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Electrical Aspects of Adsorbing Colloid Flotation. XV. Adsorption Isotherms of Mixed Surfactants

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Electrical Aspects of Adsorbing Colloid Flotation. XV. Adsorption Isotherms of Mixed Surfactants

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Abstract

A theory is developed for the calculation of absorption isotherms of binary mixtures of surfactants A and B on solid–water interfaces. The effects of the relative magnitudes of the interaction energies of A–A, A–B, and B–B nearest neighbor pairs are explored. The theory makes use of the random approximation in order to overcome mathematical difficulties which arise in the general case. The possibility of reducing surfactant costs in precipitate and adsorbing colloid flotation by the use of mixed surfactants is suggested.

INTRODUCTION

Adsorbing colloid and precipitate flotation methods have been investigated for use in industrial wastewater treatment and in the concentration of trace elements for analysis; a number of reviews summarize these developments (*1–8*). A model for adsorbing colloid and precipitate flotation which seems to be quite satisfactory is that developed by Fuerstenau and his co-workers (*9–15*) for use in the field of mineral flotation. We have analyzed this model by means of an approximate statistical mechanical technique given by Fowler and Guggenheim (*16*) for describing condensation phenomena in surface absorption (*17*). In this model, flotation of the solid becomes possible when a condensed layer of surfactant forms on the solid surface with ionic or polar heads to the solid and hydrocarbon tails to the aqueous phase; the resulting hydrophobic surface can attach to air bubbles. Currin et al. investigated the displacement of the adsorbed amphipathic ions by competing foreign ions by means of an extension of Fowler and Guggenheim's approach (*18*). Clarke et al. analyzed the effects of specifically adsorbed ions on floc surface potentials, and gave some experimental results of these effects on the flotation of flocs (*19*).

At higher concentrations of surfactant another type of cooperative phenomenon can take place—the formation of a second, reversed, monolayer of surfactant on top of the first. This makes the solid surface hydrophilic and suppresses flotation. We modeled this phenomenon (*20*) and investigated the adsorption isotherms of lauryl sulfate on ferric and aluminum hydroxides (*21*); excess adsorption was observed, but a second abrupt phase transition was not found.

Kiefer has refined and improved the model of surfactant adsorption by taking into account the effects of the spacing of the adsorption sites and the effect of the Coulombic repulsion between the ionic heads of the adsorbed surfactant ions (*22*). Brown examined the theory of the adsorption of anions and cations (including amphipathic ions) onto flocs having both positive and negative adsorption sites; he used an approximate thermodynamic approach (*23*).

One of the ways by which the economics of precipitate and adsorbing colloid flotation separations might be improved is by the use of two-component surfactant systems. One would hope to find relatively cheap "extenders" which could be used with a surfactant to give a hydrophobic hemimicellar coating to the floc at lower surfactant concentrations than would be required if the surfactant were used alone. The use of mixed systems has long been common in the field of mineral flotation. We here address the problem of calculating adsorption isotherms for such mixed systems. Again, our method of attack derives from Fowler and Guggenheim (*16*). We note, however, that our treatment here is based on the simpler of the approaches they describe in which it is assumed that the placement of the surfactant species on the lattice adsorption sites can be treated as random. We have made a persistent effort to carry out the analysis at their improved level of approximation in which the assumption of random distribution is not made. This approach, however, leads to three quadratic equations in three unknowns which must be solved simultaneously; we have not been able to progress beyond this point.

There follow the statistical mechanical analysis, a brief description of the numerical method used to calculate the adsorption isotherms, and the results of these computations.

ANALYSIS

We consider a solid–liquid interface having a total of N_S adsorption sites, N_A of which are occupied by surfactant species A and N_B of which are occupied by surfactant species B; evidently $N_A + N_B \leq N_S$. Let each site have z nearest neighbors. We let N_{AA}, N_{AB}, N_{BB}, N_{A0}, N_{B0}, and N_{00} be the numbers of pairs of adjacent sites occupied by A–A, A–B, B–B, A–vacant, B–vacant, and vacant–vacant pairs. And we let $2w_{AA}/z$, $2w_{AB}/z$, and $2w_{BB}/z$ be the interaction energy of an A–A, A–B, or B–B pair of adjacent surfactant species.

