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Minima in the Solubilities of Normal Alkane Derivatives with a Polar Group in Water

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The change in the solubility in water with the temperature was measured for alkanols, alkylamines, and alkanoic acids. It has been found that a minimum exists commonly on the solubility-temperature curve. This minimum dissolution point, P_m, may be regarded as a characteristic point with respect to the solute. The change in the solubility with the temperature has been explained in terms of the increase in the partial molar enthalpy of the solute in solution with an increase in the temperature, which results from the breakdown of the ice-like structure of water formed around the nonpolar alkyl group. Both the concentration, x_m, and temperature, T_m, at point P_m decrease with an increase in the number of carbon atoms in the alkyl group, m. The decrease in $\ln x_m$ by the addition of one methylene group is steeper in the order of alkanoic acids, alkylamines, and alkanols, while the corresponding decrease in T_m shows the reverse order. In addition, T_m is related to the cohesive energy of the solute in the pure state.

Aqueous nonionic surfactant solutions suddenly become turbid above a certain temperature, which is called the cloud point,[1)] while nicotine and like-compounds have both upper and lower critical consolution temperatures in water,[2,3)] although a substance is usually more soluble at a higher temperature in an ordinary or regular solution.[4,5)] Several concepts have been presented in attempts to interpret these anomalous solubility phenomena in water. One is that the hydrogen bonding between a water molecule and a polar group of the organic solute decreases as the temperature rises,[6)] and another is that a nonpolar hydrocarbon or rare gas molecule in water promotes the formation of the structure of water around it, while the structure gradually breaks down with a rise in the temperature.[7–9)] The above concepts, however, cannot explain the solubility phenomena quantitatively, and the states in water of organic compounds have not yet been understood sufficiently. In the present paper, in order to study the states of organic compounds in water, the change in the solubility with the temperature was measured for several normal alkane derivatives, which have a polar group in the molecule to increase the solubilities. A minimum was commonly observed on the solubility-temperature curve.

Experimental

Normal alkane derivatives as the solutes were selected from the 1-, 2-, and 3-alkanol, alkylamine, and alkanoic acid series, each of which is liquid over the temperature range under investigation. The samples are commercially available as G. R. -grade materials from Wako Pure Chemical Industries, Ltd.; the Kanto Chemical Co., Inc.; Nakarai Chemicals, Ltd.; the Sumida Chemical Co., Ltd., and the Tokyo Kasei Kogyo Co., Ltd. They were used without further treatment except for those of 1-alkanol series, which were dried over calcium oxide and kept in ampoules in contact with magnesium powder before use. The solvent was obtained by distilling ion-exchanged water from an alkaline potassium permanganate solution after refluxing for 15 h.

Twenty to thirty glass ampoules containing aqueous solutions of *ca.* 5 cm^3 of various concentrations near the solubility at room temperature for each compound were immersed in a water thermostat. The distinction between clean and turbid ampoules was made after a time long enough for equilibrium to be established, say *ca.* 2 h, at each temperature. Observations were made at 2- to 5-K intervals from 275 to 360 K. The smooth curve drawn to separate the clean and turbid regions in the concentration-temperature diagram was regarded as the solubility curve.

The heat of evaporation was estimated according to the vapor-pressure method described in a previous paper,[10)] except for using a spinning-band type of precision distillation apparatus (Tokyo Kagaku Seiki Co.).

