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Simultaneous Correlation of Excess Gibbs Energy and Enthalpy of Mixing by the UNIQUAC Equation

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Using data for excess Gibbs energy, g^E , and enthalpy of mixing, h^E , temperature dependent parameters of the UNIQUAC equation have been estimated for twenty four systems of binary mixtures. Fifteen of them include data for g^E and h^E at more than one different isotherm. These parameters are later tested in predicting the g^E and h^E data simultaneously and representing the effect of temperature on such data. The UNIQUAC equation with temperature dependent parameters represents larger values of maximum heat of mixing than does the UNIQUAC equation with the parameters independent of temperature.

Nous avons calculé à partir de données obtenues pour l'énergie d'excès de Gibbs, g^E , et l'enthalpie de mélange, h^E , des paramètres dépendants de la température de l'équation UNIQUAC pour vingt-quatre systèmes de mélanges binaires. Quinze d'entre eux comprennent des données pour g^E et h^E à plus d'un isotherme. Ces paramètres sont vérifiés par la suite par la prédiction des données de g^E et h^E simultanément et par la représentation de l'effet de la température sur ces données. L'équation UNIQUAC dont les paramètres sont dépendants de la température fournit des valeurs plus grandes de la chaleur maximale du mélange que l'équation UNIQUAC dont les paramètres sont indépendants de la température.

Keywords: excess Gibbs energy, mixing enthalpy, UNIQUAC parameters, temperature dependent parameters.

Since it was proposed by Abrams and Prausnitz (1975), the UNIQUAC equation has been used successfully in fluid phase equilibria predictions (Anderson and Prausnitz, 1978; Demirel, 1982). It is applicable to both vapour-liquid and liquid-liquid equilibria and has only two adjustable energy parameters. When the necessary care is exercised in reducing the binary data to estimate the parameters, the UNIQUAC equation provides a reliable basis for prediction of multicomponent fluid phase equilibria (Fredenslund et al., 1979; Demirel and McDermott, 1984). The UNIQUAC equation contains pure component structural parameters r and q Anderson and Prausnitz (1978) modified the UNIQUAC equation slightly and introduced new values of surface parameters, q' for alcohols and water to be used in the residual part of the equation.

Heat of Mixing

The rate of change of excess Gibbs free energy, g^E , and hence activity coefficient γ_i with temperature is proportional to heat of mixing h^E , and given by the Gibbs-Helmholtz equation.

$$\frac{h^E}{T^2} = - \left[\frac{\partial(g^E/T)}{\partial T} \right]_{p,x} \quad (1)$$

If h^E at any composition is positive, then the value of γ_i decreases with increase in temperature. But if h^E is negative then γ_i increases with increasing temperature.

The Wilson equation and the NRTL equation are not capable of correlating both g^E and h^E data for a system where the value of heat of mixing is greater than a certain maximum value of h^E at any given temperature (Murthy and Zudkevitch, 1979; Wilkinson, 1979). The limitations on the value of h^E can be eliminated by treating the energy parameters of such equations as a function of temperature. For systems with strong hydrogen bonding, such as those containing alcohols, the heat of mixing can not be represented by the Wilson parameters with linear dependence of

temperature (Novak et al., 1974). A simultaneous fit of g^E and h^E data is successfully represented by the Wilson equation whose energy parameter differences are assumed to be a quadratic function of temperature (Murthy and Zudkevitch, 1979).

Renon (1971) and Nagata et al. (1973) assumed that the NRTL parameters change with temperature in a linear form. It has been shown by Nagata et al. (1976) that by using the temperature dependent parameters, the NRTL equation is capable of representing both vapour-liquid equilibria (VLE) and heat of mixing data with a single set of parameters, for the methyl acetate-benzene and methyl acetate-cyclohexane systems. This was achieved by fitting the parameters to both types of data simultaneously. Similar results were also obtained for the systems containing alcohols (Nagata et al., 1972).

