論　文

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The Excess Enthalpies of Polarizable Nonpolar and Dipolar Solutions

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The corresponding state theory modified for polar solutions is applied to the excess enthalpies of binary mixtures of aromatic hydrocarbons and aliphatic ketones. The dispersion interaction parameter X_{12} between aromatic hydrocarbon and cyclohexanone is estimated from excess enthalpies of methylcyclohexane mixtures of corresponding aromatic hydrocarbon in which methylcyclohexane is nonpolar homologue to cyclohexanone, and heptane is used as nonpolar homologue to diethyl ketone and methyl ethyl ketone. For the parameter of dipole-dipole interaction m, the value proposed by Winnick, 1.75×10^8, is used. The dipole-induced dipole interaction parameter m' of mixtures of aromatic hydrocarbon and ketone are estimated by using these X_{12} and m parameters from excess enthalpies of mixture. The parameter m' increases in the sequence benzene > toluene > ethyl benzene. The contributions of each interaction to excess enthalpy are also estimated.

The corresponding state theories[1,2,3] have been applied to interpret thermodynamic properties of nonpolar solutions.

In this study, we have modified the Flory free volume theory[3] to apply to such polar solutions as aromatic hydrocarbon + aliphatic ketones. In such mixtures, the total intermolecular interaction may be treated as the sum of the dispersion interaction, the breaking of dipole-dipole interaction and the dipole-induced dipole interaction. Their contributions to the excess enthalpies of mixtures were estimated.

Theoretical

A theoretical derivation of the corresponding state theory for polar solution is described elsewhere[4] in detail. The resultant expressions for the excess enthalpy of mixing are briefly referred to here.

The excess enthalpy of binary mixture of nonpolar liquids is expressed as follows[3],

$$H^{\mathrm{E}} = x_1 p_1^* V_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + x_2 p_2^* V_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1}) + x_1 V_1^* \theta_2 X_{12} \tilde{v}^{-1} \qquad (1)$$

where x_i is the mole fraction of component i, θ_2 the surface fraction of component 2, p_i^* the characteristic pressure of i, V_i^* the core molar volume of i, and $\tilde{v}_i = V_i / V_i^*$ and $\tilde{v}$ are the reduced volumes of component i and mixture, respectively. Parameter X_{12} is the dispersion interaction parameter between different components. In the extension of the Flory free volume theory to the mixture of polarizable nonpolar and dipolar liquids, dipolar effects (dipole-dipole, and dipole-induced dipole interactions) are treated as the perturbation of polar effects on the dispersion interaction, assuming that the dipolar interaction is very small in comparison with the dispersion and that both mixing and orientation are random.

The contribution of polar effect on the excess enthalpy of mixture of polarizable nonpolar liquid (polarizability α_1) and dipolar liquid (dipole moment μ_2 and polarizability α_2) are divided into E_{dd}, the contribution of dipole-dipole interaction, and E_{did}, that of the interaction between the dipole of component 2 and the induced dipole of component 1. E_{dd} and E_{did} are defined by Winnick[6,7] as follow

$$E_{\mathrm{dd}} = m \mu_2^4 / RT V_2^{*2} \qquad (2)$$

$$E_{\mathrm{did}} = m' \mu_2^2 \alpha_1 / V_1^* V_2^* \qquad (3)$$

where R and T are gas constant and temperature,

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m is empirically determined as $m=1.0\times10^7$ (in cal K^{-1} mol^{-1} unit for R and Debye unit for μ) or 1.75×10^8 (in J K^{-1} mol^{-1} for R and same for μ) from the vapor pressure data for various pure substances$^{6)}$, m' is an empirical parameter determined from each binary mixture$^{7)}$.

