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**ADSORPTION CALORIMETRY AND ENHANCED
OIL RECOVERY: THREE COMPONENT SYSTEMS**

Topical Report

**By
Leo A. Noll**

March 1988

Performed Under Cooperative Agreement No. FC22-83FE60149

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



**National Energy Technology Laboratory
National Petroleum Technology Office
U.S. DEPARTMENT OF ENERGY
Tulsa, Oklahoma**

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Assistant Secretary for Fossil Energy

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ADSORPTION CALORIMETRY AND ENHANCED OIL RECOVERY: THREE COMPONENT SYSTEMS

By Leo A. Noll

ABSTRACT

One of the objectives of project BE4A is to determine the adsorptive losses of EOR chemicals on minerals in a systematic manner and expand adsorption models for incorporation as an adsorption module into chemical flooding simulators. To this end, the Woodbury-Noll adsorption model was developed during FY87, which fits both amount and heat of adsorption simultaneously.

To extend this model, two ternary systems have been selected with a view to extending the Woodbury-Noll adsorption model to these systems. In the first of these systems, DTAB/NaBr/H₂O/silica, competitive effects are not present. In the second system, methanol/toluene/heptane/silica, competitive adsorption is present. Flow adsorption calorimetry has been carried out on these ternary systems and also on their respective binaries.

Adsorption calorimetry of DTAB from solutions with added electrolyte shows that the heat and the amount of adsorption increases when the salt content was raised to 3 percent, being approximately constant thereafter. However, the increase in salinity above this amount moves the plateau region to lower surfactant concentrations. Adsorption of DTAB at 45° C resulted in lower adsorption than at 25° C, but the heat release was only slightly lower.

The heat and amount of adsorption of methanol from heptane onto silica are both markedly reduced by the presence of toluene in the solution.

The densities of the surfactant solutions and of the binaries of methanol/toluene/heptane system are also reported.

INTRODUCTION

Chemical slugs have been formulated for enhanced oil recovery (EOR) by chemical flooding for several years. Adsorption of chemicals onto reservoir minerals has always threatened such projects with failure. Preflushes have

been injected ahead of micellar slugs to reduce the concentration of divalent ions, or to change salinity. Sacrificial agents have sometimes been added to reduce adsorption. Polymers have been added to preflushes and to surfactant slugs, and as mobility control buffers behind surfactant slugs. Surfactant slugs have been formulated with various mixtures of alcohols, surfactants, cosurfactants, and cosolvents.

This complexity makes chemical flooding a very flexible EOR process, but also exposes it to the deleterious effects of adsorption, precipitation, and chromatographic separation which lead to loss of effectiveness of injected chemical formulations and possible failure of projects.

The primary thrust of this research is to develop a basic understanding and modeling of the adsorption process. Mathematical modeling of the adsorption phenomenon is a powerful tool for improving our understanding of the transport of surfactants in porous media. Most reservoir simulators simply use Henry's law (adsorption is proportional to concentration) or a Langmuir isotherm to model the adsorption of the components of a slug. These models, however, are not very realistic for describing the adsorption of aqueous surfactants onto minerals.

A thermodynamic theory of adsorption, the Woodbury-Noll model,¹ has been developed at NIPER for adsorption from binary solutions. It correctly incorporates solution properties. This model is being extended to three components and is being simplified to require one fewer parameter for the binary case.

The extension of the Woodbury-Noll model for adsorption of EOR chemicals to three-component systems requires test (and the fitting of) adsorption data from binary and from ternary solutions. Two scenarios are planned: (1) non-competitive adsorption, in which the first component serves as "solvent," the second component is actively adsorbed, and the third component has little adsorption but serves to alter the solution properties such as enthalpy and activity; and (2) competitive adsorption, in which one component serves as a more or less inert solvent and the other two of the three components compete for adsorption sites on the solid.

The system chosen for case (1) is decyltrimethylammonium bromide(DTAB)/water/sodium bromide/silica gel. The electrolyte effects

adsorption mainly by changing the solution properties. This system will be a model for adsorption of surfactant in the presence of brine. The activity and enthalpy information required will be calculated from the Burchfield-Woolley model.²⁻³

The system chosen for case (2) above is methanol(MeOH)/toluene/n-heptane(C₇)/silica gel. In this case, the methanol interacts most strongly, the toluene less so, and the heptane very little with the silica surface. This situation can arise in the petroleum reservoir with respect to a strong adsorption of surfactant, less for cosurfactant, and little for brine. Data are available in the literature for excess enthalpies of binary mixtures of methanol, toluene and heptane; and some for the ternary mixture. Activity coefficients can be estimated by chemical engineering methods.

The effect of temperature on adsorption is important; thus, in addition to these three component systems, this report will include flow adsorption calorimetry of DTAB from water onto silica at 45° C. The FY88 Annual Research Plan contains provision for a more extensive study of the effect of temperature on adsorption.

EXPERIMENTAL PROCEDURE

The calorimeter used in this work was an LKB 2107-030 flow adsorption calorimeter. The space in calorimeter the cell is about 0.5 ml. To start a run, a sample of silica gel (Davison #62, surface area 340 m²/g) is heated overnight at 300° C. It is placed in a desiccator over Drierite to cool. As soon as it has cooled, it is loaded into the cell, and the cell is placed in the calorimeter. Flow of solvent is initiated as soon as possible from a weighed solvent bottle through a valving arrangement. The valve will allow up to 15 solutions to follow the neat solvent without interfering with the flow of liquid. The heat of immersion is recorded and calibrated. Calibrations are performed on each amplification range which will be used.

After exiting from the calorimeter, the fluid flows through a Knauer differential refractometer. Reference 4 explains how the response of the refractometer is used to calculate surface excess (amount adsorbed). The refractometer trace for hydrocarbon solutions is quite difficult to read. Thus, the fluid exiting from the calorimeter is collected in weighed bottles,

with a view toward analyzing it to determine surface excess. Because of irreproducibilities caused by evaporation of hydrocarbon changing the output solution composition, all surface excess values for methanol/toluene/heptane combinations are obtained by batch adsorption experiments. In these experiments, a weighed amount of solution of known composition is added to a measured amount of silica gel, then the container is tightly capped. The solutions are agitated overnight. The initial and final compositions of the binary solutions are measured by density using a Sodev vibrating tube densimeter. The initial and final compositions of the ternary solutions are measured by gas chromatography.

DATA FITTING

Adsorption data are usually incorporated into reservoir simulators by one of three models. The first of these is the Henry's law model, which assumes that the adsorption is linearly proportional to concentration. This model has no provision for the saturation of a surface leading to plateau adsorption.

The second common model is the Freundlich isotherm. This equation is written

$$n_2^S = aC_2^{1/n} \quad (1)$$

where n_2^S is the surface excess amount C_2 is solute concentration, and a and n are adjustable parameters. Although this equation produces a curved isotherm, the isotherm never reaches a plateau value. This isotherm has been widely used to describe the adsorption of pesticides by soil.

The third common model is the Langmuir isotherm. Although this isotherm was originally developed to describe adsorption from the gas phase onto solids, it is commonly used also for adsorption out of the liquid phase. The assumptions of this model are that the solid has a fixed number of adsorption sites and that the solute forms a monolayer on the surface. The equation for this model is

$$n_2^S = \frac{n^S K C_2}{(1 + K C_2)} \quad (2)$$

where n^S is the calculated maximum or plateau value, and K is the Langmuir equilibrium constant.

To fit data, it is more convenient to convert equation 2 to a linearized form:

$$\frac{C_2}{n_2^S} = \frac{1}{Kn^S} + \frac{C_2}{n^S} \quad (3)$$

These equations are applied to the thermal data by using the enthalpy of replacement in place of the surface excess amount (n_2^S).

In this linearized model, (concentration/adsorption) is plotted against concentration. The slope and intercept of the line are determined. Then the calculated plateau value (n^S) is equal to the reciprocal of the slope; Kn^S is equal to the reciprocal of the intercept.

The features of this isotherm are that at very low concentrations, it approaches a straight line, and at higher concentrations it approaches a maximum or plateau value. However, because of its built-in assumptions, it does not fit the "S-shaped" or cooperative isotherms of surfactant adsorption.

DTAB MEASUREMENTS

This section reports on flow calorimetry measurements of system (1) above. DTAB was adsorbed from pure water, from 0.3 molal NaBr (3 percent by weight), 0.6 molal NaBr and 0.9 molal NaBr. Thus all solutions containing NaBr are three-component systems. The effect of added electrolyte on the heat and amount of adsorption is shown in this section.

The added salt is in the form of NaBr rather than NaCl so that there is one common anion (bromide) between the surfactant and the electrolyte, rather than two different anions. The results are shown in table 1. Figures 1 and 2 show the plot of the data of table 1; figure 1, the heat of replacement and figure 2, the amount adsorbed.

The isotherms of DTAB adsorption onto silica are, in general, "S-shaped," which we refer to as "showing cooperative interaction." The isotherm for DTAB

from pure water (Fig. 2) is quite low, then has a sudden increase at about 1.8 percent. This seems to occur at the critical micelle concentration (CMC) of DTAB, which is 1.8 percent.⁵ In addition, there is continued adsorption above the CMC. This increase in adsorption is caused by the change in solution properties, such as activity, occurring above the CMC. The thermal result (Fig. 1) is similar except that there is a fairly good heat effect at the lowest concentration, followed by a curve quite similar to the surface excess curve.

The effect of added electrolyte on both thermal and amount of adsorption curves is to raise them to higher plateau values and to move the onset of the plateau to lower DTAB concentrations. It also seems to decrease the amount of cooperative interaction in the adsorption. This is seen in the fact that the plots are less S-shaped.

The critical micelle concentration of DTAB in water is 1.8 percent; in 0.3 molal salt (NaCl), 1 percent; in 0.55 m salt, 0.8 percent.⁵ Mukerjee and Mysells⁵ classify these data as not of the highest quality. In our experiments with added salt, the onset of the plateau occurs at a somewhat lower concentration than the tabulated CMC, but is qualitatively similar.

Table 2 lists the plateau values. If it is assumed that the surface excess is the amount of adsorption, the calculated energy per mole is presented in column 3. The area per molecule is given in column 4. This last column indicates that there is enough room for a monolayer. The Woodbury-Noll model, however, suggests that the surface has patches with and patches without surfactant.