In the UNIQUAC equation, for each binary combination in a multicomponent mixture, there are two adjustable parameters τ_{21} and τ_{12} . These are given in terms of characteristic energies Δu_{21} and Δu_{12} by

$$\tau_{21} = \exp(-\Delta u_{21}/RT) = \exp(-a_{21}/T) \quad (2)$$

$$\tau_{12} = \exp(-\Delta u_{12}/RT) = \exp(-a_{12}/T) \quad (3)$$

Equations (2) and (3) give the primary effect of temperature on τ_{21} and τ_{12} . When the parameters a_{21} and a_{12} are used, enthalpy of mixing by the UNIQUAC equation is given as

$$h^E = R \left(\frac{q'_1 x_1 \Theta'_2 \tau_{21} a_{21}}{\Theta'_1 + \Theta'_2 \tau_{21}} + \frac{q'_2 x_2 \Theta'_1 \tau_{12} a_{12}}{\Theta'_2 + \Theta'_1 \tau_{12}} \right) \quad (4)$$

where

$$\Theta'_i = q'_i x_i / (\sum q'_i x_i)$$

If the first derivatives of h^E with respect to the parameters a_{21} and a_{12} are obtained and set equal to zero, the new

values of characteristic energies that give the maximum value of h may be evaluated. For an equimolar mixture these are

$$\frac{\tau_{21}}{(a_{21}/T - 1)} = \frac{q'_1}{q'_2} \text{ and } \frac{\tau_{12}}{(a_{12}/T - 1)} = \frac{q'_2}{q'_1} \dots (5)$$

Substituting Equation (5) into Equation (4) gives the maximum heat of mixing, h'

$$h' = RT [q'_1 x_1 (a_{21}/T - 1) + q'_2 x_2 (a_{12}/T - 1)] \dots (6)$$

Equation (6) shows that the maximum value of heat of mixing that can be predicted by the UNIQUAC equation is determined by the ratio of the surface parameters of the two components.

For the system methyl acetate-ethanol the value of a_{21} and a_{12} obtained from Equation (5), at $x_1 = x_2 = 0.5$ and $T = 45^\circ\text{C}$ are 355.27 K and 502.35 K respectively. The value of h' that can be predicted by the UNIQUAC equation is equal to 1101.5 J/mol, while the experimental value of h' is about 1552.8 J/mol. This means that, for this system, the UNIQUAC equation, with the parameters independent of temperature, may not be capable of predicting enthalpy of mixing.

Characteristic energies Δu_{21} and Δu_{12} are often weakly dependent on temperature. Abrams and Prausnitz (1975) state that when both vapour-liquid and liquid-liquid equilibrium data are used to obtain UNIQUAC parameters, they appear to be smooth functions of temperature. However this is not the case for mixtures containing hydrogen bonding, such as water and alcohols (Anderson and Prausnitz, 1978); Murthy and Zudkevitch, 1979). It is also known that $\ln \gamma_i$ varies with $1/T$ (Reid et al., 1979). Therefore in this study, the effect of temperature on the characteristic energies is expressed as

$$a_{ij} = \alpha_{ij} + \beta_{ij}/T \dots (7)$$

which is also used by Anderson and Prausnitz (1978). With the UNIQUAC parameters given in Equation (7), the enthalpy of mixing becomes

$$h^E = R \left[\frac{q'_1 x_1 \Theta'_2 \tau_{21} (\alpha_{21} + 2\beta_{21}/T)}{\Theta'_1 + \Theta'_2 \tau_{21}} + \frac{q'_2 x_2 \Theta'_1 \tau_{12} (\alpha_{12} + 2\beta_{12}/T)}{\Theta'_2 + \Theta'_1 \tau_{12}} \right] \dots (8)$$

The maximum value of h' obtained from Equation (8), using the procedure explained above, is

$$h' = RT \{q'_1 x_1 [(\alpha_{21} + 2\beta_{21}/T)/T - 1] + q'_2 x_2 [(\alpha_{12} + 2\beta_{12}/T)/T - 1]\} \dots (9)$$

Positive values of β_{21} and β_{12} increase the values of parameters a_{21} and a_{12} , thus Equation (9) represents larger values of h' than that of Equation (6).

