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Equilibrium Study of Single-Solute Adsorption of Anionic Surfactants with Polymeric XAD Resins

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Abstract

Equilibrium data for the adsorption of sodium lauryl sulfate (SLS) and sodium dodecylbenzene sulfonate (SDBS) from aqueous solutions by Amberlite XAD-4 and XAD-7 polymeric resins at temperatures in the 10–40°C range have been obtained. The specific surface area of the resins plays a major role in adsorption, and thus the best results have been obtained with XAD-4 resin. A higher adsorption of SDBS over SLS was also observed. Several adsorption isotherm models have been used to fit the experimental data. The best results have been obtained with the Redlich–Peterson and Langmuir–Freundlich equations. Estimations of the isosteric heat of adsorption, free energy, and entropy of adsorption are also reported.

INTRODUCTION

Due to their wide utilization, surfactants, particularly the anionics, are among the substances commonly found as pollutants in streams. Not only do they cause contamination problems by themselves, but they may also interfere in treatment processes for other substances.

Adsorption is one of the treatment processes available, its adoption over other alternatives being mainly dependent on economic considerations. Important factors in this sense relative to the adsorbent are cost, adsorption capacity for the particular adsorbate, regeneration, and durability.

Knowledge of the adsorption equilibrium constitutes the first step in the investigation of the possibility of using an adsorbent for a particular separation task. Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given

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application, for selection of the most appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements. Moreover, the isotherm plays a crucial functional role in predictive modeling procedures for analysis and design of adsorption systems. An additional potential use of adsorption isotherms is for theoretical evaluation and interpretation of thermodynamic parameters, such as heats of adsorption. Several equilibrium models have been developed to describe adsorption isotherm relationships. Any particular model may fit experimental data under one set of conditions but fail entirely under another. No single model has been found to be generally applicable, a fact that is understandable in light of the assumptions associated with their respective derivations.

The Langmuir and Freundlich isotherm models, although proposed a long time ago, are still the most widely used to describe adsorption processes; their success is due to their ability to fit a wide variety of data reasonably well, their simplicity, and the easy determination of the parameters. Both isotherms can be linearized, and then the parameters determined graphically or by linear regression, but a detailed examination of the results often reveals significant systematic deviations.

Langmuir isotherm can be linearized in at least three different ways, and the linear regression fit will yield different parameter values depending on the expression used, due to the fact that every transformation changes the original distribution of errors (*1*). The selection of the best transformation has been thoroughly studied, especially in the biochemistry literature. Colquhoun (*2*), after comparing the results from the linear transformations with those obtained by nonlinear regression (NLR), found the latter to be the best method because it yields parameter estimations without deviations or tendencies, with minimum variance for data with constant variance, and a normal error distribution. Sometimes, as with the other equations we tested, NLR is the only alternative.

In this work, results on the adsorption of the anionic surfactants sodium lauryl sulfate (SLS) and sodium dodecylbenzene sulfonate (SDBS) from aqueous solution with the polymeric resins Amberlite XAD-4 and XAD-7 are presented. Five isotherm models have been tested for fitting the experimental data, and values for the enthalpy, free energy, and entropy of adsorption have been estimated.

MATERIALS AND METHODS

Adsorbent

The adsorbents used in this research were the polymeric resins Amberlite XAD-4 and XAD-7 made by Rohm & Haas. They have found application as alternatives to active carbon in a number of processes including wastewater treatment. Their main characteristics are presented in Table 1. A particle size of 0.30–0.50 mm was used in the experiments.

The resins were first cleaned of preservative agents and polymerization residuals by successive washings with methanol and deionized water, dried in an oven, and then stored in a desiccator. Before use, they must be rehydrated by soaking them in methanol for some minutes and then thoroughly rinsing with deionized water.

Solutions

All solutions were prepared with deionized water. The adsorbates used, SLS and SDBS were purchased in their highest available purity. The pH of the solutions was kept close to 7.

Isotherm Procedure

A bottle point isotherm procedure was used to conduct all equilibrium studies. Fixed resin dosages of 1 or 2 g/L were contacted in 125 mL stoppered polyethylene bottles, with 100 mL of surfactant solution at four temperatures (10, 20, 30, and 40°C). SLS concentrations used were in the 0.035–0.500 mmol/L interval and SDBS in the 0.029–1.100 mmol/L. The bottles were placed in a water thermostatic bath and shaken until equilibrium was achieved, which took from several days to several weeks; the lower the temperature, the longer the equilibration time. Adsorption of SDBS and utilization of XAD-4 resin were also factors that increased the time needed to reach equilibrium. Aliquots of solution were withdrawn for analysis to determine the amounts of solute adsorbed by the resins.

