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Effects of Pressure on the Cloud Point of Nonionic Surfactant Solutions and on the Solubilization of Hydrocarbons

Shoji KANESHINA,* Osamu SHIBATA, and Makoto NAKAMURA
College of General Education, Kyushu University-01, Ropponmatsu, Chuo-ku, Fukuoka 810

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Cloud points in 1.0 wt % aqueous solutions of penta- and hexa(oxyethylene) dodecyl ether increase monotonously with an increase of pressure up to 150 MPa. The elevation of the cloud-point temperature with pressure was 1.05×10^{-7} and 1.09×10^{-7} K Pa^{-1} for respective surfactant. Both volume and enthalpy changes on the separation of the surfactant-rich phase had the positive values. The rise of cloud points on compression is attributable to the enhancement of the hydrogen bonds formation between water and ether oxygens of the poly(oxyethylene) group and partly to the disruption of the "hydrophobic bonding." The cloud-point temperature at constant pressure and the cloud-point pressure at constant temperature were also examined as a function of the amount of solubilizate such as hexane and octane. There was an optimum pressure at a given temperature, as well as an optimum temperature at a given pressure, at which the solubilizing power of surfactant is maximum.

So far a few studies have been made about the effect of pressure on the properties of surfactant solutions, especially on the critical micelle concentration of ionic surfactants.[1)] With respect to the nonionic surfactant, however, the effect of pressure on the cloud point has only been reported by Suzuki and Tsuchiya.[2)] They found that the cloud point of aqueous solution of poly(oxyethylene) *p*-nonylphenyl ether had its maximum at about 100—200 MPa.

In this paper some results of the effect of pressure on the cloud point of aqueous poly(oxyethylene) dodecyl ether solutions are presented, and then the pressure dependence of the solubilization will be elucidated from the cloud points in the presence of hydrocarbons. No information on the pressure dependences of the solubilization is available in the literature.

Experimental

Penta(oxyethylene) dodecyl ether and hexa(oxyethylene) dodecyl ether (Tokyo Kasei Kogyo Co., Ltd.,) were used without further purification. The cloud points in 1.0 wt % aqueous solution of respective surfactant were 23.5 and 48.1 °C. Hexane and octane used as solubilizate were extra-pure grade.

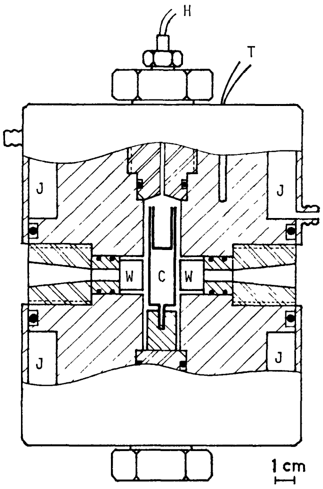
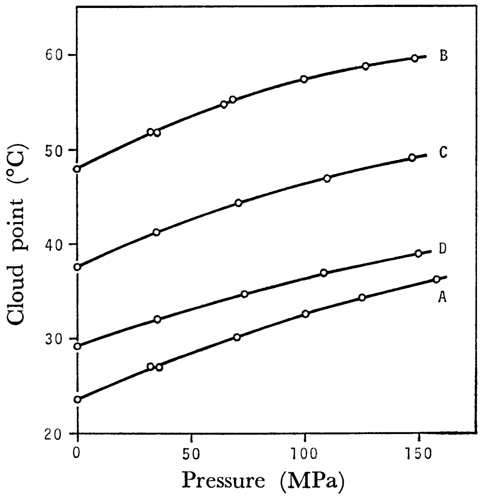


Fig. 1. Schematic diagram of the high pressure vessel equipped with optical windows. C: Syringe cell with Teflon cap in which the solution is filled, H: pressure tubing with which the pressure pump and gauge are connected, J: water jacket, T: thermocouple, W: quartz window. The pressure was sealed by means of an O-ring with a back-up ring of Teflon.

The cloud points under high pressure were determined by using the high pressure vessel with optical windows, which is shown schematically in Fig. 1. The high pressure vessel was made of stainless steel with 140 mm o.d., 20 mm i.d., and 180 mm hight. The solutions were heated or cooled slowly (0.1 °C per minute) by circulation of temperature-controlled water to the jacket. The temperature of the system was determined by the thermocouple attached to the pressure vessel. Pressures were generated by means of a screw- and hand-pump (Hikari Kikai Co.,) and measured within an accuracy of ±0.2 MPa by means of a Heise pressure gauge. Ligroin was used as pressure transmitting medium. The cloud points were decided by observing the appearence and disappearence of turbidity during the cource of heating and cooling at a given pressure. Measurements of the transmittance at 540 nm were performed with a Hitachi 139 spectrophotometer. The difference between the cloud points determined on heating and on cooling were within 1 °C.