The partition function for the system is then given by

$$pf = \sum g(N_A, N_B, N_{AA}, N_{AB}, N_{BB}) \exp\left\{-[N_{AA}w_{AA} + N_{AB}w_{BB} + N_{BB}w_{BB}] \times \frac{2}{zkT}\right\} \tag{1}$$

Here $g(N_A, N_B, N_{AA}, N_{AB}, N_{BB})$ is the number of ways we can distribute N_A molecules of A and N_B molecules of B on the adsorption sites such that we have N_{AA} A–A pairs, N_{AB} A–B paris, and N_{BB} B–B pairs. We are neglecting all the internal degrees of freedom of both A and B. Note that

$$\sum g(N_A, N_B, N_{AA}, N_{AB}, N_{BB}) = \frac{N_S!}{(N_S - N_A - N_B)!N_A!N_B!} \tag{2}$$

We then define the quantities $\bar{\bar{N}}_{AA}$, $\bar{\bar{N}}_{AB}$, and $\bar{\bar{N}}_{BB}$ by

$$(pf) = \frac{N_S! \exp\{-[\bar{\bar{N}}_{AA}w_{AA} + \bar{\bar{N}}_{BB}w_{BB} + \bar{\bar{N}}_{AB}w_{AB}]}{(N_S - N_A - N_B)!N_A!N_B!} \frac{2}{zkT} \tag{3}$$

Differentiating Eq. (1) with respect to $u = 2/zkT$ yields

$$\frac{\partial(pf)}{\partial u} = -(pf)(\bar{N}_{AA}w_{AA} + \bar{N}_{AB}w_{AB} + \bar{N}_{BB}w_{BB}) \tag{4}$$

on making use of the definitions of the average values of N_{AA}, N_{AB}, and N_{BB}, indicated by the bars. If we calculate $\partial(pf)/\partial u$ from Eq. (3), substitute for the left-hand side of Eq. (4), and cancel (pf) on both sides, we obtain

$$\bar{N}_{AA}w_{AA} + \bar{N}_{AB}w_{AB} + \bar{N}_{BB}w_{BB} = \frac{\partial}{\partial u}[u(\bar{\bar{N}}_{AA}w_{AA} + \bar{\bar{N}}_{AB}w_{AB} + \bar{\bar{N}}_{BB}w_{BB})] \tag{5}$$

We could take the X–Y pair interaction energies into account in the following way

$$4\bar{N}_{AA}\bar{N}_{00} = \bar{N}^2_{A0} \exp(-2w_{AA}/zkT) \tag{6}$$

$$4\overline{N}_{\mathrm{BB}}\overline{N}_{00} = \overline{N}^{2}_{\mathrm{B0}} \exp(-2w_{\mathrm{BB}}/zkT) \tag{7}$$

$$2\overline{N}_{00}\overline{N}_{\mathrm{AB}} = \overline{N}_{\mathrm{A0}}\overline{N}_{\mathrm{B0}} \exp(-2w_{\mathrm{AB}}/zkT) \tag{8}$$

We also have three conservation equations which must be satisfied:

$$2\overline{N}_{\mathrm{AA}} + \overline{N}_{\mathrm{A0}} + \overline{N}_{\mathrm{AB}} = zN_{\mathrm{A}} \tag{9}$$

$$2\overline{N}_{00} + \overline{N}_{\mathrm{A0}} + \overline{N}_{\mathrm{B0}} = z(N_{\mathrm{S}} - N_{\mathrm{A}} - N_{\mathrm{B}}) \tag{10}$$

$$2\overline{N}_{\mathrm{BB}} + \overline{N}_{\mathrm{B0}} + \overline{N}_{\mathrm{AB}} = zN_{\mathrm{B}} \tag{11}$$

Equations (6)–(8) are essentially equilibrium expressions relating the numbers of the various types of nearest neighbor pairs. Equation (9) enumerates the various types of pairs which have at least one A molecule; Eq. (10) enumerates those which have at least one vacancy; Eq. (11), those pairs which have at least one B molecule.

