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The Solubility Curves of Water in Normal Alkane Derivatives with a Polar Group

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Measurements were made of the solubility *vs.* temperature curves of water in normal alkane derivatives: alkanols, alkylamines, and alkanoic acids. The solubility of water increases monotonically with an increase in the temperature in alkanols and alkanoic acids, while it decreases in alkylamines. The solubility is so great that it often exceeds 1/2 in the mole fraction scale. Phase diagrams were constructed by combining such solubility curves with the solubility curves of these substances in water. The heat of solution at an infinite dilution *vs.* the temperature for 1-butanol in water is obtained by taking account of the activity coefficient of 1-butanol in its own phase.

When an organic substance containing a hydrophobic group, such as an alkyl group, is introduced to water, the water is considered to change in structure and to form an iceberg around the molecule, which breaks down gradually with a rise in the temperature.[1] As a result, such an aqueous solution shows various complicated phenomena.[2] The present authors have found that a minimum commonly exists on the solubility *vs.* temperature curve for normal alkane derivatives in water, such as alkanols, alkylamines, and alkanoic acids.[3] The heat of solution at an infinite dilution, which is the difference between the partial molar enthalpy of a solute at an infinite dilution and the molar enthalpy in its pure state, serves to elucidate the dissolution state of the solute molecule energetically.[4] The heat of solution at an infinite dilution should be obtained thermodynamically from the phase diagram of the solute and solvent if both phases at equilibrium are ideal. In order to construct the phase diagram for the binary system of water and an organic substance, it is necessary to know the mutual solubility *vs.* temperature curves, *i.e.*, the solubility curves, of the organic compound in water as well as of water in the organic phase. Measurements have not been made of the solubility of water in most normal alkane derivatives, whose solubility curves in water have been measured in a previous paper.[3]

Experimental

The materials used were the same as those described in a previous paper.[3] Twenty to thirty glass ampoules containing various compositions around the solubility of water at room temperature were immersed in a water thermostat. The distinction between clear and turbid ampoules was made after a time long enough for equilibrium to be established, say, *ca.* 2 h, at each temperature.

The behavior of the binary system of 1-pentanol and water is presented as an example in Fig. 1; here an open circle shows the most water-rich composition among the clear ampoules at each temperature and a solid one, the most 1-pentanol-rich among the turbid ones. The solubility curve is drawn smoothly between open and solid circles. The solubility curves for other compounds are similarly precise.

Results and Discussion

The solubility curves of water in the organic phases measured are expressed as the mole fraction of water, x_1^{or}, *vs.* the temperature, T, in Figs. 2 and 3. The solubility of water in either hexylamine or heptylamine could not be determined below 293 or 307 K, because these mixtures were in jelly-like states at the lower temperatures. A large amount of water dissolves in each organic phase, and x_1^{or} exceeds often 1/2; this is natural, as it has been expected that the solubility of water in an organic liquid is more than that of the organic compound in water, because the molar volume of water is generally less than that of an organic liquid.[5] Particularly, hexylamine can decrease to as low as 0.10 in the mole-fraction scale in its own phase at 300 K. As expected, the greater solubility of water is seen in the compound with the smaller number of carbon atoms in a homologous series at a given temperature.

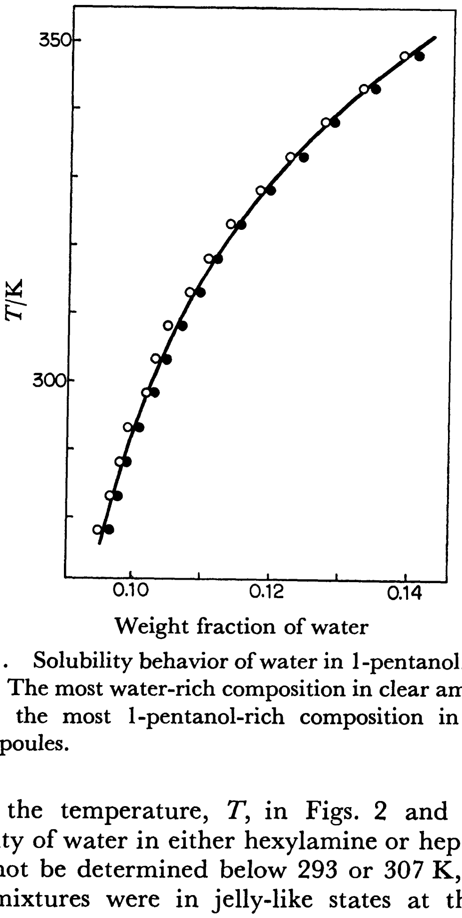

Fig. 1. Solubility behavior of water in 1-pentanol.
○: The most water-rich composition in clear ampoules, ●: the most 1-pentanol-rich composition in turbid ampoules.

