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Effect of Pressure on the Adsorption and Micelle Formation of Aqueous Dodecyltrimethylammonium Chloride-Cyclohexane System

Michio Yamanaka,*,† Makoto Aratono, and Kinsi Motomura
Department of Chemistry, Faculty of Science, Kyushu University 33,
Fukuoka 812

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The interfacial tension of aqueous dodecyltrimethylammonium chloride (DTAC) solution–cyclohexane system was measured as a function of pressure at concentrations around the critical micelle concentration (cmc). The derivative of interfacial tension with respect to pressure was observed to change abruptly at the cmc. The volume changes associated with the adsorption of DTAC from its monomeric and micellar states and the volume of micelle formation were calculated and compared with the corresponding ones of the aqueous DTAC solution–hexane system. It was found that the molar interfacial excess volume of the adsorbed film is slightly larger than the molar volume of micelle in the case of the cyclohexane system, while in the case of the hexane system the former is approximately equal to the latter. Further, it was concluded that the micellar particles solubilize molecules of the oil coexisting in equilibrium with the aqueous solution. It was also proved in the case of the present system that the micelle formation can be treated thermodynamically as the appearance of a macroscopic bulk phase in the solution.

In the preceding papers,[1,2] the interfacial tension of the aqueous solutions of dodecylammonium chloride (DAC) and dodecyltrimethylammonium chloride (DTAC) against hexane has been measured as a function of pressure. By applying the thermodynamic equations derived previously,[3] the volumes of adsorption of the surfactants from their monomeric and micellar states and the volume of micelle formation have been evaluated; the micelles of DAC and DTAC in equilibrium with hexane have been found to be similar in volumetric behavior to their adsorbed films at the solution/hexane interface. Further, our thermodynamic method has been proved to be useful.

On the other hand, organic liquids are known to have an influence on the critical micelle concentration and adsorption isotherm of surfactant.[4] Therefore, it is of interest to see if the above conclusions are drawn by using other organic liquid in place of hexane. Furthermore, it is important to investigate how the volumetric behavior of the micelle and adsorbed film of surfactant is affected by the organic liquid coexisting with its aqueous solution. In this work, we adopt cyclohexane as the organic liquid. The interfacial tension between aqueous DTAC solution and cyclohexane is measured as a function of pressure at various concentrations at a constant temperature.

Experimental

Dodecyltrimethylammonium chloride was prepared and purified as described in the previous papers.[2,5] Water was triply distilled from alkaline permanganate solution. Cyclohexane (Nakarai Chemicals, Ltd., UV spectrophotometric grade) was used after being distilled.

The equilibrium interfacial tension was measured by the pendant drop method[1,6] within an experimental error of 0.05 mN m^{-1}. The pendant drops were stood for 30 min to attain the thermodynamic equilibrium. The density of cyclohexane taken from the literature,[7] was used to calculate the interfacial tension at high pressures. The pressure range measured was from atmospheric pressure to the freezing pressure of cyclohexane (about 37 MPa). Temperature was kept constant at 298.15 K.

Results and Discussion

The interfacial tension γ between aqueous dodecyltrimethylammonium chloride (DTAC) solution and cyclohexane was measured as a function of pressure p at constant molality m_1 of DTAC and at 298.15 K. The γ vs. p curves at lower concentrations are shown in Fig. 1 and those at higher ones in Fig. 2. It is seen from Fig. 1 that the curves of the aqueous solutions of DTAC at concentrations below the critical micelle concentration (cmc; e.g., 21.89 mmol kg^{-1} at 0.1 MPa, see Fig. 5) are convex upward, while the curve of the pure water is linear. From Fig. 2, on the other hand, the curve at a concentration above the cmc is seen to be linear and have a very small slope compared to the curve of the pure water. At a concentration near the cmc, the curve has a linear portion, of which the upper limit is indicated by an arrow, at lower pressure.

The pressure effect on the adsorption can be visualized by plotting the slope of the γ vs. p curve, which is related directly to the volume change associated with the adsorption, against molality m_1 at several pressure values. Figure 3 shows the $\partial\gamma/\partial p$ vs. m_1 curves at 0.1, 15, and 30 MPa. It is seen that the $\partial\gamma/\partial p$ value varies with pressure in the concentration range below the cmc, while in the concentration range above the cmc it remains unvaried. Further, it is observed that the curve changes discontinuously at the cmc.