Ideally, one would next solve these six equations for the $\overline{N}_{XY}$'s, but this does not seem to be possible for the general case. To make further progress we have had to make the random approximation, which amounts to setting the exponentials in Eqs. (6)–(8) equal to unity. When we do this the analysis leads, after a lengthy series of successive eliminations, to the following results:

$$\overline{N}_{\mathrm{AA}} = \frac{zN_{\mathrm{A}}^{2}}{2N_{\mathrm{S}}} \tag{12}$$

$$\overline{N}_{\mathrm{AB}} = \frac{zN_{\mathrm{A}}N_{\mathrm{B}}}{N_{\mathrm{S}}} \tag{13}$$

$$\overline{N}_{\mathrm{BB}} = \frac{zN_{\mathrm{B}}^{2}}{2N_{\mathrm{S}}} \tag{14}$$

These terms are all independent of temperature, which makes the integration of Eq. (5) with respect to u trivial:

$$\int_0^u (\overline{N}_{\mathrm{AA}}w_{\mathrm{AA}} + \overline{N}_{\mathrm{AB}}w_{\mathrm{AB}} + \overline{N}_{\mathrm{BB}}w_{\mathrm{BB}})\,du = [u(\overline{\overline{N}}_{\mathrm{AA}}w_{\mathrm{AA}} + \overline{\overline{N}}_{\mathrm{AB}}w_{\mathrm{AB}} + \overline{\overline{N}}_{\mathrm{BB}}w_{\mathrm{BB}})]\,\Big|_0^u \tag{15}$$

So

$$\overline{N}_{\mathrm{AA}}w_{\mathrm{AA}} + \overline{N}_{\mathrm{AB}}w_{\mathrm{AB}} + \overline{N}_{\mathrm{BB}}w_{\mathrm{BB}} = \overline{\overline{N}}_{\mathrm{AA}}w_{\mathrm{AA}} + \overline{\overline{N}}_{\mathrm{AB}}w_{\mathrm{AB}} + \overline{\overline{N}}_{\mathrm{BB}}w_{\mathrm{BB}} \tag{16}$$

We next recall that $G = -kT \log_e (pf)$, which, together with Eqs. (3), (12)–(14), and (16), yields

$$\begin{aligned}\frac{G}{kT} = {} & -N_S \log_e N_S + N_A \log N_A + N_B \log N_B \\ & + (N_S - N_A - N_B) \log (N_S - N_A - N_B) \\ & \frac{1}{kT}\left[\frac{N_A^2 w_{AA}}{N_S} + \frac{2N_A N_B w_{AB}}{N_S} + \frac{N_B^2 w_{BB}}{N_S}\right] \qquad (17)\end{aligned}$$

We calculate chemical potentials from

$$\mu_X = \partial B / \partial N_X, \qquad X = \mathrm{A, B}$$

the results are

$$\frac{\mu_A}{kT} = \log N_A - \log (N_S - N_A - N_B) + \frac{w_{AA}}{kT} \frac{N_A}{N_S} + \frac{w_{AB}}{kT} \frac{N_B}{N_S} \qquad (18)$$

and

$$\begin{aligned}\frac{\mu_B}{kT} = {} & \log N_B - \log N_B - \log (N_S - N_A - N_B) + \frac{w_{AB}}{kT} \frac{N_A}{N_S} \\ & + \frac{w_{BB}}{kT} \frac{N_B}{N_S} \qquad (19)\end{aligned}$$

We let θ_X be the fraction of sites occupied by species X, N_X / N_S, $X = \mathrm{A, B}$, which gives

$$\log \lambda_A \equiv \frac{\mu_A}{kT} = \log \frac{\theta_A}{1 - \theta_A - \theta_B} + \frac{1}{kT} (w_{AA}\theta_A + w_{AB}\theta_B) \qquad (20)$$

and

$$\log \lambda_B \equiv \frac{\mu_B}{kT} = \log \frac{\theta_B}{1 - \theta_A - \theta_B} + \frac{1}{kT} (w_{AB}\theta_A + w_{BB}\theta_B) \qquad (21)$$

