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The Analysis of the Solubility of Hydrocarbons in Water

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Enthalpy and entropy of solution of non-polar solutes in water diverge strikingly from the normal behavior established for regular solutions. This abnormality has been considered mostly due to the iceberg formation around solute molecules in water. The abnormal solubility and enthalpy and entropy of solution of non-polar solutes in water have been explained coherently by the extension of the regular solution theory, taking into account the iceberg formation of water molecules. Unlike currently accepted views on the hydrophobic bonding, it is concluded that the enthalpy of mixing (interchange) of non-polar solute with water is large, but the enthalpy decrease due to the iceberg formation of water largely cancels the enthalpy increase of mixing (interchange). Thus, the apparent enthalpy of solution is small or negative at low temperature. It is concluded that 1) the small solubility of non-polar solutes in water is not an entropy effect, and 2) the solubility of non-polar solutes is promoted by the iceberg formation of water molecules.

Frank and Evans[1] analyzed the entropy of solution of non-polar molecules in water which diverges strikingly from the normal behavior established for regular solutions. The small or negative enthalpy of solution and large negative unitary entropy of solution lead them to the idea that the water forms frozen patches or microscopic icebergs around such solute molecules, the extent of the iceberg increasing with the size of the solute molecule. (More ordered structure formation around the solute molecule may express the phenomenon better than iceberg formation.)

In the present paper, the apparently abnormal solubility and enthalpy and entropy of solution of hydrocarbons in water due to the iceberg formation of water molecules will be explained coherently by the extension of the regular solution theory.[2]

The Enthalpy and Entropy of Solution in Regular Solutions. It is necessary to explain the dissolution in regular solutions in order to understand the dissolution of hydrocarbons in water. The enthalpy and entropy of solution of solute (2nd component) in liquid state in solvent (1st component) in regular solutions is[2];

$$\Delta\overline{S}_2 = -\boldsymbol{R}\ln X_2$$

$$\text{liquid(2 nd component)} \rightarrow \text{solute,} \qquad (1)$$

$$\Delta\overline{H}_2 = V_2\phi_1{}^2B'$$

$$\text{liquid(2 nd component)} \rightarrow \text{solute,} \qquad (2)$$

where X_2 is the solubility of 2nd component in mole fraction unit, V_2 the molar volume, ϕ_1 the volume fraction of solvent, B' the experimental constant. In the case when the 1st component is sparingly soluble in 2nd component, the 2nd component in pure liquid state and in solute state are in an equilibrium, so that the Gibbs free energy is equal, $\Delta\overline{G}_2=0$, and we obtain,

$$V_2\phi_1{}^2B' = -\boldsymbol{R}T\ln X_2\,. \qquad (3)$$

If the 2nd component is a pure solid which does not form solid solution with solvent, the enthalpy and entropy of solution is expressed as follows,

$$\Delta\overline{H}_2 = V_2\phi_1{}^2B' + \Delta H_2{}^f$$

$$\text{solid(2nd component)} \rightarrow \text{solute,} \qquad (4)$$

$$\Delta\overline{S}_2 = -\boldsymbol{R}\ln X_2 + \Delta S_2{}^f$$

$$\text{solid(2nd component)} \rightarrow \text{solute,} \qquad (5)$$

where $\Delta H_2{}^f$ and $\Delta S_2{}^f$ are the enthalpy and entropy of fusion of solid at the temperature of solution. The solid (2nd component) melts at this temperature and mixes with solvent in the process of dissolution. Additional term due to the melting is incidental to the solution of solid in liquid.[3,4] As the 2nd component in solid state and in solute state are in equilibrium, the partial molal Gibbs free energy of solution is zero.

$$\Delta\overline{G}_2 = 0\,, \qquad \Delta\overline{H}_2 = T\Delta\overline{S}_2\,. \qquad (6)$$

If we express the vapor pressure of solid by $p_2{}^s$ and that of supercooled liquid by $p_2{}^l$, the Gibbs free energy change of fusion is expressed as,

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[1] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

[2] J. H. Hildebrand and R. L. Scott "Regular Solutions," Prentice Hall, Inc., Englewood Cliffs, New Jersey (1962).