The solubility of water increases monotonically with a rise in the temperature in alkanols and alkanoic acids, while it decreases in alkylamines. The increase is steeper in alkanoic acids than in alkanols. Such behavior is significantly different from that of these substances in water.[3] When ln x_1^{or} is plotted against T^{-1}, the curve

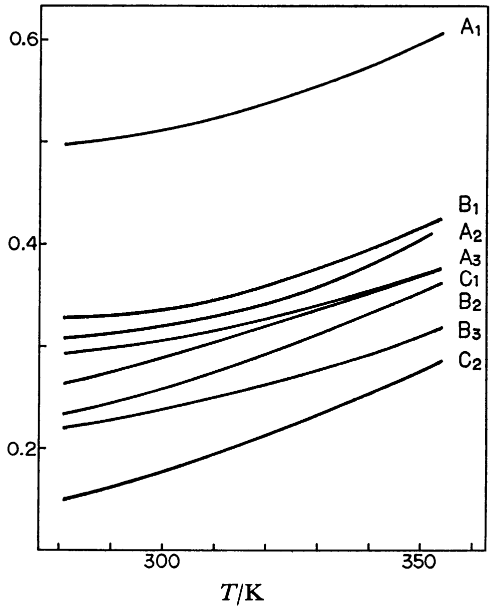

Fig. 2. Solubility curve of water in alkanols.
A_1: 1-Butanol, A_2: 1-pentanol, A_3: 1-hexanol, B_1: 2-pentanol, B_2: 2-hexanol, B_3: 2-heptanol, C_1: 3-pentanol, C_2: 3-hexanol.

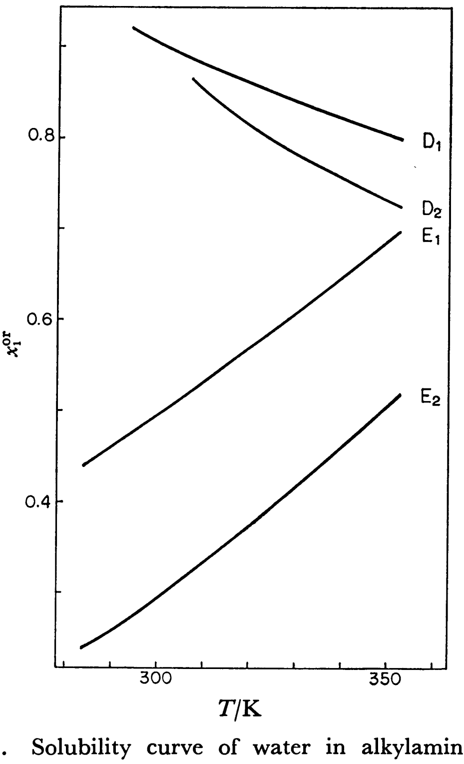

Fig. 3. Solubility curve of water in alkylamines and alkanoic acids.
D_1: Hexylamine, D_2: heptylamine, E_1: pentanoic acid, E_2: hexanoic acid.

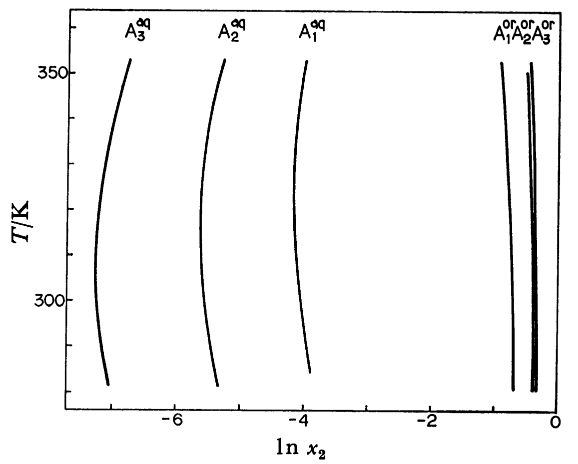

Fig. 4. Phase diagram of the binary system of water and 1-alkanol expressed as temperature *vs.* the natural logarithm of mole fraction of organic substance. Superscripts aq and or denote aqueous and organic phases, respectively.

