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**THE EFFECT OF ALKALINE AGENTS ON
RETENTION OF EOR CHEMICALS**

Topical Report

**By
Philip B. Lorenz**

July 1991

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**IIT Research Institute
National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma**



**National Petroleum Technology Office
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Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

Thomas B. Reid, Project Manager
Bartlesville Project Office
P. O. Box 1398
Bartlesville, OK 74005

Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
P. O. Box 2128
Bartlesville, OK 74005

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By Philip B. Lorenz

ABSTRACT

This report summarizes a literature survey on how alkaline agents reduce losses of surfactants and polymers in oil recovery by chemical injection. Data are reviewed for crude sulfonates, clean anionic surfactants, nonionic surfactants, and anionic and nonionic polymers. The role of mineral chemistry is briefly described. Specific effects of various alkaline anions are discussed. Investigations needed to improve the design of alkaline-surfactant-polymer floods are suggested.

INTRODUCTION

The Department of Energy has authorized research at NIPER in alkaline-surfactant-polymer (ASP) flooding for enhanced oil recovery (EOR), as part of the Department's goal to maximize the economic producibility of the domestic oil resource. ASP flooding shows promise of being cost-effective because alkali, in addition to reinforcing the activity of surfactants, reduces the depletion of surfactant and polymer by retention in the reservoir. The effectiveness of alkaline chemicals for this purpose varies widely with rock mineralogy and brine composition. In particular, effectiveness tends to increase with increasing pH. However, for most reservoirs, reaction with minerals is a serious problem for strong alkalis, and a flood needs to be operated at the lowest effective pH, about 10. Since the loss of chemicals by reaction or retention is a very important factor in the economics of ASP flooding, it is desirable to have complete information for optimizing the process.

For anionic chemicals -- sulfonates and hydrolyzed polyacrylamides -- the reduction of adsorption is most pronounced in the low pH range where the solid surface is positively charged. This is the result of the electrostatic component of adsorption. In the high-pH range, where the surface becomes negatively charged, pH usually has a less dramatic, but still significant influence on adsorption.

It is important to remember that adsorption is only one form of retention. Multivalent cations form precipitates with sulfonates. The combination of adsorption and precipitation is referred to as abstraction. Both factors are reduced by alkalis, which compete with sulfonates for multivalent cations in solution or in exchange sites. Partitioning of surfactants into residual oil is another major cause of retention, but no study of how this is affected by alkalinity has been reported. Partitioning should be increased if the addition of an alkaline agent increases the ionic strength or if natural surfactants generated from oil by an alkali lower the optimal salinity. For polymers, mechanical entrapment is often more important than adsorption¹. Again, no direct investigations of the effect of

pH have been reported. Mechanical entrapment probably will be affected by wettability, ionization, and hydrolysis, which can be altered by alkalinity; however, changes in these parameters between pH 6 and 10 are likely to be small. With polymers, retention is not always deleterious. Permeability reduction by polymer adsorption or entrapment has been shown to be a more important effect of polymers in some cases than a simple viscosity increase.²

SURFACTANTS

Crude Sulfonates

The benefits of alkalis added to surfactants as sacrificial agents have been recognized qualitatively.³⁻⁵ Qualitatively, figure 1⁶ shows an adsorption-pH curve of typical shape, with a steep decline in adsorption between pH 8 and 9. Douglas⁷ presents similar results for a petroleum sulfonate on alumina, for which the decline leveled off at about pH 6. The curve of figure 2,⁸ from results on a field core, lies in a higher pH range and has a higher minimum. This probably reflects specific properties of the carbonate rock. Some NIPER results⁹ with a carbonate alkali and PetrostepTM surfactant on Wilmington (CA) sand are similar. In other NIPER work,¹⁰ weak alkaline agents effected only a marginal reduction of adsorption of Petrostep products on crushed Berea sand (table 1). On the other hand, Krumrine et al.^{11,12} observed a markedly reduced adsorption of Petrostep on Berea by proper selection of the alkaline agents (table 2). Several investigations by Somasundaran^{6,13-14} illustrate how variable the results can be. Figure 3¹³ shows the dependence on surfactant concentration and previous history. In work on mahogany sulfonate and Berea,¹⁴ an increase in initial pH from 5 to 11 reduced adsorption only from 1.0 to 0.6 mg/g; however, the equilibrium pH values were very similar, 8.3 and 8.8, presumably because of the effect of carbonate minerals. In one study⁶ with mahogany sulfonate on agricultural limestone, the adsorption increased fourfold when pH was increased from 8 to 10, probably because of a major change in the solid surface. It is evident that meaningful results can be obtained only by controlled experiments.

Clean Anionics

The characteristic shape of adsorption-pH curves -- a rapid decline in the acid range and a slow decline in the alkaline range -- is shown in figure 4 for sodium dodecylbenzene sulfonate as measured in three laboratories. The variability of the results is seen even in systems with relative simple chemical composition. It is plausible to assume that the values of Baviere et al.¹⁵ are higher than those of Somasundaran¹⁶ because of higher salinity and isomeric purity, both of which have been found to increase adsorption.^{6,17} The large divergence of Wade and Schechter's results¹⁸ has no obvious explanation.

The point of zero charge (pZC) was reported for the latter experiments¹⁸ and corresponds roughly with the major change of slope in the adsorption curve. In figure 5, the decline of

adsorption observed by Schechter and Wade¹⁹ at higher pH corresponds with the higher pZC of alumina. The influence of electrostatic effects is confirmed in table 3,²⁰ which shows that the cationic surfactants behave in a manner converse to that of anionics. Unfortunately, not all the data conform to this neat pattern, as seen in the results of Somasundaran and Fuerstenau²¹ in figure 5.

Even, figure 6, with results all from the same laboratory,^{6,17,22-24} shows some unexpected variations. Adsorption appears to be higher on homoionic kaolinite than natural; but the opposite effect was observed by Yang et al.²⁵ Adsorption should be increased by the presence of divalent cations in exchange positions in natural clay. From table 4, which represents very systematic studies, we can conclude that the effect of pH is smaller at high salinity and the effect of salinity is larger at high pH. This is also illustrated in figure 7.²⁶

The principal conclusions to be drawn from work on clean anionics are as follows:

- (1) An increase in pH from 6 to 10 causes a modest decrease in adsorption.
- (2) The benefit of alkali in reducing adsorption is greater at low salinity.
- (3) The variations with surfactant and solid indicate that the benefit of alkali can be enhanced by tailoring the surfactant to the reservoir, but systematic data are needed to make this possible.
- (4) It is important in experimental studies to maintain careful control of conditions such as the preparation of the surface, path of approach to equilibrium, selection of position along the adsorption isotherm, and solid/liquid ratio.

Some observations of additional interest can be made:

(1) It has been found that the steep rise in adsorption with increasing acidity is more than an electrostatic effect. In acid there is a significant dissolution of trivalent aluminum from kaolinite, and this forms a precipitation with sulfonate at low concentration. The precipitate is resolubilized at higher surfactant concentration. These effects are believed to be responsible for the shape of the isotherms in the acid region shown in figure 8.

(2) Figure 9 also shows the probable effect of aluminum. In the acid range, no significant desorption occurs when surfactant concentration is reduced, even by two orders of magnitude. When pH exceeds 6, rapid desorption occurs.

(3) In figure 10, the trend toward negative adsorption at pH 11.5 is ascribed to micellar exclusion.¹⁵

(4) pH has little effect on critical micelle concentration (CMC) of alkyl-aryl sulfonates^{15,27} (figs. 10 and 11). This suggests that alkalinity as such would not change their partitioning into the oil phase. A change in CMC with pH may occur with ethoxylated anionic surfactants.

(5) A potentially significant factor is a change in the solution chemistry of surfactants with changing pH. Model calculations on potassium oleate¹³ have indicated that the acid dimeric anion $(C_{17}H_{35}COO)_2H^-$ is several orders of magnitude more strongly adsorbed than the monomer.

These effects are negligible with low- pK_a sulfonic acids, but may be important with the natural surfactants generated by alkali in contact with acidic crude oil. Hingston and Posner²⁸⁻²⁹ have shown that in the case of fairly simple weak acids such as H_3PO_4 , when $pH \approx pK_a$, the adsorption of the acid is accompanied by neutralization of the surface OH^- and can shift the pZC.

Nonionic Surfactants

The pH-scan in figure 12³⁰ shows that a change from acid to neutral causes a small decrease in adsorption of polyethoxylated alkyl phenols, but there is little effect in the mildly alkaline region. It is speculated³⁰ that one mechanism of adsorption is through hydrogen bonding to the surface hydroxyl groups $Al-OH$ and $Si-OH$, which would be altered by changes in acidity.

Figure 13 shows that there is a difference in adsorption onto hydrophilic and hydrophobic surfaces.³¹ Similar, but less clear-cut effects were observed with anionic surfactants by Yang et al.²⁵ It is doubtful that the effect of alkali in increasing water wettability is sufficient to play a role here. (This is fortunate as adsorption would change in the "wrong" direction.)

With nonionics, a major parameter in adsorption or other types of retention is nearness to the cloud point, as shown in figure 14.³² Thus, alkali will affect adsorption or partitioning if it alters the colloidal nature of the surfactant solution. One indication that this happens is the data of French et al.⁹ As shown in figure 15, alkali-extracted Wilmington (CA) crude oil, which shows no surface activity with alkali alone, displays an immediate large drop in interfacial tension when a nonionic surfactant is present with the alkali, much faster than for the surfactant without alkali. This suggests a change in the character of the surfactant in the presence of the alkali, affecting at least the kinetics of adsorption at the liquid-liquid interface.

However, results to date do not offer much encouragement for any beneficial effect of alkali in reducing retention of nonionic surfactants, except in removing divalent cations. It is probable that weakly ionic surfactants, such as ethoxylated carboxylates, will show more change in CMC, cloud point, and electrostatic adsorption with pH than purely nonionic surfactants. For each type, it would be worthwhile to carry out a systematic investigation.

POLYMERS

Adsorption of ionic polymers shows an electrostatic effect like that of ionic surfactants. Figure 16 shows strong adsorption of hydrolyzed polyacrylamide at low pH and a decrease as pH is increased.³³ Other anionic polymers behave similarly.³⁴ The inverse behavior of a cationic polymer is shown in figure 17.³⁵ The expected insensitivity to pH for a nonionic polymer is shown in figure 16. The adsorption is equal to the highest value observed with the anionic form at low pH. This illustrates that the primary attractive force is probably hydrogen bonding³⁶ through silanol and aluminol groups on the surface, which is then counteracted by electrostatic repulsion effects. When electrostatic effects are suppressed by increasing salinity, as in figure 18, the adsorption of the hydrolyzed polymer approaches that of the nonionic form.³⁷ It should be

mentioned that all the measurements for figure 18 were made at a pH well above the pZC, which was 1.5.

The effect of pH in producing an increasingly negative surface charge is only part of its effect on electrostatic repulsion. From intrinsic viscosity measurements,³⁷ it is known that the polymer molecule itself acquires an increasingly negative charge as pH increases. At very high pH, alkalinity promotes increased hydrolysis.³⁸ Adsorption of the more hydrolyzed polymers is lower and more reversible^{2,39-40} and can be suppressed by alkalinity. In contrast with the stereotypical behavior of nonionic polymers in figure 16, figures 19 and 20 show variations of adsorption in the very high and very low ranges of pH.^{23, 41}

As for surfactants, the adsorption of polymers can be reduced by deactivation of divalent cations by alkali.⁴² Insofar as alkali increases water wettability, it could be expected to increase adsorption.² However, it is speculated that this will be counteracted by reduced mechanical entrapment.⁴³ Another significant factor is hydrodynamically induced retention.⁴⁴⁻⁴⁵ No data have been reported showing the influence of pH on these effects. It is possible that they will be more pronounced as molecules expand at higher pH and lower salinity. If so, retention could increase even though adsorption decreases. It is evident that our ability to use alkalis to control polymer retention is limited by a paucity of definitive data. The important conclusion is that the impact of alkalinity on polymer retention should be studied primarily under dynamic conditions.⁴⁶

NOTES ON MINERAL CHEMISTRY

A preponderance of studies of the influence of alkali on adsorption has been with kaolinite. It would be rash to generalize to other reservoir minerals. For example, Krumrine⁴⁷ found that a silicate alkali did not reduce the adsorption of a petroleum sulfonate on montmorillonite. Figure 21 shows that in the case of calcite and gypsum, the dissolution of calcium overwhelms the simple adsorption of a sulfonate induced by electrostatic and micellar effects. It would be valuable to study the response of this solubility effect to alkali, especially in regard to kinetics. There have been few studies of adsorption on dolomite, either with or without alkali, although this is a common reservoir material and might be expected to behave differently from either calcite or magnesite.

Figure 22 shows that kaolinite has a buffering effect on brine⁴⁸⁻⁴⁹ between pH 4 and 10. This must be taken into account in experimental adjustment of pH. It is also important to monitor pH changes during adsorption, which have been observed with kaolinite,^{26, 50-52} alumina,⁵¹ and Berea sandstone.¹⁴

ALTERNATIVE ANIONS

Even though sodium hydroxide provides the highest alkalinity at the lowest cost, other alkaline agents are generally more economical because of greater effectiveness. Table 2 shows that this is particularly true with respect to suppressing retention. As in the case of interfacial activity,⁵³ the effect of various anions is not definitively correlated with pH. However, pH is one of the

factors to be considered, along with buffer capacity, ionic strength, deactivation of divalent cations, and, of course, consumption by reservoir solids.

Among the practical alternatives to sodium hydroxide, the carbonate/bicarbonate system has the simplest chemistry. Although there is evidence of slow and complex equilibria,⁵³ the system is probably the most easily controlled and stabilized. Carbonate has been shown^{8, 47, 54} to reduce adsorption of anionic surfactants to a modest extent and has been used for reservoir conditioning.^{42,55} Its effect is largely to increase pH, but it also functions by precipitating divalent cations. In flow experiments with petroleum sulfonate and Berea, Krumrine¹¹ found that surfactant was retained initially, but was released during a saline postflush following sodium carbonate. This peculiar effect is shown in figure 23.

Silicates have been recognized^{4, 11} as being very effective in reducing surfactant retention. Much of the work with silicates has been at a pH higher than that attainable with the carbonate system. Data in table 5 suggest that silicate should strongly reduce the adverse effects of magnesium and iron, but that calcium is more completely eliminated by carbonate and phosphate (especially since phosphate forms soluble complexes with calcium). However, because of the multiplicity of ionic species and crystalline forms of silicates and phosphates, the effectiveness seen in the last column of table 2 differs from that expected from tabulated solubilities. As for polymers, the performance of alkalis needs to be evaluated from flow experiments.

Silicates are characterized by the ratio $n = \text{SiO}_2/\text{Na}_2\text{O}$. A larger value of n results in anions that are larger (more SiO_2 units per unit charge) and more complex (fig. 24), so that they have more points of attachment. Multidentate ions tend to adsorb irreversibly²⁹ -- a fact well recognized with polymers. These properties promote sequestering of divalent cations by adsorption on colloidal particles, and also cause steric blocking of adsorption sites.⁵² The reduced retention of a petroleum sulfonate with an increase in n is shown in table 2. The same effect is shown for sodium dodecylbenzene sulfonate on kaolinite in figure 25. Increasing n improves the effectiveness in two ways: lower adsorption and a more rapid decrease with increasing pH. It is obvious that silicate is much superior to carbonate for this system. For an ethoxylated sulfate on Berea, comparing the results of Nelson et al.⁵⁷ with those of Peru and Lorenz,⁵⁴ it appears that silicate is superior to sodium bicarbonate by an order of magnitude in reducing adsorption.

Figure 26 shows that the performance of silicate in the system of figure 25 can be greatly improved by addition of a small amount of partly hydrolyzed polyacrylamide. The authors⁵² suggest that a large amount would have a negative effect because of the increase in ionic strength. Under flowing conditions, one would expect that the enhancing effect of polyacrylamide would be lost rapidly by retention of the polymer.