Next, let us consider the concentration dependence

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† Present address: Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Fukuoka 810.

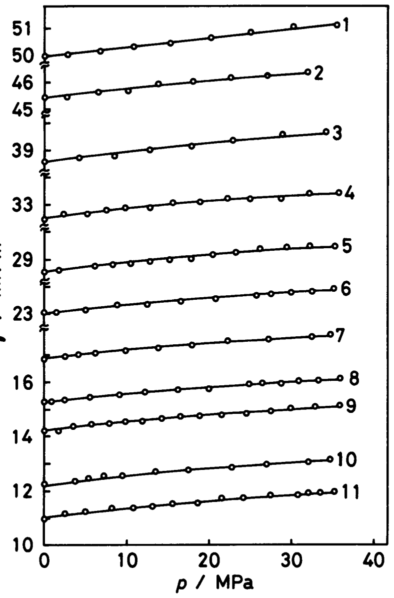

Fig. 1. Interfacial tension vs. pressure curves at constant total molality and at 298.15 K (lower concentration region). m_1=(1): 0 mmol kg^{-1}, (2): 0.20, (3): 1.03, (4): 2.61, (5): 4.02, (6): 6.94, (7): 12.04, (8): 14.00, (9): 14.97, (10): 17.71, (11): 19.56.

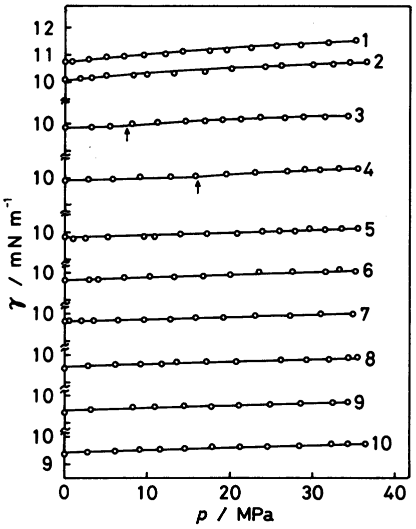

Fig. 2. Interfacial tension vs. pressure curves at constant total molality and at 298.15 K (higher concentration region). m_1=(1): 20.17 mmol kg^{-1}, (2): 21.49, (3): 22.22, (4): 22.54, (5): 23.32, (6): 25.02, (7): 27.10, (8): 30.60, (9): 35.03, (10): 40.19.

of the interfacial tension at constant pressure. In Fig. 4, the γ vs. m_1 curves, which are drawn by making use of the interpolated γ values taken from the γ vs. p curves in Figs. 1 and 2, are shown in the concentration range around the cmc. Included in this figure for comparison is the γ vs. m_1 curve of the system of aqueous DTAC solution and hexane at 0.1 MPa.[2] The γ vs. m_1 curve is observed to break at the cmc sharply enough to determine the precise value of the cmc. The dependence of the interfacial tension on pressure and concentration observed above is qualitatively similar to that made on the systems of the aqueous solutions of dodecylammonium chloride (DAC)[1] and DTAC[2] and hexane.

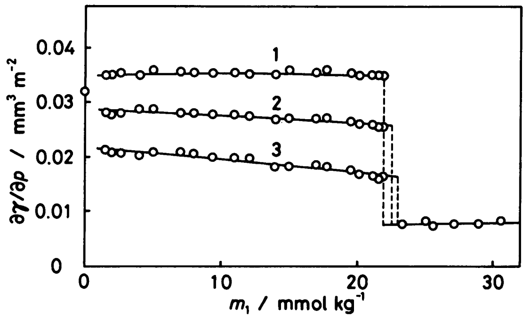

Fig. 3. Derivative of interfacial tension with respect to pressure vs. total molality curves at constant pressure and at 298.15 K. (1): 0.1 MPa, (2): 15 MPa, (3): 30 MPa.

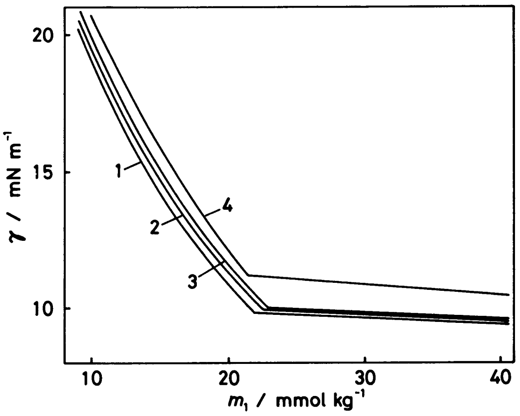

Fig. 4. Interfacial tension vs. total molality curves at constant pressure and at 298.15 K (around cmc). (1): 0.1 MPa, (2): 15 MPa, (3): 30 MPa, (4): aq DTAC/hexane, 0.1 MPa.