Analytical procedures

A variety of analytical methods for surfactants is available (*3*). The Methylene Blue Active Substance Method, MBAS (*4*), was used to de-

TABLE 1
Properties of the Amberlite XAD Adsorbents

Amberlite	XAD-4	XAD-7
Composition	Polyestyrene	Polyacrylic
Hydrated density (g/cm^3)	1.02	1.05
Specific area (m^2/g)	750	450
Mean pore diameter (Å)	50	80
Porosity (mL pore/g resin)	0.998	1.080
Dipolar moment of the groups (debyes)	0.3	1.8

termine the equilibrium concentration of each surfactant. It is based on the formation of a colored compound between the anionic surfactant and methylene blue. This is extracted in chloroform and its concentration measured by spectrophotometry at a wavelength of 652 nm against a reference blank of chloroform.

RESULTS AND DISCUSSION

Equilibrium data concerning the adsorption of SDBS and SLS from aqueous solutions are presented in Figs. 1 through 3. Figures 1 and 2 show the isotherms corresponding to the adsorption of SLS by Amberlite XAD-4 and of SDBS by XAD-7, respectively, and the results for both surfactants by both resins at 20°C are displayed in Fig. 3. Favorable adsorption isotherms were obtained in all cases. A decreasing adsorption capacity with increasing temperature is also evident, and thus the curves corresponding to high temperatures lay below the ones corresponding to lower temperatures. In every case, for a particular resin at a particular temperature,

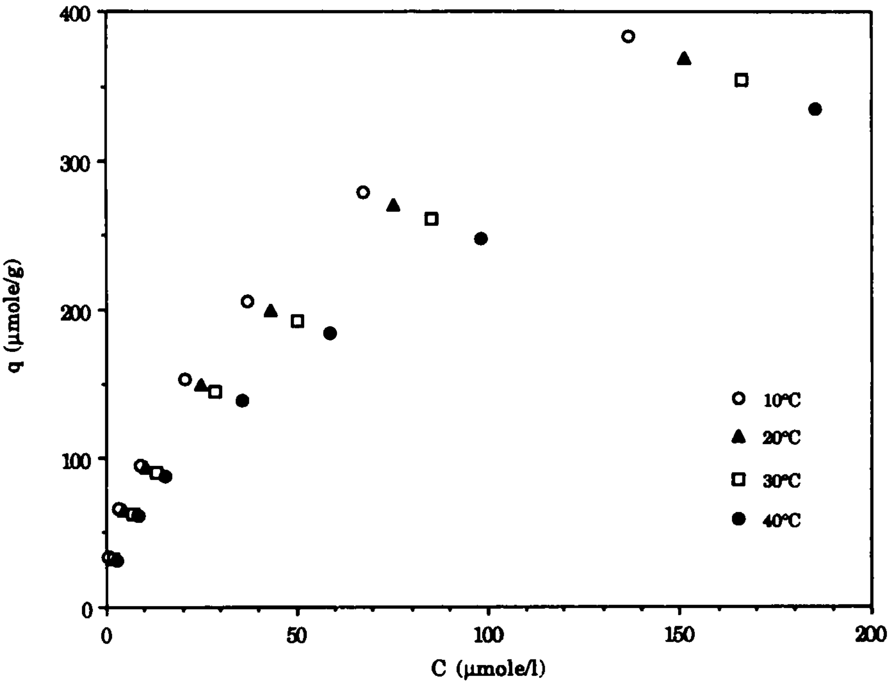

FIG. 1. Isotherms of adsorption of SLS with Amberlite XAD-4. Resin dose: 1 g/L.