Silicate solutions can come to equilibrium with purely siliceous material but are subject to consumption by aluminosilicates.⁵⁸⁻⁵⁹ To achieve pH levels that are benign with respect to mineral

reactions, it is necessary to have low concentrations along with a high value of n , as shown in figure 27.⁶⁰ However, silicate "solutions" with $n > 2$ are really colloidal dispersions (fig. 28) that are unstable on the time scale of field operations.⁶⁰

Complex phosphates, most notably the tripolyphosphate¹¹ ($P_3O_{10}^{-5}$) and hexametaphosphate²⁵ ($P_6O_{18}^{-6}$) are almost as effective as silicate in reducing retention of surfactants in the laboratory. They are also capable of effecting some desorption of polyacrylamides.⁶¹ But the complex phosphates are also unstable on the time scale of field operations, as they hydrolyze to the orthophosphate (PO_4^{-3}). For example, at pH 9 and 130° F the half-life of the tripolyphosphate is 50 days.⁶² This reaction is faster at low pH, but (unlike the silicates) the phosphate remains soluble. As shown in table 6, the orthophosphate is considerably less effective than silicate in reducing adsorption at a given pH. It is also interesting that an increase of pH enhances the benefit of silicate, but has no effect on the orthophosphate.

CONCLUSIONS

1. Alkali reduces the retention of surfactants and polymers in chemical flooding.
2. The effect is often not large in the practical pH range.
3. The benefit of alkali in reducing adsorption of ionic surfactants and polymers is greater at low salinity.
4. Observed variations with surfactant and solid indicate that the benefit of alkali can be enhanced by tailoring the surfactant to the reservoir.
5. Surfactant characteristics that need to be considered are the sensitivity to divalent cations and salt and the colloidal behavior (CMC and cloud point).
6. The effect of alkali on nonionic surfactants and polymers is minor.
7. There are no data on the effect of alkali on the mechanical entrapment of polymers, which is an important mechanism of retention.
8. The effects of specific minerals include the pH of zero charge, the solubilities of gypsum and carbonates, the effect of pH on hydroxyl groups available for hydrogen bonding, and the buffering effect of the solid. There is a paucity of data on the important minerals montmorillonite and dolomite.
9. Complex silicates and phosphates are more effective in reducing adsorption than hydroxide or carbonates, but are unstable on the time scale of field operations.

RECOMMENDED RESEARCH

1. Investigations are needed on the effect of alkalis on CMC, cloud point, and partitioning of surfactants. Emphasis should be placed on ethoxylated surfactants (nonionic, sulfonates, and carboxymethylated) with various HLB values.
2. The abundant research on adsorption on silica and kaolinite should be extended to other aluminosilicates and well-defined calcareous materials, especially dolomite.
3. Dynamic experiments should be performed to evaluate the effect of alkalis on mechanical entrapment of polymers.
4. Methods should be devised to stabilize silicates at high values of n . For example:
 - low concentrations of silicates for the specific interaction with Mg and Fe, and for blocking of adsorption sites, mixed with larger concentrations of phosphate or carbonate for buffer capacity, and
 - surfactants that solubilize the colloidal complex anions.
5. Note that the reduction of retention is just one factor in design on the surfactant-alkali process. Various requirements will have to be balanced to achieve an optimum, and retention behavior may have to be explored under less-than-ideal conditions.

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TABLE 1. - Adsorption (μ eq/g) of Petrostep B-100 (0.1 wt%) on Berea sand¹

pH	wt %	NaCl
	0.0	0.3
Batch experiments, crushed Berea, 25° C		
² 6.3	0.66	1.06
³ 10.0	0.59	0.83
Flowing experiments, high-permeability Berea, 52° C		
² 6.3	0.38	
³ 10.0	0.19	

¹From reference 10.

²Natural pH.

³0.13 eq/dm³ Na₂HPO₄, 0.065 eq/dm³ Na₂CO₃, 0.0325 eq/dm³ NaHCO₃

TABLE 2. - Effect of various alkalis on surfactant retention and effluent hardness in flowing experiments through Berea core¹

Alkali	wt %	Approximate pH	Salinity/alkalinity ² / Na ₂ O	Surfactant retained, mg/g	Effluent hardness ³ ppm CaCO ₃
None	-	7.3	-	0.68	100-300
NaOH	1.0	13.0	0.63	0.65	10-20
Na ₅ P ₃ O ₁₀	0.38	8.8	-	0.18	-
Na ₃ P ₀ ₄	0.38	11.0	0.22	0.28	10
Na ₂ CO ₃	-	10.6	0.22	0.26	20-40
SILICATE: ⁴					
n=0.5	1.0	13.0	0.44	0.25	10
n=1.6	0.43	-	⁵ 0.28	0.20	10
n=3.2	0.38	10.4	0.21	0.15	10

¹Based on data from references 11 and 12. Core was 2 in. x 1 ft. Injected slug was ca. 3 PV of 0.25% Petrostep 450 and 1.0% NaCl.

²(Conductivity in reciprocal ohm-meters)/(Na₂O content in wt%).

³Connate hardness 4,800 ppm.

⁴n = SiO₂/Na₂O (mol/mol).

⁵Interpolated.

TABLE 3. - Adsorption (μ eq/g) at CMC of cationic and anionic surfactants on kaolinite¹

Surfactant	CMC, m mol/dm ³	pH	
		3	10
CTAB ²	1	36	50
SDS ³	10	33	7

¹Data from reference 20.

²Cetyl trimethylammonium bromide.

³Sodium decyl sulfate.

TABLE 4. - Adsorption of sodium dodecylbenzene sulfonate¹
on sodium kaolinite at 30°C²

	<u>pH 6.5</u>		<u>pH 9.4</u>	
Salinity, mol/dm ³ NaCl	0.01	0.10	0.01	0.10
Adsorption, μmol/g	14.00	18.00	6.40	12.00

¹Isometric mixture, recrystallized.

²Data from reference 6.

TABLE 5. - Alkali salt solubilities in water at ~25° C¹

	Formula weight/dm ³ X 10 ⁴			
	Ca	Mg	Dolomite	Fe(II)
Carbonate	1.4	13.0	17.0	5.8
Metasilicate	8.2	10 ⁻²⁰	~0	~0
Orthophosphate	0.6	-	-	36.0

¹Data from Handbook of Chemistry and Physics, 47th Edition (1986-67);
except magnesium silicate from Thornton, NIPER-273 (1988).

TABLE 6. - Effect of metasilicate and orthophosphate on adsorption¹
at two pH levels²

	pH 6.5	pH 9.4
Adsorption at maximum in isotherm		
NaCl	1.9	1.1
Na ₂ HPO ₄	1.1	1.1
Na ₂ SiO ₃	0.4	0.0
Adsorption at concentration 50 m mol/dm ³		
NaCl	0.9	0.7
Na ₂ HPO ₄	0.4	0.4
Na ₂ SiO ₃	0.2	-0.2

¹Adsorption in $\mu\text{mol/m}^2$, recrystallized sodium dodecylbenzene sulfonate in brine at ionic strength 0.1 eq/dm^3 , on sodium kaolinite.

²Data from reference 6.

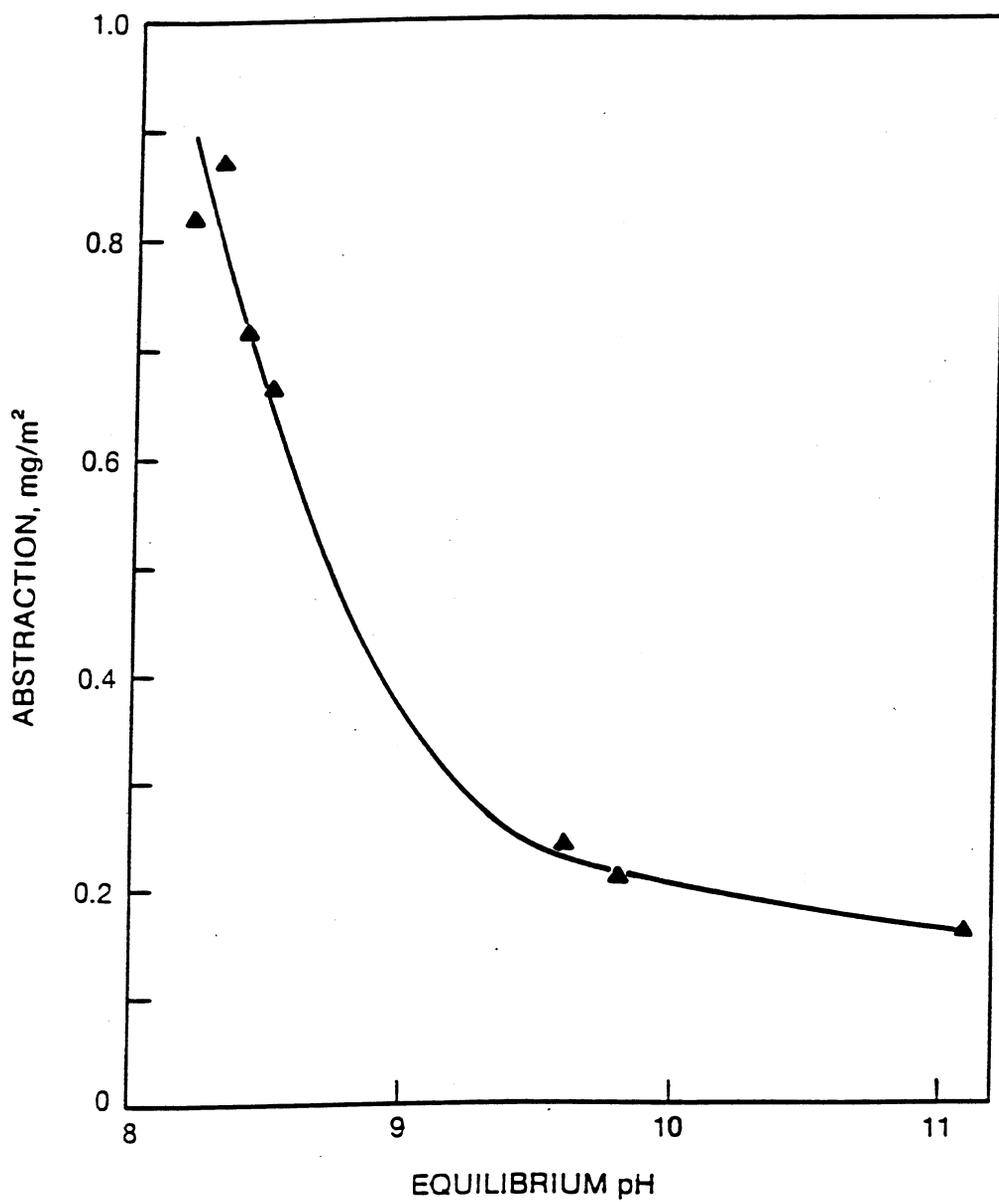


FIGURE 1. - Effect of pH on the abstraction of Mahogany AA sulfonate (initial concentration 12.6 g/dm³ active) on Bedford limestone. Solid/Liquid ratio (S/L)=1/1; 30°C; 0.01 M NaCl. (After Somasundaran and Hanna.⁶)

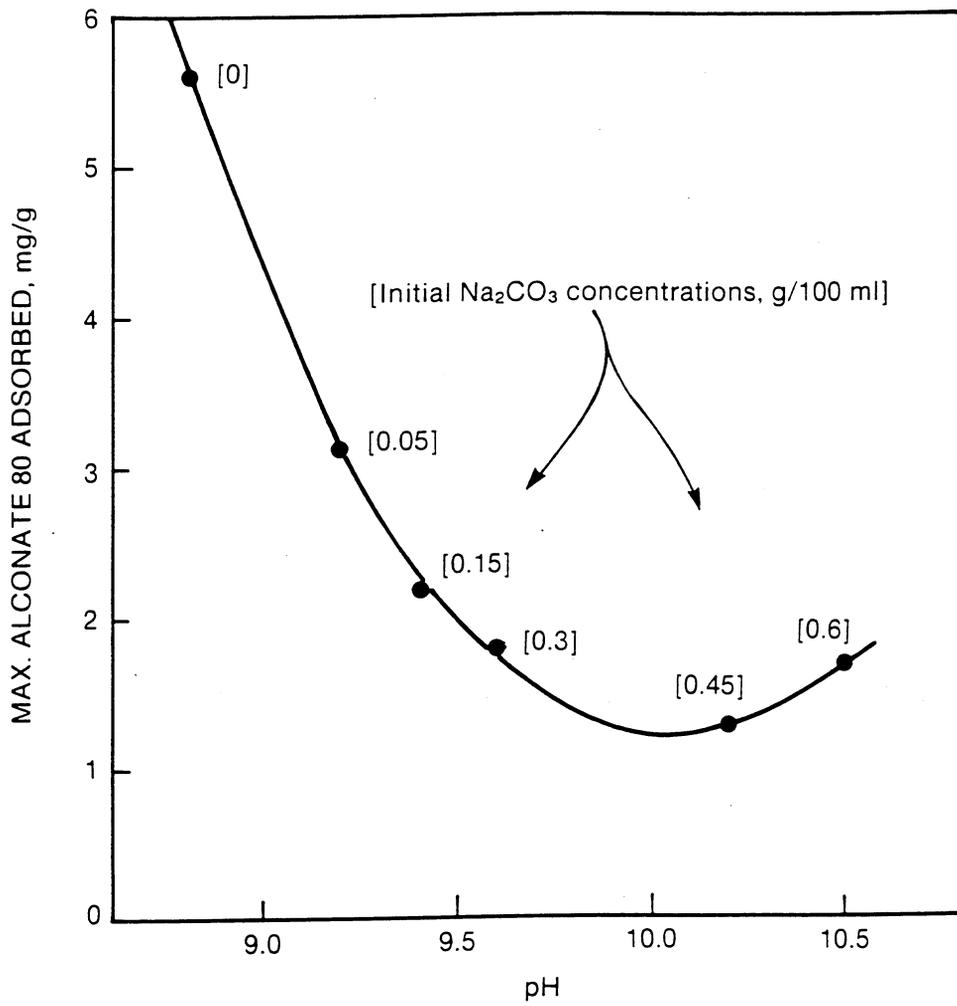


FIGURE 2. - Effect of the pH of a carbonate brine on adsorption of a petroleum sulfonate on crushed Loma Novia (TX) sandstone, 25°C. (After Hurd.⁸)

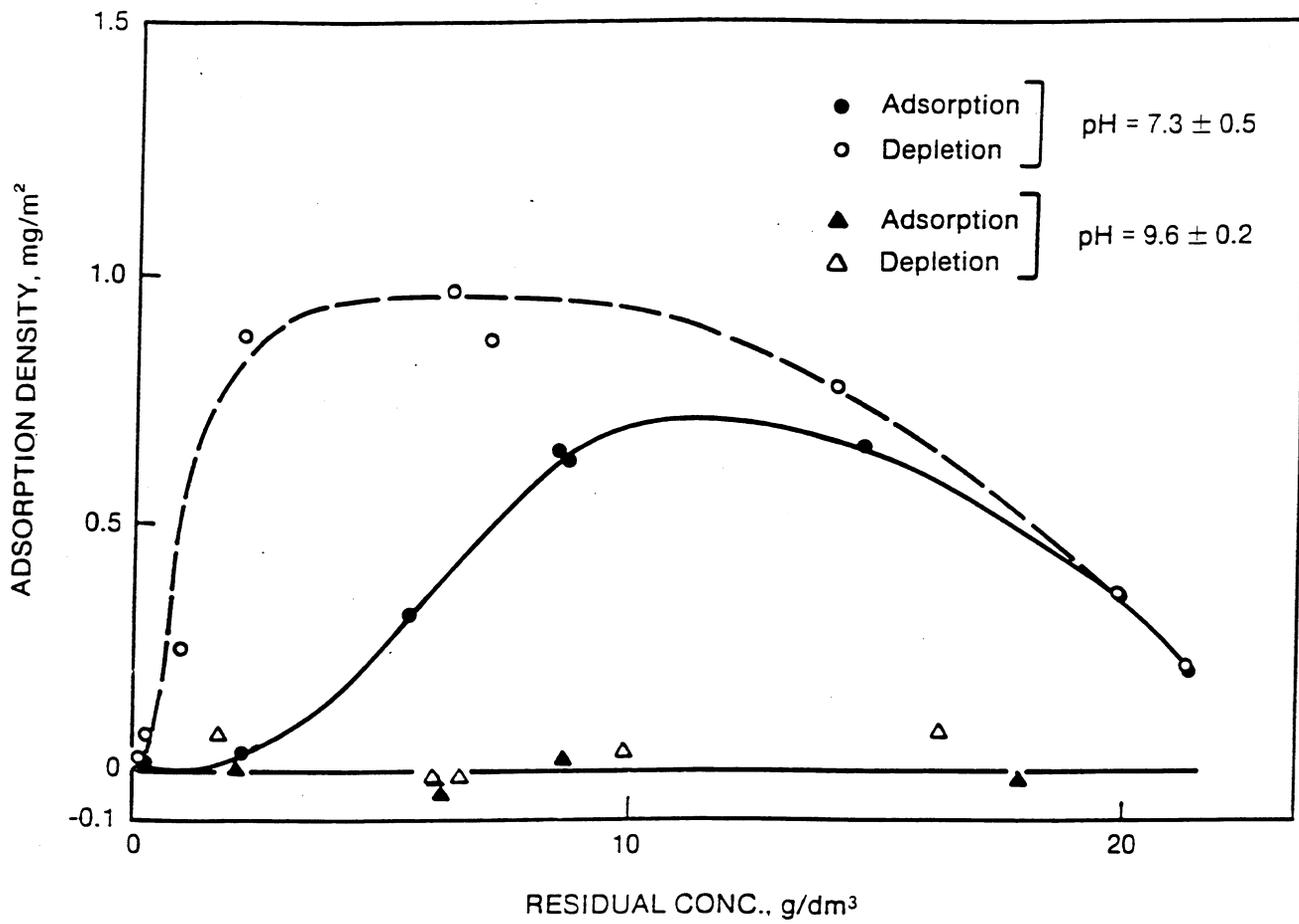


FIGURE 3. - Adsorption and depletion isotherms of a petroleum sulfonate (MW 390) on ground Berea sandstone (1.5 m²/g). S/L=2/3; 30°C; 0.2 m (NH₄)₂SO₄. (After Somasundaran.¹³)

