The Adsorption of Anionic Surfactants by Iron(III) and Aluminium Hydroxides[†]

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ABSTRACT: The adsorption of sodium dodecyl sulphate and sulphanol NP-3 by iron(III) and aluminium hydroxides was studied. The applicability of the Langmuir, Freundlich and Hill–de Boer adsorption equations for the description of the adsorption isotherms obtained experimentally was verified. Values of various parameters characterising the adsorption of the anionic surfactants investigated by iron(III) and aluminium hydroxides have been calculated. These allowed assumptions to be made about the adsorption mechanism. The possibility of using air as an adsorbent for anionic surfactants was studied.

INTRODUCTION

Studies of the adsorption of surfactants at liquid–solid and liquid–gas interfaces are important both for the further development of the theory of adsorption and for solving many practical problems (Parfitt and Rochester 1986). Information about such adsorption processes may be obtained from the relevant adsorption isotherms. For describing the various forms of surfactant adsorption isotherms, use is made of the Giles classification (Giles *et al.* 1974). According to this classification, the isotherms for the adsorption of dissolved substances from dilute aqueous solution by solid adsorbents may be divided into four classes according to their shapes. Three of these, viz. S = concave, L = Langmuir and H = convex, are curvilinear and differ in their adsorption activation energy values, whereas the fourth (class C) is rectilinear. Each class contains various types of isotherms whose shapes depend on the range of concentrations investigated.

The linear form of surfactant adsorption isotherms most often conforms to the Freundlich and Langmuir equations (Tarasyevich 1981; Pushkaryov and Trofimov 1975). In a number of cases, the isotherms have a complex form (Shinoda *et al.* 1968) and may be described by the Brunauer–Emmett–Teller (BET) equation or by equations corresponding to isotherms with inflections or maxima.

Among the large number of theories of adsorption that have been advanced, the most commonly used are those associated with monomolecular adsorption and the BET theory. Monomolecular adsorption may be described by equations advanced by Langmuir, Freundlich, Hill–de Boer, Frumkin, Parsons and others (Fyodorova and Abramzon 1993). The equation suggested by Shestakov (1983) and used by Koganovsky and Klimenko (1974) for describing the adsorption of anionic and non-ionic surfactants on carbon sorbents provides an example of a modified equation deduced on the basis of de Boer theory. Skrylev and Sviridov (1974) and Streltsova (1997) have studied the adsorption of surfactants at the liquid–gas interface, i.e. the adsorption of surfactants by gaseous adsorbents (air bubbles).

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Despite the large number of studies undertaken, quantitative knowledge regarding the adsorption of surfactants by solid and gaseous adsorbents is contradictory. Knowledge of the thermodynamic characteristics of the adsorption process is sparse with no studies having been undertaken using the Gibbs free energy as a criterion of the adsorption interaction.

The present work is devoted to a study of the adsorption of some anionic surfactants at liquid–solid and liquid–gas interfaces.

EXPERIMENTAL

Materials and methods

Aqueous solutions of anionic surfactants, i.e. sodium dodecyl sulphate (SDS) and sulphanol NP-3 (sodium dodecyl benzol sulphonate), containing 99.9% of the basic component were studied. The surfactants were purified initially by recrystallisation from a mixture of ethanol and diethyl ether (Bartnitsky *et al.* 1990). The solutions were prepared using doubly distilled water. All measurements were undertaken at a temperature of 293 K.

Iron(III) and aluminium hydroxides were used as adsorbents, iron(III) hydroxide being prepared via the hydrolysis of iron(III) chloride employing the method of Krecke (Baranova *et al.* 1983). For this purpose, a 2% solution of iron(III) chloride was added as small portions to distilled water maintained at the boiling point. The resulting solution was bright red in colour, although the colour changed on cooling the solution as a result of hydrolysis reactions which proceeded via the following equations:

$$\mathrm{FeCl_3 + 3H_2O \longleftrightarrow Fe(OH)_3 + 3HCl} \tag{1}$$

$$\mathrm{FeCl_3 + 2H_2O \longleftrightarrow Fe(OH)_2Cl + 2HCl} \tag{2}$$

$$\mathrm{Fe(OH)_2Cl + 2HCl \longleftrightarrow FeOCl + 2HCl + H_2O} \tag{3}$$

$$\mathrm{FeOCl \longleftrightarrow FeO^+ + Cl^-} \tag{4}$$

The overall composition and structure of the resulting micelles can be expressed by the following formulae (Yakovlev 1967): $[[\mathrm{Fe(OH)_3}]_m \cdot n\mathrm{Fe^{3+}} \cdot 3(n - x)\mathrm{Cl^-}]^{3+} \cdot 3x\mathrm{Cl^-}$ and $[[\mathrm{Fe(OH)_3}]m \cdot n\mathrm{FeO} \cdot (n - x)\mathrm{Cl^-}]^{+} \cdot x\mathrm{Cl^-}$.

Aluminium hydroxide was obtained by peptisation brought about by the addition of an aqueous solution of ammonia to a 1% aqueous solution of aluminium chloride (Baranova *et al*. 1983). The resulting sediment was washed a number of times by decantation with doubly distilled water and filtered. A few drops of a 0.1 M HCl solution were then added and the peptisation allowed to proceed for 2–3 h.

Experiments to determine the extent of surfactant adsorption were undertaken as follows. The relevant adsorbent at a concentration of 50 mg/l was placed in a 100-ml volume glass bulb containing 50 ml of the freshly prepared anionic surfactant solution. The bulb was well stoppered with a ground glass stopper and shaken for 0.5 h to attain equilibrium using an ABC–6c shaker (Experimental Medical Apparatus Industries, Kiev, Ukraine). The contents of the bulb were then centrifuged at 50 rpm using a CLS–3 laboratory centrifuge (‘Krasnogvardeyets’ Industries, St. Petersburg, Russia). The solution separated from the adsorbent was analysed for its anionic surfactant content (Abramzon *et al.* 1988) and the difference between the solution content before and after

