. LOW EQUIVALENT-WEIGHT PROTOSURFACTANTS ARE VERY WATER SOLUBLE[2]. FIGURE 7 SHOWS THE SOLUBILITY OF PROTOSURFACTANTS AND SURFACTANTS IN WATER AND SODIUM CHLORIDE SOLUTIONS. OUR INTEREST IS IN THE SALTING EFFECTS OF MONO- AND DIVALENT INORGANIC SALTS ON THE SOLUBILITY OF ORGANIC PROTOSURFACTANTS AND SURFACTANTS IN WATER. THE PROTOSURFACTANTS ARE NA BENZENESULFONATE (S_{AC} = 0), NA P-TOLUENESULFONATE (S_{AC} = 1), NA P-CYMENESULFONATE (S_{AC} = 4), NA 2,5-DIISOPROPYLBENZENESULFONATE (S_{AC} = 6) AND NA 2,4,6-TRIISOPROPYLBENZENESULFONATE (S_{AC} = 9). THE LAST COMPOUND HAS BEEN CLAIMED TO FORM MICELLES IN WATER[12]. THE SURFACTANTS STUDIED ARE SODIUM DODECYLSULFATE (SDS: S_{AC} = 12) AND SODIUM DODECYLBENZENESULFONATE (SDBS; HARD TYPE, I.E., ALKYL CHAIN IS BRANCHED; S_{AC} =12). THESE TWO SURFACTANTS ARE KNOWN TO FORM MICELLES IN WATER. CONCENTRATIONS OF SODIUM CHLORIDE SOLUTIONS WERE UP TO 5 MOLES NACL/KG H_2O. THE SOLUBILITIES OF PROTOSURFACTANTS AND SURFACTANTS BOTH DECREASE AS THE CONCENTRATION OF SODIUM CHLORIDE INCREASES; WITH PROTOSURFACTANT, THE GREATEST PERCENT DECREASE IS SHOWN BY NA 2,5-DIISOPROPYLBENZENESULFONATE AND THE LEAST BY SODIUM BENZENESULFONATE. THE DECREASE OF SURFACTANT SOLUBILITY WITH INCREASE IN NACL CONCENTRATION IS STRIKING, ESPECIALLY WITH SDS. ALTHOUGH THE SOLUBILITY OF SDS IS ALMOST TWO ORDERS OF MAGNITUDE HIGHER IN 0.5 M NACL THAN SDBS (THIS COMPARISON IS AT 0.5 M NACL, RATHER THAN IN WATER, BECAUSE SDBS FORMS A GEL IN WATER AT 25°C), IT IS ALMOST A FACTOR OF TEN LOWER IN 5 M NACL. THE RELATIVE DECLINE IN SOLUBILITIES OF SDBS WITH SALT CONCENTRATION ACTUALLY IS CLOSER TO NA 2,5-DIISOPROPYL- AND 2,4,6-TRIISOPROPYLBENZENSULFONATE THAN TO SDS.

PART OF THE DECREASES IN SOLUBILITY WITH INCREASING NACL CONCENTRATION IS FROM THE COMMON NA(I) ION, BUT THE SOLUBILITY DECREASES ARE MUCH MORE THAN WOULD BE EXPECTED FROM A CONSTANT PRODUCT OF SODIUM CATION AND ORGANIC ANION CONCENTRATION. AS THE CONCENTRATION OF NACL INCREASES FROM 0 TO 5 M, THE ION PRODUCT OF SODIUM 2,4,6-TRIISOPROPYLBENZENESULFONATE DECREASES BY A FACTOR OF ABOUT 34; AT THE OTHER EXTREME THAT OF NA BENZENESULFONATE DECREASES BY A FACTOR OF FOUR. FOR THE SURFACTANT SDS, THE DECREASE WAS A FACTOR OF 5.5×10^4. THE ION PRODUCTS ARE NOT SOLUBILITY PRODUCTS, BECAUSE THEY DO NOT INCLUDE ACTIVITY COEFFICIENTS NOR THE ACTIVITY OF WATER RAISED TO THE POWER OF WATERS OF HYDRATION IN THE SOLID. AT THE MOMENT WE DO NOT HAVE AVAILABLE DATA OF THE SALTING EFFECTS OF DIVALENT INORGANIC SALTS ON THE SOLUBILITY OF ORGANIC SALTS IN WATER. NEVERTHELESS, THE HIGH SOLUBILITY OF PROTOSURFACTANTS IN WATER AND IN NACL SOLUTIONS PARALLELS THE LOWER ADSORPTION OF PROTOSURFACTANT ON CLAYS AND OTHER MINERALS[13] (OR PRECIPITATION BY THEM).

DISCUSSION

THE EXTENT OF THE SOLUBILIZATION OF HYDROCARBONS IN WATER BY THE LOW-EQUIVALENT-WEIGHT PROTOSURFACTANTS CONTINUES TO SURPRISE US, ALTHOUGH IT IS NOT HIGH ENOUGH TO SUGGEST THAT IT WOULD BE FEASIBLE TO DISSOLVE OIL FROM FORMATIONS WITH THEM ALONE. THE TRENDS, HOWEVER, REMAIN INTERESTING.

AS WE DISCUSSED PREVIOUSLY,[7,8] ADDITION OF AN ALCOHOLIC COSURFACTANT (ALSO SURFACE ACTIVE) TO SYSTEMS WITH PROTOSURFACTANTS TO EFFECT A FOUR-COMPONENT SYSTEM FREQUENTLY RESULTS IN THE FORMATION OF A THIRD PHASE. THIS BEHAVIOR IS RELATED TO THE NUMBER OF QUATERNARY CONSOLUTE CURVES IN THE SYSTEM.[7] THE EXTENT OF THE THREE-PHASE REGIONS DIFFERS SUBSTANTIALLY FOR DIFFERENT HYDRO-

CARBONS AND ORGANIC SALTS. A MUCH WIDER COMPOSITIONAL RANGE OF THREE PHASES WILL RESULT BY ADDING A FIFTH COMPONENT - USUALLY INORGANIC SALTS.[9] WE ALSO FOUND THAT BY MODELING THE ENHANCED OIL RECOVERY SYSTEMS WHICH CONTAIN A HYDROCARBON, WATER, A PROTOSURFACTANT, AN ALCOHOL AND AN INORGANIC SALT, THE MISCIBILITY DIAGRAMS DO NOT UNDERGO A SHARP DISCONTINUOUS TRANSITION AS THE EQUIVALENT WEIGHT OF THE ORGANIC SALTS IS INCREASED INTO THE SURFACTANT RANGE[8-10] WHERE MICELLAR AND OTHER AGGREGATES ARE KNOWN TO FORM. THREE-PHASE REGIONS ARE FOUND WITH COMPOUNDS OF INTERMEDIATE DEGREES OF ALKYL SUBSTITUTION, AS THEY ARE WITH SURFACTANTS. THE CONCENTRATIONS OF AMPHIPHILES REQUIRED TO ATTAIN THREE-PHASE BEHAVIOR WITH PROTOSURFACTANTS ARE COMPARABLE TO THOSE REQUIRED WITH SURFACTANTS.

SCANS OF PHASE VOLUMES AS THE CONCENTRATION OF ONE COMPONENT IS CHANGED ARE QUALITATIVELY SIMILAR FOR PROTOSURFACTANTS AND SURFACTANTS, ALTHOUGH THE CONCENTRATION RANGE OVER WHICH MIDDLE PHASES PERSIST IS WIDER FOR THE PROTOSURFACTANT SYSTEMS THAN IS USUAL WITH SURFACTANTS. NEVERTHELESS THE TRANSITIONS 2 PHASES → 3 PHASES → 2 PHASES ARE VERY SHARP. LOW INTERFACIAL TENSIONS WERE OBSERVED WITH PROTOSURFACTANT SYSTEMS;[9] VALUES ARE ULTRALOW (OF THE ORDER OF 10^{-3} DYNE/CM) BETWEEN ADJACENT PHASES (LOWER VS. MIDDLE OR MIDDLE VS. UPPER) IN SOME CASES.

SURFACTANT SYSTEMS FREQUENTLY EXHIBIT A SIMILAR PROGRESSION FROM 2 PHASES → 3 PHASES → 2 PHASES WITH INCREASING ALKYL CARBON NUMBER OF THE HYDROCARBON AS WITH INCREASING EITHER OR SALINITY OR ALCOHOL CONCENTRATION. THE PATTERN APPEARS TO BE ALSO TRUE WITH LOWER-EQUIVALENT-WEIGHT SULFONATES, BUT IT IS DIFFERENT WITH EITHER LOWER-EQUIVALENT-WEIGHT CARBOXYLATE OR HYDROXY-CARBOXYLATE. WITH NA P-TERT-BUTYLBENZOATE AS PROTOSURFACTANT WITH HYDROCARBONS FROM N-PENTANE TO N-HEXADECANE, ONLY THREE-PHASE SYSTEMS OCCURRED AND PERSISTED, AND WITH NA 3,5-DIISOPROPYLSALICYLATE, THE TRANSITIONS ARE EVEN MORE SURPRISING. A TRANSITION OF 3 PHASES → 2 PHASES → 3 PHASES WAS FOUND AS THE ALKYL CARBON NUMBER OF THE HYDROCARBON INCREASES. TO DATE, THERE ARE NO DATA AVAILABLE ON HYDROCARBON SCANS WITH HIGH-EQUIVALENT-WEIGHT SALICYLATE SURFACTANTS. WE DO NOT KNOW THAT THE SALICYLATE SURFACTANTS WILL BEHAVE DIFFERENTLY FROM THE SAME CLASS OF PROTOSURFACTANT, BUT AT LEAST WE KNOW THAT THE SCAN OF HYDROCARBON ACN WITH A CARBOXYLATE PROTOSURFACTANT IS DIFFERENT FROM THAT OF A CARBOXYLATE SURFACTANT.[14] IN GENERAL, THE SCANS OF HYDROCARBON ACN SEEM TO BE MORE COMPLICATED THAN THOSE OF SALINITY OR CONCENTRATION OF COSURFACTANT OR SURFACTANT.

FINALLY, THE HIGHER SOLUBILITY OF PROTOSURFACTANTS IN WATER AND INORGANIC SALT SOLUTIONS WILL LIKELY DECREASE THE TENDENCY TO BE ADSORBED ON MINERALS AND THE HIGHER SOLUBILITIES OF SALTS OF MONO- AND DIVALENT CATIONS OF LOW-EQUIVALENT-WEIGHT SALTS WOULD BE IMPORTANT PRACTICAL ADVANTAGES IN OIL-RECOVERY APPLICATIONS, IF PROTOSURFACTANTS MET OTHER CRITERIA FOR THE PROCESS.

ACKNOWLEDGEMENTS

I AM VERY INDEBTED TO DR. J. S. JOHNSON, JR., OF THE OAK RIDGE NATIONAL LABORATORY CHEMISTRY DIVISION FOR MANY HELPFUL DISCUSSIONS, AND TO MR. T. M. BENDER FOR VALUABLE TECHNICAL ASSISTANCE.

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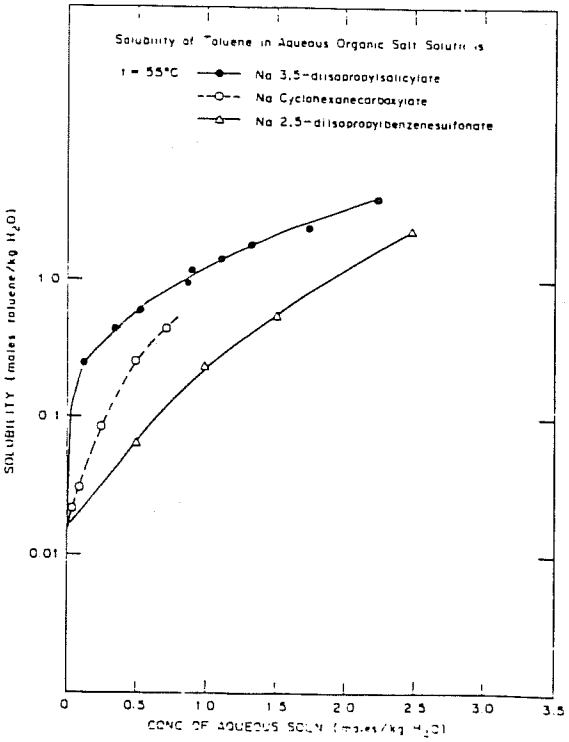

Fig. 1. Solubility of toluene in aqueous solutions of various photosurfactants (55°C).

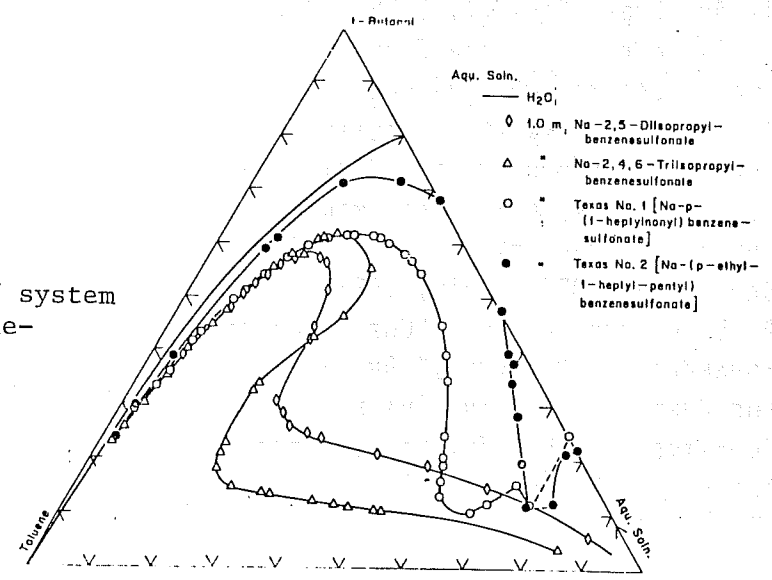

Fig. 2. Phase boundary curves of system toluene/1-butanol/1.0M Alkylbenzene-sulfonate (25°C).

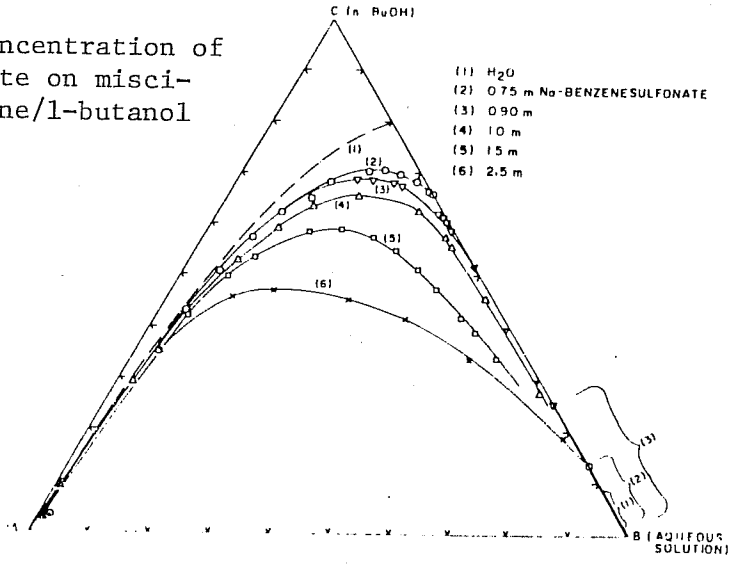

Fig. 3. Effect of concentration of sodium benzenesulfonate on miscibility of water/toluene/1-butanol systems (25°C).

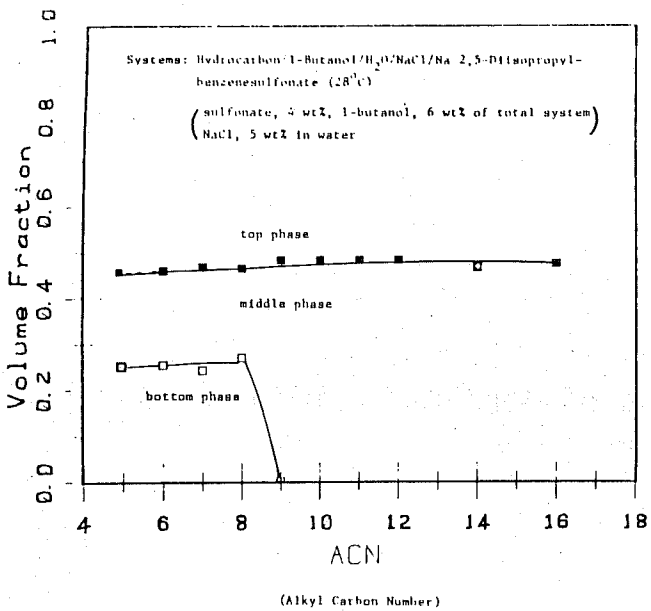

Fig. 4. Phase volumes of hydrocarbon/ 1-butanol/aqueous NaCl/Na 2,5-diiso-propylbenzene sulfonate systems (28°C): hydrocarbon scan.

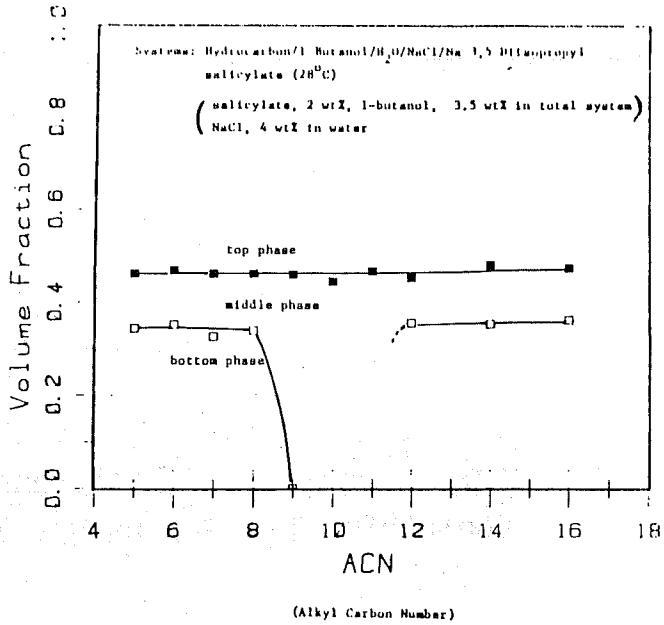

Fig. 6. Phase volumes of hydrocarbon/ 1-butanol/aqueous NaCl/Na 3,5-diiso-propylsalicylate systems (28°C): hydrocarbon scan.

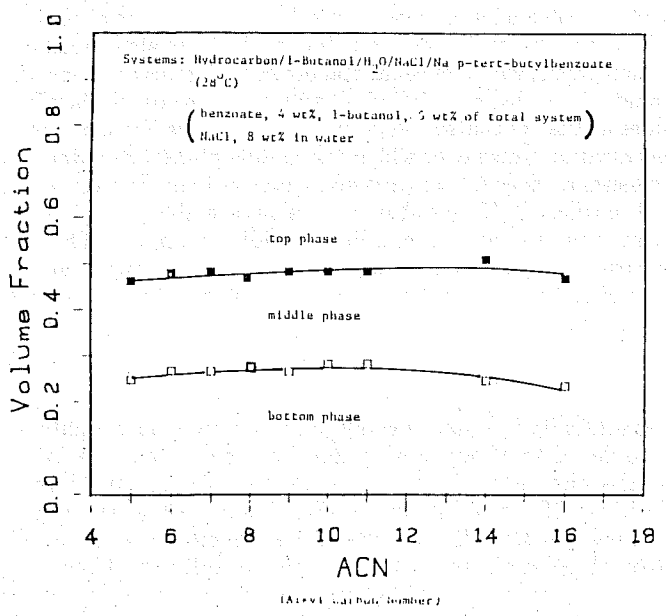

Fig. 5. Phase volumes of Hydrocarbon/ 1-butanol/aqueous NaCl/Na p-tert-butylbenzoate systems (28°C): hydrocarbon scan.

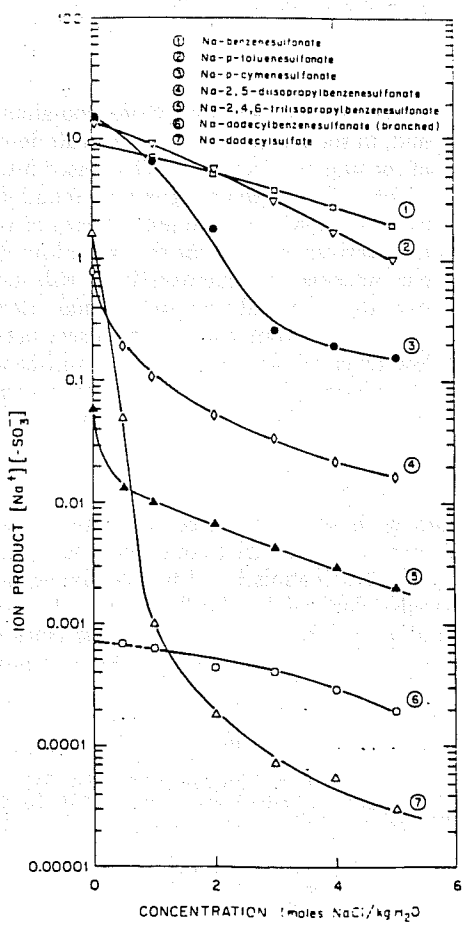

Fig. 7. Solubility of protosurfactants and surfactants in water and in aqueous NaCl solutions (25°C).

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1.2. Phases and Interfacial Tensions of Aqueous/Hydrocarbon Systems Containing Low-Equivalent-Weight Salts

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Miscibility diagrams for systems containing a hydrocarbon, water, a low-equivalent-weight organic salt, an alcohol, and, in some cases, an inorganic salt do not undergo a sharp discontinuous transition as the equivalent weight of the organic electrolyte is increased into the surfactant range, where micellar and other aggregates are known to form. Three-phase regions are found with compounds of low degrees of alkyl substitution ("protosurfactant") as they are with surfactants. Scans of phase volumes as the concentration of one component is changed are qualitatively similar for the two, although the concentration range over which the middle phase (sometimes characterized as a microemulsion with surfactants) persists is wider for the protosurfactant systems investigated here than is usual with surfactants. Low interfacial tensions (IFT) are observed; values are ultralow (of the order of 10^{-3} dyn/cm) in some cases between adjacent phases (lower vs. middle or middle vs. upper). These low tensions, the sharpness of transitions between two and three phases with compositional changes, and observations of opalescence imply that the postulation of proximity to critical end points suggested to correlate such properties of surfactant systems is also applicable here.

In recent years, we have investigated the solubilization of hydrocarbons in water by a variety of organic salts, used both with and without alcohols.[1–7] Most of the organic salts were low-molecular-weight alkylbenzenesulfonates, carboxylates, and salicylates. These are in the class referred to as "hydrotropes",[8–13] substances which enhance the solubility in water of compounds normally only slightly soluble. One of our motivations has been in elucidation of the chemistry of enhanced oil recovery by micellar flooding. The systems in micellar flooding are extremely complex; at least five classes of components—water, hydrocarbon, surfactant, cosurfactant (usually an alcohol), and inorganic salt—are involved, and several of them may be mixtures of many compounds. The criterion usually

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considered most important for mobilization of oil not accessible by primary or secondary (water-flooding) processes is attainment of ultralow interfacial tensions, in the range of mdyn/cm, between aqueous-rich and hydrocarbon-rich phases.

Many laboratories have approached these systems by study of mixtures of pure components and of fewer components than the five classes. We have tried to simplify further by using as a model for the surfactant component the low-equivalent-weight organic hydrotropic salts, which we also refer to as "protosurfactants". The alkyl chains of these compounds are shorter than what is usually considered necessary for formation of the large surfactant aggregates. In this way we hoped to unravel to some extent contributions to favorable oil recovery of micelles and of the concentration of surfactants at interfaces from other effects of the amphiphilic properties of organic salts.

In previously cited papers, we have reported solubilizations (to us surprisingly high) of hydrocarbons by protosurfactants, both in three-component systems and in systems also containing alcohols. Trends to stronger hydrotropic properties with increase in alkyl substitution of a given type of salt were found. As the system approached the composition of micellar-flood systems, the properties of the two became more similar to one another—appearance of a third, organic-salt-rich middle phase, sometimes with low interfacial tensions between phases, for example.[6,7]

The phase boundary curves in pseudo-three-component triangular representations—hydrocarbon, alcohol, and aqueous protosurfactant solutions being the apexes—between one- and more-than-one-phase regions are highly asymmetric with respect to the alcohol apex in the neighborhood of compositions giving three phases.[7] The extent of the single-phase and three-phase regions differed substantially for different hydrocarbons and organic salts. We report here the effect of inorganic salt, which changes the patterns radically and results in a much wider compositional range of three phases. Also reported are phase volumes and interfacial tensions of several five-component systems at compositions near or at which third phases exist.

Recently, it has been proposed that optimal formulations for oil recovery are at compositions near critical end points and that ultralow interfacial tensions are not a result only of the interfacial properties of surfactants but are also at least partly a result of this proximity.[14-16] Because of the high level of interest in critical phenomena at present, the results presented here on protosurfactant systems have implications beyond those for oil recovery.

Experimental Section

Materials. The sources of toluene, *n*-octane, 1-butanol, sodium *p*-cymenesulfonate, sodium 2,5-diisopropylbenzenesulfonate, sodium *p-tert*-butylbenzoate, and sodium 3,5-diisopropylsalicylate used in this paper can be found in ref 1–7. Reagent-grade sodium chloride was obtained from Fisher Scientific Co. and was dried first before using. The aqueous sodium chloride solutions were prepared with distilled water.

Methods. The phase boundary curves (Figures 1–5) were obtained by the procedures of ref 7. Concentrations of aqueous NaCl are expressed in terms of weight percent in water (g of NaCl/(g of NaCl + g of H_2O)). The concentrations of the aqueous protosurfactant solutions for phase boundary curves (Figures 1–5) are expressed in terms of mol/(kg of water) or mol/(kg of aqueous sodium chloride solution). The aqueous component (right apex) is composed of water plus protosurfactant plus NaCl.

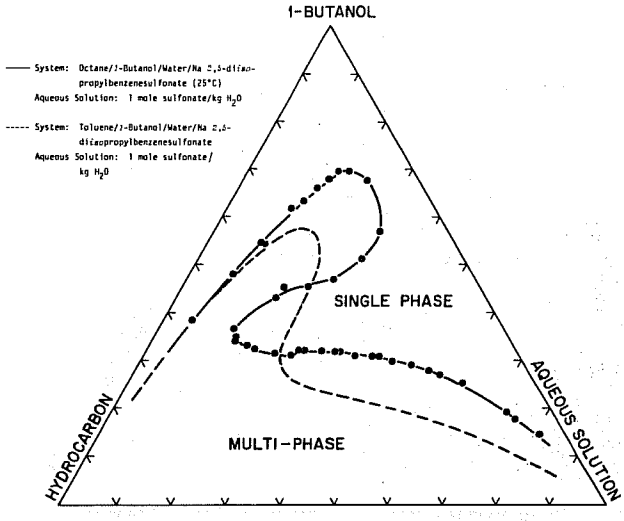

Figure 1. Phase boundary curves of systems hydrocarbon/1-butanol/(1.0 *m* sodium 2,5-diisopropylbenzenesulfonate) (25 °C).

The phase volume diagrams (Figures 6–8) in the five-component systems were determined as follows: Weighed protosurfactant, aqueous NaCl solution, 1-butanol, and *n*-octane were added one after another into a 15-mL graduated centrifuge tube with a Teflon cap. Mixing was accomplished with a Vortex mixer, and the tube was then held in a water bath at 28 °C overnight. The samples then were shaken gently every day until the volume of the phase remained constant. Most samples took only about 24 h to reach constant volumes. All quantities were determined by weighing, and compositions are presented as weight percentage. Sodium chloride is expressed as weight percent in water (g of NaCl/(g of NaCl + g of H_2O)) and all the other components are weight percent of the total systems. The ratio of water to hydrocarbon (WOR), always 1 in these experiments, is the ratio of weight of water to weight of hydrocarbon. In the phase volume diagrams, points on zero and 1 volume fraction limits indicate a transition from two to three phases within composition changes of the varied component of the width at the points.

Interfacial tensions were measured at 28 °C with a multisample spinning drop apparatus, purchase from N. B. Simpson, Tulsa, OK,[17] modified for better temperature control.[18]

Results

Phase Boundary Curves of Four- and Five-Component Systems. Miscibilities of *n*-octane/1-butanol/(aqueous solutions containing 1 mol of sodium 2,5-diisopropylbenzenesulfonate per kilogram of water) were determined to allow comparison with earlier results on a system the same except that the hydrocarbon was toluene.[7] Diagrams for similar systems with a protosurfactant of the same number of alkyl carbons, sodium 3,5-diisopropylsalicylate, were also determined.

Figure 1 presents the curve separating single- and multiphase regions of the system *n*-octane/1-butanol/(1.0 *m* aqueous sodium 2,5-diisopropylbenzenesulfonate); the

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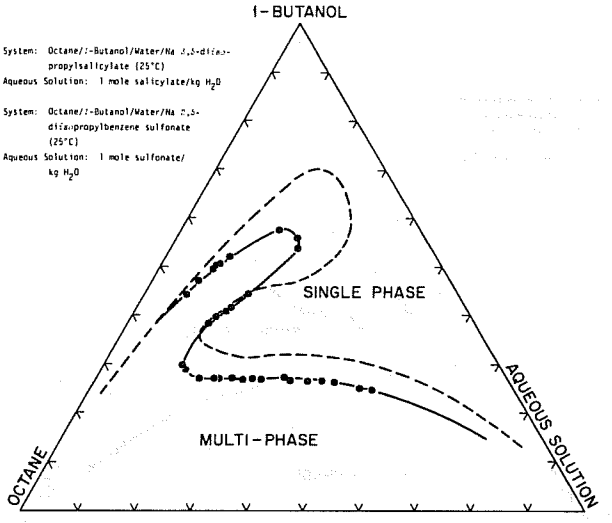

Figure 2. Phase boundary curves of systems *n*-octane/1-butanol/(1.0 *m* protosurfactant) (25 °C).

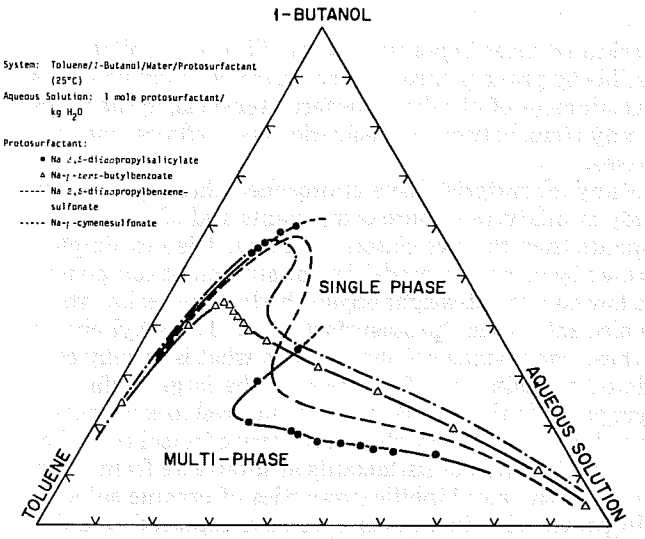

Figure 3. Phase boundary curves of systems toluene/1-butanol/(1.0 *m* protosurfactant) (25 °C).

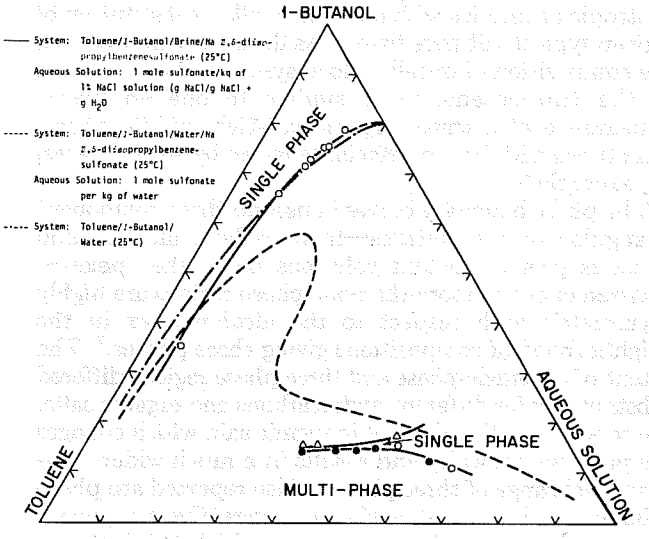

Figure 4. Phase boundary curves of systems toluene/1-butanol/(aqueous NaCl)/sodium 2,5-diisopropylbenzenesulfonate (25 °C).

phase boundary curve reported for the same system with toluene in ref 7 is dotted in. The boundary for the *n*-octane system is highly asymmetric, and the solubilization of *n*-octane by protosurfactant and 1-butanol is mostly less than with toluene, which agrees with our results in ref 5, in which we reported that alkanes with ACN (number of alkyl carbons) greater than six are less solubilized than aromatic hydrocarbons with ACN less than six. With 1-butanol is cosolvent, alkanes are more solubilized than corresponding aromatic hydrocarbons with equivalent ACN.

