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Effect of Inorganic Electrolytes on the Cloud Point of Polyoxyethylene Dodecyl Ether

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Synopsis. The cloud points of polyoxyethylene dodecyl ether in the presence of different types of inorganic electrolytes have been determined. The cloud points can be expressed by the empirical equation: $(C.P.)_s/(C.P.)_0=1+A\sqrt{C_s}+BC_s$ where $(C.P.)_s$ and $(C.P.)_0$ are the cloud points with and without an electrolyte, respectively, C_s is the electrolyte concentration, and A and B are constants.

When an aqueous solution of a polyoxyethylene-type nonionic surfactant $RO(CH_2CH_2O)_pH$ with a relatively small number of p is heated, it becomes cloudy reversibly at the temperature of incipient phase separation called the cloud point. The cloud point is rather insensitive to the concentration of the surfactant itself, but is highly dependent on the kind and the concentration of an added electrolyte.[1,2] Most of inorganic electrolytes depress the cloud point of a nonionic surfactant owing to their salt-out effect, while some electrolytes such as nitrates, iodides and thiocyanates, raise the cloud point. In addition, the cloud point is in general more influenced by the anions of added electrolytes than by the cations. However, the nature of the interaction of a nonionic surfactant with an added electrolyte (or the interaction through a change in the structure of water by an added electrolyte) is not necessarily well understood.

This note describes a systematic study on the effect of various types of inorganic electrolytes on the cloud point of polyoxyethylene dodecyl ether (abbreviated to C_{12}-POE) and proposes an empirical equation to express the cloud point as a function of an added electrolyte.

Experimental

The nonionic surfactant C_{12}POE was prepared from dodecyl alcohol of high purity by addition of ethylene oxide and purified by molecular distillation. The average number of oxyethylene units per molecule for the purified sample was found to be 6.3 from its hydroxyl value. The inorganic electrolytes examined were of guaranteed reagent grade and used without further purification.

Cloud points were photometrically measured of 2.0% C_{12}POE solutions containing electrolytes in the concentration range of 0.01—0.5 m with the apparatus shown in Fig. 1a. The transmittance of light through a sample solution and the temperature of this solution were plotted on a X–Y recorder connected with the apparatus. The solution was heated or cooled at a rate of 0.4 °C per minute across the cloud point. Fig. 1b shows the transmittance *vs.* temperature curves for the 2.0% C_{12}POE solution in the absence of an electrolyte, which were obtained by heating from below the cloud point and by cooling from above; the two curves are superimposed. The cloud point was determined as a temperature at 50% transmittance. Similar curves were obtained for other sample solutions containing electrolytes. The data were reproducible within an accuracy of ±0.05 °C.

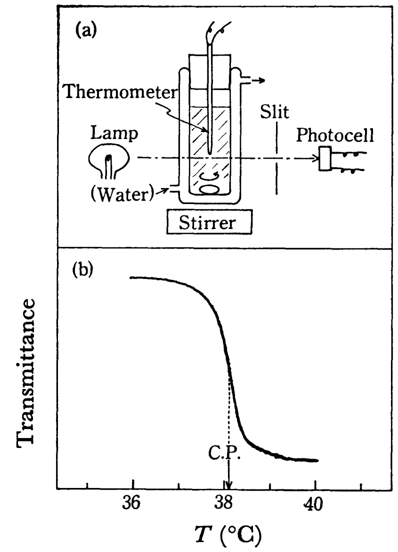

Fig. 1. (a) The apparatus used for measurement of cloud points. (b) An example of transmittance *vs.* temperature curves.

Results and Discussion

Figure 2 shows some typical examples of the effects of added electrolytes on the cloud point of the 2.0% C_{12}-POE solution. The cloud point much depends on the species of anions than on the species of cations.

Here, the present authors propose the following empirical equation, which was arrived at by analysis of the data, to describe systematically the relation of the cloud

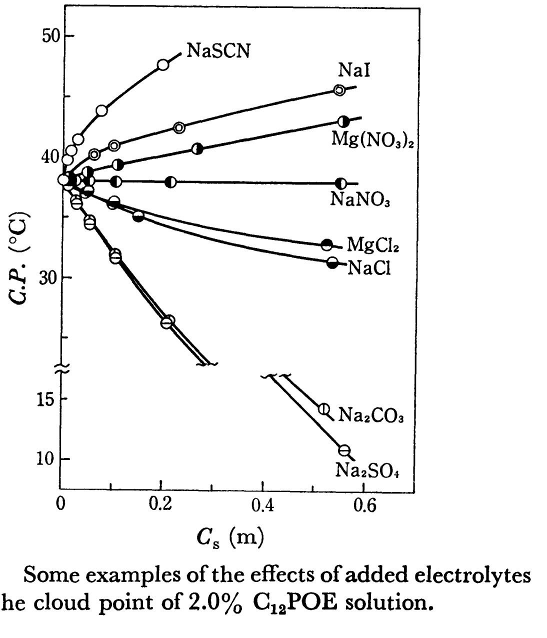

Fig. 2. Some examples of the effects of added electrolytes on the cloud point of 2.0% C_{12}POE solution.

point with the concentration of an added electrolyte.

$$(C.P.)_s/(C.P.)_0 \equiv \theta = 1 + A\sqrt{C_s} + BC_s \quad (1)$$

or

$$(\theta - 1)/\sqrt{C_s} = A + B\sqrt{C_s} \quad (2)$$

where $(C.P.)_s$ and $(C.P.)_0$ are the cloud points expressed, by absolute temperature with and without an electrolyte respectively, C_s is the electrolyte concentration in molality, and A and B are constants. If the quantity of $(\theta-1)/\sqrt{C_s}$ is plotted against $\sqrt{C_s}$, according to Eq. (2), a straight line is obtained for each electrolyte in the range of concentrations lower than about 0.25 m, as shown in Fig. 3. With chlorides and nitrates, linear relations are maintained up to a concentration of 0.5 m. The values of the constants A and B derived from the intercept and the slope of each straight line are summarized in Table 1.