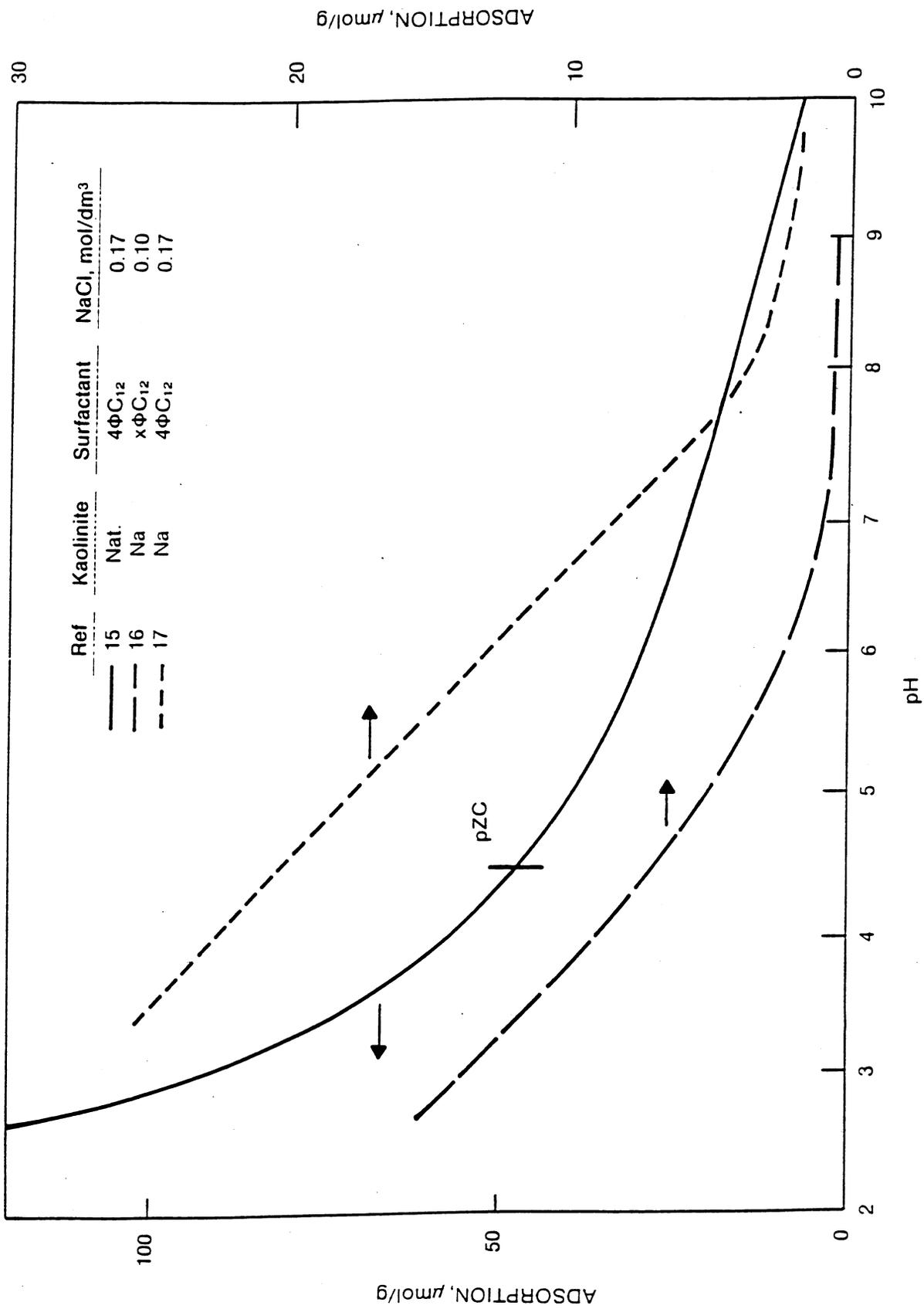


FIGURE 4. - Adsorption of sodium dodecylbenzene sulfonate on kaolinite at 30°C. nat=natural; Na=homioionic sodium; 4φC₁₂=monoisomeric, benzene on 4th carbon in chain; xφC₁₂=isomeric mixture (recrystallized).

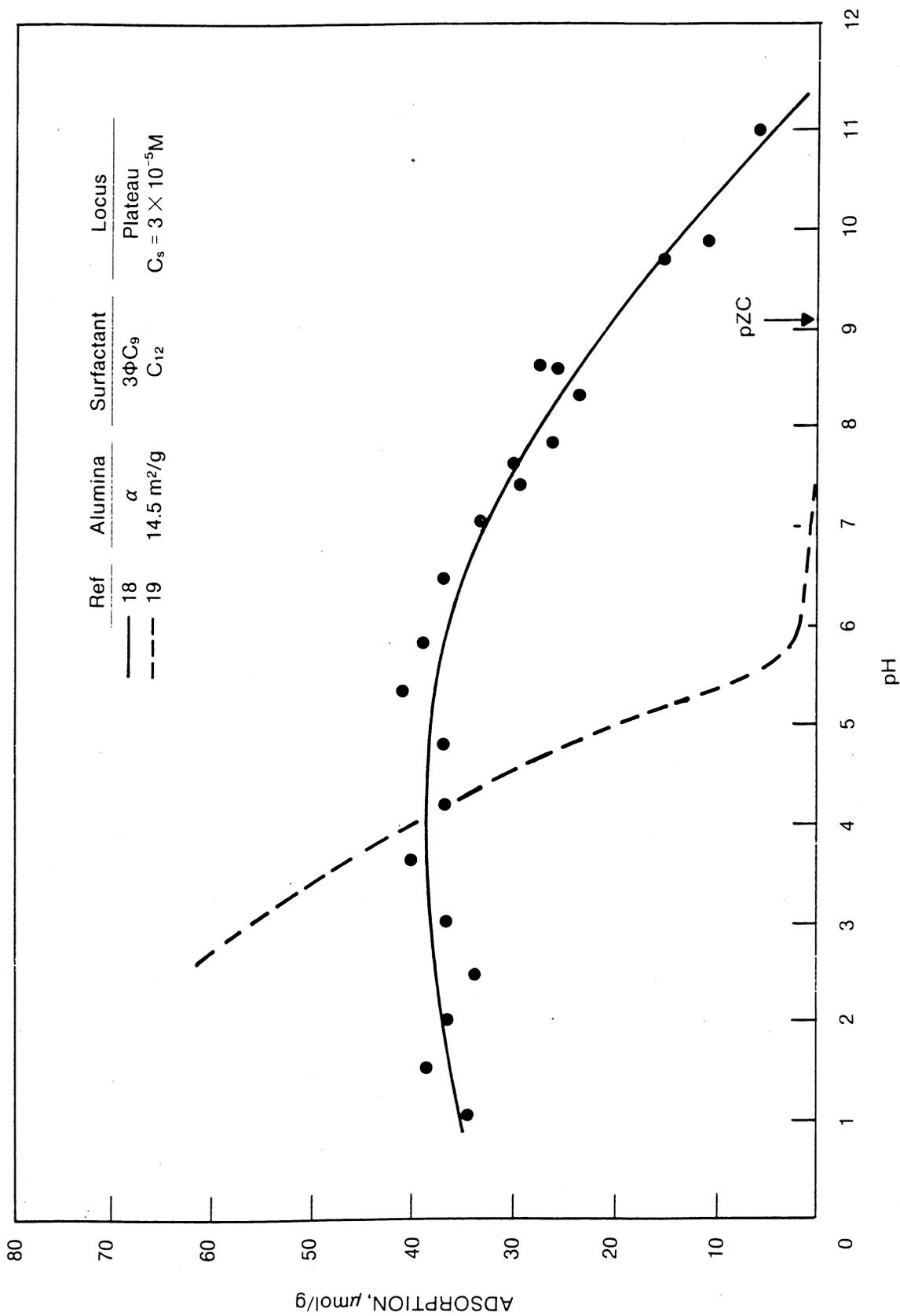


FIGURE 5. - Adsorption of sodium sulfonates on alumina. $3\phi C_{12}$ =monoisomeric, benzene attached to third carbon in nonyl chain. C_{12} = isomeric mixture of dodecyl sulfonates.

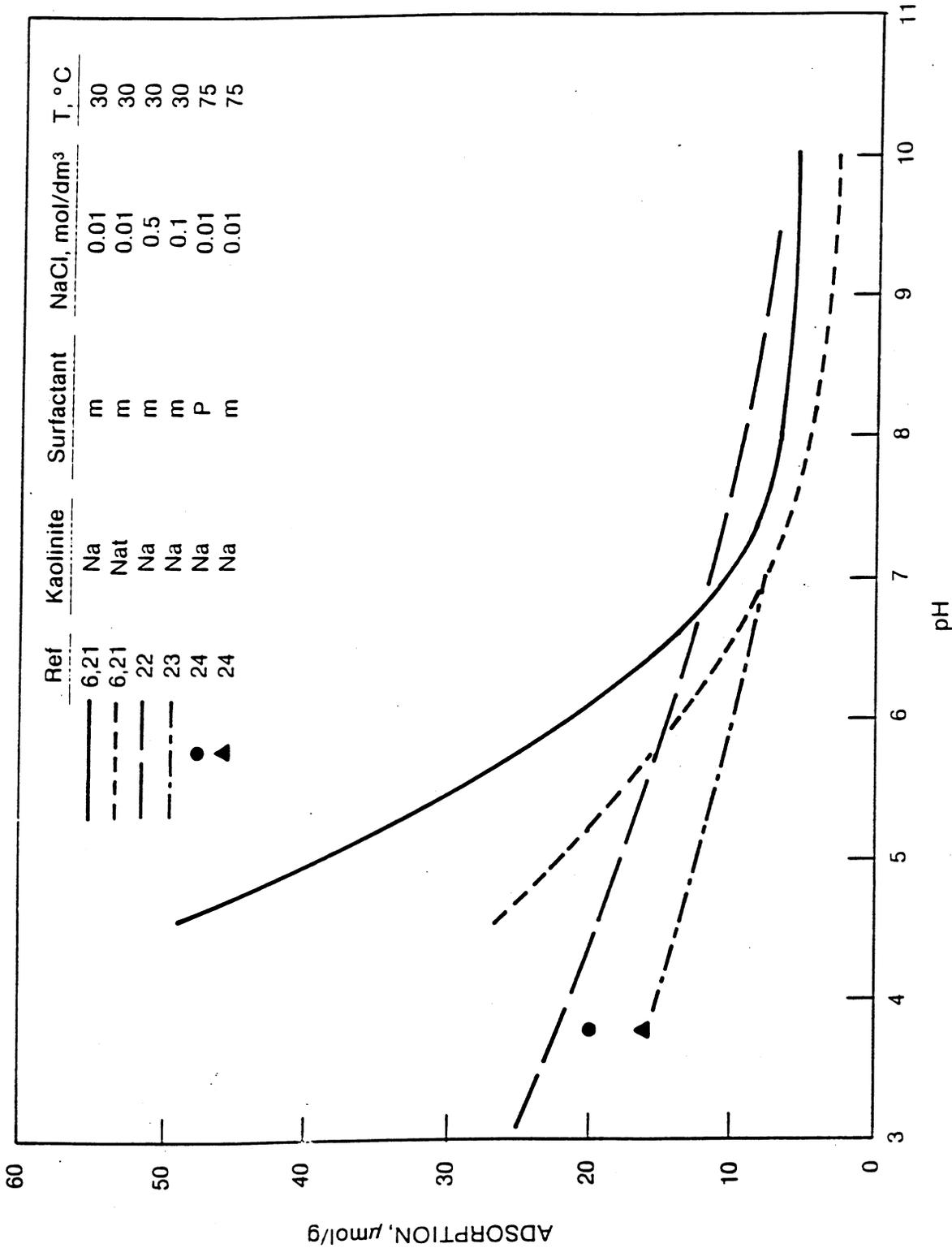


FIGURE 6. - Adsorption of sodium dodecylbenzene sulfonate on kaolinite ($\approx 10 \text{ m}^2/\text{g}$). (All after Somasundaran).
 Na=homioionic sodium; nat=natural; m=isomeric mixture; p=isomerically pure.

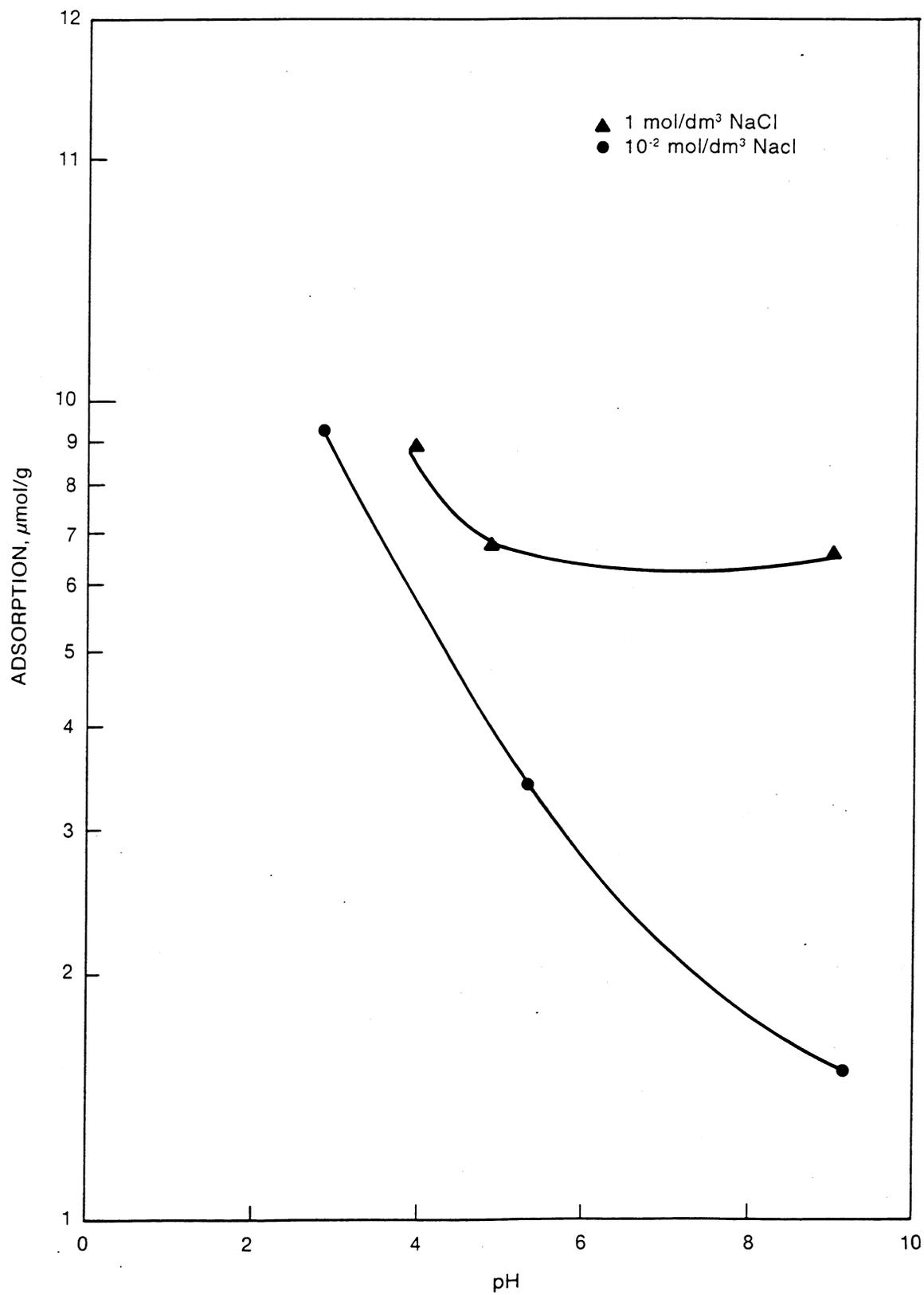


FIGURE 7. - Adsorption of sodium dodecylsulfonate (2.06 m mol/dm³) on sodium kaolinite at 30° C. S/L=1/5. (After Somasundaran.²⁶)