The total excess enthalpy of mixtures of nonpolar and dipolar liquids is represented by

$$\begin{aligned}H^{\mathrm{E}}=&\,x_1 p_1^* V_1^*(1/\tilde{v}_1-1/\tilde{v})+x_2 p_2^* V_2^*(1/\tilde{v}_2-1/\tilde{v})\\&+x_1 V_1^*\theta_2 X_{12}/\tilde{v}+x_2\, m\mu_2^4/RTV_2^{*2}(1/\tilde{v}_2-\theta_2/\tilde{v})\\&-2\,x_1\theta_2 m'\mu_2^2\alpha_1/V_1^* V_2^*\tilde{v}\end{aligned}\qquad(4)$$

Since the contribution of polar effects can be regarded as a perturbation to the dispersion interaction, the polar terms in this equation are independent of the reduced volume of solution. Equation 4 is then rewritten as

$$\begin{aligned}H^{\mathrm{E}}=&\,x_1 p_1^* V_1^*(1/\tilde{v}_1-1/\tilde{v})+x_2 p_2^* V_2^*(1/\tilde{v}_2-1/\tilde{v})\\&+x_1 V_1^*\theta_2 X_{12}/\tilde{v}+x_2\theta_1 m\mu_2^4/RTV_2^{*2}\\&-2\,x_1\theta_2 m'\mu_2^2\alpha_1/V_1^* V_2^*\end{aligned}\qquad(5)$$

The sum from the first to the third term of right hand side of equation 5 is the dispersion term H_0^{E}, the fourth term is due to the breaking of dipole-dipole interaction $H_{\mathrm{dd}}^{\mathrm{E}}$, and the last term is due to the dipole-induced dipole interaction $H_{\mathrm{did}}^{\mathrm{E}}$.

The four parameters, p^*, V^*, $\tilde{v}$, and T^*, are calculated from the thermal expansion factor α_{T} and the isothermal compressibility β_{T} by the following equations

$$\begin{aligned}&\tilde{T}=(\tilde{v}^{1/3}-1)/\tilde{v}^{4/3}\\&\tilde{v}^{1/3}=\alpha_{\mathrm{T}}T/3(1+\alpha_{\mathrm{T}}T)+1\\&p^*=(\alpha_{\mathrm{T}}/\beta_{\mathrm{T}})T\tilde{v}^2\end{aligned}\qquad(6)$$

and the polarizability α is calculated from ε by $\alpha=(\varepsilon-1)V^*/(\varepsilon+2)$.

Results and discussion

The modified corresponding state theory is applied to binary mixtures of aromatic hydrocarbons with aliphatic ketones. Benzene, toluene, and ethyl benzene are used as aromatic hydrocarbon, and cyclohexanone, diethyl ketone, and methyl ethyl ketone as ketones. The excess enthalpies of these binary mixtures were measured and reported elsewhere$^{8,9)}$.

There are three types of intermolecular interaction parameters for these mixtures, namely, dispersion interaction parameter X_{12}, dipole-dipole interaction parameter m, and dipole-induced dipole interaction parameter m'.

The contribution of the dispersion interaction to the excess enthalpy of the mixture of an aromatic hydrocarbon and cyclohexanone may be estimated by the excess enthalpy of the corresponding mixture of aromatic hydrocarbon and methylcyclohexane under the assumption that the dispersion interaction of cyclohexanone mixture could be replaced by that of methylcyclohexane similar in shape to cyclohexanone and also in molecular orientation effect. As for the corresponding mixture of diethyl ketone or methyl ethyl ketone, it is replaced by heptane mixture.

The values of excess enthalpies H^{E} were taken from our previous papers$^{8,9)}$ and literature$^{10)}$ and represented by the following equation

$$H^{\mathrm{E}}=x_1x_2\sum_{i=0}^{n}C_i(1-x_1)^i\qquad(7)$$

where suffix 1 represents an aromatic hydrocarbon, and the values of coefficients C_i are listed in table 1.

The physical properties necessary for the estimation of intermolecular interaction parameters are summarized in table 2. Among the physical values used, the dipole moments of toluene (0.31 Debye) and ethyl benzene (0.37 Debye) are neglected and assumed to be zero.

The dispersion interaction parameters X_{12} for nonpolar mixtures are given in table 3, together with the observed H^{E}(obs) and the calculated H^{E}(calc) at $x_1=0.5$.

Using these X_{12} values for the dispersion interaction parameter of the corresponding polar mixture and the dipole-dipole interaction parameter $m=1.75\times10^8$, we calculate the dipole-induced dipole interaction parameter m' by fitting H^{E} values at $x_1=0.5$ for the mixtures of aromatic hydrocarbon + ketone. The obtained values of m' are listed in table 4, together with the contributions of each interaction to H^{E} at $x_1=0.5$.

The dipole-induced dipole interaction parameter m' obviously increases in the sequence; benzene > toluene > ethyl benzene for cyclohexanone and also diethyl ketone mixtures.