Figure 2 gives the phase boundary curve of the same system, except with sodium 3,5-diisopropylsalicylate as protosurfactant. Again the pattern is asymmetric, and the one-phase area is greater with the salicylate than with the corresponding sulfonate, represented by the dotted curve. These observations appear to parallel the relative solubilizing effect of hydrocarbons by sulfonates and salicylates in three-component systems, in which toluene is more solubilized in aqueous salicylate solutions than in aqueous sulfonate solutions of the same S_{AC} (number of alkyl carbons on benzene ring of protosurfactants) in systems without alcohol.[6] However, relative solubilizing power by different protosurfactants in three-component and four-component solutions is frequently different, for different alcohols[4-6] as the fourth component.

Figure 3 summarizes the phase boundary curves for toluene/1-butanol/(1.0 *m* sodium *p-tert*-butylbenzoate or sodium 3,5-diisopropylsalicylate). The boundary curves of the same system containing sodium *p*-cymenesulfonate and sodium 2,5-diisopropylbenzenesulfonate from ref 7 are dotted in for comparison. The boundaries in the three-phase region of sodium diisopropylsalicylate were indistinct and difficult to locate. Sodium diisopropylsalicylate again proved to have the strongest hydrotropic properties among them, at least in the aqueous-rich region.

In all of these systems, compositions giving three phases are found under and near the S-shaped sector, and in some cases the three-phase regime extends into the aqueous-rich region of the pseudoternary diagram. The three-phase region for the salicylate seems to cover a particularly wide compositional range at high alcohol content. With all four protosurfactants, the weight percentage of protosurfactant of the total system in the three-phase regions was usually low, about 1–6%. The relatively strong solubilizing power of sodium diisopropylsalicylate will be confirmed in results to be presented for five-component systems (including inorganic salt). When three phases are present, the protosurfactant seems mainly in the middle phase.[19] In two-phase systems at relatively low 1-butanol concentration, the protosurfactant is concentrated in the lower aqueous phase; on the other hand, at high 1-butanol content in two-phase systems, it is predominantly in the top, hydrocarbon-rich phase.

Figure 4 compares the phase boundaries for toluene/1-butanol/(aqueous 1 mole of sodium 2,5-diisopropylbenzenesulfonate per kilogram of water[7] or per kilogram of aqueous 1 wt % NaCl). The pattern is quite different for the two; with NaCl, the single-phase region is dramatically decreased and the three-phase area increases. With added NaCl, the single-phase region near the alcohol apex is bounded by a curve not far from the curve for toluene/1-butanol/water without protosurfactant. However, there is a second opalescent single-phase region at alcohol-poor compositions (between 14% and 15% of 1-butanol). The composition range of this "single" phase is narrow in the alcohol variable. One observes on addition of alcohol a transition from cloudy opalescence to clear opalescence, then back to a cloudy opalescence. On ad-

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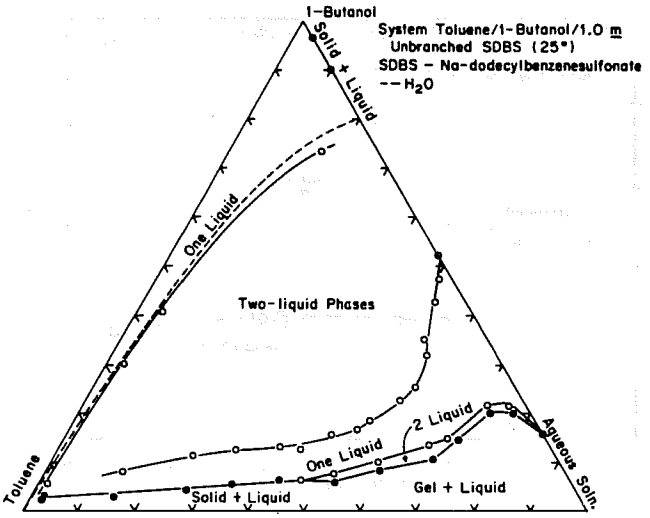

Figure 5. Phase boundary curve of systems toluene/1-butanol/(1.0 *m* sodium dodecylbenzenesulfonate) (25 °C).

dition of much more alcohol, the opalescence disappears and the solution becomes merely cloudy. Cloudy opalescent mixtures of compositions near the apparent single-phase region frequently separate into three phases on standing.

The similarity with surfactant diagrams can be striking, as an example given in Figure 5 indicates. This is for sodium 1-dodecylbenzenesulfonate, the alkyl chain being unbranched, without added NaCl. There is a single-phase region in the aqueous-rich, low-alcohol region, very like that of sodium diisopropylbenzenesulfonate with added 1% NaCl. There are, however, more variations between properties of series of chemically similar surfactants than in series of protosurfactants,[20] perhaps because of the variety of aggregation reactions that surfactants can exhibit.

Knowledge of phase diagrams (phase boundary curves) is important for understanding phase transitions.[7,21–24] The number of miscibility gaps in two-component systems and the number of critical end points (closing of miscibility gaps by variations of compositions, pressure, and temperatures, etc.) of limiting ternary systems are related to the formation of three-phase systems, interfacial tensions, and relative phase volumes.

Phase Volume Diagrams and Interfacial Tensions of Five-Component Systems. The occurrence of three phases has been found to be closely correlated with "optimal salinities"[25–27] and other optimal conditions for oil recovery and is of general interest in the context of critical phenomena. Reported here are scans of phase volumes and of interfacial tensions of five-component systems with all concentrations except that of one component fixed, carried

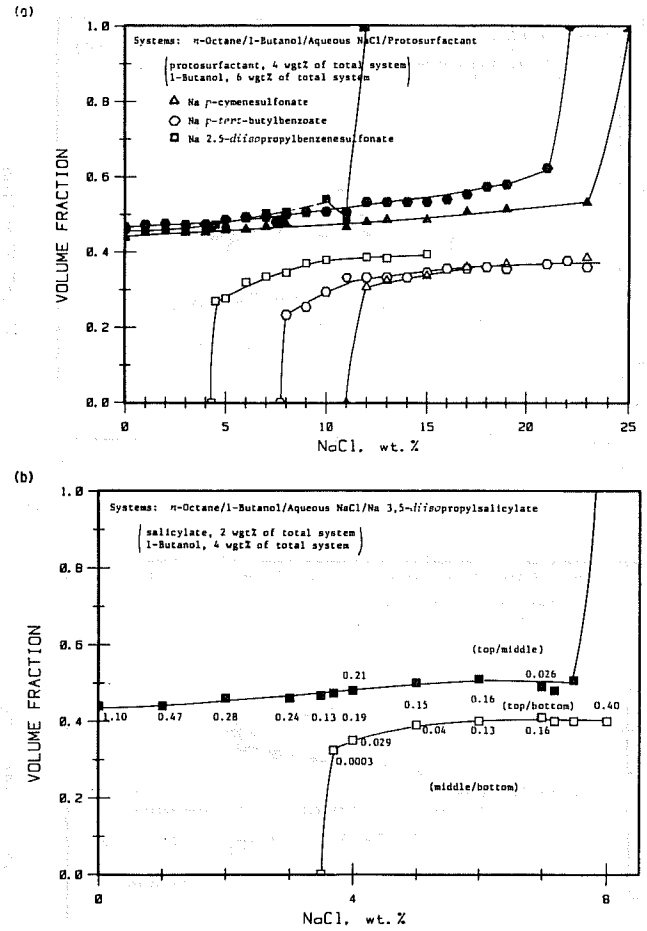

Figure 6. Phase volumes and interfacial tensions of *n*-octane/1-butanol/(aqueous NaCl)/protosurfactant systems (28 °C): salinity scan (numbers refer to interfacial tensions).

out at compositions at or near regions at which three phases coexist.

Salinity Scan. Figure 6a presents salinity scans of systems containing the two sulfonates and one benzoate: sodium *p*-cymenesulfonate, with four alkyl carbons on the benzene ring (S_{AC} = 4); sodium 2,5-diisopropylbenzenesulfonate (S_{AC} = 6); and sodium *p-tert*-butylbenzoate (S_{AC} = 4). The percentage of protosurfactant is 4 wt % of the total system and that of 1-butanol is 6 wt % of the total system. The salinity is weight percent in water. The trend is surprisingly analogous to that of surfactant systems.[28]

Figure 6b gives a salinity scan of a system containing sodium 3,5-diisopropylsalicylate (S_{AC} = 6). The weight of diisopropylsalicylate is 2% and that of 1-butanol is 4% of the total system. The salicylate and 1-butanol concentrations were chosen lower in these experiments in order to make comparisons at comparable solubilizing capabilities; the hydrotropic capability of sodium salicylate[6] is greater than those of the benzoate and sulfonate. With fixed percentages of protosurfactant and 1-butanol, at lower salinities the system has two phases, and the lower aqueous phase was rich in sodium diisopropylsalicylate (2_L). At intermediate salinities, three phases occur, and salicylate is largely in the middle phase. At higher salinity, the system reverts to two phases, and salicylate is found in the top, hydrocarbon phase (2^U).[19] (L and U refer to the phase in which the organic salt is concentrated, lower or upper). The phase transition is analogous to the Winsor

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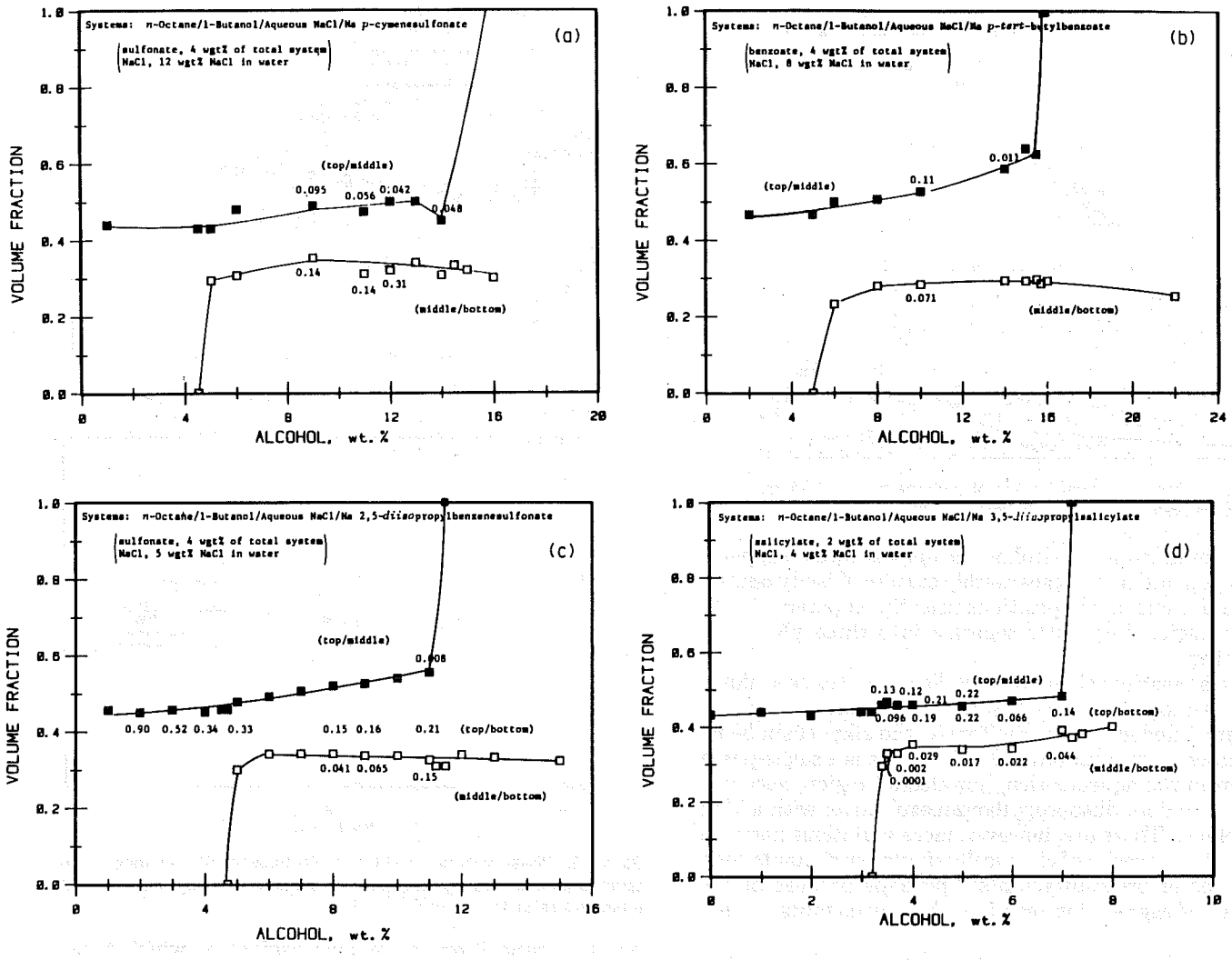

Figure 7. Phase volume and interfacial tensions of *n*-octane/1-butanol/(aqueous NaCl)/protosurfactant systems (28 °C): the effect of alcohol concentrations (numbers refer to interfacial tensions).

pattern,[29] widely used to correlate micellar-flood chemistry. In protosurfactant-containing systems, the salinity range over which middle phases occur is wider than commonly observed with surfactants. For both sodium *p*-cymenesulfonate and sodium *p-tert*-butylbenzoate, higher salinities are required to effect a middle phase than with the diisopropylbenzenesulfonate, at the same alcohol and protosurfactant concentration. This is consistent with the higher solubilities of cymenesulfonate and butylbenzoate in aqueous phases relative to their solubilities in *n*-octane which in turn are consistent with expectations from their S_{AC}. The trend with increasing alkyl substitutions is also found with surfactants.[30,31] The salicylate system is not directly comparable with the others because of composition differences. The onset of three-phase behavior occurs at lower salinity than for diisopropylbenzenesulfonate and the salinity range of three phases is less. In all the systems studied, the salinities at which the onset of three phases is observed are substantial, and the middle phase occupies a significant fraction of the total volume.

Effect of Alcohol Concentration. Figure 7a–d summarizes scans of alcohol (1-butanol) content for these four protosurfactants. In Figure 7a–c, the weight percentage of protosurfactant is 4% of the total system and the salinities are 12 wt % in water for systems with cymenesulfonate, 8% with butylbenzoate, and 5% with diisopropylbenzenesulfonate. The salinities were chosen at the onset of three phases in salinity scans. In Figure 7d the concentration of diisopropylsalicylate is 2 wt % of the total system and NaCl is 4 wt % in water.

Three-phase regions appear in the middle of the range for all four protosurfactants. Coexisting solid and liquid phases were found at 0% of 1-butanol with butylbenzoate and diisopropylbenzenesulfonate. With diisopropylsalicylate, the onset of three-phase behavior occurs at lower alcohol and persists over a narrower range of alcohol concentrations than with the other three protosurfactants; again, differences in composition preclude exact comparison. Systems with butylbenzoate have the longest range of alcohol content at which three phases coexist, and the volume of the middle phase dominates over a larger portion of the diagram. The transitions also follow the pattern of $2_L \rightarrow$ three phases $\rightarrow 2^U$. This pattern has also been observed in the four-component phase boundary curve diagram near the S-shaped sector with a fixed ratio of hydrocarbon–aqueous solutions (this is either inferred from the color of the system containing salicylate or supported by analyses in ref 7); the same phase transition occurs by increasing the amount of 1-butanol.

Effect of Protosurfactant Concentration. Figure 8a–d gives the results of scans of the concentrations of the four

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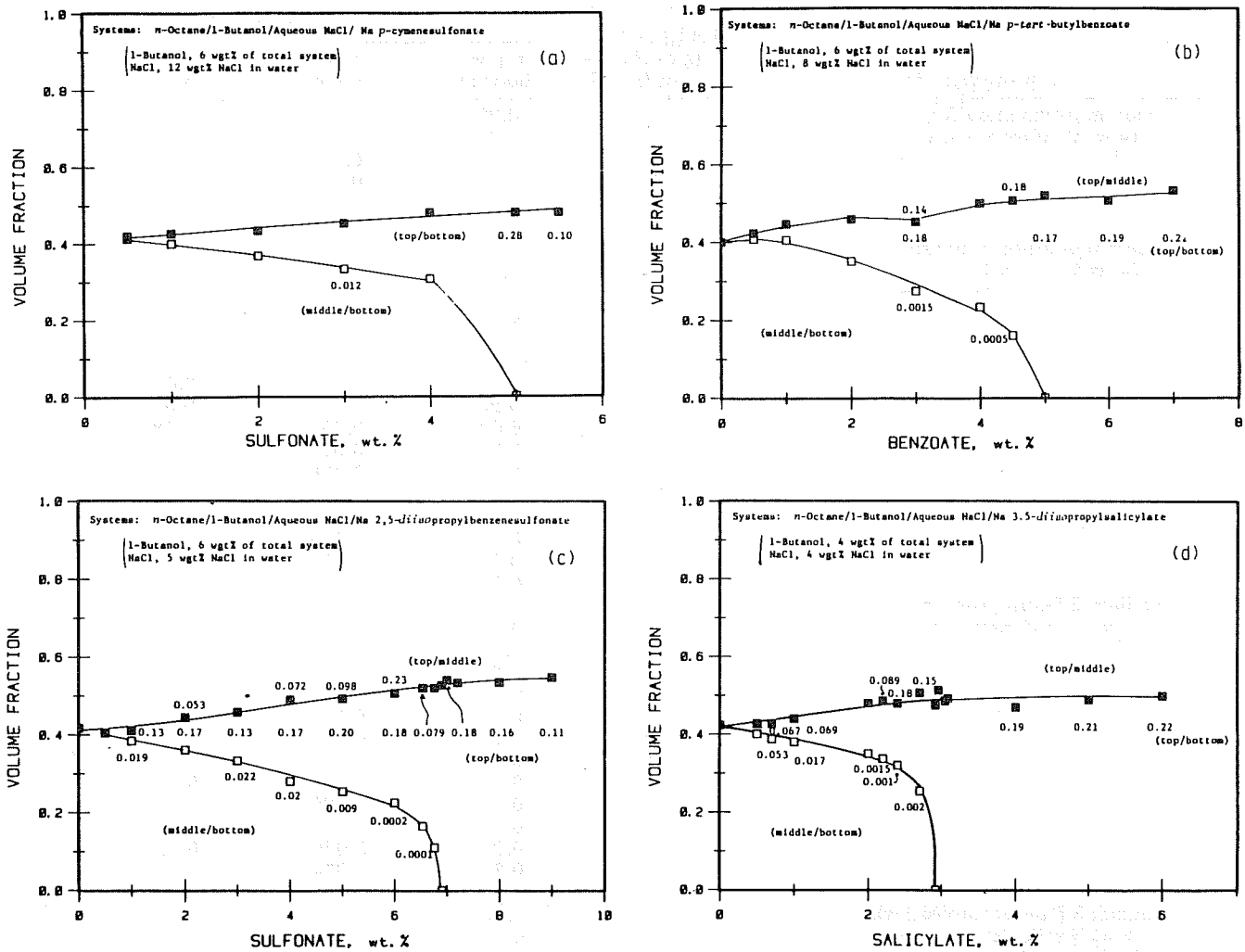

Figure 8. Phase volumes and interfacial tensions of *n*-octane/(1-butanol/(aqueous NaCl)/protosurfactant systems (28 °C): the effect of protosurfactant concentrations (numbers refer to interfacial tensions).

protosurfactants, other compositional variables being fixed. The sodium chloride and 1-butanol concentrations selected were such that three phases occurred at intermediate protosurfactant concentrations. Three phases were found with as low as 0.5 wt % of protosurfactant of the total system. The volumes of the middle phase increased with protosurfactant concentration and reached maximum values before the disappearance of the third phase; the middle and lower phases merged, while the volume of the upper phase decreased slightly. The lower and middle phases merged at ca. 2.96% of diisopropylsalicylate, 5% with either cymenesulfonate or *tert*-butylbenzoate, but with about 6.8% of diisopropylbenzenesulfonate (percentage of the total systems). In spite of the marked difference in the phase boundaries between single and multiple phases with and without NaCl in Figure 4, the ranges of protosurfactant concentration over which three phases coexist appear not to be greatly different for the two checked, diisopropyl-substituted compounds. The lower amounts of salicylate required to produce middle phases is further evidence that diisopropylsalicylate is a more powerful hydrotropic agent than the others. The results are also consistent with our earlier study,[6] in that it appears not only that the alkyl groups affect the solubilization property of those hydrotropic compounds but that other substituents are important, the charged groups, $-SO_3Na$ and $-COONa$ to a modest extent, and the unionized *o*-hydroxy group to a surprisingly large extent.

Interfacial Tensions. Interfacial tensions for compositions in and near three-phase regimes are given in Tables I–III. Values are also given in those figures near the boundary between the two phases in question where room was available. Because of sensitivity to errors in density and other reasons, these values are not considered of the highest accuracy, and lack in some sets of internal consistency, indicated by violations of Wildom's inequality rule[32] for three-phase systems, $\gamma_{max} \leq \gamma_{min} + \gamma_{middle}$, is not considered significant. In some cases, similarity of refractive indices of the two phases made measurements impossible.

Low interfacial tensions were found between top and bottom phases in many compositions. Ultralow interfacial tensions were found near the disappearance of one of the phases. With variation of either NaCl, 1-butanol, or protosurfactant, strong opalescences observed near the transition of three phases $\rightarrow 2_L$ were (frequently) correlated with interfacial tensions in the mdyn/cm range. With the transition from three phases to 2^U, opalescence was not observed as often as with three phases to 2_L, but low values of interfacial tension were often observed. The low IFT values and the strong opalescences are consistent with proximity to critical end points. Interfacial tensions are consistent with the phase volumes, in that the IFT between top (upper) and middle phases decreases as the concentration of NaCl increases and that between middle and

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TABLE I: System *n*-Octane/Water/1-Butanol/NaCl/Protosurfactant at 28 °C

protosurfactant	100[g of NaCl/ (g of NaCl + g of H_2O)]	interfacial tensions, dyn/cm		
		top vs. bottom	top vs. middle	middle vs. bottom
sodium *p*-cymenesulfonate	6	0.80		
(4 wt % sulfonate, 6 wt %	11	0.25		
1-butanol of total system)	13		0.10	0.0048
	17		0.18	
	23		0.12	0.27
	25	0.30		
sodium *p-tert*-butylbenzoate	0	1.24		
(4 wt % benzoate, 6 wt %	1	1.18		
1-butanol of total system)	3	0.49		
	7	0.25		
	7.5	0.24		
	7.7	0.11		
	8	0.31	0.22	0.0007
	9	0.28		0.005
	10	0.039	0.088	0.030
	12	0.12	0.027	
	14	0.11	0.026	0.065
	16	0.17		
	18	0.22	0.048	0.19
	19	0.11	0.0081	0.21
	21	0.22	0.0034	
	23	0.21		
sodium 2,5-diisopropylbenzenesulfonate	0	1.68		
(4 wt % sulfonate, 6 wt %	1	0.69		
1-butanol of total system)	2	0.48		
	3	0.27		
	4	0.19		
	4.5	0.15	0.13	0.001
	5	0.16	0.12	
	6	0.10		
	7	0.12		0.094
	8	0.17	0.089	0.12
	9	0.20		
	10	0.29	0.076	0.15
	11.5	0.32	0.074	0.41
	15	0.17		
sodium 3,5-diisopropylsalicylate	0	1.10		
(2 wt % salicylate, 4 wt %	1	0.47		
1-butanol of total system)	2	0.28		
	3	0.24		
	3.7	0.13		0.0003
	4	0.19	0.21	0.029
	5	0.15		0.040
	6	0.16		0.13
	7		0.026	0.16
	8	0.40		

bottom phases increases as NaCl concentration increases.

Discussion

In the composition regions in the neighborhood of coexistence of three phases, the patterns of protosurfactant-containing systems and of surfactant-containing systems are very similar in the concentration scans (Figures 6–8). The transitions from two to three phases and back again to two are reminiscent of similar plots previously cited for surfactant systems,[14–16,28] and the behavior is analogous to that represented in other formats (e.g., ref 25–27, 30, and 31).

Comparison of Figures 4 and 5 suggests that the analogies hold to some extent over the complete compositional range. The effect of NaCl in making the pattern for sodium diisopropylbenzenesulfonate (S_{AC} = 6) similar to that of sodium dodecylbenzenesulfonate (S_{AC} = 12) without added salt could be rationalized from the common sodium-ion effect in raising the activity of the organic salt in the aqueous phase. This would increase the distribution into the hydrocarbon phase, in the same direction as increasing the alkyl carbon substitution. However, some caution is in order; miscibility diagrams of other alkylbenzenesulfonates in the surfactant range did not exhibit a simple dependence on S_{AC}.[20]

The transitions in Figures 6 and 7 from two to three phases and back to two phases are frequently very sharp. A pronounced change in slope with variation of protosurfactant concentration is also seen near three-to-two-phase transitions. Most of the time phase transitions are accompanied by strong opalescence in the lower phase and sometimes by opalescence in the middle or upper phases. These indications of proximity of critical end points are supported by the low interfacial tensions frequently observed. The range of alcohol and sodium chloride concentrations over which the middle phases persist seems larger for the systems with low-equivalent-weight organic salts than for those in the literature for surfactants. This perhaps in part accounts for the nonattainment of ultralow interfacial tensions between top and bottom phases here—concentrations in the midpoints of coexistence of three phases are too far from those of critical end points. Another factor might be that the chemical potential of the protosurfactant component varies with its concentration more than that of a surfactant, because of the greater aggregation of the surfactant; by scaling laws, interfacial

TABLE II: System *n*-Octane/Water/1-Butanol/NaCl/Protosurfactant at 28 °C

protosurfactant	1-butanol, wt % of total system	interfacial tensions, dyn/cm		
		top vs. bottom	top vs. middle	middle vs. bottom
sodium *p*-cymenesulfanate	9		0.095	0.14
(4 wt % sulfonate of total system,	11		0.056	0.14
12 wt % NaCl in H_2O)	12		0.042	0.31
	14.5		0.048	
sodium *p-tert*-butylbenzoate	10		0.11	0.071
(4 wt % benzoate of total system,	14		0.011	
8 wt % NaCl in H_2O)				
sodium 2,5-diisopropylbenzenesulfonate	0	solid + liquid		
(4 wt % sulfonate of total system,	2	0.90		
5 wt % NaCl in H_2O)	3	0.52		
	4	0.34		
	5	0.33		
	6	0.17		
	7	0.12		
	8	0.15		0.041
	9	0.16		0.065
	10	0.06		
	11	0.21	0.008	0.15
sodium 3,5-diisopropylsalicylate	3.5	0.096	0.13	0.0001
(2 wt % salicylate of total system,	3.7	0.16	0.12	0.002
4 wt % NaCl in H_2O)	4	0.19	0.21	0.029
	5	0.22	0.22	0.017
	6	0.066		0.022
	7	0.14		0.044
	8	0.14		

TABLE III: System *n*-Octane/Water/1-Butanol/NaCl/Protosurfactant at 28 °C

protosurfactant	protosurfactant, wt % in total system	interfacial tensions, dyn/cm		
		top vs. bottom	top vs. middle	middle vs. bottom
sodium *p*-cymenesulfonate	3			0.012
(6 wt % 1-butanol of total system,	5.5	0.10		
12 wt % NaCl in H_2O)				
sodium *p-tert*-butylbenzoate	3	0.18	0.14	0.0015
(6 wt % 1-butanol of total system,	4.5		0.18	0.0005
8 wt % NaCl in H_2O)	5	0.17		
	6	0.19		
	7	0.22		
sodium 2,5-diisopropylbenzenesulfonate	0.5	0.13		
(6 wt % 1-butanol of total system,	1	0.13		0.019
5 wt % NaCl in H_2O)	2	0.17	0.053	0.0065
	3	0.13		0.022
	4	0.17	0.072	0.020
	5	0.20	0.098	0.009
	6	0.18	0.23	0.0002
	6.6	0.079		
	6.8	0.10		0.0001
	6.9	0.24		
	7	0.18		
	7.2	0.17		
	8	0.16		
	9	0.11		
sodium 3,5-diisopropylsalicylate	0.7	0.067		0.053
(4 wt % 1-butanol of total system,	1	0.069		0.017
4 wt % NaCl in H_2O)	2.2		0.089	0.0015
	2.4		0.18	0.0010
	2.7		0.15	0.0029
	2.9	0.018	0.002	0.0006
	4	0.19		
	5	0.21		
	6	0.22		

tension is dependent on the difference in chemical potential from the value at the critical point. A third reason might be that tensions scale down, as critical conditions are approached, from higher values for protosurfactants. However, values between oil and aqueous phases far from optimal conditions in surfactant-containing systems[15,16] are not obviously greatly lower than similar values in Tables I–III.

It has been the object of our studies to understand the fundamental chemistry underlying micellar floods and similar systems, rather than to develop compositions for them. However, if the compositional range of adequately low interfacial tension is not inherently too small, because of reasons cited above, for sufficient stability of favorable conditions, protosurfactant-containing systems would have some attractive features.

The concentrations of amphiphiles required to attain three-phase behavior with protosurfactants are comparable to those required with surfactants. The lower tendency to be adsorbed on minerals and the higher solubilities of salts of divalent cations of low-equivalent-weight salts would be important practical advantages in oil-recovery applications.[20] Exploration of only a minute fraction of the possible variables which could increase the oil-mobilization properties of these systems has been possible here. In view of the sharp differences obtained by variations in the alcohol variable alone,[6] it does not seem unlikely that conditions could be found for favorable interfacial tensions between all three phases.

In any case, many of the properties which have been attributed to the complex aggregation characteristics of surfactants seem to be also observed with protosurfactants, and some with systems in which alcohols are the only amphiphile.[33]

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1.3. Phase Composition of Aqueous/Hydrocarbon Systems Containing Organic Salts, Alcohol, and Sodium Chloride

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The phase compositions of five-component systems containing *n*-octane, water, 1-butanol, sodium chloride, and one of two low-equivalent-weight organic salts (protosurfactants) have been analyzed. The organic salts are sodium 2,5-diisopropylbenzenesulfonate or sodium 3,5-diisopropylsalicylate, both of which have six alkyl carbons on side chains of the benzene ring. The similarities earlier observed in phase behavior of protosurfactant systems and surfactant systems are extended in these results. The distribution of organic salts between phases with changes in composition follows the trends known for surfactants. Sodium chloride is concentrated in the lower phase, but significant amounts are found in the middle phase in three-phase systems. In the middle range of salinity and alcohol concentrations, at the onset of occurrence of three phases, the ratio of water to oil in the middle phase decreases as the salinity or alcohol concentration increases. The ratios of activity coefficients of sodium chloride in the middle phase to those in the aqueous phase are rather constant, and close to 1 despite the large differences in the media between the middle and bottom phases. However, the ratios of formal activity coefficients of these two protosurfactants in the middle phase to those in the aqueous phase are very small; the low activity coefficients of protosurfactants in the protosurfactant-rich phase suggest differences in aggregation in the two phases.

Introduction

In recent years, we have investigated the solubilization of hydrocarbons in water by a variety of organic salts, used both with and without alcohols.[1-7] Most of the organic salts were low-equivalent-weight alkylbenzenesulfonates, -carboxylates, and -salicylates. One of our motivations has been elucidation of the chemistry of enhanced oil recovery by micellar flooding.

In a previous paper,[8] we have reported volumes and interfacial tensions of five-component systems containing *n*-octane, water, 1-butanol, sodium chloride, and low-equivalent-weight organic salts (protosurfactant). In this paper we report analyses of coexisting phases in composition scans in the neighborhood of three-phase regions for systems containing either sodium 2,5-diisopropylbenzenesulfonate or sodium 3,5-diisopropylsalicylate and extend the comparison with similar surfactant systems containing high-equivalent-weight organic salts. From the results of phase analyses, some thermodynamic properties of protosurfactant systems can be inferred.

Other research groups[9,10] have studied surfactant systems by determination of the composition of each phase. In ref 9, Winsor type I → III → II transitions,[11] effected by varying salinity, alcohol, or surfactant concentrations and water-to-oil ratios, were investigated. Thermodynamic properties of surfactant-rich phases in equilibrium with the aqueous phase were inferred in ref 10. Here we report determinations of weight fractions of all components in each phase of five-component systems containing protosurfactants and also inferences of some thermodynamic properties.

Comparisons with the results in ref 9 and 10 are somewhat hindered by the fact that not all components were determined for the surfactant systems, the results were reported on a volume basis, and the compositions in ref 10 did not encompass three-phase regions.