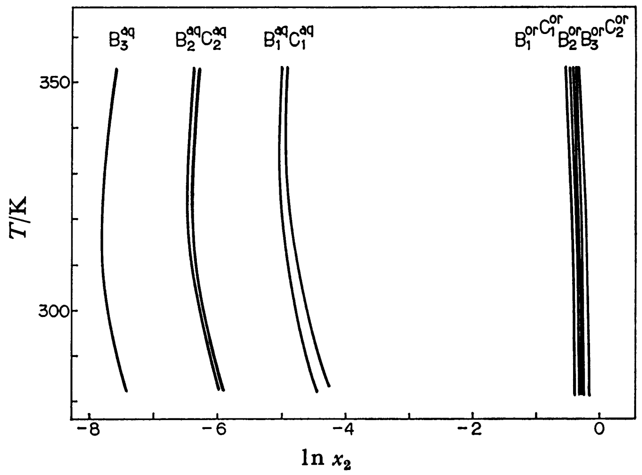

Fig. 5. Phase diagram of the binary system of water and 2- or 3-alkanol expressed as temperature *vs.* the natural logarithm of mole fraction of organic substance.

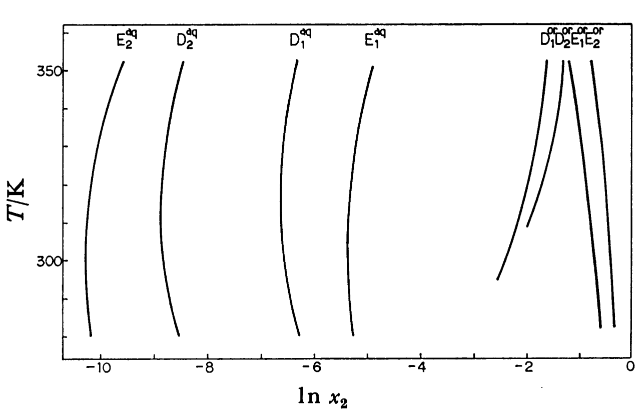

Fig. 6. Phase diagram of the binary system of water and alkylamine or alkanoic acid expressed as temperature *vs.* the natural logarithm of mole fraction of organic substance.

does not deviate very much from a straight line for any compound. This fact reveals that the structure in an organic phase does not change with the temperature so remarkably as in an aqueous phase.

The phase diagrams of the binary systems of water and one of these substances are shown in Figs. 4, 5, and 6, which were constructed by combining the solubility curves of water in Figs. 2 and 3 with the solubility curves of the substances in water reported in a previous paper.[3] The abscissa expresses the natural logarithm of the mole fraction of an organic compound. The region between two solubility curves corresponds to the turbid two-phase region; outside of this region there are clear one-phase regions.

In order to know the states of an organic substance in water, it is useful to estimate the heat of solution at an infinite dilution of the organic substance in water, $\Delta_s h_2^\ominus$.[4] If the system consists of water and an organic substance, the chemical potential of the organic substance, either in the aqueous phase, μ_2^{aq}, or in the organic one, μ_2^{or}, may be generally expressed by:[6]

$$\mu_2^{aq} = \mu_2^{\ominus aq}(T,p) + RT \ln x_2^{aq}\gamma_2^{aq}$$

and:

$$\mu_2^{or} = \mu_2^{o}(T,p) + RT \ln x_2^{or}\gamma_2^{or}.$$

When both phases are mutually saturated ($\mu_2^{aq}=\mu_2^{or}$), $\Delta_s h_2^\ominus$ can be expressed generally as:

$$\Delta_s h_2^\ominus = h_2^{\ominus aq} - h_2^{o} = \left[\frac{\partial\{\mu_2^{\ominus aq}(T,p) - \mu_2^{o}(T,p)\}T^{-1}}{\partial T^{-1}}\right]_p$$

$$= R\left[\frac{\partial \ln (x_2^{or}\gamma_2^{or}/x_2^{aq}\gamma_2^{aq})}{\partial T^{-1}}\right]_{p,\mathrm{sat.}}, \quad (1)$$

where $\mu_2^{\ominus aq}(T,p)$ and $h_2^{\ominus aq}$ are the chemical potential and the partial molar enthalpy of the organic substance in the aqueous phase at an infinite dilution at a certain temperature, T, and pressure, p, where $\mu_2^{o}(T,p)$ and h_2^{o} are the molar Gibbs free energy and enthalpy in its pure state, where x_2^{aq} and x_2^{or} $(=1-x_1^{or})$ are the mole fractions of the organic substance in aqueous and organic phases at mutual saturation, where γ_2^{aq} and γ_2^{or} are the activity coefficients of the substance in aqueous and organic phases, with reference to the infinite dilution and to the pure state respectively, and where R is the gas constant. When the aqueous phase is dilute enough to be an ideal solution ($\gamma_2^{aq}=1$), Eq. 1 is reduced to:

$$\Delta_s h_2^\ominus = R\left[\frac{\partial \ln(x_2^{or}\gamma_2^{or}/x_2^{aq})}{\partial T^{-1}}\right]_{p,\mathrm{sat.}} \cdot \quad (2)$$