In the calculation of methylcyclohexane + cyclohexanone mixture, the dispersion interaction parameter $X_{12}=9.28$ was obtained from the

Berthelot representation for X_{12}. The parameter of dipole-induced dipole interaction m' is found to be -4.36×10^4. The obtained m' is unexpectedly large negative.

Table 1. The coefficients of equation 7 for the excess enthalpy of mixtures

system	coefficients/J mol^{-1}				
1 + 2	C_0	C_1	C_2	C_3	reference
benzene + methyl cyclohexane	3122.5	−478.8	178.1	−65.1	9
toluene + methyl cyclohexane	2148.8	−48.5	94.3	32.2	9
ethyl benzene + methyl cyclohexane	1804.4	25.9	96.9	12.8	9
benzene + n-heptane	3709	−848	359		10
toluene + n-heptane	2252.9	−379.9	147.4	4.57	8
ethyl benzene + n-heptane	2166.5	−213.8	107.7	−17.0	8
benzene + cyclohexanone	−1131.5	172.3	−33.2	−75.8	9
toluene + cyclohexanone	−658.3	108.6	70.8	−110.8	9
ethyl benzene + cyclohexanone	−357.7	87.4	135.3	−103.5	9
benzene + diethyl ketone	−518.0	−156.6	201.7	95.1	8
toluene + diethyl ketone	−628.9	−189.9	142.6	−30.9	8
ethyl benzene + diethyl ketone	−194.8	−224.1	130.1	−35.5	8
ethyl benzene + methyl ethyl ketone	403.7	−173.7	139.0	−37.6	8
methyl cyclohexane + cyclohexanone	3975.9	−671.9	886.3	−684.4	9

Table 2. The physical values for calculation

material	expansion^{c} factor α_T/K	compressibility^{d} $\beta_T/10^6$atm	heat capacity^{e} C_p/J K^{-1}mol^{-1}	molar volume^{e} V/cm^3 mol^{-1}	dipole^{e} moment μ/Debye	dielectric^{e} constant ε
benzene	0.00122	97.93	135.98	89.407	0	2.275
toluene	0.00106	91.92	(157.14)^{a}	106.855	0	2.379
ethyl benzene	0.000955	86.20	(181.48)^{b}	123.074	0	2.4042
methyl cyclohexane	0.00118	135.2	134.94	128.343	0	2.020
n-heptane	0.00124	146.78	224.80	147.468	0	1.924
cyclohexanone	0.00095	70.0	(200.25)^{b}	104.18	3.01	18.3
diethyl ketone	0.00121	109.05	190.80	106.412	2.82	17.0
methyl ethyl ketone	0.00129	117.19	158.81	90.169	2.76	18.51

(　)^{a}; a value at 293.15K, (　)^{b}; a value at 303.15K.

^{c}; from reference 11, ^{d}; calculated from sound velocity of reference 12, ^{e}; from reference 13.

Table 3. The interaction parameter of nonpolar mixtures

system	parameter	excess enthalpy	
1 + 2	X_{12}/J cm^{-3}	H^E(calc)/J mol^{-1}	H^E(obs)/J mol^{-1}
benzene + methyl cyclohexane	38.32	787.5	780.6
toluene + methyl cyclohexane	23.13	540.4	537.1
ethyl benzene + methyl cyclohexane	17.88	454.6	451.1
benzene + n-heptane	43.95	939.8	927.3
toluene + n-heptane	23.51	569.5	563.2
ethyl benzene + n-heptane	20.69	545.5	541.6

According to Winnick[6)], m is empirically related to

$$m\mu^4/V^{*2}RT=(Lz/2)(\mu^4/3r^6kT) \qquad (8)$$

where L is Avogadro's number, z the coordination number, and $V^*=L\xi\sigma^3$ and $(r/\sigma)^3=V/V^*$, where ξ is the geometry factor ($4\sqrt{3}/3$ for bcc lattice, $z=8$) and σ and r are the molecular and effective diameters. The parameter m is represented by the following,