The Langmuir model has been applied to these DTAB experiments. The results are shown in figures 3-6. In these figures, the points are the calculated Langmuir relationships, and the line is the least squares fit to the points.

The figures given are for the thermal results. The results of the Langmuir fit for surface excess are similar and have not been shown. The conclusion from the lack of linearity of the points is that the Langmuir model does not fit these experiments very well. On the other hand, as the amount of added salt increases, the isotherms become more and more amenable to the Langmuir model.

The densities of DTAB solutions in water, 0.3 m and 0.6 m NaBr, were measured with a view to using these data for quantitative analysis of the solutions. These data are included here. One can calculate the partial molar volume of surfactant in these solutions from the density data. Tables 3-5 and figures 7-9 contain the density data.

In addition to these measurements, the preliminary results for the adsorption of DTAB at higher temperature are presented. The results of adsorption at 45° C are given in table 6 and figures 10 and 11. The Langmuir fit of these data is shown in figures 12 and 13. Table 7 shows the plateau values for adsorption at 45° C.

An examination of figures 12 and 13 shows that the data once again do not fit the Langmuir model. In fact, the slope of the line for the surface excess data has a negative slope, thus implying that the Langmuir "equilibrium constant" is negative.

A comparison of tables 1 and 2 with tables 6 and 7 shows that the extent of adsorption is lowered by an increase in temperature, but the heat per gram is about the same at 25° and 45° C. Thus, the heat per mole is higher at 45° C. It is our present interpretation (pending more adequate fitting of these data) that the change in DTAB solution properties with temperature is responsible for the constancy of the thermal result. The quantity which is called "heat of adsorption" or perhaps more correctly "enthalpy of replacement" is the enthalpy for taking DTAB out of aqueous (bulk) solution and placing it into the surface phase. Thus, the enthalpy of DTAB in the bulk phase has an influence on the so-called "heat of adsorption." This point is treated with thermodynamic consistency in the Woodbury-Noll model. The failure of the Langmuir model has been shown here to emphasize the need for a more adequate model for the description of the adsorption of surfactant onto mineral surfaces.

METHANOL/TOLUENE/HEPTANE/SILICA SYSTEM

The system chosen to illustrate competitive adsorption is the methanol/toluene/heptane/silica system. Flow adsorption calorimetry of the binary systems methanol/toluene (methanol from toluene), methanol/heptane and toluene/heptane was carried out. In addition to these binary systems, two ternary systems were run. In the first of these, a 10 mole percent solution

of toluene in heptane was made. Then a series of solutions of methanol in this solvent were mixed. Thus, all of the solutions referred to as "10 percent tol" refer to solutions in which the toluene:heptane mole ratio is a constant 1:9. The other series of solutions is referred to as "30 percent tol." Thus in all of these solutions, there is a constant mole ratio of toluene:heptane of 3:7. As explained in the Experimental section, the surface excess amounts were measured by bottle tests. All measurements were carried out at 25° C. The M/H binary system separates into two phases at a methanol mole fraction of 0.22. Thus, a mole fraction of 0.2 was selected as the highest concentration used for the runs in this section.

The calorimetric results are shown in table 8 and figure 14, and the surface excess results are shown in table 9 and figure 15. For simplicity and comparison purposes, the surface excess results for the ternary system given in table 9 and figure 14 are shown as though methanol is the only solute adsorbing. This is not the case, because the presence of toluene has a great influence on the behavior of the methanol, as is further discussed below. For completeness, table 10 gives a detailed account of the adsorption behavior of the system.

The plateau values of the heat of adsorption and surface excess for the M/T/H system are compiled in table 11. An examination of this table shows that the enthalpy per mole of methanol from toluene, from 10 percent toluene, and from 30 percent toluene are about equal. Another interesting thing about this table is that if we do a linear interpolation between the heat per gram for M/T and M/H, we expect that the result for M/10 percent T should be -155 J/g, and that for M/30 percent T should be -133 J/g. The observed values for these are -140 and -90 J/g, respectively. The same calculation for the surface excess yields an interpolated value of 15.9 and 13.4 mmol/g for the 10 percent and 30 percent case; the observed amounts are 11 and 7 mmol/g respectively. The conclusion of the constancy in heat/mol and the failure of the linear interpolation leads to the conclusion that the toluene competes for the surface of the silica and does not act as an inert solvent.

The Langmuir model was applied to the results of adsorption in the M/T/H system. Figures 16-20 show the Langmuir fit to the thermal data. The fit to the adsorption data is not as good as the fit to the thermal data and has not been shown. The Langmuir constants for these data are given in table 12. The

Langmuir model is much better at describing the adsorption calorimetry of the M/T/H system, but there are still systematic deviations from the lines. The density data for the binary solutions are shown in table 13. Note that the M/H system deviates most strongly from linear behavior, showing the least ideal solutions. This is the system which has a solubility gap, separating into two phases in the methanol mole fraction range 0.22 - 0.85.

MODELING OF THE THREE-COMPONENT SYSTEMS

The modeling effort described in reference 1 has continued. At this time, it is anticipated that two distinct models may be required because of the differing characteristics of adsorption in systems 1 and 2.

Modeling for the DTAB system is near completion. The following work has been carried out.

The Woodbury-Noll model for surfactant adsorption has been improved. Woodbury and Noll previously proposed a model that successfully describes the adsorption isotherms and heat of adsorption of DTAB out of water.¹ It was also shown that the adsorption isotherm of Scamehorn, et al.,⁶ for an alkyl benzene sulfonate onto alumina could also be fitted by the model. The model is now improved in the sense that the physical picture is simpler and more clear: the surfactant molecules are adsorbed either as monomers or "hemimicelles." Thus the number of parameters has been reduced by one, and the new model fits the data of Noll and Woodbury and that of Scamehorn et al. slightly better.

In addition to simplifying the present model, its extension to three-component systems is underway. It is anticipated that the fit to system 1 above will require only a different value of the model's parameters; that is, it will be a data-fitting problem for a pseudobinary system. Development of the theory for application to system 2 continues.

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TABLE 1. - Flow adsorption calorimetry of DTAB from water, 0.3 m NaBr, 0.6 m NaBr, and 0.9 m NaBr at 25° C

Solution Conc., % DTAB	Surface excess, mmol/g				Cumulative enthalpy of replacement, J/g			
	H ₂ O	.3 m NaBr	.6 m NaBr	.9 m NaBr	H ₂ O	.3 m NaBr	.6 m NaBr	.9 m NaBr
0.25	0.050	0.060	0.091	0.27	-1.04	-1.19	-1.36	-2.55
0.50	0.074	0.22	0.95	0.96	-1.27	-2.19	-4.93	-5.1
0.75	0.10	0.85	1.02	1.10	-1.45	-4.29	-5.20	-5.24
1.00	0.12	0.91	1.06	1.10	-1.59	-4.55	-5.30	-5.30
1.25	0.15	0.94	1.07	1.10	-1.72	-4.66	-5.36	-5.34
1.50	0.18	0.97	1.08	1.10	-1.85	-4.73	-5.43	-5.35
1.75	0.28	1.00	1.09	1.10	-2.14	-4.81	-5.46	-5.35
2.00	0.40	1.02	1.09		-2.72	-4.89	-5.46	
2.50	0.49	1.03	1.09		-3.12	-4.96	-5.47	
3.00	0.54	1.03	1.09		-3.33	-5.02	-5.48	
3.50	0.56	1.03	1.09		-3.47	-5.07	-5.48	
4.00	0.58	1.03	1.09		-3.57	-5.11	-5.48	

TABLE 2. - Plateau values for flow adsorption calorimetry of DTAB from indicated solvent onto silica gel at 25° C

Solvent	Surface excess, mmol/g	Enthalpy, J/g	Enthalpy, kJ/g	Parking Area nm ² /molecule
H ₂ O	0.58	-3.57	-6.2	0.97
0.3 m NaBr	1.03	-5.11	-5.0	0.55
0.6 m NaBr	1.09	-5.48	-5.0	0.52
0.9 m NaBr	1.10	-5.35	-4.9	0.51

TABLE 3. - Density of DTAB/H₂O at 25° C

DTAB mass fraction	DTAB mole fraction	Density, g/ml
0	0	0.997062
0.002500	0.0001611	0.997275
0.005000	0.0003229	0.997492
0.007500	0.0004854	0.997704
0.01000	0.0006488	0.997920
0.01250	0.0008129	0.998134
0.01500	0.0009778	0.998348
0.01750	0.001143	0.998561
0.02000	0.001310	0.998753
0.02500	0.001645	0.998097
0.03000	0.001984	0.999436
0.03500	0.002326	0.999773
0.04000	0.002671	1.000111

Least squares fit: $x_{\text{DTAB}} = 69.9375 \rho - 138.806\rho + 68.871$

TABLE 4. - Density of DTAB/0.3 m NaBr at 25° C

DTAB mass fraction	DTAB mole fraction	Density, g/ml
0	0	1.020280
0.002500	0.0001651	1.020423
0.005000	0.0003311	1.020576
0.007500	0.0004979	1.020727
0.01000	0.0006654	1.020850
0.01250	0.0008338	1.020954
0.01500	0.001003	1.021106
0.0175	0.001173	1.021197
0.0200	0.001343	1.021328
0.0250	0.001687	1.021548
0.0300	0.002034	1.021791
0.0350	0.002385	1.022023
0.0400	0.002739	1.022266

Least squares fit: $x_{\text{DTAB}} = 117.0197\rho^2 - 237.619\rho + 120.624$

TABLE 5. - Density of DTAB/0.6 m NaBr at 25° C

DTAB mass fraction	DTAB mole fraction	Density, g/ml
0	0	1.042796
0.005000	0.0003392	1.043135
0.002500	0.0001692	1.042913
0.007500	0.0005099	1.043206
0.01000	0.0006816	1.043245
0.01250	0.0008540	1.043313
0.01500	0.001027	1.043389
0.01750	0.001201	1.043458
0.02000	0.001376	1.043528
0.02500	0.001728	1.043747
0.03000	0.002084	1.043787
0.03500	0.002443	1.043866
0.04000	0.002806	1.044041