Equations (20) and (21) relate the absolute activities of the two surface active solutes to the extent to which they are adsorbed at the interface. If there are no regions in which $\partial\mu_X/\partial\theta_X$ is negative ($X = \mathrm{A}, \mathrm{B}$), that completes the problem. If $\partial\mu_X/\partial\theta_X$ is negative, the system is thermodynamically unstable. The Gibbs phase rule, extended to include surface phases, is

$$f = c + 3 - p_s - p_b \tag{22}$$

where f is the number of degrees of freedom, c is the number of components, p_s is the number of surface phases, and p_b is the number of bulk phases. If we specify one bulk phase (the substrate) and three components (water, A, B), and take the temperature and pressure as fixed (thus removing two degrees of freedom), we find that the maximum possible number of surface phases (obtained by setting $f = 0$) is 3. These would presumably be a gaseous phase in equilibrium with two condensed phases, one consisting principally of A and the other composed mainly of B. Such films might be formed with mixtures of an alcohol and a perfluorinated alcohol.

The requirements which must be satisfied in order that two surface phases 1 and 2 containing two components A and B be at equilibrium at given T and P are

$$\mu_\mathrm{A}^1 = \mu_\mathrm{A}^2 \tag{23}$$

$$\mu_\mathrm{B}^1 = \mu_\mathrm{B}^2 \tag{24}$$

and

$$\phi^1 = \phi^2 \tag{25}$$

where ϕ^i is the surface pressure of phase i. Equation (25) can be rewritten as

$$\int_{\phi^1}^{\phi^2} d\phi = 0 \tag{26}$$

which, since

$$d\phi = \Gamma_\mathrm{A}\, d\mu_\mathrm{A} + \Gamma_\mathrm{B}\, d\mu_\mathrm{B} \tag{27}$$

is equivalent to

$$\int_{\text{state 1}}^{\text{state 2}} [\theta_\mathrm{A} d \log \lambda_\mathrm{A} + \theta_\mathrm{B} d \log \lambda_\mathrm{B}] = 0 \tag{28}$$

We shall carry out the integration only along paths for which log λ_B is held constant, which leaves

$$\int_{\text{state 1}}^{\text{state 2}} \theta_A d \log \lambda_A = 0 \tag{29}$$

This guarantees that Eq. (24) is satisfied. We also require that log λ_A (state 1) = log λ_A (state 2), which makes these two states satisfy Eq. (23).

In carrying out the calculations we proceed as follows. First the desired value of log λ_B is selected. We next wish to make tables of log λ_A and θ_B as functions of θ_A for, say, 99 values of θ_A spaced evenly between 0.01 and 0.99. With log λ_B fixed, we substitute a value of θ_A, say θ_{Ai}, into Eq. (21) and solve this equation for θ_B numerically, obtaining θ_{Bi}. This and the given value θ_{Ai} are substituted into Eq. (20) to calculate log λ_{Ai}. The procedure is repeated to generate the desired tables.

We next wish to determine whether any phase transitions take place. This is done by determining those values of θ_{Ai} for which log λ_{Ai} − log λ_{Ai-1} changes sign. No sign changes indicates the presence of one phase; two sign changes, two phases; four sign changes, three phases. Let us consider the case where we have two phases. We need to find values of θ_A such that θ_A^1 is less than θ_A^{max}, θ_A^2 is greater than θ_A^{min} (see Fig. 1), that

$$\log \lambda_A(\theta_A^1, \log \lambda_B) = log\, \lambda_A(\theta_A^2, \log \lambda_B) \tag{30}$$

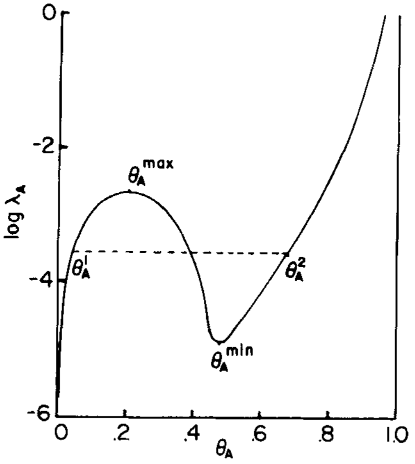

FIG. 1. Schematic of an isotherm for which a phase transition takes place.

and that Eq. (29) is satisfied. We integrate Eq. (29) by parts to get, after use of Eq. (30).

