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PRESSURE-VOLUME APPROACH TO THE ACTIVITY COEFFICIENT OF NONELECTROLYTE IN AQUEOUS MIXED SOLVENT

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The extension of McDevit and Long theory to the prediction of the activity coefficient of nonelectrolyte in aqueous mixed solvent has been made. By the use of the present approach, the characteristic composition dependences of the hydrogen gas solubility (literature data) in water-dimethyl sulfoxide (DMSO) mixtures and the observed partition coefficient of acetone and acetylacetone in the system of heptane/water-DMSO could be reasonably interpreted.

Introduction

In the course of our study to clarify the role of solvent in liquid-liquid partition of nonelectrolyte including metal chelate compounds, the most important but difficult problems to be studied are in the aqueous phase in a given system. Previously, we have examined the partition behavior of acetylacetone in the systems including water-DMSO and water-acetonitrile mixtures as aqueous phases and suggested that the observed composition dependence of the partition coefficient reflects the extent of interaction between water and the co-solvents.1)

It is quite common to discuss the solvent effect in terms of activity coefficient of solute. Hildebrand et al.2) studied widely the solubility of nonelectrolyte and succeeded to interpret many experimental results by introducing the regular solution theory. However, the solvent systems of interest such as aqueous mixtures and the electrolyte solutions are difficult to be treated by the regular solution approximation.

Recently, Hyne et al.3) have determined the internal pressure of water-DMSO mixtures of various compositions. A remarkable similarity between the composition dependence of the internal pressure and the composition dependence of partition coefficient of acetylacetone in heptane/water-DMSO system encouraged us to develop an internal pressure approach as a powerful approach to predict qualitatively an activity coefficient of solute in aqueous mixtures. Most recently, Dack has suggested in his review4) the importance of the internal pressure in solution chemistry, but there is no theoretical approach on the basis of an internal pressure concept for the present, except the attempt of McDevit and Long.5) McDevit and Long correlated the salt in/out coefficient of nonelectrolyte in aqueous solution with the effective pressure change of solvent caused by dissolved salt. However, the derivation was made under the limited condition of infinitely diluted salt solution, and hence, derived equation is not applicable to binary mixed system.

Then, we intended the extension of McDevit and Long theory to the prediction of the activity coefficient of nonelectrolyte in binary mixed solvents, including aqueous mixtures, in order to elucidate the solvent effect of an aqueous phase in liquid-liquid partition of nonelectrolyte.

Theoretical

The Helmholtz free energy of a mixed solvent can be approximately represented in a form of Taylor's expansion as follows,[2)]

$$A(V^o+\Delta V) = A(V^o) + \left(\frac{dA}{dV}\right)\cdot\Delta V - \frac{1}{2}\left(\frac{d^2A}{dV^2}\right)(\Delta V)^2 = A(V^o) - P\cdot\Delta V - \frac{(\Delta V)^2}{2\beta V}\ . \qquad (1)$$

In the above equation, a volume change ΔV upon mixing the solvents A and B is defined as $V - V^o$, in which V and V^o are the volumes of the real mixed solvent and the ideal mixed solvent, respectively, and shown as $V = n_A v_A + n_B v_B$ and $V^o = n_A v_A^o + n_B v_B^o$, where n, v, and v^o indicate the number of moles, the partial molar volume of component and the molar volume of pure solvent, respectively. β is the isothermal compressibility of mixed solvent defined in its whole composition range. McDevit and Long also started from the above equation, but in their derivation, ΔV is defined under the limited condition of dilute solution and β is over-approximated to be that of pure water.