Least squares fit: $x_{\text{DTAB}} = 117.091\rho^2 - 241.733\rho + 124.751$

TABLE 6. - Flow adsorption calorimetry of DTAB from water at 45° C

Solution conc., % DTAB	Surface excess, mmol/g	Cumulative enthalpy of replacement, J/g
0.50	0.020	-1.22
0.94	0.032	-1.40
1.49	0.052	-1.64
1.89	0.11	-2.34
2.42	0.19	-3.05
2.85	0.21	-3.25
3.69	0.24	-3.47

TABLE 7. - Plateau value for flow adsorption calorimetry of DTAB from water on silica gel at 45° C

Surface excess, mmol/g	0.24
Enthalpy, J/g	-3.47
Enthalpy kJ/mol	-14.5
Parking area, nm ² /molecule	2.35

TABLE 8. - Flow adsorption calorimetry of methanol from n-heptane (M/H), methanol from toluene (M/T), toluene from heptane (T/H), methanol from 10% toluene (M/10%T), and methanol from 30% toluene (M/30%T) on silica gel at 25° C

Concentration, mole fraction	Cumulative enthalpy of replacement		
	M/H	J/g M/T	T/H
0.001	-66.3	-9.4	-.30
0.002	-76.9	-12.8	-.50
0.003	-83.1	-19.7	-.73
0.004	-88.1	-22.3	-.93
0.006	-96.9	-26.7	-1.26
0.008	-101.0	-31.0	-1.54
0.010	-107.2	-33.6	-1.78
0.020	-115.0	-42.4	-2.78
0.030	-120.6	-45.4	-3.54
0.040	-125.0	-48.4	-4.18
0.060	-132.1	-50.6	-5.24
0.080	-142.0	-52.0	-6.06
0.100	-150.8	-53.1	-6.76
0.150	-164.2	-54.5	-7.87
0.200	-165.00	-55.2	-8.80

Concentration, mole fraction	Cumulative enthalpy of replacement,	
	J/g M/10T	M/30T
0.001	-57.9	-25.8
0.002	-64.3	-37.4
0.004	-80.7	-50.5
0.008	-94.4	-62.2
0.012	-100.	-68.4
0.025	-120.	-76.7
0.040	-124.14	-80.9
0.060	-131.	-84.1
0.080	-137.	-86.3
0.100	-140.	-87.9

TABLE 9. - Adsorption of methanol from n-heptane (M/H), methanol from toluene (M/T), methanol from 10% toluene/heptane (M/10%tol), methanol from 30% toluene/heptane (M/30%tol), and toluene from heptane (T/H) on silica gel at 25° C

M/T		M/H		T/H		M/10T		M30/T	
Conc. methanol, mole fraction	Adsorption, m mol/g	Conc. methanol, mole fraction	Adsorption, m mol/g	Conc. toluene, mole fraction	Adsorption, m mol/g	Solution conc., mole fraction	Adsorption, m mol/g	Solution conc., mole fraction	Adsorption, m mol/g
0.0395	2.41	0.0139	1.61	0.0278	0.250	0.0043	1.62	0.0061	1.98
0.0427	2.59	0.0144	2.42	0.0289	0.237	0.0083	2.06	0.012	2.11
0.0450	2.69	0.0186	6.08	0.0289	0.267	0.015	2.29	0.015	2.47
0.0696	3.26	0.0224	3.89	0.0795	0.453	0.020	2.84	0.023	3.30
0.113	3.55	0.0298	4.71	0.0816	0.372	0.036	4.49	0.035	3.93
0.136	3.79	0.0328	5.66	0.0823	0.481	0.038	7.42	0.041	4.62
0.143	3.87	0.0454	6.97	0.154	0.556	0.044	5.31	0.052	5.14
0.188	4.42	0.0501	7.32	0.155	0.542	0.052	6.83	0.070	4.90
		0.0594	11.3	0.156	0.594	0.054	7.20	0.070	5.24
		0.0644	10.8	0.246	0.609	0.069	8.97	0.080	5.45
		0.0753	12.9	0.248	0.612	0.074	6.38	0.080	6.24
		0.0936	17.2	0.253	0.632	0.089	11.9	0.100	7.11

TABLE 10. Surface excess results of the ternary system
methanol/toluene/heptane on silica at 25° C

	Initial concentration,		Grams solid	Grams liquid	Final concentration,		Surface excess			
	methanol	toluene			heptane	methanol	toluene	heptane	mmol/g	
0.0301	0.101	0.869	0.9356	5.727	0.00432	0.104	0.892	1.62	-0.17	-1.44
0.0301	0.101	0.869	0.7783	7.162	0.00831	0.103	0.889	2.06	-0.12	-1.93
0.0301	0.101	0.869	0.4890	7.234	0.0150	0.102	0.883	2.28	-0.12	-2.16
0.0301	0.101	0.869	0.2696	7.328	0.0199	0.102	0.878	2.84	-0.16	-2.67
0.0927	0.0960	0.811	0.9543	7.077	0.363	0.0999	0.863	4.49	-0.31	-4.18
0.0927	0.0960	0.811	0.7466	7.518	0.0436	0.100	0.856	5.31	-0.48	-4.82
0.0927	0.0960	0.811	0.4858	7.662	0.0523	0.0998	0.848	6.83	-0.65	-6.19
0.0927	0.0960	0.811	0.2154	6.723	0.0737	0.0973	0.829	6.39	-0.45	-5.94
0.129	0.0924	0.778	0.9961	7.353	0.0126	0.0960	0.891	7.43	-0.69	-6.74
0.129	0.0924	0.778	0.7687	6.720	0.0546	0.0997	0.845	7.20	-0.70	-6.49
0.129	0.0924	0.778	0.4853	6.503	0.0686	0.0977	0.834	8.97	-0.78	-8.19
0.129	0.0924	0.778	0.2668	7.210	0.0894	0.0961	0.874	11.88	-1.12	-10.77
0.0319	0.306	0.662	1.0424	7.617	0.00607	0.311	0.683	1.98	-0.39	-1.59
0.0319	0.306	0.662	0.7070	7.206	0.0121	0.310	0.678	2.11	-0.41	-1.71
0.0319	0.306	0.662	0.4678	6.813	0.0157	0.308	0.676	2.47	-0.33	-2.13
0.0319	0.306	0.662	0.2460	8.354	0.0228	0.308	0.669	3.31	-0.59	-2.71
0.0850	0.287	0.628	0.9940	7.157	0.0348	0.301	0.664	3.93	-1.15	-2.78
0.0850	0.287	0.628	0.7111	6.949	0.0415	0.300	0.659	4.63	-1.37	-3.25
0.0850	0.287	0.628	0.5463	7.770	0.0518	0.298	0.651	5.14	-1.68	-3.46
0.0850	0.287	0.628	0.2702	8.810	0.0702	0.291	0.639	5.24	-1.39	-3.85
0.126	0.274	0.599	0.9384	7.252	0.0697	0.290	0.640	4.90	-1.35	-3.55
0.126	0.274	0.599	0.7739	8.216	0.0805	0.287	0.633	5.45	-1.47	-3.98
0.126	0.274	0.599	0.5750	6.905	0.0799	0.287	0.633	6.24	-1.69	-4.54
0.126	0.274	0.599	0.2603	6.300	0.100	0.282	0.618	7.11	-1.97	-5.15

TABLE 11. - Plateau values for flow adsorption calorimetry of methanol/toluene/heptane on silica gel at 25° C

System	Surface excess, mmol/g	Enthalpy, J/g	Enthalpy, J/mol	Parking area, nm ² /molecule
M/H	17.2	-165	-9.6	0.033
M/T	4.4	-55	-12.5	0.13
T/H	0.63	-8.8	-14.0	0.90
M/10%T	11	-139	-12.5	0.051
M/30%T	7.1	-88	-12.4	0.08

TABLE 12. - Langmuir fitting parameters

	K	-H _M J/g
M/H	147	166
M/T	151	56
T/H	21	10
M/10%T	301	140
M/30%T	298	90

TABLE 13. - Density of methanol/toluene/heptane solutions at 25° C

M/H		M/T		T/H	
mole fraction	methanol density, g/mol	mole fraction	methanol density, g/mol	mole fraction	methanol density, g/mol
0	0.679325	0	0.861836	0	0.679351
0.02947	0.679688	0.05100	0.860137	0.05014	0.685860
0.05929	0.680346	0.08192	0.859261	0.2404	0.712717
0.09031	0.681082	0.1219	0.858020	1	0.861836
0.1231	0.681933	0.2003	0.855343		
1.	0.786433	1.	0.786433		

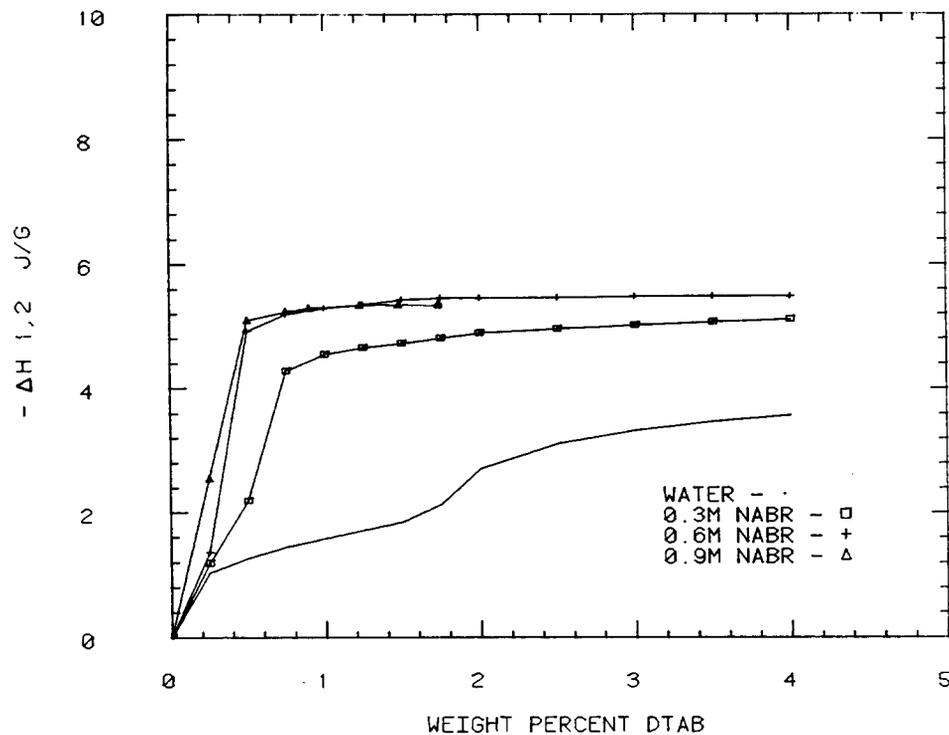


FIGURE 1. - Effect of added salt on the heat of adsorption of DTAB on silica.

