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The Estimation of the Liquid-Liquid Distribution Coefficients of Acetylacetone by Means of the Group Solution Theory

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The estimation of the liquid-liquid distribution coefficients of acetylacetone tautomers was attempted on the basis of the UNIFAC equation, and it was found that the calculated values of the reciprocals of the activity coefficients of tautomers in organic phases were linearly related to the distribution coefficients. It was verified that the estimation by the UNIFAC equation could be extended to the organic solvents with no characteristic parameter.

Acetylacetone (2,4-pentanedione), a well-known extractant, is extensively employed in the solvent extraction of various matallic elements. In the scheme of the extraction, the distribution of acetylacetone between two liquid phases plays an important role. The distribution ratio of metal elements is represented as a function of the partition coefficient of acetylacetone, the dissociation constant of acetylacetone in the aqueous phase, the formation constant of the metal acetylacetone complex, and the partition coefficient of the complex. From this point of view, the distribution of acetylacetone and its thermodynamic properties have been thoroughly investigated.

As a thermodynamic study, an interpretation of the distribution coefficients on the basis of the regular solution theory has been reported by Wakahayashi *et al.*;[1] they found a good correlation between the distribution coefficient of acetylacetone and the solubility parameter of organic solvents. The determination of the activity coefficients of each tautomer has also been tried in terms of the Wilson equation[2] and the UNIFAC equation[3] in our laboratory.[4,5] By the use of these analytical equations, the activity coefficients of tautomers could clearly be determined. Inoue *et al.* had also compared the activity coefficients of the tautomers with the distribution coefficients; they found a qualitative agreement between them.[4] For practical use, the Wilson parameters are required for all of the binary mixtures cencerned in the distribution experiments. That is, the vapor pressures of all the acetylacetone+organic solvent mixtures must be measured.

On the other hand, the calculation by the UNIFAC equation requires a smaller amount of parameters than those by the regular solution theory and the Wilson equation. Once the parameters are determined, these parameters can be employed for all the calculations for mixtures containing the same functional groups. In this study, the applicability of the UNIFAC equation to the estimation of the liquid-liquid distribution coefficients of acetylacetone was examined.

Theory

The UNIFAC Equation. The UNIFAC equation[3] consists of Eqs. 1 to 4. Eq. 1 represents the contribution of the size difference of the substances in the mixtures to the activity coefficients. In the original paper, it is named the combinatorial part, γ_i^{C}:

$$\ln \gamma_i^{\mathrm{C}} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum x_j l_j, \tag{1}$$

and:

$$\begin{aligned} &\theta_i = q_i x_i / (\sum_j q_j x_j), \quad \phi_i = r_i x_i / (\sum_j r_j x_j), \\ &l_i = z(r_i - q_i)/2 - (r_i - 1), \end{aligned} \tag{1a}$$

where x_i denotes the mole fraction of the i-th species; z, the coordination number; q_i, the parameter concerning the molecular surface area, and r_i, the parameter of the molecular volume. The q_i and r_i values are represented by the summation of the corresponding parameters, Q_k and R_k, for the functional groups by the following equations:

$$\begin{aligned} q_i &= \sum_k \nu_k^{(i)} Q_k, \\ r_i &= \sum_k \nu_k^{(i)} R_k, \end{aligned} \tag{1b}$$

and

$$\begin{aligned} Q_k &= A_{\mathrm{w},k} / (2.5 \times 10^9), \\ R_k &= V_{\mathrm{w},k} / 15.17, \end{aligned} \tag{1c}$$

where $\nu_k^{(i)}$ is the number of the k group in the i-th species. $A_{\mathrm{w},k}$ and $V_{\mathrm{w},k}$ denote the van der Waals surface area and volume of the k group respectively. In Eq. 1, the required parameters are Q_k's and R_k's, and x_i is determined by the experimental conditions.