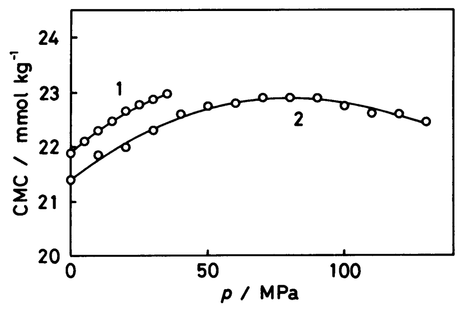

Fig. 5. Critical micelle concentration vs. pressure curves at 298.15 K. (1): aq DTAC/cyclohexane, (2): aq DTAC/hexane.

In Fig. 5, the cmc values obtained from the curves given in Fig. 4 and their analogs are shown as a function of pressure and compared with those of the aqueous DTAC solution–hexane system.[2] The values of the cyclohexane system are found to be slightly different from those of the hexane system within the pressure range measured. Taking into account that the γ vs. m_1 curve of the cyclohexane system is shifted from that of the hexane system, such a difference suggests that the cyclohexane and hexane molecules take a place in the micelle formation of DTAC molecules in the aqueous solution.

According to the thermodynamic treatment developed previously,[1,3] the partial derivative of the interfacial tension with respect to pressure at constant temperature and molality shown in Fig. 3 provides the volume change per unit area associated with the adsorption of surfactant from its monomeric state, $\Delta v(1)$, at a concentration below the cmc and that from its micellar state, $\Delta v(\mathrm{M})$, at a concentration above the cmc; they are respectively defined by

$$\Delta v(1) = \Gamma_1^{\mathrm{H}}(v^{\mathrm{H}}/\Gamma_1^{\mathrm{H}} - v_1^{\mathrm{W}}) \tag{1}$$

and

$$\Delta v(\mathrm{M}) = \Gamma_1^{\mathrm{H}}(v^{\mathrm{H}}/\Gamma_1^{\mathrm{H}} - v^{\mathrm{M}}/N_1^{\mathrm{M}}), \tag{2}$$

where v^{H} is the interfacial excess volume per unit area, v^{M} the molar volume of micelle defined as the excess one with respect to the spherical dividing surface which makes the excess number of moles of water zero,[8] v_1^{W} the partial molar volume of monomeric surfactant, Γ_1^{H} the interfacial excess number of moles of surfactant per unit area, and N_1^{M} the number of surfactant ions in the micelle particle. Therefore, the curves in Fig. 3 turn out to be the $\Delta v(1)$ vs. m_1 and $\Delta v(\mathrm{M})$ vs. m_1 curves.

The values of $\Delta v(1)$ and $\Delta v(\mathrm{M})$ at the cmc, which are obtained by extrapolation, are plotted with those of the aqueous DTAC solution–hexane system[2] against pressure in Fig. 6. It is found again that the $\Delta v(\mathrm{M})$ value is independent of pressure and the $\Delta v(1)$ value depends on pressure. Further, the $\Delta v(1)$ and $\Delta v(\mathrm{M})$ values of the cyclohexane system are seen to be larger than those of hexane system. Therefore, it is possible to say that the molar interfacial excess volume of the adsorbed film at the cmc becomes slightly larger than the molar volume of micelle though their pressure dependence is similar to each other, when cyclohexane is used in place of hexane. This may be related closely to the experimental fact that the volume of interface formation of the pure water/cyclohexane interface has a larger value than that of the pure water/hexane interface.[9]

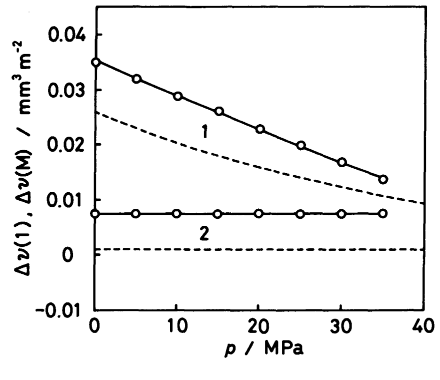

Fig. 6. Volume change associated with the adsorption from monomeric state ($\Delta v(1)$) vs. pressure and volume change associated with the adsorption from micellar state ($\Delta v(\mathrm{M})$) vs. pressure at cmc and at 298.15 K. (1): $\Delta v(1)$ vs. p, (2): $\Delta v(\mathrm{M})$ vs. p, (○): aq DTAC/cyclohexane, (— — —) aq DTAC/hexane.

