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Adsorption of Dodecyltrimethylammonium Chloride–Decylammonium Chloride Mixtures at Water/Air Interface

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The surface tension of the aqueous solution of dodecyltrimethylammonium chloride and decylammonium chloride mixture has been measured as a function of the total concentration and composition of the surfactants at 298.15 K under atmospheric pressure. It has been observed that the surface tension decreases with an increase in the composition of dodecyltrimethylammonium chloride at a fixed total concentration. A break point has been observed on the surface tension *vs.* total concentration curve. By applying the thermodynamic relations, the surface densities of surfactants have been evaluated numerically. It has been proved that the phase transition of the mixed adsorbed film takes place from a gaseous to an expanded state at the break point. By comparing the composition in the adsorbed film with that in the bulk phase, the difference between the compositions has been found to diminish as the surface tension decreases. It has been shown that the mutual relation between the compositions of the gaseous and expanded films at the transition point is described by the two-dimensional phase diagram.

The surface tension of the aqueous solution of surfactant mixture has been measured extensively and analyzed by applying the Gibbs adsorption equation.[1–14] However, most studies have been conducted in connection with the formation of mixed micelle at relatively high concentrations. In a recent paper,[15] we have investigated the adsorption of dodecylammonium chloride (DAC)–decylammonium chloride (DeAC) mixture at water/air interface in a relatively dilute concentration region; it has been shown that the phase transition of the mixed adsorbed film takes place from a gaseous state to an expanded one and its behavior can be treated thermodynamically by extending our method.[16] Further it has been shown that the two-dimensional phase diagram is useful to clarify the relation between the two coexisting phases.

In order to make sure that the occurence of the phase transition in mixed adsorbed films is a general phenomenon and our thermodynamic treatment is useful, we will investigate the mixed system of dodecyltrimethylammonium chloride (DTAC), of which the adsorbed film is accompanied by the phase transition,[17] with DeAC. The surface tension of the aqueous solution will be measured as a function of the total concentration and composition of the surfactants at constant temperature and pressure and analyzed by the thermodynamic equations advanced.

Experimental

Decylammonium chloride and dodecyltrimethylammonium chloride were synthesized and purified by the methods described previously.[15,17] Their purities were checked by the elementary analysis and guaranteed by the absence of minimum near the critical micelle concentration on the surface tension *vs.* concentration curves at 298.15 K. Water was distilled triply from alkaline permanganate.

The surface tension of solutions was measured by the drop volume technique described previously.[16] The temperature was kept constant at 298.15±0.01 K by immersing the measuring cell in a thermostat. The error estimated for the surface tension value was less than 0.05 mN m^{-1}.

Results and Discussion

The system under consideration is composed of two bulk phases and four components. Let us choose the total molality of surfactants m_t^W in the aqueous solution defined by

$$m_t^W = m_1^W + m_2^W, \tag{1}$$

and the composition of the second surfactant X_2^W defined by

$$X_2^W = m_2^W/(m_1^W+m_2^W), \tag{2}$$

as the thermodynamic independent variables at constant temperature T and pressure p. The subscripts 1 and 2 refer to DTAC and DeAC, respectively. The surface tension γ of the aqueous solution of surfactant mixture was measured as a function of m_t^W at fixed X_2^W and at 298.15 K under atmospheric pressure.

The values of γ are plotted against m_t^W at various X_2^W values in Fig. 1(a). It is seen that the curve has a break point and the m_t^W value of the break point increases, while the γ value decreases, as X_2^W increases. This can be seen more clearly from Fig. 1(b) which is the magnification of the γ *vs.* m_t^W curve in the neighborhood of the break point in Fig. 1(a). We confirmed the presence of the break by the fact that any extrapolation of the γ *vs.* m_t^W curve from concentrations above the break to zero concentration never gives, even if the experimental error is taken into account, the value for the pure water/air interface.[15] It has been proved thermodynamically that the presence of a break point on the surface tension *vs.* concentration curve means the phase transformation between two states in the adsorbed film.[15–17] Here also we may say that the phase transition takes place in the mixed adsorbed film of DTAC and DeAC.

In Fig. 2, the γ *vs.* X_2^W curves at fixed m_t^W values are illustrated, which are obtained from Fig. 1. It is found that γ increases with X_2^W and some curves have break points which are linked by the dotted line. It will be proved later that the region above and below the dotted line correspond to the gaseous and expanded states, respectively.