The following equations, Eqs. 2 and 3, represents the contribution of intermolecular interaction to the activity coefficients, in which γ_i^{R} is called the residual part, in the original paper:

$$\ln \gamma_i^{\mathrm{R}} = \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}], \tag{2}$$

$$\ln \Gamma_k = Q_k \left[1 - \ln (\sum_m \theta_m \Psi_{mk}) - \sum_m \left(\frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}} \right) \right], \tag{3}$$

where

$$\begin{aligned} \theta_m &= Q_m X_m / (\sum_n Q_n X_n), \\ \Psi_{mn} &= \exp(-a_{mn}/RT). \end{aligned} \tag{3a}$$

The Γ_k represents the group-activity coefficient, and the additivity is postulated. The $\Gamma_k^{(i)}$ is the group-activity coefficient in the pure i species, and normalizes the activity coefficient to be unity in the pure state. The a_{mn} assesses the inter-group interaction between m and n groups; these values were summarized in the original paper in the form of a_{mn}/R. R and T are the gas constant and the temperature respectively. X_m denotes the mole

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fraction of the m group in the given mixtures. In Eqs. 2 and 3, the required parameters are Q_k's and a_{mn}'s.

The activity coefficient of the i-th species, γ_i, is represented by the summation of Eqs. 1 and 2 as follows:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}}. \tag{4}$$

The Q_k and R_k values have been determined for a variety of group; the a_{mn} values have also been evaluated for the pair of principal groups. The activity coefficient in mixtures composed of well-known substances are calculated from the values of the parameters determined by Fredenslund *et al.*[6]

Distribution Coefficients. The distribution ratio, D, is generally defined by the concentration ratio of a solute in two liquid phases, ordinarily aqueous and organic phases:

$$D = C_{\mathrm{org}}/C_{\mathrm{aq}}. \tag{5}$$

The subscripts "org" and "aq" denote the organic and aqueous phases respectively. The distribution coefficients of tautomers of acetylacetone are represented as follows:

$$D = K_{\mathrm{D}}^{\mathrm{E}} f_{\mathrm{aq}}/f_{\mathrm{org}} = K_{\mathrm{D}}^{\mathrm{K}}(1-f_{\mathrm{aq}})/(1-f_{\mathrm{org}}), \tag{6}$$

where $K_{\mathrm{D}}^{\mathrm{E}}$ and $K_{\mathrm{D}}^{\mathrm{K}}$ denote the distribution coefficients of the enol and keto tautomers respectively, and where f is the enol content.

The chemical potentials, μ, of a solute in both phases are represented as follows:

$$\mu_{\mathrm{org}} = \mu^{\circ} + RT \ln x_{\mathrm{org}}\gamma_{\mathrm{org}}, \tag{7}$$

$$\mu_{\mathrm{aq}} = \mu^{\circ} + RT \ln x_{\mathrm{aq}}\gamma_{\mathrm{aq}}. \tag{8}$$

As the UNIFAC equation is defined for a symmetric ideal reference system, the μ°'s in Eqs. 7 and 8 are equal. The chemical potentials in both phases are equal in an equilibrium state:

$$\mu_{\mathrm{org}} = \mu_{\mathrm{aq}}. \tag{9}$$

Accordingly, the following relation is obtained:

$$K_{\mathrm{D,x}} = \frac{x_{\mathrm{org}}}{x_{\mathrm{aq}}} = \frac{\gamma_{\mathrm{aq}}}{\gamma_{\mathrm{org}}}. \tag{10}$$

Equation 10 is a desirable equation, as it shows that the distribution coefficient in the symmetric ideal reference system is represented by the ratio of the activity coefficients of the solute in both phases. The distribution coefficient in molarity, K_{D}, is transformed to that in the mole fraction, $K_{\mathrm{D,x}}$, by means of Eq. 11:

$$K_{\mathrm{D,x}} = K_{\mathrm{D}} v_{\mathrm{org}}/v_{\mathrm{aq}}, \tag{11}$$

where v denotes the molar volume of the solvents. From the above equations, it is possible to compare the activity coefficients of a given solute, calculated from the UNIFAC equation with the observed distribution coefficients.