Estimation of Parameters

In estimating the temperature dependent parameters, data for g^E and h^E were used simultaneously. The following objective function, which was also used by Nagata and Yamada (1973), was minimized.

$$F = \frac{1}{N} \left\{ \sum^n \frac{[100(g_{exp}^E - g_{calc}^E)/g_{exp}^E]^2}{n} \right\} + \frac{1}{M} \left\{ \sum^m \frac{[100(h_{exp}^E - h_{calc}^E)/h_{exp}^E]^2}{m} \right\} \dots (10)$$

where n and m are respectively the number of experimental g^E and h^E data points at a specified isothermal temperatures. N is the number of isothermal system temperatures for the g^E data and M is that of the h^E data. For minimizing the function F a package program called MINUIT (James, 1978) was used. The MINUIT performs minimization and analysis of the shape of a multiparameter function. It incorporates three different minimization techniques. These are the Fletcher, Monte Carlo and Simplex techniques. Each technique may be used alone or in combination with the others depending on the behaviour of the function and the requirements of the user. The MINUIT program also performs the non-linear error analysis and contour plotting that shows the confidence region. It does not require the analytical derivatives of the function, F , with respect to its free parameters.

Results and Discussions

Using data for g^E and h^E , temperature dependent parameters of the modified UNIQUAC equation (Anderson and Prausnitz, 1978) were estimated for 24 binary systems. The MINUIT program used for this purpose is rather slow, which may also be due to search for a better minimum after convergence. Estimated parameters, together with representation of g^E and h^E data and variance of the fit, are given in Table 1. Some of the systems shown in the table have the experimental value of h^E which is higher than the value that can be predicted by using the temperature independent parameters of the UNIQUAC equation. The average absolute error S was calculated as

$$S(g^E) = 1/n [|\Sigma (g_{exp}^E - g_{calc}^E)/g_{exp}^E|] \dots (11)$$

$$S(h^E) = 1/m [|\Sigma (h_{exp}^E - h_{calc}^E)/h_{exp}^E|] \dots (12)$$

The values of S were calculated at each isotherm for g^E and h^E data. These indicate the performance of the UNIQUAC equation in representing g^E and h^E data simultaneously at various isotherms. The term σ is the variance of the fit and is given by:

$$\sigma = 1/(\Sigma n_i - NP) [(g_{exp}^E - g_{calc}^E)/g_{exp}^E]^2 + 1/(\Sigma m_i - NP) [(h_{exp}^E - h_{calc}^E)/h_{exp}^E]^2 \dots (13)$$

Here Σn_i and Σm_i are the total number of data points for g^E and h^E respectively, while NP is the number of parameters.

TABLE I
Simultaneous Representation of g^E and h^E Data by the UNIQUAC Equation Using the Temperature Dependent Parameters

