NOTES

Butler-Type Isotherms of Adsorption for Equimolar Bulk Mixtures of Anionic and Cationic Surfactants in Solutions Containing Excess of Inorganic Electrolyte

INTRODUCTION

Adsorption of cationic–anionic (R^+R^-) surfactants (dissociating into R^+ and R^- ions in the bulk of the solution) in the presence of inorganic electrolyte (MeA) may be described by the adsorption isotherm, based on the generalized Butler equation (1–3)

$$x_{H_2O} \exp\{(-\pi\omega_{H_2O} - \Delta G_{H_2O})/RT\}$$
$$+ 2f_\pm[x_{R^+}x_{A^-} \exp\{(-\pi\omega_{RA} - \Delta G_{RA})/RT\}$$
$$+ x_{R^-}x_{Me^+} \exp\{(-\pi\omega_{MeR} - \Delta G_{MeR})/RT\}$$
$$+ x_{R^+}x_{R^-} \exp\{(-\pi\omega_{R^+R^-} - \Delta G_{R^+R^-})/RT\}$$
$$+ x_{Me^+}x_{A^-} \exp\{(-\pi\omega_{MeA} - \Delta G_{MeA})/RT\}]^{1/2} = 1 \quad [1]$$

where π is the surface pressure, x_i is the bulk molar fraction, ω_i is the partial molar area, ΔG_i is the free energy of adsorption of the respective component, and $f_\pm$ is the mean ionic activity coefficient in the bulk.

The last term under the square root is negligible in these systems and may be safely neglected. When the cationic surfactant (R^+A^-) and the anionic surfactant (Me^+R^-), formed from ions present in the solution differ in their surface activity, then surface solutions contain more of those organic ions, which are more surface active, e.g., $\Gamma_{R^+} > \Gamma_{R^-}$. In such cases also the term related to the single ionic surfactant of lower surface activity may be dropped out from Eq. [1]. Then, adsorption isotherm takes the form (if more surface active ions are organic cations) (4, 5)

$$x_{H_2O} \exp\{(-\pi\omega_{H_2O} - \Delta G_{H_2O})/RT\}$$
$$+ 2f_\pm[x_{R^+}x_{A^-} \exp\{(-\pi\omega_{RA} - \Delta G_{RA})/RT\}$$
$$+ x_{R^+}x_{R^-} \exp\{(-\pi\omega_{R^+R^-} - \Delta G_{R^+R^-})/RT\}]^{1/2} = 1 \quad [2]$$

The adsorption isotherm for anionic–cationic surfactants adsorbing in the absence of inorganic electrolyte is described by

$$x_{H_2O} \exp\{(-\pi\omega_{H_2O} - \Delta G_{H_2O})/RT\} + 2f_\pm(x_{R^+}x_{R^-})^{1/2}$$
$$\times \exp\{(-\pi\omega_{R^+R^-} - \Delta G_{R^+R^-})/2RT\} = 1 \quad [3]$$

This form of the adsorption isotherm may be also used for equimolar mixtures of anionic and cationic surfactants in the absence of other salts. In this case, adsorption of single ionic surfactants $(R^+A^-$ and $Me^+R^-)$ is negligible in comparison to adsorption of the cationic–anionic

surfactant (R^+R^-) and both terms describing adsorption of single ionic surfactants in Eq. [1] are negligible (6).

The last equation was next used for describing the adsorption of cationic–anionic surfactants in the presence of excess of inorganic electrolyte formed of ions common with the surfactants (7, 8).

The aim of this note is to give an answer to the questions: (i) why Eq. [3] appears satisfactory beyond the limits of its applicability (7, 8); (ii) do the parameters of adsorption, resulting from fitting Eq. [3], give the proper values of surface tension of solutions containing inorganic electrolytes; (iii) how far are the adjusted values of the free energy of adsorption from the values which would be obtained using the more adequate equation of the adsorption isotherm (Eq. [2]).

DISCUSSION

Although some mixtures described in (8) are not equimolar in organic ions in the surface (9), adjustment of Eq. [3] is satisfactory over a wide range of surfactant concentrations. The simplest reason of this fact would be obviously the constant ratio of surface concentrations of organic ions (i.e., $\Gamma_{R_nPy^+}/\Gamma_{R_nSO_3^-} = $ const.) over this range of surfactants concentrations. This is not the case however (9).

Let us find the mathematical conditions for simultaneous application of the isotherm [2] and the equation

$$x_{H_2O} \exp\{(-\pi\omega_{H_2O} - \Delta G^*_{H_2O})/RT\} + 2f_\pm(x_{R^+}x_{R^-})^{1/2}$$
$$\times \exp\{(-\pi\omega_{R^+R^-} - \Delta G^*_{R^+R^-})/2RT\} = 1 \quad [3']$$

to the results presented in (7, 8), where the values $\Delta G^*_{H_2O}$ and $\Delta G^*_{R^+R^-}$ are the apparent values of these parameters, resulting from fitting Eq. [3']. Both values of ΔG_{H_2O} and $\Delta G^*_{H_2O}$ are usually low (4–8, 10) and not much different. So, as $\Delta G_{H_2O} \approx \Delta G^*_{H_2O}$ and $x_{R^+} = x_{R^-} = x_R$, we obtain

