Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article García-Delgado, R. A. , Cotoruelo, L. M. and Rodríguez, J. J.(1992) 'Adsorption of Anionic Surfactant Mixtures by Polymeric Resins', Separation Science and Technology, 27: 8, 1065 — 1076
To link to this Article: DOI: 10.1080/01496399208019024
URL: http://dx.doi.org/10.1080/01496399208019024

SEPARATION SCIENCE AND TECHNOLOGY, 27(8 & 9), pp. 1065–1076, 1992

Adsorption of Anionic Surfactant Mixtures by Polymeric Resins

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Abstract

Results concerning the single-solute adsorption of two anionic surfactants were presented in a previous paper; this paper deals with their mixtures. Equilibrium adsorption isotherms of mixtures of sodium lauryl sulfate and sodium dodecylbenzene sulfonate in aqueous solution by Amberlite XAD-4 and XAD-7 polymeric resins at 10 and 30°C have been obtained and are compared to the predictions given by several multicomponent adsorption models that make use of the single solute adsorption data already available. Reasonable agreement has been achieved in some cases, especially when predicting total surfactant adsorption.

INTRODUCTION

Purification of water by adsorption usually requires dealing with several solutes capable of sorbing. For design purposes it's necessary to have the corresponding equilibrium data, and given the great number of possible multicomponent systems, those needed won't likely be available in the literature. Therefore it becomes necessary to predict the equilibrium data from single solute adsorption data or the minimum number of binary experiments.

There are a number of ways to reach this objective. On the one hand we have multicomponent models derived as extensions of isotherm equations such as the modified Langmuir's and Freundlich's isotherms. There are also semitheoretical models that, although developed from well-founded theoretical concepts, use empirical parameters to simplify their use when compared to the purely theoretical ones, and that are accurate

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enough for engineering applications (*1–3*). On the other hand, many theories have been proposed based on thermodynamic and physicochemical considerations, and they have modeled the process with varied complexity and success (*4–6*). Among the main models that have been discussed in the literature are 1) the Polanyi adsorption potential theory, developed by Manes and others (*7–9*); 2) the net adsorption energy concept formalized by Suffet and McGuire (*10*); and 3) the solvophobic approximation adopted by Belfort and others (*11*, *12*).

A significant advance in the ability to predict multicomponent adsorption equilibria came with the work of Radke and Prausnitz (*13*) who presented a thermodynamic method to predict the multicomponent adsorption in the aqueous phase from single solute adsorption data. This method, which makes use of the ideal solution concept of Myers and Prausnitz for gases (*14*), is based on a minimum number of hypotheses and is not derived from a specific molecular model but from thermodynamic arguments appropriate for dilute solutions.

There is abundant literature on the application of the IAST to multicomponent adsorption and on a number of modifications needed in order to attain the faster calculations (*15–17*) essential when dealing with a large number of components. Nevertheless, predicted adsorption equilibria do not always agree with experimental data. For this reason, some variations that account for factors such as nonideal competition among the solutes for the adsorption sites, interaction among the sorbed species, and irreversible adsorption have been implemented (*18*, *19*).

In this work the results on the adsorption of mixtures 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 and compared to predictions obtained from multisolute models that make use of the single solute adsorption data reported in an earlier paper (*20*).

MATERIALS AND METHODS

Since most of this section remains the same as for the description given in the first work on single solute adsorption, we shall limit its extent here.

Adsorbent. The adsorbents used in this research were the polymeric resins Amberlite XAD-4 and XAD-7 made by Rohm and Haas. A particle size of 0.10–0.20 mm was used in the experiments in order to shorten equilibration times.

Preservative agents and polymerization residuals were first removed from the resins by consecutive washings with methanol and deionized water. The beads were dried in an oven and then stored in a dissicator.

The cleaning step is important in order to avoid interferences in the analysis when using UV absorption spectrophotometry. Before using them, the resins must be rehydrated by soaking them in methanol for some minutes and then thoroughly rinsing them with deionized water to displace the methanol.

Solutions. All solutions were prepared with deionized water. The sorbates used, sodium lauryl sulfate (SLS) and sodium dodecylbenzene sulfonate (SDBS), were purchased in their highest available purity. The pH of the solutions was kept close to 7.