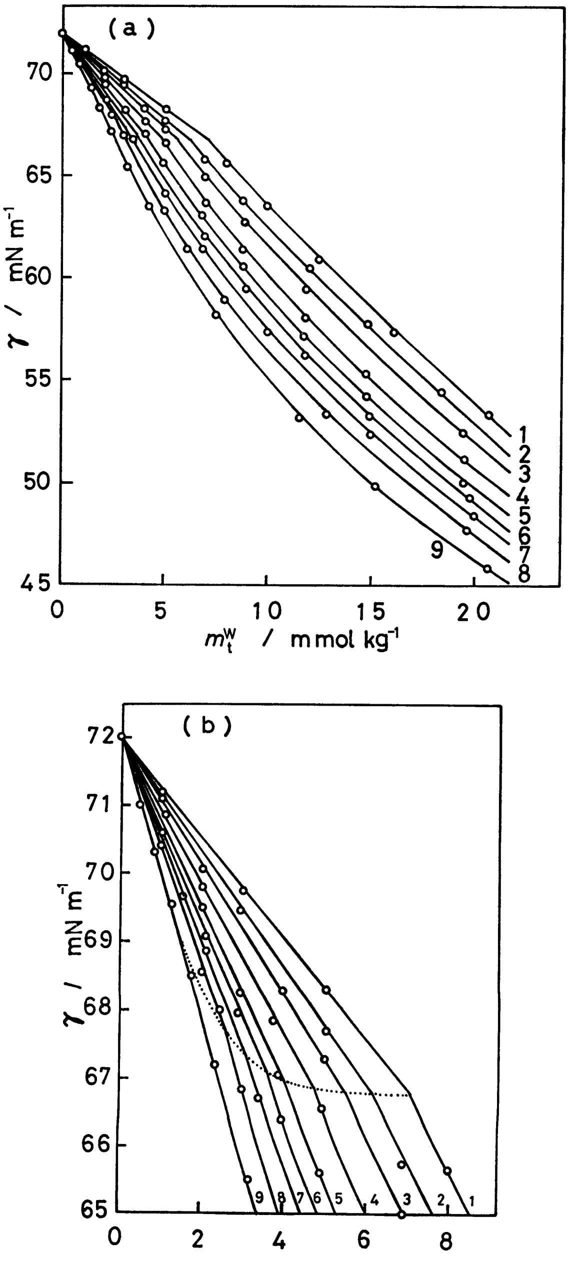

Fig. 1. Surface tension *vs.* total molality curves at constant bulk composition. (1) $X_2^W=1$, (2) 0.950, (3) 0.894, (4) 0.800, (5) 0.697, (6) 0.601, (7) 0.498, (8) 0.300, (9) 0.

Now let us consider the evaluation of the surface excess number of moles per unit area, Γ_i^H, of surfactant *i* defined with respect to the two dividing planes which are positioned so as to make the surface excess numbers of moles of water and air be zero.[18] Both surfactants in the present study are uni-uni valent strong electrolytes, which have the common anion and dissociate completely into ions. Then the surface tension can be expressed as a function of the total molality m_t^W and the composition X_2^W at constant temperature and pressure as[15]

$$d\gamma = -2RT[(\Gamma_1^H+\Gamma_2^H)/m_t^W]dm_t^W$$
$$-RT[(X_1^W\Gamma_2^H-X_2^W\Gamma_1^H)/X_1^WX_2^W]dX_2^W. \quad (3)$$

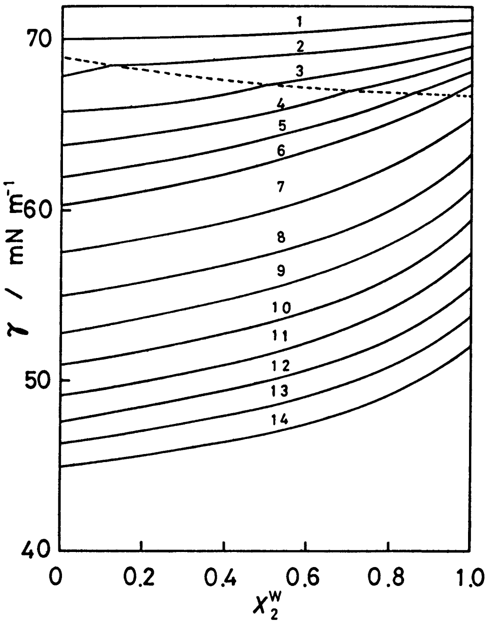

Fig. 2. Surface tension *vs.* bulk composition curves at constant total molality. (1) $m_t^W=1$ mmol kg^{-1}, (2) 2, (3) 3, (4) 4, (5) 5, (6) 6, (7) 8, (8) 10, (9) 12, (10) 14, (11) 16, (12) 18, (13) 20, (14) 22.