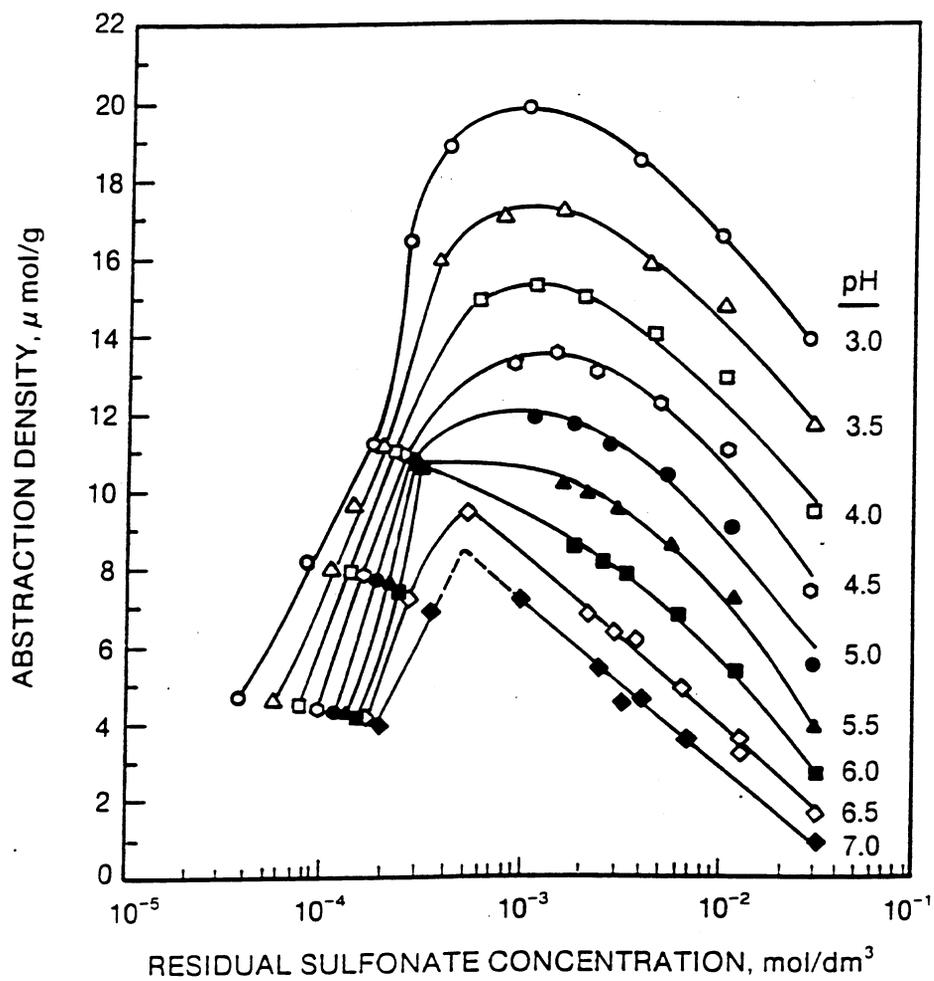


FIGURE 8. - Abstraction isotherms for sodium dodecylbenzene sulfonate (recrystallized isomeric mixture) on sodium kaolinite. S/L=1/5; 30° C; 0.1 M NaCl. (After Siracusa and Somasundaran.²⁴)

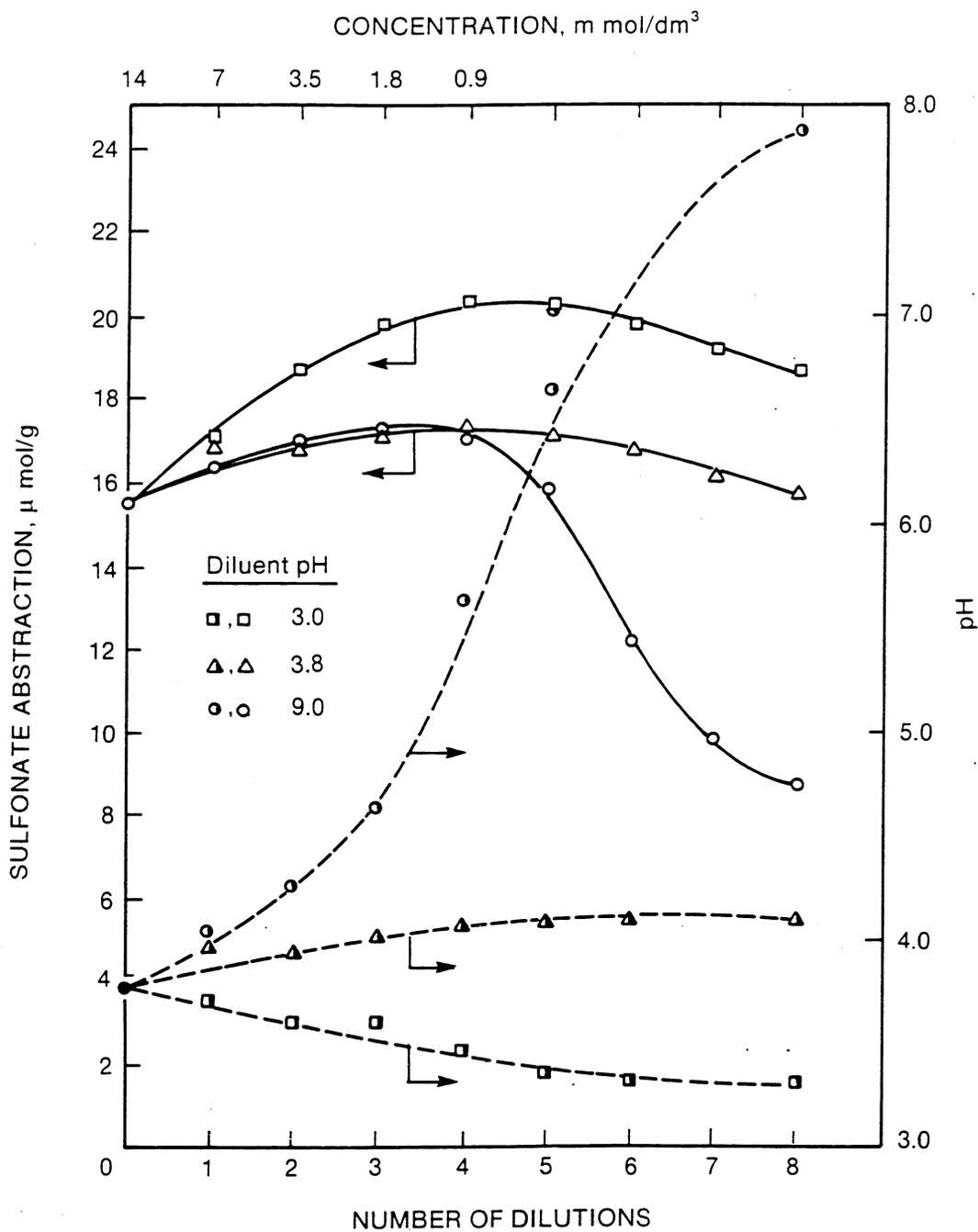


FIGURE 9. - Change in abstraction and system pH in a series of pH-adjusted 50% dilutions of sodium dodecylbenzene sulfonate (recrystallized isomeric mixture) on sodium kaolinite. Original pH 3.8. S/L maintained at 1/5; 30° C; 0.1 M NaCl. (After Siracusa and Somasundaran.²⁴)

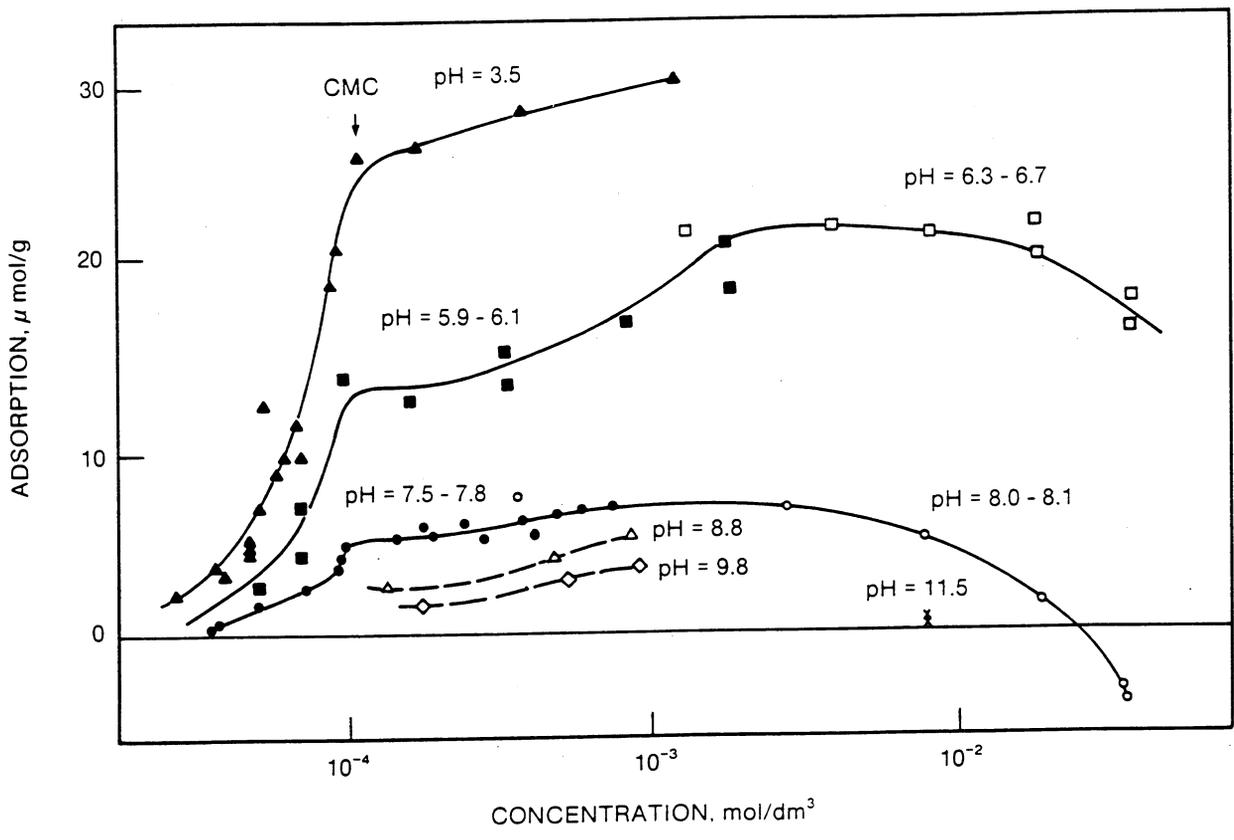


FIGURE 10. - Effect of pH on adsorption of monoisomeric sodium dodecylbenzene sulfonate (benzene on fourth carbon in chain) on homoionic sodium kaolinite. S/L=1/119; 30° C; 0.17 M NaCl. (After Baviere et al.¹⁵)

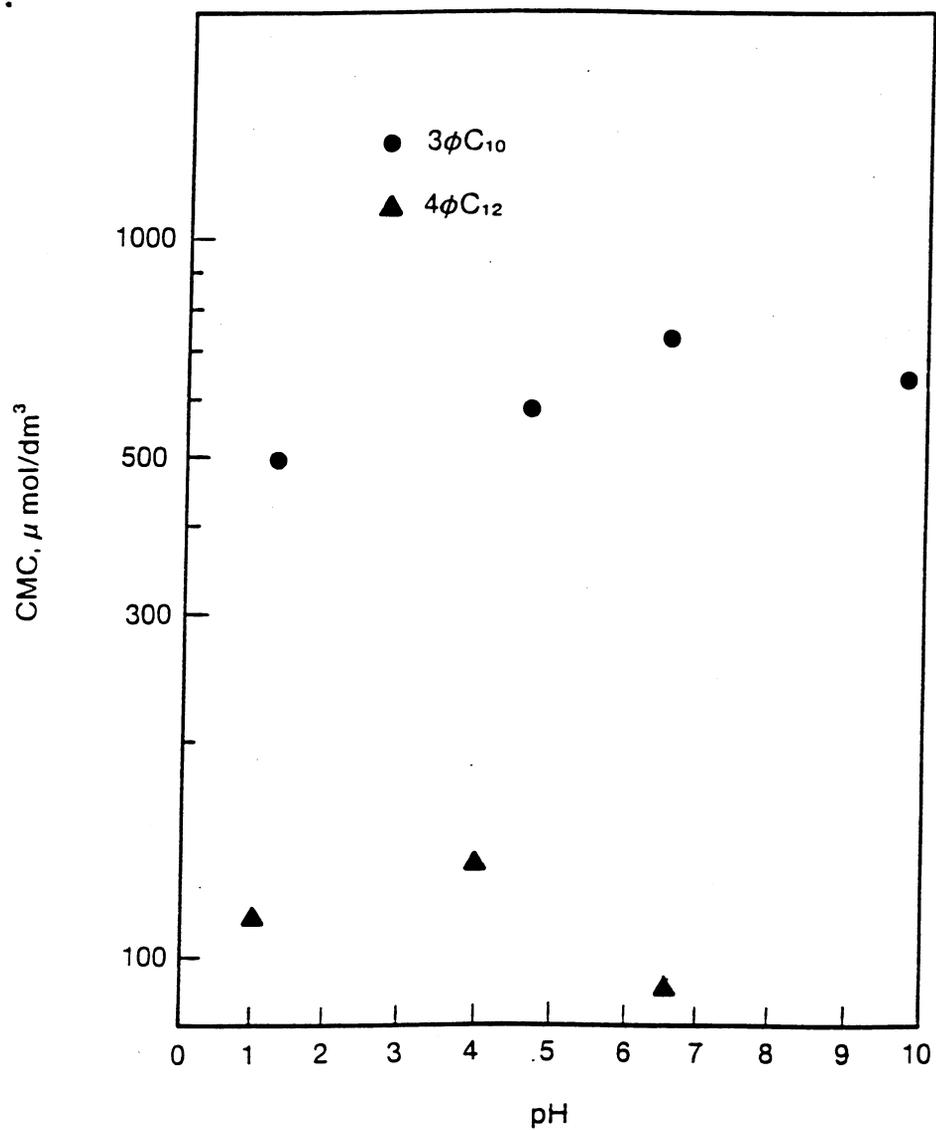


FIGURE 11. - Effect of pH on CMC of isomerically pure sodium alkylbenzene sulfonates. $3\phi\text{C}_{10}$ =benzene on third carbon of decyl chain; $4\phi\text{C}_{12}$ =benzene on fourth carbon of dodecyl chain. 25°C; 0.17 M NaCl. (After Scamehorn et al.²⁷)

