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Electrical Aspects of Adsorbing Colloid Flotation. XVII. Quasi-Chemical Method for Adsorption of Mixed Surfactants

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Electrical Aspects of Adsorbing Colloid Flotation. XVII. Quasi-Chemical Method for Adsorption of Mixed Surfactants

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Abstract

The quasi-chemical approximation is applied to the calculation of adsorption isotherms for two-component surfactant systems. No further approximations are necessary. The effects of the relative sizes of the interaction energies of the various nearest neighbor pairs are investigated, and plots of representative adsorption isotherms are given. Some possible applications of the theory to foam flotation and other surface chemical separation techniques are suggested.

INTRODUCTION

Flotation methods have been used for ore beneficiation (*1, 2*) for many years. More recently they have been investigated for use in the concentration of trace elements for analysis, for metals recovery from ore leachates, and for industrial wastewater treatment; this work is summarized in a number of reviews (*3–11*). The model developed by Fuerstenau and his co-workers for surfactant adsorption in mineral flotation (*12–18*) appears to be appropriate also for adsorbing colloid and precipitate flotation. We have analyzed their model within the framework of the quasi-chemical approximation of statistical mechanics (*19, 20*) for describing condensation phenomena in

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surface adsorption (*21*). According to the model, flotation of the solid becomes possible when a condensed monolayer of surfactant forms on the solid surface with polar or ionic heads to the solid and hydrocarbon tails to the aqueous phase; this makes the surface hydrophobic and permits the attachment of air bubbles. Currin et al. extended the quasi-chemical method to investigate the displacement of the adsorbed amphipathic ions by competing foreign ions (*22*). Clarke et al. analyzed the effects of specifically adsorbed ions on the surface potentials of the flocs, and gave some experimental results of these effects on the flotation of $Fe(OH)_3$ (*23*).

At higher concentrations of surfactant a second, reversed monolayer of surfactant can be adsorbed on top of the first, making the solid surface hydrophilic and suppressing flotation. We modeled this with the quasi-chemical approximation (*24*), and determined adsorption isotherms of lauryl sulfate on $Fe(OH)_3$ and $Al(OH)_3$ (*25*); excess adsorption occurs, but there does not appear to be a second abrupt surface-phase transition.

Kiefer improved the model of surfactant adsorption by including the effects of the spacing of the adsorption sites and the Coulombic repulsions between the ionic heads of the adsorbed surfactant ions (*26*). Brown developed a theory for the adsorption of anions and cations (including amphipaths) onto flocs having both positive and negative adsorption sites; he used an approximate thermodynamic approach (*27*).

We have been interested in improving the selectivity and the economics of precipitate and adsorbing colloid flotation methods by the use of two-component surfactant systems, a technique of long standing in mineral flotation. Our first attempt to use the quasi-chemical method ended in a humiliating morass of algebraic complexity, and we fell back on the much simpler Bragg-Williams approximation, in which it is assumed that the placement of the surfactant species on the lattice adsorption sites can be treated as random (*28*). This evidently requires that the interaction energies w_{AA}, w_{AB}, and w_{BB} between the adsorbed surfactants A and B be small compared to kT, which they are not. This casts some doubts on the propriety of using the Bragg-Williams approximation in this context, and limits one's confidence in interpreting the results.

We present below a quasi-chemical statistical mechanical analysis of the cooperative adsorption of two surfactants. We have found this to be possible for the case where the differences between the interaction energies w_{AA}, w_{AB}, and w_{BB} are not too large compared with kT. We first give a much simpler rederivation of our Bragg-Williams results, then an outline of the rather lengthy statistical mechanical analysis, then a short description of the numerical procedure used to compute the adsorption isotherms, and finally the results.

ANALYSIS

Let us consider a solid–liquid interface having M adsorption sites, N_A of which are occupied by species A and N_B of which are occupied by species B. The lattice is such that each site has c nearest neighbors, and we consider nearest neighbor interactions only. We define $N_{AA}, N_{AB}, N_{BB}, N_{A0}, N_{B0}$, and N_{00} as the number of pairs of adjacent sites occupied by A–A, A–B, B–B, A–vacant, B–vacant, and vacant–vacant pairs. Also we let w_{AA}, w_{AB}, and w_{BB} be the interaction energies of the three types of pairs of occupied sites. These will, in general, be negative.

By way of introduction, we show a much simpler derivation of the chemical potentials of A and B within the framework of the Bragg-Williams approximation. This approximation assumes that the interaction energies w_{AA}, w_{BB}, and w_{AB} are all small in magnitude compared to kT. We assume that the canonical partition function can be written as

$$Q(N_A, N_B, M, T) = \frac{M! q_A^{N_A} q_B^{N_B}}{N_A! N_B! (M - N_A - N_B)!} \exp\left[-\frac{1}{k\mathrm{T}}(\bar{N}_{AA} w_{AA} + \bar{N}_{AB} w_{AB} + \bar{N}_{BB} w_{BB})\right] \tag{1}$$

where

$$\bar{N}_{AA} = cN_A^2/2M \tag{2}$$

$$\bar{N}_{AB} = cN_A N_B/M \tag{3}$$

$$\bar{N}_{BB} = cN_B^2/2M \tag{4}$$

Here we have assumed that the distribution of pairs is completely random, so that the $\bar{N}_{XY}$ may be calculated on purely statistical grounds. Also, q_A and q_B are the partition functions for the internal degrees of freedom of A and B, respectively. Then

$$Q = \frac{M! q_A^{N_A} q_B^{N_B}}{N_A! N_B! (M - N_A - N_B)!} \exp\left[\frac{-c}{MkT}\left(\frac{N_A^2 w_{AA}}{2} + N_A N_B w_{AB} + \frac{N_B^2 w_{BB}}{2}\right)\right] \tag{5}$$

Taking logs yields

$$\log Q = M \log M - M - N_A \log N_A + N_A - N_B \log N_B + N_B$$
$$- (M - N_A - N_B) \log (M - N_A - N_B) + (M - N_A - N_B)$$
$$+ N_A \log q_A + N_B \log q_B$$
$$\frac{-c}{MkT}\left[\frac{N_A^2 w_{AA}}{2} + N_A N_B w_{AB} + \frac{N_B^2 w_{BB}}{2}\right] \tag{6}$$

The surface pressure Φ is then given by

$$\frac{\Phi}{kT} = \left(\frac{\partial \log Q}{\partial M}\right)_{N_A,N_B,T} = \log M - \log (M - N_A - N_B)$$
$$+ \frac{c}{kTM^2}\left(\frac{N_A^2 w_{AA}}{2} + N_A N_B w_{AB} + \frac{N_B^2 w_{BB}}{2}\right) \tag{7}$$

$$= \log \frac{1}{1 - \theta_A - \theta_B} + \frac{c}{kT}\left(\frac{w_{AA}}{2}\theta_A^2 + w_{AB}\theta_A\theta_B + \frac{w_{BB}}{2}\theta_B^2\right) \tag{8}$$

where $\theta_X = (N_X/M)$, the fraction of sites occupied by species X.

