Adsorption of Ammonium Perfluorooctanoate at the Air–Water Interface

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The adsorption of ammonium perfluorooctanoate has been investigated at the air-water interface as a function of surfactant concentration at various concentrations of ammonium chloride. The area occupied by the surfactant ion was then calculated from the Gibbs equation with allowance for the presence of salt ions. Independently, the area per surfactant ion at the interface was determined by the technique of neutron reflectiviy. Within experimental error the two sets of measurements were in good agreement.

INTRODUCTION

One of the most useful and widely used equations in interfacial science is that developed by Gibbs in his treatise on heterogeneous systems.[1] In the case of simple nonelectrolytes, once a thermodynamic decision has been made with regard to the location of the dividing plane and the surface excess of the medium, it has been used extensively to measure adsorption isotherms, particularly at the air-water interface.[2] In the case of electrolytes which dissociate at the interface the situation becomes more complex particularly in the case of ionic surface active materials, which may be the only salt present, or which may have salt added either with an ion in common with the surfactant, or with a different salt to that of the surfactant ion.

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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When Egon Matijević came to Cambridge in 1957 he produced in collaboration with Brian Pethica several papers on the behaviour of sodium dodecylsulphate at the air-water interface, which considered the problem of ionised surfactants at the air-water interface using the Gibbs equation.[3] This work enabled calculations to be made from appropriate experimental data of interfacial tension aqainst the logarithm of the surfactant concentration to obtain the area occupied by a surfactant ion at the interface.

However, at that time it was not possible to obtain a definite independent check on the results obtained from the Gibbs equation using a totally different technique although attempts were made using radio-labelled surfactant ions.[4,5]

Over the last decade or so, however, the technique of neutron reflectivity has developed rapidly and now forms an excellent method for examining the behaviour of molecules at interfaces,[6,7] since it provides information about the thickness of the film as well as the area occupied by the molecules in it.

In a recent paper[8] we reported extensive data on the adsorption of ammonium perfluorooctanoate, APFO, at the air-water interface in the presence of ammonium chloride, a salt with a common ion, NH_4^+. The use of the Gibbs equation to calculate the limiting area occupied by a perfluorooctanoate ion as a function of salt concentration was also discussed. In addition, some very preliminary neutron reflectivity results under the same conditions were reported and a comparison made of the areas per surfactant ion obtained by the two techniques.[8,9] This work has now been considerably extended.

In previous work[10] we have reported a small angle neutron scattering examination of APFO in water and admixed with ammonium alkanoates. Our interest in the APFO molecule stems from the fact that it reduces the surface tension of water to very low values,[11] *ca.* 18 mN m^{-1}, and can by adsorption on solid surfaces make them both hydrophobic and oleophobic. In molecular terms the perfluorocarbon chain is also very stiff compared with the more flexible hydrocarbon chain and it is, therefore, of interest to examine the influence these differences have on molecular packing at interfaces.

EXPERIMENTAL

Materials

All the distilled water used in the surface tension experiments was obtained by double-distillation from an all-Pyrex still. The surface tension was repeatedly checked and found to be 72.0 mN m^{-1} at 25 °C. For neutron reflection work the water was also of high purity and was obtained from an Elga UHQ water purifier.

Deuterium oxide (D_2O) was obtained from Aldrich as 99.8% atom percent deuterated material.

Ammonium perfluorooctanoate (APFO) was Rimar material. This was recrystallised from diethyl ether before use and was the same material as used in earlier studies[8].

Ammonium chloride was BDH Analar material.

Surface Tension Measurements

These were carried out by the procedures described previously.[8]

Neutron Reflectivity Measurements

These measurements were made using the neutron reflectometer CRISP at ISIS, the spallation neutron division of the Rutherford Appleton Laboratory. Measurements were made over a momentum transfer, Q, range, normal to the surface, of 0.05 to 0.4 Å^{-1}. The instrument was calibrated with reference to a D_2O surface. The procedure used has been previously described in some detail.[7,9]