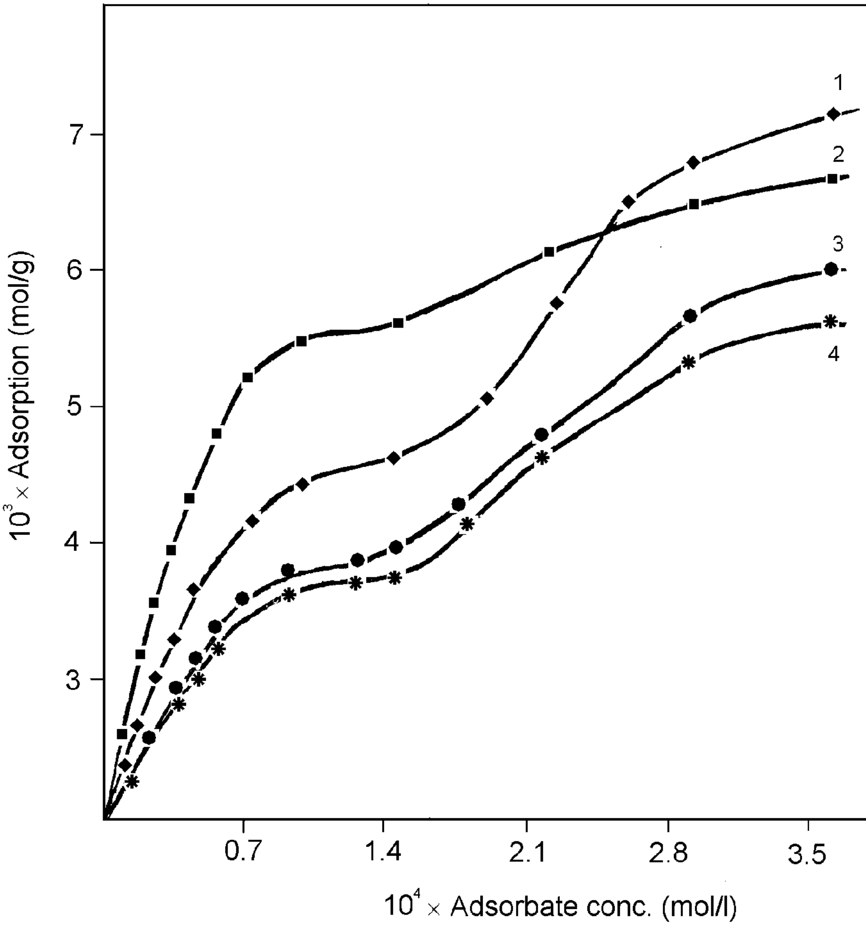

Figure 1. The adsorption isotherms for SDS (curves 1 and 2) and sulphanol NP-3 (curves 3 and 4) on to iron(III) (curves 2 and 3) and aluminium (curves 1 and 4) hydroxides at pH 7.5.

adsorption calculated. The data thus obtained were used for the construction of the relevant adsorption isotherms (see Figure 1).

The surface tension values of the solutions were determined using the Vylgelmy method to an accuracy of ± 0.5 mJ/m^2 at 293 ± 1 K.

RESULTS AND DISCUSSION

The results obtained showed that the adsorption isotherms of SDS and sulphanol NP-3 on iron(III) hydroxide (Figure 1, curves 1 and 3) and aluminium hydroxide (Figure 1, curves 2 and 4) exhibited a complex S-form, caused on the one hand by the heterogeneity of the adsorbate (as a result of the presence of the dissolved anionic surfactant in a colloidal form) and on the other hand by the polymolecular character of the adsorption process.

In order to obtain the basic characteristics of the adsorption interaction between SDS, sulphanol NP-3 and the adsorbents, viz. iron(III) and aluminium hydroxides, an attempt was made to apply some adsorption theories developed for solid–gas interfaces to the isotherm data obtained experimentally. In this way, the suitability of the Langmuir and de Boer adsorption theories as well as the Freundlich equation was verified. The fit between the adsorption equation and the experimental data was estimated by the method of linearisation, i.e. the equation was reduced to that of a straight line and the dependence was plotted in appropriate coordinates. The theory (and consequently the corresponding equations) was adjudged suitable if the isotherm or the part of the isotherm could be presented as a straight line in the appropriate coordinates.

The Langmuir equation may be expressed as:

$$\frac{C_p}{A} = \frac{1}{\beta A_\infty} + \frac{C_p}{A_\infty} \tag{5}$$

where A is the adsorption corresponding to the equilibrium concentration C_p, A_∞ is the maximum (limiting) adsorption and β is a constant linked to the adsorption equilibrium constant via the expression:

$$K = \gamma{\cdot}\beta\frac{S_p}{S_a} \tag{6}$$

where γ is the number of moles of solvent in 1 kg of its mass, and S_a and S_p are the areas occupied on the adsorbent surface by the adsorbate molecules and solvent molecules, respectively.

The corresponding expression for the Freundlich equation may be written as:

$$\ln A = \ln k + 1/n \ln C_p \tag{7}$$

where k and n are constants. This equation was suitable for the description of the initial parts of the isotherm corresponding to monomolecular adsorption (over the concentration range $0.2–1.4 \times 10^{-4}$ mol/l).

The Hill–de Boer equation (Hill 1946; de Boer 1953) may be expressed as:

$$\frac{\theta}{1-\theta} + \ln\left(\frac{\theta}{1-\theta}\right) - \ln C_p = \ln K_1 - K_2\theta \tag{8}$$

where $\theta = A/A_\infty$ is the degree of filling of the adsorbent surface by the adsorbate, and K_1 and K_2 are constants describing the interaction between the adsorbed ions and molecules with the adsorbent surface on the one hand and between themselves, respectively. This equation describes that part of the experimental isotherms corresponding to limited filling of the adsorbent surface by the adsorbate ($\theta = 0.4–0.6$).