$$0 = \log \lambda_A(\theta_A^1, \log \lambda_B)(\theta_A^2 - \theta_A^1) - \int_{\theta_A^1}^{\theta_A^2} \log \lambda_A \, d\theta_A \qquad (31)$$

We select as our first approximation for θ_A^1 the first value of θ_{A_i} less than $\theta_A^{\max}$, determine $\log \lambda_A(\theta_A^1)$, and integrate to that value of θ_A greater than $\theta_A^{\min}$ for which $\log \lambda_A = \log \lambda_A(\theta_A^1)$, which we take as our first approximation to θ_A^2. If this integral is negative, we decrease i by 1 and repeat. This procedure is continued until the integral changes sign, at which point we have obtained our best approximations for θ_A^1 and θ_A^2. If a third phase exists it is that for which $\log \lambda_A(\theta_A^3, \log \lambda_B) = \log \lambda_A(\theta_A^1, \log \lambda_B)$.

We found that taking $\theta_{A_i} - \theta_{A_{i-1}} = 0.01$ in the calculations provided us with all the accurary necessary for making the plots needed, and use of a smaller interval (say 0.001) resulted in spurious maxima and minima because of the extremely large percentage errors in the differences between very similar values of $\log \lambda_A$. It took about 32 s of computer time on a DEC 1099 to calculate a set of four runs such as are shown in Fig. 2.

RESULTS

Space constraints prevent the presentation of results demonstrating the effects of all the various parameters on the shapes of the adsorption isotherm plots, $\log \lambda_A(\theta_A, \log \lambda_B)$. Variation in the binding energies of the polar or

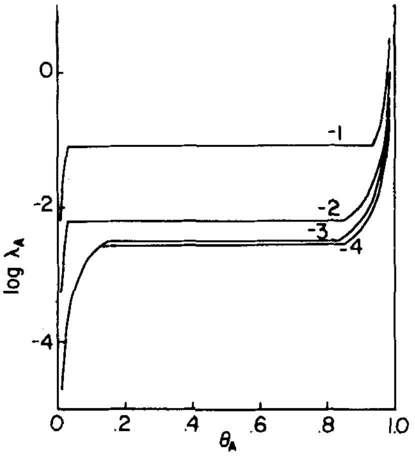

FIG. 2a. Adsorption isotherms for species A, with $\log \lambda_B = -4, -3, -2, -1$ as indicated. Here $z = 6$, $T = 298°K$, $w_{AA} = w_{BB} = -2.1 \times 10^{-13}$ erg, $w_{AB} = -0.6 \times 10^{-13}$ erg.

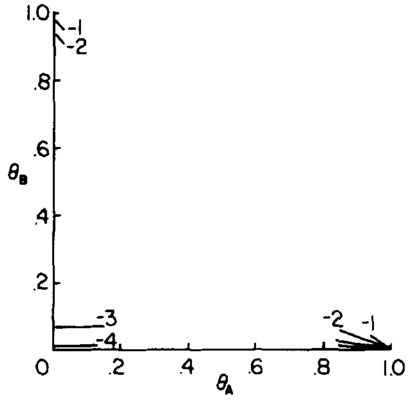

FIG. 2b. The dependence of θ_B on θ_A for the isotherms is Fig. 2a.

ionic heads of the surfactants to the adsorption sites results only in shifts in the values of of λ_A and log λ_B at which the various features of the plots are observed. This is described in our earlier work (*17–23*). The effects of increasing temperature are the same as those of decreasing the cooperative interaction energies of the surfactant species, w_{XY} (X, Y = A, B); this result is expected, since the temperature dependence occurs only in the form w_{XY}/kT. We therefore focus on the effects of the interplay of the magnitudes of w_{AA} and w_{BB}.