Experimental Section

Materials. The sources of *n*-octane, 1-butanol, sodium 2,5-diisopropylbenzenesulfonate, sodium 3,5-diisopropylsalicylate, and NaCl used in this paper can be found in ref

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TABLE I

	uncertainty	overall uncertainty	uncertainty on material balance
compositional analyses			
GC determination (H_2O, 1-butanol, octane)	±5% (each)	±16%	±28%
UV analyses—protosurfactant	within 1%		
chloride analyses	within 1%		
phase volume reading	±10%	±15%	
phase density measurement	±5%		

TABLE II: Phase Compositions of System *n*-Octane/Water/1-Butanol/NaCl/Protosurfactant (28 °C) (Water/*n*-Octane Weight Ratio, 1:1)

Protosurfactant	$\frac{g\ NaCl}{gNaCl+gH_2O} \times 100$	Phase	Composition (Wt% in Phase) H_2O	1-BuOH	n-Octane	Protosurfactant	NaCl	Total	Phase Volume Fraction	Phase Density (g/cc)
Na 2,5-diisopropylbenzenesulfonate (4 wt% sulfonate. 6 wt% 1-butanol of total system)	3	t	0.045	5.1	96.8	0.034	0.003	101.9	0.54	0.70
		b	85.9	7.9	2.5	8.8	1.7	106.8	0.46	1.04
	6	t	0.04	6.0	90.8	--	--	96.9	0.51	0.70
		m	57.7	7.4	6.5	25.0	3.1	99.7	0.17	0.96
		b	87.1	3.0	0.3	1.0	8.0	99.4	0.32	1.06
	10	t	1.3	7.1	91.5	1.0	0.02	100.9	0.46	0.71
		m	29.4	17.0	22.6	24.5	1.0	94.5	0.16	0.96
		b	80.9	2.1	3.2	0.5	9.9	96.6	0.38	1.09
	11	t	6.5	9.1	75.8	0.6	0.06	92.1	0.51	0.74
		m	13.7	11.9	52.3	29.0	1.9	108.8	0.14	0.96
		b	73.7	1.7	0.3	0.4	12.1	88.2	0.35	1.09
	15	t	12.6	7.9	68.6	7.9	--	97.0	0.61	0.94
		b	87.5	0.9	0.45	0.2	15.8	104.9	0.39	1.19
Na 3,5-diisopropylsalicylate (2 wt% salicylate. 4 wt% 1-butanol of total system)	1	t	0.07	2.0	95.3	0.008	--	97.4	0.56	0.70
		b	84.7	4.6	0.8	3.7	1.0	94.4	0.44	1.02
	4	t	0.06	2.1	92.4	0.026	---	94.6	0.52	0.70
		m	48.1	11.7	13.9	14.3	2.0	90.0	0.13	0.93
		b	85.7	2.4	--	0.3	4.6	93.0	0.35	1.04
	6	t	0.27	2.3	88.7	0.43	--	91.7	0.49	0.70
		m	40.0	13.1	26.3	17.1	1.7	98.2	0.11	0.93
		b	84.4	1.94	0.054	0.2	5.8	92.3	0.40	1.10
	7	t	0.13	4.8	90.9	0.7	0.01	93.7	0.51	0.70
		m	28.9	13.9	37.8	20.0	0.9	101.5	0.08	0.87
		b	83.3	1.85	0.06	0.16	7.9	93.3	0.41	1.10
	8	t	2.54	4.8	82.7	3.1	0.1	93.4	0.60	0.74
		b	81.9	1.9	0.095	0.1	8.9	92.6	0.40	1.05

t - top phase, m - middle phase, b - bottom phase

1–8. 2-Propanol (certified ACS grade with boiling point range 81.7–82.1 °C (Fisher Scientific Co.)), which was used for preparation of GC standards and for sample dilutions, was dried over sodium metal and distilled. Only the portion with a boiling point range of 82.1–82.3 °C was collected. The water content of the fresh distilled 2-propanol was less than 0.1% (GC).

Methods. The samples were prepared as in ref 8. All quantities were determined by weighing, and compositions are presented as weight percentage. Sodium chloride is expressed as weight percent in water (g of NaCl/(g of H_2O + g of NaCl)) and all the other components are weight percent of the total systems. The ratio of water to hydrocarbon (WOR) is the weight ratio of water to hydrocarbon and is 1 throughout the study.

Protosurfactant and Sodium Chloride. The concentrations of protosurfactant in each phase were determined spectrophotometrically with a Perkin-Elmer UV–vis 559; sulfonate at 255–280 nm and salicylate at 255–315 nm. Sodium chloride was assayed by chloride analysis with a Buchler-Cotlove Chloridimeter. Precision of UV analyses is within ±1% and chloride analysis within ±1%.

n-Octane, 1-Butanol, and Water. The amounts of *n*-octane, 1-butanol, and water in each phase were determined by gas chromatography. A Perkin-Elmer Sigma 3 with hot wire detector equipped with a Spectra-Physics integrator was used. A 6 ft × $^1/_8$ in. o.d. stainless-steel column packed with 80–100 mesh Porapak Q (Waters Associates) was used. Column temperature was programmed from 90 (4-min hold) to 200 °C with an increase of 10 °C/min. Helium carrier gas with inlet pressure at 75 psig was used. The instrument was calibrated by using standard solutions of *n*-octane, 1-butanol, and water in 2-propanol. They were prepared by weight. The amounts of 1-butanol in all three phases, water in the top phase, and *n*-octane in the bottom phase were determined with samples directly withdrawn from each phase. Aliquots of top, middle, and bottom phases were diluted with 2-propanol in order to determine the large quantity of water and *n*-octane in these phases. Accuracies of gas-chromatographic analyses were about ±5%.

The density of each phase was determined by weighing an empty 100-μL microsyringe with a Sartorius semimicrobalance first, and then the syringe with 100 μL of sample. Duplicates agreed to within 5%.

Deviations arise from many sources. The estimated uncertainties of compositional analyses and their formal effect on overall material balances are summarized in Table I. The actual overall material balances for the total system generally were much better than the estimate of approximately 30% uncertainty (usually less than 5%). However, the material balances for individual components in the total system (particularly NaCl) sometimes approached this deviation.

Results

The analyses of coexisting phases in the neighborhood of three phase regions are presented in the same pattern as in the previous paper on phase volumes, as scans of one compositional variable, i.e., salinity, alcohol, or protosur-

TABLE III: Weight Ratios of Protosurfactant to 1-Butanol in Coexisting Phases

Protosurfactant	Wt% protosurfactant in total system	Wt% 1-Butanol in total system	gNaCl / (gH$_2$O + gNaCl) %	Wt Ratio protosurfactant/1-butanol: In total system	Top phase	Middle phase	Bottom phase	Number Phases
Na 2,5-diisopropylbenzene sulfonate	4	6	3	0.67	0.007		1.11	2
	4	6	6	0.67	---	3.38	0.33	3
	4	6	10	0.67	0.14	1.44	0.24	3
	4	6	11	0.67	0.065	2.44	0.24	3
	4	6	15	0.67	1.00		0.22	2
	4	3	5	1.00	---		1.34	2
	4	9	5	0.44	0.04	1.49	0.26	3
	4	10	5	0.40	0.04	0.57	0.19	3
	4	12	5	0.33	0.28		0.20	2
	4	15	5	0.27	0.28		0.18	2
	3	6	5	0.50	0.005	1.04	0.76	3
	5	6	5	0.83	---	0.83	0.65	3
	8	6	5	1.33	0.007		2.27	2
Na 3,5-diisopropylsalicylate	2	4	1	0.50	0.004		0.80	2
	2	4	4	0.50	0.012	1.22	0.13	3
	2	4	6	0.50	0.19	1.31	0.10	
	2	4	7	0.50	0.15	1.44	0.09	3
	2	4	8	0.50	0.65		0.05	2
	2	3	4	0.67	---		0.77	2
	2	4	4	0.50	0.012	1.22	0.13	3
	2	6	4	0.33	0.065	0.96	0.069	3
	2	7	4	0.29	0.082	0.82	0.05	3
	2	8	4	0.25	0.40		0.067	2
	1	4	4	0.25	0.012	0.95	0.069	3
	2.2	4	4	0.55	0.038	0.94	0.094	3
	4	4	4	1.00	0.047		1.14	2
	5	4	4	1.25	---		1.28	2

factant, the others being fixed.

Effect of Salinity. Table II gives the phase compositions as the salinity increases in the systems of *n*-octane/water/1-butanol/NaCl/protosurfactant. In the system with sodium 2,5-diisopropylbenzenesulfonate, sulfonate is 4% and 1-butanol is 6% of the weight of the total system. The weight percentage of sodium 3,5-diisopropylsalicylate is 2% and 1-butanol is 4% of the total system in the system with sodium diisopropylsalicylate as protosurfactant. The salinity in both systems is expressed as g of NaCl/(g of NaCl + g of H_2O).

The information available is sufficient to define tie surfaces of three-phase systems whose apexes locate the composition of coexisting phases. However, with five components, representation in a plane or in a three-dimensional space is not possible. To convey an impression of the effect on three-phase composition of the component scanned, we have plotted the three-phase results in a tetrahedron with two components combined in one apex. In Figure 1, a and b, are plotted the planes of the pseudo-tie triangle with one apex the fixed protosurfactant–alcohol ratios of total system (the ratio of sulfonate to 1-butanol is 2:3 and salicylate to 1-butanol is 1:2). The ratios of protosurfactant to alcohol in each phase however are not constant (see Table III), as they also are not in surfactant systems.[9,10,12–14] In Figure 1, a and b, higher salinity increases the water content of the octane-rich (top) phase and lowers the total amphiphilic (alcohol plus protosurfactant) concentration in the aqueous (bottom) phase.

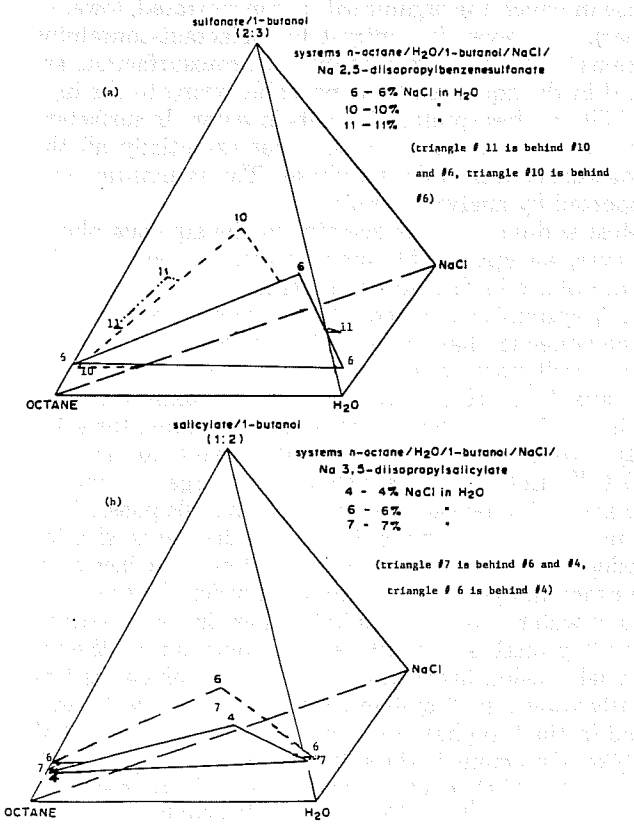

Figure 1. Pseudo-tie triangles of *n*-octane/1-butanol/H_2O/NaCl/protosurfactant systems: salinity scan.

At low salinity (below 5% NaCl in the sulfonate systems and 4% NaCl in the salicylate systems), the systems are of type 2_L; i.e., the system is two phase and the protosurfactant is rich in the aqueous (lower) phase. On in-

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TABLE IV: Phase Compositions of System *n*-Octane/Water/1-Butanol/NaCl/Protosurfactant (28 °C) (Water/*n*-Octane Weight Ratio, 1:1)

Protosurfactant	Wt% 1-Butanol of Total System	Phase	Composition (wt% in phase) H_2O	1-BuOH	n-Octane	Protosurfactant	NaCl	Total	Phase Volume Fraction	Phase Density (g/cc)
Na 2,5-diisopropylbenzenesulfonate 4 wt% sulfonate of total system. 5 wt% NaCl in H_2O	3	t	0.045	0.4	94.1	—	—	94.5	0.55	0.70
		b	70.4	5.8	2.4	7.8	4.8	91.2	0.45	1.03
	9	t	0.15	9.4	92.0	0.4	—	102.0	0.47	0.71
		m	56.1	13.6	11.6	20.2	1.0	101.3	0.19	0.92
		b	83.7	3.4	0.2	0.9	5.8	94.0	0.34	1.04
	10	t	0.4	9.2	92.4	0.4	—	102.4	0.46	0.74
		m	29.4	27.4	26.9	15.5	0.8	100.0	0.20	0.92
		b	84.0	3.6	0.2	0.7	5.3	93.8	0.34	1.04
	12	t	26.6	16.6	49.6	4.7	—	97.5	0.66	0.82
		b	80.1	3.0	0.07	0.6	5.8	89.6	0.34	1.10
	15	t	24.9	22.9	53.9	6.5	—	108.2	0.68	0.82
		b	85.6	2.8	0.14	0.5	5.8	94.8	0.32	1.10
Na 3,5-diisopropylsalicylate (2 wt% salicylate of total system. 4 wt% NaCl in H_2O)	3	t	0.07	2.0	89.2	—	—	91.1	0.56	0.70
		b	73.1	4.8	3.0	3.7	3.9	88.1	0.44	1.02
	4	t	0.06	2.1	92.4	0.026	—	94.6	0.52	0.70
		m	48.1	11.7	13.9	14.3	2.0	90.0	0.13	0.93
		b	85.7	2.4	—	0.3	4.6	93.0	0.35	1.04
	6	t	0.15	3.1	96.9	0.2	—	100.4	0.53	0.70
		m	41.0	14.5	20.2	13.9	0.7	90.3	0.13	0.96
		b	86.6	2.9	2.8	0.2	4.3	96.8	0.34	1.03
	7	t	1.0	9.7	87.7	0.8	—	99.2	0.52	0.70
		m	36.7	15.3	25.5	12.6	1.1	91.2	0.09	0.96
		b	86.0	3.9	0.3	0.2	4.8	95.2	0.39	1.03
	8	t	5.6	12.2	70.4	4.9	0.1	93.2	0.60	0.73
		b	86.5	3.0	0.1	0.2	5.0	94.8	0.40	1.03

t - top phase, m - middle phase, b - bottom phase

creasing salinity, three phases occur, and protosurfactant is largely in the middle phase. At higher salintiy, the system reverts to two phases, and protosurfactant is found mostly in the organic phase (2^U) (L and U refer to the phase in which the organic salt is concentrated, lower or upper). However, in contrast to surfactant-containing systems,[9,10] fairly large amounts of protosurfactant are found in the aqueous phase, probably owing to the high solubility of these protosurfactants in water. In surfactant systems, it is usually assumed that essentially all the surfactant is in the micellar phase. The assumption was supported by analysis in ref 9.

Most sodium chloride remains in the aqueous phase; however, an appreciable amount can be found in the middle phase in three-phase systems.

In 2_L systems, large amounts of *n*-octane are dissolved in the aqueous phase, about 0.26 mol of *n*-octane/kg of H_2O in sulfonate systems at 3% NaCl and 0.08 mol of *n*-octane/kg of H_2O in the salicylate systems with 1% NaCl. Without protosurfactant and 1-butanol, the solubility of *n*-octane in water is only about 5.8×10^{-7} mol/kg of H_2O.[15] In three-phase systems, very large amounts of *n*-octane and water can be found in the middle phase. The amount of water in the middle phase decreases with increasing salinity, whereas the amount of *n*-octane increases. In surfactant systems, the salinity in which the (volume) ratio of water to oil in the middle phase is 1 is referrd to as the "optimal" salinity.[16] At this composition, the interfacial tension between oleic and water phases is frequently lowest. In 2^U systems, a large amount of water was found in the top phase (organic phase), about 10 mol of H_2O/kg of *n*-octane in the sulfonate system at 15% NaCl and 2 mol of H_2O/kg of *n*-octane in the salicylate system at salinity of 8% NaCl. The literature[17] solubility of water in *n*-octane alone is only 0.08 mol of H_2O/kg of *n*-octane.

Effect of Alcohol Concentration. The phase analyses of the scans of alcohol (1-butanol) content for systems

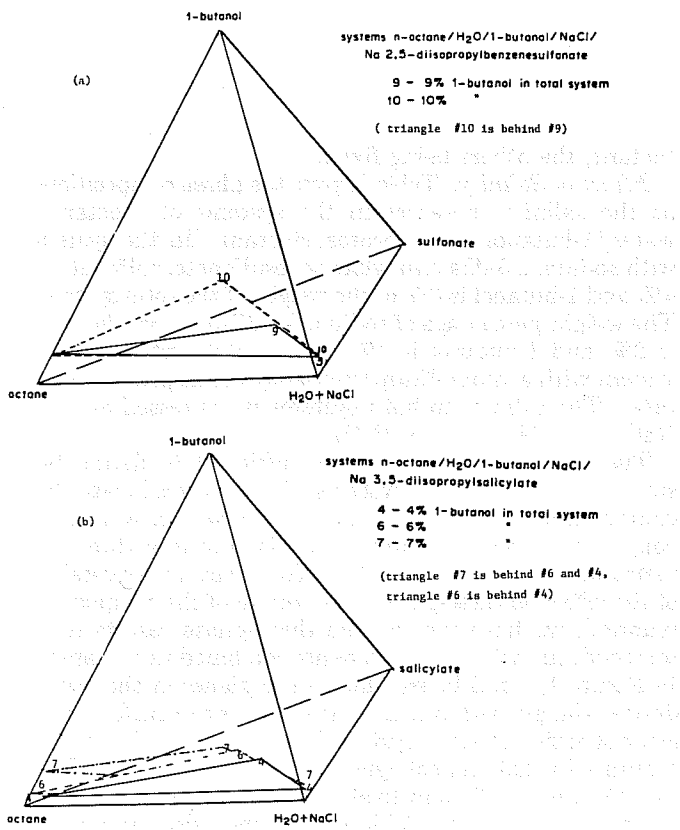

Figure 2. Pseudo-tie triangles of *n*-octane/1-butanol/H_2O/NaCl/protosurfactant systems: the effect of alcohol concentrations.

containing these two protosurfactants are given in Table IV. In systems with sulfonate, sodium sulfonate is 4% of the weight of the total system and salinity is 5 wt% NaCl in water; in systems with salicylate, sodium salicylate is 2% of the total system, and salinity is 4 wt % in water. The salinities were chosen at the onset of three phases in the salinity scans discussed above. The planes of the pseudo-tie triangle in Figure 2, a and b, were plotted in a tetrahedron with *n*-octane, 1-butanol, protosurfactant,

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TABLE V: Phase Compositions of System *n*-Octane/Water/1-Butanol/NaCl/Protosurfactant (28 °C) (Water/*n*-Octane Weight Ratio, 1:1)

Protosurfactant	Wt% Protosurfactant in Total System	Phase	Composition (wt% in phase) H_2O	1-BuOH	n-Octane	Protosurfactant	NaCl	Total	Phase Volume Fraction	Phase Density (g/cc)
Na 2,5-diisopropylbenzenesulfonate (6 wt% 1-butanol of total system. 5 wt% NaCl in H_2O)	3	t	0.15	4.4	92.4	0.02	0.002	97.0	0.54	0.72
		m	52.2	13.7	11.8	14.2	2.0	93.9	0.13	0.96
		b	85.7	2.5	4.3	1.9	5.5	99.9	0.33	1.02
	5	t	0.09	4.4	86.3	–	–	90.8	0.51	0.72
		m	64.4	13.0	8.5	10.8	3.2	99.9	0.24	0.99
		b	84.0	3.4	0.4	2.2	6.0	96.0	0.25	1.02
	8	t	0.04	1.4	97.5	0.01	0.009	99.0	0.46	0.70
		b	63.0	6.7	5.0	15.2	3.9	93.8	0.54	1.02
Na 3,5-diisopropylsalicylate (4 wt% 1-butanol of total system. 4 wt% NaCl in H_2O)	1	t	0.11	3.4	91.9	0.04	0.003	95.5	0.56	0.70
		m	45.6	15.3	22.1	14.6	1.4	99.0	0.06	0.96
		b	92.2	2.9	0.05	0.2	4.2	99.3	0.38	1.01
	2.2	t	0.09	1.2	102.0	0.046	–	103.3	0.51	0.70
		m	56.7	13.9	11.7	13.0	1.8	97.2	0.15	0.96
		b	80.4	3.2	0.23	0.3	4.4	88.5	0.34	1.01
	4	t	0.3	1 5	94.0	0.07	–	95.8	0.53	0.70
		b	69.8	5.8	6.4	6.6	3.8	92.4	0.47	1.02

t - top phase, m - middle phase, b - bottom phase

and NaCl + H_2O as the four apexes. The distribution of protosurfactant in each phase at fixed salinity with the variation of alcohol concentration is similar to salinity scans; i.e., at lower alcohol concentration most protosurfactant and NaCl are in the aqueous phase (2_L). At intermediate concentration, most protosurfactant is in the middle phase and a substantial amount of sodium chloride is also in the middle phase, although NaCl stays predominantly in the aqueous phase. At high alcohol concentration, large amounts of protosurfactant are in the top phase (2^U). The *n*-octane and 1-butanol distributions follow a pattern similar to the salinity scans. The transitions from $2_L \rightarrow 3$ phases $\rightarrow 2^U$ can be effected by adding alcohol just as by adding salt. The behavior again parallels that of surfactant systems.

Effect of Protosurfactant Concentration. Table V gives the results of scans of protosurfactant concentration, the other compositional variables being fixed. The sodium chloride and 1-butanol concentrations were selected to emphasize the three-phase region. Three phases occurred with as low as 0.5% (of total system) sodium 2,5-diisopropylbenzenesulfonate and with less than 0.5% sodium 3,5-diisopropylsalicylate. The volume of the middle phase increases with increasing protosurfactant concentrations and reaches a maximum value before the disappearance of the third phase. At the same time, the weight fraction of water in the middle phase increases, and that of *n*-octane decreases. It is interesting to find that the volume of the middle phase increases with increasing ratio of water to oil in the phase and reaches a maximum before the transition to two-phase systems. Figure 3, a and b, was plotted by the same way as in Figure 2, in that the planes of the triangles of the three-phase systems are shown within a tetrahedron with NaCl + H_2O as a pseudocomponent. As the protosurfactant concentration in the total system increases, the altitude of the pseudo-tie triangle gradually reduces and finally the middle phase merges with the aqueous phase. From the phase compositions in Table V, the amount of NaCl in the middle phase was fairly large in three-phase systems.

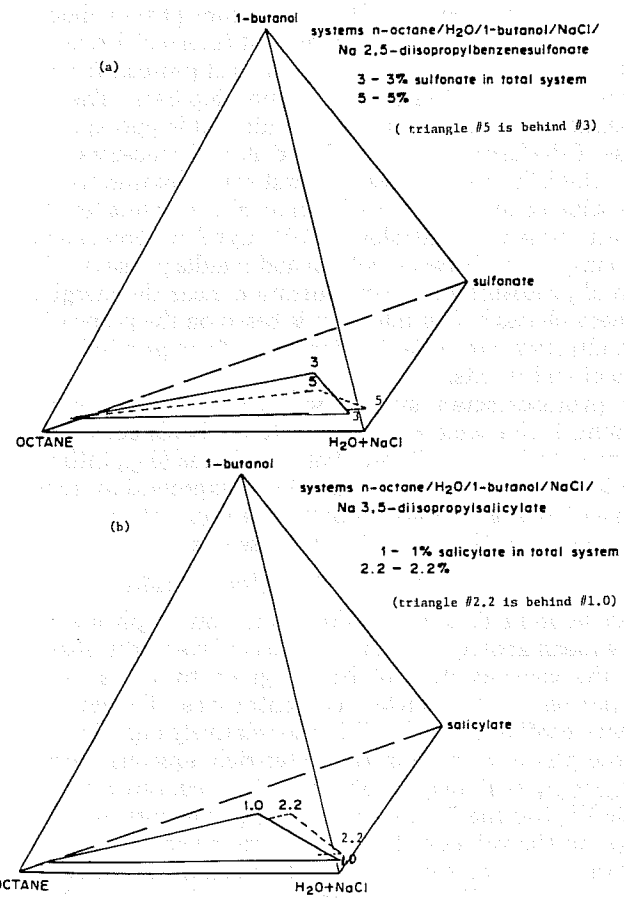


Figure 3. Pseudo-tie triangles of *n*-octane/1-butanol/H_2O/NaCl/protosurfactant systems: the effect of protosurfactant concentrations.

Discussion

From analyses of phases of at systems, Baviere et al.[9] found that there is a linear relationship between the logarithm of water-to-oil ratio (volume ratio) in the middle phase and salinity (or alcohol content). In these protosurfactant systems, we find also that, when the logarithms of water-to-oil (weight) ratios of the middle phase in three-phase systems are plotted vs. salinity or 1-butanol content, a linear relationship holds (Figure 4, a and b), although the number of data points in the sulfonate systems is limited, and the points somewhat scattered.

According to Healy and Reed[16] at salinity (or alcohol content) where the (volume) ratio of solubilized water to solubilized oil is about equal to 1, the interfacial tension between top (oil) and bottom (aqueous) phase should be a minimum, and the curves for IFT between top and

TABLE VI: Salt Activity Ratios in Middle and Bottom Phases of Protosurfactant Systems (Water/*n*-Octane Weight Ratio, 1:1)

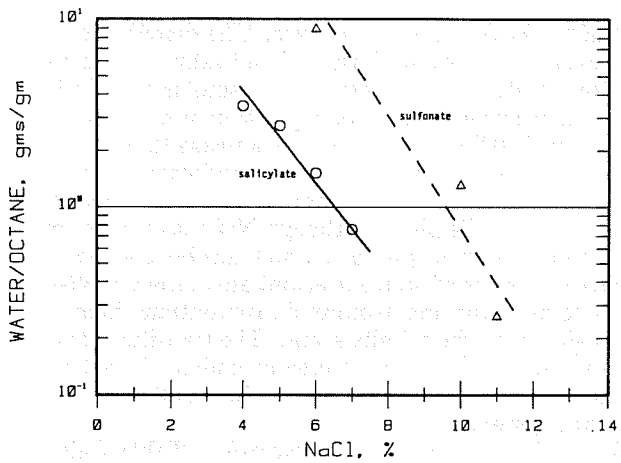
Protosurfactant	wt% protosurfactant in total system	wt% 1-butanol in total system	$\frac{g\ NaCl}{gH_2O + gNaCl}$ %	$\left(\frac{moles\ Na^+}{kg\ H_2O}\right) \times \left(\frac{moles\ Cl^-}{kg\ H_2O}\right)$ bottom phase	middle phase	Γ	$\left(\frac{moles\ Na^+}{kg\ H_2O}\right) \times \left(\frac{moles\ SO_3^-\ (or\ CO_2^-)}{kgH_2O}\right)$ bottom phase	middle phase	Γ′
Na 2,5-diisopropylbenzenesulfonate	3	6	5	1.3	1.1	1.1	0.099	1.7	0.24
	5	6	5	1.6	1.26	1.1	0.14	0.94	0.39
	4	6	6	2.6	2.4	1.0	0.07	4.2	0.13
	4	6	10	4.4	2.2	1.4	0.05	11.8	0.07
	4	6	11	8.0	23.0	0.6	0.06	47.3	0.04
	4	9	5	1.45	0.5	1.7	0.05	2.24	0.15
	4	10	5	1.2	1.1	1.0	0.04	4.92	0.09
Na 3,5-diisopropylsalicylate	1	4	4	0.61	0.95	0.8	0.007	2.4	0.054
	2.2	4	4	0.9	0.8	1.1	0.0145	1.4	0.10
	2	4	4	0.66	0.4	0.7	0.013	2.3	0.076
	2	4	6	1.4	1.8	0.9	0.01	4.3	0.05
	2	4	7	2.6	1.8	1.2	0.013	9.5	0.04
	2	6	4	0.7	0.5	1.2	0.008	2.33	0.06
	2	7	4	0.9	0.98	0.96	0.009	2.7	0.06

middle and between middle and bottom phases should intersect. With the small changes of interfacial tension with salinity (or alcohol content) scans of protosurfactant systems,[8] we cannot verify this relationship here. The low dependence of IFT on salinity or alcohol is perhaps because of the large range of NaCl and alcohol concentrations over which the middle phases persist with protosurfactant. The wide concentration region may also account for the nonattainment of ultralow ($<10^{-3}$ dyn/cm) interfacial tensions, except between bottom and middle phases in the scan of protosurfactant concentration, near the merging of these phases.[8] This inference is based on the proposal[18] that ultralow interfacial tension arises from proximity to critical end points.

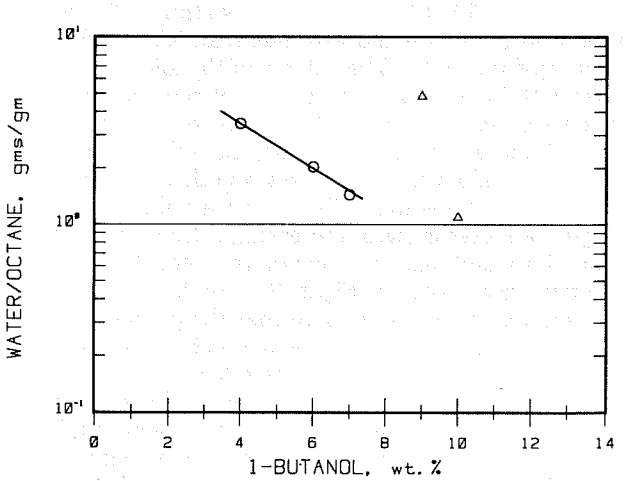
In protosurfactant systems with three phases in equilibrium, if the same reference state for NaCl activity is assigned for the middle and bottom phases (e.g., infinite dilution in water), and concentration is expressed in terms of mol of ions/kg of water in both phases (m), the equality of activities of NaCl may be expressed as

$$(m_{Na})_b(m_{Cl})_b(\gamma_\pm)_b^2 = (m_{Na})_m(m_{Cl})_m(\gamma_\pm)_m^2$$

where m and b denote the middle and bottom phases, $\gamma_\pm$ is the mean activity coefficient of electrolyte in the phase, and the concentration of Na^+ is given by the sum of chloride and protosurfactant concentrations. The ratio of activity coefficients of NaCl in the relatively organic-rich middle phase to those in the water-rich aqueous phase, $(\gamma_\pm)_m/(\gamma_\pm)_b = \Gamma$, may be obtained from concentrations. Table VI gives the Γ values of all three-phase systems. The ranges in the values of these ratios are all small, despite the large differences in the media between the middle and bottom phases. The narrow range of Γ values of NaCl is at first glance surprising. Analogous behavior is known to occur, however, in organic ion-exchange resins, which Bauman and Eichhorn[19] suggest can be considered highly ionized salt solutions. Values of Γ within a factor of 2 of unity are computed from measurements of co-ion uptake[20,21] in contact with solutions of moderate to high outside electrolyte concentrations. Analysis of the small concentrations of water and chloride in the *n*-octane-rich top phases here are not sufficiently accurate to compute the meaningful values of Γ, but in any case, at very low water contents, Γ is not expected to be close to 1.[22]



Ratio of Weight of Water to Weight of Hydrocarbon in the Middle Phase as a function of gms NaCl/(gms NaCl + gms water)
Composition (wgt % of total system)
○ 2% sodium 3,5 diisopropyl salicylate, 4% 1-butanol
△ 4% sodium 2,5 diisopropyl benzene sulfonate, 6% 1-butanol
water/n-octane wgt ratio, 1/1



Ratio of Weight of Water to Weight of Hydrocarbon in the Middle Phase as a Function of Weight Percentage 1-Butanol in Total System
○ 2% sodium 3,5-diisopropylsalicylate, 4% NaCl in water
△ 4% sodium 2,5-diisopropylbenzene sulfonate, 5% NaCl in water
Water/n-octane wgt ratio, 1/1

Figure 4. Ratio of weight of water to weight of hydrocarbon in the middle phase as a function of g of NaCl/(g of NaCl + g of water) (or of weight percentage 1-butanol in total system).

(18) Fleming, P. D., III; Vinatieri, J. E.; Glinsmann, G. R. *J. Phys. Chem.* **1980**, *84*, 1526.
(19) Bauman, W. C.; Eichhorn, J. J. *J. Am. Chem. Soc.* **1947**, *69*, 2830.
(20) Gregon, H. P.; Gottlieb, M. H. *J. Am. Chem. Soc.* **1953**, *75*, 3539.
(21) Nelson, F.; Kraus, K. A. *J. Am. Chem. Soc.* **1958**, *80*, 4154.