Analytical Procedures. Spectrophotometric procedures were used to determine the concentration of the surfactants in solution. SDBS was directly determined by UV absorption at a wavelength of 223 nm against a blank of deionized water; the presence of SLS does not interfere in this determination. Once the concentration of SDBS was known, the Methylene Blue Active Substance Method, MBAS (*21*), was used to determine the concentration of SLS from a calibration of absorbance versus the concentration of each surfactant. This resulted in a linear function of their concentrations and was fitted by multiple linear regression.

Isotherm Procedure. A bottle point isotherm procedure was used to conduct all equilibrium studies. Fixed resin dosages of 1 g/L were contacted in 125 mL stoppered polyethylene bottles, with 100 mL solutions of both surfactants having concentrations in the 0.03–0.42 mmol/L range. Five molar ratios of SDBS:SLS (1:3, 2:3, 1:1, 3:2, and 3:1) were used in the experiments which were carried out at 10 and 30°C. The bottles were placed in a water thermostatic bath and shaken until equilibrium was achieved, which took from several days to several weeks.

RESULTS AND DISCUSSION

Representative adsorption isotherms obtained are presented in Figs. 1 through 4. For the sake of readability of the graphs, only some of the molar ratios are presented in each graph. A competition between the surfactants for the adsorption sites is evident. Every surfactant was increasingly adsorbed as its proportion in the mixture increased and also with decreasing temperature. For example, SDBS was more adsorbed at 10 than at 30°C and when it was in a 3:1 ratio with respect to SLS than when it was in a 1:3 ratio. It can also be seen that SDBS was always more adsorbed than SLS, the same as was observed in single-solute adsorption (*20*), and that XAD-4, the resin with the highest specific surface area (750 m^2/g) presented a higher adsorption capacity than XAD-7 (450 m^2/g). All of these are again in agreement with the individual single solute data available. SDBS adsorption on XAD-7 was not as affected by competitive

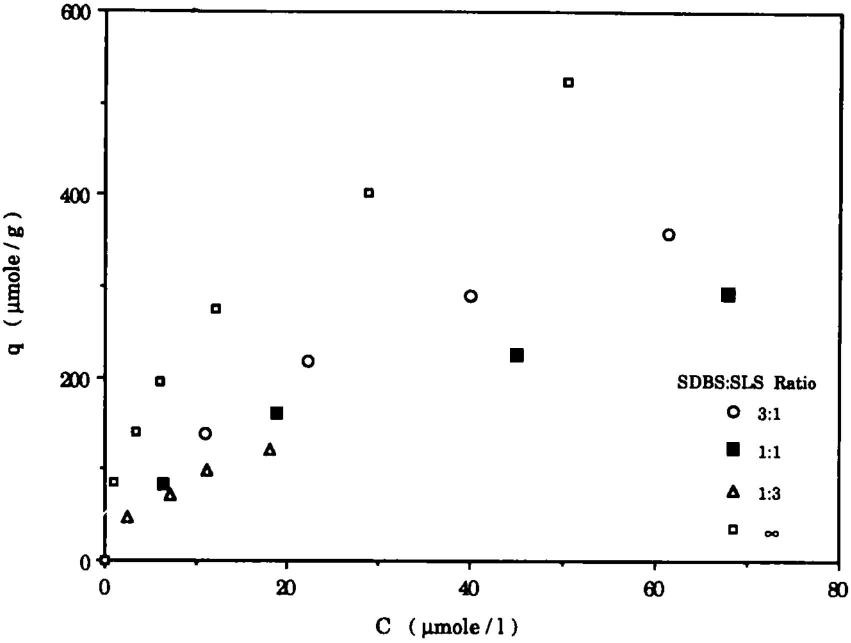

FIG. 1. Adsorption of SDBS from aqueous mixtures of (SDBS + SLS). Resin: Amberlite XAD-4. Temperature: 10°C.

adsorption of SLS as it was on XAD-4, that is, the isotherms corresponding to the different molar ratios are much closer, almost coincident, whereas on XAD-4 there is a clear difference between isotherms. This is due to the fact that adsorption on XAD-4 occurs to a greater extent than in XAD-7 and also to the fact that while both surfactants adsorb in similar quantities on XAD-4, XAD-7 sorption of SDBS is about twice as much as that of SLS.