By assuming that the addition of nonelectrolyte into the mixed solvent causes an additional volume change V_n, an analogous equation to eq. (1) holds for a nonelectrolyte-mixed solvent system. And then, the differentiation of the equation with respect to V_n and the introduction of the relation $(dG/dV)_{T,p} = (dA/dV)_{T,p} + P$ give the next equation in the condition of vanishingly small amount of the nonelectrolyte

$$\lim_{V_n\to 0}\left(\frac{dG}{dV_n}\right)_{T,p} = -\frac{\Delta V}{\beta V}\ . \qquad (2)$$

If we introduce formally the relationships, $V_n = n_n v_n^\infty$ and $(dG/dn_n) = RT\ln f_n$ and replace β with $\alpha T/P_i$, we obtain the final equation of the pressure-volume approach to mixed solvent system,

$$\lim_{n_n\to 0}(\ln f_n) = \frac{v_n^\infty}{RT}\cdot\frac{P_i}{\alpha T}\left(\frac{\bar{v}^o}{\bar{v}} - 1\right) \qquad (3)$$

where f_n and v_n^∞ are the activity coefficient and the partial molar volume of the nonelectrolyte at infinit dilution, and v^o and v refer to the mean molar volumes of ideal mixed solvent and real mixed solvent, and α is the coefficient of thermal expansion of the mixed solvent. Equation (3) shows that the molar excess free energy, $RT\ln f_n$, of the solute is represented by the volume term, v_n^∞, and the pressure term, $(P_i/\alpha T)\cdot\{(\bar{v}^o/\bar{v}) - 1\}$.

Results and Discussion

Equation (3) should be examined by comparison with the experimental observation. Unfortunately, we are not accessible to the internal pressure data available for mixed solvent for the present, except a few system reported by Hyne et al.[3)] In the present examination, the water-DMSO binary system was chosen because this is one of the most interesting systems known as a typical "structured" mixture.[5)] Now the pressure term in eq. (3), $(P_i/\alpha T)\cdot\{(\bar{v}^o/\bar{v}) - 1\}$, can be evaluated as a function of mole fraction of DMSO. The value of α is estimated from $\ln \rho_T$ vs T plot based on the relation $\alpha = -(\partial \ln \rho_T/\partial T)$, where ρ_T is the density of the mixture at temperature T.[7)] The values of $\bar{v}^o/\bar{v}$ are also obtained from the density data. Several data of the estimated pressure term are also summerized in Table 1 and this term exhibits a maximum at ca. 0.25 mole fraction of DMSO.

Table 1. Activity coefficient of hydrogen in water-DMSO mixtures at 25 °C

Mole fraction of DMSO	$\ln f_n$ a)	$\ln f_n$ b)	$\frac{P_i}{\alpha T}(\frac{\bar{v}^o}{\bar{v}} - 1)$ c)
0.000	0.000	0.000	0.0
0.202	0.703 0.717	0.713	16.2
0.401	0.711 0.731	0.691	15.7
0.590	0.434 0.458	0.406	9.3
0.779	0.200 0.226	0.168	3.8
1.000	0.000	0.000	0.0

a) Duplicate values are calculated corresponding to the two original data reported as hydrogen solubility in DMSO.[8)]
b) calculated from eq. (3).
c) cal cm^{-3}.

First, we examined the hydrogen gas solubility as an example of an inert solute. Original solubility data were already given by Symons.[8)] The activity coefficient of hydrogen in the water-DMSO mixture can be estimated from the experimental data and the following intuitive equation,[9)]

$$\ln f_n = (1-\phi_s) \ln x_n^o + \phi_s \ln x_n^1 - \ln x_n \tag{4}$$

where ϕ_s is the ideal volume fraction of DMSO defined as

$$\phi_s = x_s v_s^o / (1 - x_s) v_w^o + x_s v_s^o \tag{5}$$

in which x_s and v_s^o are the mole fraction and the molar volume of DMSO, respectively, v_w^o is the molar volume of water, and x_n^o, x_n^1, and x_n are the solubility of hydrogen on mole fraction scale in pure water, in pure DMSO and in the mixed solvent, respectively. The values of $\ln f_n$ estimated from eqs. (4) and (5) at 25 °C are listed in Table 1. Predicted values of $\ln f_n$ from eq. (3) by employing the value of 26 cm^3 mol^{-1}[10)] as the partial molar volume of hydrogen and the pressure term in Table 1 are also listed in this table. Agreement of the experimental results with the predicted ones is satisfactorily good. In Fig. 1 is shown the good correlation between the experimental and the predicted activity coefficients over the whole composition range and at different temperatures, 25 °C and 65 °C.