[3] J. H. Hildebrand, *J. Phys. Chem.*, **64**, 370 (1960).

[4] K. Shinoda and J. H. Hildebrand, *ibid.*, **62**, 292 (1958).

$$\Delta G_2{}^f = \Delta H_2{}^f - T\Delta S_2{}^f = \boldsymbol{R}T\ln(p_2{}^l/p_2{}^s)\,. \tag{7}$$

Combining Eqs. (4), (5) and (6), we obtain

$$T\Delta S_2{}^f - \Delta H_2{}^f = \boldsymbol{R}T\ln X_2 + V_2\phi_1{}^2B'\,. \tag{8}$$

Substituting Eq. (7) into (8), we obtain

$$\begin{aligned}\boldsymbol{R}T\ln(p_2{}^s/p_2{}^l) &= \boldsymbol{R}T\ln a_2\\ &= \boldsymbol{R}T\ln X_2 + V_2\phi_1{}^2B'\,.\end{aligned} \tag{9}$$

The enthalpy of solution and the temperature dependence of solubility is related as follows,

$$-\boldsymbol{R}\left(\frac{\partial \ln a_2}{\partial \ln X_2}\right)_T\left(\frac{\partial \ln X_2}{\partial\, 1/T}\right)_{\mathrm{sat}} = \Delta\overline{H}_2 = T\Delta\overline{S}_2\,, \tag{10}$$

where $(\partial \ln a_2/\partial \ln X_2)_T \approx 1$ in dilute solution.

It is clear from Eqs. (10) and (4) that the temperature dependence of the logarithm of solubility is proportional to the enthalpy of solution and increases discontinuously by the amount $\Delta H_2{}^f$ below the melting point of solute. However, the enthalpy and entropy of fusion cancel each other, so that the solubility is scarcely affected by the increased enthalpy of solution slightly below the melting point.

The Enthalpy and Entropy of Solution of Non-polar Solutes in Water. In the process of solution of non-polar solutes in water the iceberg formation[1] and hydrogen bond breaking occurs around the hydrocarbon chains. In dilute solution of this system, the amount of water which forms icebergs and the hydrogen bond breaking increases proportionally to the number of moles of solute, but does not increases with the amount of added solvent. Thus, the iceberg formation of water and the hydrogen bond breaking affect the partial molal quantity of solute, but they little affect that of solvent in dilute solution. This statement is clear from the general partial molal equation for a binary system,

$$n_1\mathrm{d}\overline{Y}_1 + n_2\mathrm{d}\overline{Y}_2 = 0,$$

where Y is any extensive property of the solution. According to the equation, $\mathrm{d}\overline{Y}_1$ is negligibly small in dilute solution, because n_2/n_1 is very small (about 10^{-3} at the present system). If n mol of water form icebergs and n' units of hydrogen bonds are destroyed per mole of solute, the enthalpy and entropy of solution of non-polar solutes in water is expressed as follows,

$$\Delta\overline{H}_2 = V_2\phi_1{}^2B' - n\Delta\overline{H}_i{}^f + n'\Delta\overline{H}_h$$

$$\text{non-polar liquid} \rightarrow \text{solute in } H_2O\,, \tag{11}$$

$$\Delta\overline{S}_2 = -\boldsymbol{R}\ln X_2 - n\Delta\overline{S}_i{}^f + n'\Delta\overline{S}_h$$

$$\text{non-polar liquid} \rightarrow \text{solute in } H_2O\,, \tag{12}$$

where $-n\Delta\overline{H}_i{}^f(-n\Delta\overline{S}_i{}^f)$ is the partial molal enthalpy(entropy) change of 2nd component due to the iceberg formation of n moles of the surrounding water and $n'\Delta\overline{H}_h(n'\Delta\overline{S}_h)$ is the partial molal enthalpy(entropy) change due to the hydrogen bond breaking. As the effect of iceberg formation seems predominant in aqueous solution, only the iceberg formation may be taken into account as an abnormality in the present paper. The iceberg formation proceeds with the temperature decrease and n increases with the temperature depression. On the other hand, the solubility and the enthalpy of solution approach to the regular values at higher temperature.