Tosch et al.[10] have determined the distribution ratios of water, alcohol, and electrolytes in equilibrated micellar and aqueous phases of systems containing hydrocarbon, alkylarylsulfonate, isopropyl alcohol, water, and sodium sulfate. If the same reference state for Na_2SO_4 activity is assigned for the micellar phase (top phase in this reference) and aqueous phase (bottom phase), and concentration is also expressed as mols/kg of H_2O, the ratios of activity coefficients of Na_2SO_4 in micellar phase to those in aqueous phase are found to be in the range of 0.5–0.9. We have also checked three-phase surfactant systems either with mixtures of hydrocarbon and mixtures of surfactants[12] or with pure components[13,14] and calculated the ratios of activity coefficients of inorganic electrolyte in the micellar phase (middle phase in all three references) to those in water-rich phase in the same way as above and found the Γ_{NaCl} value to be in the vicinity of unity. (For example, in Table II of ref 12, the amounts of TRS-410 in middle phases of the listed four sets of samples were 0.178, 0.384, 0.519, 0.617 mols/kg of H_2O and zero in all bottom phases. The amounts of NaCl in middle phases were 0.153, 0.093, 0.090, 0.059, and in bottom phases were 0.177, 0.248, 0.267, 0.303 mol/kg of H_2O correspondingly. The calculated Γ_{NaCl} values are 0.79, 1.18, 1.14, and 1.52.) This thermodynamic property of protosurfactant systems is thus similar to surfactant systems.

Table VI gives the ratio of activity coefficients of protosurfactant in the relatively organic-rich middle phase to those in the water-rich aqueous phase. The data were treated the same way as with NaCl and the concentration of Na^+ ion was again taken as the sum of chloride and of protosurfactant. The values are found to be very small; the low activity of protosurfactants in the protosurfactant-rich phase suggests differences in aggregation or association in the two phases. It seems likely that the aggregates involve other components. Since literature reports in surfactant systems known to us assume that there is essentially no surfactant in aqueous phases coexisting with a micellar phase, the ratios of activity coefficient of surfactant in the micellar rich phase to those in the aqueous phase cannot be compared to protosurfactant systems. To the extent this assumption is correct, Γ of the surfactants is much smaller than Γ for protosurfactants.

In representations of phase behavior of systems of more than three components in two dimensions, two of the components are frequently combined into a single apex, as in several of the figures here. It is generally recognized that this procedure is only exact in locating boundaries between single-phase and multiphase regions, because the ratios of the two are in general not the same in the coexisting phases (i.e., tie lines cannot be accurately drawn). Table II illustrates the wide variations in the ratios of surfactant surrogate/alcohol in the systems reported here. Combination of these two components is common in the literature of micellar-flood systems. Analyses of the surfactant in other than the microemulsion phase are rarely reported, but, in a salinity scan, values of the ratio in the middle phase of surfactant to isobutyl alcohol[12] vary from 1.85 to 4.17 and the ratio in the oil phase for the 4.17 value was 0.45. Definition of pseudocomponents, which may include contributions of positive or negative amounts of all actual components, for each apex has been proposed to allow a more accurate representation of phase behavior.[23]

The ratios in Table III strain the accuracy of analysis, but through the scatter some trends are apparent. The ratios of protosurfactant to cosurfactant are generally higher in the protosurfactant-rich phases. Although the ratios of the two are far from constant, there is a tendency for alcohol concentration to be highest in the phases in which the protosurfactant is highest.

Acknowledgment. We are very much indebted to Dr. J. S. Johnson, Jr., of the Oak Ridge National Laboratory Chemistry Division for many helpful suggestions and discussions. This research was sponsored by the Office of Oil, Gas, and Shale, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide corp.

Registry No. *n*-Octane, 111-65-9; 1-butanol, 71-36-3; sodium chloride, 7647-14-5; sodium 2,5-diisopropylbenzenesulfonate, 15763-80-1; sodium 3,5-diisopropylsalicylate, 79427-97-7.

(22) Kraus, K. A.; Raridon, R. J.; Baldwin, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 2571.

(23) Fleming, P. D., III; Vinatieri, J. E. *J. Chem. Phys.* **1977**, *66*, 3147.

2. Osmotic Coefficients of Protosurfactant Solutions

Although formation of large micelles by the low-alkyl-carbon organic salts we call protosurfactants is not expected, complexes comprised of a few units would not be surprising. Low values of activity coefficients, in comparison with those of simple inorganic salts, might give an indication of the presence of aggregates. We have carried out isopiestic measurements of water activity in aqueous solutions of alkylbenzene sulfonates and carboxylates, and of salicylates, and computed solute activities from them. Our analysis of results with the sulfonates has progressed enough to be reported in the following. Briefly, in compounds having four or more alkyl carbons, the results are consistent with the formation of small complexes, but it is not feasible to conclude which species dominate.

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OSMOTIC COEFFICIENTS OF LOW-EQUIVALENT-WEIGHT ORGANIC SALTS+

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ABSTRACT

Results of isopiestic measurements at 25°C for aqueous solutions of sodium *p*-toluenesulfonate, sodium 2,4-dimethylbenzenesulfonate, sodium 2-methyl-5-*iso*propylbenzenesulfonate(Na *p*-cymenesulfonate), and sodium 2,5-di*iso*propylbenzenesulfonate are reported. Values of the osmotic coefficients decline more rapidly with increasing molality for compounds of higher alkyl substitution. Activity coefficients were computed from least-squares fits to the water activities.

Low-equivalent-weight organic salts fall between simple inorganic salts, such as NaCl, and surfactants. We are interested here in this intermediate class, which we refer to as <u>protosurfactants.</u> The results to be reported involve compounds of up to six alkyl carbons. In aqueous solutions, such salts are not usually presumed to form the micellar aggregates, comprised of tens of molecules, or the even more complicated liquid crystal structures, that salts with polar groups and long alkyl chains frequently do. Nevertheless, systems containing them share many properties typical of those containing surfactants.

It has been recognized that many protosurfactants are effective hydrotropes, i.e., they can solubilize substantial quantities of hydrocarbons in water; in some cases, their ability to effect this equals or exceeds the ability of many compounds in the surfactant class.[1,2] With alcohols (1-butanol for example) added to the system, solubilization of hydrocarbons is greatly increased at high protosurfactant concentrations,[2-6] and at lower concentrations, middle phases rich in the protosurfactant component may occur.[7] If inorganic salt as a fifth component is also present, the phase volumes as a function of NaCl or of alcohol concentration, the other concentrations being fixed, frequently exhibit[8] a pattern common in surfactant-containing systems:[9] a progression from two phases, protosurfactant predominantly in the lower; to three phases, the middle rich in protosurfactant, and again to two phases, the organic salt now largely in the upper (hydrocarbon-rich) phase. In some cases, interfacial tensions between adjacent phases are low, of the order of 10^{-2} dynes/cm, in protosurfactant systems.

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#Undergraduate Cooperative Education Student from the University of Tennessee, Knoxville.
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These parallels suggest that much of the chemical behavior sometimes attributed to the propensity of surfactants to form micellar aggregates has other origins. In fact, it has been proposed that many of these properties are related to proximity of critical points.[10-12] It is of course also possible that low-equivalent-weight organic salts also are aggregated to some degree or at least that the organic ions may interact strongly with one another.

Free energies of aqueous solutions might shed some light on this question. With respect to solutes closely related to those investigated here, values are available in the literature for alkali metal toluene-sulfonates[13,14,15] and for toluenesulfonic[15,16] acid alone or mixed with its sodium salt[14] or HCl.[17] Bonner and coworkers also report measurements on acids or salts of benzenesulfonate,[18] p-ethylbenzene-sulfonate,[18] 2,5-dimethylbenzene-sulfonate,[18,19] and 2,4,6-trimethyl-benzenesulfonate.[18] Several of these papers also provide data on disulfonates, the ionic group either on the same benzene ring[19] or on separate rings.[19,20,21] Sodium benzoate and hydroxy benzoates have been investigated by Desnoyers, et al.[22]

We report here isopiestic results for aqueous solutions of several sodium alkylbenzenemonosulfonates and for one system containing both a sulfonate and NaCl. All measurements were at 25°C.

EXPERIMENTAL

The organic electrolytes have been described in a previous paper.[1] Osmotic coefficients were measured by

$$\phi = -(55.51/\sum_i m_i)\ln a_S \qquad (1)$$

the isopiestic method, in which solutions are equilibrated to the same vapor pressure with a solution of a reference salt of known dependence of solvent activity (a_S, pure solvent being the standard state) on molality. The reference salts (subscript r) were NaCl or KCl, and the osmotic coefficients of NaCl and KCl were taken from ref. 13. The number 55.51 is for an aqueous solution and refers to the moles of water/kg solvent, and $\sum_i m_i$ is the total number of moles of solute ions/kg of solvent. Solute or solution of known molality, m, is initially weighed into cups, and the concentration determined after equilibration by weighing. Osmotic coefficients were computed from the equation

$$\phi = \frac{\nu_r m_r \phi_r}{\sum m_i} \qquad (2)$$

ν being the number of moles of ions per mole of electrolyte (here 2). The apparatus used allows simultaneous equilibration of twelve samples in platinum cups; two of these were usually duplicate reference and five other duplicates were unknown. A series was started with concentrated solutions, and after each equilibration, solvent was added to the cups, in different amounts to the duplicates, so that equilibrium was approached from different molalities. The apparatus and procedure is described in more detail in ref. 23.

RESULTS

TABLE 1 REPORTS THE RESULTS FOR TWO-COMPONENT SYSTEMS. REPRODUCIBILITY BETWEEN DUPLICATE CUPS AVERAGES ABOUT ± 0.002 IN ϕ FOR SODIUM DIISOPROPYLBENEZENESULFONATE, THE WORST CASE, AND THE RANGE WAS CONSIDERABLY SMALLER IN THE OTHERS.

FOR ONE OF THE PROTOSURFACTANTS, LITERATURE DATA ARE AVAILABLE.[24] FIGURE 1 COMPARES OUR RESULTS FOR SODIUM *p*-TOLUENESULFONATE WITH THOSE CALCULATED FROM THE ISOPIESTIC MOLALITIES IN REF. 24 WITH THE SAME EQUATION FOR ϕ OF THE STANDARD USED TO COMPUTE OUR VALUES. DIFFERENCES IN ϕ OF AS MUCH AS 0.025 BETWEEN THE TWO SETS OCCUR. BECAUSE IT IS DIFFICULT TO PREPARE THESE COMPOUNDS AS PURE OR AS WELL CHARACTERIZED AS COMMON INORGANIC SALTS, SOME DISCREPANCY BETWEEN SETS WOULD NOT BE SURPRISING. HOWEVER, IT IS NOT CLEAR WHY VALUES FOR THE INDIVIDUAL SETS ARE NOT CONSISTENTLY HIGHER OR LOWER THAN ONE ANOTHER. HERE, OUR ϕ VALUES ARE HIGHER AT LOW AND LOWER AT HIGH MOLALITY THAN THOSE OF ROBINSON. A FEW OF HIS VALUES FOR CONCENTRATIONS WHICH APPEARED TO BE HIGHER THAN THE SOLUBILITY WERE OMITTED FROM FIGURE 1.

TO CHECK THAT NO DEFICIENCIES HAD DEVELOPED IN THE EQUIPMENT OR IN OUR TECHNIQUE, KCL WAS RUN vs. NACL. WITH NACL[13] TAKEN AS STANDARD, VALUES OF ϕ_{KCL} AGREED WITH LITERATURE VALUES FROM THE SAME REFERENCE WITH AN AVERAGE DIFFERENCE OF ABOUT 0.002 IN ϕ.

THE OSMOTIC COEFFICIENTS WERE FIT TO AN EQUATION HAVING A DEBYE-HÜCKEL TERM (s = -1.1708 FOR 25°C IN AQUEOUS SOLUTIONS) AND A POWER SERIES IN IONIC STRENGTH, I (FOR THESE 1,1 ELECTROLYTES, THE SAME AS m),

$$\phi = 1 + \frac{\alpha^{DH}}{2} + \tfrac{1}{2}[a^{(1)}I + a^{(2)}I^2 + a^{(3)}I^3 + a^{(4)}I^4] \quad (3)$$

$$\alpha^{DH} = (2s/a^3 I)[1 + aI^{\frac{1}{2}} - \frac{1}{1 + aI^{\frac{1}{2}}} - 2\,\ln(1 + aI^{\frac{1}{2}})] \quad (4)$$

a BEING THE DEBYE-HÜCKEL DISTANCE-OF-CLOSET-APPROACH PARAMETER. THE LOWER LIMIT OF MOLALITY FOR WHICH ϕ CAN BE MEASURED WITH FAIR ACCURACY BY THIS TECHNIQUE IS TOO HIGH TO DETERMINE A PRECISE VALUE OF THE DEBYE-HÜCKEL a PARAMETER. CONSEQUENTLY, INSTEAD OF VARYING a IN THE LEAST-SQUARES ANALYSIS WE RAN FITS FOR EACH SOLUTE FOR A SERIES OF VALUES BETWEEN 1.0 AND 3.0 AT INTERVALS OF 0.5. FROM THE DEVIATIONS BETWEEN OBSERVED AND COMPUTED, WE SELECTED RATHER ARBITRARILY a's OF 2.0 FOR SODIUM TOLUENE- AND DIMETHYLBENZENESULFONATE, AND 2.5 FOR SODIUM CYMENE- AND DI*iso*-PROPYLBENZENESULFONATE, AND FIXED THESE IN THE FITS, FOR WHICH THE PARAMETERS ARE REPORTED IN TABLE 2. (FOR SODIUM *p*-CYMENE-SULFONATE, WE ALSO LIST IN TABLE 2 PARAMETERS WITH a FIXED AT 1.5, FOR PURPOSES OF DISCUSSION OF SOLUBILITIES.)

OTHER REASONABLE CHOICES FOR a WOULD HAVE HAD LITTLE INFLUENCE ON THE COMPUTED VALUES OF ϕ. TERMS THROUGH $a^{(4)}$ IMPROVED THE FITS. THE DEVIATIONS FROM THE LEAST SQUARES FIT WERE GREATER THAN THE ONE TO A FEW THOUSANDTHS IN ϕ WE HAVE CUSTOMARILY ATTAINED WITH SOLUTIONS OF INORGANIC SALTS (TABLES 1 AND 2 AND FIGURE 2). ALSO, EXCEPT FOR SODIUM *p*-TOLUENESULFONATE, THE ABSOLUTE MAGNITUDES OF

THE $a^{(\ )}$ POWER SERIES TERMS NECESSARY TO FIT THE DATA WERE MUCH GREATER THAN FOUND FOR STRONG INORGANIC ELECTROLYTES[25] NOT SUSPECTED OF FORMING POLYNUCLEAR SPECIES; THEY ARE LARGE EVEN COMPARED TO THOSE OF A 1:4 ELECTROLYTE, TUNGSTOSILICIC ACID.[26]

FROM THESE COEFFICIENTS, VALUES OF ACTIVITY COEFFICIENTS MAY BE COMPUTED BY THE EQUATION[27]:

$$\ln \gamma_{\pm} = \frac{SI^{\frac{1}{2}}}{1 + aI^{\frac{1}{2}}} + \tfrac{1}{2}(2a^{(1)}I + \frac{3}{2}a^{(2)}I^2 + \frac{4}{3}a^{(3)}I^3 + \frac{5}{4}a^{(4)}I^4) \qquad (5)$$

VALUES OF ϕ AND $\gamma_{\pm}$ AT ROUNDED MOLALITIES FROM THESE FITS ARE GIVEN IN TABLE 3.

THE ANALYSIS OF THE SODIUM *p*-CYMENESULFONATE (NA 2-METHYL-5-*iso*-PROPYLBENZENESULFONATE)-NACL-H_2O RESULTS (TABLE 4) WAS CARRIED OUT BY SIMILAR EQUATIONS FOR THREE-COMPONENT SYSTEMS.[28,29] THE EQUATION FOR OSMOTIC COEFFICIENTS INVOLVES α TERMS CALCULATED FROM THE COEFFICIENTS FROM THE FITS TO THE TWO-COMPONENT SYSTEMS AND β TERMS FROM FITS TO RESULTS FOR THE MIXTURES.

$$\phi = 1 + \frac{I}{\nu_A m_A + \nu_B m_B}\{\alpha_A + (\alpha_B - \alpha_A)\, y_B + \beta_{AB}^{(0)} y_B(1 - y_B) + \beta_{AB}^{(1)} y_B(1 - y_B)(1 - 2y_B)\} \qquad (6)$$

WHERE

$$\alpha_J = \frac{2S}{\mathbf{a}_J{}^3 I}\left[1 + \mathbf{a}_J I^{1/2} - \frac{1}{1 + \mathbf{a}_J I^{1/2}} - 2\ln(1 + \mathbf{a}_J I^{1/2})\right] + a_J{}^{(1)} I + a_J{}^{(2)} I^2 + a_J{}^{(3)} I^3 + a_J{}^{(4)} I^4 \qquad (7)$$

$$\beta_{AB}^{(0)} = b_{AB}^{(0,1)} I + b_{AB}^{(0,2)} I^2 + b_{AB}^{(0,3)} I^3 \qquad (8)$$

$$\beta_{AB}^{(1)} = b_{AB}^{(1,2)} I^2 + b_{AB}^{(1,3)} I^3 \qquad (9)$$

THE SUBSCRIPT A REFERS HERE TO THE PROTOSURFACTANT AND B TO NACL. y_J IS THE IONIC STRENGTH FRACTION OF COMPONENT J ($= I_J/\bar{I}$).

FOR MODERATELY GOOD FITS, CROSS TERMS $b_{AB}^{(0,1)}$, $b_{AB}^{(0,2)}$, $b_{AB}^{(0,3)}$, $b_{AB}^{(1,2)}$, AND $b_{AB}^{(1,3)}$ WERE ALL NEEDED (TABLE 5). FOR SUCH LOW IONIC STRENGTH SOLUTIONS, BOTH THE NUMBER AND THE NUMERICAL MAGNITUDE OF THESE CROSS-COEFFICIENTS ARE LARGE IN COMPARISON WITH SIMPLE INORGANIC SALTS.[25] (AN ALTERNATIVE SET OF PARAMETERS (B) IS GIVEN FOR THE DEBYE-HÜCKEL a SET AT 1.5.)

THE EQUATIONS FOR ACTIVITY COEFFICIENTS ARE AS FOLLOWS:

$$\ln \gamma_{\pm A} = \frac{I_A}{\nu_A m_A}[A_A + \alpha_A + (\alpha_B - \alpha_A)\, y_B + \beta_{AB}^{(0)} y_B + (B_{AB}^{(0)} - \beta_{AB}^{(0)})\, y_B{}^2 + \beta_{AB}^{(1)} y_B + 3(B_{AB}^{(1)} - \beta_{AB}^{(1)})\, y_B{}^2 - 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)})\, y_B{}^3] \qquad (10)$$

$$\ln \gamma_{\pm B} = \frac{I_B}{\nu_B m_B}[A_B + \alpha_B + (\alpha_A - \alpha_B)\, y_A + \beta_{AB}^{(0)} y_A + (B_{AB}^{(0)} - \beta_{AB}^{(0)})\, y_A{}^2 - \beta_{AB}^{(1)} y_A - 3(B_{AB}^{(1)} - \beta_{AB}^{(1)})\, y_A{}^2 + 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)})\, y_A{}^3] \qquad (11)$$

WHERE

$$(A_J + \alpha_J) = \frac{2SI^{1/2}}{1 + \mathbf{a}_J I^{1/2}} + 2a_J{}^{(1)} I + {}^3/_2 a_J{}^{(2)} I^2 + {}^4/_3 a_J{}^{(3)} I^3 + {}^5/_4 a_J{}^{(4)} I^4 \qquad (12)$$

$$B_{AB}^{(0)} = b_{AB}^{(0,1)}I + {}^1/_2 b_{AB}^{(0,2)}I^2 + {}^1/_3 b_{AB}^{(0,3)}I^3 \quad (13)$$

$$B_{AB}^{(1)} = {}^1/_2 b_{AB}^{(1,2)}I^2 + {}^1/_3 b_{AB}^{(1,3)}I^3 \quad (14)$$

VALUES OF OSMOTIC COEFFICIENTS AND ACTIVITY COEFFICIENTS AT ROUNDED VALUES OF IONIC STRENGTH AND IONIC STRENGTH FRACTIONS ARE GIVEN IN TABLE 6.

DISCUSSION

DESPITE THE EXPERIMENTAL SCATTER OF THE RESULTS, THERE ARE INFORMATIVE TRENDS. IN FIGURE 2, A TREND TOWARD STEEPER DECLINE IN ϕ WITH MOLALITY IS IMMEDIATELY APPARENT AT HIGHER DEGREES OF ALKYL SUBSTITUTION. VALUES AT LOW MOLALITIES FALL BELOW THOSE COMPUTED FROM THE DEBYE-HÜCKEL FOR REASONABLE VALUES OF THE $\dot{a}$ PARAMETER, A BEHAVIOR REFLECTED IN THE SUBSTANTIAL NEGATIVE VALUES OF THE POWER SERIES COEFFICIENTS (TABLE 3).

BONNER ET AL. REPORTED (PRESUMABLY SMOOTHED) ϕ-VALUES AT ROUNDED CONCENTRATIONS. FOR CONSISTENT COMPARISON WITH OUR RESULTS, WE FITTED THEM TO EQUATION 3, WITH DEBYE-HÜCKEL a PARAMETERS OF 2.0 FOR SODIUM BENZENESULFONATE, SODIUM 2,5-DIMETHYL-BENZENESULFONATE, AND SODIUM *p*-ETHYL-BENZENESULFONATE AND 2.5 FOR SODIUM 2,4,6-TRIMETHYLBENZENESULFONATE. THESE VALUES CORRESPOND TO THOSE ADOPTED FOR OUR RESULTS FOR SOLUTES OF COMPARABLE ALKYL SUBSTITUTION. THE ACTIVITY COEFFICIENTS IN FIGURE 3 ARE COMPUTED FROM EQUATION 5 WITH THE PARAMETERS OBTAINED FROM THE FIT. THEY DIFFER BUT LITTLE FROM THE ACTIVITY COEFFICIENTS REPORTED BY BONNER, ET AL, EVALUATED BY THE INTEGRATION PROCEDURE THEY USED. THE TREND OF STEEPER DECLINE IN $\gamma_\pm$ WITH INCREASING ALKYL SUBSTITUTION PARALLELS THOSE OF ϕ.

IN THE EXPERIMENTAL RANGE COVERED BY FIGURE 4, THE OSMOTIC COEFFICIENTS OF SODIUM *p*-CYMENESULFONATE-NACL THREE-COMPONENT SOLUTIONS ARE SEEN TO FALL BETWEEN THOSE OF NACL-H_2O AND PROTOSURFACTANT-H_2O, EXCEPT AT LOW IONIC STRENGTH. THE RISE ABOVE THOSE OF NACL-H_2O IN THE LAST CASE PRESUMABLY ARISES FROM THE CONTRIBUTION OF THE LARGER DEBYE-HÜCKEL a PARAMETER OF THE ORGANIC SALT (EQUATION 6 AND 7). IN THE REST OF THE RANGE THERE IS LITTLE, IF ANY, INDICATION OF AN EFFECT OF INCREASING CONCENTRATION OF THE SODIUM COUNTERION TO INCREASE THE EXTENT OF AGGREGATION, AS DECREASES IN OSMOTIC COEFFICIENTS OF INORGANIC SALT-SURFACTANT SOLUTIONS HAVE BEEN INTERPRETED.[30]

SOLUBILITY. WE HAVE MEASURED THE SOLUBILITY OF SEVERAL OF THESE SULFONATES IN NACL SOLUTIONS. PRELIMINARY VALUES WERE REPORTED IN REFERENCE 31, AND RESULTS OF MORE EXTENSIVE MEASUREMENTS FOR SODIUM *p*-CYMENE SULFONATES ARE GIVEN IN TABLE 7. FROM THESE, IF THE COMPOSITION OF THE SOLID PHASE IS KNOWN, RATIOS OF ACTIVITY COEFFICIENTS OF THE SULFONATES IN SATURATED SOLUTIONS IN NACL TO ACTIVITY COEFFICIENTS IN WATER MAY BE COMPUTED, BY THE EQUATION:

$$\frac{(\gamma_\pm)_{sat/NaCl}}{(\gamma_\pm)_{sat/H_2O}} = \frac{(m_{sulf})_{sat/H_2O}}{[m_{Na}(m_{sulf})]^{\frac{1}{2}}_{sat/NaCl}} \cdot \left(\frac{(a_{H_2O})_{sat/H_2O}}{(a_{H_2O})_{sat/NaCl}}\right)^{n/2} \quad (15)$$

WHERE n IS THE NUMBER OF MOLES OF WATER PER MOLE OF SULFONATE IN THE SOLID PHASE. FOR SODIUM *p*-CYMENESULFONATE, MEASUREMENT OF SOLID COMPOSITION OVER A RANGE OF WATER ACTIVITIES INDICATED THAT THE SOLID CONTAINED 2.5 WATERS OF HYDRATION. TABLE 7 COMPARES THE VALUES OF THE ACTIVITY COEFFICIENT RATIOS OBTAINED FROM SOLUBILITIES WITH THOSE COMPUTED FROM THE LEAST-SQUARES PARAMETERS OBTAINED FROM THE ISOPIESTIC RESULTS. THE IONIC STRENGTH OF THE SATURATED SOLUTIONS IN 4 AND 5 *M* NACL ARE CONSIDERABLY OUTSIDE OF THE RANGE OF THE ISOPIESTIC RESULTS FOR TWO-COMPONENT SOLUTIONS OF THE PROTOSURFACTANT, AND THE VALUES COMPUTED FROM THE ISOPIESTIC RESULTS THEREFORE REPRESENT EXTRAPOLATIONS.

THE FIRST THREE VALUES FOR MIXED SYSTEMS ARE FOR COMPOSITIONS WITHIN THE SPAN OF THE ISOPIESTIC MEASUREMENTS, ALTHOUGH APPROACHING THE EDGES, AND THE AGREEMENT IS CONSIDERED SATISFACTORY, IN VIEW OF THE PRECISION OF THE SOLUBILITY MEASUREMENTS. THE LAST ARE OUTSIDE THE RANGE, AND THE AGREEMENT IS POOR. THE DIFFERENCES IN THE EXTRAPOLATED RANGE APPEAR GROSS. WE HAVE OBSERVED PREVIOUSLY THAT EXTRAPOLATIONS FROM FITS TO FREE-ENERGY DATA FOR EVEN INORGANIC ELECTROLYTE TAKEN OVER A RESTRICTED CONCENTRATION RANGE WERE NOT VERY RELIABLE WHEN CHECKED AGAINST FITS TO MORE EXTENDED DATA WHEN THEY BECAME AVAILABLE. IN THESE CASES, THE ASSUMED SPECIES PRESUMABLY REPRESENTED WELL THE ACTUAL SPECIES IN SOLUTION, AND PROBABLY BECAUSE OF THIS, THE ABSOLUTE MAGNITUDE OF THE FITTING COEFFICIENTS WAS RELATIVELY SMALL. HERE THESE COEFFICIENTS ARE LARGE ENOUGH TO SUGGEST THAT COMPLEX SPECIES ARE FORMED AND THAT $\nu=2$ (THE BASIS FOR COMPUTATIONS OF STOICHIOMETRIC OSMOTIC AND ACTIVITY COEFFICIENTS) DOES NOT CORRESPOND TO THE ACTUAL SITUATION. TO ILLUSTRATE THE SENSITIVITY OF RATIOS COMPUTED FROM ACTIVITY COEFFICIENTS TO FITS IN THE EXTRAPOLATION RANGE, WE ALSO GIVE THE RATIO IN TABLE 7 FOR THE PARAMETER SET B, OBTAINED BY A FIT WITH THE DEBYE-HÜCKEL a SET AT 1.5. THE FIT TO EXPERIMENTAL OSMOTIC COEFFICIENTS ON THIS ASSUMPTION WAS NOT AS GOOD AS WITH THE a FOR PROTOSURFACTANT SET AT 2.5, BUT IT WAS NOT RIDICULOUSLY WORSE. IN THE EXPERIMENTAL RANGE OF OSMOTIC COEFFICIENTS, THE AGREEMENT WITH RATIOS FROM SOLUBILITIES IS FAIRLY GOOD FOR BOTH a-VALUES. HOWEVER, IN THE EXTRAPOLATED RANGE (4 AND 5 *m* NACL), THE DIFFERENCES ARE LARGE, AND ACTUALLY IN DIFFERENT DIRECTIONS FOR THE TWO VALUES OF a.

WE CONCLUDE THAT IT IS LIKELY THAT THE SOLUBILITY VALUES OF THE ACTIVITY COEFFICIENT RATIOS ARE CLOSER TO CORRECT THAN THOSE COMPUTED FROM FITS TO WATER ACTIVITIES IN THE CASE OF 4 AND 5 MOLAL NACL, BECAUSE OF THE UNCERTAINTY OF EXTRAPOLATIONS OF ISOPIESTIC MEASUREMENTS WITH THIS HIGHLY NON-IDEAL SYSTEM.

AGGREGATION. THE OSMOTIC COEFFICIENTS IN FIGURE 2 DO NOT EXHIBIT IN THE CONCENTRATION RANGE OF THESE MEASUREMENTS THE SHARP DISCONTINUITIES SEEN AT CRITICAL MICELLE CONCENTRATIONS OF SURFACTANTS.[32,33,34] HOWEVER, THE VALUES, PARTICULARLY FOR COMPOUNDS SUBSTITUTED WITH FOUR OR MORE ALKYL CARBONS, ALL FALL BELOW THOSE PREDICTED FOR REASONABLE DEBYE-HÜCKEL PARAMETERS. THE ATTRACTIVE INTERACTION BETWEEN SOLUTE PARTICLES IMPLIED DOES NOT HOWEVER SEEM SUFFICIENTLY LARGE TO SUGGEST FORMATION OF LARGE MICELLES. THIS INFERENCE IS REINFORCED BY THE LACK OF EFFECT OF ADDED SALT, PREVIOUSLY DISCUSSED.

THE MAGNITUDE OF THE POWER SERIES COEFFICIENTS, WHICH REFLECTS THE SUBSTANTIAL DEPARTURE FROM BEHAVIOR OF SIMPLE ELECTROLYTES, DO SUGGEST THAT COMPLEX SPECIES MAY BE FORMED. IN SUCH CASES, WHEN SOLUTES ARE ESSENTIALLY NON-IONIZED, SO THAT SPECIES ACTIVITY COEFFICIENTS VARIATIONS ARE SMALL ENOUGH TO IGNORE OR CAN BE REPRESENTED SIMPLY,[34,35,36] THERMODYNAMIC DATA CAN BE ANALYZED WITH FAIR PROSPECT OF SUCCESS IN TERMS OF AGGREGATION EQUILIBRIA. HOWEVER, WHEN IONIC SPECIES REACT

$$pM^- \rightleftharpoons P^{-p}$$

$$K = \frac{(m_P)(\gamma_{\pm B_p P})^{p+1}}{(m_M)^P(\gamma_{\pm BM})^{2p}} \qquad (16)$$

(B^+ BEING THE COUNTERION), EVEN IF ONLY A SINGLE P SPECIES IS FORMED, LARGE VARIATIONS IN THE RATIO OF ACTIVITY COEFFICIENTS OF THE SPECIES, DIFFICULT TO PREDICT A PRIORI, CAN BE EXPECTED. BECAUSE IN FITTING OF RESULTS, VARIATIONS IN THE ACTIVITY COEFFICIENT RATIO CAN BE COMPENSATED TO A CONSIDERABLE EXTENT BY VARIATIONS IN THE EQUILIBRIUM CONSTANT, K, IT IS DIFFICULT TO ARRIVE AT AN UNIQUE INTERPRETATION FROM FREE-ENERGY DATA ALONE.

WE HAVE ATTEMPTED HOWEVER TO SEE IF SUCH AN INTERPRETATION WOULD BE AT LEAST PLAUSIBLE FOR TWO-COMPONENT SOLUTIONS OF SODIUM DI*iso*PROPYLBENZENE SULFONATE. THE ACTIVITY COEFFICIENT OF THE MONOMERIC (M) AND POLYMERIC (P) SPECIES ARE TAKEN TO BE GIVEN BY EQUATIONS OF THE FORMS 10 AND 11. TO KEEP THE NUMBER OF PARAMETERS TO A MANAGEABLE LEVEL, WE SET THE DEBYE-HÜCKEL PARAMETER AT 2.5 FOR BOTH SPECIES, AND IN ALL EXCEPT ONE CASE FOR COMPARISON, RESTRICTED THE CONCENTRATION POWER SERIES OF EACH SPECIES TO TERMS LINEAR IN IONIC STRENGTH, AND SET THE B INTERACTION COEFFICIENTS AT ZERO. BECAUSE THE EVALUATION OF STOICHIOMETRIC ACTIVITY COEFFICIENTS (TABLE 3) WAS ON THE SAME BASIS (ν=2) AS THE MONOMERIC SPECIES IN EQUATION 16, THE STOICHIOMETRIC ACTIVITY IS THE SAME AS THE ACTIVITY OF THE MONOMERIC SPECIES, $m_{ST}\gamma_{\pm ST} = m_M\gamma_{\pm M}$. THE COMPUTATION INVOLVES A LEAST-SQUARES FIT OF VALUES OF THE ACTIVITY OF THE MONOMERIC SPECIES TO THE EXPERIMENTAL STOICHIOMETRIC VALUES, WITH VARIATION OF K, $a_M^{(1)}$, AND $a_P^{(1)}$ (PLUS EXTENDED PARAMETERS, IN ONE CASE).