Then, we examine the dependence of the partition coefficients of acetone and acetylacetone in the two phase system of heptane/water-DMSO at 25 °C on the pressure term of the mixture phase. The curve A in Fig. 2 shows the observed partition coefficients of acetone on mole fraction scale. The experimental procedure to obtain the partition coefficient of acetone is the same for acetylacetone.1)

For the partition coefficient also, an analogous idea to eq. (4) can be introduced as follows,

$$\Delta \ln P = \ln P - (1 - \phi_s) \ln P^o - \phi_s \ln P^1 \qquad (6)$$

where P^o and P^1 are the partition coefficients in heptane/water and heptane/DMSO, respectively. The curve B in Fig. 2 represents a contribution of the first two terms on the right-hand side of eq. (6), hence the difference between the curves A and B gives the value of $\Delta \ln P$. The $\Delta \ln P$ corresponds to $\ln f_n$ and can be correlated with pressure term as given in eq. (3). In Fig. 3, the $\Delta \ln P$ is plotted against the pressure term of the mixed solvent phase. From the good linear relationship, it is concluded that the observed maximum in the partition coefficient of acetone in Fig. 2 is caused by the increase of the pressure term of the mixed solvent phase. For the partition data of acetylacetone1) also, similar analysis has been attempted. Since acetylacetone is the mixture of keto and enol forms and the two tautomers are not expected to behave in the same manner in solution, the plotting in Fig. 3 has been made for each partition coefficient which has been estimated in the previous paper.1) A satisfactory linear relation is observed for the keto form. A quite large scatter observed for the enol form may be ascribable to a probable hydrogen bonding interaction between the enol form and water.11)

From the above results, the importance of the pressure term as a new solvent parameter for aqueous mixed solvent will be concluded.

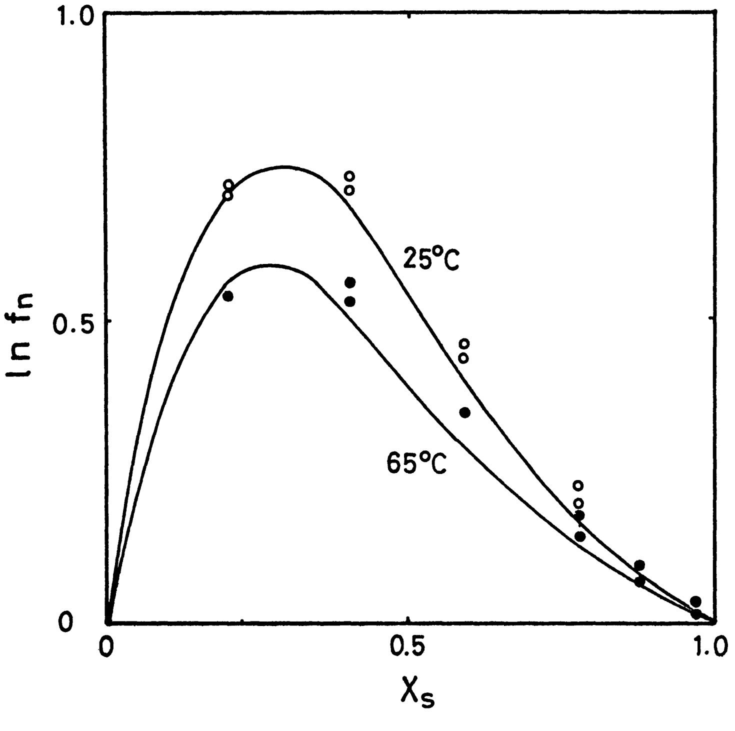

Fig. 1. Activity coefficients of hydrogen at different temperatures. The plots are the experimental values8) and the solid lines are estimated from eq. (3).