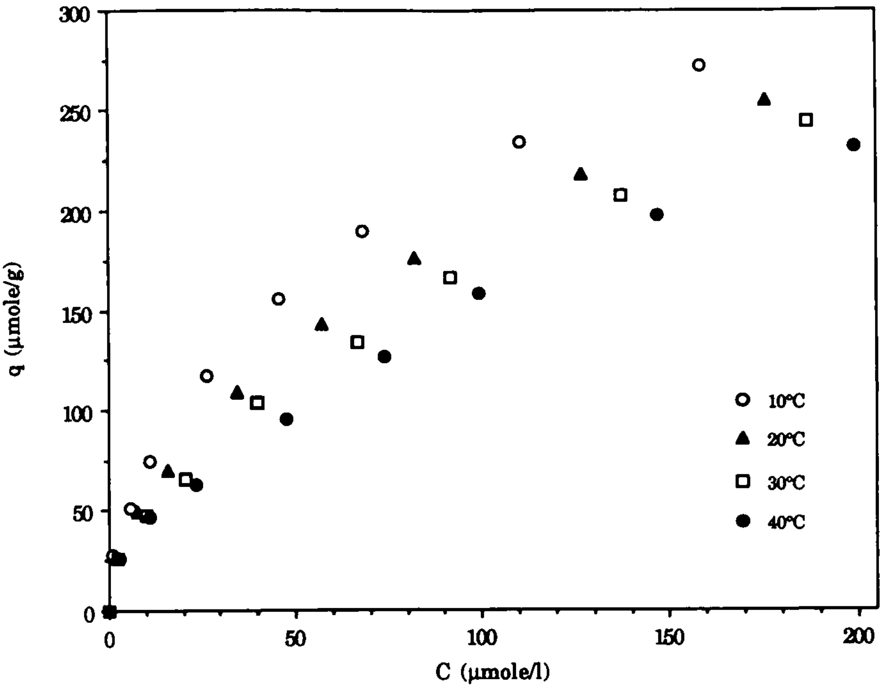

FIG. 2. Isotherms of adsorption of SDBS with Amberlite XAD-7. Resin dose: 1 g/L.

SDBS was more extensively adsorbed than SLS. This can be explained by the polar nature of the solvent (water) and the dual nature (polar and apolar groups) of the surfactants, whose hydrophobicity increases as their hydrocarbon skeletons increase in size (SDBS > SLS) as do their affinities for the relatively apolar resins. Similar tendencies have been found by other authors for compounds in an homologous series, provided the sorbate molecules are not so large that they can't enter the pores of the resin, and have been reported in the literature (*5*).

Amberlite XAD-4 (750 m^2/g) had a higher adsorption capacity than XAD-7 (450 m^2/g). Yields in elimination at low surfactant concentrations (30 ppm of SDBS and 10 ppm of SLS at 10°C) were 99% for SDBS and 98% for SLS using XAD-4 (1 g/L) versus 96% (1 g/L) and 82% (2 g/L), respectively, obtained with XAD-7 in the same conditions. Specific surface area then plays a major role in the adsorption of these substances. The pore size is not a significant factor in the adsorption of the surfactants by these adsorbents, which implies that there is no major hindrance to the

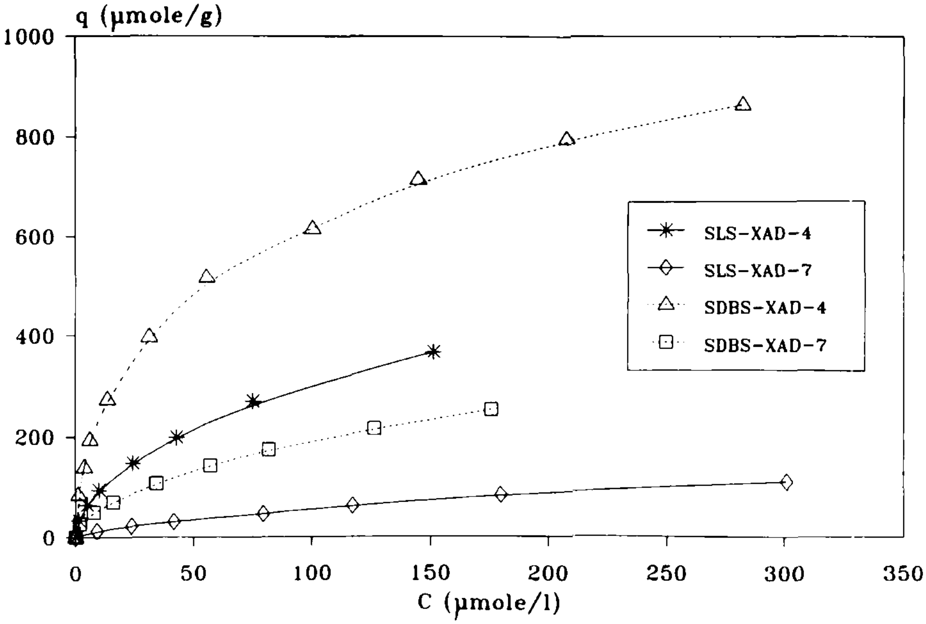

FIG. 3. Comparison of the adsorption at 20°C of SLS and of SDBS with Amberlite XAD-4 and with XAD-7.

diffusion of the adsorbates into the resin beads. The different polarities of the resins are not a decisive factor either.