When the organic phase is also ideal ($\gamma_2^{or}=1$), Eq. 2 gives:

$$\Delta_s h_2^\ominus = R\left[\frac{\partial \ln(x_2^{or}/x_2^{aq})}{\partial T^{-1}}\right]_{p,\mathrm{sat.}} \cdot \quad (3)$$

If, further, the amount of water in the organic phase in equilibrium with the aqueous phase is either zero or independent of the temperature, Eq. 3 is reduced to:

$$\Delta_s h_2^\ominus = -R\left[\frac{\partial \ln x_2^{aq}}{\partial T^{-1}}\right]_{p,\mathrm{sat.}} \cdot \quad (4)$$

Equation 4 has frequently been used to obtain the heat of solution from the solubility curve of a solid substance.[7] Such a value is almost entirely correct, because the solvent is rarely dissolved in a solid substance and $\ln x_2^{or}$ may be regarded as zero. On the other hand, $\Delta_s h_2^\ominus$ has been evaluated from the solubility curve in water for several substances which are in the liquid state under the conditions measured.[8-11] Such a solubility curve corresponds to the curve with the superscript aq on the left-hand side in Figs. 4, 5, and 6. The conditions for Eq. 4, however, would fail for most liquid organic substances, since the solubilities of water in them must exceed their solubilities in water.[5] Equation 4 cannot be used, of course, for the substances studied here, because neither $\ln x_1^{or}$ nor its derivative with respect to T is zero, as is shown by the right-hand side curves with the superscript or in Figs. 4, 5, and 6. If the mutual solubility is small and both aqueous and organic phases are ideal, $\Delta_s h_2^\ominus$ can be obtained by means of Eq. 3 from the phase diagrams shown in Figs. 4, 5, and 6. In the present cases, however, the organic phases cannot be assumed to be ideal, because the solubilities of water x_1^{or} are as high as between 0.15 and 0.90 as is shown in Figs. 2 and 3, while the aqueous phases are dilute enough to be assumed to be ideal.[3] Unfortunately, $\Delta_s h_2^\ominus$ cannot be evaluated from the phase diagram only, but it can with the use of Eq. 2. The activity coefficient, γ_2^{or}, however, is not available from the literature for most of the substances investigated in the present paper. For 1-butanol, though, the values of γ_2^{or} at 298 K have been found over a wide range of compositions.[12] If γ_2^{or} is assumed to be independent of the temperature at an equal composition,[13] $\Delta_s h_2^\ominus$ for 1-butanol can be estimated from the phase diagram in Fig. 4 by applying Eq. 2. Thus, the difference in $\Delta_s h_2^\ominus$ according to the respective assumption can be checked here for the 1-butanol–water system. The relation between the $\Delta_s h_2^\ominus$ estimated from Eq. 2 and the T for 1-butanol is shown as Curve 2 in Fig. 7. It is expected that the value for $\Delta_s h_2^\ominus$ obtained by Eq. 1 is not so very different from that on Curve 2, since the solubilities of the organic substances are small enough to be ideal. The most likely values of $\Delta_s h_2^\ominus$ shown by Curve 2 increase with an increase in the temperature. The increment of Curve 2 corresponds to the increase in the partial molar enthalpy of 1-butanol in water at an infinite dilution with the rise in the temperature, because the heat of evaporation is almost independent of the temperature.[3] The values for $\Delta_s h_2^\ominus$ which are

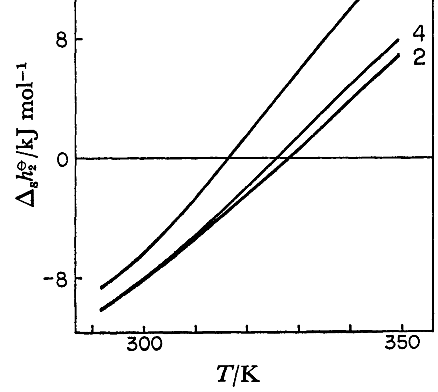

Fig. 7. Heat of solution at infinite dilution *vs.* temperature curves for 1-butanol in water estimated by three different methods.
2: Eq. 2, 3: Eq. 3, 4: Eq. 4.

obtained by the use of Eqs. 3 and 4 are also shown as Curves 3 and 4 respectively in Fig. 7 for the purposes of comparison. It is very impressive that Curve 3 is distant from Curve 2 as a result of our neglecting the deviation of γ_2^{or} from unity and that Curve 4 again approaches Curve 2 as a result of our further neglecting the solubility of water in the organic phase. This suggests that the $\Delta_s h_2^{\ominus}$ value obtained by the simplest method using Eq. 4 may be close to the real value because of the compensation of the two effects of x_2^{or} and γ_2^{or}.

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