Let us now consider the volume of micelle formation $\Delta_{\mathrm{W}}^{\mathrm{M}} v$ defined by

$$\Delta_{\mathrm{W}}^{\mathrm{M}} v = v^{\mathrm{M}}/N_1^{\mathrm{M}} - v_1^{\mathrm{W}}. \tag{3}$$

The value of $\Delta_{\mathrm{W}}^{\mathrm{M}} v$ can be evaluated by use of the equation[8]

$$\Delta_{\mathrm{W}}^{\mathrm{M}} v = 2(RT/\mathrm{cmc})(\partial \mathrm{cmc}/\partial p)_T. \tag{4}$$

The $\Delta_{\mathrm{W}}^{\mathrm{M}} v$ vs. p curve obtained from the cmc vs. p curve in Fig. 5 is compared with that of the hexane system in Fig. 7. It is seen from this figure that the micelle formation in the cyclohexane system shows the volumetric behavior slightly different from that in the hexane system. Therefore, we may say that the micelle particles solubilize molecules of the oil coexisting in equilibrium with the aqueous solution.

Finally, let us examine whether the micelle particle behaves thermodynamically like a macroscopic bulk phase. Combining Eqs. 1, 2, and 3, the following equation is obtained:

$$\Delta v(1) - \Delta v(\mathrm{M}) = \Gamma_1^{\mathrm{H}} \Delta_{\mathrm{W}}^{\mathrm{M}} v. \tag{5}$$

The left side of Eq. 5 is the difference between the $\Delta v(1)$ and $\Delta v(\mathrm{M})$ values given in Fig. 6 and the right side the product of the Γ_1^{H} value, which is evaluated

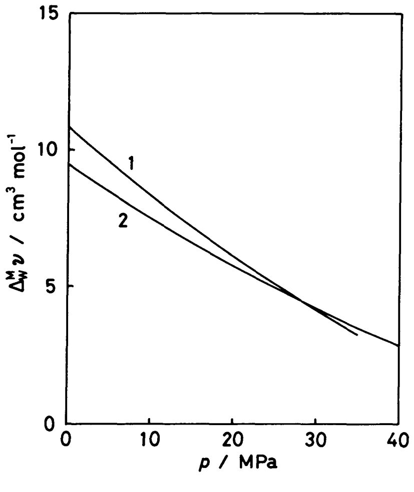

Fig. 7. Volume of micelle formation vs. pressure curves at 298.15 K. (1): aq DTAC/cyclohexane, (2): aq DTAC/hexane.

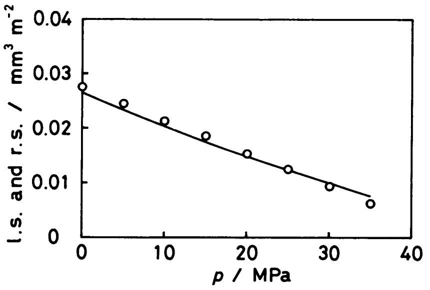

Fig. 8. Comparison between left side ($\Delta v(1)-\Delta v(\mathrm{M})$) and right side ($\Gamma_1^{\mathrm{H}}\Delta_{\mathrm{W}}^{\mathrm{M}}v$) of Eq. 5. (○): left side, (——): right side.

from the γ vs. m_1 curve in Fig. 4, and the $\Delta_{\mathrm{W}}^{\mathrm{M}}v$ value given in Fig. 7; both the sides are compared in Fig. 8. They are in good agreement with each other over the entire pressure range measured. Therefore, we again arrive at the conclusion that irrespective of the phase coexisting in equilibrium with its aqueous solution, the micelle formation of surfactant can be treated thermodynamically as the appearance of a macroscopic bulk phase.[1-3,5]

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