$$m=2.19\times10^8(V^*/V)(\xi^2 z) \quad \text{(in J unit)} \qquad (9)$$

Winnick found empirically $m=1.0\times10^7$ (in cal unit) $=1.75\times10^8$ (in J unit) from a fit of vapor pressure data of various pure substances. Since the dipole-induced dipole interaction in cyclohexanone cannot be separated from the dipole-dipole interaction, its contribution is included in parameter m, which is empirically determined without the division between these two interactions and the parameter of the dipole-induced dipole interaction produced in pure dipolar liquid is assumed to be zero. Consequently, the parameter m' is due to the dipole-induced dipole interaction newly formed between different species in mixture and must be positive contrary to the result of calculation of methylcyclohexane + cyclohexanone mixture. m is originally the constant characteristic for the substances, as given in equation 9, and the value of parameter m estimated from vapor pressure data may be different from the value estimated from excess enthalpy of mixing.

A trial which is treated with $X_{12}=9.28$ by Berthelot's expression and $m'=0$ gives a value of 6.28×10^8 to m from the excess enthalpy of methylcyclohexane + cyclohexanone, on the assumption of the contributions of dispersion and dipole-dipole interactions. The parameter m' of the mixture of aromatic hydrocarbon + cyclohexanone was recalculated, as a trial, by using new value of parameter $m=6.28\times10^8$, and was also recalculated for the other ketone systems by use of the same value of m as that of cyclohexanone. The obtained $m'/10^4$ is 9.92 (cyclohexanone) and 10.10 (diethyl ketone) for benzene, 8.33 (cyclohexanone) and 8.42 (diethyl ketone) for toluene, and 8.02 (cyclohexanone), 8.08 (diethyl ketone) and 7.87 (methyl ethyl ketone) for ethyl benzene, and larger than the value in table 4.

In conclusion, the negative value of m' for methylcyclohexane + cyclohexanone may be ascribed to the value of m which must be varied with the function of reduced volume and also the polarizability of polar component neglected in theory, and then parameter m' is considered to be a difference between the dipole-induced dipole interaction in pure dipolar liquid and that newly produced in solution.

Another probable cause may be the contribution from the molecular orientation correlation effect in solution. This effect may make the value of m larger than in the case of random orientation, because of the increment of the contribution of the more stable orientation. Consequently the value of dipole-dipole interaction parameter m in solution must be estimated as physical constant of materials or case by case.

The corresponding state theory for polar solution may be useful to interpret the contribution to the excess enthalpy from the molecular interaction, such as dispersion, dipole-dipole, and dipole-induced dipole, in consideration of these

Table 4. The interaction parameters and their contributions to the excess enthalpy of polar solutions

system	parameters		contribution/J mol^{-1} (at $x_1=0.5$)			
1 + 2	X_{12}/J cm^{-3}	$m'/10^4$	H_0^E	H_{dd}^E	H_{did}^E	H^E(obs)
benzene + cyclohexanone	38.33	7.02	725.4	191.2	−1198.7	−282.9
toluene + cyclohexanone	23.13	5.19	506.7	204.9	−876.7	−164.6
ethyl benzene + cyclohexanone	17.88	4.57	435.8	215.7	−740.2	−89.4
benzene + diethyl ketone	43.95	7.47	853.3	154.3	−1135.3	−129.3
toluene + diethyl ketone	23.15	5.57	515.1	165.4	−836.8	−157.2
ethyl benzene + diethyl ketone	20.69	4.95	491.2	174.0	−712.8	−48.7
ethyl benzene + methyl ethyl ketone	20.69	3.84	453.3	240.2	−593.0	100.9
methyl cyclohexane + cyclohexanone	9.28*	−4.36	217.2	216.2	560.8	994.0

*; from Berthelot's expression

points.

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〔会員の頁〕

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IS-2	電気	電気，物理，電気工学，コンピューター関係の用語と短文。ギリシア文字とその読み方，数式の読み方，中学の物理程度の電気，光に関する口語体のやさしい表現。
IS-3	機械	機械工学，熱力学，材料，物性，プロセスの用語，道具の名称と短文，エンジンを中心とした会話練習。図形と英語。モーター，発電機，温度についての短い英文。
IS-4	薬学	薬学，有機化学，薬品名，病名。短い句と表現。小数，分数の簡単な表現と読み方。英語論文を書くときの短い必須表現（175例）。アメリカの会社名の読み方。
IS-5	医学	医学，生物学関係の用語とその説明または定義。医者と患者の対話。主な血管，筋肉，神経の名前など。
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