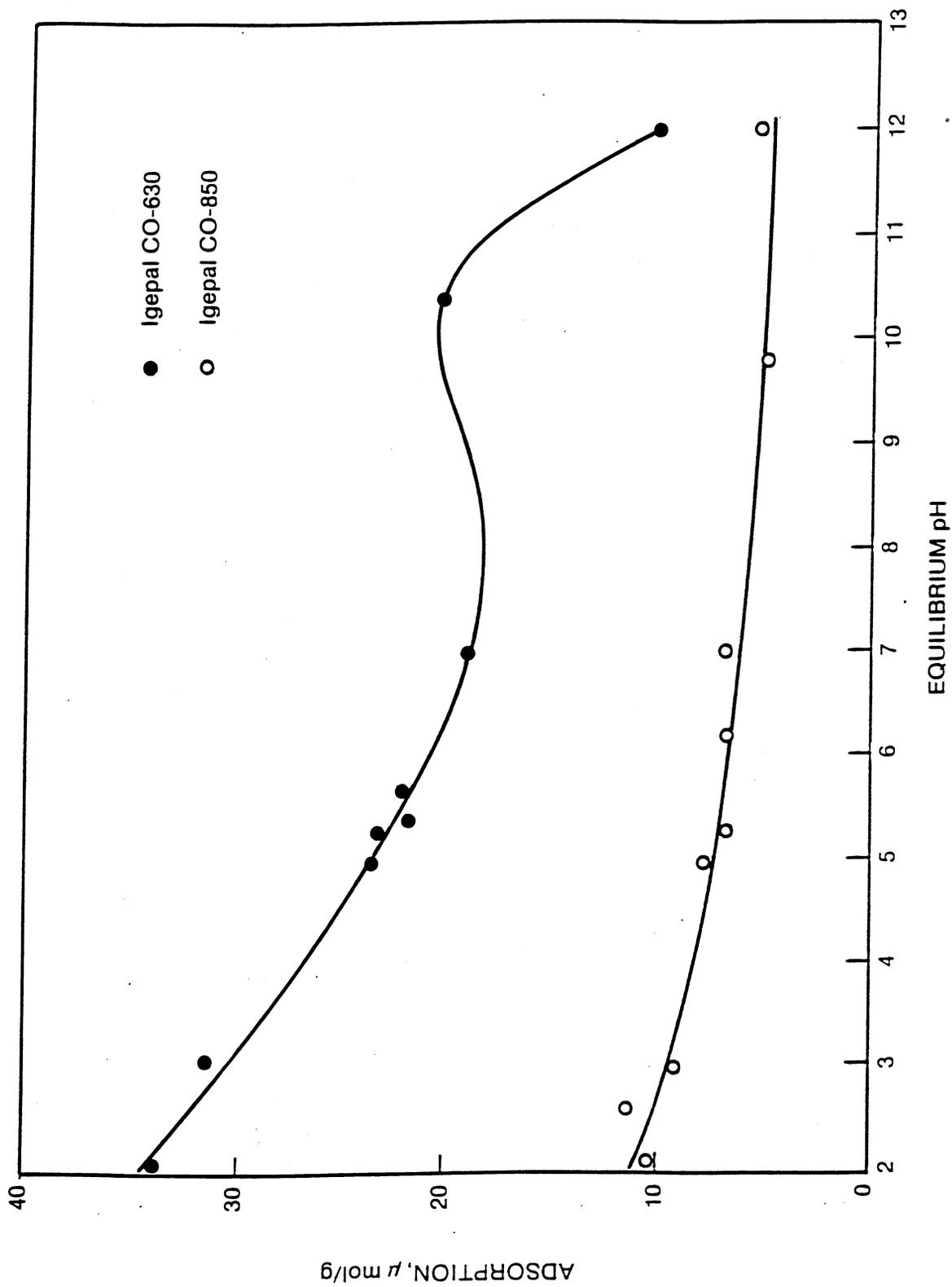


FIGURE 12. - Effect of pH on adsorption of Igepals on Kaolinite. 30° C; 0.1 M NaCl. (After Schechter and Wade.³⁰)

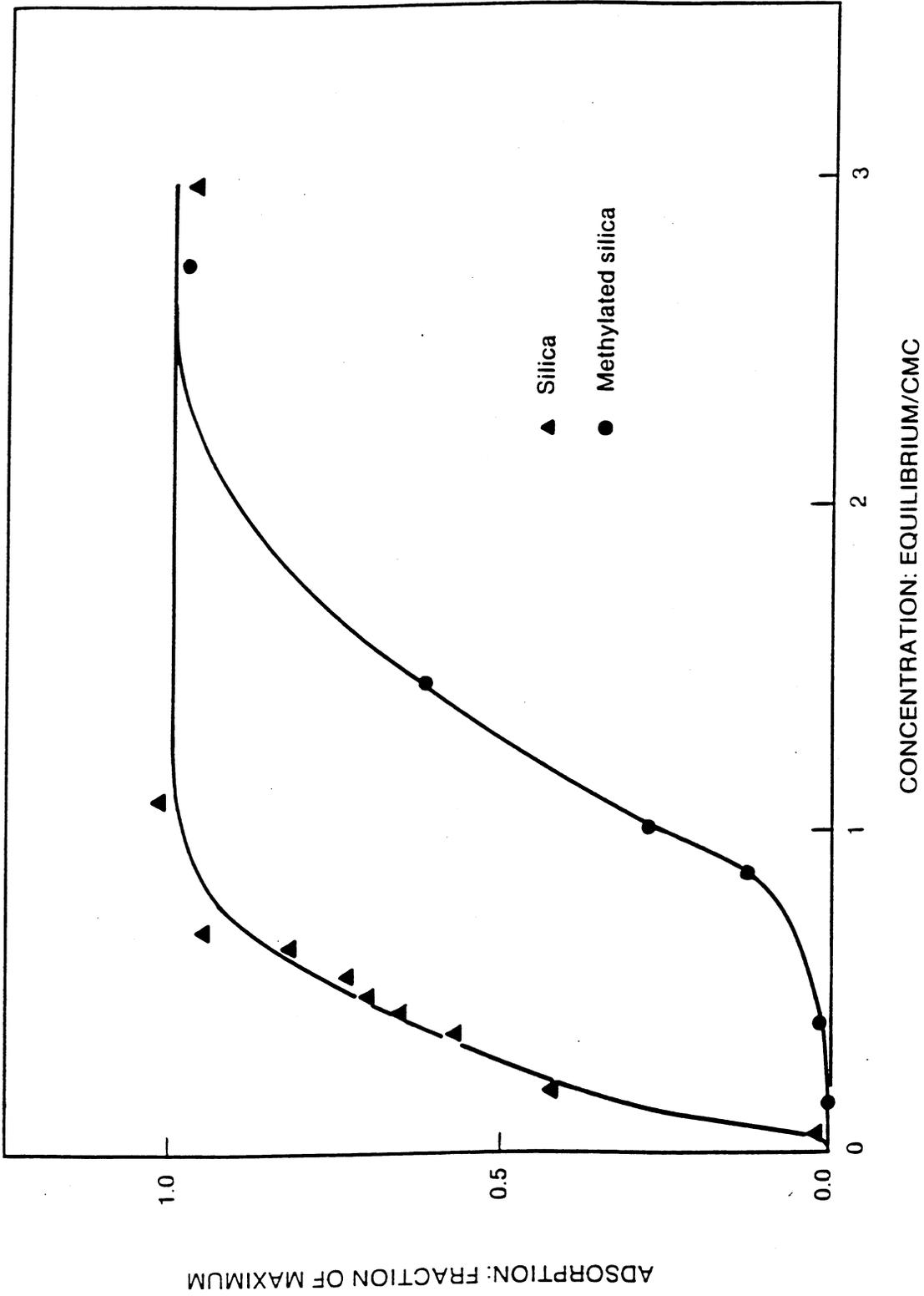


FIGURE 13. - Adsorption of ethoxylated nonylphenol C₉O(EO)₉ on precipitated silica (62 m²/g) and on silica treated with trimethyl chlorosilane. (After Furlong and Aston.³¹)

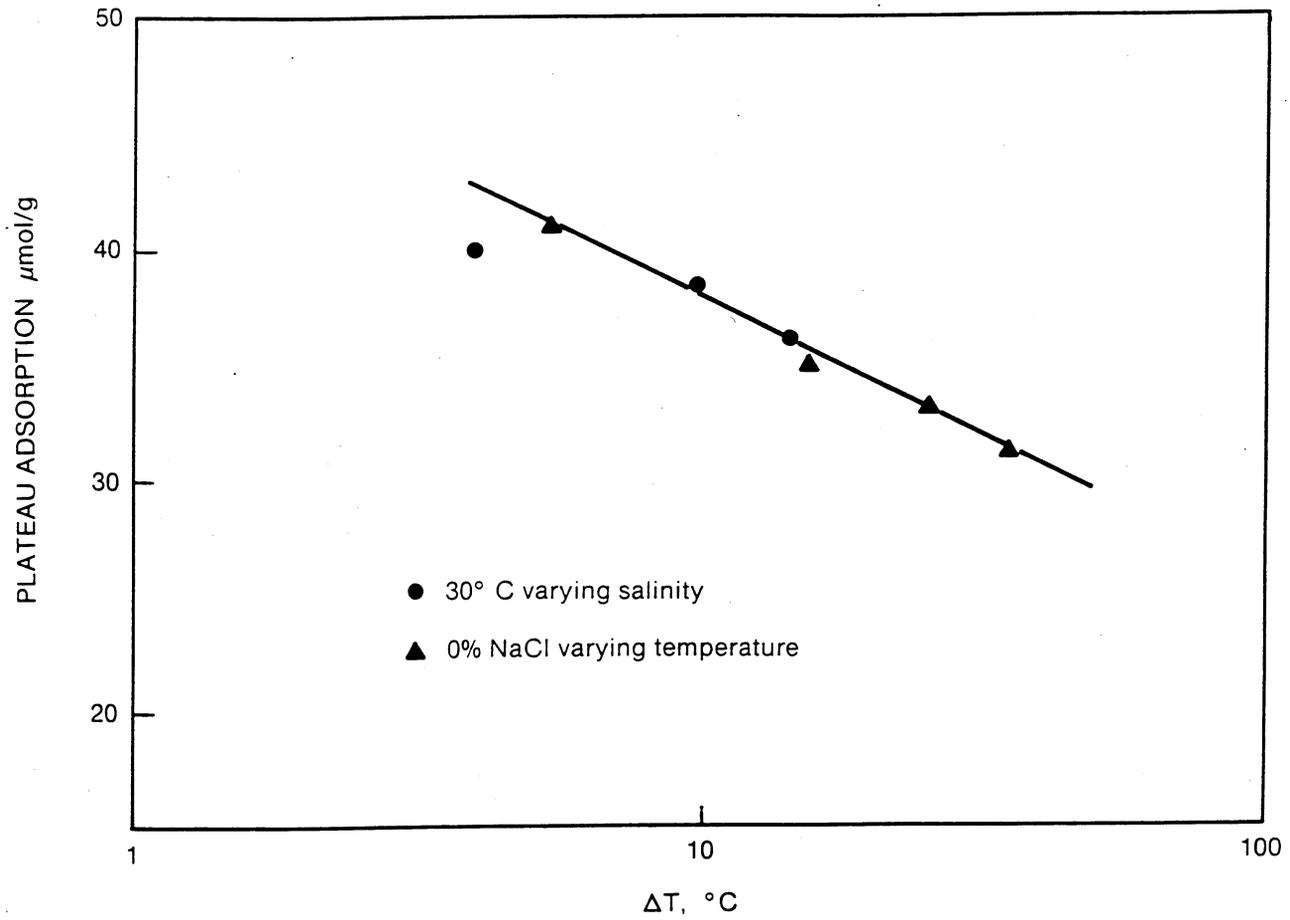


FIGURE 14. - The effect of cloud point on adsorption of Igepal CO-630 on kaolinite. ΔT = cloud point - adsorption temperature. (After Verkruyse and Salter.³²)

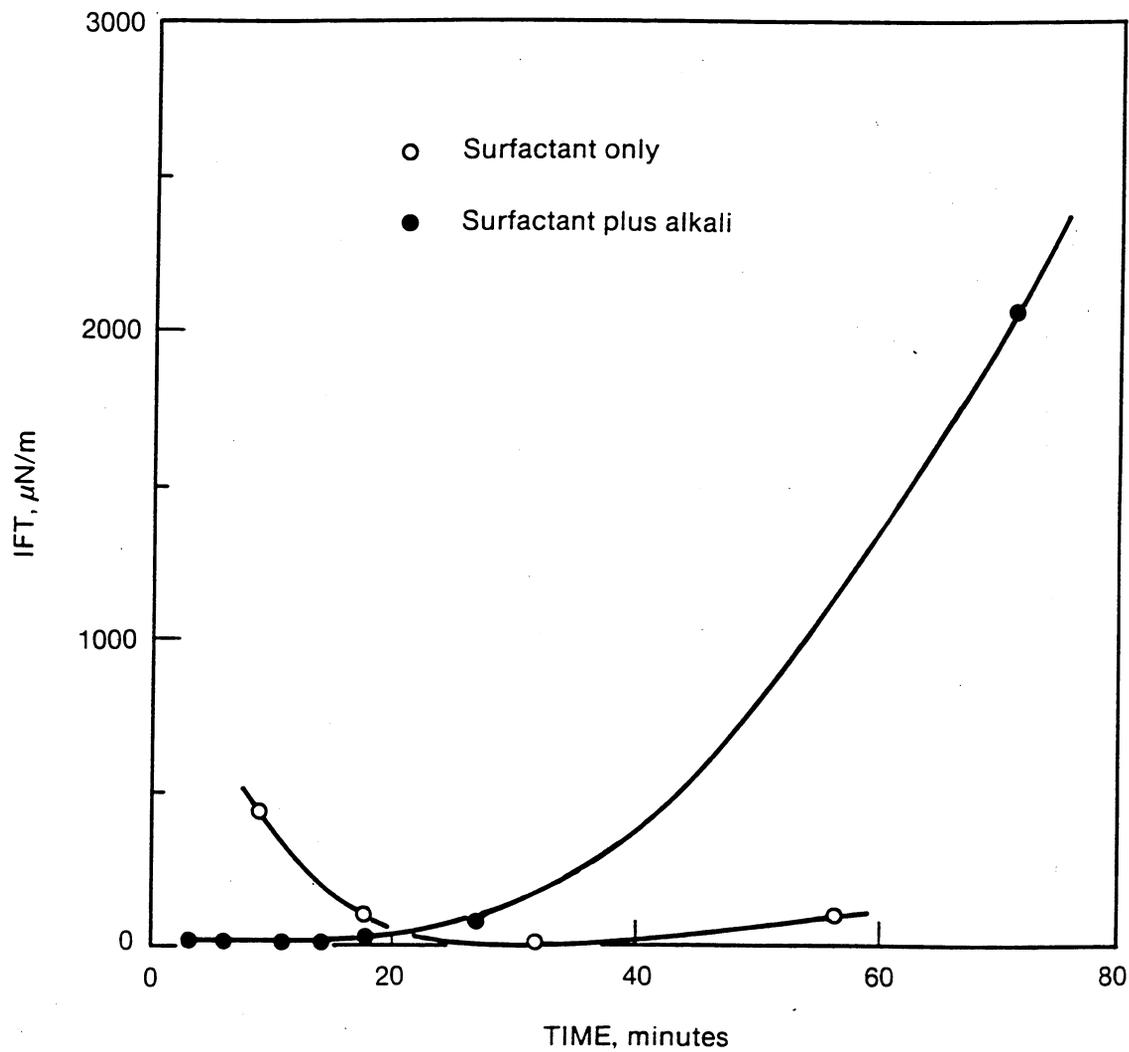


FIGURE 15. - Transient interfacial tension of deacidified Wilmington (CA) crude oil and 0.1% Neodol 25-9. Alkali is 0.19 N equimolar mixture of Na_2CO_3 and NaHCO_3 , pH 10.8. (After French et al.⁹)