Fitting of the Experimental Results to Several Isotherm Equations

Langmuir, Freundlich, Redlich–Peterson, Langmuir–Freundlich, and Toth isotherm models, some with a theoretical basis and others purely empirical, were used to fit the experimental results for the adsorption of SLS and SDBS. The mathematical equations, number of fitting parameters, and asymptotic properties are presented in Table 2.

A nonlinear least-squares computer program based on Marquardt's algorithm was used to fit the data. Some transformations or grouping of the parameters were made, when necessary, in order to keep some physical meaning in their values. An example is keeping the value of the maximum adsorption capacity (*M*) positive.

Figure 4 shows typical Langmuir, Freundlich, and Redlich–Peterson fits. Overall results are shown in Fig. 5, where the averaged relative errors between the fitted and experimental values at the four temperatures are presented for every resin, surfactant, and isotherm model tested. As can

TABLE 2
Characteristics of the Isotherm Models Used

Isotherm	Equation	Adjustable parameters	Asymptotic properties: Lineal at $C \to 0$	Asymptotic properties: Adsorption maximum at $C \to \infty$
Langmuir	$q = KCM/(1 + KC)$	2	Yes	Yes = M
Freundlich	$q = KC^n$	2	No	No
Langmuir–Freundlich	$q = KC^{\beta}M/(1 + KC^{\beta})$	3	No	Yes = M
Redlich–Peterson	$q = KCM/(1 + KC^{\beta})$	3	Yes	No
Toth	$q = KCM/(1 + KC^{\beta})^{1/\beta}$	3	Yes	Yes = M

be seen, the equations that globally best reproduce the experimental data are the Redlich–Peterson for SLS and the Langmuir–Freundlich for SDBS. Mean relative errors were less than 7.0% in all cases. The Freundlich and Toth models provided remarkably good fits. The Langmuir isotherm doesn't reproduce the experimental data satisfactorily, with the larger deviations, sometimes over 20%, corresponding to the lower temperatures.

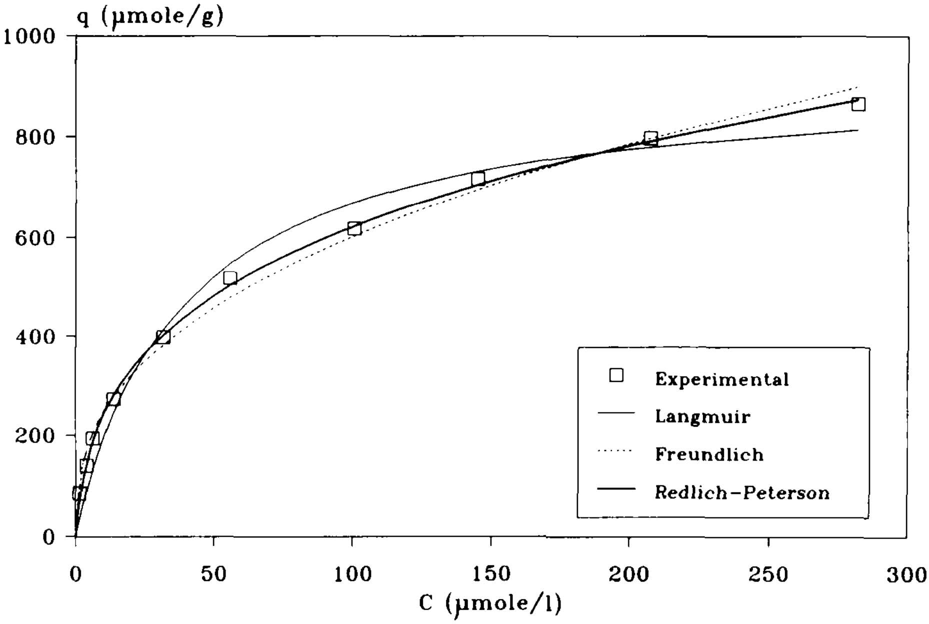

FIG. 4. Results of the fitting of the isotherm of adsorption of SDBS with XAD-4 at 20°C by different isotherm models.