Prediction of the Mixture Adsorption Data

Three models have been considered in order to predict the adsorption of surfactant mixtures. First the Ideal Adsorbed Solution Theory (IAST) was tried by using the Freundlich equation and then the Redlich–Peterson equation to describe the individual adsorption isotherms. Finally a nonideal competition model, the ISIAS model of Yonge and Keinath (*18*), was applied.

The IAST model, developed by Radke and Prausnitz, is based on the assumption than the adsorbed phase is ideal. The following five basic

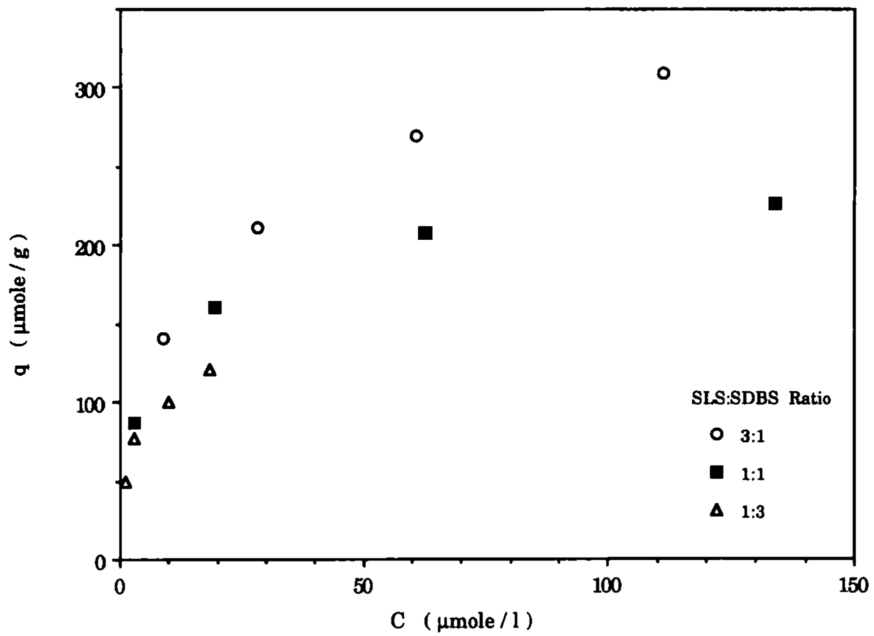

FIG. 2. Adsorption of SLS from aqueous mixtures of (SDBS + SLS). Resin: Amberlite XAD-4. Temperature: 10°C.

equations are used to predict multicomponent adsorption from single-solute isotherms:

$$q_T = \sum_{i=1}^{N} q_i \tag{1}$$

$$z_i = q_i/q_T, \qquad i = 1 \text{ to } N \tag{2}$$

$$C_i = z_i C_i^0, \qquad i = 1 \text{ to } N \tag{3}$$

$$1/q_T = \sum_{i=1}^{N} z_i/q_i^0 \tag{4}$$

$$\frac{\pi_m A}{RT} = \int_0^{q_i^0} \frac{d \ln C_i^0}{d \ln q_i^0} dq_i^0 = \frac{\pi_i^0 A}{RT}, \qquad i = 1 \text{ to } N \tag{5}$$

Equation (1) defines q_T, the total surface loading. Equation (2) defines z_i, the mole fraction on the surface of the adsorbent for component i.