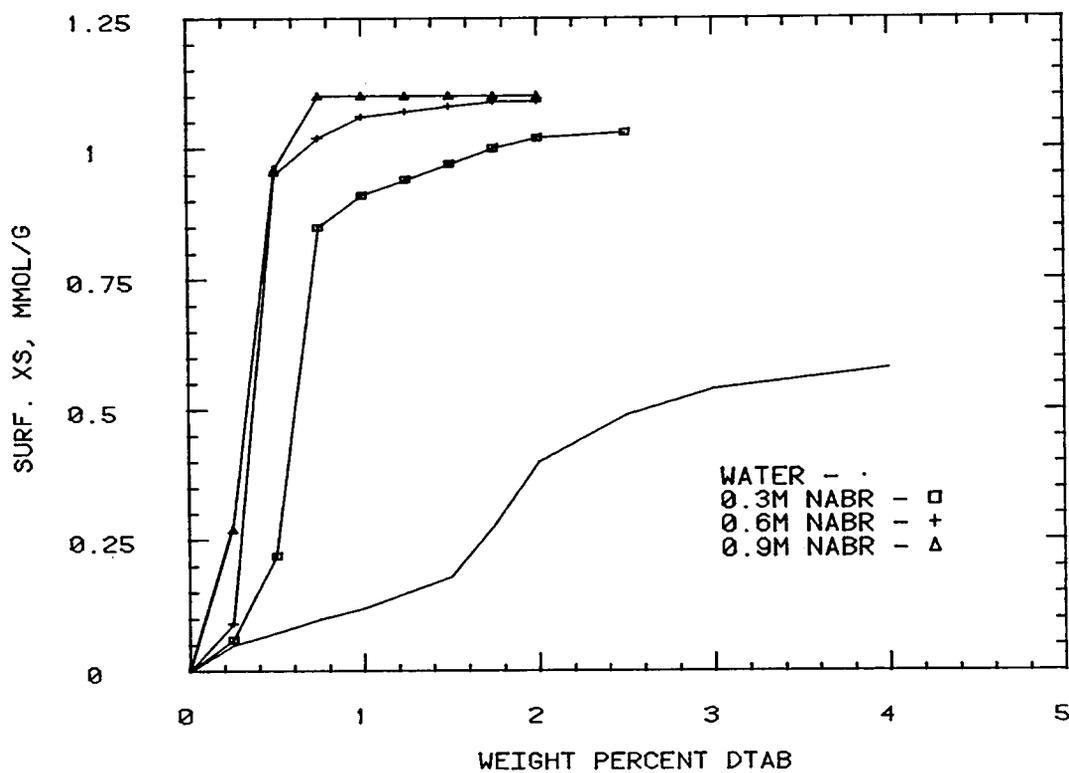


FIGURE 2. - Effect of added salt on the extent of adsorption of DTAB on silica.

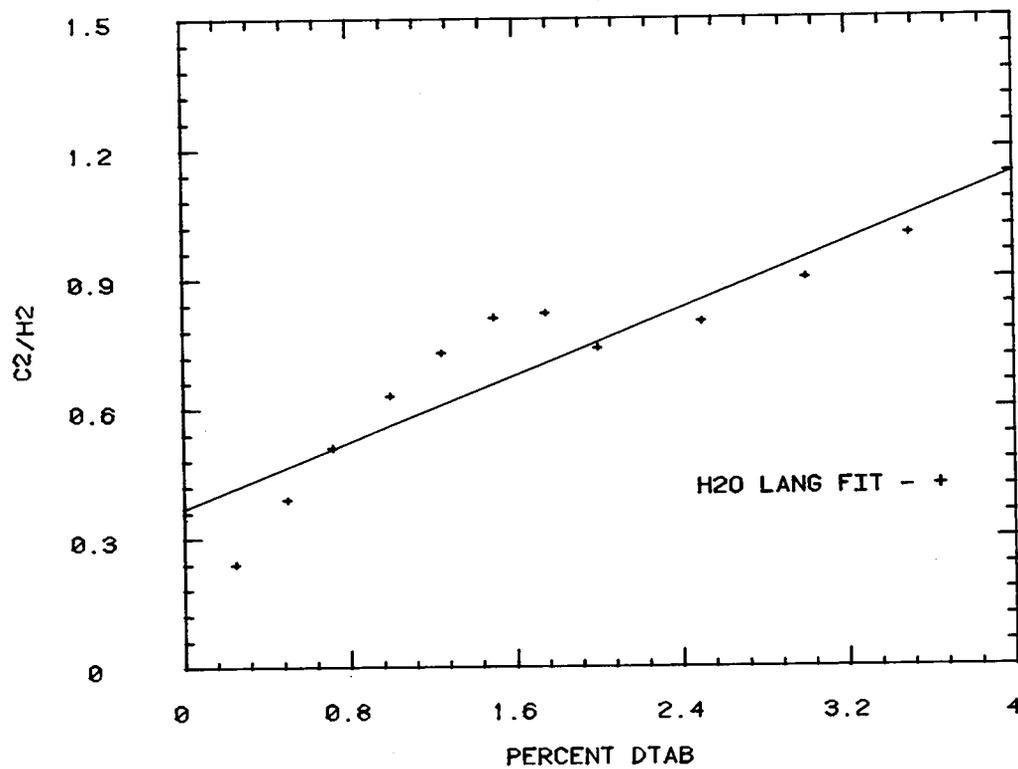


FIGURE 3. - Langmuir fit for the heat of adsorption of DTAB out of water.

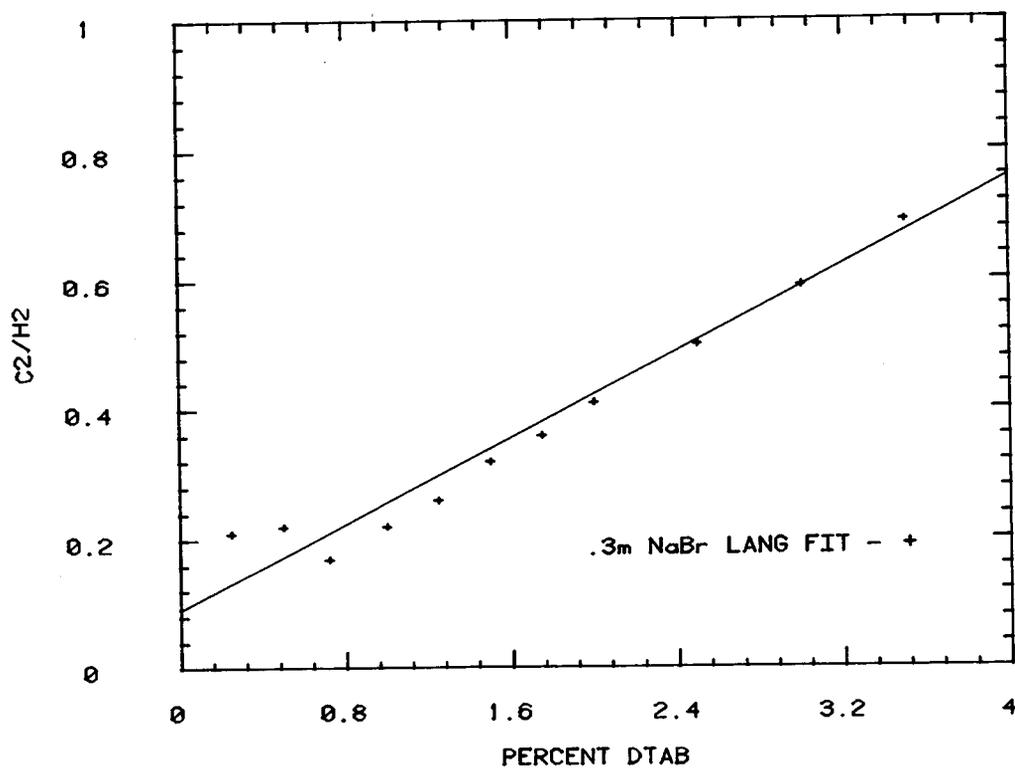


FIGURE 4. - Langmuir fit for the heat of adsorption of DTAB out of 0.3 m NaBr.

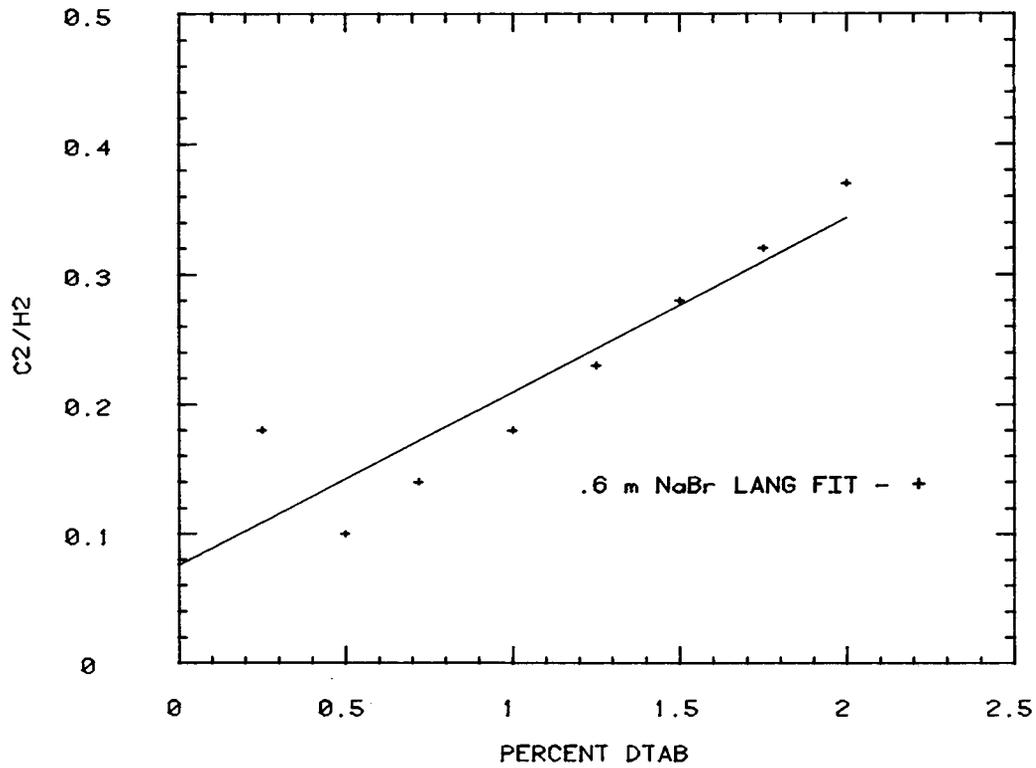


FIGURE 5. - Langmuir fit for the heat of adsorption of DTAB out of 0.6 m NaBr.