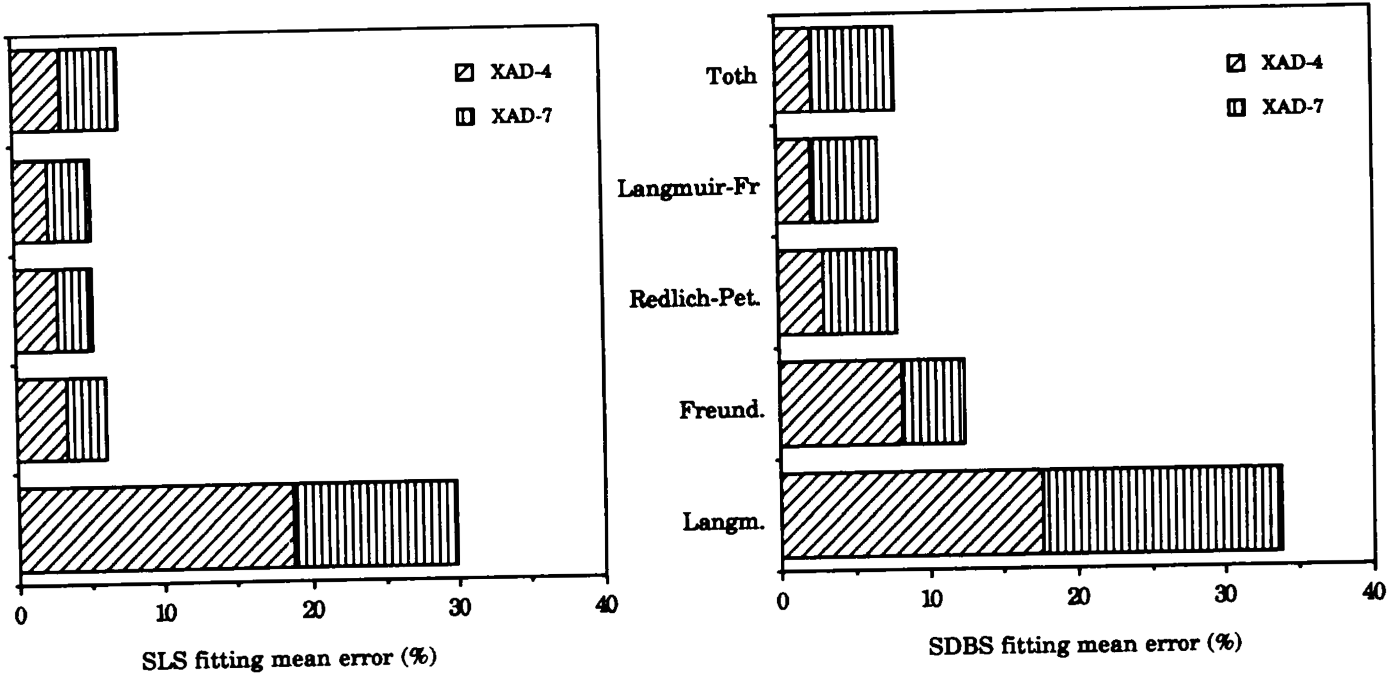

FIG. 5. Averaged relative errors between fitted and experimental adsorption values.

TABLE 3
Experimental and Predicted (extrapolated) Surfactant Adsorption at High Concentrations (adsorption values in mmol/g)

Surfactant	Resin	Experimental	Freundlich	Langmuir–Freundlich	Redlich–Peterson
SLS	XAD-4	0.77	0.95	0.77	0.90
SLS	XAD-7	0.30	0.29	0.24	0.28
SDBS	XAD-4	1.38	1.55	1.15	1.35
SDBS	XAD-7	0.57	0.58	0.58	0.58

Experiments were carried out using surfactant concentrations higher than those employed to fit the equations. The results are summarized in Table 3 together with adsorption values extrapolated from Freundlich, Langmuir-Freundlich, and Redlich-Peterson fits. Agreement is very good in most cases, which indicates that these equations may be applied with confidence in a concentration range bigger than that used in their calculation.

Thermodynamics of the Adsorption of Single Solutes

Estimations of the isosteric heat of adsorption, free energy, and entropy were calculated from data interpolated using the best fitting isotherm. The values obtained were dependent upon the extent of surface coverage of the adsorbent. While the estimated heats of adsorption are probably not accurate because of the assumptions involved in their calculation, they are considered to be the correct order of magnitude. Comparisons by other authors between results from this method to those obtained by calorimetric measurements showed order of magnitude agreement.