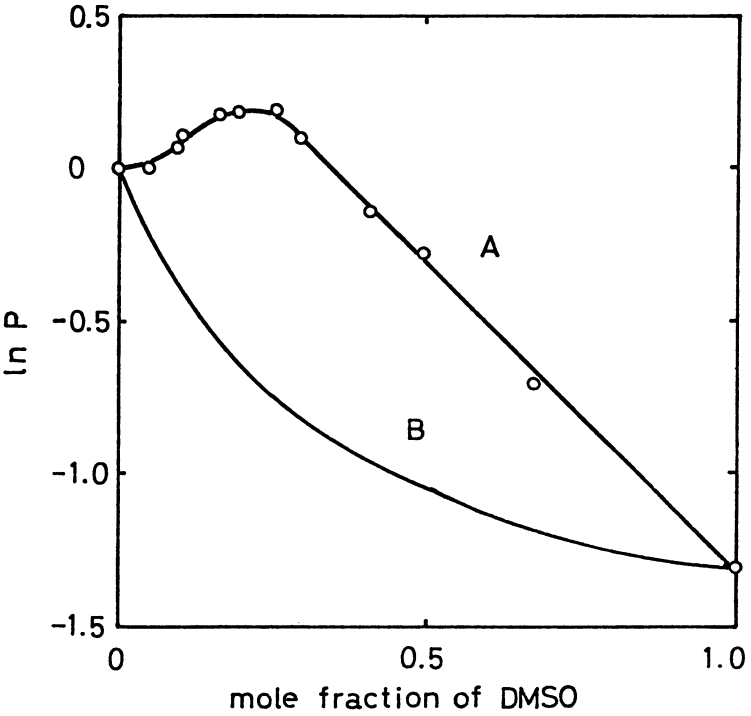

Fig. 2. The partition coefficients of acetone in the systems of heptane/water-DMSO mixtures at 25 °C. Curve A: Experimental result. Curve B: $\ln P = (1 - \phi_s) \ln P^0 + \phi_s \ln P^1$.

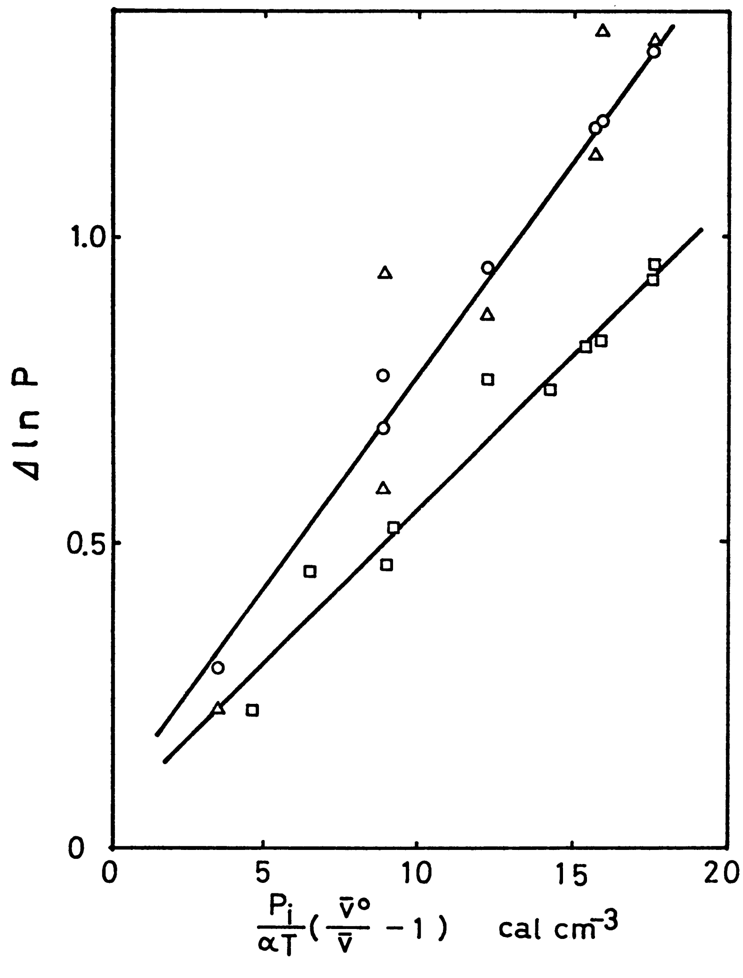

Fig. 3. The dependence of Δ ln P on the pressure term of mixed solvent phase. □ ; Acetone, ○; Keto form of acetylacetone, △; Enol form of acetylacetone.

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