The chemical potential of A is given by

$$\frac{\mu_A}{kT} = -\left(\frac{\partial \log Q}{\partial N_A}\right)_{M,N_B,T} = -[-\log N_A + \log (M - N_A - N_B)]$$
$$+ \log q_A - \frac{c}{MkT}(N_A w_{AA} + N_B w_{AB}) \tag{9}$$

$$= \log \frac{\theta_A}{1 - \theta_A - \theta_B} - \log q_A + \frac{c}{kT}(w_{AA}\theta_A + w_{AB}\theta_B) \tag{10}$$

Similarly

$$\frac{\mu_B}{kT} = \log \frac{\theta_B}{1 - \theta_A - \theta_B} - \log q_B + \frac{c}{kT}(w_{BB}\theta_B + w_{AB}\theta_A) \tag{11}$$

This approach, which follows Hill's treatment of the one-component system, eliminates a lengthy algebraic reduction and an integration which were necessary in our earlier treatment (*28*) and which cause serious trouble when one attempts to use the quasi-chemical approximation.

With this preliminary out of the way, we turn to the quasi-chemical approximation. The notation is as above.

By drawing lines from each site occupied by A to all the neighboring sites, we find that

$$cN_A = 2N_{AA} + N_{A0} + N_{AB} \tag{12}$$

Similarly

$$cN_B = 2N_{BB} + N_{B0} + N_{AB} \tag{13}$$

and

$$c(M - N_A - N_B) = 2N_{00} + N_{0A} + N_{0B} \tag{14}$$

Thus, of our six different pair numbers $N_{AA} \ldots N_{00}$, only three are independent. We choose N_{A0}, N_{B0}, and N_{AB} as independent, leaving

$$N_{AA} = \frac{c}{2} N_A - \frac{N_{A0}}{2} - \frac{N_{AB}}{2} \tag{15}$$

$$N_{BB} = \frac{c}{2} N_B - \frac{N_{B0}}{2} - \frac{N_{AB}}{2} \tag{16}$$

$$N_{00} = \frac{c}{2} (M - N_A - N_B) - \frac{N_{A0}}{2} - \frac{N_{B0}}{2} \tag{17}$$

Also, the number of

$$\text{OA ordered pairs} = N_{A0}/2 \tag{18}$$

$$\text{AO ordered pairs} = N_{A0}/2 \tag{19}$$

$$\text{OB ordered pairs} = N_{B0}/2 \tag{20}$$

$$\text{BO ordered pairs} = N_{B0}/2 \tag{21}$$

$$\text{AB ordered pairs} = N_{AB}/2 \tag{22}$$

$$\text{BA ordered pairs} = N_{AB}/2 \tag{23}$$

Now the total number of pairs of $cM/2$, so, if we approximate the pairs as independent, the degeneracy of the state specified by N_{A0}, N_{B0}, N_{AB} is given by

$$\omega(M, N_A, N_B, N_{A0}, N_{B0}, N_{AB} = \frac{(cM/2)!}{X!Y!Z!\left[\frac{(N_{A0})!}{2}\right]^2\left[\frac{(N_{B0})!}{2}\right]^2\left[\frac{(N_{AB})!}{2}\right]^2} \tag{24}$$

where

$$X = \frac{1}{2}(cN_A - N_{A0} - N_{B0}) \tag{25}$$

$$Y = \frac{1}{2}(cN_B - N_{B0} - N_{AB}) \tag{26}$$

$$Z = \frac{1}{2}[c(M - N_A - N_B) - N_{A0} - N_{B0}] \tag{27}$$

Now we know that ω overcounts the pairs (since it assumes that they are independent), and we also have that

$$\sum_{N_{A0}} \sum_{N_{B0}} \sum_{N_{AB}} g(M, N_A, N_B, N_{A0}, N_{B0}, N_{AB}) = \frac{M!}{N_A!N_B!(M - N_A - N_B)!} \tag{28}$$

from simple combinatorial considerations, where g is the true degeneracy of the state specified by N_{A0}, N_{B0}, N_{AB}. We therefore construct a correction factor for ω as follows: Let

$$\frac{M!}{N_A!N_B!(M - N_A - N_B)!} = C(M, N_A, N_B) \cdot \sum_{N_{A0}} \sum_{N_{B0}} \sum_{N_{AB}} \omega \tag{29}$$

We use the maximum term method to evaluate the triple sum on the right-hand side of Eq. (29), a common crime in statistical mechanics. To find the maximum term, proceed as below.

$$\begin{aligned}\log_e \omega = \log (cM/2)! - & \Bigg\{\frac{1}{2}(cN_{\mathrm{A}} - N_{\mathrm{A0}} - N_{\mathrm{AB}}) \log \frac{1}{2}(cN_{\mathrm{A}} - N_{\mathrm{A0}} - N_{\mathrm{AB}}) \\ & - \frac{1}{2}(cN_{\mathrm{A}} - N_{\mathrm{A0}} - N_{\mathrm{AB}}) + \frac{1}{2}(cN_{\mathrm{B}} - N_{\mathrm{B0}} - N_{\mathrm{AB}}) \\ & \log \frac{1}{2}(cN_{\mathrm{B}} - N_{\mathrm{B0}} - N_{\mathrm{AB}}) - \frac{1}{2}(cN_{\mathrm{B}} - N_{\mathrm{B0}} - N_{\mathrm{AB}}) \\ & + \frac{1}{2}[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}] \\ & \log \frac{1}{2}[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}] \\ & - \frac{1}{2}[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}] \\ & - \frac{1}{2}[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}] \\ & + 2\Bigg[\frac{N_{\mathrm{A0}}}{2} \log \frac{N_{\mathrm{A0}}}{2} - \frac{N_{\mathrm{A0}}}{2} + \frac{N_{\mathrm{B0}}}{2} \log \frac{N_{\mathrm{B0}}}{2} - \frac{N_{\mathrm{B0}}}{2} \\ & + \frac{N_{\mathrm{AB}}}{2} \log \frac{N_{\mathrm{AB}}}{2} - \frac{N_{\mathrm{AB}}}{2}\Bigg]\Bigg\} \qquad (30)\end{aligned}$$

We obtain the maximum term from this by using Stirling's formula for $\log X!$ and setting

$$\begin{aligned}\frac{\partial \log \omega}{\partial N_{\mathrm{A0}}} = 0 = - & \Bigg\{-\frac{1}{2} \log \frac{1}{2}(cN_{\mathrm{A}} - N_{\mathrm{A0}} - N_{\mathrm{B0}}) \\ & - \frac{1}{2} \log \frac{1}{2}[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}] + \log \frac{N_{\mathrm{A0}}}{2}\Bigg\} \qquad (31)\end{aligned}$$

$$\begin{aligned}\frac{\partial \log \omega}{\partial N_{\mathrm{B0}}} = 0 = - & \Bigg\{-\frac{1}{2} \log \frac{1}{2}(cN_{\mathrm{B}} - N_{\mathrm{B0}} - N_{\mathrm{AB}}) \\ & - \frac{1}{2} \log \frac{1}{2}[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}] + \log \frac{N_{\mathrm{B0}}}{2}\Bigg\} \qquad (32)\end{aligned}$$

$$\frac{\partial \log \omega}{\partial N_{\mathrm{AB}}} = 0 = - \Bigg\{-\frac{1}{2} \log \frac{1}{2}(cN_{\mathrm{A}} - N_{\mathrm{A0}} - N_{\mathrm{AB}})$$

$$-\frac{1}{2}\log\frac{1}{2}(cN_B - N_{B0} - N_{AB}) + \log\frac{N_{AB}}{2}\Bigg\} \tag{33}$$