BECAUSE OF THE COUPLED NATURE OF THE EQUILIBRIUM CONSTANT AND ACTIVITY COEFFICIENT RATIO, THE LEAST-SQUARES ADJUSTMENT WAS UNSTABLE, AND IT WAS NECESSARY, AT LEAST IN EARLY PHASES OF THE FIT, TO DAMP THE PARAMETER ADJUSTMENTS BETWEEN CYCLES. THE RESULTS IN TABLE 8 ARE CONVERGED VALUES. THE FITS, AS INDICATED BY THE DEVIATIONS, WERE REASONABLY GOOD, APPROXIMATELY EXPERIMENTAL UNCERTAINTY. HOWEVER, THE UNCERTAINTIES IN THE PARAMETERS IN THE MONOMER-TRIMER CASE, AND THE LARGE ABSOLUTE VALUES OF THE $a_M^{(1)}$ COEFFICIENT FOR THE MONOMER-TETRAMER AND MONOMER-PENTAMER EQUILIBRIUM DO NOT LEND CONFIDENCE IN THE PHYSICAL SIGNIFICANCE OF THE MODELS. THE RESULTS ARE CONSISTENT WITH POSTULATION OF THE FORMATION OF SMALL AGGREGATES, ALTHOUGH THEY BY NO MEANS CONCLUSIVELY ESTABLISH WHICH, IF ANY, EXIST.

CONCLUDING REMARKS. FREE ENERGIES OF PROTOSURFACTANT SOLUTIONS, IN COMMON WITH MANY OTHER PROPERTIES, APPEAR TO BE INTERMEDIATE BETWEEN SOLUTIONS OF

SIMPLE INORGANIC OR ORGANIC SALTS AND THOSE OF SURFACTANTS, THE PROPERTIES APPROACHING THOSE OF SURFACTANTS MORE CLOSELY WITH INCREASING DEGREES OF ALKYL SUBSTITUTION. THE TRENDS ARE NOT ALWAYS UNIFORM HOWEVER; PROTO-SURFACTANTS ARE SOMETIMES ABLE TO SOLUBILIZE ON A MOLE PER MOLE BASIS MORE HYDROCARBON IN AQUEOUS MEDIA THAN MICELLE-FORMING SURFACTANTS, AT LEAST THAN SOME IN THE LOW-EQUIVALENT-WEIGHT RANGE (COMPARE E.G., DATA IN REF. 2 WITH THOSE IN REF. 37 AND 38). THE PHASE BEHAVIOR OF AQUEOUS-HYDROCARBON SYSTEMS CONTAINING PROTOSURFACTANTS, FOR EXAMPLE, SALINITY SCANS,[8] ALSO RESEMBLES SURFACTANT-CONTAINING SYSTEMS, A PARALLEL WHICH ALSO EXISTS WITH OTHER LOW-MOLECULAR-WEIGHT AMPHIPHILES, SUCH AS ALCOHOLS.[39]

ALTHOUGH THE NON-IDEALITIES IN ACTIVITIES OF THE PROTOSURFACTANTS OF HIGHER DEGREES OF ALKYL SUBSTITUTION ARE GREAT ENOUGH IN COMPARISON WITH THOSE OF SIMPLE ELECTROLYTES TO SUGGEST FORMATION OF COMPLEXES, WE WERE NOT ABLE TO INFER FROM OUR RESULT UNIQUE INTERPRETATION IN TERMS OF SPECIES. DESNOYERS, ET AL.[34] CARRIED OUT SEVERAL THERMODYNAMIC MEASUREMENTS ON A SERIES OF NON-IONIC AMPHIPHILES, ALKYL DIMETHYLAMINE OXIDES. WITH THESE NONCHARGED SPECIES, ACTIVITY COEFFICIENT VARIATIONS SHOULD BE RELATIVELY MANAGEABLE. THEY CONCLUDED THAT THERE WAS EVIDENCE OF AGGREGATION WHEN THE ALKYL GROUP WAS BUTYL, THAT COMPLEXES COMPRISED OF ABOUT FIVE MONOMERS WERE FORMED FOR HEXYL (ALTHOUGH NOT ON THE BASIS OF THEIR OSMOTIC COEFFICIENTS), AND THAT THERE WAS A CLEAR CMC WITH ABOUT FIFTEEN MONOMERS/MICELLE WHEN THE ALKYL GROUP WAS DECYL. STENIUS[40] REPORTS WATER ACTIVITY MEASUREMENTS ON NACL-FATTY ACID SODIUM SALT SOLUTIONS, AND FROM DEPARTURES FROM LINEAR RELATIONSHIPS INFERS SLIGHT AGGREGATION OF SODIUM BUTYRATE AND LARGE AGGREGATES OF SODIUM HEXANOATE AT HIGH CONCENTRATIONS. PRELIMINARY SMALL-ANGLE NEUTRON SCATTERING RESULTS WE HAVE OBTAINED ON PROTOSURFACTANT SOLUTIONS APPEAR ALSO CONSISTENT WITH SOME AGGREGATION, ALTHOUGH A DEFINITIVE CONCLUSION AWAITS THEORETICAL DEVELOPMENT OF STRUCTURAL FACTORS TO DEAL WITH THE STRONG INTERACTION BETWEEN PARTICLES IMPLIED BY THE PEAKS IN INTENSITY AS A FUNCTION OF SCATTERING ANGLE.

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Table 1. Isopiestic Molalities and Osmotic Coefficients for the Two-Component Systems (Alkylbenzenesulfonate-Water).

Alkylbenzenesulfonate	m^a_{KCL}	m^b_{NaCl}	Sulfonate m	Sulfonate φ obsd.	Sulfonate φ calc.
Na p-toluene-sulfonate		0.400	0.406	0.908	0.909
		0.487	0.498	0.901	0.902
	0.630		0.632	0.895	0.890
		0.639	0.665	0.888	0.888
	0.883		0.916	0.864	0.865
	0.898		0.934	0.861	0.864
		1.001	1.104	0.848	0.848
		1.132	1.275	0.833	0.833
	1.186		1.278	0.833	0.833
		1.670	2.077	0.776	0.774
	2.218		2.726	0.746	0.747
		2.483	3.467	0.724	0.723
Na 2,4-dimethyl-benzenesulfonate	0.124		0.123	0.932	0.934
	0.313		0.309	0.917	0.916
	0.537		0.538	0.897	0.895
	0.630		0.644	0.879	0.882
	0.883		0.950	0.834	0.833
	1.186		1.380	0.773	0.773
Na p-cymenesulfonate	0.124		0.127	0.903	0.891
	0.313		0.357	0.794	0.786
		0.487	0.674	0.665	0.663
	0.537		0.784	0.615	0.626
	0.630		1.016	0.557	0.559
		0.639	1.098	0.537	0.540
	0.883		1.652	0.479	0.466
	0.898		1.686	0.478	0.464
		1.001	1.989	0.471	0.462
	1.090		2.067	0.474	0.465
		1.132	2.255	0.471	0.474
	1.186		2.262	0.472	0.474
	1.301		2.446	0.479	0.484
	1.380		2.569	0.484	0.491
		1.538	3.003	0.491	0.487
Na 2,5-Diisopropyl-benzenesulfonate	0.124		0.126	0.893	0.902
		0.232	0.263	0.815	0.800
		0.285	0.376	0.701	0.708
		0.320	0.459	0.642	0.646
		0.400	0.694	0.530	0.526
	0.479		0.907	0.476	0.481
		0.487	0.936	0.480	0.476

[a] Reference electrolyte was KCl

[b] Reference electrolyte was NaCl

TABLE 2. PARAMETERS FOR THE TWO-COMPONENT SYSTEMS[+]

PARAMETERS	SODIUM SULFONATES OF											
	P-TOLUENE		2,4-DIMETHYL-BENZENE		P-CYMENE				2,5-DIISOPROPYL-BENEZENE		NACL[*]	
		±		±	(A)	±	(B)	±		±		±
α	2.0		2.0		2.5		1.5		2.5		1.5	
$\alpha^{(1)}$	-0.057045	0.010665	-0.10916	0.05643	-0.90455	0.059188	-0.7508	0.067378	-0.16266	0.35289	0.03684	0.001167
$\alpha^{(2)}$	-0.14517	0.018347	0.13522	0.22913	-0.01200	0.10534	-0.078814	0.11253	-5.4630	2.0162	0.02108	0.00117
$\alpha^{(3)}$	0.063618	0.0091851	-0.44166	0.28628	0.18977	0.057325	0.18666	0.057815	8.0665	3.5557	-0.001307	0.0003467
$\alpha^{(4)}$	0.007899	0.0013927	0.20246	0.10921	-0.039965	0.0096875	-0.035831	0.0091947	-3.4095	1.9470	0.0	
DEVIATIONS[≠]												
	0.0021		0.0028		0.0095		0.0123		0.0121		0.0006	

[+] DEBYE-HÜCKEL α FIXED AT LISTED VALUES.
[*] FROM FIT TO VALUES OF ϕ IN REF. (13). USED IN ANALYSIS OF THREE-COMPONENT MEASUREMENTS.

[≠] $$\left(\frac{\Sigma(\text{OBSERVED } \phi - \text{COMPUTED } \phi)^2}{\text{NUMBER OBSERVATIONS} - \text{NUMBER OF VARIED PARAMETERS}}\right)^{1/2}$$

Table 3. Osmotic and Activity Coefficients of Alkylbenzenesulfonates
(At rounded concentration from least-squares fit)

	ϕ Sodium Sulfonate of				$\gamma_{\pm}$ Sodium Sulfonate of			
molality	p-toluene	2,4-dimethyl benzene	p-cymene	2,5-diisopropyl benzene	p-toluene	2,4-dimethyl benzene	p-cymene	2,5-diisopropyl benzene
0.1	0.938	0.937	0.905	0.918	0.792	0.789	0.743	0.772
0.2	0.927	0.925	0.856	0.850	0.747	0.744	0.652	0.668
0.3	0.918	0.917	0.811	0.769	0.718	0.714	0.583	0.571
0.4	0.910	0.908	0.768	0.689	0.694	0.691	0.526	0.488
0.5	0.902	0.899	0.728	0.619	0.675	0.670	0.477	0.421
0.6	0.894	0.887	0.689	0.563	0.657	0.649	0.436	0.369
0.7	0.885	0.874	0.654	0.524	0.640	0.629	0.400	0.331
0.8	0.876	0.859	0.621	0.499	0.624	0.608	0.368	0.303
0.9	0.867	0.842	0.591	0.482	0.609	0.588	0.341	0.280
1.0	0.585	0.824	0.564	0.463	0.595	0.568	0.318	0.260
1.5	0.815	0.771	0.477		0.534	0.494	0.239	
2.0	0.779		0.462		0.486		0.202	
2.5	0.755		0.487		0.450		0.184	
3.0	0.739		0.487		0.423		0.168	

Table 4. Isopiestic Ionic Strengths $\underline{I}$, and Osmotic Coefficients for the System Na p-cymenesulfonate (A) + NaCl (B) + H_2O

m_{NaCl} [a] (mol kg^{-1})	I [b] (mol kg^{-1})	y_B [c]	ϕ obsd.	ϕ calc.
0.232	0.236	0.29	0.908	0.902
0.320	0.330	0.29	0.893	0.882
0.425	0.450	0.29	0.869	0.857
0.410	0.410	0.50	0.920	0.914
0.410	0.403	0.75	0.935	0.939
0.666	0.696	0.50	0.885	0.885
0.666	0.658	0.75	0.936	0.937
0.728	0.909	0.29	0.742	0.760
1.137	1.621	0.29	0.661	0.653
1.109	1.295	0.50	0.806	0.819
1.109	1.117	0.75	0.934	0.929
1.585	1.947	0.50	0.782	0.778
1.585	1.661	0.75	0.917	0.919
1.687	2.475	0.29	0.658	0.655
2.238	2.775	0.50	0.802	0.806
2.238	2.403	0.75	0.927	0.923

[a] NaCl as reference solute

[b] $\underline{I} = \underline{m}_{NaCl} + \underline{m}_{Na\ p\text{-cymenesulfonate}}$

[c] y_B = ionic strength fractions of NaCl

TABLE 5. PARAMETERS FOR THE THREE-COMPONENT SYSTEM
NA *p*-CYMENESULFONATE (A) + NACL (B) + H_2O

α	$b_{AB}^{(0,1)}$	$b_{AB}^{(0,2)}$	$b_{AB}^{(0,3)}$	$b_{AB}^{(1,2)}$	$b_{AB}^{(1,3)}$	DEVIATION+ IN ϕ
2.5	1.9171	-1.3744	0.26265	-0.44331	0.15711	0.0094
±	0.11423	0.12984	0.03441	0.13853	0.060387	
1.5	2.1134	-2.0091	0.34604	-0.74628	0.12830	
±	0.19772	0.22473	0.05956	0.23978	0.10452	

+ $$\left(\frac{\Sigma(\text{OBSERVED } \phi - \text{COMPUTED } \phi)^2}{\text{NUMBER OBSERVATIONS} - \text{NUMBER OF VARIED PARAMETERS}}\right)^{1/2}$$

Table 6. Isopiestic Ionic Strengths I, Ionic Strength Fraction y_B of NaCl, Osmotic Coefficients ϕ and Activity Coefficients $\gamma_{\pm}$, for Na p-cymenesulfonate (A) + NaCl (B) + H_2O (At rounded concentration from least-squares fit)

I(mol kg^{-1})	y_B	ϕ	$\gamma_{\pm NaCl}$	$\gamma_{\pm ps}$
0.1	0.0	0.905	0.831	0.743
0.1	0.25	0.928	0.818	0.765
0.1	0.50	0.942	0.806	0.789
0.1	0.75	0.943	0.793	0.814
0.1	1.00	0.934	0.781	0.840
0.5	0.0	0.728	0.819	0.477
0.5	0.25	0.833	0.783	0.542
0.5	0.50	0.906	0.748	0.627
0.5	0.75	0.938	0.715	0.738
0.5	1.00	0.922	0.684	0.886
1.0	0.0	0.564	0.807	0.318
1.0	0.25	0.719	0.769	0.383
1.0	0.50	0.850	0.729	0.489
1.0	0.75	0.931	0.691	0.665
1.0	1.00	0.936	0.659	0.969
1.5	0.0	0.477	0.782	0.239
1.5	0.25	0.638	0.756	0.290
1.5	0.50	0.800	0.718	0.389
1.5	0.75	0.922	0.682	0.590
1.5	1.00	0.957	0.659	1.024
2.0	0.0	0.462	0.769	0.202
2.0	0.25	0.609	0.762	0.241
2.0	0.50	0.777	0.723	0.327
2.0	0.75	0.918	0.684	0.527
2.0	1.00	0.983	0.670	1.051
2.5	0.0	0.487	0.780	0.184
2.5	0.25	0.632	0.797	0.218
2.5	0.50	0.788	0.747	0.293
2.5	0.75	0.925	0.694	0.483
2.5	1.00	1.012	0.690	1.052

$\underline{I} = \underline{m}_{NaCl} + \underline{m}_{ps}$ (ps - Na p-cymenesulfonate)

TABLE 7. RATIOS OF ACTIVITY COEFFICIENTS OF NA *p*-CYMENESULFONATE AT SATURATION MOLALITIES IN NACL SOLUTIONS TO WATER SOLUTIONS.

NACL (MOLES/KG H_2O)	SOLUBILITY OF NA *p*-CYMENESULFONATE (MOLES/KG H_2O)	$\gamma_{\pm}$ SAT./NACL / $\gamma_{\pm}$ SAT./H_2O FOR DH a = 2.5		FOR DH a = 1.5	
		SOLUBILITY	ISOPIESTIC	SOLUBILITY	ISOPIESTIC
	(A) (B)				
0	3.04 ± 0.14				
1	2.29 ± 0.17	1.2	1.3	1.2	1.7
2	0.47 ± 0.02	3.0	3.5	3.0	3.6
3	0.113 ± 0.04	5.5	5.4	5.6	7.4
4	0.044 ± 0.0056	8.2	5.1	8.3	12.2
5	0.021 ± 0.0032	11.4	3.6	11.5	22.8

(A) AVERAGE
(B) STANDARD DEVIATION

TABLE 8. TESTS OF FITS TO ACTIVITIES OF SODIUM DI *iso*PROPYLBENZENESULFONATE BY AGGREGATION MODELS.

EQUILIBRIUM	K	$a_M(1)$	$a_P(1)$	$a_M(2)$	$a_P(2)$	$b_{MP}(0,1)$	DEV.
MONOMER-TRIMER	0.349	-0.080	-0.024	(0)	(0)	(0)	0.0023
±	0.276	0.481	0.051				
MONOMER-TETRAMER	0.071	-0.487	0.037	(0)	(0)	(0)	0.0012
±	0.008	0.050	0.010				
	0.734	-0.336	0.051	-0.439	0.015	0.857	0.0003
±	0.207	0.504	0.024	0.041	0.012	0.046	
MONOMER-PENTAMER	0.012	-0.614	0.104	(0)	(0)	(0)	0.0016
±	0.0015	0.041	0.017				

NOTES: (0) DENOTES PARAMETER FIXED AT ZERO.
DEV. SIGNIFIES SQUARE ROOT OF THE SUM OF THE SQUARES OF THE DIFFERENCES BETWEEN VALUES OF $m\gamma_{\pm}$ LISTED IN TABLE 3 AND $\tilde{m}_M\gamma_{\pm M}$ COMPUTED FROM THE LEAST-SQUARES FIT, DIVIDED BY NUMBER OF VALUES OF ACTIVITIES LESS THE NUMBER OF VARIED PARAMETERS.

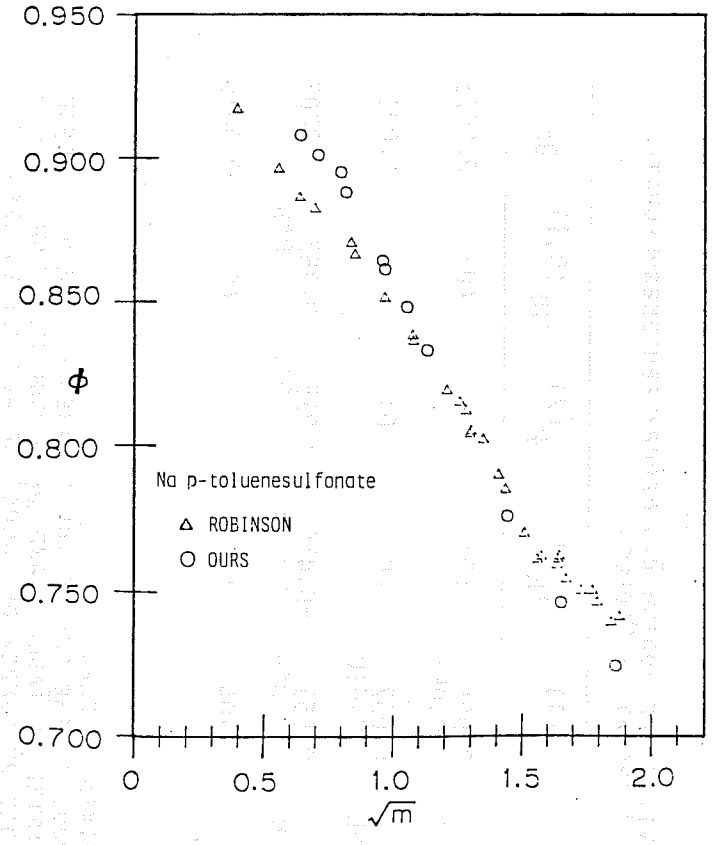

Figure 1. Comparison of osmotic coefficients of Na p-toluenesulfonate between literature (Ref. 13) values and our results.

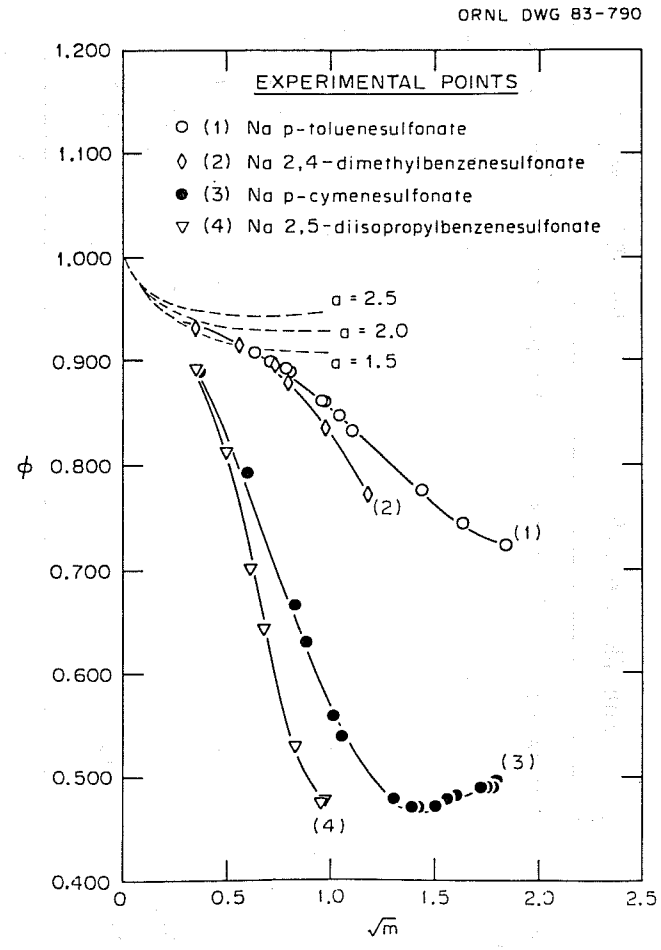

Figure 2. Osmotic coefficients of aqueous solutions of organic salts. Dashed curves, Debye-Huckel with indicated values of distance-of-closest-approach parameter. Solid curves, calculated from least-square fit. Points, experimental points, (○) Na p-toluenesulfonate, (◊) Na 2,4-dimethylbenzenesulfonate, (●) Na p-cymenesulfonate, (▽) Na 2,5-diisopropylbenzenesulfonate.

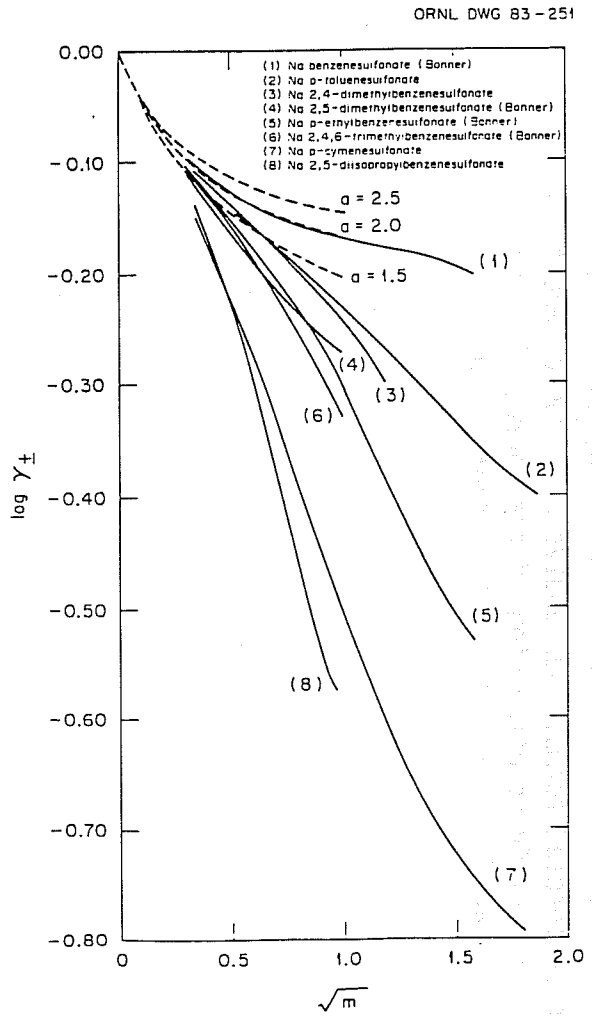

Figure 3. Activity coefficients of sodium alkylbenzenesulfonates. Dashed curves, Debye-Huckel with indicated values of a. Data of Bonner et al., from Ref. 18, computed with least-squares fit.

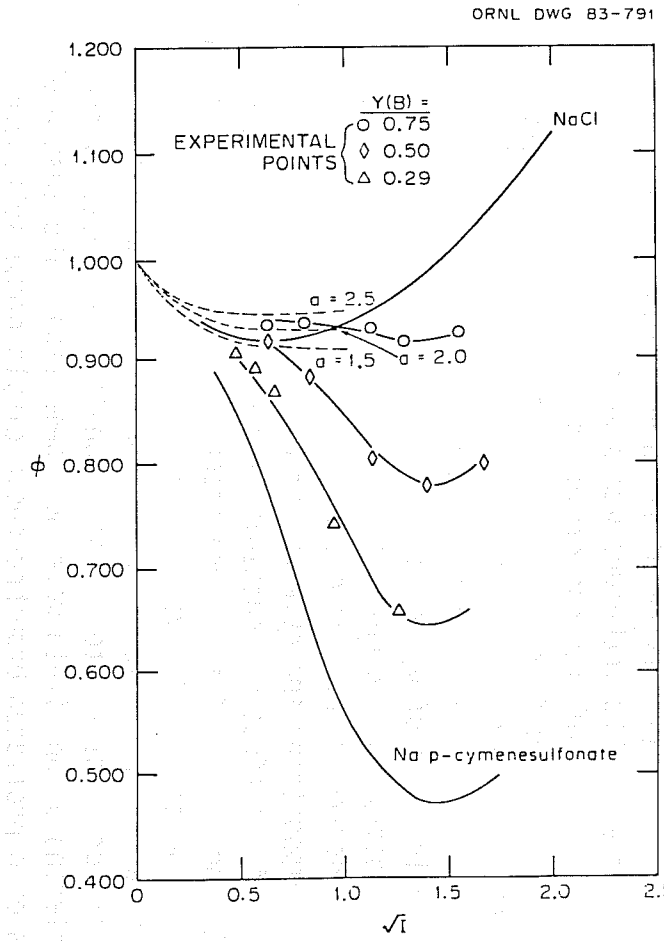

Figure 4. Osmotic coefficients of Na p-cymenesulfonate/NaCl/H_2O solutions. Dashed curves, Debye-Huckel with indicated values of a. Solid curves, calculated from least-square fit. Points, experimental points with Y(B) = 0.75 (○), 0.50 (◊), 0.29 (△).

3. SMALL-ANGLE NEUTRON SCATTERING OF MICELLAR SYSTEMS

In long-range projections for both this and our late collateral program, Chemicals for Enhanced Oil Recovery, growing emphasis on small-angle neutron scattering (SANS) studies was planned. The technique was seen to have great promise in resolving many questions of long standing concerning the structure of micelles and of microemulsions. The diminishing funds available have truncated the effort possible. However, interest in the problems for which SANS might be helpful has continued among several formerly associated with oil-recovery research at the Laboratory. These are now principals of groups at the University of Tennessee, Knoxville, Wake Forest University, and the University of Palermo, Italy, and collaborators in continued research in the subject area.

Initially we have been emphasizing the development of experimental techniques and methods of data analysis for surfactant-containing systems, in the course of studying systems of significance in the field. One account, incorporated in the last report of the Chemicals for Enhanced Oil Recovery program (Compere et al., 1983), dealt with micelles of branched-chain alkylbenzene sulfonates. Here we reproduce three papers. One deals with critical scattering of a non-ionic surfactant, and another with critical scattering of an oil-in-water microemulsion. The last deals with contrast measurements on a protiated branched-chain alkylbenzene sulfonate in media of varying H_2O/D_2O ratios (or as a function of contrast between the scattering power of the solute and of the solvent). The main objective was verification of the mean spherical approximation for computation of structural factors from interparticle interactions of charged micelles. We have carried out preliminary studies of water-in-oil microemulsions; of aqueous protosurfactants; of surfactants selectively deuterated in various regions; and of a salinity scan of a five-component (surfactant, alcohol, hydrocarbon, salt, and water) system with different components in deuterated forms. Our analysis of these results has not progressed to the point of justifying discussion of them here. Some brief reports have been given in the Bartlesville Energy Technology Center's quarterly progress reviews.

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3.1. Small-Angle Neutron Scattering from Aqueous Micellar Solutions of a nonionic Surfactant as a Function of Temperature

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Solutions of 0.029 M *n*-dodecyl hexa(oxyethylene glycol) monoether ($C_{12}E_6$) in D_2O have been investigated by small-angle neutron scattering at a series of temperatures from 14.3 to 47.3 °C. The sample displays a lower consolute temperature of 47.4 ± 0.05 °C. The scattering curves are fit best by assuming that (1) spherical micelles are present at all temperatures investigated and (2) the observed increases in the scattered intensity with increasing temperature in the low-angle region are due to critical concentration fluctuations. The angular dependence in this region can be approximated by the Ornstein–Zernike relation, with the correlation lengths obtained following a power law dependence on the reduced temperature $(T_c - T)/T_c$.

Introduction

Until recently light-scattering measurements on dilute aqueous solutions of nonionic amphiphiles have generally been interpreted in terms of a large increase in micellar molecular weight as the lower consolute temperature (T_c, often called a "cloud point") is approached.[1,2] (T_c as used in this paper should be considered an apparent critical temperature, since the substitution of D_2O for H_2O may shift the critical concentration somewhat.) A few investigators, however, recognized that the large increases in turbidity might be due to the increasing dominance of critical fluctuations as $T_c - T$ decreased.[3-5] Recently Corti and Degiorgio[6] have reinvestigated aqueous solutions of *n*-dodecyl hexa(oxyethylene glycol) monoether ($C_{12}E_6$) (the same surfactant used in ref 1 and 2) by static and dynamic light scattering. They postulate that critical phenomena dominate the observed scattering in the temperature range 30–50 °C (T_c = 50.35 °C).

The effective hydrodynamic radius[7] of $C_{12}E_6$ micelles at 5 °C has been reported to be 31 Å. It has been predicted that nonionic micelles should increase only slightly in size as the temperature is increased,[3,8] and there is indirect evidence from NMR data (^1H resonance line widths and spin–lattice relaxation times) that $C_{12}E_6$ micelles in D_2O do grow slowly.[9] We decided to employ small-angle neutron scattering (SANS) in order to establish directly whether small micelles are present in D_2O solutions of $C_{12}E_6$ at temperatures up to T_c. SANS differs from light scattering in the range of values of K (the modulus of the scattering vector) which is accessible. Here $K = (4\pi/\lambda) \sin \theta$, where 2θ is the scattering angle and λ is the wavelength of the scattered radiation (λ = 4.75 Å in our SANS measurements). In particular, SANS permits measurements to be made at K values where the single-particle scattering function, $P(K)$, for small micelles shows angular dependence.

Here we present the results of SANS measurements on 0.029 M $C_{12}E_6$ in D_2O at several temperatures. This is the critical concentration in H_2O solutions.[6] The study was undertaken to determine whether the scattering could be described over a large K range in terms of the occurrence of approximately spherical micelles at all temperatures plus critical concentration fluctuations characterized by a simple power-law dependence on the reduced temperature. However, upon examining the scattering curves obtained, it occurred to us that a second model should be tested: the occurrence of spherical micelles at temperatures below 15 °C which grow into larger and larger cylindrical micelles ($R_{cyl} \simeq R_{sph}$) as $T \rightarrow T_c$. This model essentially assigns the temperature-dependent intensity increases observed at low K's to micelle growth; we designate it model 1. Model 2 will be used to designate the small micelle plus critical scattering hypothesis; of the two, it gives a more plausible explanation of all results.