The isosteric heat of adsorption at different adsorption levels can be easily calculated from the expression

$$\ln\left(\frac{1}{C}\right) = \ln(K_0) + \left(\frac{-\Delta H}{RT}\right) \tag{1}$$

which is derived from the Van't Hoff equation by a procedure shown elsewhere (*5*). Equation (1) yields a straight line when representing the logarithm of the inverse of the equilibrium concentrations corresponding to a determined value of q versus the inverse of the absolute temperature. The slope of this plot, which is determined by least-squares analysis of the data obtained at various temperatures, yields the enthalpy over the universal gas constant. A close distribution of the experimental points with respect to the lines can be observed. Correlation coefficient values were in the range 0.985–1.000. Figure 6 shows some of these curves for the SLS–XAD-4 system.

Values for the free energy of adsorption can be obtained using an expression derived from the Gibbs adsorption isotherm by a procedure shown elsewhere (*6*). In the end we get

$$\Delta G = -RT \int_{o}^{X} q \frac{dX}{X} \tag{2}$$

where X represents the molar fraction of the adsorbate in solution. q was then replaced by the Redlich–Peterson isotherm equation, and the resulting expression was integrated numerically using Romberg's algorithm, and values of ΔG at different q values were obtained. The use of the Freundlich isotherm would lead to a value for the free energy independent of q.

Entropy variation values can be estimated using previously calculated

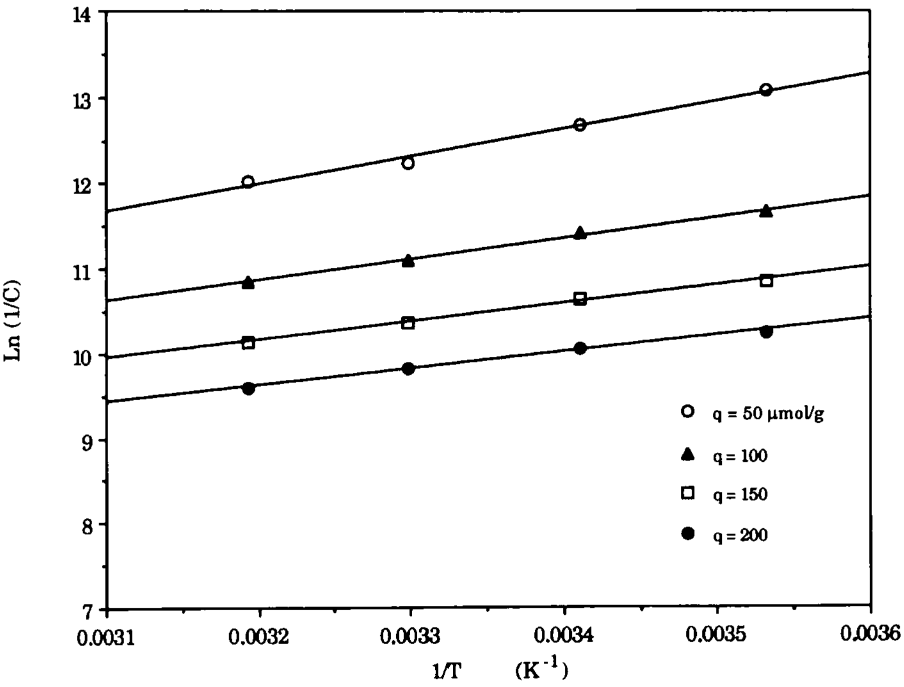

FIG. 6. Enthalpy determination curves for the adsorption of SLS with XAD-4.

ΔH and ΔG values and the Gibbs–Helmholtz equation

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{3}$$

Table 4 shows a summary of the estimated values for these three thermodynamic properties at various adsorbate loadings. Values of the enthalpy (always negative) are indicative of an exothermic process, and their magnitudes (10–30 kJ/mol) manifest a physisorption process. Absolute values decrease as the adsorption increases, a common situation when dealing with adsorption on nonhomogeneous surfaces which can be related to the preferential occupation of the superficial locations energetically more favorable. As depicted in Fig. 7, the slopes of the curves representing the variation of adsorption enthalpy versus the percentage of adsorption show a tendency to stabilize at high adsorption levels at values very similar for the two adsorbates and independent of the resin, values that should correspond approximately to the condensation heat of the adsorbate. A slight increase, up to 4 kJ/mol, in the heat of adsorption of SDBS with XAD-4, which may be attributed to interactions among the adsorbed molecules, can be observed at high surface coverage.