According to the magnitudes of A and B, the electrolytes examined may be classified into the following two types. *Type I—carbonates, sulfates, and chlorides.* These electrolytes have negative values of A and B, as given in Table 1, and only small differences in A are seen among the electrolytes. The constant B varies, depending on the species of anions rather than cations. *Type II—nitrates, iodides, and thiocyanates.* The values of A for these electrolytes are positive, or negative but very close to zero. The values of B are slightly positive.

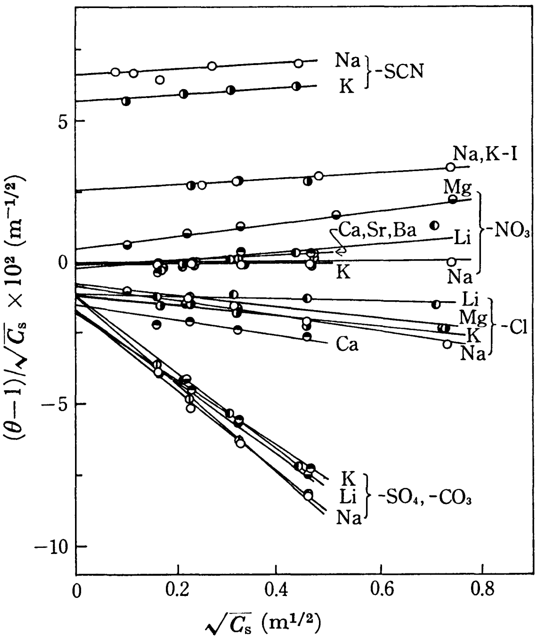

Fig. 3. Plots of $(\theta-1)/\sqrt{C_s}$ *vs.* $\sqrt{C_s}$ for various electrolytes.

Table 1. Values of A and B for various electroytes

Type I			Type II		
Electrolyte	$A\times10^2$ (m$^{-1/2}$)	$B\times10^2$ (m^{-1})	Electrolyte	$A\times10^2$ (m$^{-1/2}$)	$B\times10^2$ (m^{-1})
Na_2CO_3	−1.2	−16.2	$LiNO_3$	−0.2	1.3
K_2CO_3	−1.2	−13.5	$NaNO_3$	0	0.1
Li_2SO_4	−1.7	−12.9	KNO_3	0.1	0.1
Na_2SO_4	−1.7	−14.3	$Mg(NO_3)_2$	0.5	2.1
K_2SO_4	−1.8	−11.8	$Ca(NO_3)_2$	−0.1	0.9
LiCl	−1.1	−0.4	$Sr(NO_3)_2$	−0.1	0.9
NaCl	−0.9	−2.6	$Ba(NO_3)_2$	−0.1	0.9
KCl	−1.2	−1.7	NaI	2.6	1.0
$MgCl_2$	−0.7	−1.8	KI	2.6	1.0
$CaCl_2$	−1.5	−2.7	NaSCN	6.6	1.1
			KSCN	5.7	1.1

The solubility of nonionic surfactants in solutions of electrolytes may be discussed in terms of two factors: i) hydration of the ions, with a consequent change in the water structure nearby, which affects the affinity of the water molecules to the ether oxygens of the surfactant, and ii) binding of the ions or salts of polyvalent metals to the ether oxygens *via* cation complexation at high concentrations, resulting in an increase in solubility of the surfactant.

The structure of water in electrolyte solutions has been discussed from viscosity[3,4] and NMR[5] data with the conclusion that the effectiveness in destrusturing water around anions is in the order of $I^- > NO_3^- > Cl^- > SO_4^{2-} > CO_3^{2-}$, in which CO_3^{2-} and SO_4^{2-} ions are rather structure-forming. Their conclusion is in accordance with the magnitude of B shown in Table 1. These results would suggest that the constant B has some close relation to the extent of destructure of water by added electrolytes, although differences in B between iodides and nitrates, and between sulfates and carbonates, are not so distinctive. Probably, added electrolytes, especially their anions, would affect the solubility of the nonionic surfactant through changes in the structure of water around them, depending on their structure-breaking or -forming ability.

The difference in A between electrolytes of the types I and II cannot be explained at the present stage: the constant A might be concerned with a factor not being related to the structure of water, presumably, with an interaction of ions (or salts) with the ether oxygens of the nonionic surfactant. Interpretation of the constant A requires additional information.

According to current views, thiocyanate ions are destructive of water,[6,7] and unassociated water hydrates nonionic surfactant molecules better than hydrogen-bonded, associated water, which results in raising the cloud point. Therefore, the positive values of B for thiocyanates could also be ascribed to their destruction of water structure. The large values of A are to be noted, which seem to be related to an increase in cloud point although the detailed mechanism is not clear.

The behavior of cations in nonionic surfactant solutions may be discussed in terms of complex formation.[8] For example, differences in A and B between $NaNO_3$ and $Mg(NO_3)_2$ could be explained in part by the complex formation of Mg^{2+} ions with the ether linkages of the surfactant.

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