PARTIAL MISCIBILITY IN WATER-NICOTINE AND WATER β-PICOLINE SYSTEMS

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Abstract—the significant structure theory of liquids has been applied to the partially miscible systems, of which the temperature-composition phase diagrams are of closed loop type.

In this paper, the sublimation energy of a mixture is expressed as a quadratic form of surface area fractions of components, and the energy correction parameter between one component and the other is assumed to be a second order function of temperature for simplicity, although it is a higher order function of temperatures and compositions. The calculated partial miscibilities are in good agreement with the experiment.

Considered mixture systems are water-nicotine and water-β-picoline systems.

INTRODUCTION

We live in a world of mixtures-the air we breathe, the food we eat, the gasoline in our automobiles. Wherever we turn, we find that our lives are linked with materials which consist of a variety of chemical substances. Many of the things we do are concerned with the transfer of substances from one mixture to another; for example, in our lungs, we take oxygen from the air and dissolve it in our blood, while carbon dioxide leaves the blood and enters the air; in our coffee maker, water-soluble ingredients are leached from the coffee grain into the water. In each of these common daily experiences, as well as in many others in physiology, home life, industry, and so on, there is a transfer of a substance from one phase to another. This occurs because when two phases are brought into contact, they tend to exchange their consitituents until the composition of each phase attains a constant value; when that state is reached it is said that the phases are in equilibrium. The equilibrium compositions of two phases are often very much different from one another and it is precisely this difference which enables us to separate mixtures by distillation, extraction, and other phase-contacting operations. The final, or equilibrium, phase compositions depend on many variables, such as temperature and pressure, and on the chemical nature and concentration of the various substances involved. Phase-equilibrium thermodynamics seeks to establish the relations between the various properties (in particular, temperature, pressure, and composition) which ultimately prevail when two or more phases reach a state of equilibrium wherein all tendency for further change has ceased.

Since so much of life is concerned with the interaction between different phases, it is evident that phase-equilibrium thermodynamics is a subject of fundamental importance in many sciences. It is of special interest in chemistry and chemical engineering since so many operations in the manufacture of chemical products consist of phase-contacting. For example, extraction, adsorption, distillation, leaching, and absorptions are essential unit operations in chemical industry and an understanding of any one of them is based on the science of phase equilibrium.

Many partially miscible binary liquid mixture which form a single homogeneous phase at high temperature possess an upper critical solution temperature (UCST) below which phase separation occurs. On the contrary, it has been observed[1] that most polymer-polymer pairs exhibiting partial miscibility decrease in solubility as temperature is increased. That is, many polymer-polymer pairs possess an lower critical solution temperature (LCST) above which phase separation occurs. In addition, mixtures such as nicotine and β-picoline with water[2] possess both LCST and UCST, producing a egg-shaped temperature composition diagrams, and many other types of unusual phase behaviors[2] are found in binary liquid mixtures.

In order to interpret and predict the phase equilibrium phenomena, we depend on thermodynamics. Over the years there have been two kinds of developments in the thermodynamics. One, the classical thermodynamics, pioneered by Gibbs provides broad relationships between microscopic properties, but it is not concerned with quantitive prediction of these properties. The other, the statistical thermodynamics, initiated by Boltzmann seeks to establish relationships between macroscopic properties through partition function, which contains microscopic informations. There are two methods of the statistical thermodynamics. One, the formal approach, provides the aesthetic pleasure of initial rigor but, at some stage of the development, approximations have always crept in to make the mathematics tractable. When such difficulties are overcome, a noteworthy advance will have been achieved. The alternative method is the model approach, in which one visualizes a physical model of molecules, translates the picture into mathematical language, i.e., a partition function. If the model is reasonable, the theory will predict the experimental values with sufficient faithfulness.

One of the most widely used model theories is the significant structure theory of liquids [3]. The theory has been applied to various liquids, and was extended to binary mixtures [4-6]. Using the theory, Lee et al[7] explained the partial miscibility of O_2-O_3 system possessing UCST, and later Jung and Jhon[8] explained the LCST behavior which occurs commonly in polymer-polymer systems. In this work, based on the previous applications, the authors explained the phase behavior of a closed loop type temperature-composition phase diagram using the theory.