Results and Discussion

The solubilities in the mole fraction, x_2, measured are plotted against the temperature, T, in Figs. 1 and 2. Alkanols, alkylamines, and alkanoic acids commonly show decreasing and increasing solubilities with temperature in lower- and higher-temperature regions respectively. Each curve, then, has a minimum point

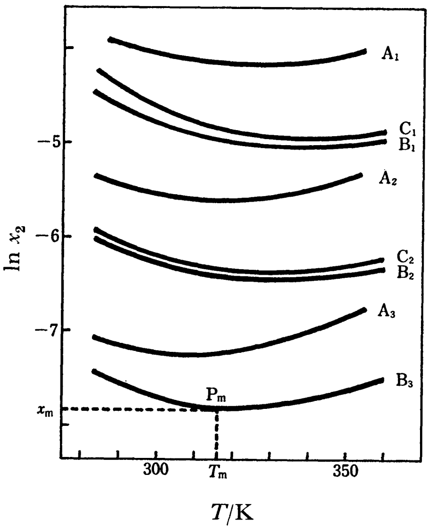

Fig. 1. Solubility of alkanol series in water as a function of temp.

A_1: 1-Butanol, A_2: 1-pentanol, A_3: 1-hexanol, B_1: 2-pentanol, B_2: 2-hexanol, B_3: 2-heptanol, C_1: 3-pentanol, C_2: 3-hexanol, P_m: minimum dissolution point, x_m: minimum dissolution concn, T_m: minimum dissolution temp.

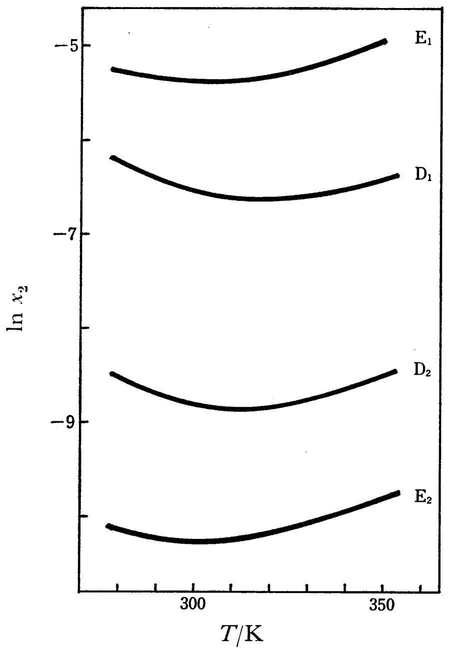

Fig. 2. Solubility of alkylamine and alkanoic acid series in water as a function of temp.
D_1: Hexylamine, D_2: heptylamine, E_1: pentanoic acid, E_2: hexanoic acid.

in solubility, which is referred to as the minimum dissolution point, P_m, as is indicated in Fig. 1. This minimum point may be regarded as a characteristic point with respect to the solute in water as a solvent. The concentration and temperature at that point are termed the minimum dissolution concentration, x_m, and the minimum dissolution temperature, T_m, respectively. The appearance of these minima resembles the dependence of the critical micelle concentration, CMC, on the temperature, T, for aqueous surfactant solutions measured by Shinoda.[9] He has described how the iceberg formation of water molecules around the monodisperse solute rather enhances the CMC, the logarithm of which would be decreased linearly with T^{-1} if the solution behaved regularly, and the iceberg formation increases with the temperature depression.