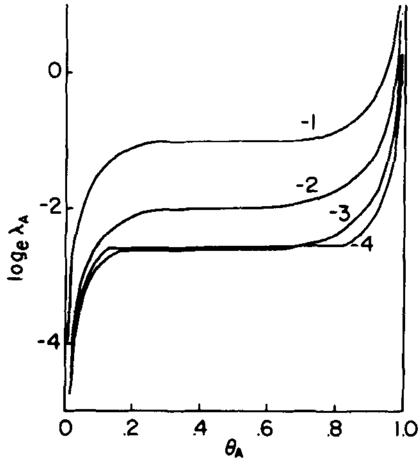

FIG. 3a. Adsorption isotherms for species A, with log $\lambda_B = -4, -3, -2, -1$ as indicated. $w_{AB} = -1.2 \times 10^{-13}$ erg, other parameters as in Fig. 2a.

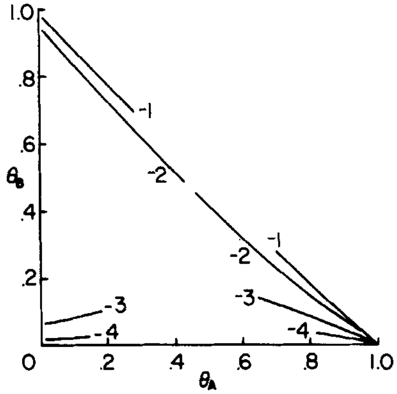

FIG. 3b. θ_B as a function of θ_A for the isotherms in Fig. 3b.

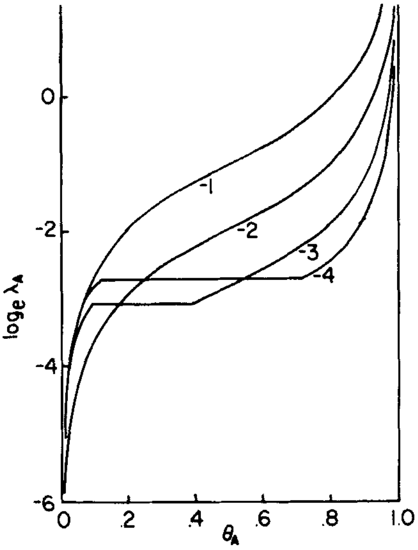

FIG. 4a. Adsorption isotherms for species A, with log $\lambda_B = -4, -3, -2, -1$ as indicated. $w_{AB} = -1.8 \times 10^{-13}$ erg, other parameters as in Fig. 2a.

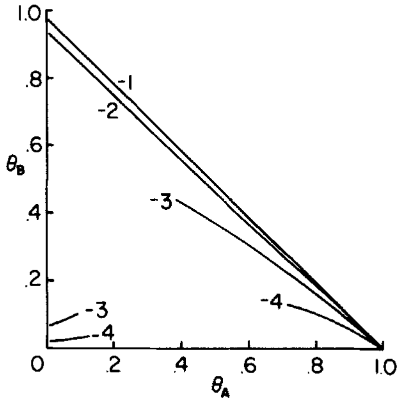

FIG. 4b. θ_B as a function of θ_A for the isotherms in Fig. 4b.

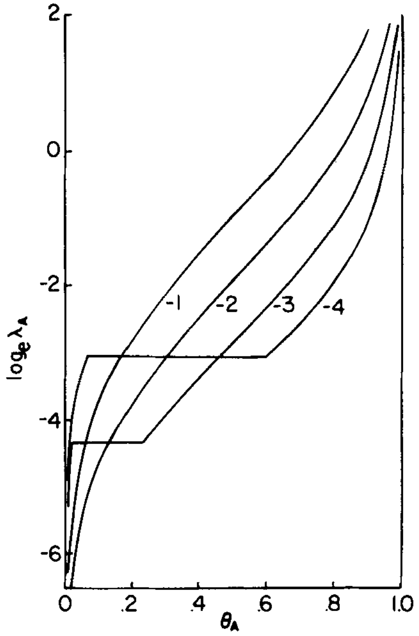

FIG. 5a. Adsorption isotherms for species A, with log $\lambda_B = -4, -3, -2, -1$ as indicated. $w_{AB} = -2.4 \times 10^{-13}$ erg, other parameters as in Fig. 2a.