THEORY

The Gibbs Equation

In a general form of the Gibbs equation the change in surface tension at the air-water interface, $d\gamma$, with change of chemical potential, $d\mu$, of the solution components is related to the surface excess concentration per unit area, Γ, at constant temperature and pressure by,

$$-d\gamma = \Sigma_i\, \Gamma_i\, d\mu_i \qquad (1)$$

As discussed in previous work[3,8] with ionic surfactants there are several important cases, only two of which we shall discuss in the present work. For APFO in water, without any additional electrolyte added, and also in the absence of hydrolysis then the ionisation process can be written as,

$$APFO = A^+ + PFO^-$$

when,

$$-d\gamma = 2\, \Gamma^{\sigma}_{PFO}\, RT\, (1 - 0.577 m^{1/2}_{APFO})\, d\ln m_{APFO} \qquad (2)$$

with Γ^{σ}_{PFO} the surface excess, following the Guggenheim convention[12] and m_{APFO} = the concentration of APFO in molal units, R = the gas constant and T the absolute temperature.[13,14]

If the activity term in parentheses is neglected then,

$$-\mathrm{d}\gamma = 2\ \Gamma^{\sigma}_{\mathrm{PFO}}\ RT\ \mathrm{d}\ \ln\ C_{\mathrm{APFO}} \qquad (3)$$

Secondly, as in the present work, where in addition to experiments using solutions of APFO only, solutions were also used which contained various concentrations of ammonium chloride in addition to APFO then the solution contains a surfactant and an ion in common, *i.e.* NH_4^+. For this situation it has been shown[3] that,

$$-\mathrm{d}\gamma = \Gamma^{\sigma}_{\mathrm{PFO}}\ RT\ \left[1 + \frac{C_{\mathrm{APFO}}}{C_{\mathrm{APFO}} + C_{\mathrm{NH_4Cl}}}\right]\ \mathrm{d}\ \ln\ C_{\mathrm{APFO}} \qquad (4)$$

In the absence of added salt, equation (4) when put into activity units reverts to equation (2).

The equations (2) and (4) have the general form,

$$-\mathrm{d}\gamma = f\Gamma^{\sigma}_{\mathrm{PFO}}\ RT\ \mathrm{d}\ \ln\ C_{\mathrm{APFO}} \qquad (5)$$

when according to conditions used f can be calculated from the appropriate section of either equation (2) or equation (4).

In the present work surface pressure $\Pi = \gamma_\mathrm{o} - \gamma$, is used with γ_o = the surface tension of clean water and γ the surface tension of the surfactant solution, hence, $\mathrm{d}\Pi = -\mathrm{d}\gamma$.

Neutron Reflectivity

A planar surface film of adsorbed surfactant can be assumed to form a layer of thickness, d, and coherent scattering length density, ρ_f, between the liquid substrate and air as illustrated in Figure 1. When an incident neutron beam of intensity, I_o, is directed on to the surface at an angle θ_o then part of the beam is reflected with an intensity I_r ; the other part is transmitted through the layer and passes into the lower phase with an intensity I_t.

The reflectivity, R, of a single uniform film in optical terms is given by the expression,

$$R = I_\mathrm{r} / I_\mathrm{o} = \left[(r_{01} + r_{12}\exp(2i\beta)) / (1 + r_{01}r_{12}\exp(2i\beta))\right]^2 \qquad (6)$$

where r_{ij} is the Fresnel coefficient[15] at the ijth interface such that,

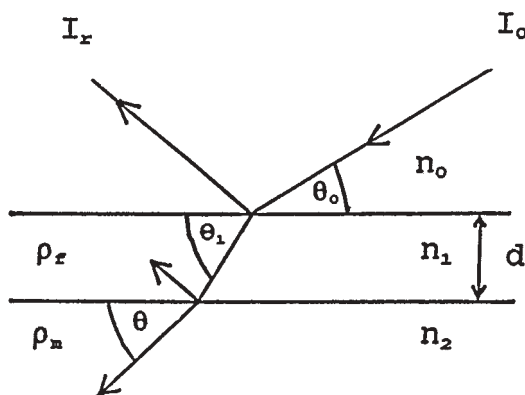$$r_{ij} = (p_i - p_j) / (p_i + p_j)$$

Figure 1. Schematic illustration of neutron reflectivity from a film covered planar interface.

with $p_i = n_i \sin\theta_i$ and $\beta = 2\pi n_1 d \sin\theta_1/\lambda$. Although developed for optical measurements[15,16] the basic theory can also be applied to the use of neutron beams.[6,7] For specular reflection of a neutron beam the refractive index is given by

$$n_i = 1 - \lambda^2 \rho_i / 2\pi$$

with ρ_i a coherent scattering length density and λ the wavelength of the beam; for neutrons $1-n_i$ is of order 10^{-6}.