Bohon and Claussen[11] have estimated the heat of solution from such solubility curves for aromatic compounds by assuming that the heat of solution is proportional to the tangent of the curve of $\ln x_2$ *vs.* T^{-1}. This assumption, however, is valid only when the organic phase in equilibrium with the aqueous solution contains no water or a constant amount of it, regardless of the temperature. It may be reasonable, nevertheless, to consider that the change in the solubility with the temperature shown in Figs. 1 and 2 is predominantly due to the increase in the heat of solution at an infinite dilution with the temperature, because the solubility of water in an organic phase is expected to vary less with the temperature. The heat of solution at an infinite dilution is the difference between the partial molar enthalpy of the solute in an infinitely dilute solution and the molar enthalpy in the pure state of the solute; in addition, the heat of solution is equal to the sum of the heat of evaporation of the pure solute and the heat of condensation of the solute from the vapor phase to the solution, according to Hess' law. The heat of evaporation may be assumed to be constant in the measured temperature range for each solute, because the logarithm of the vapor pressure decreases linearly with T^{-1}, as is shown in Figs. 5 and 6. The increase in the heat of solution, therefore, may be attributed mainly to the increase in the partial molar enthalpy of the solute in the solution through the heat of condensation, which shows that some endothermic changes proceed on and/or around the solute molecules with the temperature rise. Since all the solubility curves in Figs. 1 and 2 are similar in shape, regardless of the nature of the polar group, such endothermic changes may be attributed commonly to the nonpolar alkyl group. Frank and Evans[7] have described how the rare gases and hydrocarbon gases form icebergs when they dissolve in cold water; how, as the temperature is raised, these icebergs melt, giving rise to the enormous partial molar heat capacity of these gases in water, and how, at still higher temperatures, the heat of evaporation from the aqueous solution becomes negative. The solubility of most gases in water shows a minimum when plotted against the temperature. Following the above description, the solubility curves in Figs. 1 and 2 can be explained by considering that the ice-like structure of water is also formed around the nonpolar alkyl group of alkanol, alkylamine, or alkanoic acid in water, which structure breaks down as the temperature is raised.

The relations between $\ln x_m$ and the number of carbon atoms in an alkyl chain, m, for the respective series are shown in Fig. 3. The value of $\ln x_m$ decreases linearly with m for the 1- and 2-alkanol series, and these two lines are nearly parallel to each other. The decrease in $\ln x_m$ from 3-pentanol to 3-hexanol is nearly equal

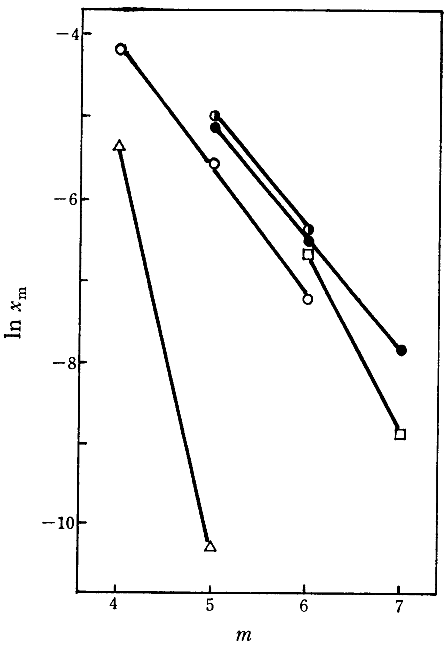

Fig. 3. Minimum dissolution concn as a function of number of carbon atom in alkyl group.
○: 1-Alkanol, ●: 2-alkanol, ◑: 3-alkanol, □: alkylamine, △: alkanoic acid.

to the slopes of the straight lines for the 1- and 2-alkanol series. The decrease of $\ln x_m$ by the addition of one methylene group is different according to the kind of polar group attached to the molecule; the order is as follows:

$$\text{-COOH} > \text{-NH}_2 > \text{-OH}.$$

It has previously been determined[12] that the slopes of the logarithm of solubility *vs.* *m* values of more than 9 both for the alkanoic acid series at 298 K and for the alkylamine series at 295 K are very close to the slope for the alkanol series in Fig. 3. The larger decrease for the alkylamine or alkanoic acid series in Fig. 3 can then be expected to be reduced gradually to that for the alkanol series, when *m* increases up to the range out of the influence of the polar group. These phenomena may be interpreted in terms of a higher free energy of a methylene group under the influence of the attached polar group than that out of the influence of the polar group.[13] The farther the methylene group is apart from the polar group, the easier is the structure of water to be formed around it, since the effect of the polar group decreases with the distance. The steeper decrease in $\ln x_m$ for the alkanoic acid series than for the alkylamine series in Fig. 3 can be explained by the smaller carbon number, *m*, in the former series, although the former series have slightly weaker polarities or dissociation constants.[14] In addition, in the alkanol series, the closer the OH groups are to the center, the more soluble they are when they have the same *m*, as is shown in Fig. 3. This may be explained in terms of the increasing number of methylene groups within the influence of an OH group as the OH group is closer to the center of the molecule, but the difference between the 2- and 3-alkanol series is not appreciable.