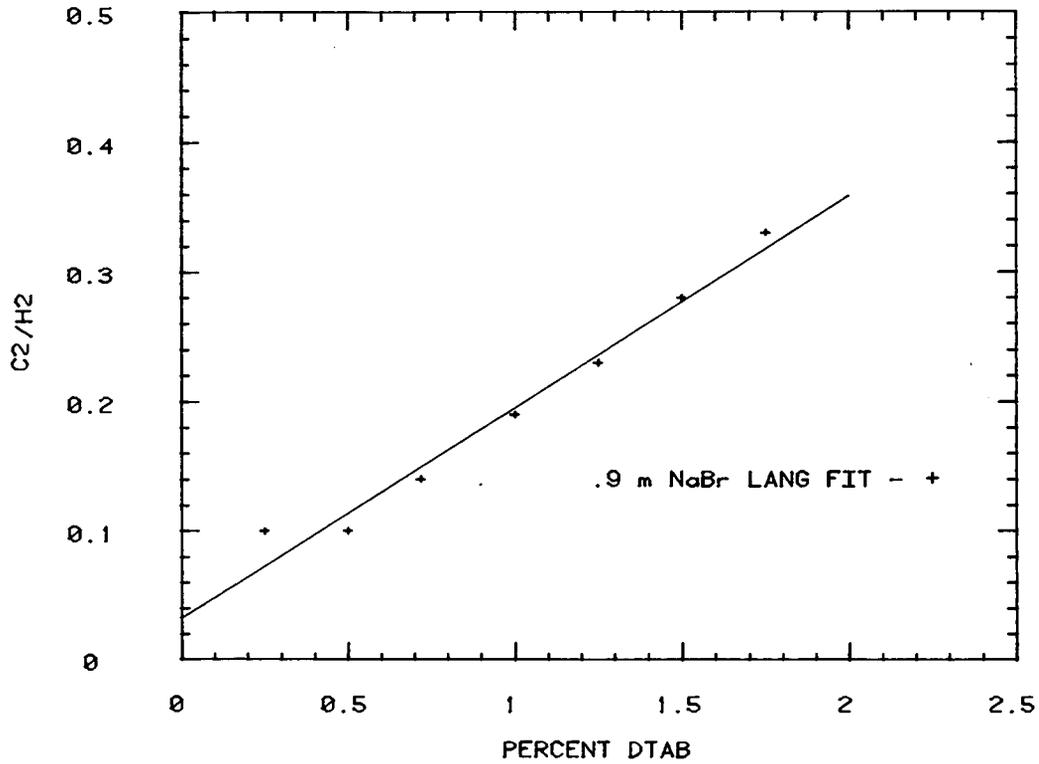


FIGURE 6. - Langmuir fit for the heat of adsorption of DTAB out of 0.9 m NaBr.

DTAB/Water

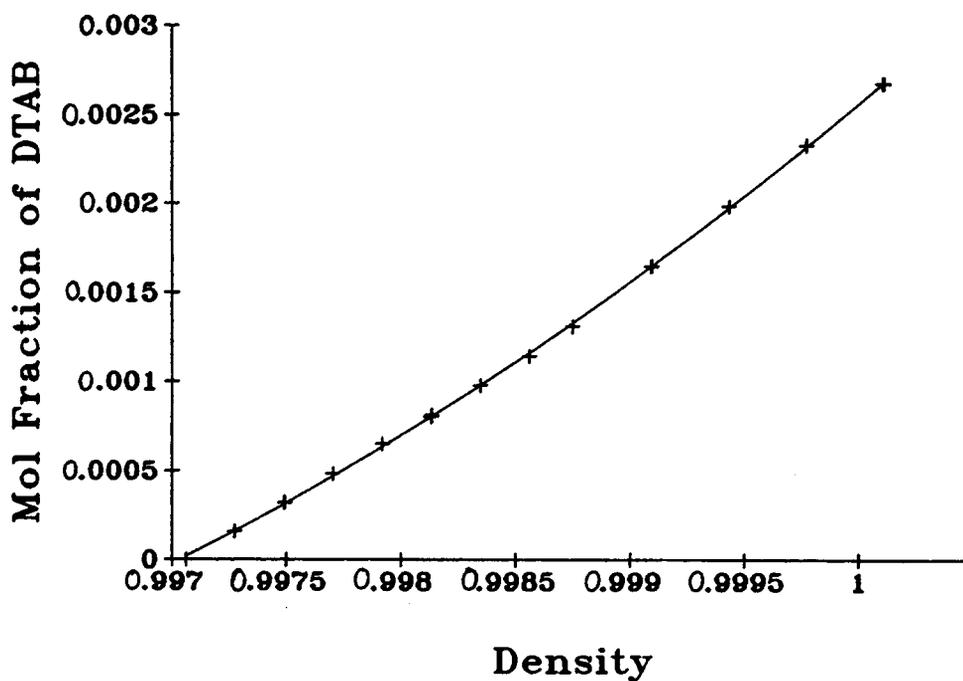


FIGURE 7. - Density of DTAB/water solutions; line is the least squares fit to the data.

DTAB/Water/.3 molal Brine

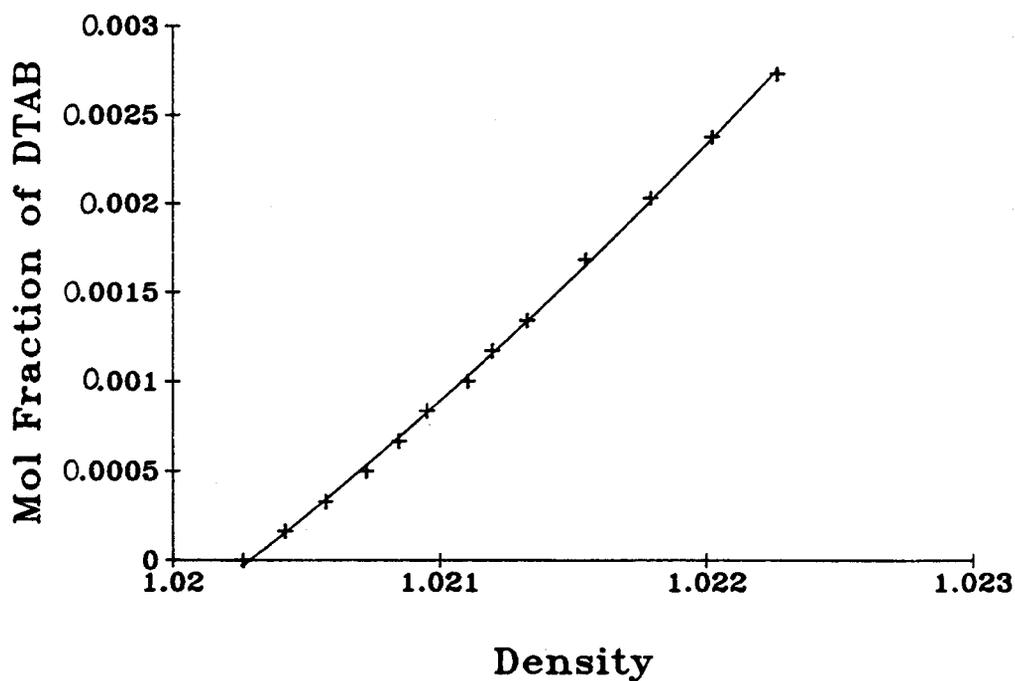


FIGURE 8. - Density of DTAB/0.3 m NaBr solutions; line is the least squares fit to the data.

DTAB/.6mNaBr/HOH

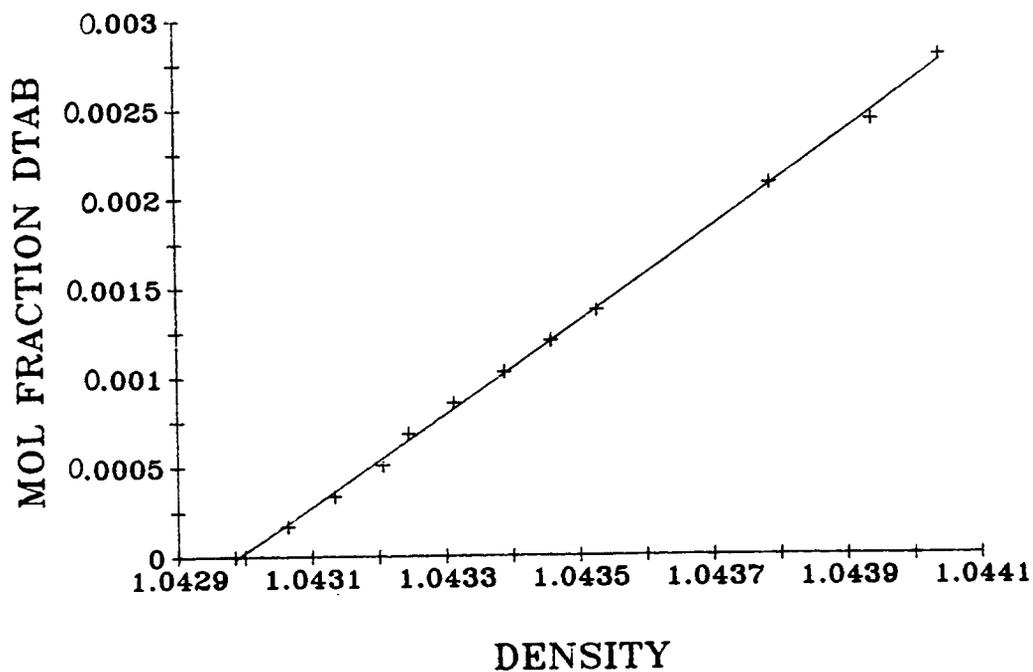


FIGURE 9. - Density of DTAB/0.6 m NaBr solutions; line is the least squares fit to the data.