Results and Discussion

Effect of Pressure on the Cloud Point. The cloud points in 1.0 wt % aqueous solution of nonionic surfactants are shown in Fig. 2 as a function of pressure. The cloud points for all the surfactant solutions increase monotonously with an increase of pressure up to 150 MPa. This elevation of cloud points on compression is within that caused by an increase of one oxyethylene unit in the poly(oxyethylene) chain. In other words, the alteration in the hydrophilic-lipophilic balance (HLB) of the surfactant by the compression up to 150 MPa seems to be less than that by the addition of one oxyethylene group in the poly(oxyethylene) chain. It is clear from Fig. 2 that the pressure up to 150 MPa is favorable for the dissolution of surfactant molecules in water although most of dissolved-surfactant molecules are in the micellar state. The cloud point for aqueous solutions of surfactants is generally taken to be the point where separation of the surfactant-rich phase is casued by the dehydration of ether oxygens of the poly(oxyethylene) group. Le Chatelier's principle brings about the positive volume change on separation of the sur-



Eig. 2. Effect of pressure on the cloud point of nonionic surfactant solutions. Curve A: 1.00 wt % penta(oxyethylene) dodecyl ether solution, B: 1.00 wt % hexa(oxyethylene) dodecyl ether solution, C: 1.02 wt % hexa(oxyethylene) dodecyl ether solution containing hexane of 2.42 g/kg H_2O, D: 1.02 wt % hexa(oxyethylene) dodecyl ether containing hexane of 4.26 g/kg H_2O.

factant-rich phase. From data of apparent molal volumes of nonionic surfactants and polyethylene glycol(PEG) oligomers with various lengths of poly(oxyethylene) chain the apparent molal volume assigned for one oxyethylene group can be calculated. The values assigned for the group are 37.1 cm^3/mol for surfactant in micellar state[3] and 36.9 cm^3/mol for PEG,[4] which are found to be apparently smaller than the molal volume assigned for an oxyethylene unit in the state of pure liquids, 38.9—39.1 cm^3/mol.[4,5] That is, the volume change on formation of hydrogen-bonds between water and ether oxygens of the poly(oxyethylene) group is negative, and the increase of pressure enhances the formation of hydrogen bonds.

In the two-component, two-phase system, the Clausius-Clapeyron type equation is written as follows:[6]

$$\left(\frac{\partial T}{\partial P}\right)_{x_2}=\frac{T(y_1\Delta\bar{v}_1+y_2\Delta\bar{v}_2)}{y_1\Delta\bar{h}_1+y_2\Delta\bar{h}_2}, \tag{1}$$

where subscripts 1 and 2 refer to components 1 and 2, x and y the mole fraction in the phase α and β, respectively. $\Delta\bar{h}$ and $\Delta\bar{v}$ are the change of partial molal enthalpy and volume, respectively, on the transfer from phase α to β. In the present system, we choose surfactant as component 2 and the micellar solution as the phase α. Assuming $y_1 \ll y_2$,

$$\left(\frac{\partial T}{\partial P}\right)_{x_2}=\frac{T\Delta\bar{v}_2}{\Delta\bar{h}_2}. \tag{2}$$

As is seen from Fig. 2, $(\partial T/\partial P)_{x_2}$ is positive. That is, $\Delta\bar{h}_2$ and $\Delta\bar{v}_2$ have the same sign. The dehydration of the poly(oxyethylene) chain, *i.e.*, the hydrogen bond breaking contributes to the positive change in both $\Delta\bar{h}_2$ and $\Delta\bar{v}_2$. Further, the positive volume change is also caused by the elimination of hydrocarbon–water contact. This "hydrophobic bonding" also brings about the positive contribution to $\Delta\bar{h}_2$ because of the breakdown of ice-like structure around the hydrocarbon chain. Therefore, the rise of cloud points on compression is attributable to the enhancement of the hydrogen bonds formation and partly to the disruption of the hydrophobic bonding.

The values of $(\partial T/\partial P)_{x_2}$ are $1.05(\pm0.05)\times10^{-7}$ K Pa^{-1} for penta(oxyethylene) dodecyl ether and $1.09(\pm0.03)\times10^{-7}$ K Pa^{-1} for hexa(oxyethylene)dodecyl ether. The value for poly(oxyethylene) *p*-nonylphenyl ether is found to be $(0.8—1.3)\times10^{-7}$ K Pa^{-1} for the various compositions.[2] Assuming that the hydrophillic-lipophilic property of surfactant balances at the cloud point, the pressure of about 10 MPa is required for the temperature rise of 1 °C to keep the original HLB.

Effect of Solubilizate on the Cloud Point. The cloud points in the presence of solubilizate as hexane and octane increase monotonously with an increase of pressure. Some results are included in Fig. 2.