Experimental

The acetylacetone and chlorobenzene (guaranteed reagents of commercial origin) were distilled with a distillator with 80 to 100 theoretical plates, and the middle portions were submitted to vapor-pressure measurements. Redistilled water was used. No signal due to impurities was detected on a gas chromatogram.

The apparatus for the vapor pressure measurements was previously reported by our laboratory.[7] The thermostat was controlled at 298.15±0.001 K.

The enol content of acetylacetone in water and chlorobenzene was determined from the signal area of the terminal methyl groups of each tautomer in an NMR spectrogram at 298±1 K.

The concentrations of the liquid and vapor phases were determined from their densities.

Results

The observed vapor pressures are listed in Table 1, along with the activity coefficients of the component substances. In this table, x_{acac} denotes the mole fraction of acetylacetone in the liquid phase; y_{acac}, that in the vapor phase, and p, the total pressure. Table 2 summarizes the dependence of the enol content, f, on the concentration of acetylacetone. The enol content in chlorobenzene mixtures was smoothed by the least-squares method as follows:

$$10^2 f = 2\ 538 x_{\mathrm{acac}}^2 + 7.393 x_{\mathrm{acac}} + 8\ 525. \tag{12}$$

No concentration dependence of the enol content in the mixtures containing water was found in diluted solutions.

TABLE 1. OBSERVED ACTIVITY COEFFICIENTS OF THE TAUTOMERS OF ACETYLACETONE, γ^{E} AND γ^{K} AND A SOLVENT, $\gamma^{\mathrm{solvent}}$, AT 298.15 K

x_{acac} a)	y_{acac} b)	p c) / mmHg d)	γ^{E}	γ^{K}	$\gamma^{\mathrm{solvent}}$
		Acetylacetone + Chlorobenzene			
0.0	0.0	11.64	—	—	1.0
0.103	0.099	11.47	1.038	2.118	0.990
0.219	0.194	11.45	0.965	1.768	1.015
0.345	0.293	11.41	0.934	1.523	1.058
0.420	0.355	11.21	0.920	1.405	1.071
0.519	0.440	10.90	0.907	1.268	1.090
0.635	0.558	10.87	0.951	1.201	1.131
0.734	0.657	10.38	0.937	1.086	1.150
0.846	0.789	9.97	0.952	1.003	1.174
0.936	0.897	9.69	0.963	0.941	1.340
1.0	1.0	9.67	1.013	0.936	—
		Acetylacetone + Water			
0.0	0.0	23.41	—	—	1.0
0.0022	0.057_4	24.44	300.8	13.94	0.986
0.0070	0.138	25.30	235.2	10.90	0.938
0.0114	0.149	26.49	163.3	7.57	0.974

a) Mole fraction of acetylacetone in the liquid phase. b) Mole fraction of acetylacetone in the vapor phase. c) Total pressure. d) 1 mmHg≈133.322 Pa.

TABLE 2. DEPENDENCE OF THE ENOL FRACTION, f, UPON THE CONCENTRATION OF ACETYLACETONE AT 298 K

x_{acac}	$10^2 f$ a)	x_{acac}	$10^2 f$ a)	x_{acac}	$10^2 f$ a)
		Acetylacetone + Chlorobenzene			
0.151	90.3	0.498	83.6	0.787	85.4
0.294	90.2	0.729	85.5	0.845	84.5
0.422	88.5				
		Acetylacetone + Water			
0.0078	15.8	0.863	82.0	0.923	81.9
0.0146	16.9	0.869	81.9	0.928	80.4
0.0207	17.3				

a) f = [enol]/[acac].

Table 3. Inter-group interaction energy parameters, a_{mn}/R, along with quoted values from Ref. 6

a_{mn}/R	CH_2	CH_2CO	E.R.[a]	ACH	$ACCH_2$	ACCl	$CHCl_3$	CCl_4
CH_2	0	476.4[b]	610	61.13[b]	76.50[b]	321.5[b]	24.90[b]	104.3[b]
CH_2CO	26.77[b]	0	−130	140.1[b]	365.8[b]	150.0	−354.6[b]	−39.20[b]
E.R.[a]	570	310	0	220	70	150	−160	10
ACH	−11.12[b]	25.77[b]	190	0	167.0[b]	538.2[b]		
$ACCH_2$	−69.70	−52.10[b]	600	−146.8[b]	0			
ACCl	−141.3[b]	60	280	−237.7[b]		0		
$CHCl_3$	36.7[b]	552.1[b]	240				0	
CCl_4	−78.45[b]	372[b]	550					0

a) Denotes the enol ring. b) Quoted from Ref. 6.