A straightforward but rather lengthy reduction leads to

$$N_{A0} = cM\theta_A(1 - \theta_A - \theta_B) \tag{34}$$

$$N_{B0} = cM\theta_B(1 - \theta_A - \theta_B) \tag{35}$$

$$N_{AB} = cM\theta_A\theta_B \tag{36}$$

where

$$\theta_A = N_A/M \tag{37}$$

$$\theta_B = N_B/M \tag{38}$$

These values of N_{A0}, N_{B0}, and N_{AB} allow us to calculate the maximum value of ω:

$$\omega_{\max} = \left(\frac{cM}{2}\right)! \Bigg/ \Bigg\{ \left(\frac{cN_A^2}{2M}\right)! \left(\frac{cN_B^2}{2M}\right)! \left(\frac{c}{2M}(M - N_A - N_B)^2\right)! \left[\left(\frac{c}{2M}(M-N_A-N_B)N_A\right)!\right]^2 \left[\left(\frac{c}{2M}(M-N_A-N_B)N_B\right)!\right]^2 \left[\left(\frac{c}{2M}N_AN_B\right)!\right]^2 \Bigg\} \tag{39}$$

Use of Stirling's approximation and a lengthy reduction finally lead to

$$\omega_{\max} = \left[\frac{M!}{N_A!N_B!(M - N_A - N_B)!}\right]^c \tag{40}$$

so that our normalizing constant $C(M, N_A, N_B)$ becomes (on use of $\omega_{\max}$ for the triple sum in Eq. 29)

$$C(M, N_A, N_B) = \left[\frac{M!}{(M - N_A - N_B)!N_A!N_B!}\right]^{1-c} \tag{41}$$

Now the canonical partition function for this system is given by

$$Q(N_{\mathrm{A}}, N_{\mathrm{B}}, M, T) = q_{\mathrm{A}}{}^{N_{\mathrm{A}}} q_{\mathrm{B}}{}^{N_{\mathrm{B}}} \sum_{N_{\mathrm{A0}}} \sum_{N_{\mathrm{B0}}} \sum_{N_{\mathrm{AB}}} g(M, N_{\mathrm{A}}, N_{\mathrm{B}}, N_{\mathrm{A0}}, N_{\mathrm{B0}}, N_{\mathrm{AB}})$$

$$\exp\left[\frac{1}{kT}\,(N_{\mathrm{AA}}w_{\mathrm{AA}} + N_{\mathrm{BB}}w_{\mathrm{BB}} + N_{\mathrm{AB}}w_{\mathrm{AB}})\right] \tag{42}$$

We substitute $g = C\omega$ (where C is given in Eq. 41 and ω is given by Eq. 24) and we replace N_{AA} and N_{BB} by the use of Eqs. (15) and (16). The resulting series is again intractable, so we use the maximum term method. Let t be one of the terms in Q; then

$$\log t = \log \left\{ q_{\mathrm{A}}^{N_{\mathrm{A}}} q_{\mathrm{B}}^{N_{\mathrm{B}}} \left[\frac{M!}{(M - N_{\mathrm{A}} - N_{\mathrm{B}})!N_{\mathrm{A}}!N_{\mathrm{B}}!}\right]^{1-c} \frac{(\mathrm{cM})!}{2} \right.$$

$$\left. \exp\left\{-\frac{\beta c}{2}\,(w_{\mathrm{AA}}N_{\mathrm{A}} + w_{\mathrm{BB}}N_{\mathrm{B}})\right\}\right\}$$

$$+ \log\left(\exp\left(N_{\mathrm{A0}}\frac{w_{\mathrm{AA}}\beta}{2}\right) \exp\left(\frac{N_{\mathrm{BO}}w_{\mathrm{BB}}\beta}{2}\right) \exp\left(\frac{N_{\mathrm{AB}}\beta}{2}(w_{\mathrm{AA}} + w_{\mathrm{BB}} - 2w_{\mathrm{AB}})\right)\right)$$

$$-\frac{1}{2}(cN_{\mathrm{A}} + N_{\mathrm{A0}} + N_{\mathrm{AB}}) \log \frac{1}{2}\,(cN_{\mathrm{A}} - N_{\mathrm{A0}} - N_{\mathrm{AB}}) + \frac{1}{2}\,(cN_{\mathrm{A}} - N_{\mathrm{A0}} - N_{\mathrm{AB}})$$

$$-\frac{1}{2}(cN_{\mathrm{B}} - N_{\mathrm{B0}} - N_{\mathrm{AB}}) \log \frac{1}{2}\,(cN_{\mathrm{B}} - N_{\mathrm{B0}} - N_{\mathrm{AB}}) + \frac{1}{2}\,(cN_{\mathrm{B}} - N_{\mathrm{B0}} - N_{\mathrm{AB}})$$

$$-\frac{1}{2}\,[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}] \log \frac{1}{2}[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}]$$

$$-\frac{1}{2}\,[c(M - N_{\mathrm{A}} - N_{\mathrm{B}}) - N_{\mathrm{A0}} - N_{\mathrm{B0}}]$$

$$-2\left\{\frac{N_{\mathrm{A0}}}{2}\log\frac{N_{\mathrm{A0}}}{2} - \frac{N_{\mathrm{A0}}}{2} + \frac{N_{\mathrm{B0}}}{2}\log\frac{N_{\mathrm{B0}}}{2} - \frac{N_{\mathrm{B0}}}{2} + \frac{N_{\mathrm{AB}}}{2}\log\frac{N_{\mathrm{AB}}}{2} - \frac{N_{\mathrm{AB}}}{2}\right\} \tag{43}$$

where $\beta = 1/kT$.