THEORY

Partition functions for the pure components

According to the significant structure theory of water proposed by Jhon et al,[9] the partition function for water is written as follows

$$f=\left\{\frac{e^{Es/RT}}{(1-e^{-\theta/T})^6}\cdot f_{deg}\cdot K^{\frac{K}{46(1+K)}}\cdot f_{vib}\right\}^{N\frac{Vs}{V}}\cdot\left\{\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{eV}{Na}\cdot f_{rot}\cdot f_{vib}\right\}^{N\frac{V-Vs}{V}} \qquad (1)$$

where V is a molar volume of the liquid, V_s a molar volume of the solid at the melting poit, E_s the sublimation energy, θ the Einstein characteristic temperature, K the equilibrium constant between Ice-I-like molecules and Ice-III-like molecues, f_{vib} the vibrational partition function, f_{rot} the rotational partition function, f_{deg} the partition function of the positional degeneracy and the other symbols have their usual statistical mechanical significance. Here f_{deg} is expressed as follows

$$f_{deg}=1+n\left(\frac{V}{V_s}-1\right)\exp\left\{-\frac{aE_sV_s}{(V-V_s)RT}\right\} \qquad (2)$$

where n is the number of holes next to a molecule, and a the characteristic parameter appearing in the theory. Partition function for the other components are written as follows.

$$f=\left\{\frac{e^{ES/RT}}{(1-e^{-\theta/T})^6}\cdot f_{deg}\cdot f_{vib}\right\}^{N\frac{Vs}{V}}\left\{\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{eV}{Na}\cdot f_{vid}\cdot f_{rot}\right\}^{N\frac{V-Vs}{V}} \qquad (3)$$

The notations are the same as in Eqn. (1). Here we assume that the rotations of the solid-like molecules for nicotine and β-picoline do not occur since no solid state transitions[10] have been observed and the volume increase upon melting is not sufficient to permit the rotation of solid like molecules in the liquid.

Partition function for a mixture

The significant structure theory of liquids was extended to a binary mixture assuming the followings [4-6]. (a) Non-random mixing is negligible, (b) the same Einstein characteristic temperatures of vibration, θ, are retained for mixtures that were used for the pure substance, (c) molecules of both components continue to possess their gas-like translations degrees of freedom, (d) the degeneracy term has the same form as for a pure liquid, and (e) the parameters E_s, V_s, a, and n are taken as suitable averages of the parameters for the pure components. Then, the partition function of the binary mixture chosen in this work be written as

$$f_{mixture}=\frac{(N_1+N_2)!}{N_1!N_2!}\left\{\frac{1}{(1-e^{-\theta_1/T})^6}\cdot K^{\frac{K}{46(1+K)}}\cdot f_{vib_1}\right\}^{N_1\frac{Vs}{V}}\cdot\left\{\frac{(2\pi m_1kT)^{3/2}}{h^3}\cdot\frac{eV}{Na}\cdot f_{rot_1}\,f_{vib_1}\right\}^{N_1\frac{V-Vs}{V}}\cdot\left\{\frac{1}{(1-e^{-\theta_2/T})^6}\cdot f_{vib_2}\right\}^{N_2\frac{Vs}{V}}\left\{\frac{(2\pi m_2kT)^{3/2}}{h^3}\cdot\frac{eV}{Na}\cdot f_{rot_2}\cdot f_{vib_2}\right\}^{N_2\frac{V-Vs}{V}}\cdot\left(f_{deg}e^{ES/RT}\right)^{(N_1+N_2)\frac{Vs}{V}} \qquad (4)$$

where

$$f_{deg}=1+n(V/Vs-1)\ \exp\left\{-\frac{aE_sV_s}{(V-V_s)RT}\right\} \qquad (5)$$

$$V_s=x_1V_{s1}+x_2V_{s2} \qquad (6)$$

$$n=x_1n_1+x_2n_2 \qquad (7)$$

$$a=x_1a_1+x_2a_2 \qquad (8)$$

$$E_s=\theta_1^{*2}E_{s1}+\theta_2^{*2}E_{s2}+2\theta_1^*\theta_2^*(1+\delta_E)\sqrt{E_{s1}E_{s2}} \qquad (9)$$

Here subscript "1" denotes water, subscript "2" the other component, x_i a mole fraction of i-th component and θ_i is a surface area fraction of i-th compoent, assuming the molecules are spherical for simplicity.