Discussion

In applying the UNIFAC equation to the mixtures containing acetylacetone, the parameters for the enol tautomer should be defined as a modified value. Because the enol ring forms a resonance structure, it is reasonable to consider that it should be treated as one functional group. The details of the definition were described in Ref. 3. As more accurate data for the temperature dependence of the vapor pressure of acetylacetone were reported by Inoue *et al.*,[4] the values of a_{mn}/R were recalculated; they are listed in Table 3, along with the values reported by Fredenslund *et al.*[6] An example of the analysis by means of the UNIFAC equation is shown in Fig. 1 for acetylacetone+chlorobenzene mixtures.

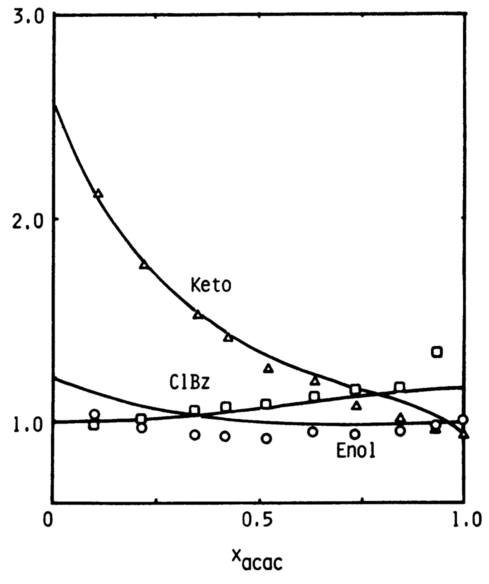

Fig. 1. Activity coefficients of the components in acetylacetone+chlorobenzene mixture at 298.15 K. ○ denotes enol tautomer, △ is keto tautomer, and □ is chlorobenzene. Solid lines represent the values calculated from the UNIFAC equation.

Correlation between $K_{D,x}$ and the Ratio of γ. As has been described above, the distribution coefficients, $K_{D,x}$, are represented as a ratio of the activity coefficients of a solute in two phases. In this study, the dependence of the distribution coefficients upon the activity coefficient in organic phases was considered.

When the activity coefficients of acetylacetone tautomers in several organic solvents were calculated by the UNIFAC equation, the concentration of acetylacetone was determined to be 10^{-3} in the mole fraction. This concentration nearly corresponds to 10^{-2} mol dm^{-3}. It has been found that the distribution coefficients of acetylacetone are independent of the concentration of acetylacetone in this concentration range.[1]

The calculated activity coefficients are listed in Table 4. In this table, D denotes the distribution coefficients of acetylacetone reported by Johansson and Rydberg.[8] The f_{org} values estimated from the equation reported by Pawling and Bernstein[9] are used because of the scarcity of experimental data. $K^E_{D.x}$ and $K^K_{D.x}$ denote the distribution coefficients of enol and keto tautomers respectively in the mole fraction. In Table 4, the systems containing benzene, toluene, chloroform, carbon tetrachloride, and chlorobenzene were used for the determination of the a_{mn}/R values. However, the activity coefficients in the mixtures of xylene, mesitylene, ethylbenzene, and some alkanes were calculated without any characteristic parameter for solvent molecules.