To get the values of N_{A0}, N_{B0}, N_{AB} which make t a maximum, we set

$$\frac{\partial \log t}{\partial N_{A0}} = \frac{\partial \log t}{\partial N_{B0}} = \frac{\partial \log t}{\partial N_{AB}} = 0 \tag{44}$$

which gives us

$$\begin{aligned} 0 = {} & \frac{\beta w_{AA}}{2} + \frac{1}{2} \log \frac{1}{2} (cN_A - N_{A0} - N_{AB}) \\ & + \frac{1}{2} \log \frac{1}{2} [c(M - N_A - N_B) - N_{A0} - N_{B0}] - \log \frac{N_{A0}}{2} \end{aligned} \tag{45}$$

$$\begin{aligned} 0 = {} & \frac{\beta w_{BB}}{2} + \frac{1}{2} \log \frac{1}{2} (cN_B - N_{B0} - N_{AB}) \\ & + \frac{1}{2} \log \frac{1}{2} [c(M - N_A - N_B) - N_{A0} - N_{B0}] - \log N_{B0} \end{aligned} \tag{46}$$

$$\begin{aligned} 0 = {} & \frac{\beta}{2} (w_{AA} + w_{BB} - 2w_{AB}) + \frac{1}{2} \log \frac{1}{2} (cN_A - N_{A0} - N_{AB}) \\ & + \frac{1}{2} \log (cN_B - N_{B0} - N_{AB}) - \log \frac{N_{AB}}{2} \end{aligned} \tag{47}$$

Another lengthy reduction leads to

$$N_{AB} = D_{AB} \cdot \frac{N_{A0}\, N_{B0}}{[c(M - N_A - N_B) - N_{A0} - N_{B0}]} \tag{48}$$

$$\begin{aligned} 0 = {} & c^2 N_A (M - N_A - N_B) - N_{A0} c (M - N_B) \\ & - cN_A N_{B0} + N_{A0} N_{B0} (1 - D_{AB}) + N_{A0}^2 (1 - D_{AA}) \end{aligned} \tag{49}$$

$$\begin{aligned} 0 = {} & c^2 N_B (M - N_A - N_B) - N_{B0} c (M - N_A) \\ & - cN_B N_{A0} + N_{A0} N_{B0} (1 - D_{AB}) + N_{B0}^2 (1 - D_{BB}) \end{aligned} \tag{50}$$

$$D_{XY} = \exp(-\beta w_{XY}); \qquad X,\ Y = \mathrm{A, B} \tag{51}$$

This pair of simultaneous quadratics is roughly the place where our previous attempts on this problem have foundered. To make further progress we assume that the differences between w_{AA}, w_{AB}, and w_{BB} are not large in comparison to kT, in which case we expect that

$$\frac{N_{B0}}{N_B} \cong \frac{N_{A0}}{N_A} \tag{52}$$

is a reasonable first approximation. We therefore substitute $N_{B0} = N_B N_{A0}/N_A$ in Eq. (49) and $N_{A0} = N_A N_{B0}/N_B$ in Eq. (50). Equation (49) then yields

$$N_{A0} = \frac{cM - \left[(cM)^2 - 4\left\{\frac{N_B}{N_A}(1 - D_{AB}) + (1 - D_{AA} \right\} c^2 N_A (M - N_A - N_B)\right]^{1/2}}{2\left[\frac{N_B}{N_A}(1 - D_{AB}) + (1 - D_{AA})\right]} \tag{53}$$

and Eq. (50) yields

$$N_{B0} = \frac{cM - \left[(cM)^2 - 4\left\{\frac{N_A}{N_B}(1 - D_{AB}) + (1 - D_{BB})\right\} c^2 N_B (M - N_A - N_B)\right]^{1/2}}{2\left[\frac{N_A}{N_B}(1 - D_{AB}) + (1 - D_{BB})\right]} \tag{54}$$

We rewrite these equations in terms of

$$f_{A0} = N_{A0}/cM \tag{55}$$

and

$$f_{B0} = N_{B0}/cM \tag{56}$$

which yields for our first approximation

$$f_{A0} = \frac{\theta_A\{1 - [1 - 4(\theta_B(1 - D_{AB}) + \theta_A(1 - D_{AA}))\,(1 - \theta_A - \theta_B)]^{1/2}\}}{2[\theta_B(1 - D_{AB}) + \theta_A(1 - D_{AA})]} \tag{57}$$

$$f_{B0}=\frac{\theta_B\{1-[1-4(\theta_A(1-D_{AB})+\theta_B(1-D_{BB}))\,(1-\theta_A-\theta_B)]^{1/2}\}}{2[\theta_A(1-D_{AB})+\theta_B(1-D_{BB})]}\tag{58}$$

Improved values of f_{A0} and f_{B0} are obtained by rewriting Eqs. (49) and (50) as

$$\begin{aligned}&f_{A0}{}^2(1-D_{AA})+f_{A0}[(1-D_{AB})f_{B0}-1+\theta_B]\\&\quad+[\theta_A(1-\theta_A-\theta_B)-\theta_A f_{B0}]=0\end{aligned}\tag{59}$$

and

$$\begin{aligned}&f_{B0}{}^2(1-D_{BB})+f_{B0}[(1-D_{AB})f_{A0}-1+\theta_A]\\&\quad+[\theta_B(1-\theta_A-\theta_B)-\theta_B f_{A0}]=0\end{aligned}\tag{60}$$

We substitute the first approximation for f_{B0} from Eq. (58) into Eq. (59) and solve the resulting quadratic for f_{A0}; we similarly take f_{A0} from Eq. (57) and use this in Eq. (60), solving the resulting quadratic for f_{B0}. These results are then used iteratively in the same manner until convergence of the roots occurs. One must use the positive sign in the quadratic formula in order that $f_{X0}=0$ when $\theta_X=0$, $X=$ A or B.

After we have obtained f_{A0} and f_{B0}, we calculate $f_{AB}=N_{AB}/cM$ from Eq. (48) in the form

$$f_{AB}=\frac{D_{AB}f_{A0}f_{B0}}{1-\theta_A-\theta_B-f_{A0}-f_{B0}}\tag{61}$$

On using the maximum term method again, we have $\log Q=\log t_{\max}$. We wish to calculate the chemical potentials of A and B from $\log Q$ in order to get their adsorption isotherms. We know that the chemical potential μ_A is given by

$$\frac{-\mu_A}{kT}=\left(\frac{\partial\log Q}{\partial N_A}\right)_{N_B,M,T}=\frac{\partial\log t_{\max}}{\partial N_A}\tag{62}$$

and likewise for μ_B. This gives us

$$\frac{-\mu_A}{kT}=\log\left[q_A\exp\left(\frac{\beta c w_{AA}}{2}\right)\right]+\left(\frac{\partial\log t}{\partial N_A}\right)_{N_B,N_{0A},N_{0B},N_{AB},M,T}$$

$$+\frac{\partial \log t}{\partial N_{0A}}\frac{\partial N_{0A}}{\partial N_A}+\frac{\partial \log t}{\partial N_{0B}}\frac{\partial N_{0B}}{\partial N_A}+\frac{\partial \log t}{\partial N_{AB}}\frac{\partial N_{AB}}{\partial N_A} \tag{63}$$