The coherent neutron scattering lengths for H_2O and D_2O are -0.56×10^{-6} Å^{-2} and 6.35×10^{-6} Å^{-2} respectively. Consequently, for a mixture of 8% H_2O and 92% D_2O the scattering length density is zero and therefore this medium is non-reflecting. In this work all the experiments were carried out using this medium as the substrate. Under these conditions with a film of a fluorinated surfactant, of coherent scattering length density 4.30×10^{-6} Å^{-2}, the neutron reflectivity arises solely from the adsorbed surfactant film. As pointed out, for example, by Penfold[7] this is related directly to the surface excess, Γ^σ, and hence to the area occupied by the surfactant molecule or ion in the film. In the present work the film has been treated as a single layer whence the area per molecule is, given by,

$$A = \Sigma n_i b_i / \rho_f \times d$$

where b_i is the scattering length of the ith isotope and n_i the number of isotopic atoms in the molecule. The parameters ρ_f, the scattering length density of the film and d, the thickness of the film are obtained from the

reflectivity results using an iterative fitting procedure »FITFUN«.[17] The value of $\Sigma n_i b_i$ for PFO⁻ was taken as 1.49×10^{-3} Å using the values for ^{19}F, ^{12}C and ^{16}O given by Bacon.[18] The product $\rho_f \times d$ is a length density.

RESULTS

Surface Pressure

Figure 2 presents results for APFO in the form of Π against log ([APFO] /mol dm^{-3}) in the absence of added salts and in the presence of 0.05, 0.10 and 0.20 mol dm^{-3} ammonium chloride. The most extensive data was obtained in the absence of added salt and it was also established that, within experimental error, the same results were obtained with both null reflecting water and D$_2$O solutions of APFO. As can be seen from the figure the lowest surface pressures were obtained, above the c.m.c., with APFO alone. With increase in salt concentration in this region the surface pressure increased and also the c.m.c. moved to lower values. As the c.m.c. was approached, in
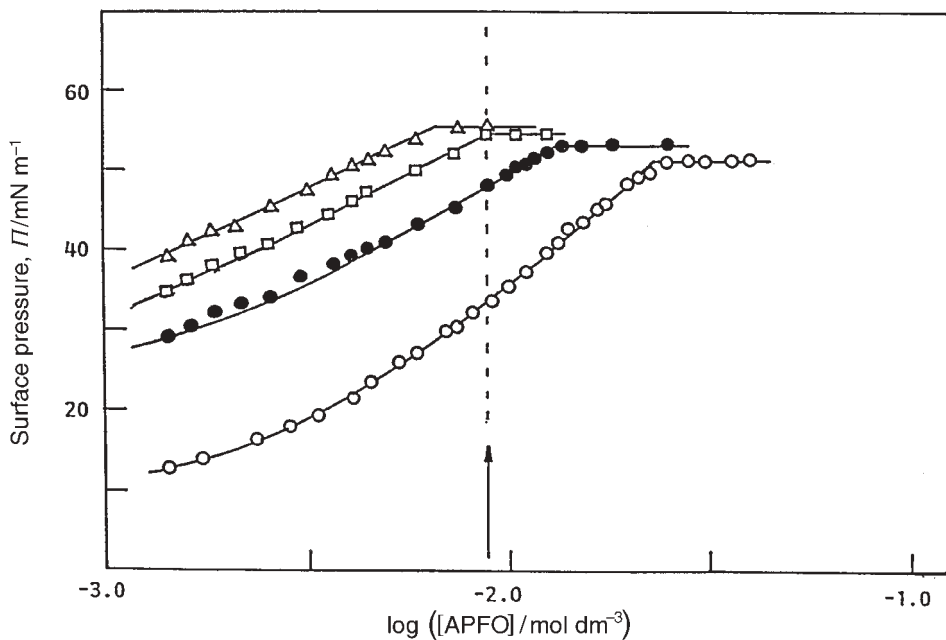