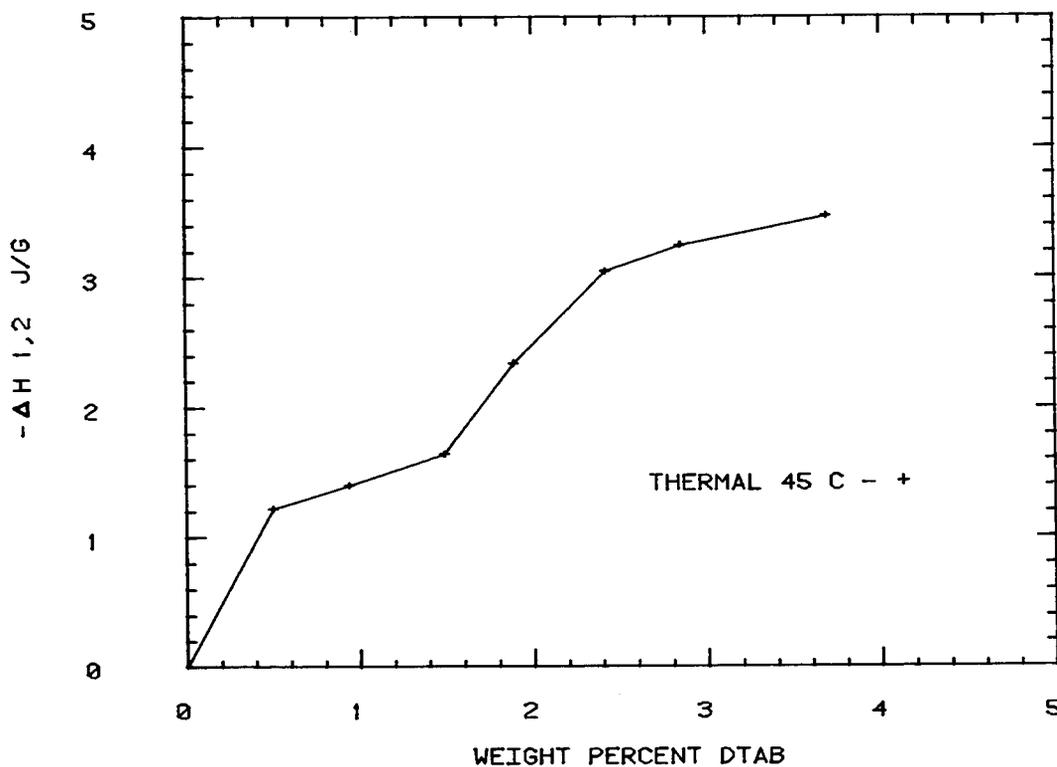


FIGURE 10. - Heat of adsorption of DTAB out of water onto silica gel at 45° C.

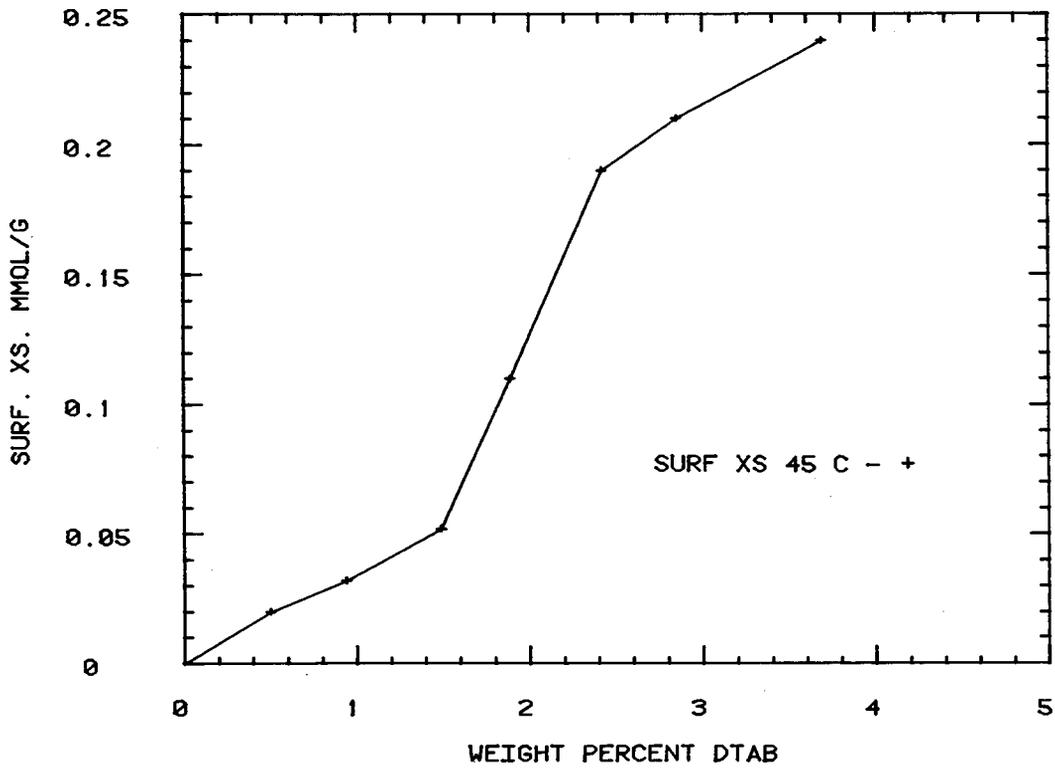


FIGURE 11. - Surface excess of DTAB out of water onto silica gel at 45° C.

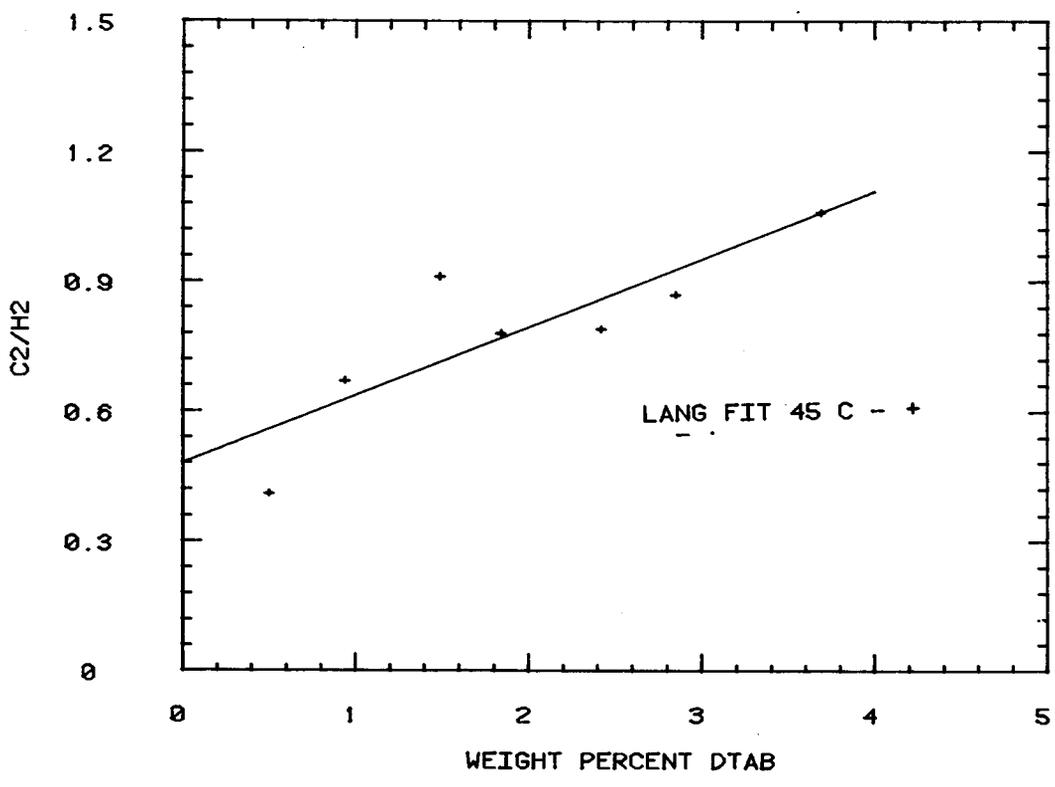


FIGURE 12. - Langmuir fit for the heat of adsorption of DTAB out of water onto silica gel at 45° C.

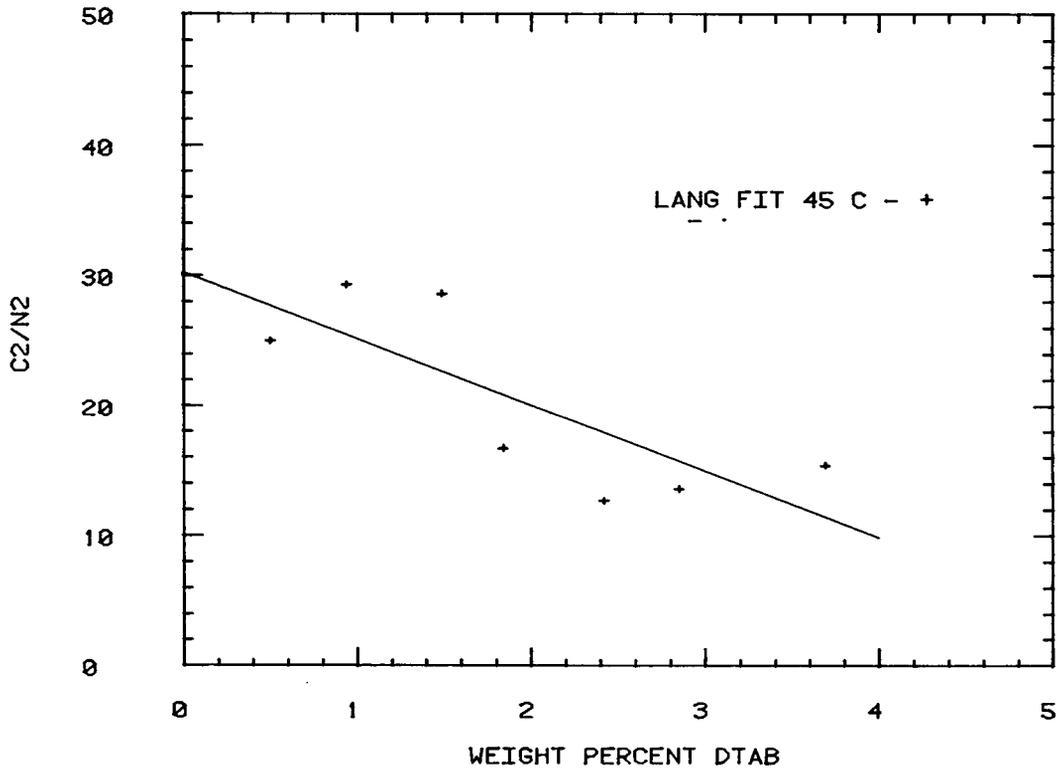


FIGURE 13. - Langmuir fit for the surface excess of DTAB out of water onto silica gel at 45° C.