Recall, however, that the last three products vanish by virtue of Eq. (44). Equation 63 therefore reduces to

$$-\frac{\mu A}{kT}=\log\left[q_A \exp\left(-\frac{\beta c w_{AA}}{2}\right)\right]+(1-c)[\log(M-N_A-N_B)-\log N_A]$$
$$-\frac{c}{2}\log\frac{1}{2}(cN_A-N_{A0}-N_{AB})+\frac{c}{2}\log\frac{1}{2}\,[c(M-N_A-N_B)-N_{A0}-N_{B0}] \tag{64}$$

which gives

$$\log\left[\lambda_A q_A \exp\left(\frac{-\beta c w_{AA}}{2}\right)\right]$$
$$=\log\left[\left\{\frac{\theta_A}{1-\theta_A-\theta_B}\right\}^{1-c}\left\{\frac{\theta_A-f_{A0}-f_{AB}}{1-\theta_A-\theta_B-f_{AB}-f_{B0}}\right\}^{c/2}\right] \tag{65}$$

where $\lambda_A=\exp\mu_A/kT$ is the absolute activity of A. We have an equation similar to Eq. (65) for λ_B:

$$\log\left[\lambda_B q_B \exp\left(\frac{-\beta c w_{BB}}{2}\right)\right]$$
$$=\log\left[\left\{\frac{\theta_B}{1-\theta_A-\theta_B}\right\}^{1-c}\left\{\frac{\theta_B-f_{B0}-f_{AB}}{1-\theta_A-\theta_B-f_{B0}-f_{A0}}\right\}^{c/2}\right] \tag{66}$$

From Eqs. (65) and (66) we can calculate $\log\lambda'_A$ and $\log\lambda'_B$ as functions of θ_A and θ_B. (Here $\lambda'_X=\lambda_X q_X$, $X=$ A, B.) Usually what we wish to do, however, is to hold $\log\lambda'_B$ fixed and construct tables of $\log\lambda'_A$ and θ_B as functions of θ_A. This can be done fairly readily as follows. One selects $\log\lambda'_B$ and θ_A and then solves Eq. (66) for θ_B numerically with the aid of Eqs. (55)–(61). Then $\log\lambda'_A$ is calculated from Eq. (65).

If the plot of $\log\lambda'_A$ as a function of θ_A is monotonically increasing, our task is complete. If this plot shows maxima and minima, we shall have separation of the system into two or possibly three phases. For two phases this situation is handled in the usual way (*19, 20*) as follows. We let superscripts 1 and 2 refer to the two phases. Then chemical equilibrium gives

(we drop the primes henceforth)

$$\log \lambda_{\mathrm{A}}^{1} = \log \lambda_{\mathrm{A}}^{2} \tag{67}$$

$$\log \lambda_{\mathrm{B}}^{1} = \log \lambda_{\mathrm{B}}^{2} \tag{68}$$

and the requirement that the surface pressures of the two phases be equal gives us

$$0 = \int_{\text{State 2}}^{\text{State 2}} d\Phi = \int \theta_{\mathrm{A}} d \log \lambda_{\mathrm{A}} + \int \theta_{\mathrm{B}} d \log \lambda_{\mathrm{B}} \tag{69}$$

Since in our table of log λ_{A} as a function of θ_{A}, log λ_{B} is held constant, we can carry out the integration over a path of constant log λ_{B}, thereby obtaining

$$0 = \int \theta_{\mathrm{A}} \, d \log \lambda_{\mathrm{A}} \tag{70}$$

We integrate by parts to obtain

$$0 = \theta_{\mathrm{A}}^{2} \log \lambda_{\mathrm{A}}^{2} - \theta_{\mathrm{A}}^{1} \log \lambda_{\mathrm{A}}^{1} - \int_{\theta_{\mathrm{A}}^{1}}^{\theta_{\mathrm{A}}^{2}} \log \lambda_{\mathrm{A}}(\theta_{\mathrm{A}}, \log \lambda_{\mathrm{B}}) \, d\theta_{\mathrm{A}} \tag{71}$$

Use of Eq. (68) converts this to

$$\log \lambda_{\mathrm{A}}^{1}(\theta_{\mathrm{A}}^{2} - \theta_{\mathrm{A}}^{1}) = \int_{\theta_{\mathrm{A}}^{1}}^{\theta_{\mathrm{A}}^{2}} \log \lambda_{\mathrm{A}}(\theta_{\mathrm{A}}, \log \lambda_{\mathrm{B}}) \, d\theta_{\mathrm{A}} \tag{72}$$

This result indicates that the horizontal tie line in our plot of log λ_{A} (ordinate) versus θ_{A} passes through the loops of the curve such that the area of the loop above the tie line is equal to the area of the loop below the tie line. This provides us with a criterion for the selection of θ_{A}^{1} and θ_{A}^{2}. (The tie line must be horizontal because of Eq. 68). We locate the maximum and minimum of the plot, corresponding to values $\theta_{\mathrm{A}}^{\mathrm{max}}$ and $\theta_{\mathrm{A}}^{\mathrm{min}}$ as shown in Fig. 1. We wish to find values θ_{A}^{1} and θ_{A}^{2} such that θ_{A}^{1} is less than $\theta_{\mathrm{A}}^{\mathrm{max}}$, θ_{A}^{2} is greater than $\theta_{\mathrm{A}}^{\mathrm{min}}$, that Eq. (68) is satisfied, and that Eq. (72) is satisfied. We take as our first approximation for θ_{A}^{1} the first value of $\theta_{\mathrm{A}i}$ less than $\theta_{\mathrm{A}}^{\mathrm{max}}$, determine log $\lambda_{\mathrm{A}}(\theta_{\mathrm{A}}^{1})$, and integrate the right-hand side of (72) to that value of θ_{A} greater than $\theta_{\mathrm{A}}^{\mathrm{min}}$ for which log λ_{A} = *log* $\lambda_{\mathrm{A}}(\theta_{\mathrm{A}}^{1})$; this is our first approxima-

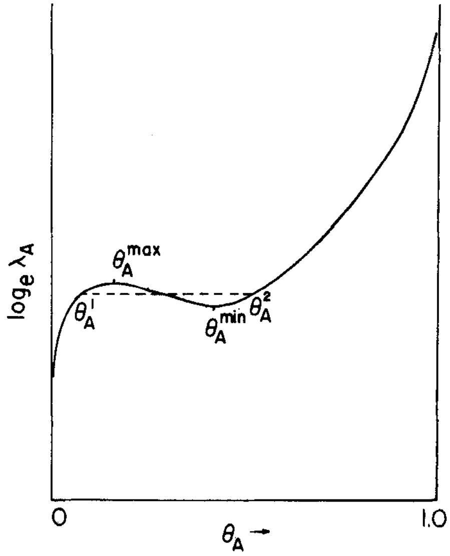

FIG. 1. Schematic of an isotherm exhibiting a phase transition.

tion to θ_A^2. If the integral is less than $\log \lambda_A(\theta_A^1, \log \lambda_B)$ $(\theta_A^1 - \theta_A^2)$, we decrease i by one (take the next lower value of θ_A), and repeat. We continue this procedure until the integral first becomes larger than the left-hand side of Eq. (60). This gives us our best approximations for θ_A^1 and θ_A^2. If a third phase exists, its value of θ_A, θ_A^3, is that for which $\log \lambda_A$ $(\theta_A^3, \log \lambda_B) = \log \lambda_A(\theta_A^1, \log \lambda_B)$ and for which $\log \lambda_A$ is increasing with increasing θ_A.