Introducing the total surface density Γ_t^H defined by

$$\Gamma_t^H = \Gamma_1^H + \Gamma_2^H, \quad (4)$$

Γ_t^H is found to be related to the change in γ with m_t^W at fixed X_2^W by the expression

$$\Gamma_t^H = -(m_t^W/2RT)(\partial\gamma/\partial m_t^W)_{T,p,X_2^W}, \quad (5)$$

which is derived from Eq. 3. On the other hand, the derivative of γ with respect to X_2^W at constant m_t^W is related to X_2^H in the form

$$X_2^H = X_2^W - (X_1^WX_2^W/RT\Gamma_t^H)(\partial\gamma/\partial X_2^W)_{T,p,m_t^W}, \quad (6)$$

where X_2^H is the composition of DeAC in the adsorbed film defined by

$$X_2^H = \Gamma_2^H/\Gamma_t^H. \quad (7)$$

Combination of Eqs. 5 and 6 gives the values of Γ_1^H and Γ_2^H. Further, Eq. 6 provides information regarding the difference between the compositions of surfactants in the adsorbed film and aqueous solution under the condition that *T*, *p*, and m_t^W are kept constant. It is noteworthy that the relation between X_2^H and X_2^W, when *T*, *p*, and γ are specified, is given by

$$X_2^H = X_2^W - (2X_1^WX_2^W/m_t^W)(\partial m_t^W/\partial X_2^W)_{T,p,\gamma}. \quad (8)$$

By applying Eq. 5 to the experimental data shown in Fig. 1, the value of Γ_t^H can be evaluated numerically. The Γ_t^H *vs.* m_t^W curves at various X_2^W values are drawn in Fig. 3. It should be noted that the values of Γ_t^H increase monotonously with increase in X_2^W although they change discontinuously at the m_t^W value of the break point in Fig. 1. Taking into account that the values of Γ_t^H at the discontinuous point are similar in magnitude to those of the DAC–DeAC system,[15] we can conclude that the phase transition occurs between a gaseous and an expanded state. It deserves further attention that the difference in the Γ_t^H value

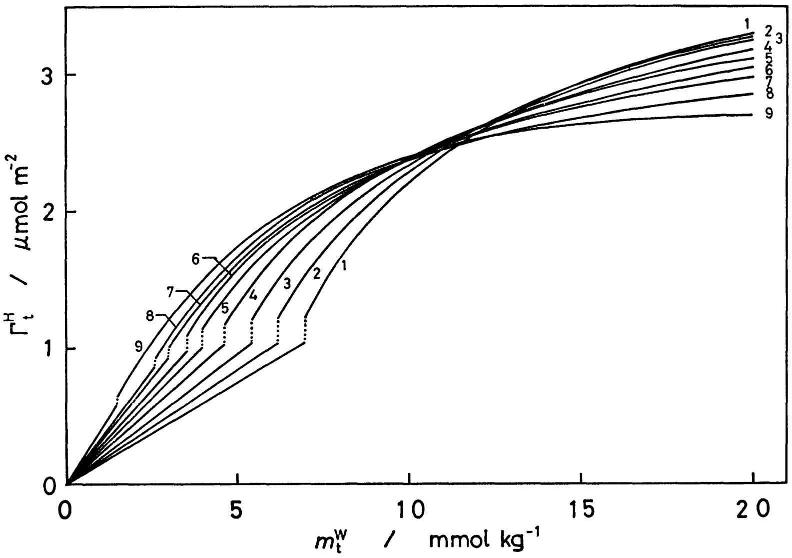

Fig. 3. Total surface density *vs.* total molality curves at constant bulk composition. (1) $X_2^{\rm W}=1$, (2) 0.950, (3) 0.894, (4) 0.800, (5) 0.697, (6) 0.601, (7) 0.498, (8) 0.300, (9) 0.