Experimental Section

SANS Measurements. Neutron-scattering measurements were performed with the 30-m (source-to-detector) SANS instrument of the National Center for Small Angle Scattering Research, located at the High Flux Isotope Reactor, Oak Ridge National Laboratory. Scattering intensities were recorded in the K range 0.002–0.20 Å^{-1} (only part of the range at some temperatures), which corresponds to sample-to-detector distances of 2.6–15.1 m for neutrons of wavelength λ = 4.75 Å. The samples were contained in cylindrical spectrophotometric cells of 5-mm pathlength. A specially built cell holder allowed the sample to be aligned in the beam by means of micrometric adjustments. The temperature was kept constant to ±0.05 °C by means of circulation from an external bath. Scattering from sample and solvent (D_2O) was corrected for detector background, detector sensitivity, empty cell scattering, (computed) incoherent scattering, and sample transmission, and solvent intensity was subtracted from that of sample at each position. The differences were converted to radial-average intensity (with an error due to counting

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statistics for each point) vs. K by programs provided by the Center, and absolute cross sections $d\Sigma/d\Omega$ in cm^{-1} were computed from calibrations based on the known scattering from pure water or from a vanadium single crystal. The calibrations, also provided by the Center, were determined independently for different source slits and gave results for the runs at different distances which were within ±10%. Solvent scattering ranged from a few tenths of a percent of that of the sample at the low end of the K range to more than half above $K = 0.15$.

Sample Preparation. Homogeneous $C_{12}E_6$ was obtained from Nikko Chemicals, Tokyo, in crystalline form. D_2O was obtained from Aldrich Chemical Co. The surfactant sample (13.1 mg/cm^3) was prepared by volume in D_2O at 25 °C under N_2 prior to introducing it into the cell. A decrease in scattering intensity with an increase in temperature indicated that the sample separated into two liquid phases at 47.40 ± 0.05 °C. This agrees with a visual determination of cloud-point temperature. It is about 3 °C lower than T_c in H_2O; however, other investigators have found similar isotope effects for D_2O solutions of nonionic surfactants.[10] Scattering curves at 29.1 and 47.3 °C obtained before and after the sample was cycled through phase separation were essentially identical.

Data Analysis. Provided the structure function, $S(K)$, is unity and the micelles are monodisperse, the samples' coherent scattering cross section may be expressed by eq 1,[11a] in terms of the number of micelles per cm^3 (N_p), the

$$d\Sigma/d\Omega = N_p V_p^2(\rho_M - \rho_S)^2 P(K) = I_{0,mic}P(K) \quad (1)$$

volume per micelle (V_p, in Å^3), the scattering length densities of the micelles and solvent (ρ_M and ρ_S, respectively, in cm/Å^3), and the single-particle scattering function. $I_{0,mic}$ is the scattering by micelles at $\theta = 0$. Equations 2 and 3 present normalized $P(K)$ for spheres (of radius R) and cylinders (of radius R and length = 2 H) respectively,[12] where $J_1(X) = (\sin X - X \cos X)/X^2$.

$$(P(K))_{sph} = \left(3\frac{\sin KR - KR\cos KR}{(KR)^3}\right)^2 \quad (2)$$

$$(P(K))_{cyl} = \int_0^{\pi/2} \frac{\sin^2(KH\cos\phi)}{(KH\cos\phi)^2}\,\frac{9(J_1(KR\sin\phi))^2}{(KR\sin\phi)^2}\sin\phi\, d\phi \quad (3)$$

Model 1 consists of employing eq 1 with $P(K)$ given by eq 3. This assigns the observed increase in $I(K)$'s as the temperature is increased almost entirely to an increase in H.

In model 2 as T_c is approached, the observed intensity increases may be represented as critical concentration fluctuations (of correlation length ξ) and $d\Sigma/d\Omega$ is then given by

$$\frac{d\Sigma}{d\Omega}(K) = \frac{I_{0,crit}}{1 + K^2\xi^2}(P(K))_{sph} + N_p V_p^2(\rho_M - \rho_S)^2(P(K))_{sph} + B \quad (4)$$

where $I_{0,crit}$ is the zero-angle critical scattering and B is a term (K independent) for residual background scattering. The observed scattering is thus composed of a contribution from the micelles proper and a contribution from critical scattering, whose $S(K)$ component is represented by the Ornstein–Zernike relationship ($I_{0,crit}/(1 + K^2\xi^2)$). It should be noted that this relationship has an accuracy worse than 10% only at fairly large $K\xi$ values[13,14] (e.g., $K\xi > 21$); except at temperatures within ca. two degrees of T_c, our maximum K's are not large enough for this to be a serious problem. We have also not included the critical exponent η in our treatment, since it likewise represents a small correction.[13] In eq 4, the $P(K)$ used is that defined in eq 2.

A weighted (by the reciprocal of the square of the statistical error of the individual points) nonlinear least-squares fitting routine was used in applying model 1 to the experimental scattering curves. (An equally weighted fit failed completely in the $K > 0.05$ region.) The variables were R, H, the constant background term B, and an I'_0 term (collection of constants) equal to $2\pi N_p V_p(\rho_M - \rho_S)^2$. Note that $N_p V_p$ is the volume (in Å^3) per cm^3 of solution occupied by micelles and therefore is a function of surfactant concentration and partial specific volume and therefore does not change with R (nor H).

In the case of model 2 both unequally weighted and equally weighted fits were made; the $K > 0.05$ region is fit significantly better with a weighted fit, because the lower absolute values of the errors in this region gives the points more influence on the fit, relative to those in the low K region. Equally weighted fits were adequate for the temperatures for which only the low-K range was measured, because the range of error magnitudes was not large. The variables were R, ξ, $I_{0,crit}$, $I'_{0,mic}$ ($\equiv (4/3)\pi N_p V_p(\rho_M - \rho_S)^2$), and B. For the full scattering curves, the values of ξ and $I_{0,crit}$ reported are from the equally weighted fits, since we wish to compare these parameters with those obtained at temperatures for which only the low K region ($K < 0.05$) was examined. Attempts to fit the results by eq 4 without the term $N_p V_p^2(\rho_M - \rho_S)^2 P(K)_{sph}$ failed.

The values of B obtained in the least-squares fit were small, usually less than 0.1 in $d\Sigma/d\Omega$.

Results and Discussion

Figure 1, which presents scattering curves for the full K range for three temperatures, illustrates the general features of the results. Intensity values are essentially zero at $K > 0.15$. Values are similar for all temperatures in the K range 0.05–0.15, and the values increase rapidly with temperature at lower K. The results insensitive to temperature suggest the previously mentioned approximately constant dimension. Low-K values are shown for more temperatures and in more detail in Figure 2. It is in this region that the two models may be distinguished.

Interpretation of the Scattering Observed at 14.30 °C. The observed scattering curve at this temperature is consistent with the presence of approximately spherical $C_{12}E_6$ micelles. Equations 1 and 2 fit the data very well, giving a value of 27.6 ± 0.2 Å for the sphere's radius. However, as Tanford[15] has demonstrated, other experimental data on $C_{12}E_6$ micelles are consistent with their being oblate ellipsoids. By using Tanford's equation, on the assumption that the ethylene oxide chains are in the meander configuration,[7] the semiminor axis (b) is calculated to be 23.8 Å. If the volume of the particles is taken to be that of a sphere with R = 27.6 Å, the value of the ellipsoid's major

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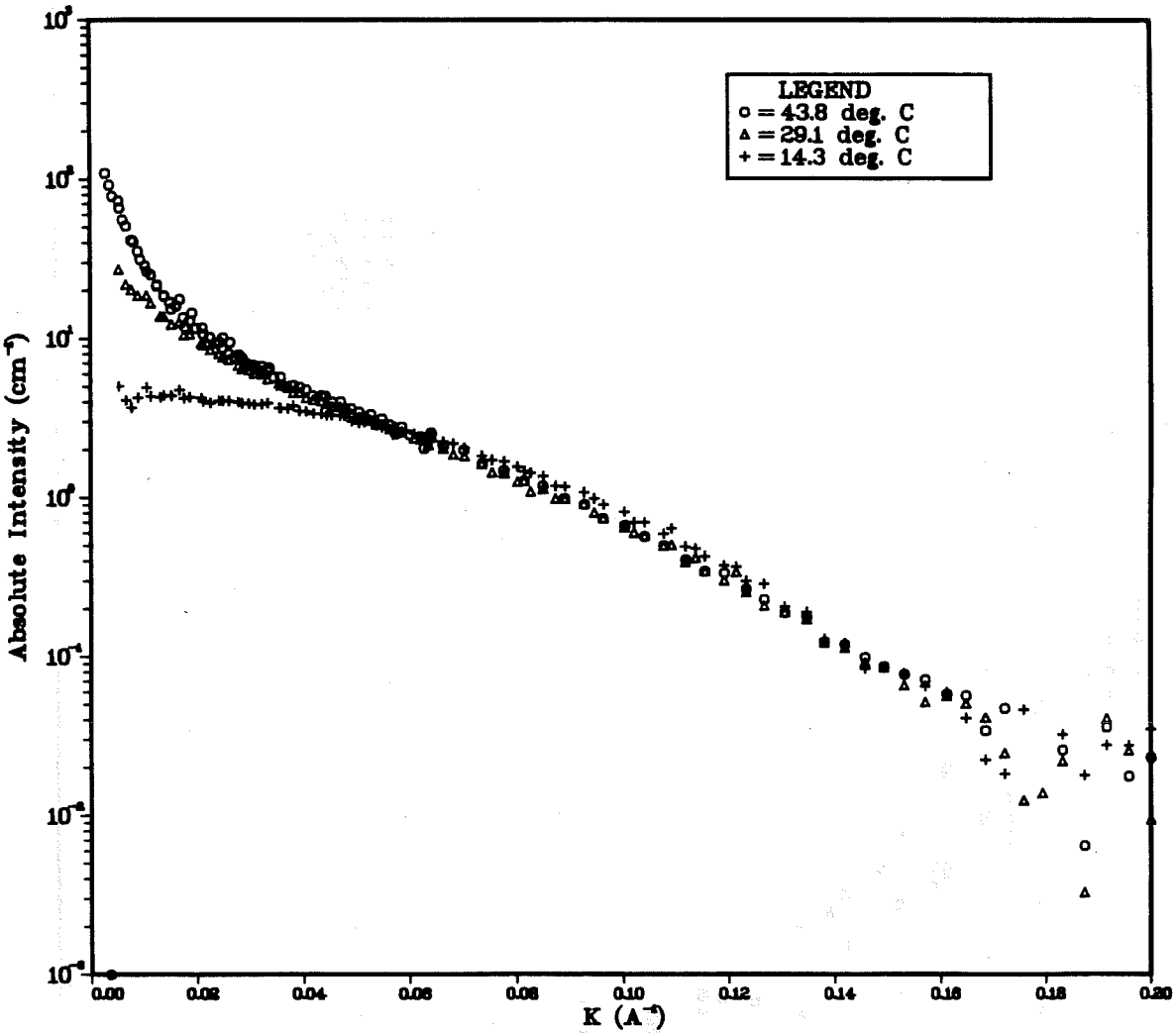

Figure 1. Scattering from $C_{12}E_6$ vs. temperature: full K range.

axis, a, from $V = (4/3)\pi a^2 b$ would be 29.7 Å. The resulting axial ratio is too small to cause $P(K)$ to deviate much from the expression given in eq 2. Indeed, it is difficult to distinguish between a modest deviation from sphericity and the occurrence of some polydispersity in sphere radii.

The micelle volume of a sphere of 27.6 Å is 8.81×10^4 Å^3; 8.30×10^4 Å^3 of that volume is occupied by surfactant ($\bar{v} = 1.001$ mL/g for micellized[2] $C_{12}E_6$ and the aggregation number[2] is 111 at 15 °C in D_2O). This implies that only ca. 1.5 D_2O molecules per monomer penetrates the micelles deeply enough to be detected by the SANS measurement. Most of the water of hydration probably is associated with the outermost portions of the micelle, in a region having a scattering length density very close to ρ_S. Using the appropriate scattering lengths,[11b] and the simplifying assumption of a homogeneous ρ_M, one can compute ρ_M to be 6.59×10^{-15} cm/Å^3 and ρ_S to be 6.37×10^{-14} cm/Å^3, which gives a value of 3.26×10^{-27} cm^2/Å^6 for $(\rho_M - \rho_S)^2$. This is in qualitative agreement with the value, 3.64×10^{-27} cm^2/Å^6, computed from I_0 at 14.30 °C.

Model 1: Cylinders. The parameters determined as a result of fitting the full scattering curves obtained from 24.15 to 43.85 °C to model 1 are presented in Table I. A scattering curve obtained at 47.30 °C is qualitatively consistent with the trends of those measured at lower temperatures, but because the temperature is within 0.10 °C of T_c, and our temperature control is only ±0.05 °C, it is not included in our analysis. At and especially above 38.9 °C, the parameters are not well determined; the fit obtained at 43.8 °C is shown in Figure 3. Note that the errors on the cylinder length were very large (i.e., the fit was insensitive to their values), despite the fact that an unequally weighted fit was used. For comparison, Table I includes cylinder H's estimated by using the apparent molecular weights (M_{app}) obtained from ultracentrifugation[2] and light scattering,[1] with an assumed cylinder radius[7] of 27 Å. Note that because of the isotope effect on T_c, 42 °C in D_2O is equivalent (roughly) to 45 °C in H_2O; this was taken into account in the estimation above.

Balmbra et al.[1] proposed that M_{app} grows exponentially with T in $C_{12}E_6/H_2O$ solutions over the temperature range 25–45 °C. Corti and Degiorgio[6] noted that their M_{app} results were in good agreement with Balmbra's in that temperature range, with deviations from the exponential dependence becoming very large from 45 °C up to T_c. Our I_0 values show the same behavior, increasing much more rapidly in the temperature range 44.8–46.8 °C than predicted by the exponential dependence of I_0 on T observed below ca. 43 °C.

Model 2: Spheres + Critical Scattering. Table II collects the values obtained for the micelles' radii, the solutions' correlation length ξ, and $I_{0,crit}$ at all temperatures above 14.3 °C which were investigated. The parameters are better determined than those for the cylinder in Table I. Note particularly that the errors in ξ, the parameter especially important at low K, are much smaller than the

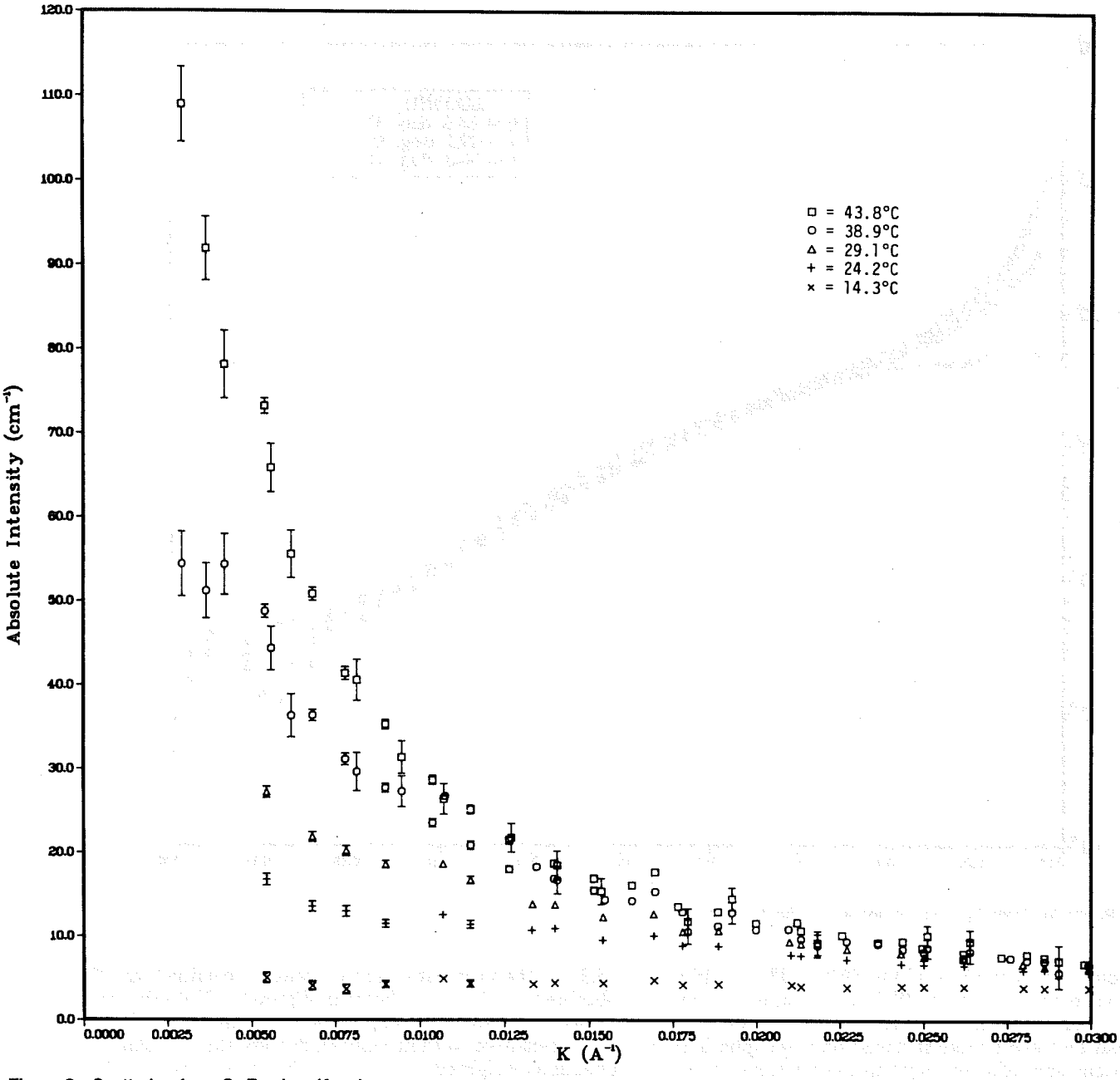

Figure 2. Scattering from $C_{12}E_6$: low K region.

TABLE I: Parameters of Fits to Cylinder Model (Eq 1 and 3)

temp, °C	R, Å	H, Å SANS	H, Å lit.[a]	$10^4(2\pi N_p V_p \cdot (\rho_M - \rho_S)^2)$	$I_{0,mic}$[b]	χ^2
24.15	21.9 ± 2.9	99.9 ± 22.8	90.5	2.81 ± 0.67	14	7.34
29.10	23.8 ± 1.1	182.4 ± 34.6	148	2.53 ± 0.22	26	4.78
38.90	25.5 ± 3.3	1106 ± 951	433	2.33 ± 0.54	167	9.35
43.85	26.4 ± 14.0	1700 ± 11900	871	2.42 ± 2.22	287	27.0

[a] Values in H_2O interpreted or extrapolated from light scattering and ultracentrifugation, ref 1 and 2, at comparable $T_c - T$ values. [b] $I_{0,mic} = 2\pi R^2 H N_p V_p (\rho_M - \rho_S)^2$.

errors in H at temperatures close to T_c. Equation 4 was used at temperatures where full scattering curves had been determined. At temperatures where only the low K region was investigated, values for $I_{0,crit}$ and ξ were obtained with eq 4 without the $I_{0,mic}P(K)$ term, after its contribution had been essentially eliminated by subtracting the experimental scattering curve obtained at 14.3 °C. Figure 4 presents the fit to the full scattering curve at 43.85 °C. In the low K region, it is appreciably better than the cylinder model in Figure 3, and the residuals appear to scatter more randomly than those for the cylinder model. Values of χ^2 for the critical scattering plus spheres model were less than for the cylinder model for three temperatures and slightly greater for the fourth (Tables I and II). Table II includes the correlation lengths determined by Corti and Degiorgio[6] in their light scattering study.

Figure 5 shows the dependence of ξ and $I_{0,crit}$ on the reduced temperature $\epsilon = (T_c - T)/T_c$, along with lines

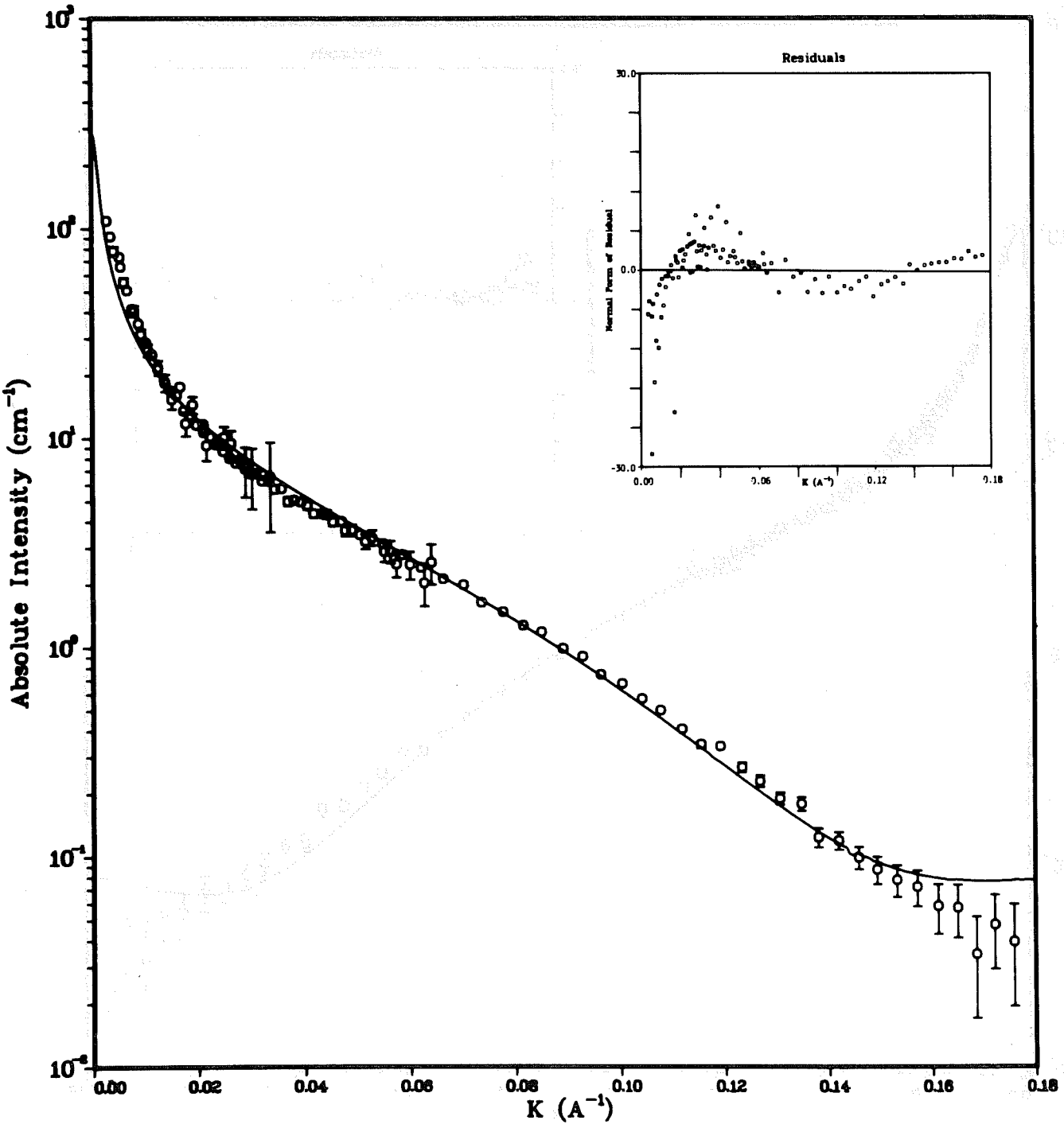

Figure 3. Fit to scattering at 43.8 °C by cylinder model. The inset shows the residuals (computed minus experimental, divided by error).

TABLE II: Parameters of Fits to Critical Scattering Plus Spheres

temp, °C	R, Å[a]	ξ, Å: SANS	ξ, Å: light scattering[b]	$I_{0,crit}$	$10^4[(4/3)\pi N_p V_p \cdot (\rho_M - \rho_S)^2]$	$I_{0,mic}$[c]	$I_{0,comp}$[d]	χ^2
24.15	27.0 ± 0.6	63.7 ± 0.3	80.4	12.3 ± 0.0	1.53 ± 0.06	3.0	15.3	2.71
29.10	27.7 ± 1.6	92.7 ± 0.5	91.3	26.4 ± 0.1	1.48 ± 0.15	3.1	29.5	5.81
34.00		116 ± 1	108	46.5 ± 0.4				
38.90	28.4 ± 1.6	135 ± 4	137	60.7 ± 0.8	1.46 ± 0.15	3.3	64	5.35
43.85	28.5 ± 2.8	211 ± 5	217	141 ± 3	1.55 ± 0.28	3.6	145	8.45
44.80		315 ± 7	257	317 ± 10				
45.80		342 ± 45	332	386 ± 80				
46.30		536 ± 250	405	729 ± 464				
46.80		652 ± 175	558	1370 ± 610				

[a] Where R is listed, results were available over range of K wide enough for least-squares analysis for all parameters of eq 4. Otherwise, critical parameters were obtained by fitting intensities at temperature minus intensities at 14.3 °C, with R in $(P(K))_{sph}$ fixed at 27.6 Å. [b] Interpolated from ref 6. [c] $(4/3)\pi R^3 N_p V_p (\rho_M - \rho_S)^2$. [d] $I_{0,mic} + I_{0,crit}$.

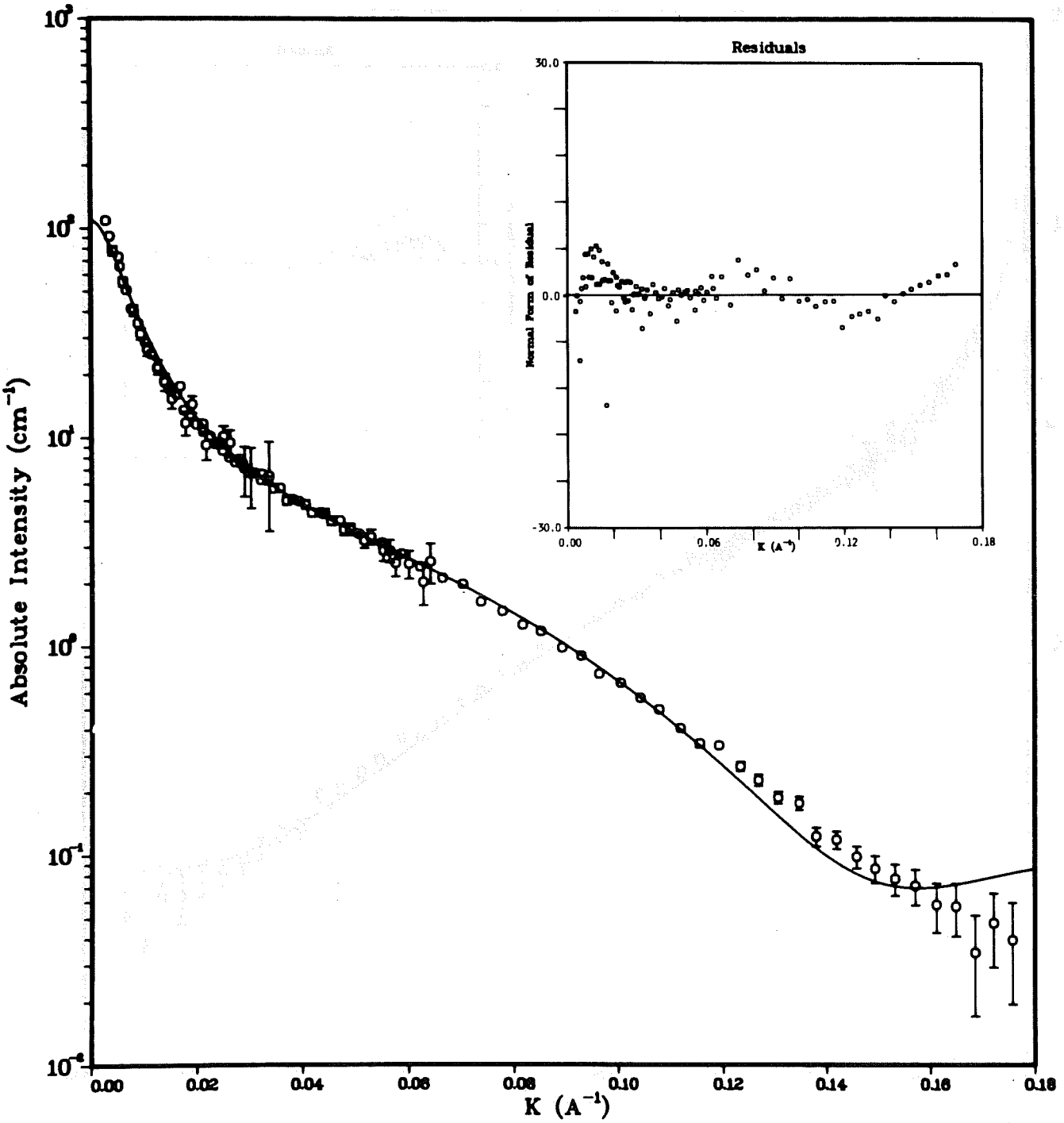

Figure 4. Fit to scattering at 43.8 °C by spheres plus OZ model. The inset shows the residuals (computed minus experimental, divided by error).

obtained by least-squares fit. At 29.1 °C and above, the correlation length, ξ, follows the power law $\xi = \xi_0\epsilon^{-\nu}$, with $\nu = 0.57 \pm 0.06$ and $\xi_0 = 17.9 \pm 3.0$. Similarly, $I_{0,\mathrm{crit}}$ is proportional to $\epsilon^{-\gamma}$, with $\gamma = 1.11 \pm 0.09$. We note that the critical exponents γ and ν are close to those reported by Corti and Degiorgio[6] (and are close to those predicted by mean-field theory). It is possible that at temperatures closer to T_c crossover to nonclassical exponents occur, but we were unable to detect it. Error bars at these temperatures are very large, which is probably due to temperature fluctuations within our thermostatted cell block. In future work we hope to use more accurate thermostatting and purer sample of surfactant than that available commercially.[16]

(16) Dr. John Lang of Procter and Gamble has agreed to supply us with a sample of specially purified $C_{12}E_6$.

Conclusions

SANS measurements on 0.029 M $C_{12}E_6$ in D_2O at several temperatures are consistent with an approximately spherical micelle. The high K portions of the scattering curves are dominated by $P(K)$ for these spheres. As $T \rightarrow T_c$ the low K region is increasingly dominated by critical effects; the K dependence in this region can be approximated by the Ornstein–Zernike relation. The resulting correlation lengths and $I_{0,\mathrm{crit}}$ values are described by simple power law behavior; the resulting critical exponents are classical.

We favor model 2, critical scattering plus spheres, over an alternative of cylinders of approximately constant radii whose length increases with temperature, although the R_{cyl} parameter does remain fairly constant with temperature. Our preference is based on the better fit given by model

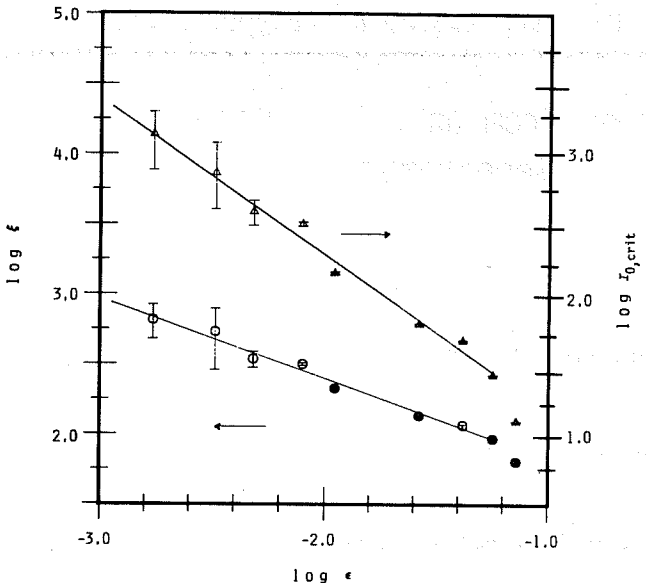

Figure 5. Evaluation of critical parameters: filled, results for wide K range, fit to all parameters; open, results at low K, intensities minus 14.3 °C values fit to critical parameters.

2, and on the fact that one would in any case expect a contribution of critical scattering in this system and the large increases in intensity can be fit by reasonable critical parameters (in this regard, it is pertinent that an attempt to include an Ornstein–Zernike contribution to a cylinder fit did not improve matters).

The results confirm the value of the high K range attainable with SANS, in allowing inferences concerning particle dimensions to be made at temperatures in the neighborhood of critical points. The technique can therefore complement light scattering, in which scattering from solutes is swamped by that from critical fluctuations.

Acknowledgment. This research was supported by the Office of Oil, Gas, and Shale, U.S. Department of Energy, under Contract No. W-7405-eng-26 with Union Carbide Corp. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the work at the University of Tennessee. This research was performed at the National Center for Small-Angle Scattering Research (NCSASR). The NCSASR is funded by National Science Foundation Grant No. DMR-77-244-58 through Interagency Agreement No. 40-637-77 with the Department of Energy (DOE) and is operated by the Union Carbide Corp. under Contract No. W-7405-eng-26 with the DOE. We thank Elijah Johnson, George D. Wignall, and J. Shelten for helpful discussions and assistance in analysis of results. The holder for liquid samples was constructed by Frank Ward of the Oak Ridge National Laboratory Plant and Engineering Division.