Then

$$\theta_i^* = \frac{V_{Si}^{2/3} x_i}{V_{S1}^{2/3} x_1 + V_{S2}^{2/3} x_2} \qquad i=1,2 \tag{10}$$

In our systems, water molecule differs largely from the other molecule in their size. Therefore, the number of contacting sites between molecules is considered to be a function of surface area fractions rather than that of mole fractions. δ_E is the energy correction parameter containing high order terms of temperatures and compositions.

Thermodynamic Condition for Phase Separation

The equation of the coexistence curve called the binodal is written as[11]

$$\triangle\mu_i(x_1, T, P) = \triangle\mu_i(x_1', T, P) \qquad i=1,2 \tag{11}$$

wherre

$$\triangle\mu_i = \left(\frac{\partial\triangle G_{mixing}}{\partial N_i}\right)_{T,P,N_j\neq i} \tag{12}$$

ΔG_{mixing} is the Gibbs free energy change of mixing By the thermodynamic relationships at constant pressure,

$$\triangle G_{mixing} = \triangle A_{mixing} + P\triangle V_{mixing} \tag{13}$$

where ΔA_{mixing} is the Helmholtz free energy change of mixing and ΔV_{mixing} is a volume change of mixing. ΔA_{mixing} is related to the partition function by[12]

$$\triangle A_{mixing} = -kT \ln\frac{f_{mixture}}{f_1 f_2} \tag{14}$$

Since the volume changes of mixing in the systems are negligible,[13] then

$$\triangle G_{mixing} = \triangle A_{mixing} \tag{15}$$

From Eqn.'s (12) to (14)

$$-\frac{\triangle\mu_1}{kT} = \left(\frac{\partial}{\partial N_1}\ln\frac{f_{mixture}}{f_1 f_2}\right)_{T,P,N_2} \tag{16}$$

$$-\frac{\triangle\mu_2}{kT} = \left(\frac{\partial}{\partial N_2}\ln\frac{f_{mixture}}{f_1 f_2}\right)_{T,P,N_1} \tag{17}$$

From Eqn.'s (1) to (4), Eqn.'s (16) and (17) become

$$-\frac{\triangle\mu_1}{kT} = -\ln x_1 + \frac{V_s}{V}B_1 - \frac{V_{s_1}}{V_1}B_1^* + \ln\frac{V}{V_1} + \frac{V_s}{V}\ln f_{deg} - \frac{V_{s_1}}{V_1}\ln f_{deg_1} + \frac{V_s}{V}\frac{E_s}{RT} - \frac{V_{s_1}}{V_1}\frac{E_{s_1}}{RT} + Q(x_1, x_2)\cdot x_2 \tag{18}$$

$$-\frac{\triangle\mu_2}{kT} = -\ln x_2 + \frac{V_s}{V}B_2 - \frac{V_{s_2}}{V_2}B_2^* + \ln\frac{V}{V_2} + \frac{V}{V}s^2\ln f_{deg} - \frac{V_{s_2}}{V_2}\ln f_{deg_2} + \frac{V_s}{V}\frac{E_s}{RT} - \frac{V_{s_2}}{V_2}\frac{E_{s_2}}{RT} - Q(x_1, x_2)\cdot x_1 \tag{19}$$

where

$$B_1 = \ln\left[\frac{1}{(1-e^{-\theta_1/T})^6}K^{\frac{K}{46(1+K)}} \Big/ \left\{\frac{(2\pi m_1 kT)^{3/2}}{h^3}\frac{eV_1}{N_a}f_{rot_1}\right\}\right]$$