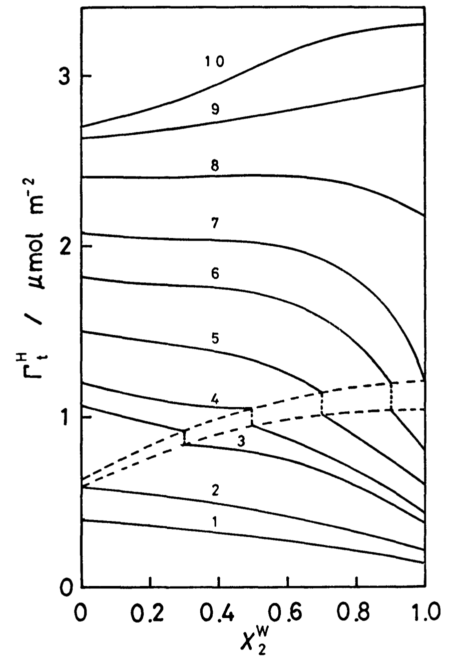

Fig. 4. Total surface density *vs.* bulk composition curves at constant total molality. (1) $m_t^{\rm W}=1$ mmol kg^{-1}, (2) 1.5, (3) 2.6, (4) 3, (5) 4, (6) 5.45, (7) 7, (8) 10, (9) 15, (10) 20.

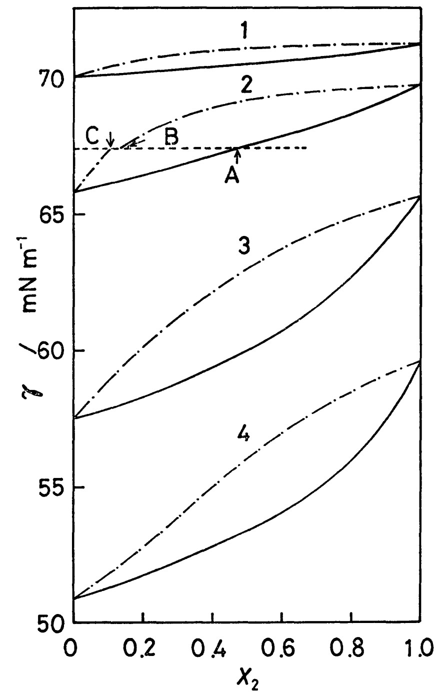

Fig. 5. Surface tension *vs.* composition curves at constant total molality. (1) $m_t^{\rm W}=1$ mmol kg^{-1}, (2) 3, (3) 8, (4) 14, (——) γ *vs.* $X_2^{\rm W}$, (----) γ *vs.* $X_2^{\rm H}$.

between the two states becomes large as $X_2^{\rm W}$ increases.

In Fig. 4, the variation of $\Gamma_t^{\rm H}$ with $X_2^{\rm W}$ is drawn at constant $m_t^{\rm W}$. It is seen that the value of $\Gamma_t^{\rm H}$ decreases with increasing $X_2^{\rm W}$ at a smaller value of $m_t^{\rm W}$. However, the dependence of $\Gamma_t^{\rm H}$ on $X_2^{\rm W}$ reverses at about 11 mmol kg^{-1} in the expanded film. This observation seems to indicate that the hydrocarbon chain length of the surfactant has a great influence on the adsorption at water/air interface when the value of $\Gamma_t^{\rm H}$ is relatively small, but the effect of the size of ionic head group of DTAC becomes predominant as the value of $\Gamma_t^{\rm H}$ increases.

Next let us evaluate the composition of surfactants in the adsorbed film at given T, p, and $m_t^{\rm W}$. Applying Eq. 6 to the γ *vs.* $X_2^{\rm W}$ curve shown in Fig. 2, the value of $X_2^{\rm H}$ can be calculated as a function of $X_2^{\rm W}$. In Fig. 5, the results are illustrated in the form of the γ *vs.* $X_2^{\rm H}$ as well as the corresponding γ *vs.* $X_2^{\rm W}$ curve at various $m_t^{\rm W}$ values. We can read the relation between $X_2^{\rm H}$ and $X_2^{\rm W}$ at a given value of γ from the diagram indicated by 1 in the gaseous film and from the diagrams 3 and 4 in the expanded film. They are similar