Figure 2. Surface pressure against log ([APFO]/mol dm^{-3}) for various ammonium chloride concentrations: (○) zero; (●) 0.050; (□) 0.10; (△) 0.20 mol dm^{-3}. (↑) concentration used for neutron reflectivity.
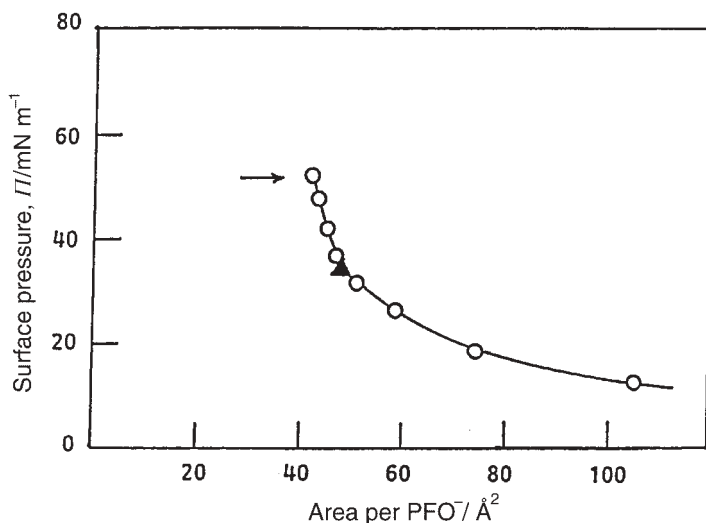
Figure 3. Surface pressure against area per PFO⁻ in absence of added salt. ($\rightarrow$) Π_{cmc}, ($\blacktriangle$) neutron reflectivity value.

all cases, the surface pressure appeared to increase linearly with the log of the APFO concentration.

For the data obtained in the absence of salt all the data up to the c.m.c. were fitted by least squares to a quadratic equation; from this fitted curve the gradient $d\Pi / d \log [\text{APFO}]$ was then obtained and hence from equation (5) the surface excess $\Gamma^\sigma_{\text{PFO}}$. This was converted into the area occupied per PFO⁻ ion, A, using $A = \Gamma^\sigma_{\text{PFO}} N_A$ with N_A = Avogadro's number. f was calculated using the bracketed terms in either equation (2) or (4).

TABLE I

Data from surface pressure measurements

[NH$_4$Cl] / mol dm^{-3}	[APFO] / mol dm^{-3}	f	A / Å^2	Π / mN m^{-1}
zero	9.00×10^{-3}	1.945	44 ± 2	33.5
zero	$2.60 \times 10^{-2*}$	1.811	41 ± 2	51.6
0.050	9.00×10^{-3}	1.153	41 ± 2	48.0
0.050	$1.05 \times 10^{-2*}$	1.174	42 ± 2	53.4
0.10	$8.91 \times 10^{-3*}$	1.091	41 ± 2	54.6
0.20	$6.60 \times 10^{-3*}$	1.032	41 ± 3	55.3

*c.m.c. value

The curve of Π against A is illustrated in Figure 3. As the value of A decreases Π rises very steeply and at Π_{cmc}, the value of A becomes 42 Å^2. The data for the other salt concentrations were over a more limited concentration range but the limiting areas were also calculated using a least squares procedure to obtain the limiting gradient. The results are listed in Table I. Since the neutron reflectivity measurements were all made at an APFO concentration of 9.0×10^{-3} mol dm^{-3} values at this concentration are also listed.

Neutron Reflection

Figure 4 shows the results of the neutron experiments presented as curves of reflectivity, R, against the wave vector transfer, Q, over the range 0.05 to 0.2 Å^{-1}. The results are all for APFO at a concentration of 9.00×10^{-3} mol dm^{-3} in null reflecting water both in the absence of added salt and in the presence of 0.050, 0.10 and 0.20 mol dm^{-3} ammonium chloride. A distinct shift is visible between the result in zero added salt and that in 0.2 mol dm^{-3} salt; the results obtained at 0.050 and 0.10 mol dm^{-3}, however, appear to be quite close together.
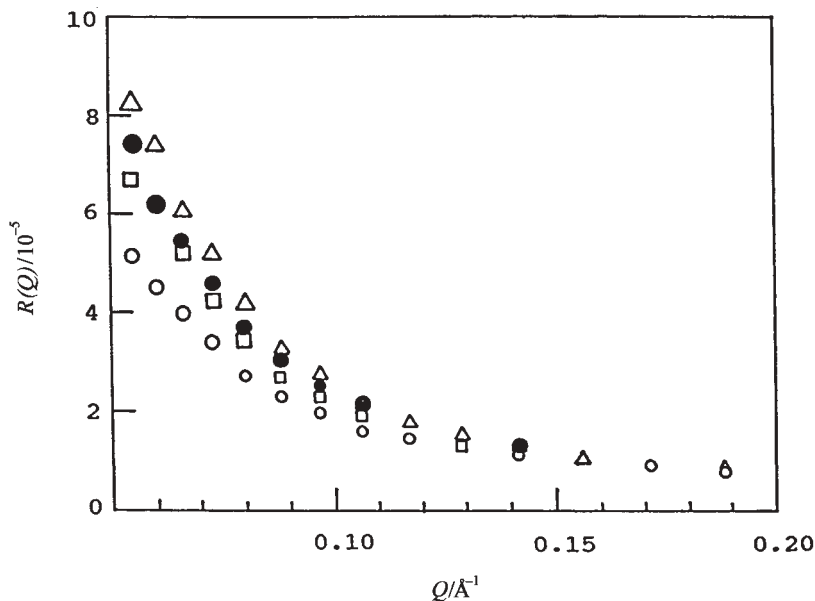