RESULTS

A FORTRAN computer program was written to calculate adsorption isotherms on the DEC 1099 of the Vanderbilt University Computer Center. About 6 minutes of CPU time was required to calculate the four runs plotted in Fig. 2. This is about 12 times the time required to do a similar set of Bragg-Williams calculations. We note that it is necessary to multiply the interaction energies w_{XY} used in this paper by $c/2$ to make them comparable with the w_{XY} used in our earlier calculation (28) using the Bragg-Williams approximation. In all our work reported here, we assumed $c = 6$ (six nearest neighbors).

We present here a sampling of the effects of some of the model parameters on the shapes of the adsorption isotherm plots. Variation in the binding energies of the polar or ionic heads of the surfactants to the adsorption sites on the surface only causes shifts in the values of log λ_A and log λ_B at which the various features of the plots are observed. This is discussed in earlier papers (*21–26*). The results of increasing the temperature are similar to those of decreasing the w_{XY} insofar as the shapes of the isotherms are concerned, since Eqs. (59), (60), (61), (65), and (66) depend on temperature only in the form w_{XY}/kT, with the temperature dependencies of q_A and q_B in Eqs. (65) and (66) merely changing the origins of the log λ_A and log λ_B axes. For these reasons we focus, as before, on the effects of variations in w_{AA}, w_{BB}, and w_{AB}.

Figures 2a, 3a, 4a, and 5a show plots of the adsorption isotherms $\log_e \lambda_A(\theta_A, \log_e \lambda_B)$ for sets of values of log λ_B (−4, −3, −2, −1) as functions of θ_A. In these figures $w_{AB} = -1, -2, -3$, and -4×10^{-14} erg, respectively. Figures 2b, 3b, 4b, and 5b show plots of θ_B (θ_A, $\log_e \lambda_B$) for the same runs; gaps in these plots occur where there are phase transitions. The plots all show features qualitatively similar to the Bragg-Williams isotherms calculated earlier, despite the fact that the w_{XY} are here comparable in magnitude to kT (4.11×10^{-14} erg). We see in Figs. 2 and 3 the formation of two separate condensed phases when $\log_e \lambda_B$ is large; we expect this for $|w_{AB}|$ substantially smaller than $|w_{AA}|$ and $|w_{BB}|$, and had observed it in our Bragg-Williams calculations. As we let $|w_{AB}|$ increase we see an increased tendency for condensed phases to form at lower values of log λ_A due to the increased ability of the B species at a given activity to attract and stabilize A molecules in a single mixed condensed surface phase. This is particularly evident in Figs. 5a and b.

In Figs. 6–10 we show a similar set of plots for systems having $w_{AA} = w_{BB} = -3.5 \times 10^{-14}$ erg; $w_{AB} = -.5, -1.5, -2.5, -3.5$, and -4.5×10^{-14} erg. In each set of runs log $\lambda_B = -5, -4, -3, -2$, and -1. For reasons of space we omit the plots of θ_B versus θ_A. This group of runs shows features similar to the first, except that a somewhat higher surface "vapor pressure" in the sparse surface phase is needed to bring about condensation, as one would expect. Again we find that for $|w_{AB}|$ substantially less than $|w_{AA}|$ and $|w_{BB}|$, we may have two condensed phases in equilibrium with each other. For example, the plots of θ_B versus θ_A for the top two isotherms in Fig. 6 exhibit this behavior.

In Figs. 11a, and 11b we see plots of log λ_A and θ_B versus θ_A for $w_{AA} = -3$, $w_{BB} = -4$, $w_{AB} = -3.5 \times 10^{-14}$ erg. We see that this system shows only a single mixed condensed phase for $\log_e \lambda_B = -1, -2$, or -3, and that the isotherms for $\log_e \lambda_B = -4$ and -5 almost exhibit condensation. The maxima in the plots of θ_B versus θ_A (Fig. 11b) show the ability of A to coadsorb B into the surface phase.

The use of mixtures of surfactants is not uncommon in the field of ore flotation, where the selection of collectors is based on experience, chemical

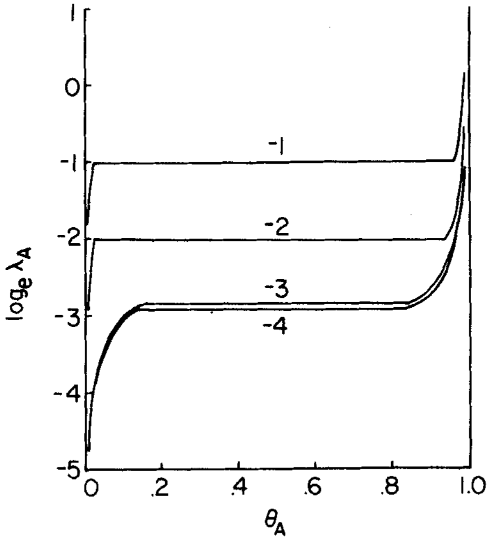

FIG. 2a. Adsorption isotherms for Species A. $c = 6$; $T = 298$ K; $\log_e \lambda_B = -1, -2, -3, -4$ as indicated; $w_{AA} = w_{BB} = -4$, $w_{AB} = -1 \times 10^{-14}$ erg.

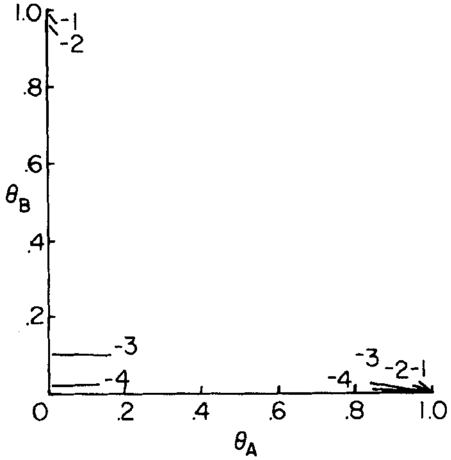

FIG. 2b. The dependence of θ_B on θ_A for the isotherms in Fig. 2a.

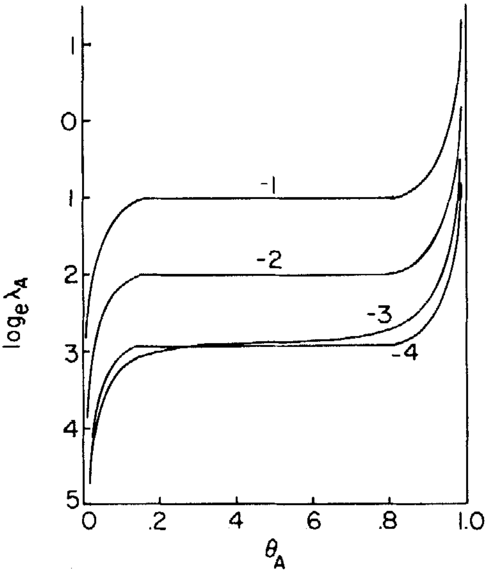

FIG. 3a. Adsorption isotherms for Species A. $w_{AA} = -4$, $w_{BB} = -4$, $w_{AB} = -2 \times 10^{-14}$ erg; other parameters as in Fig. 2a.