Analysis of the Temperature Dependence of the Solubility of Alkanes in Water. The solubility of alkanes (C_1—C_4) at 1 atm as a function of temperature has been published.[5-7] In order to gain an insight into the dissolution phenomena, the solubility of alkanes at 1 atm pressure was recalculated to that of hypothetical liquid alkanes. The recalculation has been performed as follows. The fugacity of liquid alkanes divided by the critical pressure of respective alkanes, f°/p_c, at various temperature was obtained from the empirical diagram drawn by Prausnitz based on the principle of corresponding state.[8] The solubility at 1 atm multiplied f° is the solubility of hypothetical liquid alkanes. The recalculated solubility was plotted in Fig. 1.

As the iceberg formation decreases with the temperature rise, n in Eqs. (11) and (12) decreases

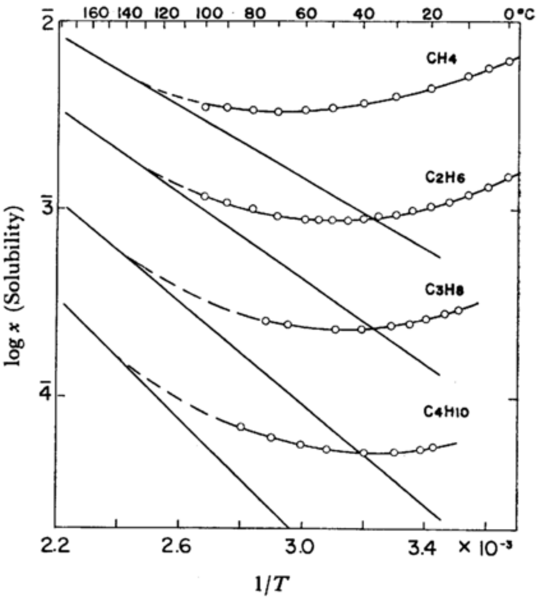

Fig. 1. The solubility of hypothetical liquid alkanes in water as a function of temperature. Calculated from the data at 1 atm (Refs. 5, 6 and 7).

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5) W. F. Claussen and M. F. Polglase, *J. Am. Chem. Soc.*, **74**, 4817 (1952).

6) T. J. Morrison and F. Billet, *J. Chem. Soc.*, **1952**, 3819.

7) L. W. Winkler, *Ber.*, **36**, 1408 (1901).

8) J. M. Prausnitz, *J. Phys. Chem.*, **66**, 640 (1962).

TABLE 1. THE ANALYSIS OF THE ENTHALPY AND ENTROPY OF SOLUTION OF LIQUID HYDROCARBONS IN WATER AT 25°C

Enthalpy of solution $= \Delta\bar{H}_2 = -\boldsymbol{R}\left(\dfrac{\partial \ln X_2}{\partial\, 1/T}\right)_{\text{sat}}$; Entropy of solution $= \Delta\bar{H}_2/T$

Enthalpy of mixing $= V_2\phi_1{}^2B'$ (estimated) ; Entropy of mixing $= -\boldsymbol{R}\ln X_2$

Enthalpy of iceberg formation $= -n\Delta\bar{H}_i{}^f$; Entropy of iceberg formation $= -n\Delta\bar{S}_i{}^f$