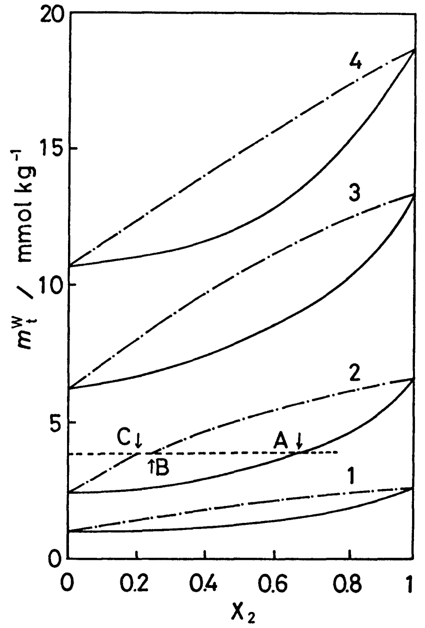

Fig. 6. Total molality *vs.* composition curves at constant surface tension. (1) $\gamma=70\,\mathrm{mN\,m^{-1}}$, (2) 67, (3) 60, (4) 55, (——) m_t^W *vs.* X_2^W, (----) m_t^W *vs.* X_2^H.

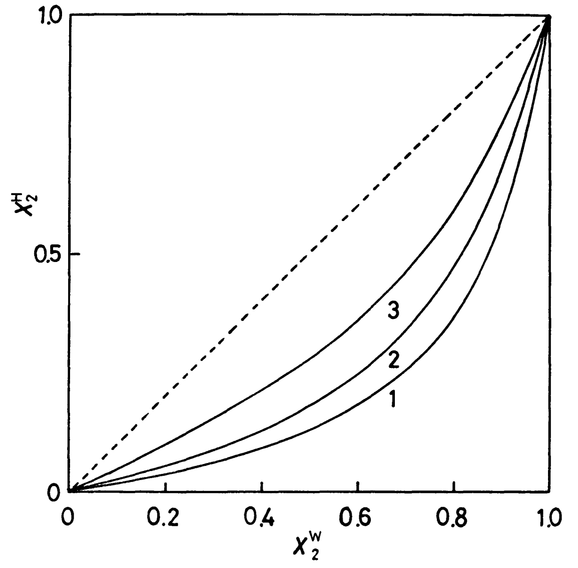

Fig. 7. Surface composition *vs.* bulk composition curves at constant surface tension. (1) $\gamma=70\,\mathrm{mN\,m^{-1}}$, (2) 60, (3) 50.

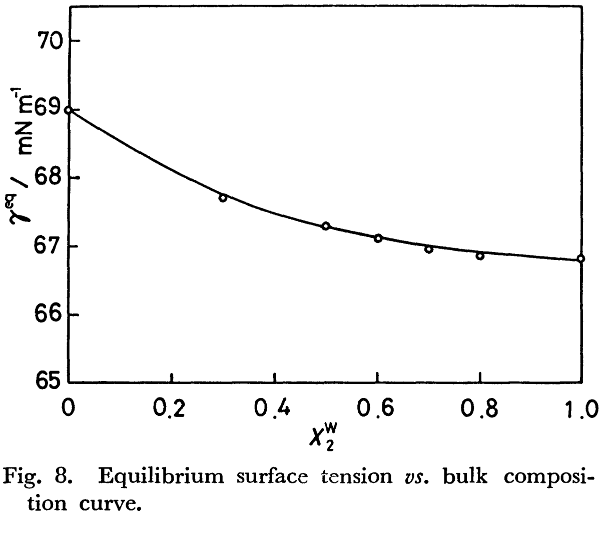

Fig. 8. Equilibrium surface tension *vs.* bulk composition curve.

in form to each other although the former takes the shape of a deflated cigar and the latters of a swollen cigar. However the diagram is slightly complex when the phase transition takes place in the adsorbed film. At $m_t^W=3\,\mathrm{mmol\,kg^{-1}}$ (the diagram 2), the γ *vs.* X_2^W curve breaks at the point A and the γ *vs.* X_2^H curve changes discontinuously from the point B of the gaseous film to the point C of the expanded film. It should be noted that the alteration in the slope at A is related closely to the difference between the X_2^H values of B and C.