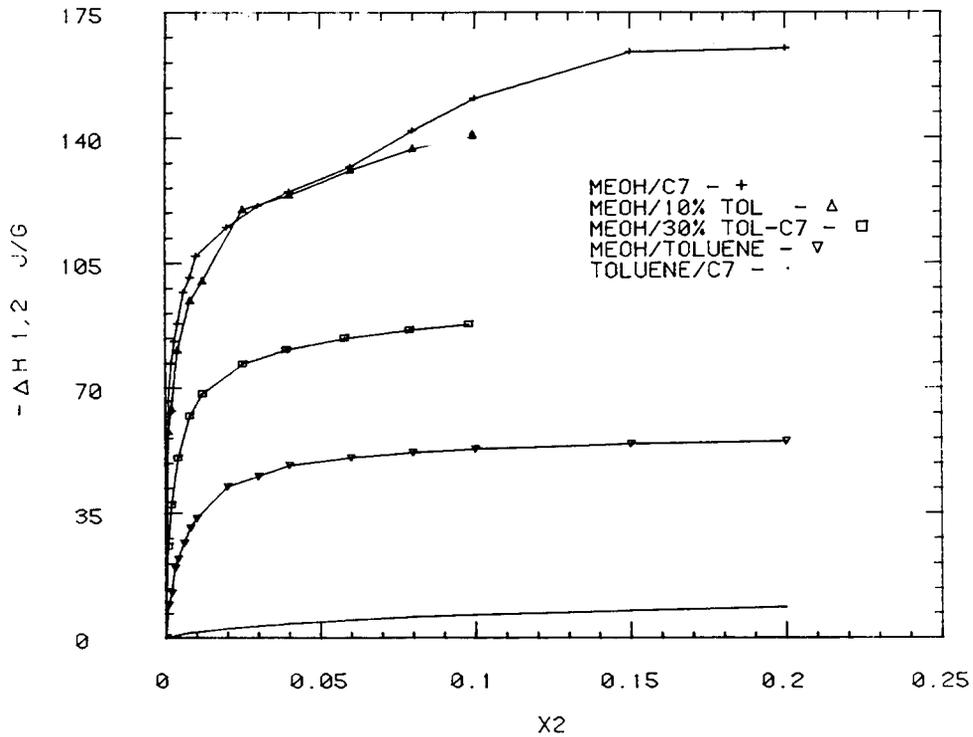


FIGURE 14. - Thermal results for the adsorption calorimetry of the methanol/toluene/heptane system on silica gel.

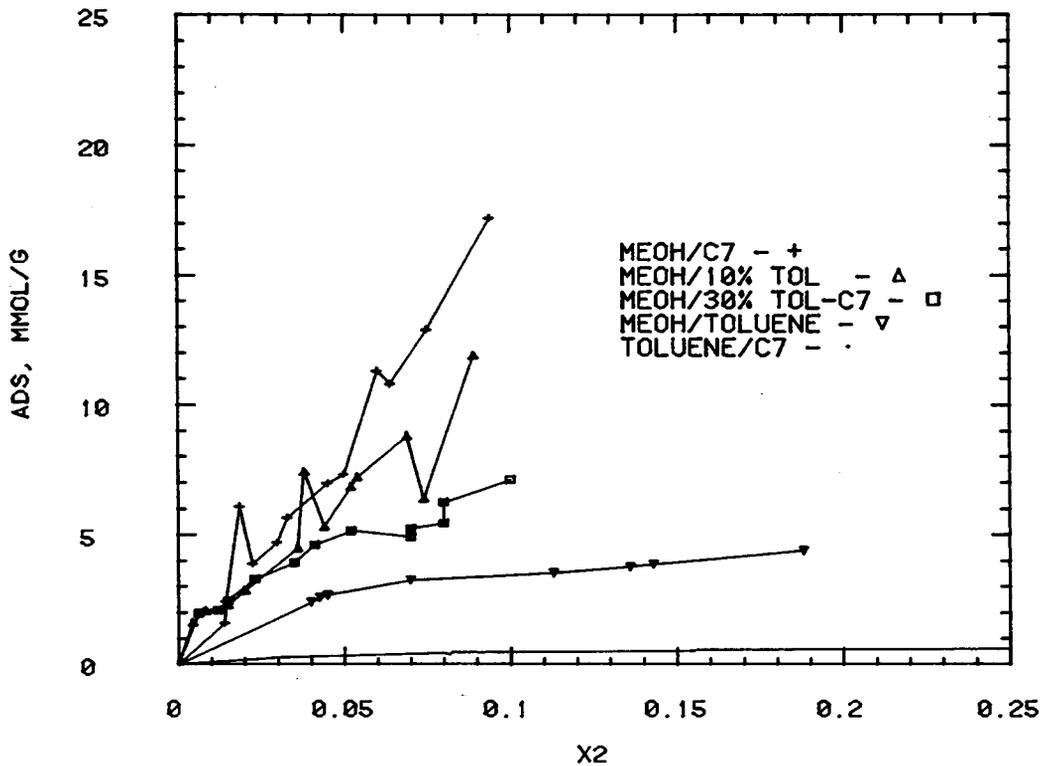


FIGURE 15. - Surface excess results for the adsorption of the methanol/toluene/heptane system on silica gel.

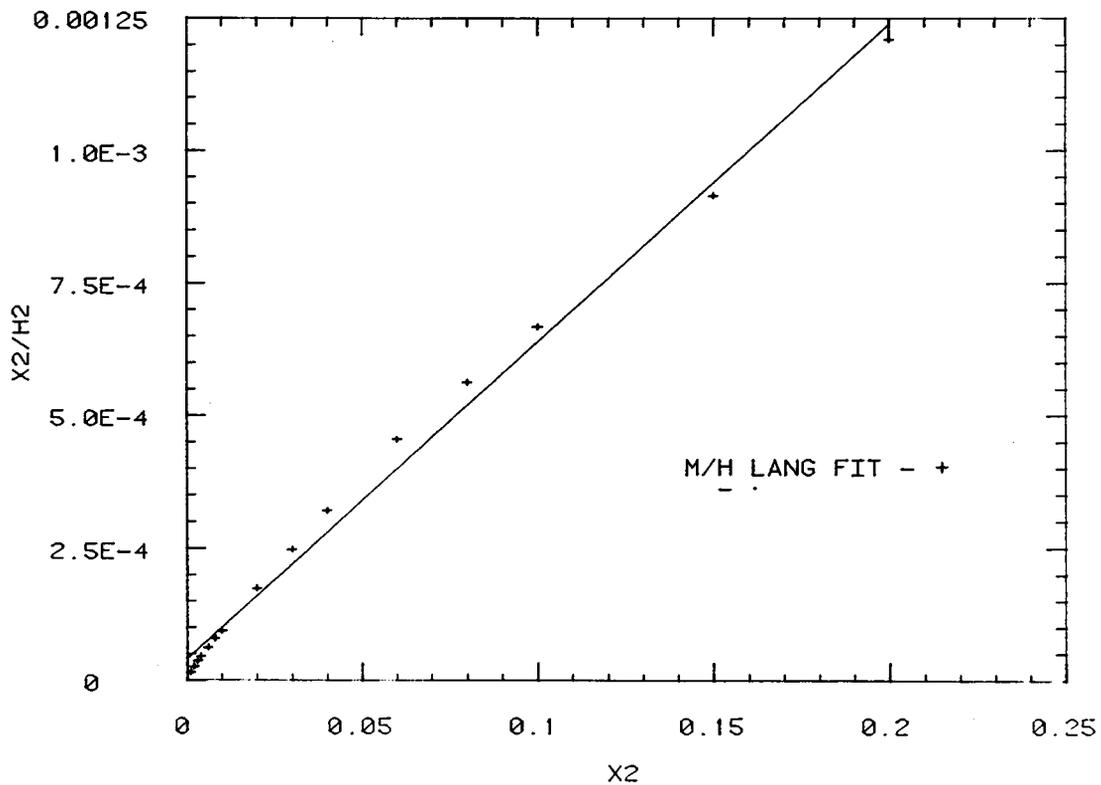


FIGURE 16. - Langmuir fit of the M/H/silica data. The line is the least squares fit to the points.