The various parameters calculated by application of equations (6)–(8) to the experimental data arising from the adsorption of the anionic surfactants on to iron(III) and aluminium hydroxide are listed in Table 1. The values of the Gibbs free energy for the adsorption process calculated according to the equation:

TABLE 1. Parameters for the Adsorption of Surfactants at the Liquid–Solid Interface

Surfactant	Adsorbent	10^3A (mol/g)[a]	k	n	$-\Delta G^0_{ads}$ (kJ/mol)	10^3K (l/mol)	K_1 (l/mol)	K_2 (l/mol)
SDS	$Fe(OH)_3$	5.6	11.22	4.5	35.5	1665	99	2.0
	$Al(OH)_3$	4.5	10.03	5.3	35.0	1332	55	3.0
Sulphanol NP-3	$Fe(OH)_3$	3.7	7.94	2.9	33.8	827	55	5.0
	$Al(OH)_3$	3.7	7.59	2.8	33.7	812	54	4.7

[a] A = adsorption.

$$\Delta G^0_{ads} = -RT \ln K \tag{9}$$

are also listed in the table. Analysis of the calculated data showed that the adsorption of SDS and sulphanol NP-3 by iron(III) and aluminium hydroxide was mainly of a chemical nature (the values of ΔG^0_{ads} being high and close to those expected for chemisorption). The systems investigated correspond to those exhibiting an increased adsorption selectivity (K values of 812–1665 × 10^3 l/mol). The values of n [equation (7)], which describe the degree of association of the surfactant molecules in the adsorption layer, were greater than unity, indicating that ions, molecules and surfactant micelles all participated in the adsorption process at the same time (Giles *et al.* 1974).

From a comparison of the experimental and calculated data with those in the literature (Pushkaryov and Trofimov 1975; Koganovsky and Klimenko 1974), it seemed reasonable to suggest that the adsorption of the surfactants investigated on the dispersed iron(III) and aluminium hydroxide surfaces proceeded, on the one hand, via interaction of the ionic groups of the anionic surfactants with the positively charged adsorbent surfaces and, on the other hand, via coagulation interaction.

As the content of iron(III) and aluminium hydroxide in the system was increased, a corresponding increase occurred in the extent of surfactant adsorption from solution (Figure 2). Thus, the presence of 50 mg/l adsorbent in the solution led to the maximum degree of adsorption for both SDS and sulphanol NP-3 (surfactant concentration = 100 mg/l).

To evaluate the efficiency of using a gaseous adsorbent (flotation), the adsorption of both SDS and sulphanol NP-3 was also investigated at the liquid–gas interface. By using the experimentally obtained surface tension isotherms (Figure 3), the extent of adsorption was calculated using the Gibbs equation:

$$\Gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc} \tag{10}$$

where σ is the surface tension of the surfactant solution. The area occupied by a single molecule in the saturated adsorption layer was calculated from the formula:

$$S_0 = \frac{1}{\Gamma_\infty \cdot N_A} \tag{11}$$

where N_A is Avogadro's number and Γ_∞ is the limiting adsorption.