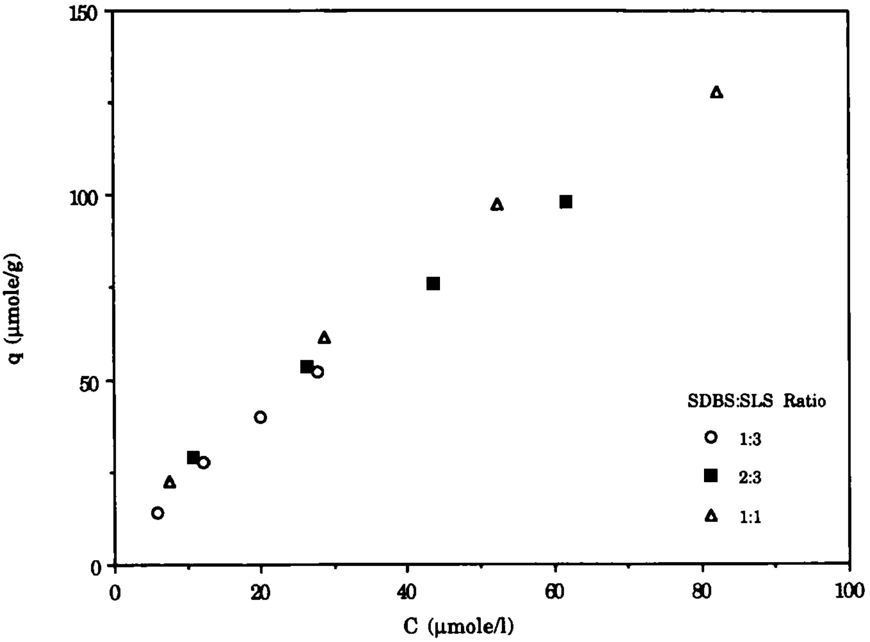

FIG. 3. Adsorption of SDBS from aqueous mixtures of (SDBS + SLS). Resin: Amberlite XAD-7. Temperature: 10°C.

Equation (3) is analogous to Raoult's law, where C_i^0 is the single-solute liquid-phase concentration in equilibrium with q_i^0. The single-solute surface loadings, q_i^0, are the loadings that cause the same spreading pressure or reduction in surface tension as the mixture. Equation (4) is the expression for no area change per mole upon mixing in the mixture from the single-solute isotherms at the spreading pressure of the mixture. Equation (5) equates the spreading pressures of the pure component systems to that of the mixture. Finally, it is necessary to know the expression of the single-solute isotherms, $q_i^0 = f(C_i^0)$. We have used the following in this work:

Freundlich $$q = KC^n \tag{6}$$

Redlich–Peterson $$q = KCM/(1 + KC^{\beta}) \tag{7}$$

Tables 1 and 2 show the parameter values corresponding to the fits for Freundlich's and Redlich–Peterson's isotherms of the single-solute adsorption data used in these calculations, together with the corresponding

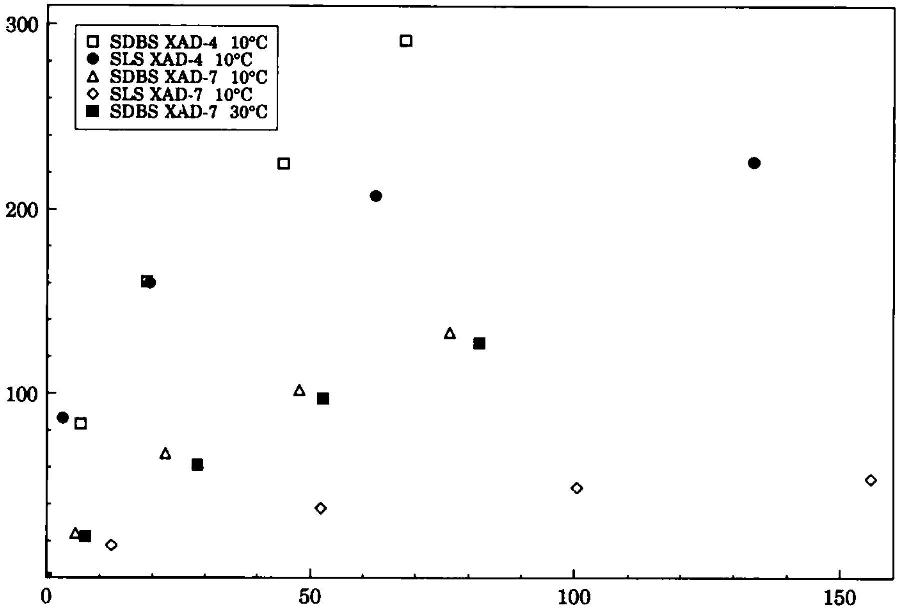

FIG. 4. Comparison of SDBS and SLS adsorption in 1:1 mixtures.