In Fig. 3, the cloud-point temperatures of the solutions containing 1.0 wt % hexa(oxyethylene) dodecyl ether at constant pressure are shown as a function of the amount of solubilized hexane. The solubilization end points, below which the excess hydrocarbon separates from micellar solution, are also shown only at an atmospheric pressure. As is seen from Fig. 3, the region between the cloud-point temperature isobar and solubilization curve is a homogeneous transparent phase. According to Shinoda,[7] in the region (denoted by II_{W-D}) above the cloud-point temeperature isobar the nonionic surfactant phase containing oil separates. On the other hand, the excess oil separates in the II_{W-O} region below the solubilization curve. In Fig. 4, the cloud-point temperatures of the system with solubilized octane are shown as a function of the amount of octane. The pattern of isobars is analogous in both the systems; namely, the isobars are shifted to higher

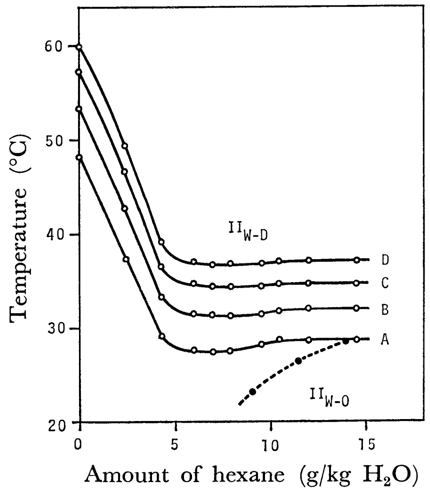


Fig. 3. The cloud-point temperature as a function of the amount of hexane solubilized at 0.1 MPa (curve A), 50 MPa (B), 100 MPa (C), and 150 MPa (D). The solubilization end points (●) are also shown only at an atmospheric pressure.

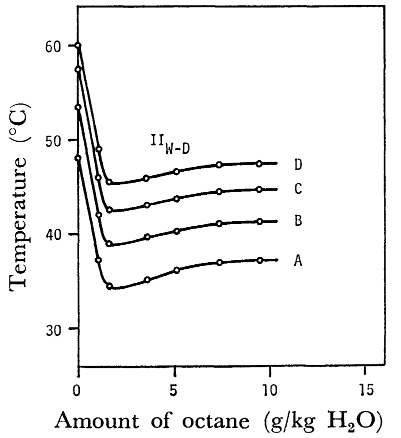


Fig. 4. The cloud-point temperature as a function of the amount of octane solubilized at 0.1 MPa (curve A), 50 MPa (B), 100 MPa (C), and 150 MPa (D).

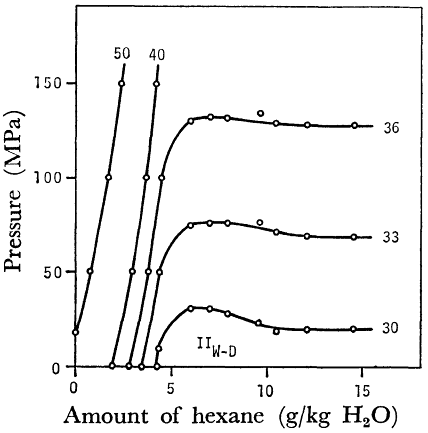


Fig. 5. The could-point pressure as a function of the amount of hexane solubilized. Numerical values refer to the temperature in °C.

temperature as the pressure increases. The cloud-point temperature is initially depressed by the addition of solubilizate and then approaches a definite temperature *via* a minimum. At the definite temperature the solubilizing power of surfactant becomes maximum. The compression up to 100 MPa elevates the optimum temperature by 6.0 and 7.6 °C for the systems with solubilized hexane and octane, respectively.

The cloud-point pressure of the solutions containing 1.0 wt % hexa(oxyethylene) dodecyl ether at constant temperature are shown in Figs. 5 and 6 as a function of the amount of solubilized hexane and octane, respectively. The cloud-point pressure isotherms for all the systems with solubilized hexane and octane are similar; the higher the pressure, the larger the area of homogeneous phase. The cloud-point pressure of the solution containing solubilized hexane more than 6 g/kg H_2O is little affected by the additional

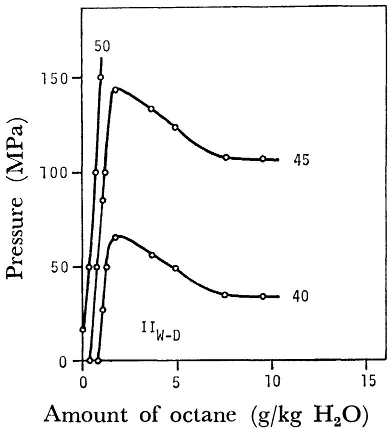


Fig. 6. The cloud-point pressure as a function of the amount of octane solubilized. Numerical values refer to the temperature in °C.

solubilization of hexane. That is, there is the optimum pressure for the maximum solubilization at a given temperature. The solubilizing power of surfactant becomes maximum at a slightly higher pressure than the pressure in the plateau region of isotherms. Also in the system with solubilized octane, there is an optimum pressure for the solubilization. The higher the temperature, the higher the optimum pressure in both systems.

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