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3.2. Small-Angle Neutron Scattering from an Oil-in-water Microemulsion as a Function of Temperature

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A multicomponent oil-in-water microemulsion containing CTAB ($C_{16}H_{33}NMe_3Br$), *n*-octane, 1-butanol, NaBr, and D_2O has been studied by small-angle neutron scattering at several temperatures. The size of the microemulsion droplets was found to be independent of temperature. Correlation lengths for the critical concentration fluctuations agree with those determined earlier by light scattering.

1. Introduction

Recently Nicoli et al. [1,2] have investigated by static and dynamic light scattering at several temperatures an oil-in-water microemulsion composed of CTAB ($C_{16}H_{33}\dot{N}Me_3Br$), *n*-octane, 1-butanol, NaBr, and water. The data are qualitatively consistent with the presence of droplets whose size (≈75–80 Å) is independent of temperature, but the Q region [$Q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle] where the single-particle scattering function, $P(Q)$, shows angular dependence for these droplets is not experimentally accessible by light scattering. The system has a parabolic phase boundary in the NaBr concentration–temperature. The temperature dependence of the scattered intensity along a constant [NaBr] path has been analyzed to provide correlation radii (ξ) for the system; these radii show a maximum at 37.5°C, which corresponds to the [NaBr] minimum for the phase-boundary curve [1]. Thus the physical picture which emerges is of a microemulsion system containing particles whose size is approximately temperature independent, but which shows critical-type behavior (characterized by critical fluctuations whose correlation length, ξ, diverges as the critical point is approached).

The use of small-angle neutron scattering (SANS) is particularly appropriate for this CTAB microemulsion, since it permits measurements to be made at Q values where $P(Q)$ shows angular dependence. It is thus possible to obtain direct evidence about the particle size in the system. In this paper we report scattering curves for this microemulsion at 1.35 wt % NaBr, using D_2O instead of H_2O as the continuous phase. The solvent substitution shifts the phase-boundary curve ≈0.2% (wt/vol basis) lower in NaBr concentration but does not displace it in temperature space. In this preliminary analysis of our results we find that our neutron-scattering data support the inference of Nicoli et al.; the aggregate

size is indeed approximately independent of temperature and the observed temperature dependence in the low-Q region arises from changes in the mean correlation range for the cooperative diffusion of these aggregates.

2. Experimental

2.1. SANS measurements

Neutron-scattering measurements were performed with the 30 m (source-to-detector) SANS instrument of the National Center for Small-Angle Scattering Research, located at the High Flux Isotope Reactor, Oak Ridge National Laboratory. Scattering intensities were recorded in the Q range 0.005–0.20 $Å^{-1}$ (only part of the range at some temperatures), which corresponds to sample-to-detector distances of 2.6–15.1 m for neutrons of wavelength $\lambda = 4.75$ Å. The samples were contained in cylindrical spectrophotometric cells of 5 mm pathlength. A specially built cell holder allowed the sample to be aligned in the beam by means of micrometric adjustments. The temperature was kept constant to ±0.05°C by means of circulation from an external bath. Scattering from sample and solvent (D_2O) was corrected for detector background, detector sensitivity, empty-cell scattering, (computed) incoherent scattering, and sample transmission, and solvent intensity was subtracted from that of the sample at each position. The differences were converted to radial-average intensity (with an error due to counting statistics for each point)

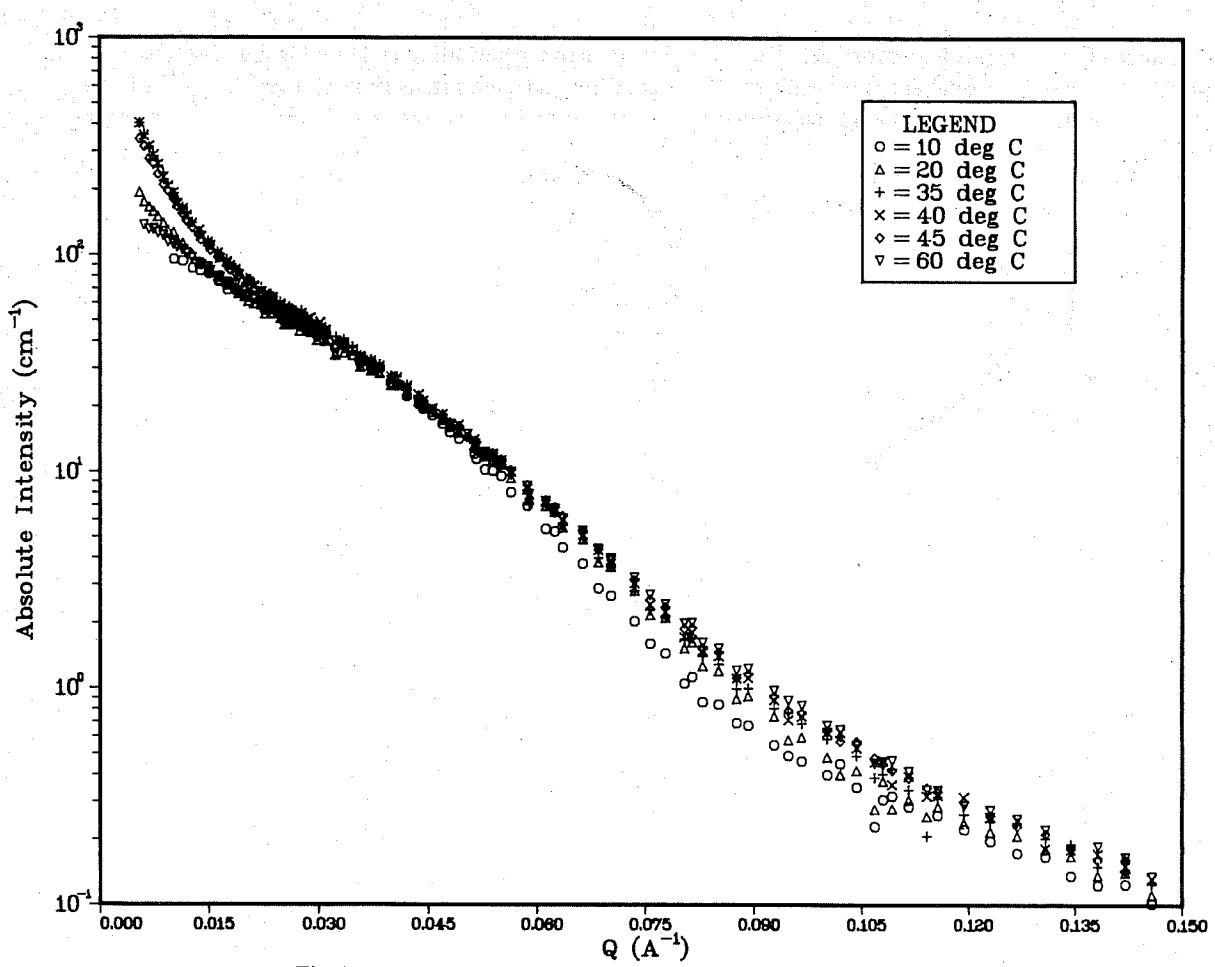

Fig. 1. Scattering from the CTAB microemulsion versus temperature.

versus Q by programs provided by the Center, and absolute cross sections $d\Sigma/d\Omega$ in cm^{-1} were computed from calibrations based on the known scattering from pure water or from a vanadium single crystal. The calibrations, also provided by the Center, were determined independently for different source slits and gave results for the runs at different distances which were within ±10%. Solvent scattering ranges from a few tenths of a percent of that of the sample at the low end of the Q range to more than half above $Q = 0.15$.

2.2. Sample preparation

CTAB (City Chemical Corp.) was recrystallized from CCl_4 and its purity evaluated by molecular-weight determination (titration with $AgNO_3$) and determination of its critical micelle concentration in H_2O at 25°C (9.1×10^{-4} M, EMF measurement). *n*-octane, 1-butanol, and D_2O (all from Aldrich) were used as received. Sodium bromide (Fisher) was dried before use. The microemulsion (prepared by weight) corresponds to the Nicoli system in H_2O, with D_2O being substituted for H_2O on a volume basis. Thus the components had the following wt/vol percents in D_2O: 2.30% CTAB, 2.30% *n*-octane, 4.60% 1-butanol, and 1.35% NaBr.

3. Results and discussion

Full scattering curves obtained for the microemulsion at several temperatures are given in fig. 1. The curves are essentially coincident at $Q > 0.05$ Å^{-1} (except at 10°C), which is consistent with aggregates of approximately constant radius. The intensities obtained at 35 and 40°C are essentially the same, which is consistent with the observed minimum in the phase-boundary curve.

It is expected that most of the *n*-octane present will be solubilized in the aggregates' core, with the outer layer containing the CTAB, a portion of the 1-butanol, the remainder of the *n*-octane and undoubtedly (vide infra) some penetrating D_2O molecules. Fig. 2 shows that the scattered intensity at $Q > 0.045$ Å^{-1} is indeed consistent with this core plus shell model for the aggre-

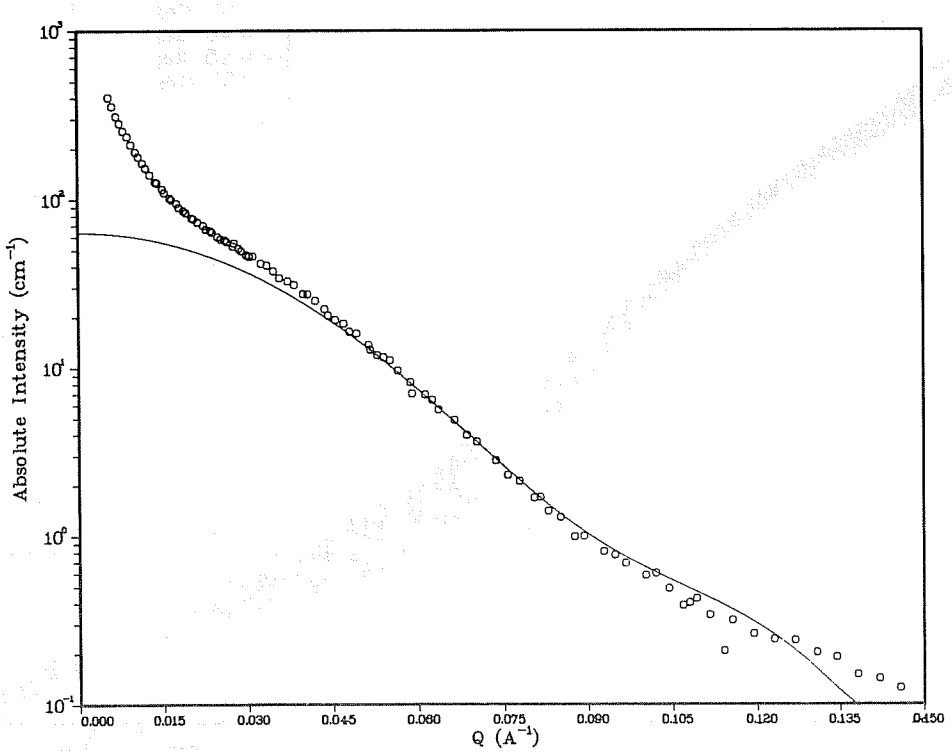

Fig. 2. Fit of the data at $Q > 0.045$ Å^{-1} using eq. (1).

gates. Thus the equation

$$I(Q) = \mathrm{d}\Sigma(Q)/\mathrm{d}\Omega = N_\mathrm{p}\,[V_1(\rho_1 - \rho_2)\,\phi(QR_1) + V_2(\rho_2 - \rho_s)\,\phi(QR_2)]^2 + B\,, \qquad (1)$$

where the core's scattering length density (ρ_1) was fixed at the value for n-octane (-5.5×10^{-15} cm/Å^3), and N_p (the number of aggregates per cm^3), R_1 (the core radius in Å), R_2 (the aggregate radius in Å), and ρ_2 (the scattering length density of the outer shell) were allowed to vary, provides a satisfactory fit of the high-Q data (fig. 2). Here $V_n = (4/3)\pi R_n^3$, $\phi(x)$ equals $(3.0/x^3)(\sin x - x\cos x)$, and B is a term (Q-independent) for residual background scattering. The least-squares fit gave for the core radius, R_1, 32.5 ± 6.1 Å. The particle radius R_2 is not well defined, 68.0 ± 40.0 Å, but is in reasonable agreement with the value from light scattering [1]. The value of ρ_2, $(5.42 \pm 0.4) \times 10^{-14}$ cm/Å^3, indicates substantial D_2O penetration; the value for ρ_{D_2O} is 6.34×10^{-14} cm/Å^3.

It is difficult to determine the boundary between the lowest Q values where critical scattering dominates and the region where interparticle ordering arising from repulsion between the aggregates [3] is most important; the regions may not be distinguishable. The high salt concentrations tend to screen the mutual repulsion, and under conditions near critical, critical scattering probably should to a first approximation dominate. In these cases, the equation

$$\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega = [I_{0,\mathrm{crit}}/(1 + Q^2\xi^2)]\,[\phi(QR_2)]^2 + B \qquad (2)$$

is appropriate, with ξ representing the correlation length for the critical concentration fluctuations. Fig. 3 shows the fit of the low-Q region using eq. (2) for the 35°C data; the value of ξ is 178 ± 35 Å. The profile of the temperature dependence of the correlation length (fig. 4) inferred from eq. (2) agrees qualitatively with that inferred by Nicoli et al., from dynamic scattering, for a 1.6% NaBr and H_2O, a composition probably closer to critical than the 1.35% NaBr and D_2O of this study.

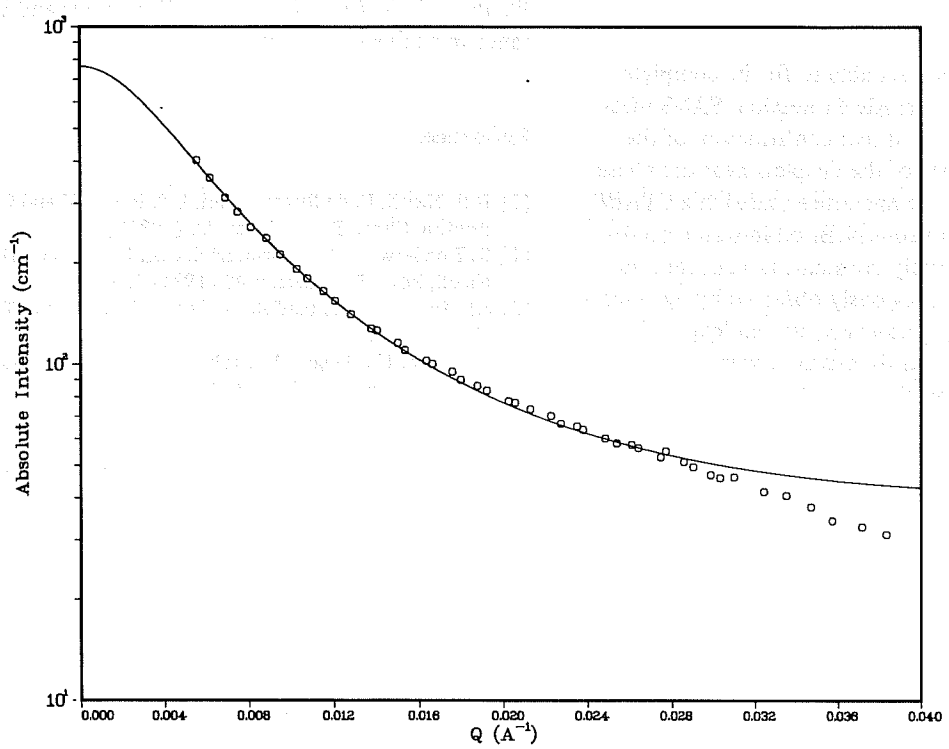

Fig. 3. Fit of the low-Q region using eq. (2).

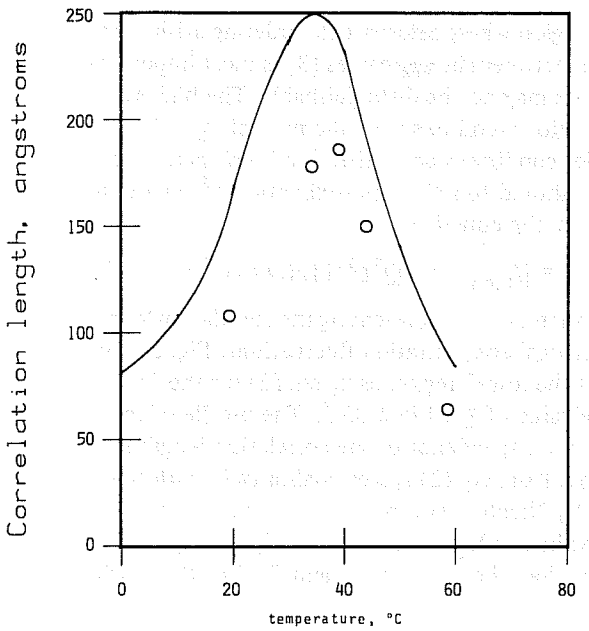

Fig. 4. Temperature dependence of the microemulsion's correlation length. Curve: light scattering, Nicoli et al. [1], 1.6% NaBr–H_2O. Points: SANS, 1.35% NaBr–D_2O.

4. Conclusions

Although we are not yet able to fit the complete scattering curves with a single expression, SANS measurements have provided direct confirmation of the hypothesis that the size of the droplets near the phase boundary (in [NaBr]–temperature space) in a CTAB/1-butanol/*n*-octane/aqueous NaBr oil-in-water microemulsion is approximately constant. In addition, the critical-type behavior previously observed by light scattering [1,2] is also seen here; correlation lengths for the critical concentration fluctuations were obtained at several temperatures. Similar behavior has been found previously [4] for the binary system n-$C_{12}H_{25}O(CH_2CH_2O)_6H$–$D_2O$, and we are currently investigating additional examples of micellar and microemulsion systems which show critical-type behavior.

Acknowledgement

This research was supported by the Office of Oil, Gas, and Shale, U.S. Department of Energy, under Contract No. W-7405-eng-26 with Union Carbide Corporation. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the work at the University of Tennessee. One of the authors (RT) acknowledges partial support from the "Progetto Finalizzato Fine e Secondaria" of CNR (Rome). This research was performed at the National Center for Small-Angle Scattering Research (NCSASR). The NCSASR is funded by National Science Foundation Grant No. DMR-77-244-58 through Interagency Agreement No. 40-637-77 with the Department of Energy (DOE) and is operated by the Union Carbide Corporation under Contract No. W-7405-eng-26 with the DOE. We thank H.R. Child for helpful discussions and assistance in analysis of results.

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3.3. Small-angle Neutron Scattering from H_2O/D_2O Solutions of a Sodium Alkylbenzenesulfonate Having a Branched Alkyl Group

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Small-angle neutron scattering results from 0.055 *M* sodium *p*(1-pentylheptyl)benzenesulfonate solutions in D_2O–H_2O solutions of 57% to 100% volume percent D_2O are reported. Strong interaction peaks indicate interparticle ordering. Good fits to the results can be obtained taking account of hard-sphere and electrostatic repulsion with the mean spherical approximation. The model used is a spherical micelle, comprising a hydrocarbon core of 11.9 Å radius surrounded by a shell. The thickness of the shell derived from the results is 8.9 Å, implying a rough micellar surface. The measured geometry and change are essentially independent of the contrast between the micelles and the solvent.

INTRODUCTION

Micelles are molecular aggregates formed in solutions of surfactants, i.e., molecules in which a nonpolar "tail" and a polar (ionic, zwitterionic, or nonionic) "head" coexist. Basically, the formation of micelles is a consequence of a net gain of free energy on aggregation. The extent of aggregation, in turn, is limited by the balance between attractive forces (between the chains, between the heads and the solvated counterions, and between the heads and the solvent molecules) and the repulsive forces involving essentially the polar heads. As a consequence, ionic micelles show smaller aggregation numbers than similar nonionic molecules. In the case of ionic micelles, strong micelle–micelle interactions generate a considerable amount of local order which is evidenced in static or dynamic scattering experiments at low values of momentum transfer. A great deal of work aimed at describing the static and dynamic behavior of dispersions and/or solutions of spherical strongly interacting particles has been published in the last few years.[1–5]

More recently, the use of the mean spherical approximation (MAS) has been proposed independently by Triolo and Floriano[6] and Hayter and Penfold.[7,8] The latter authors, however, have shown convincingly that the use of MSA is a plausible and correct approach. They matched the static structure factor $S(k)$ of sodium dodecyl (SDS) solutions with the values obtained experimentally by dynamic small angle neutron scattering.[9] Their work has now opened a new way to interpret scattering data from micellar solutions in terms of the internal structure of the micelle and of intermicellar interactions. In addition, Hayter's approach, especially in the recent[8] rescaled form, allows the extension of the above method to arbitrarily low densities for which the standard MSA was of little use. The rescaled mean spherical approximation (RMSA) uses a rescaling argument based on the generalization of a procedure due to Gillan[10] which preserves the analytical form of the original MSA solution.

Finally, we want to stress the fact that, while for high concentrations corresponding to packing fractions $n \geq 0.2$, the RMSA and the MSA give essentially the same results, for packing fractions of the order of $\eta \cong 10^{-3}$ or lower RMSA describes the system with the same accuracy as the hypernetted chain approximation (HNC) but with a substantial saving in computing time. This provides an inexpensive but sufficiently accurate way to test potential models and to estimate the surface potential of interacting colloidal particles with fairly good precision.

EXPERIMENTAL

In this paper, we present a structural study of 0.055 *M* solution of sodium *p*-(1-pentylheptyl)benzenesulfonate (6 Ph C12 SNa) in D_2O/H_2O mixtures at 45 °C, with the purpose of gaining information about the internal structure of the micelles formed by this surfactant and of confirming this information using contrast variations. The 6 Ph C12 SNa was the same as was used in previous work.[11]

Neutron scattering (SANS) measurements were performed on the 30 m (source to detector) SANS instrument of the National Center for Small Angle Scattering Research (NCSASR) at the High Flux Isotope Reactor (HFIR) in Oak Ridge (USA). D_2O was an Aldrich product.

[a]Research supported in part by Oil, Gas, and Shale Technology, U. S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

H_2O was obtained by distilling deionized water in quartz. Scattered intensities were recorded in the k range 0.02–0.18 Å^{-1}; $k=(4\pi \sin\theta)/\lambda$ where 2θ is the scattering angle and λ (4.75 Å) is the wavelength of the neutrons used. The samples were contained in quartz spectrophotometric cells having 0.1, 0.2, or 0.5 cm path lengths. The temperature of the specially built cell holder was kept constant at 45.0 ± 0.1 °C by circulating fluid from an external bath. Two stock solutions of the surfactant in D_2O and H_2O were mixed in the measuring cell in the ratio required to obtain the various H_2O/D_2O volume ratios.

Scattering from samples and solvents was corrected for detector background and sensitivity, empty cell scattering, (computed) incoherent scattering, and sample transmission. Solvent intensity was subtracted from that of the sample at each position. These differences were converted to radial-average intensities vs k and absolute cross sections $d\Sigma/d\Omega$ were computed from calibrations based on the known scattering from pure water or from a vanadium single crystal.

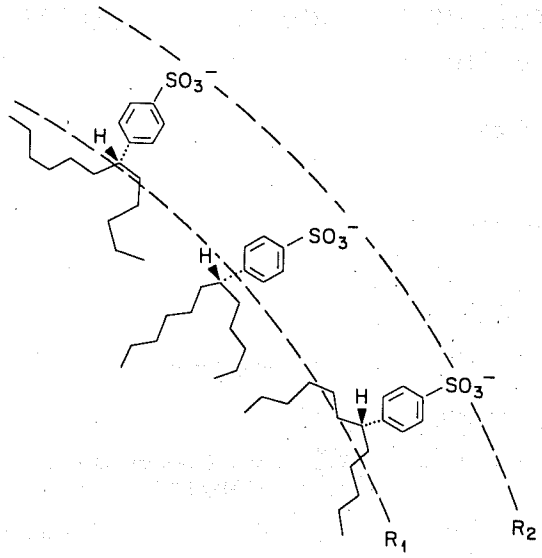

FIG. 2. Model of micelle used in this analysis.

RESULTS AND DISCUSSION

The data have been analyzed by describing the system as a solution of monodisperse charged hard spheres interacting via a screened Coulombic potential due to the interaction of the double layers associated with the spheres. In dimensionless form, this potential

$$V(x)=\beta^{-1}\gamma \exp(-Kx)/x\ , \quad x>1\ ,$$

where $x=r/\sigma$, $K=\kappa\sigma$, $\beta^{-1}=k_BT$ (with k_B = Boltzmann constant), and γ is a dimensionless parameter which is a function of the dielectric constant ϵ, the diameter σ, the surface potential ψ_0, and the inverse Debye screening length κ:

$$\gamma=\beta\pi\epsilon\,\psi_0^2\sigma\exp(K)\ .$$

The Ornstein–Zernike equation[12] together with the MSA closure[13] for this potential form a closed set that can be solved analytically following the prescription of Hayter, Penfold, and Hansen[7,8] to yield the micelle–micelle structure factor $S(k)$. This is related to the absolute measured intensity through the following equation:

$$I(k)=\alpha\cdot P(k)\cdot S(k)\ , \tag{1}$$

where α is a proportionality constant which is a function of the concentration as well as of the units used for the scattering length, and $P(k)$ is the single micelle scattering factor. This quantity is a function of the micellar geometry and composition and can be obtained from scattering data, once $S(k)$ is obtained. For example, for a typical Hartley model (core of radius R_1 surrounded by a shell of radius R_2), the single particle form factor $P(k)$ can be calculated by means of the equation

$$P(k)=[4\pi R_1^3(\rho_1-\rho_2)\,\phi(kR_1)+4\pi R_2^3(\rho_2-\rho_s)\,\phi(kR_2)]^2\ ,$$

where ρ_1, ρ_2, and ρ_s are the scattering length densities of the core, the first shell (of radius $R_2=\sigma/2$), and the solvent, respectively, and

$$\phi(x)=\frac{\sin x - x\cos x}{x^3}$$

Figure 1 shows a typical SANS pattern obtained by combining two runs made at different detector distances.[14] It is clear that we can locate three angular regions: The first one at small values of k is essentially dominated by the compressibility of the system and hence by the thermodynamic limits of $S(k)$. The second region, at intermediate values of k, is dominated by the first peak of the structure factor $S(k)$. The third region, at high values of k, is dominated by $P(k)$ since beyond ~0.08 Å^{-1} (~3.3 on the dimensionless units of the abscissa) $S(k)$ oscillates around 1 and the amplitude of the oscillations, already small, is damped further by the quickly decreasing $P(k)$.

Clearly the experimental intensities $I(k)$ can be fitted to Eq. (1) using the diameter σ and the charge Z of the micelle as fitting parameters, provided a model to calculate $P(k)$ is available.

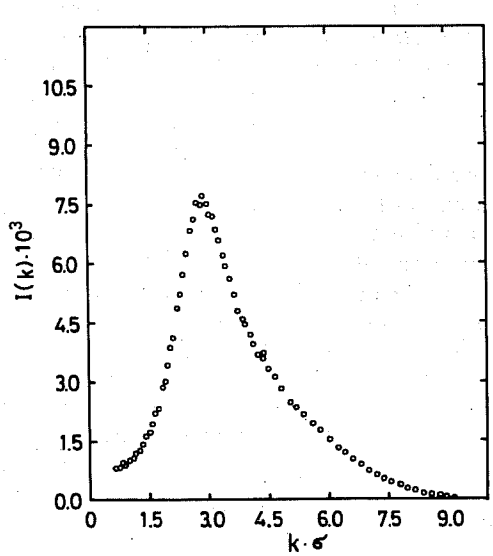

FIG. 1. Small-angle neutron scattering from 0.055 M sodium p(1-pentylheptyl)benzenesulfonate in D_2O.

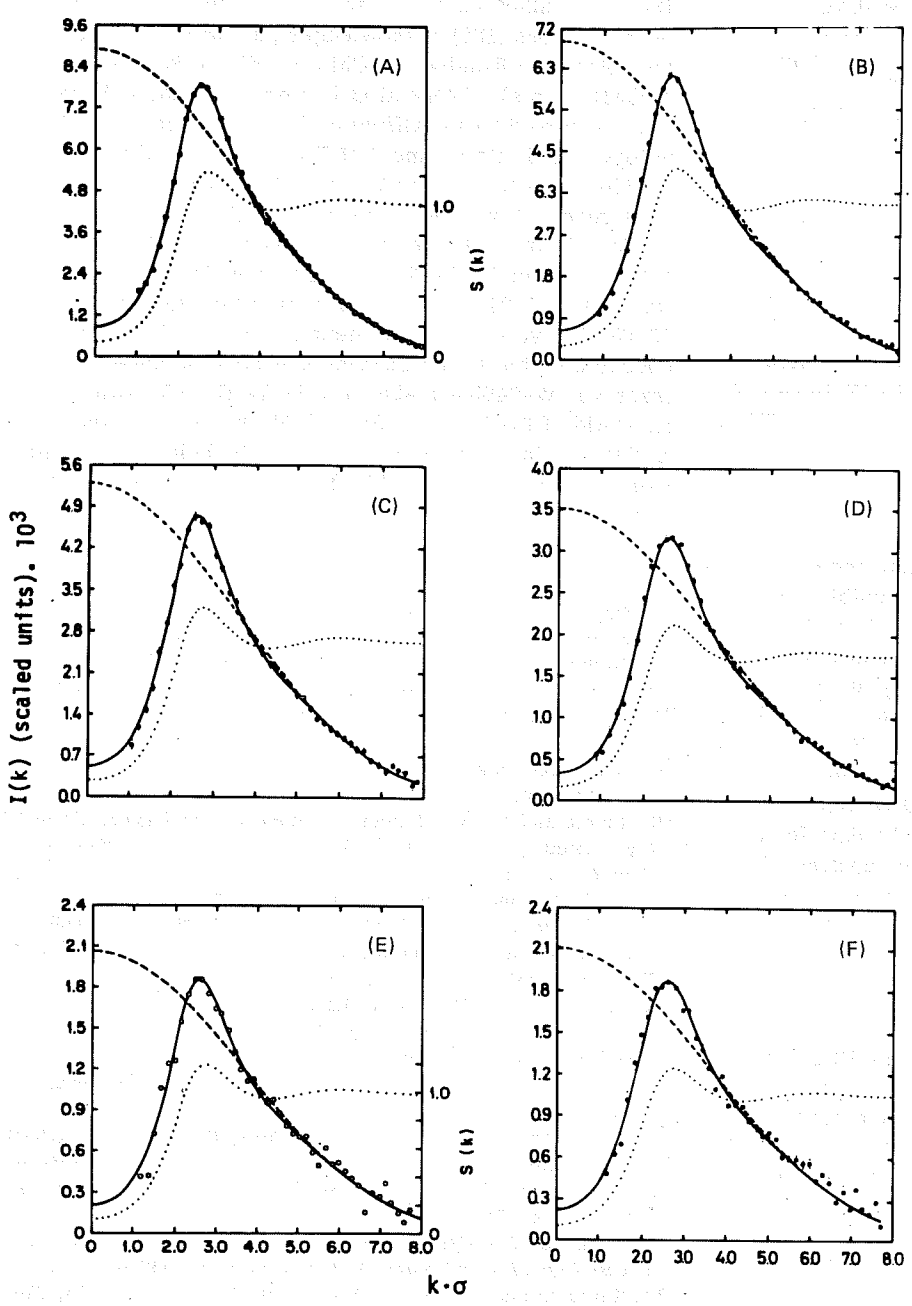

FIG. 3. MSA fits to contrast patterns of 0.055M sodium p(1-pentylheptyl) benzene sulfonate solutions. --- particle scattering formation, $P(k)$; ••• structural functions, $S(k)$; —computed intensities.

	D_2O Vol%	
(A) 100	(C) 80	(E) 57%
(B) 90	(D) 70	(F) 57% (repeat)

We have tried several models for the micelle. We have found that a shell model (Fig. 2) with a core of radius $R_1 = 11.9$ Å containing all the methyls and $(9-2\delta)$ methylenes/monomer, and a spherical shell of thickness $(\sigma/2 - R_1)$ containing the remaining methylenes plus all the CH, C_6H_4, solvated head groups and solvated counter ions was able to fit the SANS data for 0.055 M 6 Ph C12 SNa in all the D_2O/H_2O mixtures studied. Volumes of the groups comprising the surfactant were taken from the literature.[15,16] We recognize that 11.9 Å exceeds the extended length of a seven-carbon chain terminated by a methyl group (~10.4 Å), and there is consequently an approximation in the model. However, a deeper penetration of a small fraction of the monomers in the micelle or a slight departure from spherical shape would serve to fill empty space in the center of the aggregate. The extent necessary of either of these variations would probably not be detectable in the scattering pattern.