Figure 4. Reflectivity against Q for APFO at 9.0×10^{-3} mol dm^{-3} at various ammonium chloride concentrations in: (○) zero; (●) 0.050; (□) 0.10; (△) 0.20 mol dm^{-3}.
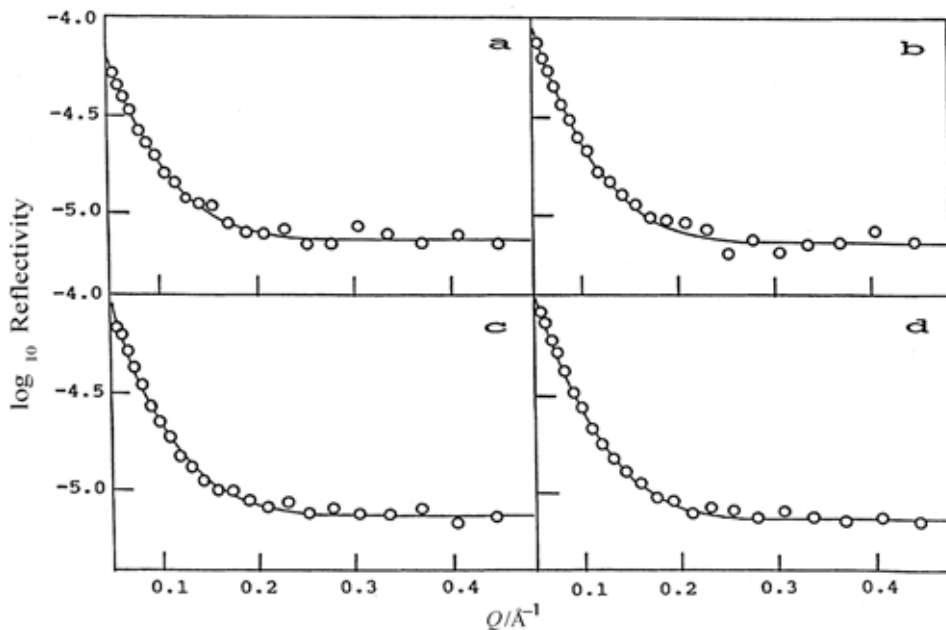
Figure 5. Logarithm of reflectivity against Q to illustrate fits to the experimental data at various ammonium chloride concentrations in mol dm^{-3}: a) zero, b) 0.050, c) 0.10, d) 0.20.

Figure 5 shows the fitted curves and the experimental points for the four sets of conditions. After estimating the background reflectivity from the solvent fits were made from the two parameters, ρ_f, the scattering length density of the film and the thickness, d, and hence the product $\rho_f \times d$. The area occupied per PFO⁻, at the interface, was calculated using equation (7). The results are given in Table II.