The minimum dissolution temperature, T_m, also decreases with an increase in the number of carbon atoms, *m*, for those series, as is shown in Fig. 4. The decrease in T_m upon the addition of one methylene group is steeper in the reverse order of that of $\ln x_m$ in Fig. 3. The T_m values show the following order:

$$\text{3-alkanol} > \text{2-alkanol} > \text{alkylamine} >$$
$$\text{1-alkanol} > \text{alkanoic acid},$$

if *m* is constant in the range of 5 and 6.

The characteristic point, P_m, of a solute in an aqueous solution is expected to be related to the characteristics of the solute itself, especially, for example, the cohesion between molecules. The heat of evaporation, $\Delta_e h_2^\circ$, can be considered a measure of the cohesive energy.[10] The vapor pressures, *p*, of the solutes in their pure states

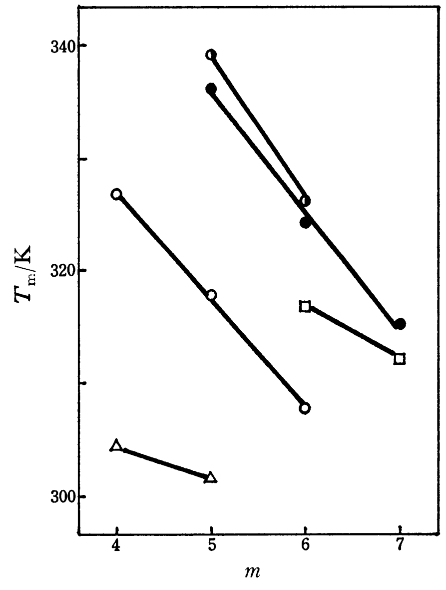

Fig. 4. Plots of minimum dissolution temp *vs.* number of carbon atom in alkyl group.
○: 1-Alkanol, ●: 2-alkanol, ◑: 3-alkanol, □: alkylamine, △: alkanoic acid.

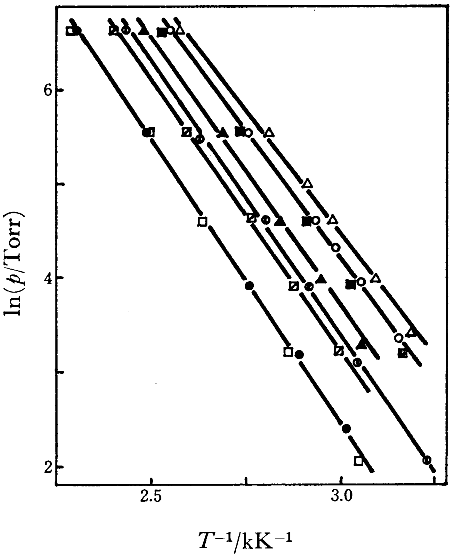

Fig. 5. Vapor pressure of alkanol series as a function of temp.
○: 1-Butanol, ⦶: 1-pentanol, ●: 1-hexanol, ■: 2-pentanol, ▨: 2-hexanol, □: 2-heptanol, △: 3-pentanol, ▲: 3-hexanol.