$$x_{R^+}x_{A^-} \exp\{(-\pi\omega_{RA} - \Delta G_{RA})/RT\}$$
$$+ x_R^2 \exp\{(-\pi\omega_{R^+R^-} - \Delta G_{R^+R^-})/RT\}$$
$$= x_R^2 \exp\{(-\pi\omega_{R^+R^-} - \Delta G^*_{R^+R^-})/RT\} \quad [4]$$

and

$$\pi = \left(\frac{\omega_{R^+R^-} - \omega_{RA}}{RT}\right)^{-1}\left[\ln x_R - \ln x_A\right.$$
$$\left. + \ln\left\{\exp\frac{\Delta G_{RA} - \Delta G^*_{R^+R^-}}{RT} - \exp\frac{\Delta G_{RA} - \Delta G_{R^+R^-}}{RT}\right\}\right]$$

$$[5]$$

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In all previous papers, discussed here, the values of ΔG and ΔG^* were taken as composition independent. Thus, Eq. [5] corresponds to a linear relationship (x_{A^-} = const., when the sufficient excess of inorganic electrolyte is present)

$$\pi = A + B \ln x_R \qquad [6]$$

where

$$B = \left(\frac{\omega_{R^+R^-} - \omega_{RA}}{RT}\right)^{-1}$$

$$A = B\left[-\ln x_{A^-} + \ln\left\{\exp\frac{\Delta G_{RA} - \Delta G^*_{R^+R^-}}{RT}\right.\right.$$
$$\left.\left. - \exp\frac{\Delta G_{RA} - \Delta G_{R^+R^-}}{RT}\right\}\right]$$

Thus, a satisfactory adjustment of Eq. [3'] to the experimental data on surface tension of equimolar bulk mixtures of anionic and cationic surfactants differing in surface activity, in the presence of inorganic electrolyte excess, may be expected over a region of saturation adsorption.

Application of Eq. [6] makes possible estimation of the real values of $\Delta G_{R^+R^-}$ from the apparent values of $\Delta G^*_{R^+R^-}$ if values of ΔG_{RA} are also known.

Possibility of satisfactory adjustment Eq. [3'] to the experimental data for systems of surface highly assymetric in organic ions, over a range of π changing linearly with x_R has been confirmed for the data presented earlier [10]. Such procedure leads however to the values $\Delta G^*_{R^+R^-}$ more negative than the values $\Delta G_{R^+R^-}$ resulting from Eq. [2], as if the cationic–anionic surfactant was more surface active than it is itself. For example, the value of $\Delta G^*_{R^+R^-}$ resulting for dodecyltrimethylammonium hexylsulfate from Eq. [3'] is equal to about -15.7 kcal/mole for mixtures of dodecyltrimethylammonium perchlorate with sodium hexylsulfate in 0.01 M NaClO$_4$. The same $\Delta G^*_{R^+R^-}$ value is about -14.7 kcal/mole for mixtures of dodecyltrimethylammonium bromide with sodium hexylsulfate in 0.25 M NaBr. Fitting Eq. [2] gives for $\Delta G_{R^+R^-}$ one value of -14.4 kcal/mole for both systems (10).

Assuming $\omega_{R^+R^-} = 50$ A^2/molecule (4, 5, 7, 8) one may expect the change of $\Delta G_{R^+R^-}$ (in kcal/mole) equal to about 0.07 change of π (in mN/m): $\delta\Delta G_{R^+R^-} \approx 0.07\delta\pi$. It means that if all other parameters of adsorption remained constant, a change in the value of $\Delta G_{R^+R^-}$ equal to 0.3 kcal/mole would lead to variation in π of about 4 mN/m.

The region of satisfactory adjustment of Eq. [3'] in (8) is broader than a linear relationship of π vs ln c_R (9), so there should be also another answer to the first question. It comes out straight from experimental data. It has been shown (10, 11) that over a range of inorganic electrolyte concentration, its addition to the equimolar mixtures of cationic and anionic surfactants, differing in surface activity, affects only little the surface pressure of solutions, although it changes the ratio of organic anions and cations in the surface. The region of practically invariant π would be obviously much narrower for the systems containing such ions as ClO$_4^-$ (10) or I$^-$ (12). So long as variations of π upon addition of inorganic salt to the mixed solutions of oppositely charged organic ions are not significant, fitting Eq. [3'] to the experimental data is possible and would lead to the values of $\Delta G^*_{R^+R^-}$ similar to those which would be obtained for simple aqueous solutions, i.e., in the absence of added inorganic electrolyte. Thus, the values $\Delta G^*_{R^+R^-}$ will be reasonable, and hence also the values of surface pressure and of the sum ($\Gamma_{R^+} + \Gamma_{R^-}$), corresponding to the range of satisfactory adjustment of Eq. [3'], obtained from this equation, will also be reasonable. On the other hand, Γ_{R^+}, Γ_{R^-}, $x^s_{R^+}$, and $x^s_{R^-}$ resulting from Eq. [3'] would be erroneous, indicating surface layers totally symmetric in organic ions, which is not true.

Concluding, one may state that application of Eq. [3'] leads to the real values of the free energy of cationic–anionic surfactants adsorption in the absence of inorganic electrolyte. The values of $\Delta G^*_{R^+R^-}$ obtained in the presence of inorganic salts are numerically equal to the real values of $\Delta G_{R^+R^-}$ as long as addition of electrolyte does not effectively influence the surface tension of solutions.

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