Variations of the adsorption free energy with temperature as well as with superficial coverage are always small. This confirms the physical character

TABLE 4
Thermodynamic Properties of the Systems Tested

				ΔG (kJ/mol)		ΔS (J/mol·K)	
Surfactant	Resin	q (μmol/L)	ΔH (kJ/mol)	10°C	30°C	10°C	30°C
SLS	XAD-4	50	−26.6	−4.73	−3.47	−77.3	−76.4
		100	−20.4	−4.81	−3.83	−55.1	−54.7
		150	−17.7	−4.83	−4.06	−45.3	−44.9
SLS	XAD-7	30	−17.5	−3.88	−3.68	−48.2	−45.7
		50	−14.3	−3.93	−3.73	−36.9	−35.0
		70	−13.1	−3.96	−3.77	−32.4	−30.6
SDBS	XAD-4	100	−13.0	−3.00	−3.23	−35.3	−32.2
		150	−10.6	−3.25	−3.52	−26.0	−23.4
		300	−10.3	−3.96	−4.30	−21.7	−19.8
SDBS	XAD-7	30	−27.9	−3.51	−3.70	−85.9	−79.7
		90	−23.7	−4.16	−3.99	−68.9	−65.0
		150	−19.2	−4.45	−4.10	−51.9	−49.7

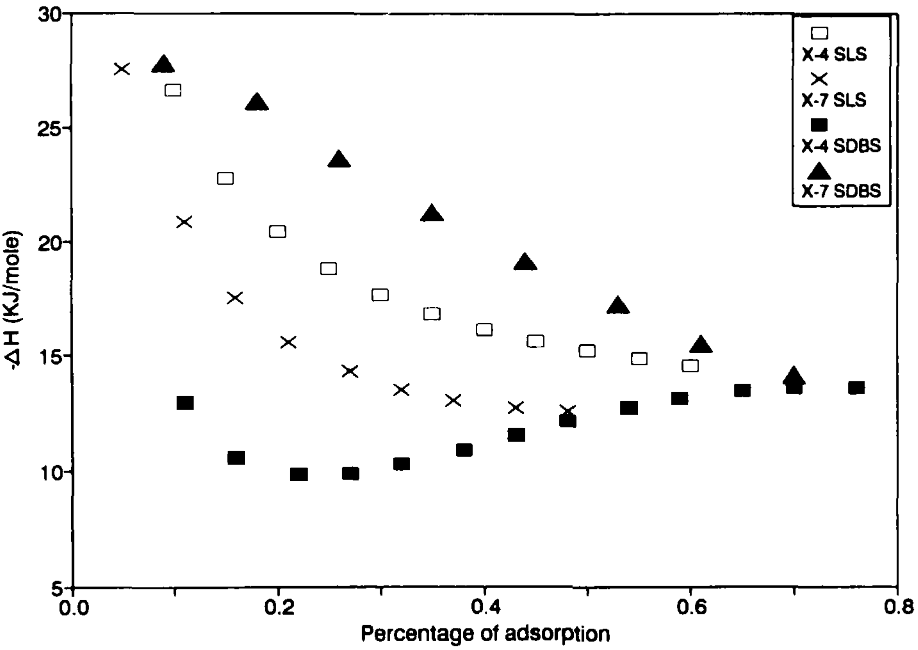

FIG. 7. Variation of the enthalpy of adsorption with the amount of adsorbed surfactant.

of the adsorption process and also indicates a compensation effect of the entropic contribution at low adsorption levels.

Finally, the negative values of the adsorption entropy are consistent with restricted mobilities of the adsorbed molecules of SDBS and SLS as compared with those in solution. Absolute entropy values decrease slightly with increasing temperature; this is more marked with increasing coverage. Bottani (7) has presented some values for gas–solid adsorption with this same tendency. The reason can be attributed to the superficial heterogeneity of the adsorbent (and this effect would be more manifest at low surface coverages) and to the influence of the configurational factor at high adsorption levels. This factor accounts for entropy changes due to the configuration of the adsorbate molecules on the surface, which may change with increasing coverage, versus those due to the mobility of the adsorbate molecules.

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