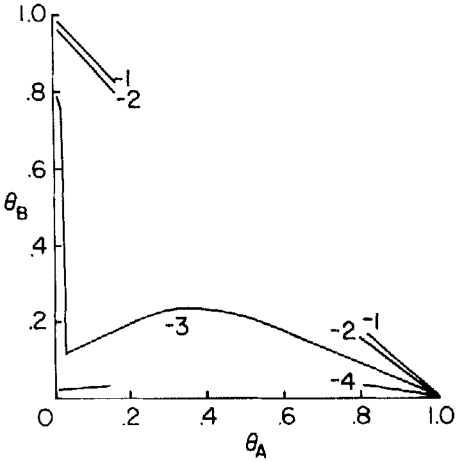

FIG. 3b. The dependence of θ_B on θ_A for the isotherms in Fig. 3a.

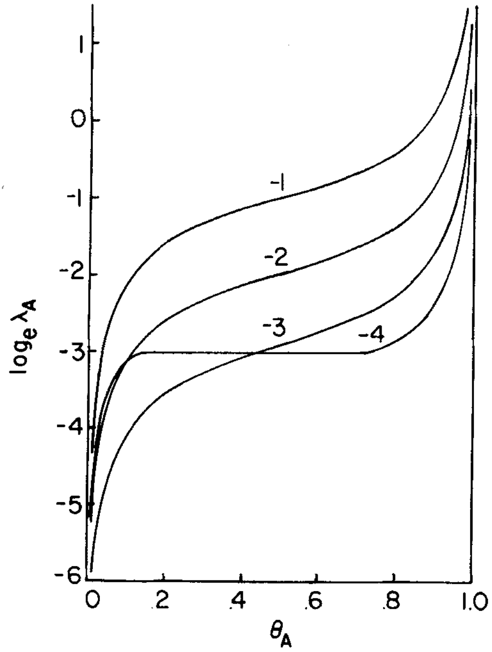

FIG. 4a. Adsorption isotherms for Species A. $w_{AA} = -4$, $w_{BB} = -4$, $w_{AB} = -3 \times 10^{-14}$ erg; other parameters as in Fig. 2a.

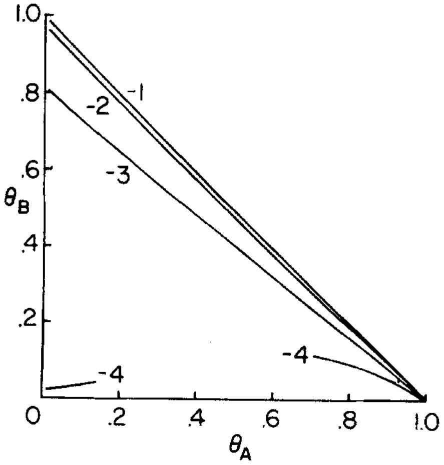

FIG. 4b. The dependence of θ_B on θ_A for the isotherms in Fig. 4a.

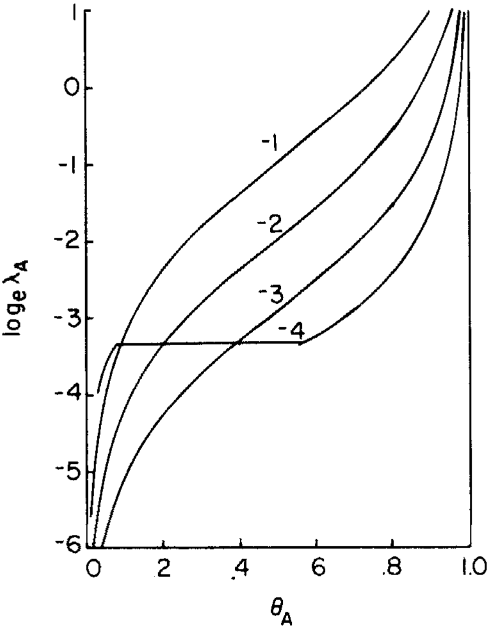

FIG. 5a. Adsorption isotherms for Species A. $w_{AA} = -4$, $w_{BB} = -4$, $w_{AB} = -4 \times 10^{-14}$ erg; other parameters as in Fig. 2a.

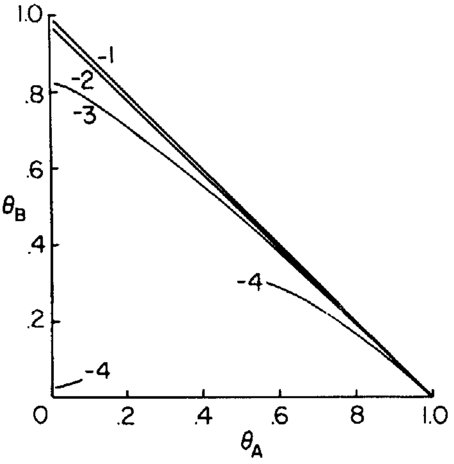

FIG. 5b. The dependence of θ_B on θ_A for the isotherms in Fig. 5a.

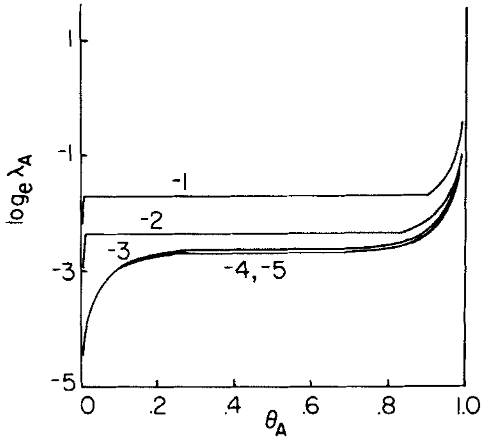

FIG. 6. Adsorption isotherms for Species A. $w_{AA} = -3.5$, $w_{BB} = -3.5$, $w_{AB} = -0.5 \times 10^{-14}$ erg; $\log_e \lambda_B = -1, -2, -3, -4, -5$ as indicated; other parameters as in Fig. 2a.

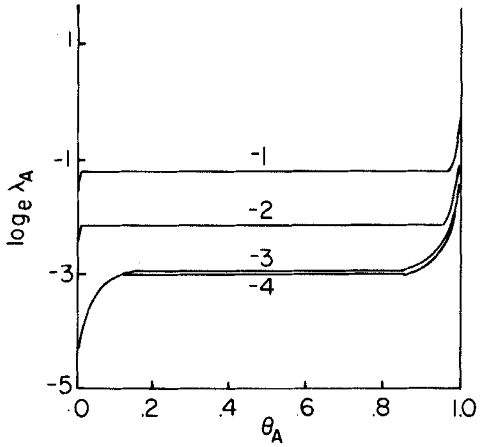

FIG. 7. Adsorption isotherms for Species A. $w_{AA} = -3.5$, $w_{BB} = -3.5$, $w_{AB} = -1.5 \times 10^{-14}$ erg; other parameters as in Fig. 2a.