$$B_1^* = \ln\left[\frac{1}{(1-e^{-\theta_1/T})^6}K^{\frac{K}{46(1+K)}} \Big/ \left\{\frac{(2\pi m_1 kT)^{3/2}}{h^3}\frac{eV_1}{N_a}f_{rot_1}\right\}\right]$$

$$B_2 = \ln\left[\frac{1}{(1-e^{-\theta_2/T})^6} \Big/ \left\{\frac{(2\pi m_2 kT)^{3/2}}{h^3}\frac{eV}{N_a}f_{rot_2}\right\}\right]$$

$$B_2^* = \ln\left[\frac{1}{(1-e^{-\theta_2/T})^6} \Big/ \left\{\frac{(2\pi m_2 kT)^{3/2}}{h^3}\frac{eV_2}{N_a}f_{rot_2}\right\}\right]$$

and

$$Q(x_1, x_2) = \frac{\partial}{\partial x_1}\left(\frac{V_2}{V}\right)\left(x_1 B_1 + x_2 B_2 + \ln f_{deg} + \frac{E_s}{RT}\right) + \left(1-\frac{V_s}{V}\right)\frac{\partial \ln V}{\partial x_1} + \frac{V_s}{V}\frac{\partial \ln f_{deg}}{\partial x_1} + \frac{V_s}{V}\frac{\partial}{\partial x_1}\left(\frac{E_s}{RT}\right)$$

Substituting Eqn. s (18) and (19) into Eqn. (11), the coexistence curve can be obtained.

RESULTS AND DISCUSSION

The significant structure theory of liquids was applied to water-nicotine and water-β-picoline systems.

The same input data as those of Jhon et al [9], are used for water in this work. The input data for nicotine and β-picoline are listed in Table 1. Here the experimental values were used for a molar volume V [13], V_s's were obtained from estimated relations [14], E_s for nicotine was obtained using the similar method described by Cho et al.[15] E_s for β-picoline was calculated from the experimental heat capacity data [10], and a, n, and θ were evaluated by the relations described in Ref. [3]. The moment of inertia, I_{ABC}, for calculations of the rotational partition functions were estimated from the crystalline structures [16,17]. The volume changes of mixing were neglected since the volume changes are negligibly small [13].

The theoretical prediction for the phase diagrams are compared with the experimental values in Figures 1 and 2. In these calculations, the energy correction parameter

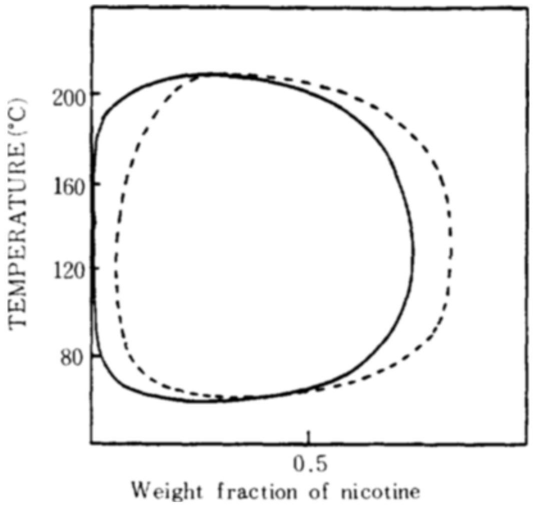

Fig. 1. Phase diagram for water-nicotine system
$\delta_E = 9.225\times10^{-6}t^2 - 2.557\times10^{-3}t + 0.01617$, t : °C
--- : eperimental — : calculated