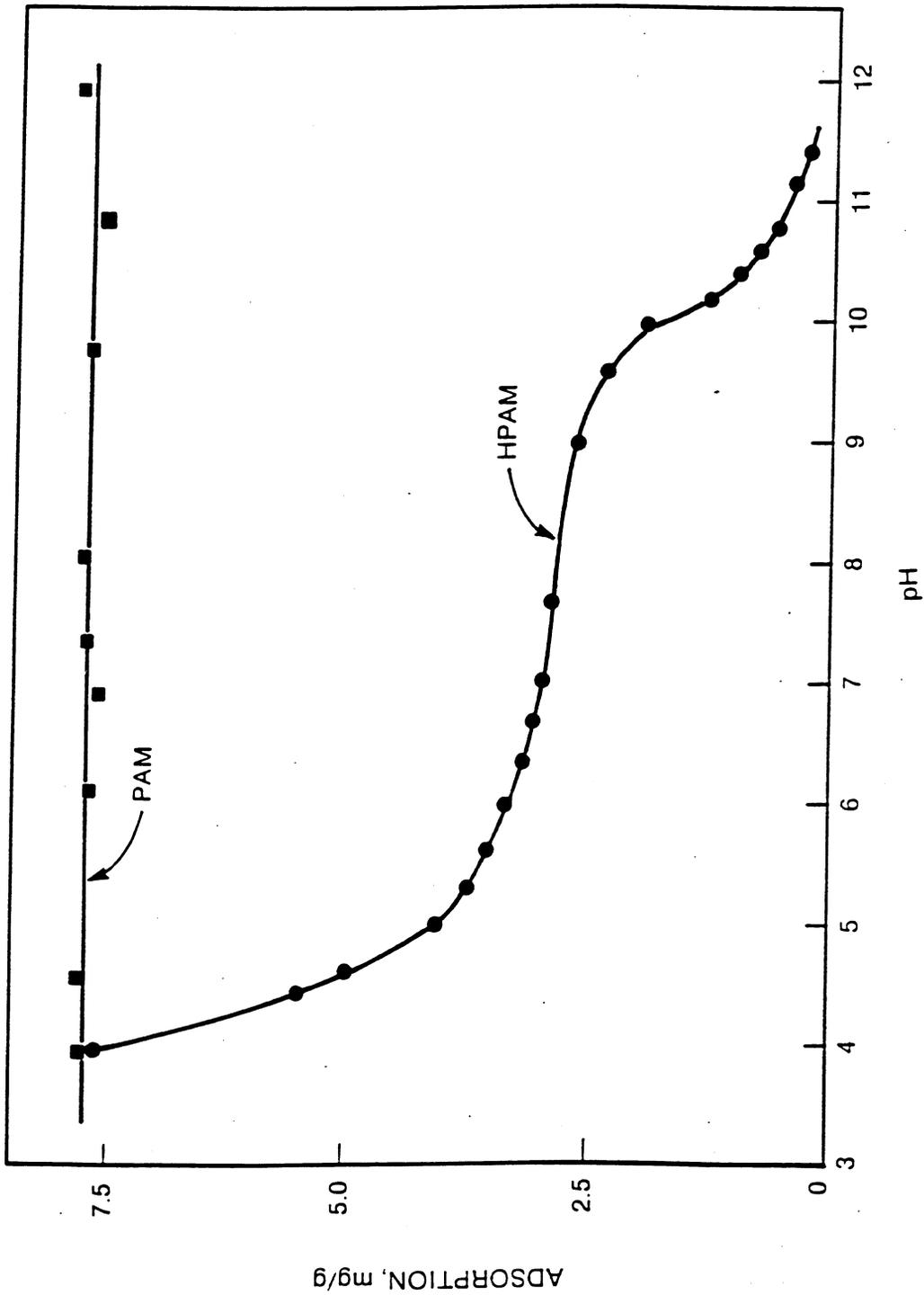


FIGURE 16. - Adsorption of polyacrylamide ($MW \approx 8 \times 10^6$ dalton) on sodium kaolinite (lateral surface area $5 \text{ m}^2/\text{g}$) in the presence of 0.34 M NaCl ; polymer $> 100 \text{ ppm}$). PAM: 1% hydrolyzed. HPAM: 17% hydrolyzed. pH above 9 adjusted by addition of Na_2CO_3 . (After Chauveteau, LeCourtier, and Lec.33)

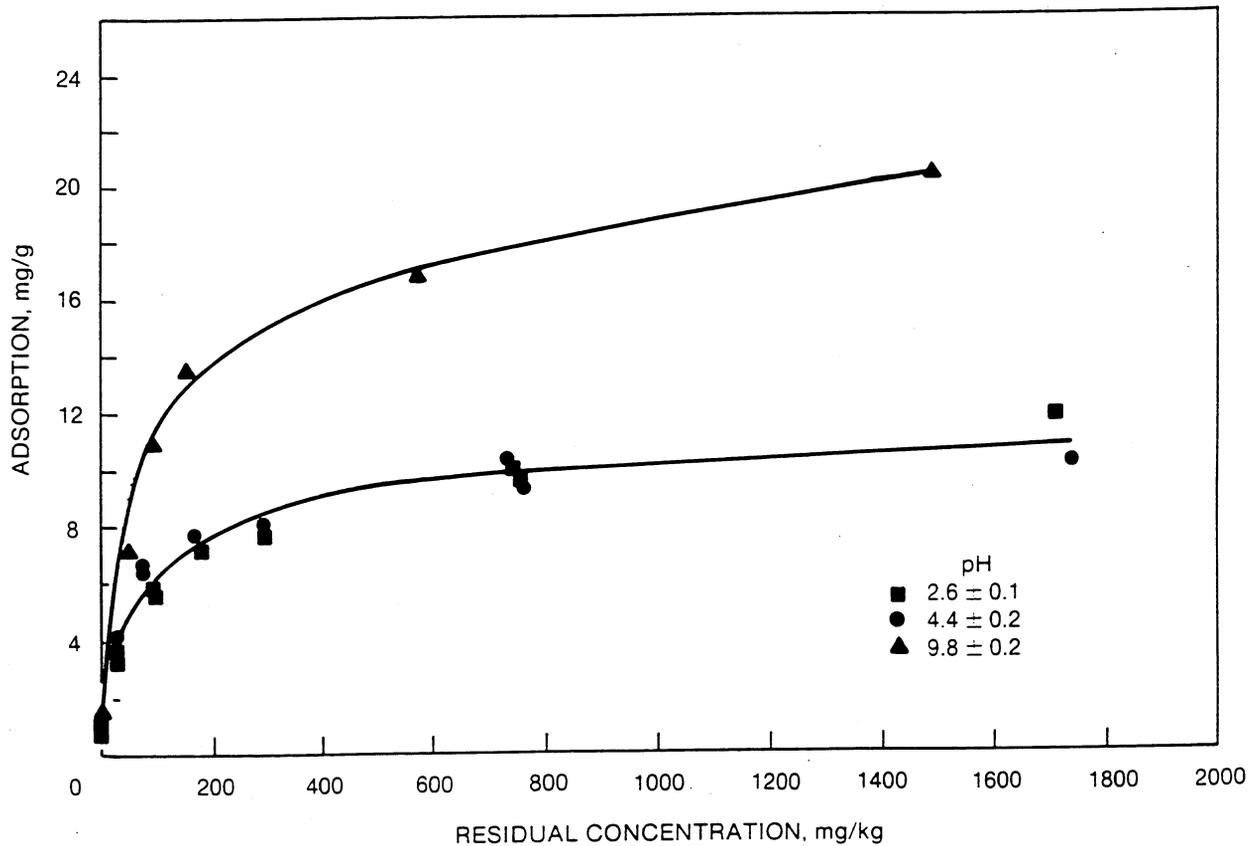


FIGURE 17. - Adsorption isotherms for aminated polyacrylamide (10 mol% positive charge) on silica (Biosil).
 S/L=1/40; 25°C; 0.03 M NaCl. (After Somasundaran and Gryte.³⁵)

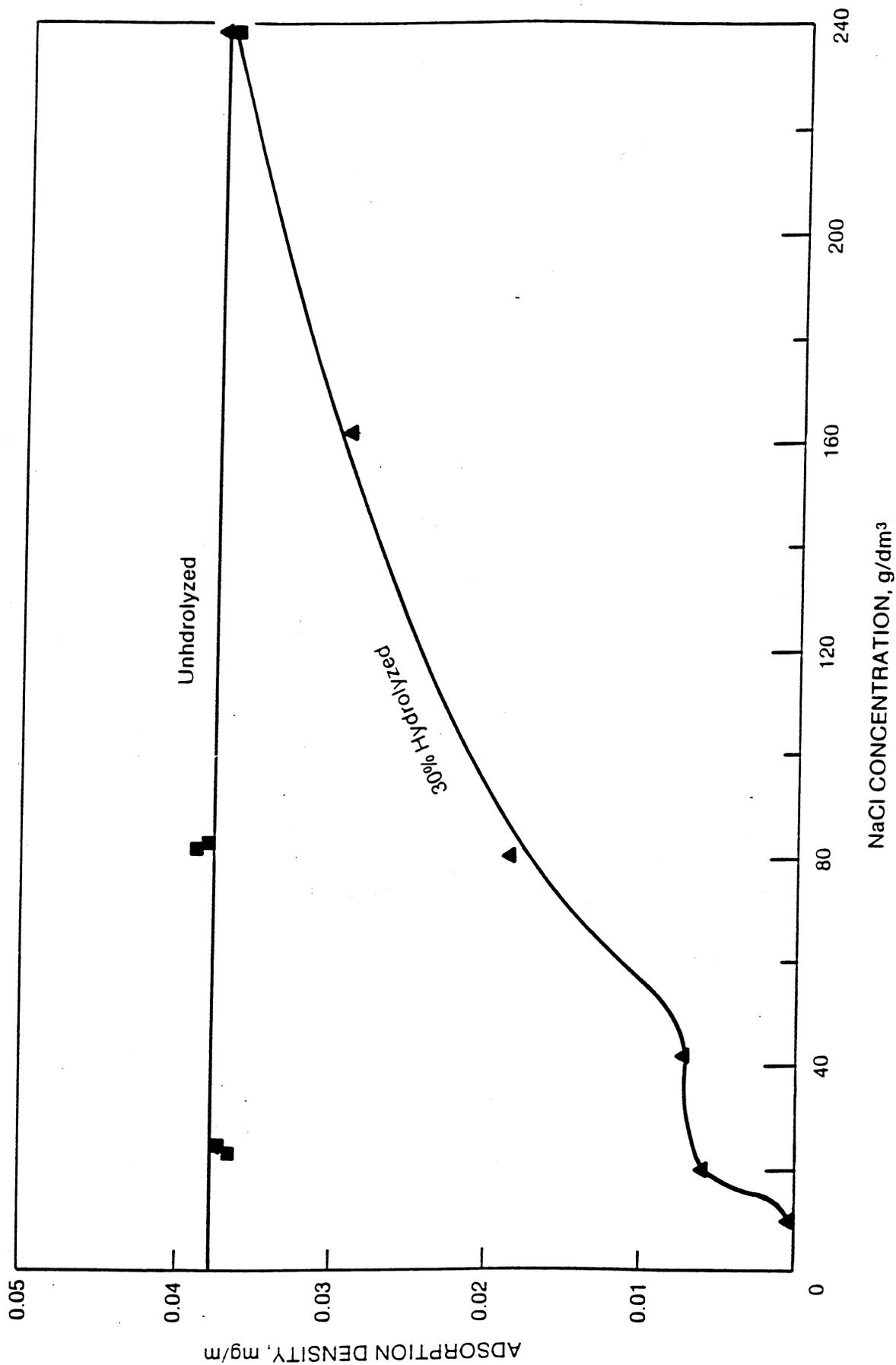


FIGURE 18. - Adsorption of polyacrylamide (MW=7.5x10⁶ dalton) on sand (0.1 m²/g), from a solution at 150 ppm in 0.34 M NaCl at pH 7. (After LeCourtier, Lee, and Chauveteau.³⁷)

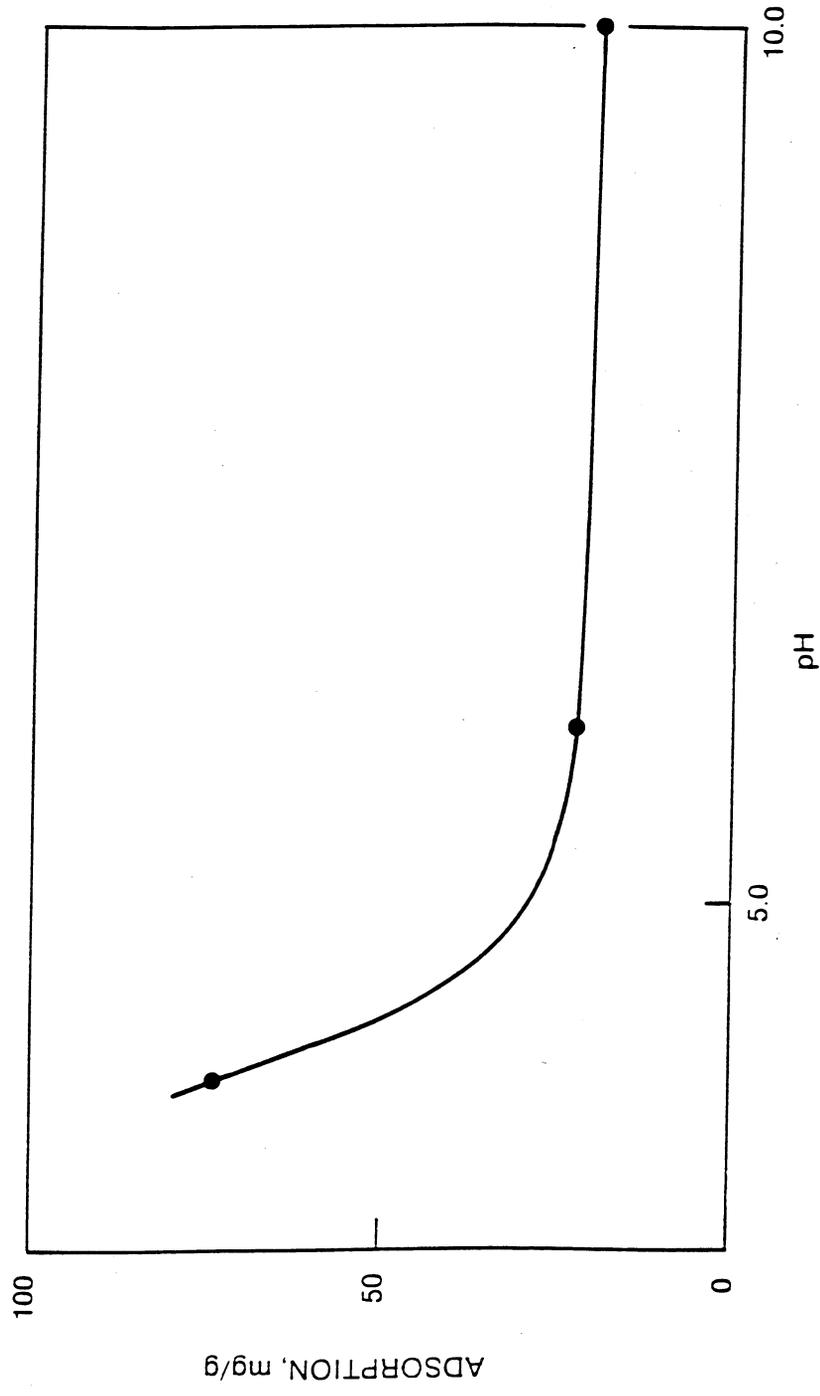


FIGURE 19. - Adsorption of polyacrylamide (MW 1.2×10^6 dalton, <1% hydrolyzed) on sodium kaolinite (lateral surface area $8.3 \text{ m}^2/\text{g}$) at 24°C . Plateau concentration $\approx 150 \text{ ppm}$. (After Nabzar and Pefferkom.41)

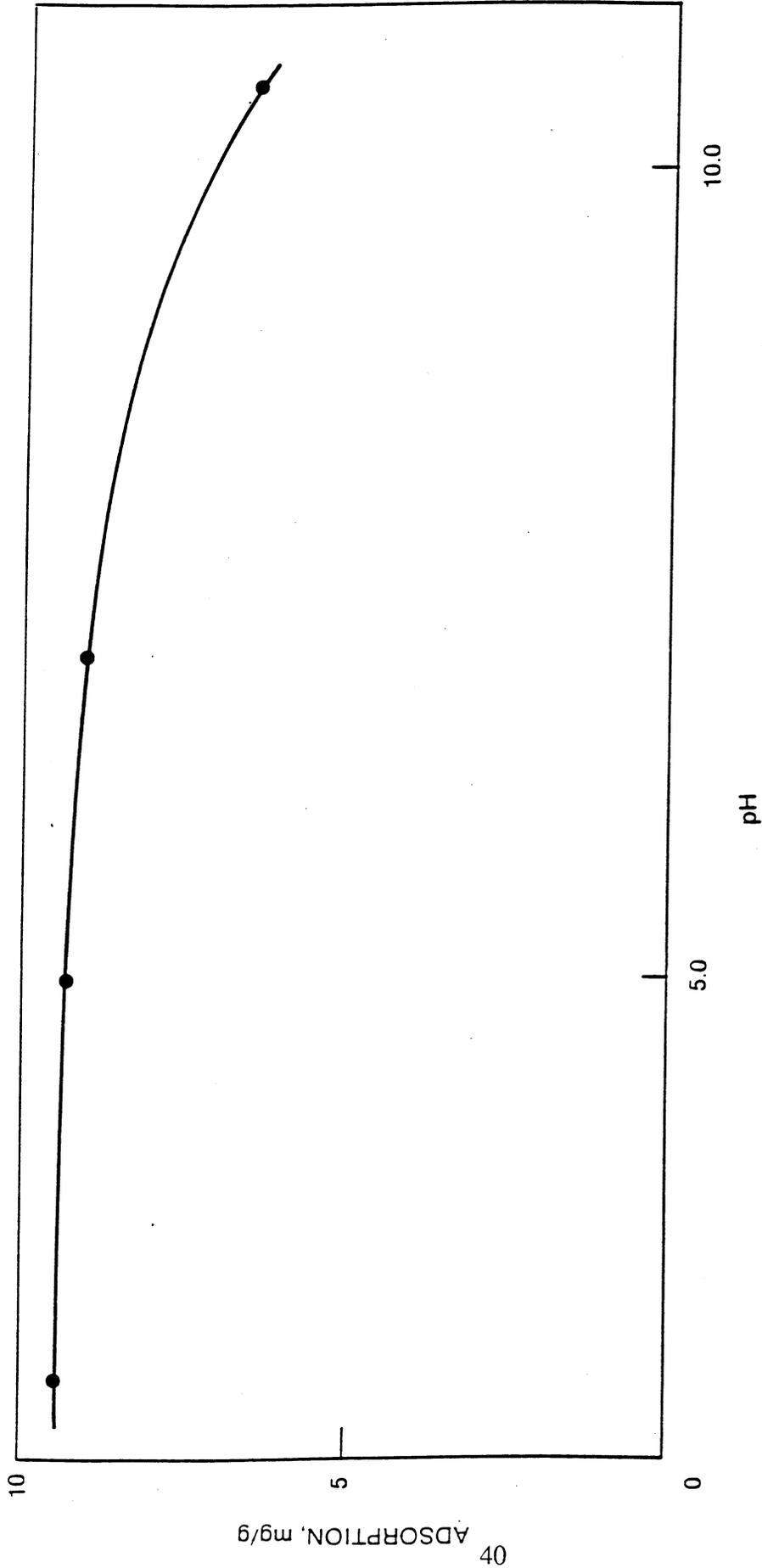


FIGURE 20. - Adsorption of unhydrolyzed polyacrylamide on sodium kaolinite (9.8 m²/g). Equilibrium concentration 100 ppm; 0.01 M NaCl; 30° C. (After Somasundaran.²³)