Figure 2 shows the correlation between $K^E_{D.x}$ and the

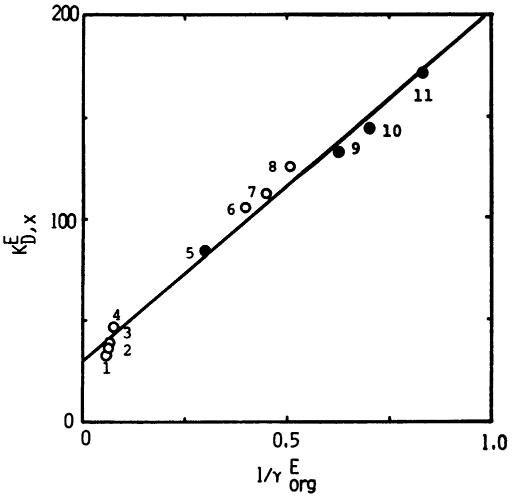

Fig. 2. Correlation between $K^E_{D.x}$ and $1/\gamma^E_{org}$ at 298.15 K. The open circles denote the systems having no characteristic parameters for solvent. (1-cyclohexane, 2-hexane, 3-heptane, 4-dodecane, 5-carbon tetrachloride, 6-mesitylene, 7-ethylbenzene, 8-xylene, 9-toluene, 10-benzene, and 11-chlorobenzene).

TABLE 4. DISTRIBUTION COEFFICIENTS AND ACTIVITY COEFFICIENTS OF TAUTOMERS OF ACETYLACETONE AT 298.15 K

Solvent	D	f_{org}	$K^{\mathrm{E}}_{\mathrm{D,x}}$ a)	$1/\gamma^{\mathrm{E}}_{\mathrm{org}}$ b)	$K^{\mathrm{K}}_{\mathrm{D,x}}$ a)	$1/\gamma^{\mathrm{K}}_{\mathrm{org}}$ b)
Benzene	5.93	0.89	144.3	0.70	3.94	0.31
Toluene	4.57	0.89	132.9	0.63	3.63	0.27
Xylene	3.69	0.89c)	124.0	0.51	3.39	0.27
Mesitylene	2.73	0.89c)	103.7	0.40	2.83	0.28
Ethylbenzene	3.31	0.89c)	110.8	0.45	3.03	0.21
Cyclohexane	1.03	0.96	32.8	0.059	0.303	0.0098
Hexane	0.95	0.95	36.3	0.061	0.422	0.0104
Heptane	0.89	0.97	38.8	0.063	0.265	0.0106
Dodecane	0.69	0.97c)	46.7	0.076	0.320	0.0126
Chlorobenzene	5.98	0.92	170.8	0.83	3.51	0.39
Chloroform	23.80	0.87	507.2	4.12	17.51	5.24
Carbon tetrachloride	3.31	0.96	94.2	0.30	0.87	0.058

a) Calculated from Eqs. 6 and 11. b) Calculated from the UNIFAC equation. c) Estimated from the equation proposed by Pawling and Bernstein.[9]

reciprocal of the activity coefficient of the enol tautomer, $1/\gamma^{\mathrm{E}}_{\mathrm{org}}$. The open circles denote a system with no characteristic parameter. The linearity of this figure is satisfactory. The correlation is represented by the least-squares method as follows:

$$K^{\mathrm{E}}_{\mathrm{D,x}} = 171.04/\gamma^{\mathrm{E}}_{\mathrm{org}} + 30.69. \qquad (13)$$

The correlation coefficient was 0.992, omitting the chloroform system. Figure 3 shows the similar plots for the keto tautomer. The correlation by the least-squares method, except for chlorobenzene, mesitylene and chloroform, was as follows:

$$K^{\mathrm{K}}_{\mathrm{D,x}} = 12.43/\gamma^{\mathrm{K}}_{\mathrm{org}} + 0.20. \qquad (14)$$

The correlation coefficient was 0.997. When only the data for chloroform were excluded,

$$K^{\mathrm{K}}_{\mathrm{D,x}} = 11.75/\gamma^{\mathrm{K}}_{\mathrm{org}} + 0.22. \qquad (15)$$

The correlation coefficient was 0.986. As the amounts of the keto tautomer were very small in an organic solvent, the inaccuracy in enol contents strongly contributed to the calculated results. These two figures show that a good linear correlation exists between the distribution coefficient and the reciprocal of the activity coefficient in the organic phase.