TABLE 1
Values of the Parameters for Freundlich's Isotherm Fits of Single-Solute Data (for q in mmol/g and C in mmol/L)

	T (°C)	K	n	R^2	Error[a] (%)
XAD-4					
SLS	10	1.0083	0.4839	0.998	4.5
SLS	30	0.9303	0.5303	0.998	3.8
SDBS	10	1.4962	0.3798	0.993	8.1
SDBS	30	1.3334	0.3779	0.993	8.1
XAD-7					
SLS	10	0.2491	0.5864	0.999	2.9
SLS	30	0.2270	0.6574	0.999	1.7
SDBS	10	0.6657	0.4770	0.998	3.8
SDBS	30	0.6313	0.5641	0.998	4.2

[a] Calculated as $\frac{1}{n}\sum_{i}^{n}\frac{|q_{i_{\mathrm{exp}}} - q_{i_{\mathrm{fit}}}|}{q_{i_{\mathrm{exp}}}} \times 100$.

TABLE 2
Values of the Parameters for Redlich–Peterson's Isotherm Fits of Single-Solute Data (for q in mmol/g and C in mmol/L)

	T (°C)	M	K	β	R^2	Error[a] (%)
XAD-4						
SLS	10	0.9988	446.3800	0.5235	0.998	5.3
SLS	30	0.8681	35.3533	0.5438	0.999	2.7
SDBS	10	1.3458	75.1317	0.7066	0.999	4.2
SDBS	30	1.2134	67.3944	0.7097	0.999	2.7
XAD-7						
SLS	10	0.2491	335.3522	0.4171	0.999	3.0
SLS	30	0.2303	38.6596	0.3623	0.999	2.0
SDBS	10	0.6325	80.2307	0.5658	0.998	5.3
SDBS	30	0.6295	235.4799	0.4425	0.998	4.5

[a] Calculated as in Table 1.

regression coefficients and mean relative errors of the fitted isotherms with respect to the experimental values.

All these equations were algebraically reduced to a set of nonlinear equations which were solved numerically by the Newton–Raphson method alone in the case of Freundlich's isotherm, which allows an analytical integration of Eq. (6), and by the Newton–Raphson method coupled with Romberg's method for the numerical evaluation of the integrals in that expression when using the Redlich–Peterson isotherm.

To account for nonideal competition, the ISIAS model of Yonge and Keinath (*18*) was used. This employs single-solute adsorption isotherm parameters (Freundlich's fit) and competition factors whose values are determined from the multicomponent equilibrium data. The equations of the model are of the form

$$q_i = K'^{(n'-1)/n'} \left[\frac{k_i C_i^{n_i}}{\eta_i} \right]^{1/n'} \left[\sum_{i=1}^{N} \left(\frac{k_i C_i^{n_i}}{\eta_i K'} \right)^{1/n'} \right]^{(n'-1)} \tag{8}$$

where: q_i = solid-phase equilibrium concentration of solute
n_i, k_i = empirical Freundlich constants for single-solute adsorption
C_i = liquid-phase equilibrium concentration of solute i
n' = average value of n_i
K' = average value of k_i calculated as $\Sigma\ (k_i/\eta_i)/N$
η_i = competition factor for species i

By adding the equations corresponding to each of the surfactants, an expression for the total amount of surfactants adsorbed is reached:

$$q_T = \left[\sum_{i=1}^{N}\left(\frac{k_iC_i^{n_i}}{\eta_i}\right)^{1/n'}\right]^{n'} \tag{9}$$

The equation was solved by nonlinear regression, and the calculated values of η_i are shown in Table 3. Values of the competition factors are always greater than 1 for SDBS and are determined with a smaller standard error than for SLS. This is likely due to the indirect procedure used to determine the concentrations.