Figure 3 shows the agreement obtained between the experimental data and the values of $I(k)$ calculated with the parameters listed in Table I. A second pattern taken at 57% D_2O indicates reproducibility.

The first conclusion that can be drawn is that, considering the parameter δ, the model shows a degree of roughness that is considerably greater than the one found for other "small" micelles like SDS,[17] cetyl trimethylammonium bromide (CTAB),[18] and sodium octanoate.[19] Whether this is due to branched alkyl chain or to the presence of the phenyl group next to the polar head is not now clear, and more experimental data on similar systems is needed for a clearer resolution of this point.

TABLE I. Parameters derived from fit to SANS data.

Fraction D_2O	Aggregation number	Charge Z	δ[a]	Diameter σ, Å
1.00	54	19	3.2	42.0
0.90	53	20	3.1	41.6
0.80	52	19	3.1	41.6
0.70	52	19	3.1	41.6
0.57	51	18	3.0	41.0
0.57 (repeat)	50	17	3.0	41.0
Average	52	18	3.1	41.5

[a]Number of methylenes per branch in shell (2δ per surfactant monomer).

The second conclusion is that the present model of the 6 Ph C12 SNa micelles seems very plausible. In fact, changing the scattering length of the solvent with respect to that of the micelles makes the scattering experiment dependent solely on the detailed geometry of the micelle, as $S(k)$ for all D_2O/H_2O compositions will be essentially independent of the contrast. Hence, a "wrong" model of the micelle which gives agreement with the experimental result at a given D_2O/H_2O ratio by coincidence, should not be able to fit the data for a different D_2O/H_2O ratio. The results also confirm that there is essentially no effect on the micelle structure because of changing the solvent from light to heavy water.

CONCLUSION

SANS data on a 0.055 M solution of 6 Ph C12 SNa in several D_2O/H_2O mixtures can be described in terms of a model of spherical micelles formed by a core of radius $R_1 = 11.9$ Å surrounded by a spherical shell 8.9 Å thick. The core of the micelles contains, on the average, only half of each chain, giving a picture of a rough dynamic entity substantially different from the two-shell Hartley model.

ACKNOWLEDGMENTS

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4. Distribution of Inorganic Ions Between Saline Solutions and Hydrous Oxides

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The results discussed here were obtained partially with support of the discontinued program aimed at identifying conditions under which adsorption of inorganic ions is low enough for them to serve as tracers for water flow through formations. It was completed under the other sponsor, the Office of Nuclear Waste Isolation. Accounts have been published in the open literature[1,2] and only a brief discussion will be given here.

The equilibrium between inorganic salts in solution and in a contacting solid phase (salts of a monovalent anion and of divalent and monovalent cations are taken for examples here) is given by equality of their activities, $\underline{a}$, if the same reference state is selected for the two phases:

$$\underline{a}_{MX} = \underline{m}_M \underline{m}_X \gamma^2_{\pm MX} = \bar{\underline{a}}_{MX} = \bar{\underline{m}}_M \bar{\underline{m}}_X \bar{\gamma}^2_{\pm MX} \quad (1a)$$

$$\underline{a}_{BX_2} = \underline{m}_B \underline{m}_X^2 \gamma^3_{\pm BX_2} = \bar{\underline{a}}_{BX_2} = \bar{\underline{m}}_B \bar{\underline{m}}_X^2 \bar{\gamma}^3_{\pm BX_2}, \quad (1b)$$

$\underline{m}$ denoting concentrations, conveniently in moles/kg water in each phase; $\gamma_\pm$, mean ionic activity coefficient; and the bar over the symbols indicating the solid phase. By dividing (1b) by (1a) squared, one obtains

$$1/\Gamma = \frac{\bar{\underline{m}}_B \underline{m}_M^2}{\underline{m}_B \bar{\underline{m}}_M^2}, \quad (2)$$

where Γ is the quotient of the activity coefficients. Values of Γ for uptake of electrolytes from concentrated aqueous solutions by organic ion exchangers are frequently close to unity, even though the values of $\gamma_\pm$ in the individual phases may vary over an order of magnitude.[3] Salt rejection by dynamically formed ion exchange membranes, which depends on coion invasion, also can be represented with economy in adjustable parameters by this approach.[4]

The value of one for the equilibrium constant is a consequence of assignment of the same reference state to the two phases. If the solid has a fixed negative charge (cation-exchange capacity, $\underline{C}^*$), uptake of the anion (here the coion) will be repressed by the high concentration of cations on the solid (equations 1a and 1b), and it may be a satisfactory approximation to neglect coion uptake. In such cases and when also one cation (here B) is present at very low concentration relative to the other,

$$1/\Gamma = \frac{\bar{\underline{m}}_B \underline{m}_M^2}{\underline{m}_B \underline{C}^{*2}} = \underline{D}_B \frac{\underline{m}_M^2}{\underline{C}^{*2}} \quad (3a)$$

or

$$d \log \underline{D}_B = -2\, d \log \underline{m}_M - d \log \Gamma \quad (3b)$$

where $\underline{D}_B$ is the distribution coefficient of B. For constant Γ, a plot of log $\underline{D}_B$ <u>vs</u> log $\underline{m}_M$ will be linear, of slope-2 for the example here of a monovalent/divalent ion exchange. With these restrictions, the expressions are the same as one obtains by the conventional representation of ion exchange reactions, $B^{2+} + 2\,\bar{M}^+ \rightleftarrows \bar{B}^{2+} + 2\,M^+$ here.

With many minerals, particularly clays, results obtained by ourselves and others have shown that equation 3b correlates behavior to a good approximation. However, with some inorganic solids, there are obvious departures. Figure 1 summarizes some measurements of Sr(II) at low loading on alumina. Slopes are clearly much less than two. Some, confronted by such discrepancies, have maintained that an ion-exchange model is not useful.

This view neglects the analogy of weak-electroyte ion-exchange resins. Hydrous oxides have characteristics in common with ion-exchangers with carboxylic or non-quaternary amine groups; in acidic media, they tend by reaction with protons to have a fixed positive chage, i.e., to be anion exchangers; and in basic, by reaction with hydroxide, cation exchangers.[5] Figure 2 summarizes uptakes of Br^- and Na^+ by alumina. The trend with pH is obvious, and the higher uptakes with increasing salt concentration are also in the direction expected from equation 1.

The approximation identifying $\underline{m}_M$ in equation 3 with a constant $\underline{C}^*$ is therefore not good in this case. The more general equations 1 and 2 for equilibria of ions between solid and liquid phases are useful in discussing such systems. The measurements of anion uptake in Figure 2 were carried out with bromide ions because of the availability of a convenient gamma tracer. The assumption that chloride uptake is similar is probably good. The variation of ion exchange capacity with concentration of macro salt is estimated from the results in Figure 2, and introducted into equation 3b, to obtain the predicted slopes listed in Table 1. Agreement with the experimental slopes is seen to be good.[2]

Although, as we observed above, the trends of uptakes of sodium and bromide ions in Figure 2 are qualitatively as expected, they do not follow quantitatively equation 1a, with $M = Na^+$ and $x = Br^-$. The half filled points in Figure 3 are for the experimental points from the range of conditions in Figure 2, for which the differences between solution concentration before and after equilibration were sufficient for concentrations of ions in the solid determined by material balance to be reasonably precise. Because we have no information on the water content of the solid, concentrations in the solid phase are per kg of dry solid, indicated by parentheses, rather than per kg of water as in the equations. Water content probably does not vary greatly over the range of conditions here. Only the spread of the ordinate values is of significance, not the actual values.

Values of the quotients of sodium and bromide concentration products for solutions and solid phases vary over several orders of magnitude. Much more constant quotients are obtained for acid and base activities in the solutions divided by the square of bromide or square of sodium concentrations on the solid, respectively. The constancy implies bromide is taken up along with a proton (thus the square of bromide on solid = (H^+) (Br^-)) and sodium along with a hydroxide, the sites of anion and cation adsorption being physically separated. We are not altogether comfortable with this model. However, in any case, the departure of the slopes of the logarithm of distribution coefficients of trace cations vs NaCl concentration from the negative of charge on the tracer ions can be explained by the variation of effective ion exchange capacity with salt concentration.

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Table 1.

COMPARISON OF THEORY AND EXPERIMENT FOR ADSORPTION ON ALUMINA AT HIGH pH

	Cs(I)	Sr(II)
$\frac{d\ LOG\ D}{d\ LOG\ m_{Na}}$ - exp.	-0.48	-0.72
$\frac{d\ LOG\ D}{d\ LOG\ m_{Na}}$ - predicted	-0.38	-0.76

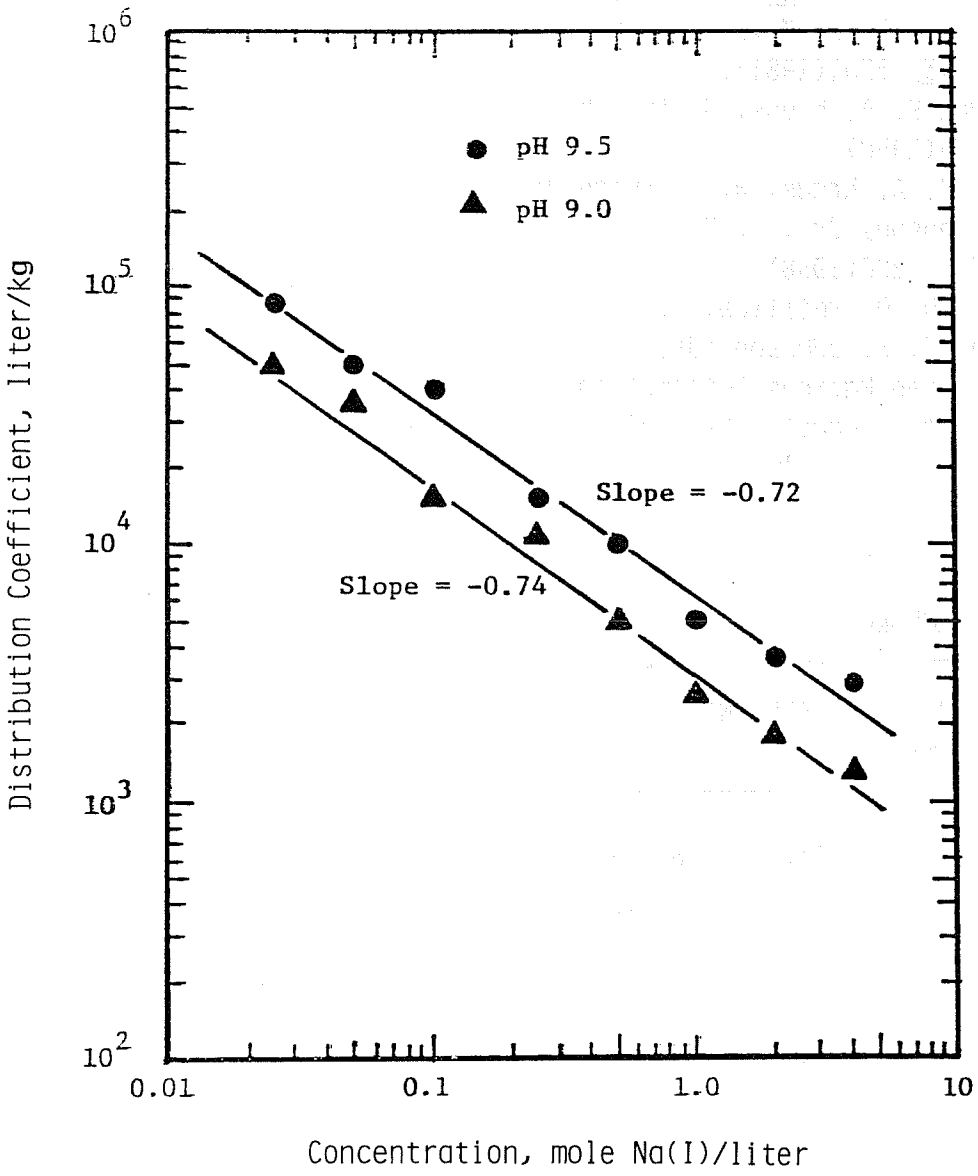


Fig. 1. Adsorption of Sr(II) on the Na form of Al_2O_3

ORNL DWG 80-1406R

THE ANION AND CATION UPTAKE ON Al_2O_3

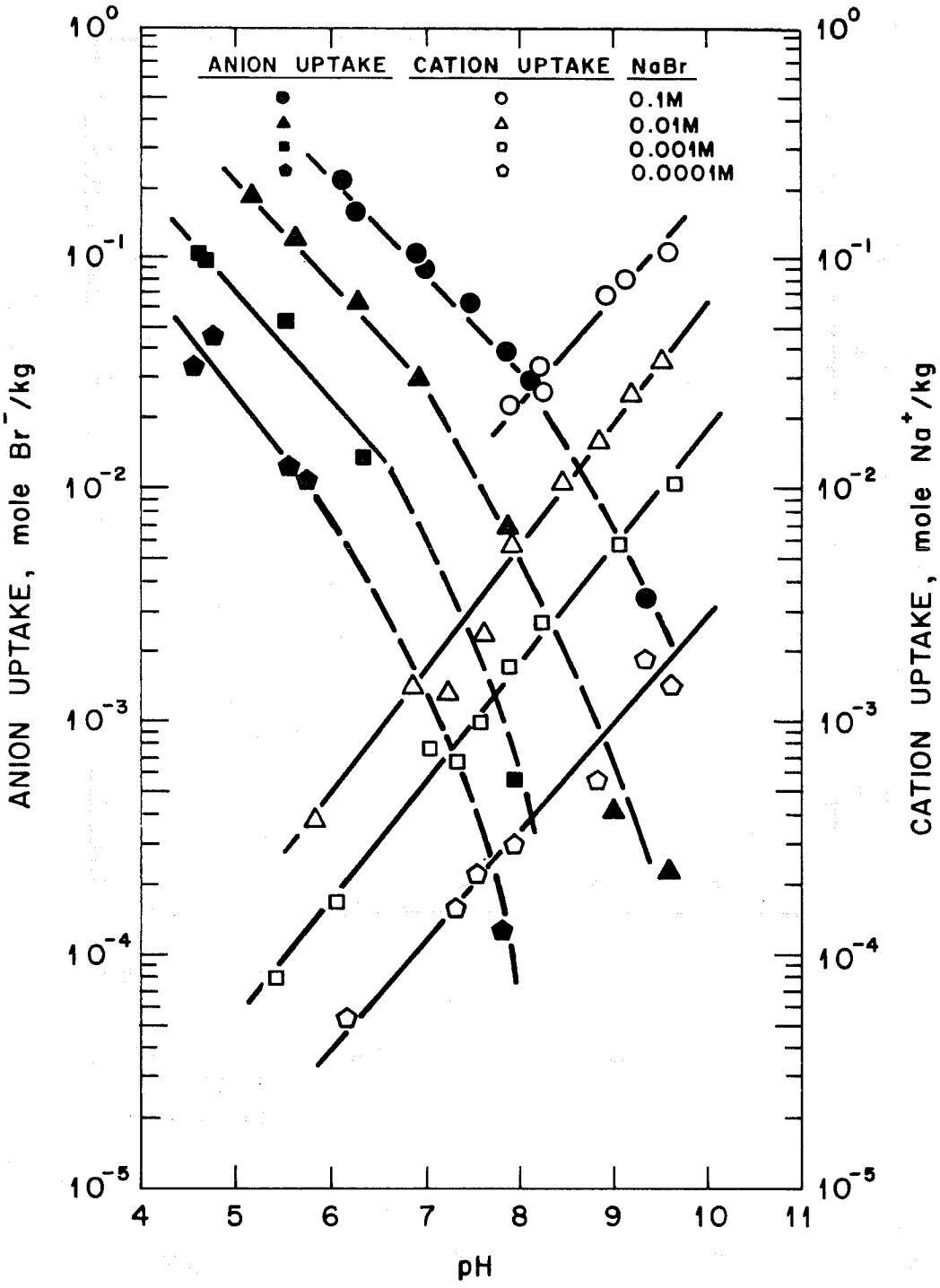
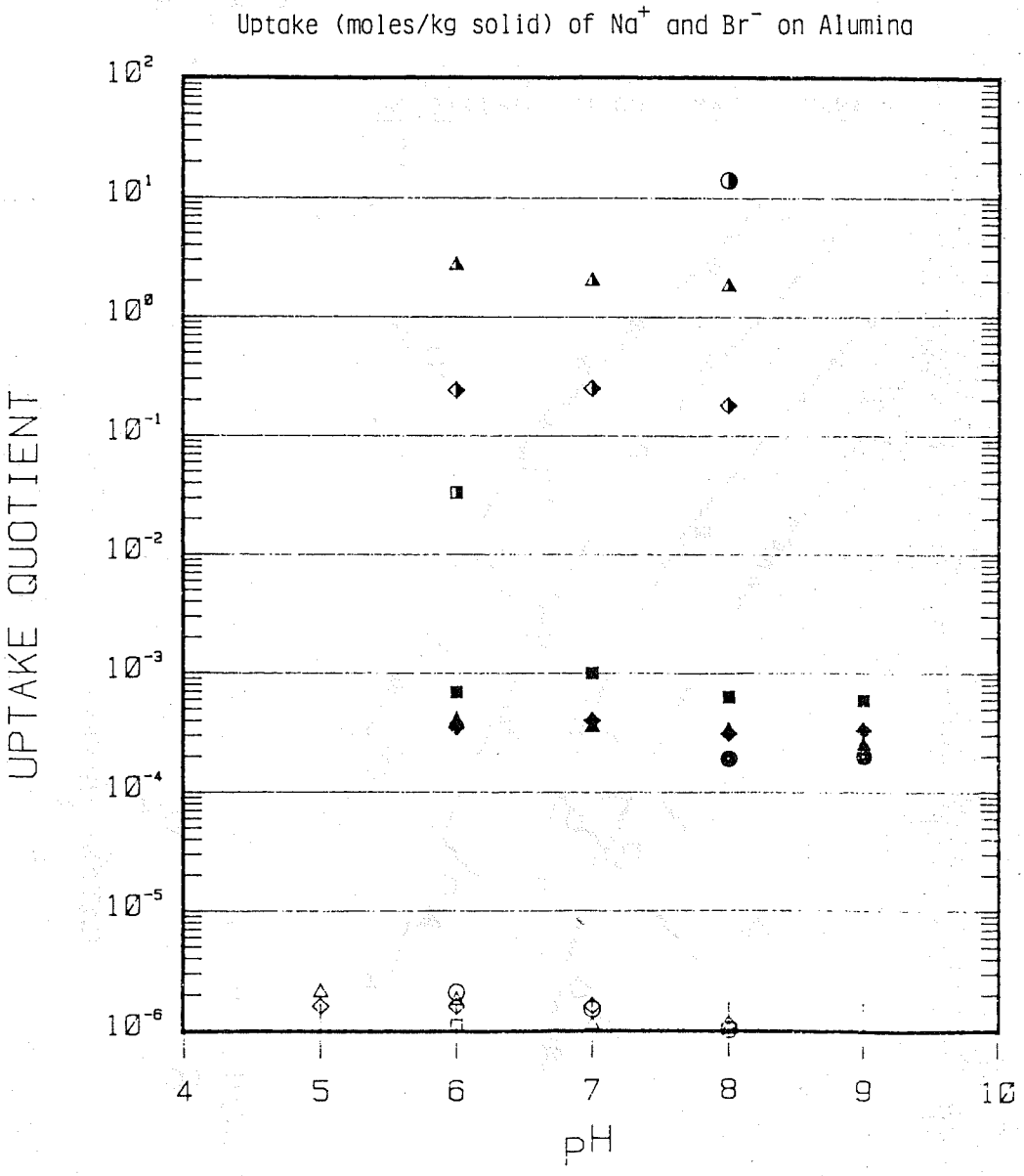


Fig. 2



Uptake Quotients, solution over solid

m_{NaBr}	$\frac{m_H m_{Br}}{(Br)^2}$	$\frac{m_{Na} m_{Br}}{(Na)^2}$	$\frac{m^2_{NaBr}}{(Na)(Br)}$
0.1	○	●	◑
0.01	△	▲	◭
0.001	◇	◆	◩
0.0001	□	■	◨

Fig. 3

5. PROGRAM HISTORY

The program was initiated in April, 1977, under the name "Ion-Exchange Characteristics of Enhanced Oil Recovery Systems," at the same time as another began, "Multiple Tracers for Enhanced Oil Recovery." A collateral program, "Chemicals for Enhanced Oil Recovery," had been previously underway about a year. Although all three had the furtherance of oil recovery as the goal, and the research was frequently mutually supportive, the motivations and specific objectives were different.

The chemicals program aimed at reducing barriers to implementation of enhanced recovery arising from the high costs or limited supply of chemicals used in micellar floods. It grew out of interests in microbiological processes used in the treatment of waste streams by various methods and recovery of useful products. The background of the ion exchange program was long-term research in aqueous-organic systems, primarily though not exclusively with relation to ion exchange and membrane processes. It has been more fundamental than the other two. The rationale of the tracers was to take advantage of our experience in ion-exchange, particularly on inorganic materials, to find and evaluate potential new tracers for water movement in formations. Many of the modifications of experimental technique which had to be developed in this task were also useful in one topic of this program, equilibria of hardness ions between minerals and ground waters in oil-bearing formations.

Concurrent were research programs of our group in inorganic and separations chemistry supported by the Division of Chemical Sciences, Basic Energy Sciences/DOE and in adsorption of nuclides of interest in permanent disposal of reactor wastes, supported by the Office of Nuclear Waste Isolation.

An outline of the history of the chemicals program was included in the last report of the program (A. L. Compere et al., "Chemicals for Enhanced Oil Recovery", Report DOE/BETC/OR-21 for October 1980 - September 1981). As the present report is in all likelihood the last from this program, now entitled "Amphiphilic Compounds in Enhanced Oil Recovery," it seems also appropriate to review briefly the activities under it, as well as those in the tracer work. A list of publications from both programs follows, as well as a separate list of papers on related topics from research supported by others (identified by (O) by the report number), to facilitate discussion.

<u>Adsorption of inorganic ions on minerals</u>. There are many minerals which might adsorb tracers (added to monitor water movement) and thereby retard them relative to water. Other minerals serve as reservoirs of multivalent cations, deleterious to properties of surfactants needed in oil recovery. Of such minerals, clays are probably the class most harmful in these respects, and hydrous oxides next. These are emphasized in our work. We covered wide ranges of salinity, to establish the reservoir water compositions in which tracers might be useful or predictions from adsorption parameters might be valid. Refs. 5 & 7 show that Ca(II)-Na(I) equilibria between solutions and montmorillonite from many sources, as well as other clays of lower ion-exchange capacity, can be described adequately for most practical

purposes in this application by simple ion-exchange equilibria. The adsorption of Sr(II) and perhaps other alkaline earth ions in exchange with sodium are low enough to imply they may be useful as tracers in formations of relatively high salinity, say over one mole/liter (4, 6(0)).

Anionic species have advantages as tracers, because most minerals tend to carry negative charges, or to be cation exchangers, at the pH of the waters in most natural formations. The usefulness of bromide, iodide, and strong complexes such as those of cyanide reflect this situation. We evaluated ions which form chloride complexes at moderate chloride concentrations as tracers. It appears that adsorption of Cd(II) may be low enough under some conditions (6). The pertechnetate ion is also but little adsorbed under oxic conditions (9(0)). However, TcO_4^- may be reduced to valence states lower than VII in oil formations. In addition, its convenient gamma tracer, ^{95m}Tc, is expensive and of relatively short half-life (about two months); radiation from the abundantly available ^{99}Tc is a weak beta, relatively difficult to detect.

The axial filter was demonstrated to be a convenient technique for study of adsorption on minerals, particularly for establishing short-time reversibility of reactions (4(0), 5(0)). The adsorbent is suspended in a chamber surrounding a rotor wrapped with a membrane which passes liquid but not adsorbent. Solution containing the adsorbate is pumped into the chamber, and the concentration of filtrate followed as a function of time. After the adsorbent is loaded, solution without adsorbate may be introduced, and desorption monitored. From the time dependence of filtrate concentration, distribution coefficients may be determined.

Adsorption equilibria of hydrous oxides are more complicated than on clays, which resemble strong-acid or strong-base organic ion exchangers. Hydrous oxides are usually relatively weak acids or bases. They are typically anion-exchangers in acidic solutions, in which the net charge of the solid tends to be positive, and cation-exchangers in basic solution, in which the net charge becomes negative; the ion-exchange "capacity" refers to readily exchangeable counterions taken up by the solid to neutralize the matrix charge. The nature of the exchanger (anion or cation) and its capacity at a given pH depend also on the acidity of the central ion forming the oxide and the concentration and type of other ions in the solution.

These aspects of the hydrous oxide of Al(III), widely distributed in natural formations, are illustrated in two papers (8, 8(0)), and the applicability of an ion-exchange model is discussed further in this report.

Adsorption on mixtures of minerals is predictable by additivity, unless solubility of one of them changes the composition of the medium (7(0)).

<u>Phase behavior of aqueous-hydrocarbon systems</u>. We had earlier been impressed by the ability of hydrotropic salts, such as inorganic perchlorates, to solubilize components in mixes used for casting desalination membranes or in solutions which were models for membrane components. We have therefore approached the properties of amphiphiles and their use in oil recovery from a somewhat different perspective than others in the field. Initially, we examined the ability of inorganic and

organic salts to solubilize hydrocarbons in water, by themselves or in conjunction with another amphiphile, usually an alcohol. Inorganic perchlorates were found, for example, to be roughly as effective as benzene sulfonate, on a mole basis, in solubilizing toluene, as indicated by the amount of butylcellosolve necessary to effect a one-phase system (9). The solubilizing power of organic salts of a given class however increases rapidly as the number of alkyl carbon substituents increases (1,2,9) and varies with the nature of the organic salt, e.g., aromatic sulfonates or carboxylates, salicylates being particularly high 2(0),9). For a given set of amphiphiles, higher concentrations of them are necessary to attain miscibility as the hydrocarbon molecular weight increased (3). We designated the low-equivalent-weight organic salts as "protosurfactants."

These trends are probably what one might have expected. There were, to us at least, two surprising aspects, however. One was the large solubilization of hydrocarbons in water, both alone and in conjunction with alcohols, by protosurfactants, considerably greater on a mole/mole basis than those reported for low-molecular-weight surfactants. The other was the rather large difference between classes of protosurfactants, particularly between salicylates and others. We are not aware of any data which would allow similar comparisons of surfactants of corresponding hydrophilic groups.

Even though the solubilizations are high, in no systems we have investigated are they high enough to suggest that attainment of complete miscibility of oil in formations would be a practical route to oil recovery. In systems of lower ratio of protosurfactant to water, patterns diverge from those having high ratio (3(0),9). If a representation on a triangular compositional diagram with hydrocarbon, alcohol, and aqueous protosurfactant at the three apices, miscibility boundaries are relatively symmetrical with respect to the alcohol at high protosurfactant concentrations, but become highly asymmetric at low protosurfactant/water ratios, much more alcohol being required to effect a single phase in the hydrocarbon-rich region. Patterns with surfactants are frequently qualitatively similar, although they may be more complex (12). In the neighborhood of these asymmetries on the water-rich side, third phases frequently are present, and the single phase solutions are often opalescent, an observation suggesting the proximity of critical compositions. This inference is strengthened by the fact that interfacial tensions are frequently low in this region.

Compositional regions in which third phases exist are of course those favorable for oil recovery. By addition of a fifth component, inorganic salt, and by carrying out scans of the effect of varying the concentration of individual components, we have shown in work reported elsewhere in this report that the behavior of protosurfactant-containing systems parallels that of otherwise similar systems containing organic salts in the surfactant range.

Although we are unable to pursue these systems, a list of some of the topics we would have liked to investigate may be of interest. Further exploration of specific effects of functional groups and comparison of

alkyl with alkyl/aromatic protosurfactants, as well as non-ionic protosurfactants; mixtures of surfactants and protosurfactants; adsorption of protosurfactants on minerals; effect of divalent cations on properties; further small-angle neutron scattering studies of the structure of the systems and free-energy measurements, discussed below. The sparse information we have obtained indicates that loss by adsorption on minerals or by precipitation will be much less than with surfactants, and if a formulation causing low enough interfacial tensions could be developed, a flood in which favorable conditions are maintained should be much easier to design. The recipes we have tried so far do not provide adequate capillary numbers, but they are not so far away that optimization from a systematic study seems futile. In any case, the information accumulated should be useful as background for the more complex surfactant systems.

Free energies. We have measured water activities of solutions of sodium alkyl benzene sulfonates, alkyl benzene carboxylates, and alkyl-substituted salicylates, and of a few of these also containing NaCl. An account of the sulfonates is in this report. Behavior of the salicylates is similar. With the carboxylates, there is in some cases a surprising peak in osmotic coefficients as a function of concentration. Although similar observations have been reported for sodium alkyl carboxylates by Robinson and for sodium benzoate by Desnoyer and coworkers, we would like to be sure that the peak is not an artifact from adsorption of atmospheric carbon dioxide by these solutions (the solutes are salts of weak acids) before investing substantial effort in analysis of results.

With the sulfonates of higher alkyl substitution than toluene, osmotic coefficients, and the solute activity coefficients derived from them, decline more steeply with increasing concentration than those of common inorganic salts. The decline becomes steeper with increasing nos. of alkyl carbons. The results are consistent with existence of complex species comprised of a few anions, but not with formation of large micellar aggregates.

Small-angle neutron scattering (SANS). The species formed in micellar floods are complex and in some cases even broad aspects are not well established. It is generally agreed that in the two-phase region, closed surfactant aggregates incorporating other components exist, but details of their structure are controversial. In the middle phase near optimal salinities, some postulate, in contrast to discrete aggregates, a bicontinuous arrangement of extended domains, primarily aqueous and primarily hydrocarbon, separated by surfactant layers.

Small-angle neutron scattering has appeared to us and to many others to be a technique having great promise of contributing to the resolution of many of these questions. The distances important in scattering neutrons over the angular range accessible to detection are in the range of the dimensions of micelles and microemulsions. Scattering is primarily by hydrogen isotopes, abundant in the compositions to be investigated. Scattering by protons and deuterons is very different, and information on the arrangement of individual components and of parts of molecules can be inferred by use of deuterated components or compounds isotopically labelled

in regions of interest.

Experimental results from complicated systems are usually complicated to interpret, and SANS from micellar solutions is no exception. Factors influencing scattering include size and shape of particles, polydispersity, interparticle interactions, and proximity of critical points. Because the availability to the general scientific community of equipment to carry out SANS experiments is rather recent, much effort is at present directed to working out techniques to obtain and analyze data. Some of our attempts to contribute are reported elsewhere in the report. They involve mainly structural factors arising from proximity of critical points and from interparticle structure resulting from repulsion between charged micelles.

We have also measured scattering from solutions of surfactants deuterated at different positions, from the microemulsion phases over a salinity scan, with different components deuterated; and from protosurfactant solutions, among other systems. Although many interesting inferences may be made, we have not yet had time to work out other than very preliminary analyses of these results.

It is perhaps worth mentioning that these techniques should also be very useful in study of the water-soluble polymers used for mobility control. Delineation of size and shape, and changes with ionic environment and degradation should be feasible.

PUBLICATIONS

Listed below are publications from the program from its start through the period of the report. Publications dealing with adsorption of inorganic ions on minerals from this title and from "Selection of Multiple Tracers for Enhanced Oil Recovery Systems," a presently inactive program, are included. Papers on related topics supported by other DOE sponsors are compiled separately and designated by a number plus (O), for discussion of the program.

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PRESENTATIONS AT MEETINGS

1. Ho, P. C., and Kraus, K. A. The effect of hydrotropic salts on phase relationships involving hydrocarbons, water, and alcohols. Presented at the SPE Fifth International Symposium on Oilfield and Geothermal Chemistry, Stanford University, California, May 1980.
2. Ho, P. C. Phase boundary curves in toluene, 1-butanol, and aqueous sodium alkylbenzenesulfonate systems. Presented at the 181st ACS National Meeting, Atlanta, Georgia, March 1981.
3. Ho, P. C. Amphiphilic properties of low-equivalent organic salts. Presented at 1983 Spring National Meeting and Petro Expo '83, American Institute of Chemical Engineers, Houston, Texas, March 1983.
4. Ho, P. C. Phase and interfacial tensions of aqueous hydrocarbon systems containing low-equivalent-weight amphiphilic compounds. Presented at the 186th ACS National Meeting, Washington, D. C., August 1983.
5. Magid, L. J. Light scattering and microemulsion phase behavior. Gordon Research Conference, Fluids in Permeable Media, Tilton School, New Hampshire, July 25-29, 1983.