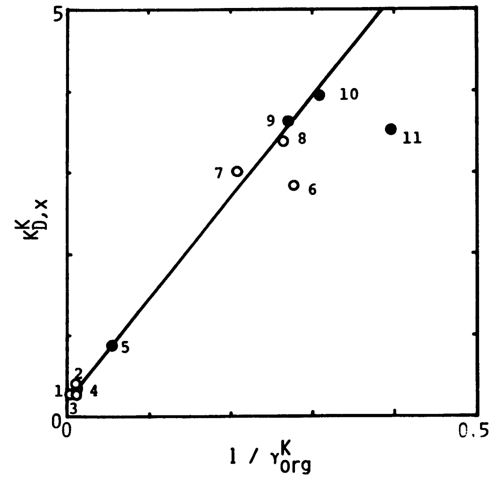

Fig. 3. Correlation between $K^{\mathrm{K}}_{\mathrm{D,x}}$ and $1/\gamma^{\mathrm{K}}_{\mathrm{org}}$ at 298.15 K. The open circles denote the systems having no characteristic parameters for solvent. The numbers are corresponding to that in Fig. 2.

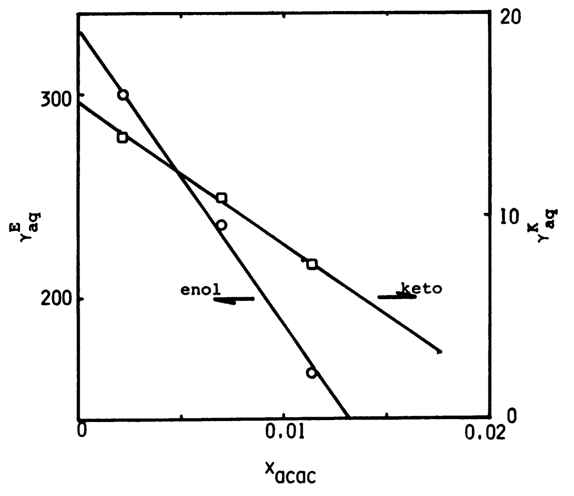

Fig. 4. Activity coefficients of acetylacetone tautomers in water at 298.15 K.

Comparing Eqs. 13 to 15 with Eq. 10, it is found that the slopes in Figs. 2 and 3 correspond to the activity coefficients of tautomers in the aqueous phase. As is shown in Fig. 4, the observed activity coefficient of the enol tautomer in an aqueous mixture was about 330, while that of the keto tautomer was 15.6 at an infinite dilution. The slope for the enol tautomer in Fig. 2 remarkably disagreed with the observed activity coefficient, and an intercept appeared. The disagreement of slopes indicates a smaller distribution coefficient than that calculated from the activity coefficient. The activity coefficients calculated from the UNIFAC equation were slightly greater than the observed values. The plots of Fig. 2 obtained by the use of the observed activity coefficients show a small intercept, but the same slope. As the concentration of electrolytes in the aqueous phase was 10^{-3} mol dm^{-3} of $\mathrm{HClO_4}$,[8] it is considered that the activity coefficient of the enol tautomer takes the same value as the value in Fig. 4. In the experiment of distribution, small amounts of water were found in the organic phase. Recently, it has been found that acetylacetone, particularly its enol tautomer, associates with water in a benzene solution.[10] This fact supports the greater activity coefficient in distribution experiments than that in vapor-pressure measurements, and smaller distribution coefficients than those calculated from the activity coefficients.

Conclusion

The activity coefficients of tautomers of acetylacetone were clearly determined by the UNIFAC equation, and it was found that the distribution coefficients were linearly related to the calculated activity coefficients. This fact shows that the UNIFAC equation is applicable to the estimation of the liquid-liquid distribution coefficients. As the UNIFAC equation can be easily extended to multi-component mixtures, it is expected that the foregoing presentation can be extended to the distribution by mixed solvents. The estimation of distribution coefficients by the UNIFAC equation can be considered to be a very useful method.

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