Solute	$\Delta\bar{H}_2 = V_2\phi_1{}^2B' - n\Delta\bar{H}_i{}^f$ (cal/mol)	$\Delta\bar{S}_2 = -\boldsymbol{R}\ln X_2 - n\Delta\bar{S}_i{}^f$ (cal/deg/mol)	$\Delta\bar{H}_i{}^f/\Delta\bar{S}_i{}^f$ (°K)
CH_4	$-1900=4300-6200$	$-6.4=10.8-17.2$	360
C_2H_6	$-2000=5100-7100$	$-6.7=13.7-20.4$	348
C_3H_8	$-1880=6100-7980$	$-6.3=16.5-22.8$	350
C_4H_{10}	$-820=7200-8020$	$-2.7=19.6-22.3$	359
C_6H_6	$+580=5100-4520$	$+1.9=15.4-13.5$	335
$CH_3C_6H_5$	$+640=6050-5410$	$+2.2=17.9-15.7$	345
$C_2H_5C_6H_5$	$+390=7000-6610$	$+1.4=20.4-19.0$	348

and the slope of $-\partial\ln X_2/\partial(1/T)$ increases with the temperature rise as shown in Fig. 1. The change of the slope with temperature, $-[\partial^2\ln X_2/\partial(1/T)^2]$, decreases with temperature and is almost zero at 120—160°C at which the iceberg formation seems mostly disappear. We can evaluate the solubility at this temperature by extrapolation and then calculate the enthalpy of solution by the aid of Eqs. (2), (3) and (10). The straight lines in Fig. 1 express the hypothetical solubility of alkanes in water assuming no iceberg formation. The temperature dependence of solubility, $-(\partial\ln X_2/\partial 1/T)$, decreases with the temperature depression as shown in Fig. 1 and the solubility increases relatively with the iceberg formation of water. Similar relation is observed for aromatic hydrocarbons[9,10] and the analysis of the data is listed in Table 1.

The straight line and the experimental solubility curve approaches asymptotic at high temperature. This is an important finding, because the entropy of solution of hydrocarbon from the pure liquid state to the solute state in water is then given by,

$$\Delta\bar{S}_2 = -\boldsymbol{R}\ln X_2 = \bar{S}_2 - S_2{}^\circ. \tag{13}$$

As the partial molal entropy of hydrocarbon (2nd component) in aqueous solution, $\bar{S}_2$, and the hypothetical standard entropy of hydrocarbon in which the mole fraction is formally taken as unity, $\bar{S}_2{}^\circ$, are related as,

$$\bar{S}_2 = \bar{S}_2{}^\circ - \boldsymbol{R}\ln X_2, \tag{14}$$

the fact implies the assertion that the hypothetical standard entropy of the 2nd component as a solute is equal to the standard entropy of that component as a pure liquid,

$$\bar{S}_2{}^\circ = S_2{}^\circ. \tag{15}$$

This relation holds in regular liquid-liquid mixtures regardless the difference between δ_1 and δ_2, as can be derived from Eq. (1) or (13),

$$\bar{S}_2{}^\circ = \bar{S}_2 + \boldsymbol{R}\ln X_2 = \bar{S}_2 - (\bar{S}_2 - S_2{}^\circ) = S_2{}^\circ. \tag{16}$$

Namely, the enthalpy of mixing in regular solutions is purely energetic and the cratic entropy compensates the enthalpy change to give $\Delta G_2=0$. If the dissolution involves phase change such as the melting of solute, both the enthalpy and entropy changes with the process of melting as shown in Eqs. (4) and (5). In this case both changes largely cancel each other and the cratic entropy to compensate the difference, $\Delta H_2{}^f - T\Delta S_2{}^f$, is small. It is evident from Eq. (5) that

$$\bar{S}_2{}^\circ - S_2{}^\circ = \Delta S_2{}^f \quad \text{(solid} \rightarrow \text{solute).} \tag{17}$$