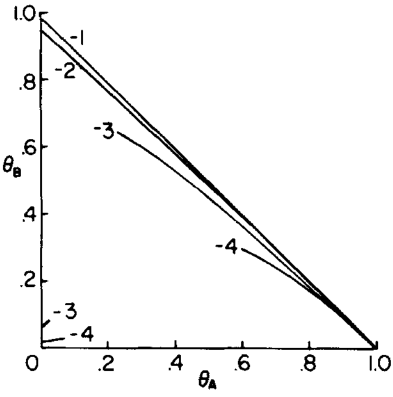

FIG. 5b. The dependence of θ_B on θ_A for the Fig. 5a values of log λ_B.

Figures 2–5 portray a series of sets of adsorption isotherms for which w_{AA} and w_{BB} are held constant (at -2.1×10^{-13} erg) and w_{AB} is decreased from -6.0×10^{-14} to -2.4×10^{-13} erg. In each set of isotherms log λ_B is given the values −4.0, −3.0, −2.0, and −1.0. In Fig. 2, for which $w_{AB} = -0.6 \times 10^{-13}$ erg, we see that phase transitions occur in all the plots. If log λ_B is −3 or −4 we see from Fig. 2b that the transition is from a gaseous film to a film which is mainly B to a condensed film which is mainly A. The same general pattern is seen in Fig. 3 for which $w_{AB} = -1.2 \times 10^{-13}$ erg, except that the two condensed phases show much broader ranges of composition, as one would expect with the increased magnitude of the interaction between A and B. As w_{AB} is decreased still further, to -1.8×10^{-13} erg, the A–B interaction becomes sufficiently strong that there is no phase transition as one goes from a condensed film of A to a condensed film of B. At the lower values of log λ_B we still observe the expected phase transition from a mixed gaseous film to a mixed condensed film as log λ_A increases. The same general features are observed in Fig. 5 in which $w_{AB} = -2.4 \times 10^{-13}$ erg. The phase transition, where it occurs, takes place at lower values of log λ_A than is the case in Fig. 4, due to the greater tendency of B to bring about condensation when the strength of the A–B bonding interactions is increased.

Figures 6 and 7 show the effects of decreasing all the w's from −1.8 to -2.1×10^{-13} erg; decreasing the cooperative interaction energies w_{XY} (increasing the strength of the binding interactions) results in a shift of the condensation points to lower values of log λ_A, as one would expect.

In Fig. 8 there is included a plot in which apparently three phases are present simultaneously; this is the curve for which $\lambda_B = -2.0$, which exhibits

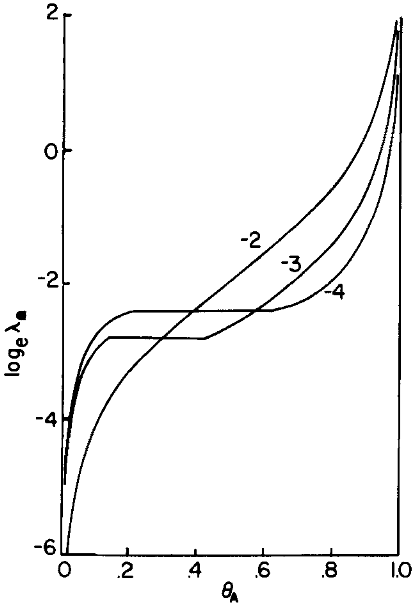

FIG. 6a. Adsorption isotherms for species A, with log $\lambda_B = -4, -3, -2$. $w_{AA} = w_{BB} + w_{AB} = -1.8 \times 10^{-13}$ erg, other variables as in Fig. 2a.

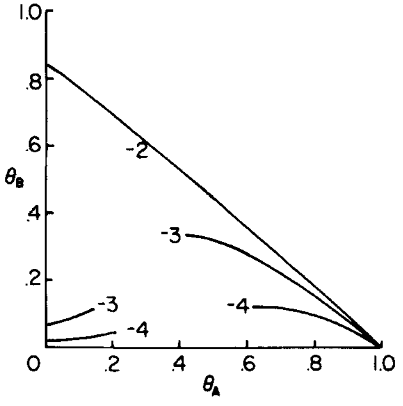

FIG. 6b. θ_B as a function of θ_A for the runs in Fig. 6a.