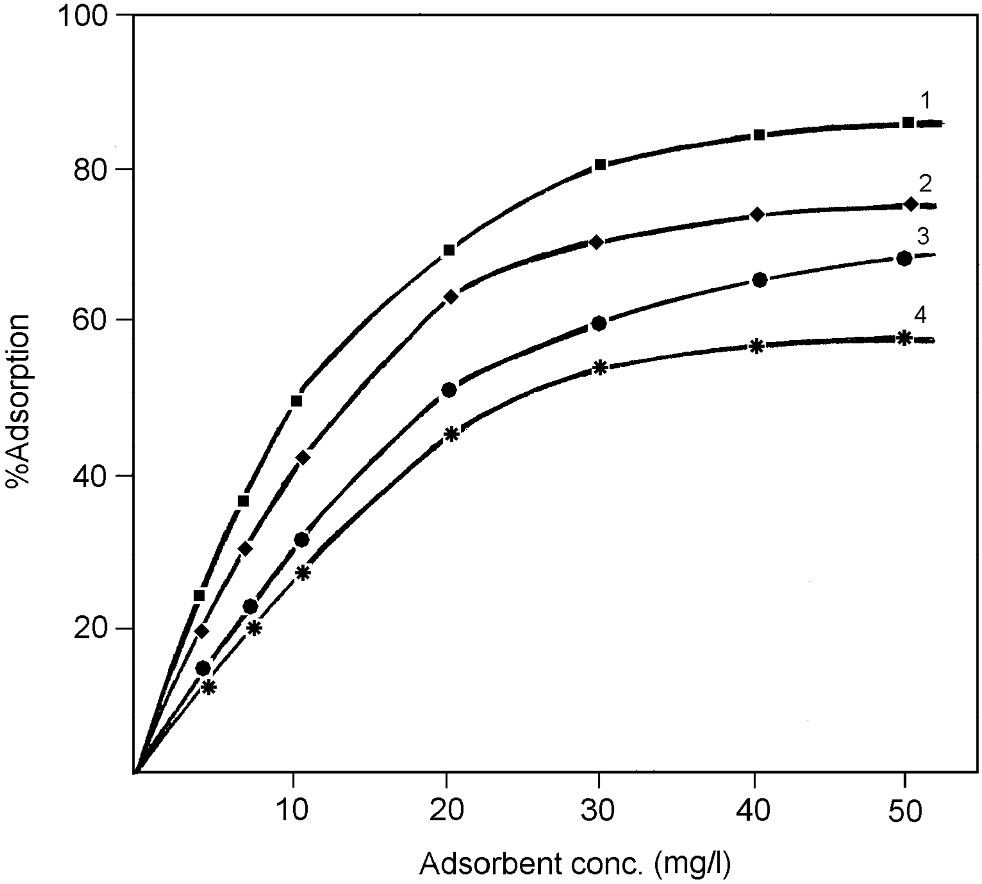

Figure 2. The dependence of the adsorption of SDS (curves 1 and 2) and sulphanol NP-3 (curves 3 and 4) on the content of iron(III) (curves 1 and 3) and aluminium (curves 2 and 4) hydroxide in the system.

The superficial activity was calculated via the expression:

$$g = -\left(\frac{d\sigma}{dc}\right)_{c\to 0} \tag{12}$$

and the Gibbs free energy of adsorption with the Langmuir equation:

$$\Delta G_{ads} = -RT \ln\left(\frac{\Gamma}{\delta \cdot c}\right) \tag{13}$$

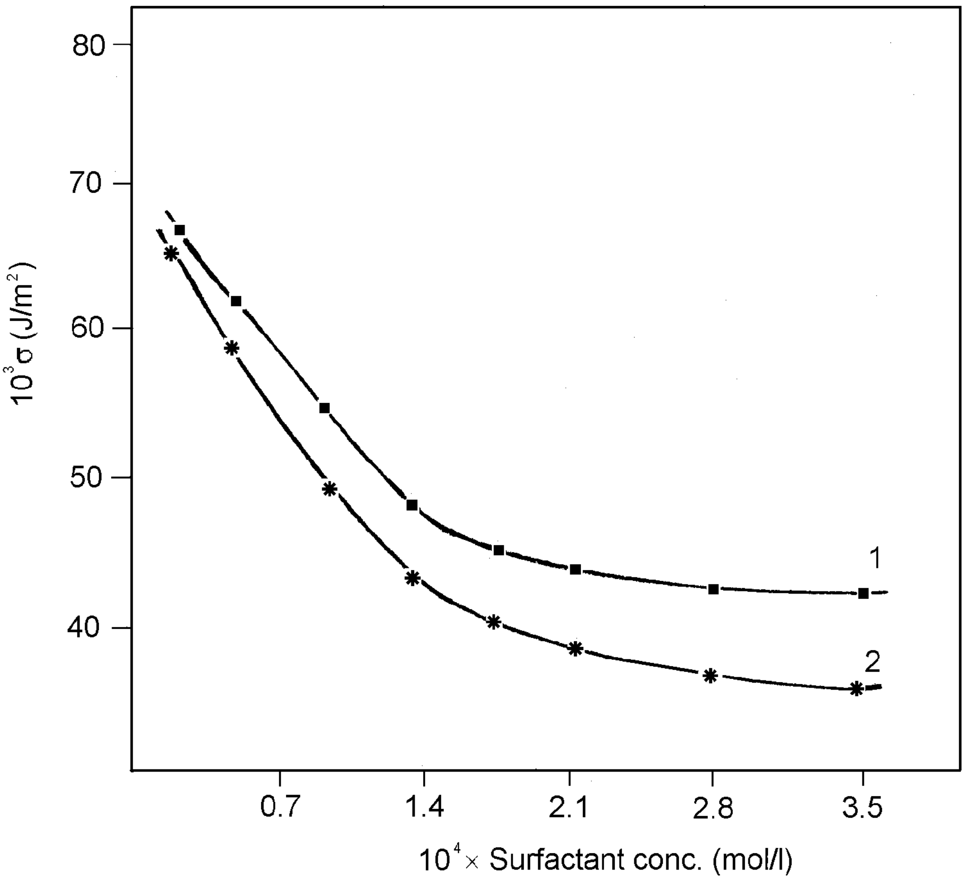

Figure 3. The surface tension isotherms for aqueous solutions of sulphanol NP-3 (curve 1) and SDS (curve 2).

where δ is the thickness of the superficial layer of surfactant, which as a first approximation was equal to 9×10^{-10} m (Abramzon 1981). The values of ΔG_{ads} thus obtained were extrapolated to zero surfactant concentration, i.e. to the situation in an ideal solution.

The values of the various parameters describing the adsorption of SDS and sulphanol NP-3 at liquid–gas interfaces accord with the literature data (Plakatina *et al.* 1993) and demonstrate the high surface activity of the anionic surfactants investigated, with the formation of an extremely saturated monolayer in which the surfactant molecules are oriented vertically (Phrolov 1982). The formation of an adsorption layer of SDS or sulphanol NP-3 at the solution–gas interface was accompanied by a smaller change in the Gibbs free energy than when the same adsorption occurred at the liquid–solid interface (see data listed in Table 2). Thus, for the solution–gas interface, $-\Delta G^0_{ads}$ = 27.0–27.6 kJ/mol whereas for the liquid–solid interface the corresponding value was $-\Delta G^0_{ads}$ =

TABLE 2. Parameters for the Adsorption of Surfactants at the Liquid–Gas Interface

Surfactant	$10^6\Gamma$ (mol/m^2)	S_0 (Å^2)	g [(J m)/mol]	$-\Delta G^0_{ads}$ (kJ/mol)
SDS	7.30	22.7	0.3	27.6
Sulphanol NP-3	7.06	23.5	0.2	27.0

33.7–35.5 kJ/mol. Hence, a gas (air) is a less effective adsorbent for the anionic surfactants investigated compared with iron(III) and aluminium hydroxide.

However, despite the fact that the adsorption of anionic surfactants at the liquid–air interface is less advantageous thermodynamically than at the liquid–solid interface, the availability of air and the opportunity to carry out adsorption processes using simple flotation devices makes the use of air as an adsorbent worth considering (Streltsova 1997).

CONCLUSIONS

The following conclusions arise from the work undertaken:

1. The Langmuir and Freundlich equations have been shown to be suitable for the description of the initial parts of the experimental isotherms for the adsorption of SDS and sulphanol NP-3 on to iron(III) and aluminium hydroxide surfaces. This demonstrated that such equations were capable of describing monolayer formation by the surfactants studied, whereas the Hill–de Boer equation could only be applied to part of the region where an increase in the isotherm occurred.
2. Despite the fact that the adsorption of the anionic surfactants studied at the solution–air interface was thermodynamically less advantageous than at the liquid–solid [iron(III) and aluminium hydroxide] interface, the use of air as an adsorbent (flotation) is worthy of consideration.

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