The iceberg formation resembles to the phase change. Both enthalpy and entropy are lost due to the process as expressed in Eqs. (11) and (12). Standard entropy of solute decreases due to the iceberg formation of water, but this abnormality diminishes gradually with the temperature rise. The hydrogen bond breaking on the other hand, increases the enthalpy and entropy of solute. These two abnormalities decrease with the temperature and cancel each other at 120—160°C. Because, the experimental entropy of solution at this temperature is equal to $-\boldsymbol{R}\ln X_2$ (*cf.* Eq. (12)). As the effect of iceberg formation is so large at lower temperature that $n'\Delta\bar{S}_h$ and $-n\Delta\bar{S}_i{}^f$ (at 120°C) were neglected from the following discussion.

Estimation of Respective Factors to the Enthalpy and Entropy of Solution of Hydrocarbons in Water at 25°C (First Approximation). The enthalpy and entropy of solution of liquid hydrocarbons in water at 25°C are calculated from the temperature dependence of the solubility

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[9] R. L. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, **73**, 1571 (1951).

[10] D. M. Alexander, *J. Phys. Chem.*, **63**, 1021 (1959).

and shown in Table 1. The enthalpy of solution assuming regular behavior is obtained from the slope of straight lines in Fig. 1, then the enthalpy change of iceberg formation, $n\Delta\bar{H}_i{}^f$, is readily obtained by the aid of Eq. (11). The entropy of mixing is calculated from the solubility,[11] and $n\Delta\bar{S}_i{}^f$ is obtained by the aid of Eq. (12) assuming $-n\Delta\bar{S}_i{}^f$ (at 120°C)$+n'\Delta\bar{S}_h$ (25°C) is small. All these values are summarized in Table 1.

The enthalpy of mixing is approximately proportional to the molal volumes of respective alkanes, and the ratio of $\Delta\bar{H}_i{}^f/\Delta\bar{S}_i{}^f$ (mean freezing point of iceberg formation) is nearly constant, 350°K, for all hydrocarbons examined. As the iceberg formation proceeds at above room temperature, this is a reasonable value as a first approximation. These relations support the consistency of the present theory. Unlike currently accepted views,[12,13] it is evident from Fig. 1 and Table 1 that the enthalpy of mixing is a large positive value as would be expected on the basis of the intermolecular forces. Small negative enthalpy of solution, $\Delta\bar{H}_2$, is resulted from a large positive enthalpy of mixing and a large negative enthalpy of iceberg formation.

Introducing the relation $\Delta\bar{H}_2=T\Delta\bar{S}_2$ in Eqs. (11) and (12), (and neglecting $n'\Delta\bar{H}_h-n'T\Delta\bar{S}_h$ as a first approximation,) we obtain,

$$n\Delta\bar{H}_i{}^f - nT\Delta\bar{S}_i{}^f = \boldsymbol{R}T\ln X_2 + V_2\phi_1{}^2B' . \quad (18)$$

The left hand side of Eq. (18) corresponds to the free energy term of 2nd component, $\boldsymbol{R}T\ln a_2$. Unlike the process of solid (2nd component) in liquid, the relative activity is larger than 1 in the process of mixing liquid in liquid accompanied with iceberg formation. Equation (18) is useful to understand that the small solubility of hydrocarbons in water is mainly resulted from the large positive enthalpy of mixing and the enthalpy decrease of the iceberg formation is largely cancelled[1,14] by the accompanying entropy decrease (about 83% cancelled) at 25°C, and that the solubility increases as much as $\exp(n\Delta\bar{H}_i{}^f-n\Delta\bar{S}_i{}^f)/\boldsymbol{R}T$ times due to the iceberg formation.

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11) K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, **61**, 789 (1957).

12) W. Kauzmann, *Advances in Protein Chem.*, **14**, 1 (1959).

13) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).

14) H. S. Frank, *Federation Proc. Suppl.*, **24**, 1 (1965).