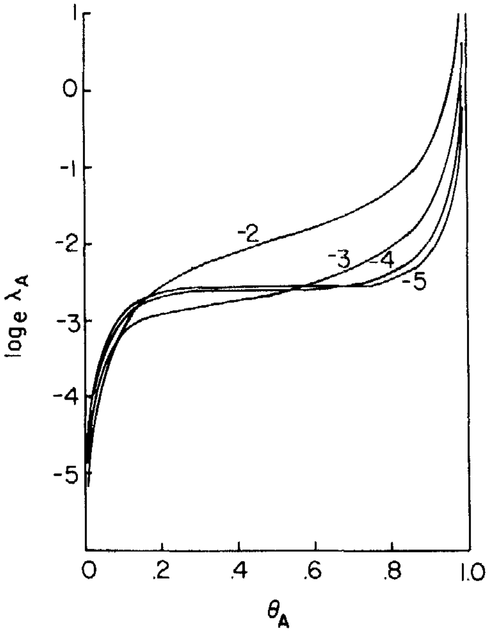

FIG. 8. Adsorption isotherms for Species A. $w_{AA} = -3.5$, $w_{BB} = -3.5$, $w_{AB} = -2.5 \times 10^{-14}$ erg; $\log_e \lambda_B = -1, -2, -3, -4, -5$; other parameters as in Fig. 2a.

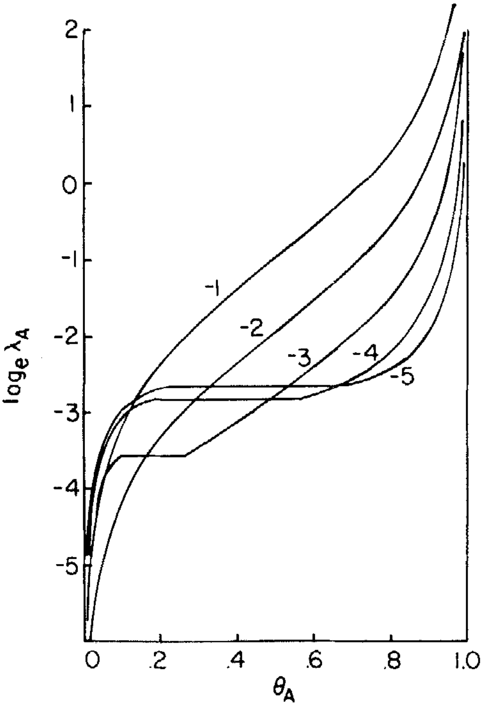

FIG. 9. Adsorption isotherms for Species A. $w_{AA} = -3.5$, $w_{BB} = -3.5$, $w_{AB} = -3.5 \times 10^{-14}$ erg; $\log_e \lambda_B = -1, -2, -3, -4, -5$; other parameters as in Fig. 2a.

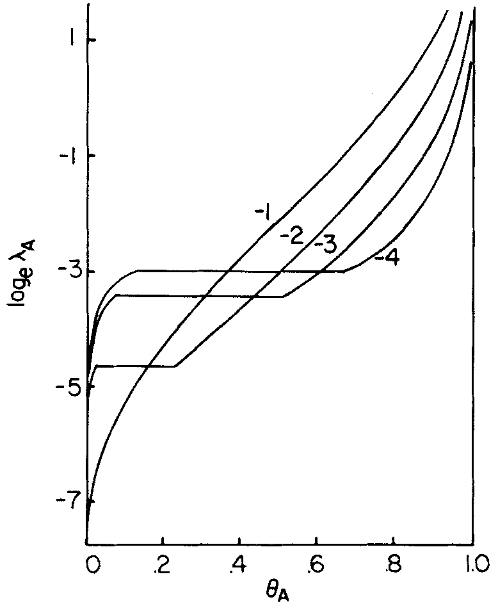

FIG. 10. Adsorption isotherms for Species A. $w_{AA} = -3.5$, $w_{BB} = -3.5$, $w_{AB} = -4.5 \times 10^{-14}$ erg; $\log_e \lambda_B = -1, -2, -3, -4$; other parameters as in Fig. 2a.

intuition, and low cunning. To our knowledge, the use of mixtures of surfactants has not yet been systematically investigated in connection with other foam separations. This might well be worth study, and the model discussed here may prove useful in designing experiments and selecting and optimizing combinations of surfactants for such use.

Also, this model suggests the further study of the surface chemical separation of materials which might be co-adsorbed into the condensed surface phase of a surfactant in a foam from either the gas or the liquid phase and then recovered from the subsequently collapsed foamate. This model (or the simpler Bragg-Williams approach) could readily be used for preliminary optimization of such separations.

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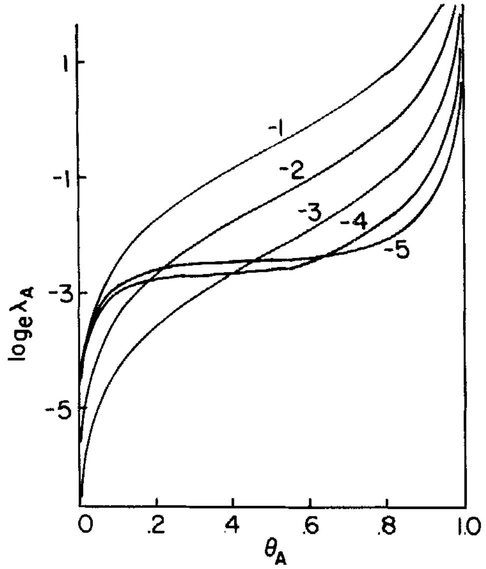

FIG. 11a. Adsorption isotherms for Species A. $w_{AA} = -3$, $w_{BB} = -4$, $w_{AB} = -3.5 \times 10^{-14}$ erg; $\log_e \lambda_B = -1, -2, -3, -4, -5$; other parameters as in Fig. 2a.

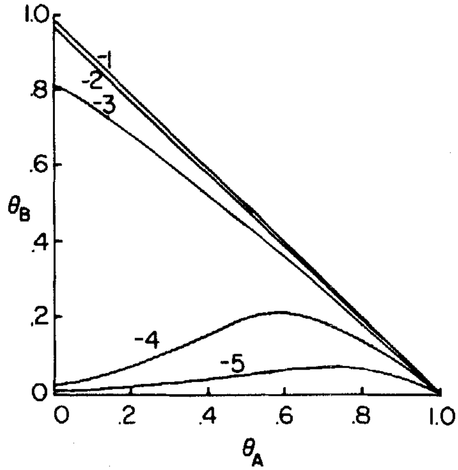

FIG. 11b. The dependence of θ_B on θ_A for the isotherms in Fig. 11a.

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