The results shown in Table II can be compared with those obtained from surface tension measurements and analysis using the Gibbs equation. The

TABLE II

Neutron reflection: APFO at 9.0×10^{-3} mol dm^{-3}

[NH₄Cl]/mol dm^{-3}	d / Å	ρ_f / 10^{-6} Å^{-2}	$\rho_f \times d$ / 10^{-5} Å^{-1}	A / Å^2
zero	20.19	1.585	3.20	47 ± 2
0.050	20.51	1.897	3.89	40 ± 2
0.10	20.51	1.783	3.66	41 ± 3
0.20	20.51	2.012	4.13	36 ± 2

result obtained in zero added salt, which was obtained below the c.m.c., at an APFO concentration corresponding to surface pressure of 33.5 mN m^{-1} (Figure 2) gives an occupied area of 47 ± 2 Å^2. This is in remarkably good agreement with the value of A obtained from Figure 3, *i.e.* the Π against A curve. For 0.050 and 0.1 mol dm^{-3} salt the reflectivity results are again, within experimental error, in agreement with those obtained from surface tension data. In 0.20 mol dm^{-3} ammonium chloride the result from reflectivity is somewhat lower than that obtained from surface tension. However, the neutron experiment was carried out above the c.m.c and the surface tension value from the limiting slope of the surface tension against log concentration plot at the c.m.c.

DISCUSSION

The results presented give a direct comparison, by two completely independent experimental techniques, of the areas per PFO$^-$ ion occupied at the air-water interface well below the c.m.c., just below the c.m.c., at the c.m.c and above the c.m.c. Within the experimental errors involved in both techniques there appears to be quite good agreement between them. These support the use of the Gibbs equation in the form given in equations (2), (4) and (5).

The measurement of the vertical direction, or thickness d, of the film by the reflection technique provides interesting new information. The dimension obtained of 20 ± 2 Å is considerably longer than the extended length of the perfluorooctanoate chain. An estimation of the latter gives a value of *ca.* 15 Å as the maximum possible length of a PFO$^-$ unit. Hence, the value of 20 ± 2 Å would suggest that the PFO$^-$ chains must have a staggered conformation at the interface.

An additional factor from the analysis is that ρ_f ranges from 1.59×10^{-6} Å^{-2} in the absence of salt to 2.01×10^{-6} Å^{-2} in 0.20 mol dm^{-3} salt. This value can be compared with the value for the bulk molecule of APFO of 4.30×10^{-6} Å^{-2}. Consequently, it suggests that less than half of the volume of the film is occupied by the PFO$^-$ ions or APFO molecules since there will be some association of the head groups with the ammonium counter-ions. In null reflectivity water there will be some exchange occurring so that the counter-ions will be a mixture of NH$_4^+$ and NH$_3$D$^+$. The former has an $\Sigma n_i b_i$ value of -0.556×10^{-4} Å and the latter 0.485×10^{-4} Å; the net result for a mixture would seem to be close to zero. Therefore, reflection from the counter-ions has been ignored in the present work.

Thus the remaining volume of the film would have to be either null reflecting water or air. Of the two the latter seems to be the more probable in

the knowledge of the known hydrophobicity of perfluorinated chains. In fact both the limiting areas and the scattering length density of the film would suggest that the chains are not in a tightly compressed state. The estimated cross-sectional area of a perfluorocarbon chain as calculated from molecular models[19] is 22 Å^2 and X-ray crystallographic data for a close packed hexagonal layer of perfluorocarbon chains gives[20] 25.5 Å^2.

Since perfluorooctanoic acid is quite a strong acid pK_a *ca.* 2.0[21] then electrostatic interaction between the head groups would be anticipated. However, this would be almost completely damped out in 0.20 mol dm^{-3} salt leading to the expectation of a condensed film of tightly packed molecules. One possible explanation is that although the head group region is »wet« the chains, as far as possible, prefer to be »wetted« by air. In addition the stiffness of the chains has to be taken into account as well as possible stereochemical effects of the type reported by Albrecht.[22]

Further work[23] is in progress to explore temperature effects and the effect of changing the coherent scattering length density of the substrate; this will include an analysis using the kinematic approach.[24]

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SAŽETAK

Adsorpcija amonijeva perflourooktanoata na međupovršini voda–zrak

Geraldine A. Ottewill i Ronald H. Ottewill

Adsorpcija amonijeva perflourooktanoata na međupovršini voda-zrak istraživana je u ovisnosti o koncentraciji površinski aktivne tvari pri različitim koncentracijama amonijeva klorida. Površina zaposjednuta ionima površinski aktivne tvari izračunana je pomoću Gibbsove jednadžbe prilagođene dopuštenoj prisutnosti iona soli. Površina, zaposjednuta ionima površinski aktivne tvari, na međupovršini neovisno je određena tehnikom neutronske refleksije. Dva navedena skupa mjerenja dobro se slažu unutar pogreške mjerenja.