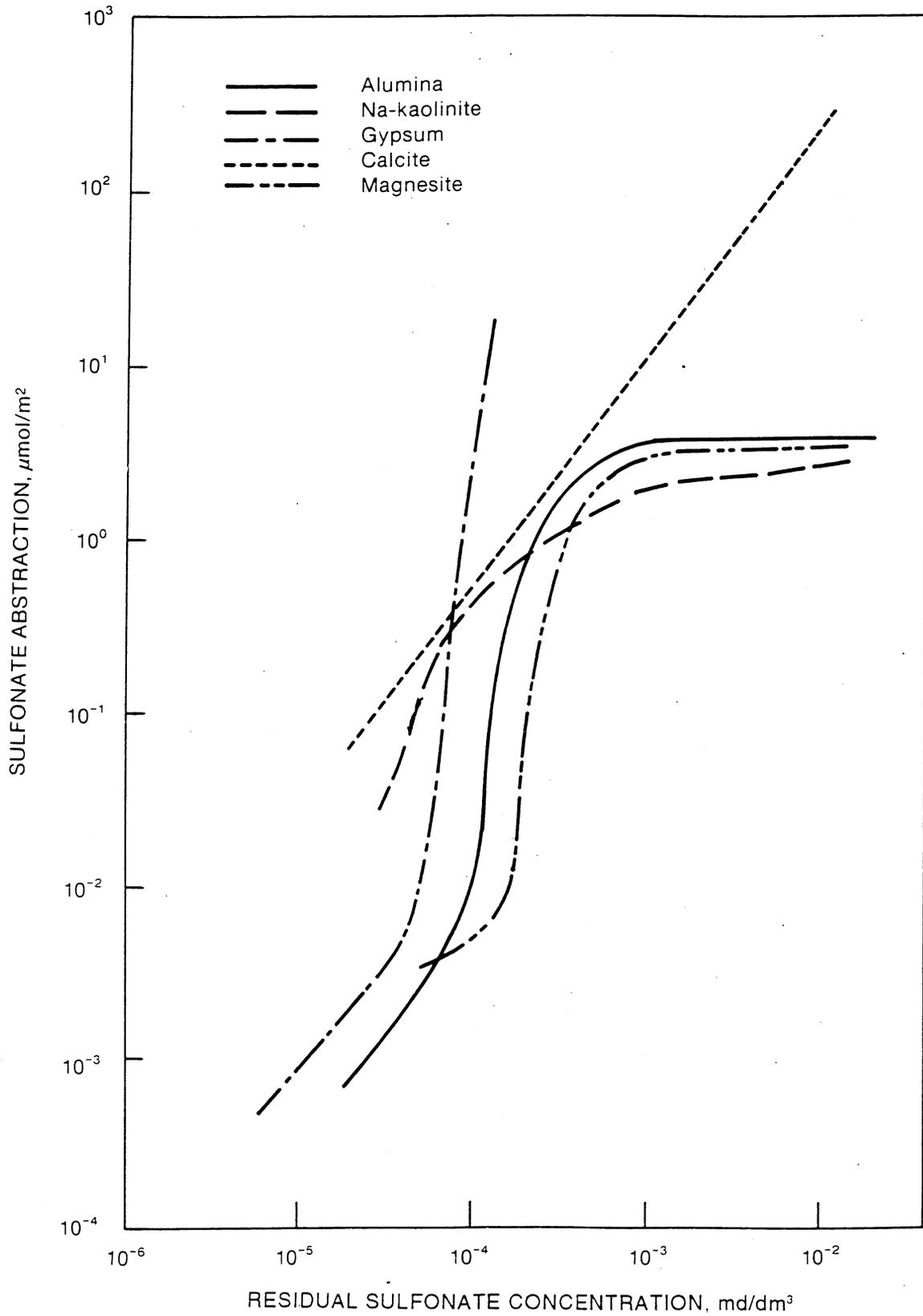


FIGURE 21. - Adsorption isotherms for sodium n-decylbenzene sulfonate on various minerals. $S/L=1/10, 1/5$; 57°C ; 0.1 M NaCl ; natural pH. (After Somasundaran and Gryte.¹⁶)

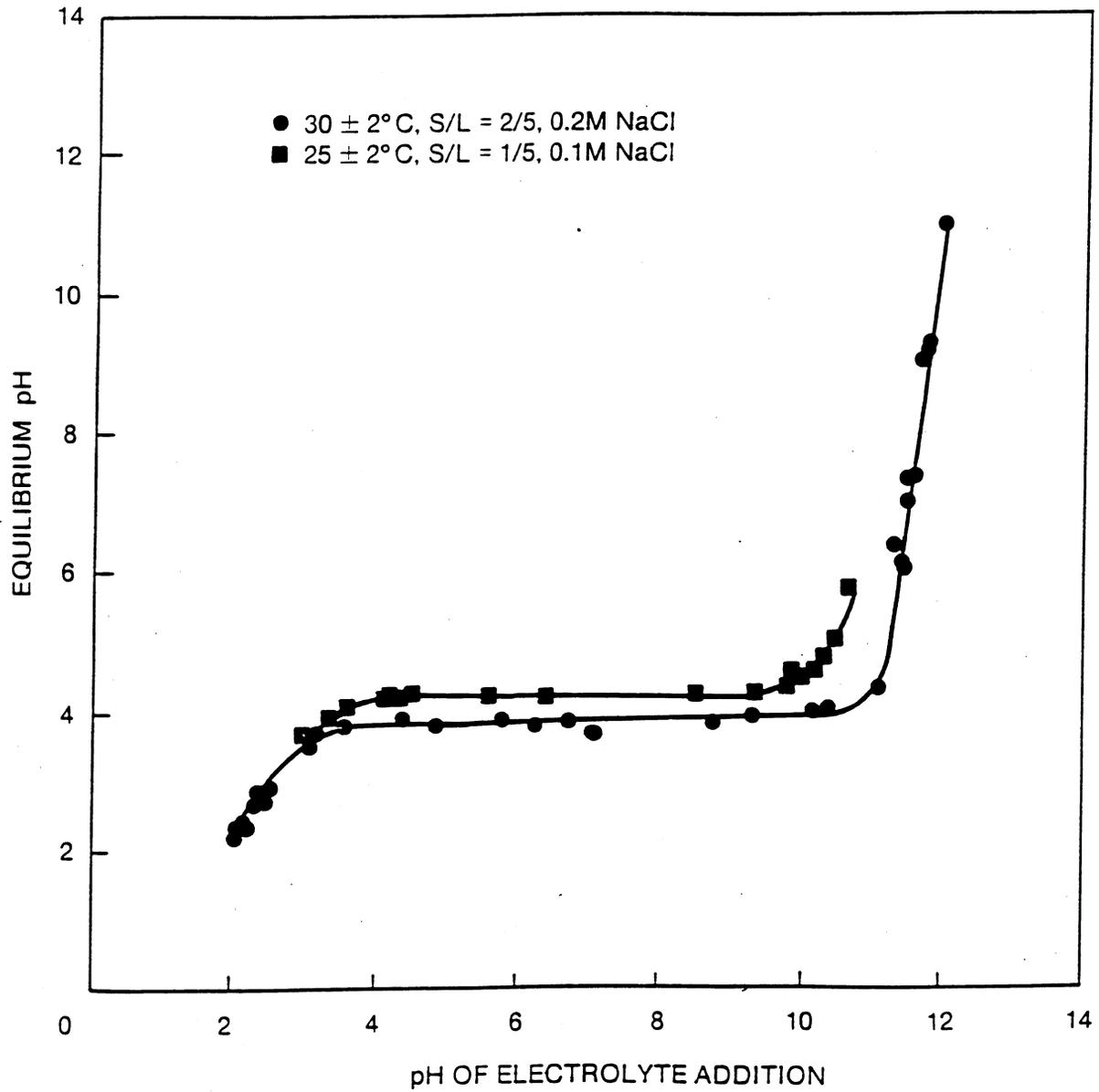


FIGURE 22. - Equilibrium pH obtained by contacting sodium kaolinite with pH-adjusted solutions of sodium chloride. (After Somasundaran.⁴⁸)

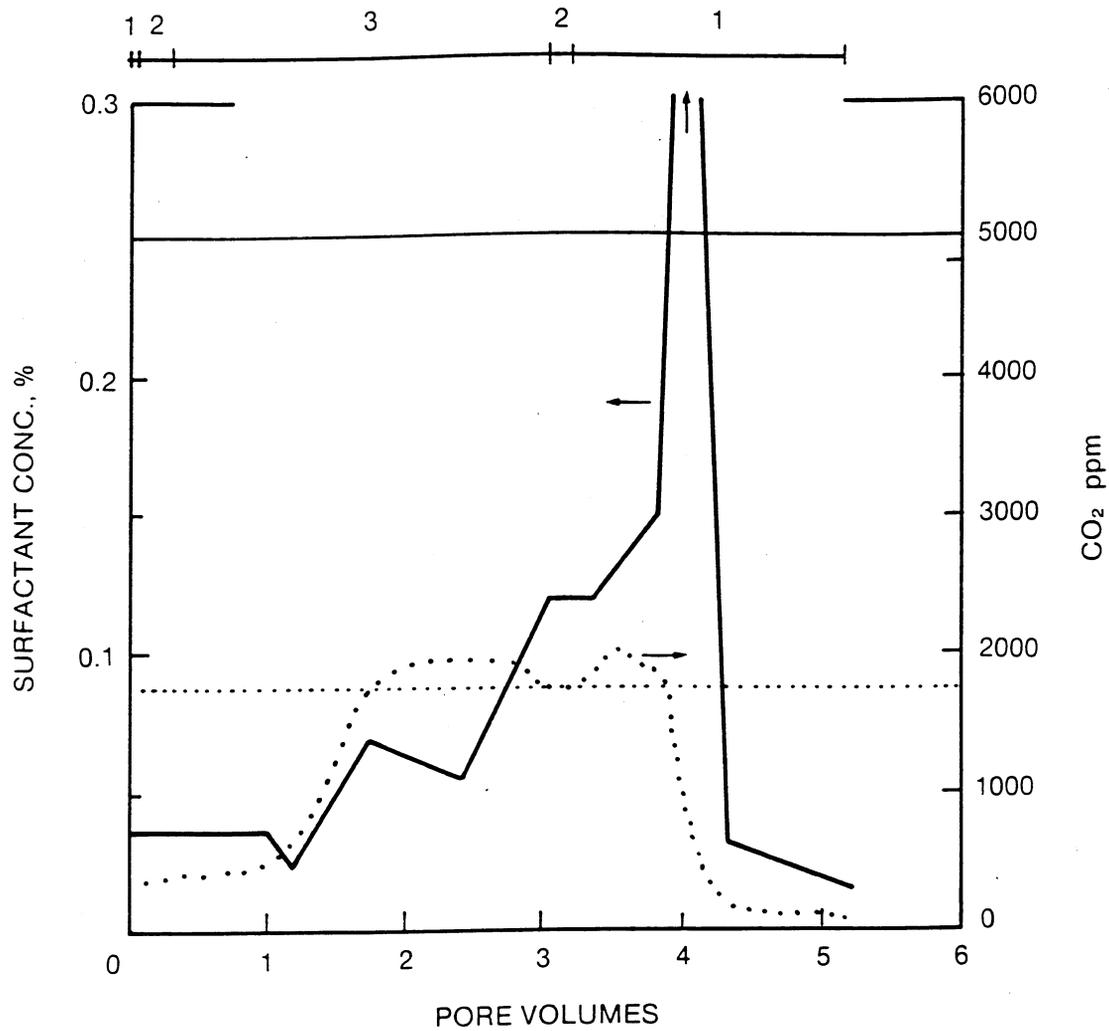


FIGURE 23. - Effluent profiles in a dilute surfactant flood enhanced by sodium carbonate (no oil) in Berea cores (2 in. x 1 ft). 1 = hard brine (1,920 ppm Ca); 2 = saline preflush/postflush (0.017 M NaCl); 3 = surfactant-alkaline slug: injection concentrations shown by horizontal lines. (After Krumrine and Falcone.¹¹)

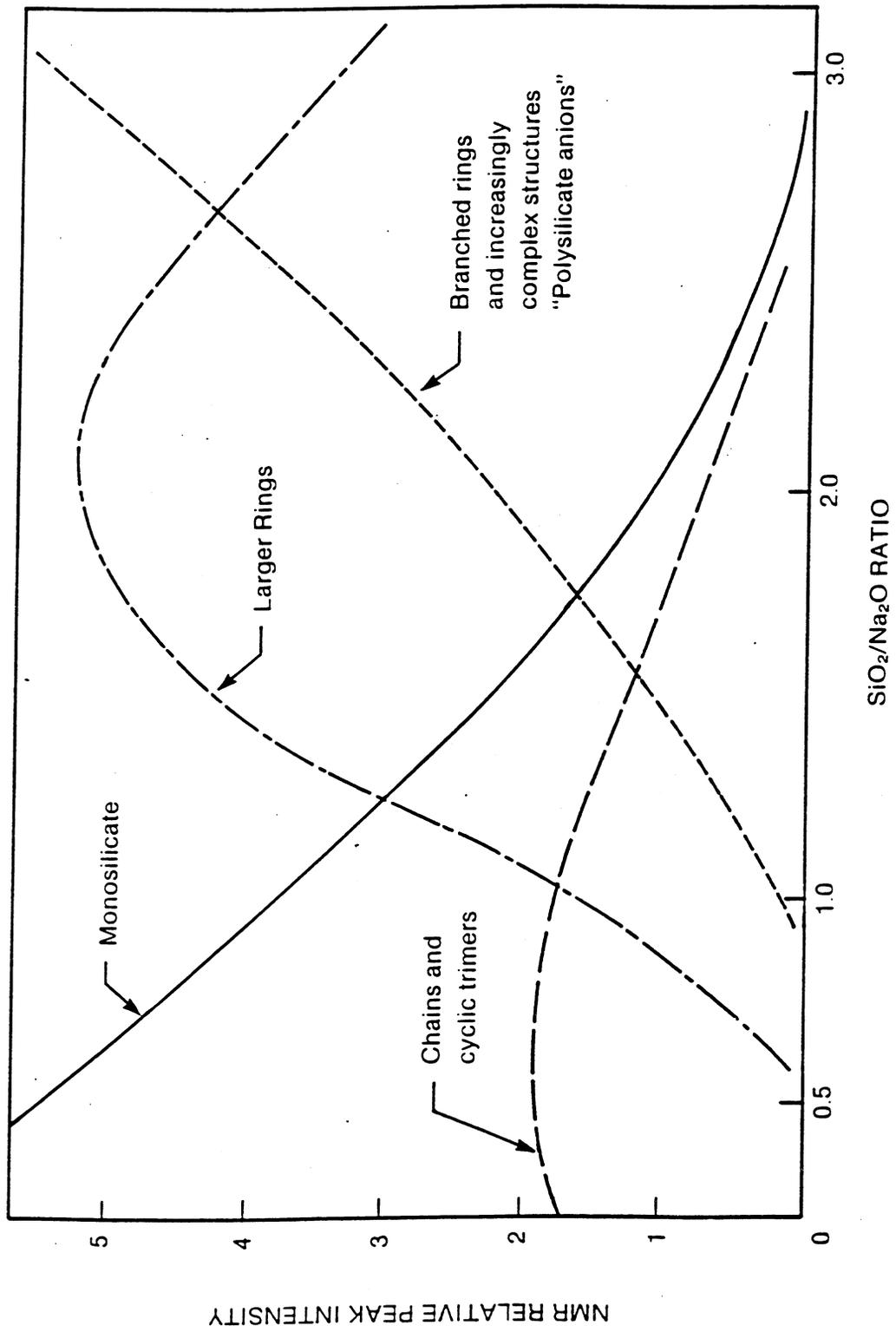


FIGURE 24. - Qualitative interpretation of silicate ion structure equilibria. (After Falcone, cited by Krumrine.⁵⁶)