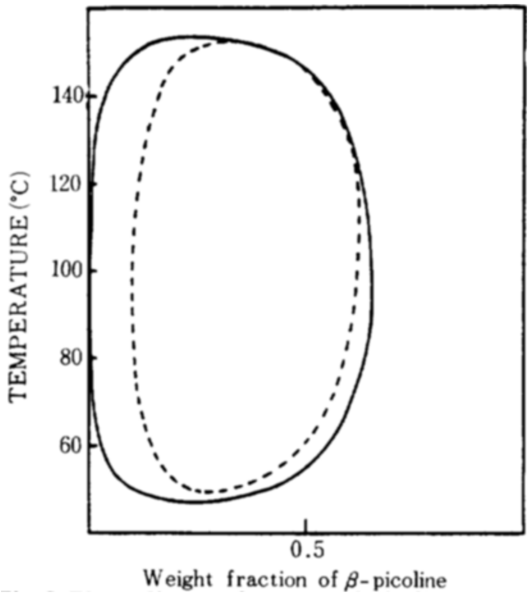

Fig. 2. Phase diagram for water-β-picoline system
$\delta_E = 1.396\times10^{-5}t^2 - 2.904\times10^{-3}t - 0.03070$, t: °C
--- : experimental | — : calculated

in Eqn. (9) is considered approximately as a second order function of temperature, i.e. $\delta_E = \alpha + \beta t + \gamma t^2$. were α, β, and γ are constant, although δ_E is a higher order function of temepratures and compositions. The values of α, β, and γ are taken as the best fitted values because of lack in experimental data of E_{s12}. The figures show that δ_E ranging between -0.1 and -0.2 with positive γ and negative β, causes the closed loop temperature composition diagram in our systems. This is expected from the following reasons. i) For the phase separation, $E_{s12} = (1 + \delta_E)\sqrt{E_{s1}E_{s2}}$ must be less than both E_{s1} and E_{s2}, or largely less than E_{s1} or E_{s2} [7,8]. ii) The closed loop diagrams indicate that the composition range for phase separation increases with temperature below the certain temperature and decreases with temperature above the certain temperature. Therefore it is expected that δ_E decreases with temperature below the certain temperature since the width of the composition range for phase separation increases as $E_{s12} = (1+\delta_E)\sqrt{E_{s_1}E_{s_2}}$ decreases. This means that δ_E of a second order function of temperature with positive γ and negative β causes the closed loop temperature-composition diagram, and it is observed that the larger α and γ, the smaller the magnitude of the egg-shaped phase diagram and that the smaller β, the higher the phase diagram locates along the temperature-axis, although the results are not presented in this paper because of lack in experimental data to be compared with. This results from the fact that the smaller δ_E, the more likely phase separation occurs. The percent deviations between the experiment and the calculated values are listed in Table 2.

CONCLUSION

The partial miscibilities with the closed loop temperature-composition diagrams have been examined for water-nicotine and water-β-picoline systems in terms of the significant structure theory of liquid mixtures. Reasonable results are obtained between the theory and the experiment. It has been shown that the energy correction parameter δ_E of a second order function of temperature with positive γ and negative β causes the closed loop temperature composition diagrams.

For the more exact description of partial miscibilities, it is considered that δ_E may contain composition terms as well as temperature terms.

Table 1. Input data for nicotine and β-picoline

	E_s(kJ/kmol)	V_s(m^3/kmol)	a	n	θ(K)	I_{ABC}(kg^{3}m^6)	d(kg/m^3)$\times10^{-3}$
nicotine	62700	142.6×10^{-3}	0.001443	11.33	39.32	1.018×10^{-132}	$1.0239-0.7041\times10^{-3}t-0.964\times10^{-6}t^2$
β-picoline	76740	81.6×10^{-3}	0.00848	10.36	69.16	2.5×10^{-134}	$0.9723-0.745\times10^{-3}t-2.25\times10^{-6}t^2$

Table 2. Percent deviations between the experiment and the calculated values

water-nicotine	T(°C)	70	90	110	130	150	170	190
system	% deviation	7.5	8.7	7.9	7.5	8.2	7.7	9.8
water-β-picoline	T(°C)	70	90	110	130	150		
system	% deviation	7.2	7.6	7.6	6.0	6.0		

% deviation = $\{|w_1\text{ (exptl.)} - w_1\text{ (calc.)}| + |w_1'\text{ (exptl.)} - w_1'\text{ (calc.)}|\}/2 \times 100\%$
w_1 and w_1': weight fractions of component 1 on the coexistence curve at given temperature

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