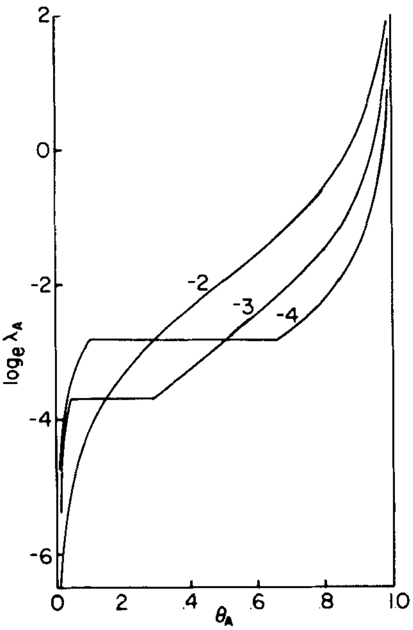

FIG. 7a. Adsorption isotherms for species A, with $\log \lambda_B = -4, -3, -2$. $w_{AA} = w_{BB} = w_{AB} = -2.1 \times 10^{-13}$ erg, other variables as in Fig. 2a.

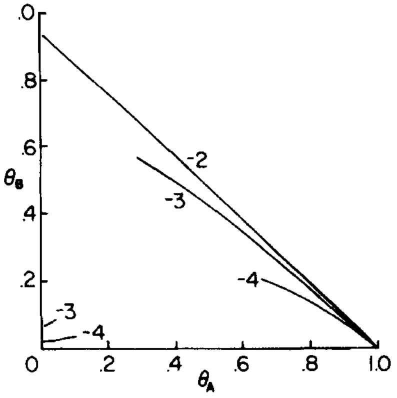

FIG. 7b. The relationship between θ_B and θ_A for the runs in Fig. 7a.

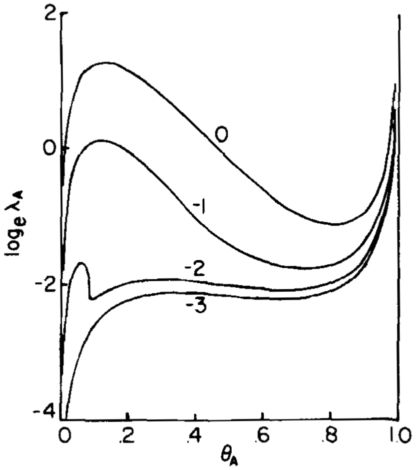

FIG. 8a. Adsorption isotherms for species A, with $\log \lambda_B = -3, -2, -1, 0$. The construction of the tie lines joining the phases present at phase transition has not been carried out so as to exhibit the appearances of the initial plots more clearly. Here $w_{AA} = -1.8$, $w_{BB} = -1.8$, $w_{AB} = 0.0 \times 10^{-13}$ erg, and the other parameters are as in Fig. 2a. Note the two maxima and minima in the isotherm for which $\log \lambda_B = -2$; this may be associated with the formation of three surface phases.

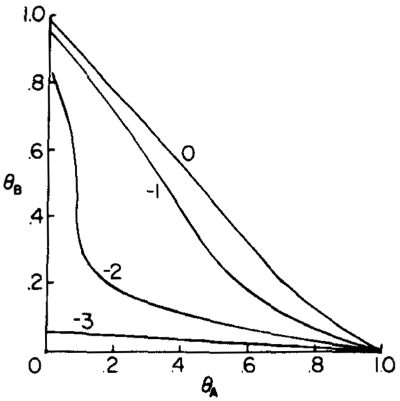

FIG. 8b. The relationship between θ_B and θ_A for the runs in Fig. 8a.

two maxima and two minima. One is a bit uncertain about trusting interpretations of small features of isotherms based on a model which contains such a severe assumption as our randomness approximation. And it does seem a most remarkable coincidence that log $\lambda_B = -2.00$ should turn out to give the "triple point" surface concentration for this system. We therefore restrain our enthusiasm somewhat, and conclude that this plot suggests the possibility of a surface "triple point" somewhere in the vincinity of log $\lambda_A = -2$, log $\lambda_B = -2$.

We conclude that surface phase transitions of mixed surfactant system on solid–water interfaces show sufficient variability to warrant their experimental investigation with an eye to improving the economics of precipitate and adsorbing colloid foam flotation separations.

Acknowledgment

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