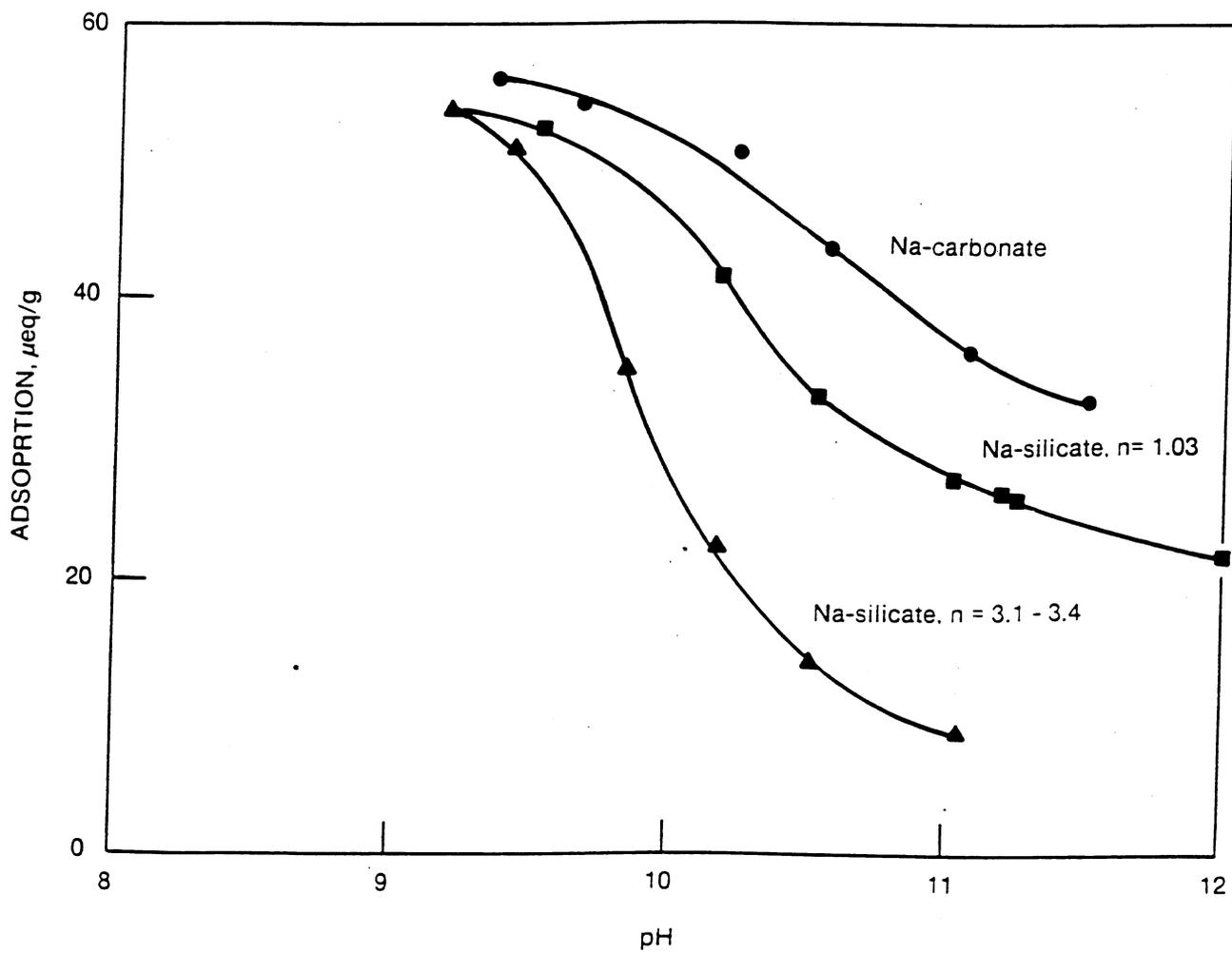


FIGURE 25. - Adsorption as a function of pH with various alkalis. Sodium dodecylbenzene sulfonate on kaolinite. (After Yang and Han.⁵²) The exact experimental conditions are not clear.

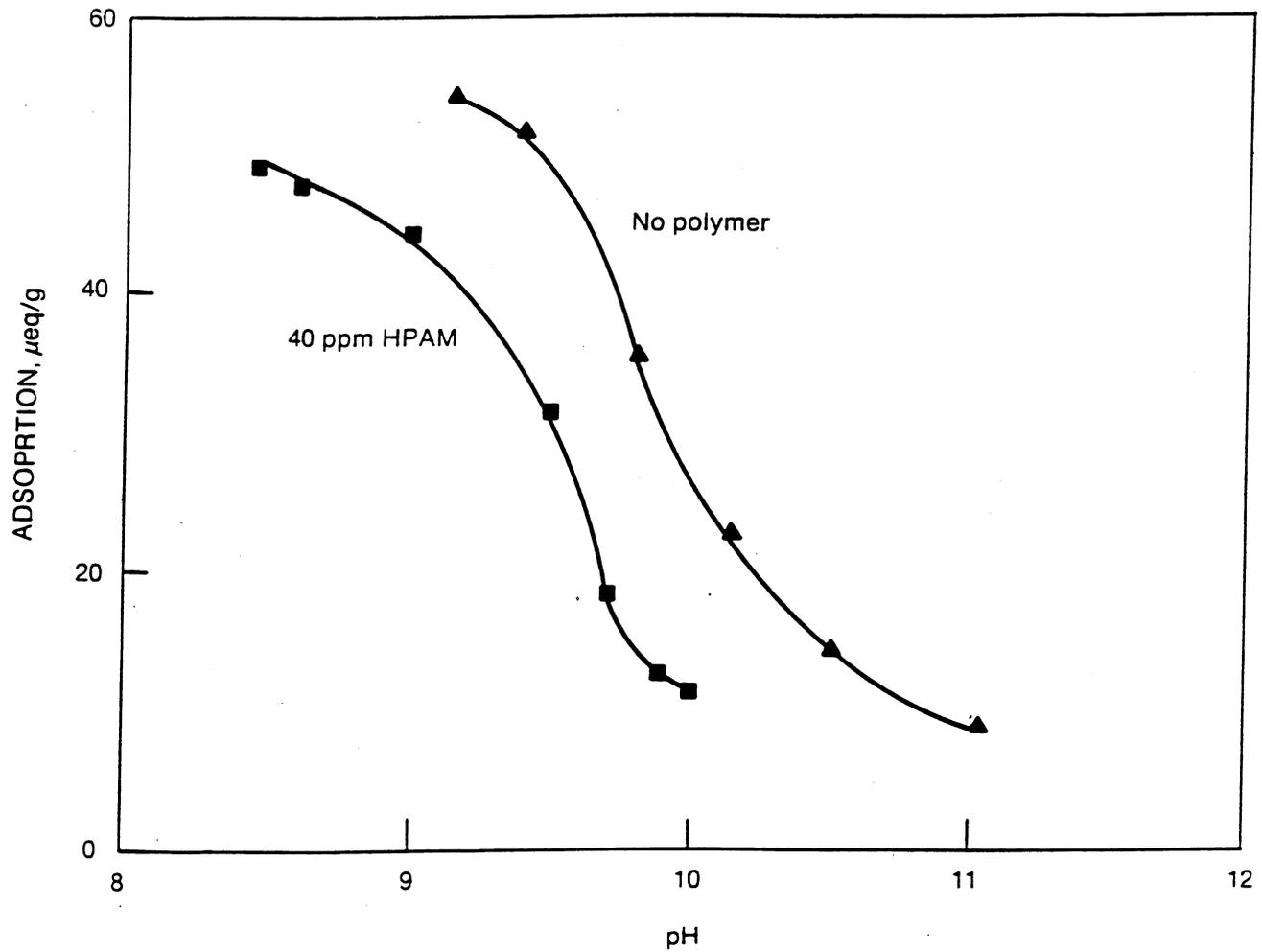


FIGURE 26. - The effect of partly hydrolyzed polyacrylamide, 40 ppm, on the adsorption isotherms for n+3 silicate of figure 25. (After Yang and Han.⁵²)

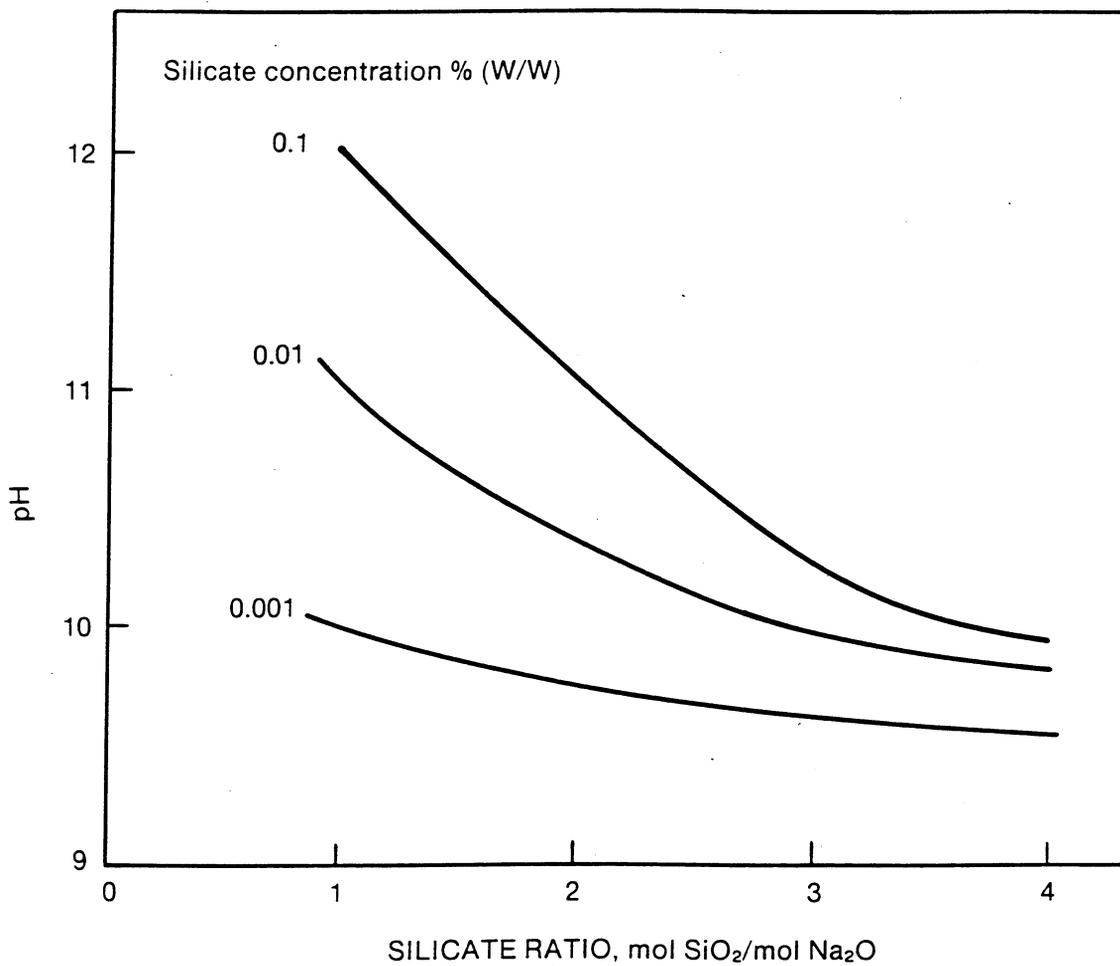


FIGURE 27. - pH values for silicate solutions of different concentrations and silicate ratios. (After Krumrine and Falcone.⁶⁰)

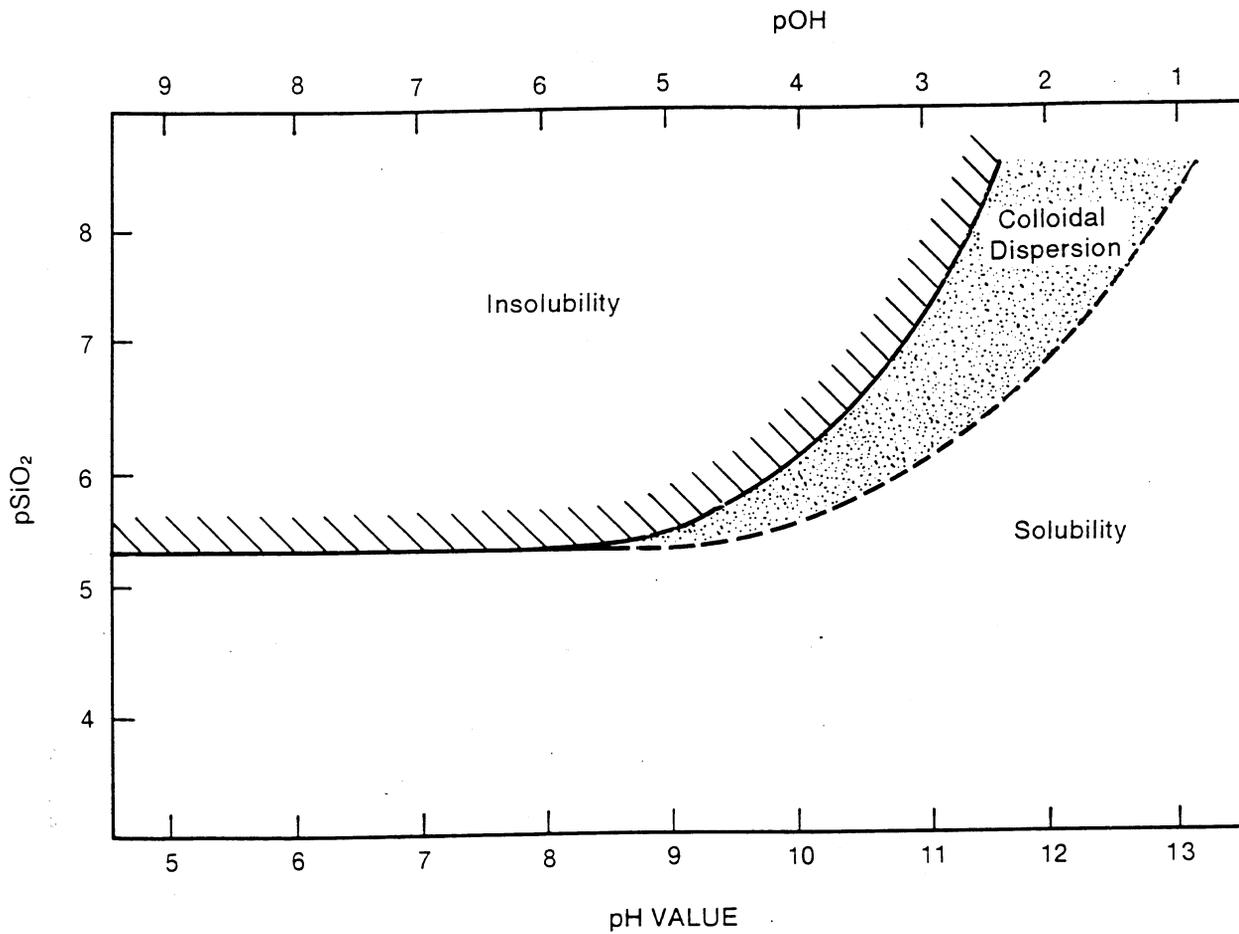


FIGURE 28. - Domains of solubility, colloidal dispersion, and insolubility for silicates. (After Krumrine and Falcone.⁶⁰)