The three models used predict an SLS adsorption which is less than the experimental value and an SDBS adsorption higher than the experimental value in all cases. As can be seen in Table 4, both effects compensate to a certain extent when the total surfactant adsorption is predicted; the relative error was always less than 20% with a mean value of about 5%. The IAST model integrated with Redlich–Peterson's isotherm equation yielded the best approximation for Amberlite XAD-4 and was only slightly worse than ISIAS for Amberlite XAD-7. A summary of the results can be found in Table 4. Figures 5 and 6 show a comparison between experimental and predicted values for each surfactant and for the total amount adsorbed with resin Amberlite XAD-4, respectively.

IAST-Freundlich yielded the worse predictions because, as already discussed in the literature (*22–24*), even when Freundlich's equation fits the experimental single-solute adsorption data well over a concentration range, predictions using it in IAST over the same interval carry an error which may be considerable due to the fact that Freundlich's isotherm equation does not reduce to Henry's law (a linear isotherm) at low coverages, instead $\lim_{C\to 0}(q/C) = \infty$. This induces an overestimation of the spreading pressure in Eq. (5), and from it an error in the concentration calculated to exert that pressure.

TABLE 3
Values of the Competition Factors for the Adsorption of SLS + SDBS

Amberlite	T (°C)	η_{SLS}	Standard error	η_{SDBS}	Standard error	R^2
XAD-4	10	0.9417	0.0623	1.1765	0.0395	0.960
XAD-4	30	1.3218	0.1453	1.1193	0.0281	0.979
XAD-7	10	0.9374	0.0468	1.2320	0.0217	0.990
XAD-7	30	0.8832	0.0645	1.0882	0.0285	0.984

TABLE 4
Mean Relative Deviations (%) between Experimental and Predicted Adsorption Values Using IAST and ISIAS Methods[a]

	10°C			30°C		
	SLS	SDBS	Total	SLS	SDBS	Total
XAD-4						
IAST-Fr.	17.1 (26)	7.2 (−13)	4.5 (15)	20.4 (28)	11.6 (−18)	3.7 (9)
IAST-Red.	9.1 (13)	5.4 (−10)	2.6 (2)	10.7 (14)	9.7 (−16)	1.9 (−2)
ISIAS	10.7 (13)	3.6 (−6)	6.2 (7)	27.2 (39)	8.7 (−12)	8.3 (26)
XAD-7						
IAST-Fr.	36.2 (13)	15.4 (−13)	4.6 (1)	33.1 (12)	12.2 (−8)	5.3 (3)
IAST-Red.	24.7 (9)	13.1 (−11)	3.8 (−3)	35.0 (11)	12.0 (−8)	5.1 (3)
ISIAS	25.6 (13)	6.1 (−13)	4.6 (1)	22.2 (6)	6.5 (−4)	4.2 (2)

[a] Mean relative deviations in % calculated as $\frac{1}{n}\sum_{i}^{n}\frac{|q_{i_{\text{exp}}} - q_{i_{\text{cal}}}|}{q_{i_{\text{exp}}}} \times 100$, where q_{cal} corresponds to the values calculated for the experimental initial concentrations. Values in parentheses are mean deviations in μmol/g, calculated as $\frac{1}{n}\sum_{i}^{n} q_{i_{\text{exp}}} - q_{i_{\text{cal}}}$.