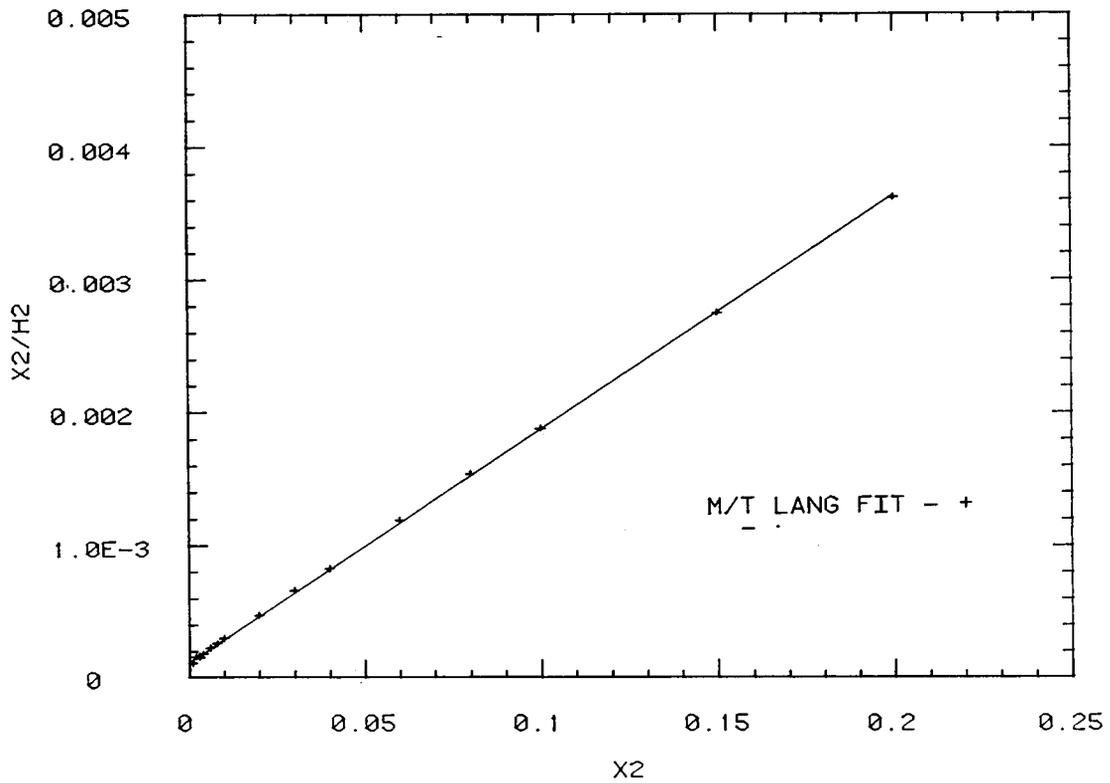


FIGURE 17. - Langmuir fit of the M/T/silica data. The line is the least squares fit to the points.

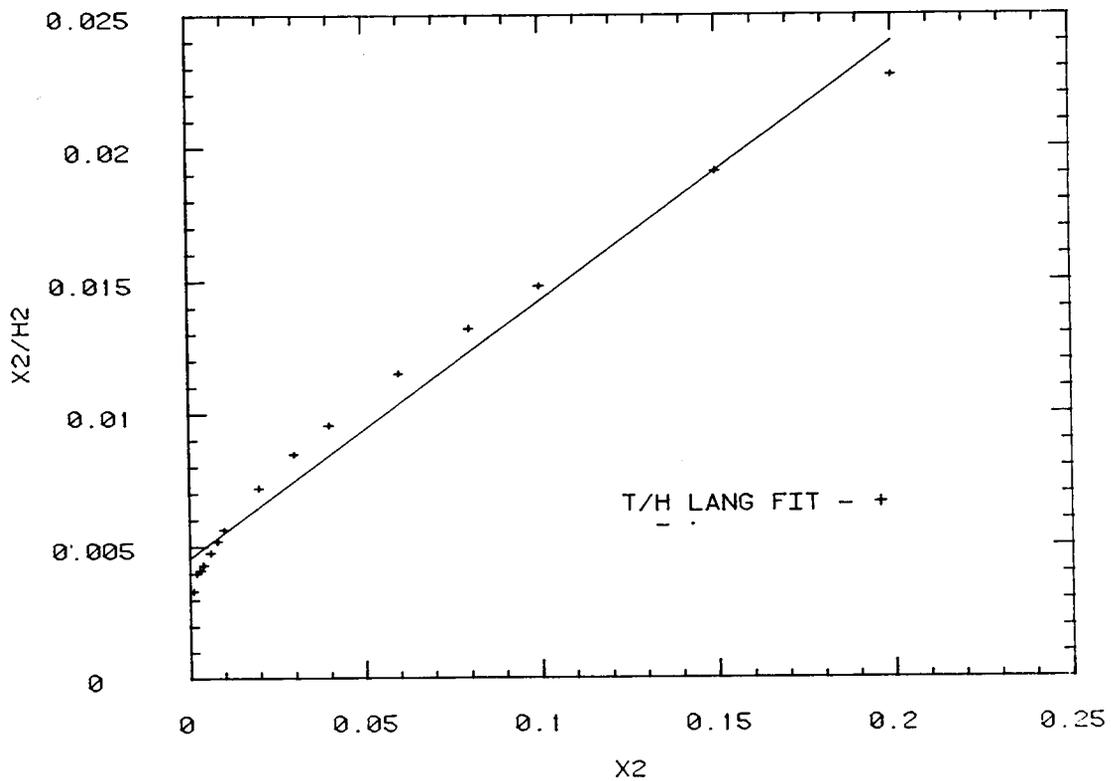


FIGURE 18. - Langmuir fit of the T/H/silica data. The line is the least squares fit to the points.

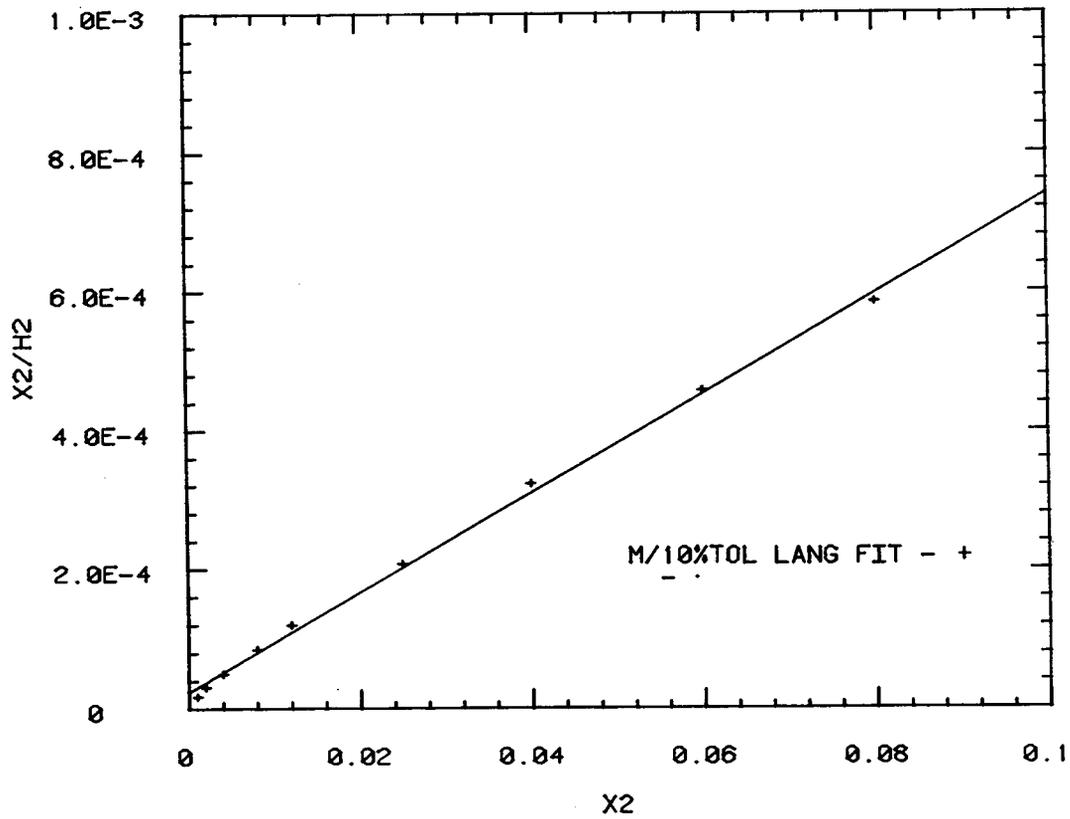


FIGURE 19. - Langmuir fit of the M/10%T/silica data. The line is the least squares fit to the points.

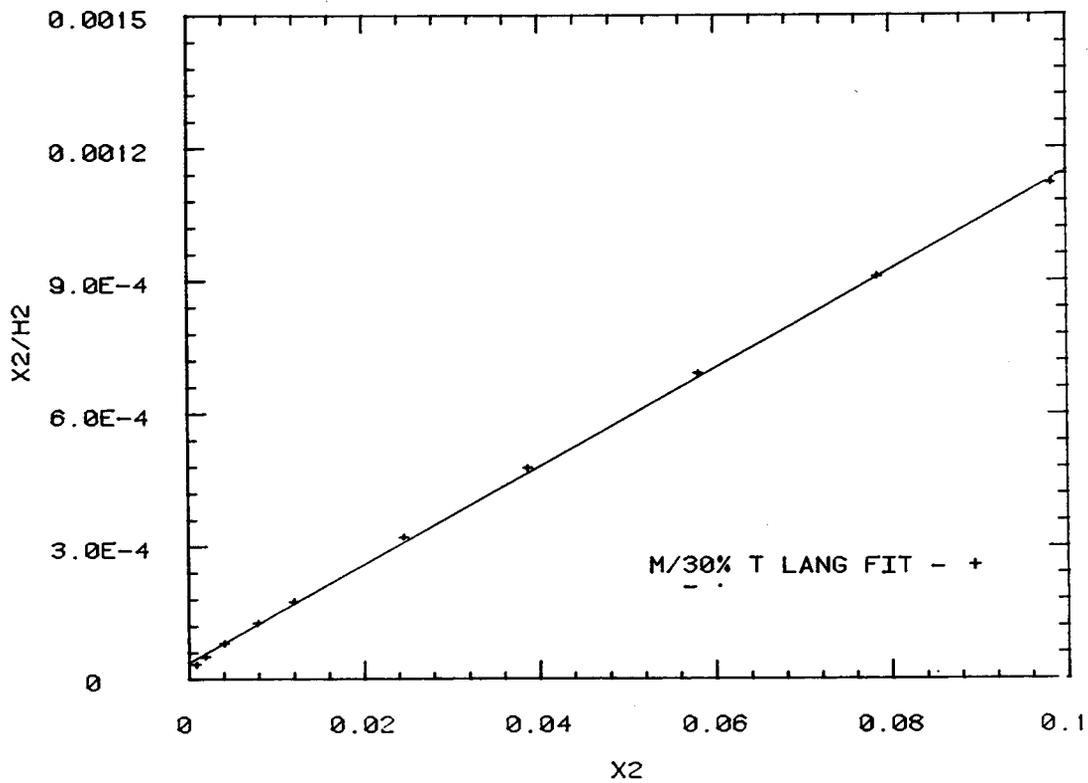


FIGURE 20. - Langmuir fit of the M/30%T/silica data. The line is the least squares fit to the points.