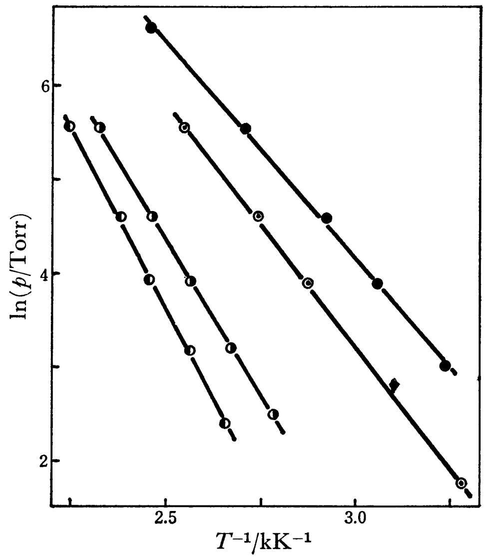

Fig. 6. Vapor pressure of alkylamine and alkanoic acid series as a function of temp.
●: Hexylamine, ⊙: heptylamine, ◑: pentanoic acid, ◐: hexanoic acid.

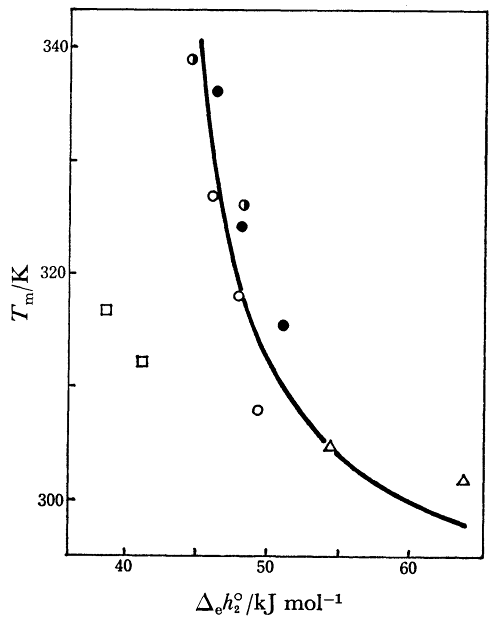

Fig. 7. Plots of minimum dissolution temp *vs.* heat of evaporation.

○: 1-Alkanol, ●: 2-alkanol, ◑: 3-alkanol, □: alkylamine, △: alkanoic acid.

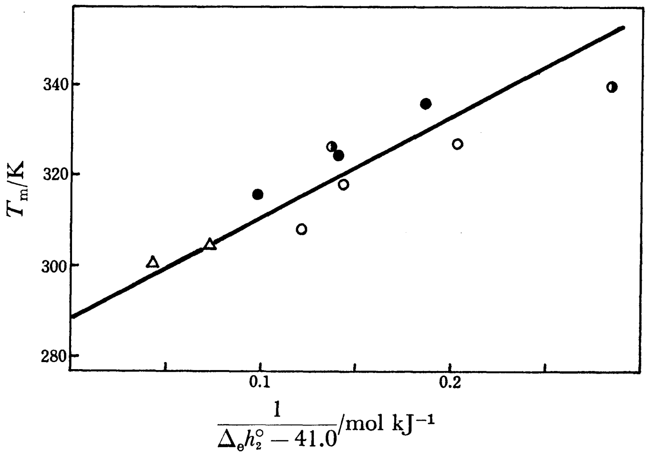

Fig. 8. T_m *vs.* $\frac{1}{\Delta_e h_2^\circ - 41.0}$ plots.

Marks are the same as in Fig. 7.

were measured in the temperature range between 305 and 445 K. As has been mentioned above, $\ln p$ decreases linearly with T^{-1} for each solute, as is shown in Figs. 5 and 6. The heat of evaporation, $\Delta_e h_2^\circ$, was estimated from the slope according to the Clausius-Clapeyron equation. It has been found that $\Delta_e h_2^\circ$ has a certain relation to T_m except for the alkylamine series, as is shown in Fig. 7. The relation may be expressed by

$$T_m = \frac{223}{\Delta_e h_2^\circ - 41.0} + 288, \qquad (1)$$

as is shown as the straight line in Fig. 8 and as the curve in Fig. 7. It should be noted that Eq. 1 should be applied to the compounds having $\Delta_e h_2^\circ$ values higher than 41.0 kJ mol^{-1} and T_m values larger than 288 K.

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