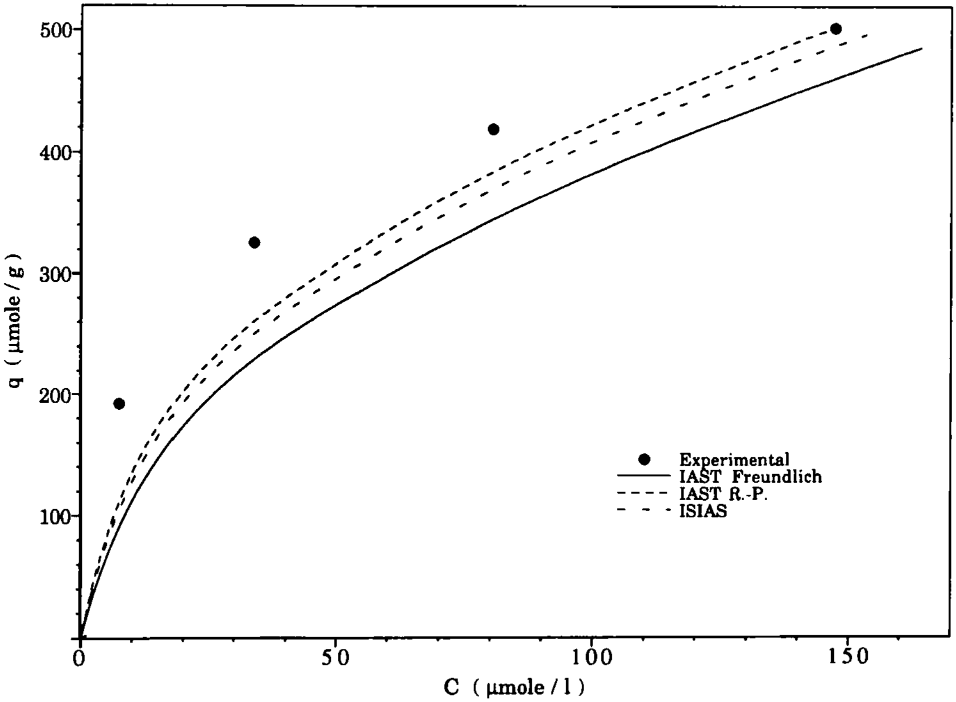

FIG. 5. Comparison of experimental and predicted SLS and SDBS adsorption from 1:1 mixtures. Resin: XAD-4. Temperature: 10°C.

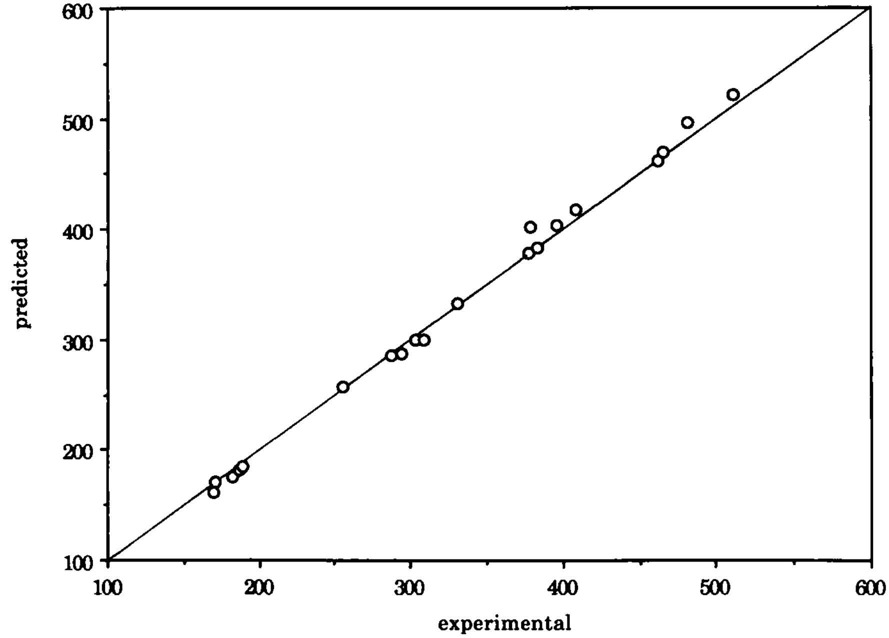

FIG. 6. Comparison of experimental and predicted total surfactant adsorption using the IAST R.-P. model. Resin: XAD-4. Temperature: 30°C.

CONCLUSIONS

IAST and ISIAS models for multicomponent adsorption provide qualitative (and in some cases quantitative) estimations for the adsorption of these surfactants. The use of an isotherm equation which is linear at low concentrations (IAST-R.P.) or the introduction of competition factors determined from the bisolute equilibrium data significantly improves the accuracy of the predictions, which are better when referring to total surfactant adsorption.

Acknowledgments

The authors express their acknowledgement to the Spanish DGCYT for a grant to one of us (R.A.G.-D.) and to Rohm & Haas Spain who provided the resins used in this work. Professor David J. Wilson of Vanderbilt University kindly reviewed this manuscript and that of the preceding paper on single-solute adsorption. We want to express our gratitude to him.

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Received by editor May 20, 1991
Revised November 26, 1991