Further the value of X_2^H at constant T, p, and γ can be calculated by use of Eq. 8. The m_t^W *vs.* X_2^H and m_t^W *vs.* X_2^W are shown in Fig. 6. It is seen that the essential form of the diagram is quite similar to that in Fig. 5. It is important to note that the diagram 2, like the diagram 2 in Fig. 5, has a break point on the m_t^W *vs.* X_2^W curve and a discontinuous change on the m_t^W *vs.* X_2^H curve.

An interesting feature is manifested by plotting the value of X_2^H against X_2^W. The results at constant γ is illustrated in Fig. 7. We can see that the curve recedes from the diagonal line as the surface tension increases, *i.e.*, the difference between the compositions in the bulk phase and in the adsorbed film becomes large as the surface tension increases. This observation coincides with our previous result of the mixed system of DAC and DeAC.[15] Taking into account that DTAC and DAC are more surface active than DeAC, these facts indicate that the fraction of the more surface active molecule in the adsorbed film is enhanced remarkably at a larger value of γ.

Next, we shall elucidate the mutual relation between the compositions of the gaseous and expanded films at the phase transition point in connection with the two-dimensional phase diagram. When the two phases coexist in equilibrium, $X_2^{H,g}$ and $X_2^{H,e}$ are related to the equilibrium surface tension γ^{eq} by the expression

$$X_2^{H,g}-X_2^{H,e}=[X_1^W X_2^W(1/\Gamma_t^{H,e}-1/\Gamma_t^{H,g})/RT] \times(\partial\gamma^{eq}/\partial X_2^W)_{T,p}\,. \qquad (9)$$

It is important to recognize that the variation in γ^{eq} with X_2^W, which is illustrated in Fig. 8, is determined by the difference $X_2^{H,g}-X_2^{H,e}$. By virtue of the diagram 2 in Fig. 5 and analogues, attended by the phase transition, we can obtain the γ^{eq} *vs.* $X_2^{H,g}$ and γ^{eq} *vs.* $X_2^{H,e}$ curves which are drawn in Fig. 9. It was found that the numerical value of $X_2^{H,g}-X_2^{H,e}$ calculated by applying Eq. 9 to the curve in Fig. 8 is approximately equal to the corresponding one in Fig. 9. This fact thermodynamically proves that the phase transition does take place at the break point on the γ *vs.* m_t^W curves.

It is seen in Fig. 9 that the value of $X_2^{H,e}$ is smaller than that of $X_2^{H,g}$. This means that the fraction of the more surface active component in the expanded film is larger than that in the gaseous film. A similar

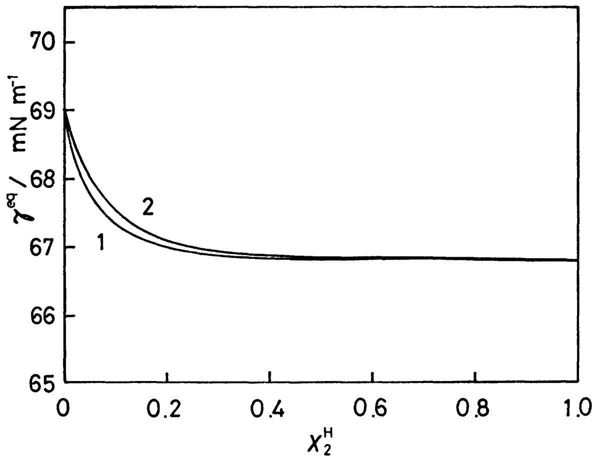

Fig. 9. Equilibrium surface tension *vs.* surface composition curves. (1) γ^{eq} *vs.* $X_2^{H,e}$, (2) γ^{eq} *vs.* $X_2^{H,g}$.

result has been obtained for the mixed adsorbed film of DAC and DeAC.15) It is important to note that such a behavior has been observed in the case of mixed insoluble films on water if their equilibrium surface pressure *vs.* composition curves have no extremum.19) Therefore, Fig. 9 is the two-dimensional phase diagram of the transition between the gaseous and expanded states of DTAC–DeAC mixed adsorbed film at 298.15 K under atmospheric pressure. It may be concluded that the phase transition in the mixed adsorbed film is described by the phase diagram like that in the mixed insoluble monolayer.

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