System	T (°C)	h' (Eq.6) (J/mol)	$T(g^E)$ (°C)	n	$T(h^E)$ (°C)	m	α_{12} (K)	α_{21} (K)	$S(g^E)$	$S(h^E)$	$(\sigma)^{1/2}$
Reference		h_{max}^E (exp) (J/mol)					β_{12} (K ²)	β_{21} (K ²)	$S*100$		
1. methyl acetate benzene Nagata (1973)	35	1771.2 274.2	30 40 50	10 7 11	25 35	13 6	147.84 -16617	-176.17 32494	20.05 11.66 14.50	5.22 6.58	0.2490
2. methyl acetate cyclohexane Nagata (1973)	45	2049.2 1776.5	35 40	8 9	25 35 45	11 11 9	-31.19 20259	-18.83 45916	1.98 3.21	4.75 3.82 4.36	0.0678
3. methanol ethyl acetate Nagata (1975)	35	1188.1 1029.5	55	11	25 35	12 12	-291.19 52222	554.28 17903	1.23	4.53 5.22	0.0796
4. *ethanol ethyl acetate Nagata (1975)	35	1157.2 1328.4	55	10	25 35	12 16	-411.46 77730	467.8 53564	2.61	4.06 4.04	0.0721
5. *2-propanol ethyl acetate Nagata (1975)	35	1135.5 1803.2	55	10	25 35	13 18	-227.58 28830	-318.11 217080	22.76	3.25 4.59	0.3621
6. *1-propanol ethyl acetate Nagata (1975)	45	1172.3 1686.6	55	11	25 35 45	11 20 9	-348.16 62570	68.91 133520	6.63	3.36 2.13 2.42	0.1048
7. ethyl formate methanol Nagata (1976)	45	1128.4 864.8	45	12	25 35 45	8 11 9	616.43 -14273	-229.80 42798	1.68	10.42 4.71 7.82	0.0903
8. *ethyl formate ethanol Nagata (1976)	45	1100.1 1228.9	45	12	25 35 45	6 13 9	541.03 24831	-359.86 72397	2.58	10.54 4.59 7.85	0.0945
9. *ethyl formate 1-propanol Nagata (1976)	45	1079.1 1529.8	50	8	25 35 45	8 13 9	518.21 24689	-471.91 101090	5.24	10.09 3.11 8.42	0.1113
10. *ethyl formate 2-propanol Nagata (1976)	45	1081.1 1736.3	45	11	25 35 45	13 12 11	586.43 11773	-542.86 121640	4.48	8.09 1.43 8.46	0.1054
11. *methyl acetate methanol Nagata (1972)	45	1126.5 1107.7	35 45	13 13	25 35 45	14 16 10	233.02 69416	-145.54 24272	4.94 4.07	3.58 1.25 4.02	0.0834
12. *methyl acetate ethanol Nagata (1972)	45	1101.5 1552.8	45 55	10 13	25 35 45	11 12 7	286.02 86704	-406.33 81606	9.13 12.9	6.54 2.55 6.26	0.1943
13. *ethanol toluene Van Ness (1967)	60	1226.8 1284.9	30 45 60	18 18 17	30 45 60	26 23 26	-239.68 37137	-120.92 352160	1.97 2.41 2.78	10.43 6.2 8.2	0.1118
14. *2-propanol n-heptane Van Ness (1967)	60	1417.4 1443.2	30 45 60	17 17 16	30 45 60	24 22 21	-400.33 72080	-407.5 545930	3.23 3.16 2.95	11.95 9.14 13.86	0.1529
15. n-pentanol n-hexane Sayegh (1976), Nguyen (1975)	25	1394.4 527.2	25	9	25	9	-373.29 56104	1149.9 -66894	2.14	3.32	0.0653
16. n-pentanol 2,3-dimethyl butane Sayegh (1976), Nguyen (1975)	25	1393.8 507.7	25	8	25	9	-386.98 57578	1113 -31836	2.69	4.21	0.0795
17. n-pentanol 2-methyl pentane Sayegh (1976), Nguyen (1975)	25	1318.2 590.5	25	9	25	9	-415.47 62506	1084.4 -41149	2.51	4.67	0.0862

TABLE 1 (continued)
Simultaneous Representation of g^E and h^E Data by the UNIQUAC Equation Using the Temperature Dependent Parameters

System	T (°C)	h' (Eq.6) (J/mol)	$T(g^E)$ (°C)	n	$T(h^E)$ (°C)	m	α_{12} (K)	α_{21} (K)	$S(g^E)$	$S(h^E)$	$(\sigma)^{1/2}$
Reference		h_{max}^E (exp) (J/mol)					β_{12} (K ²)	β_{21} (K ²)	S^*100		
18. iso-pentanol n-hexane Sayegh (1976), Nguyen (1975)	25	1395.6 568.1	25	9	25	9	-388.81 59164	1097 -39689	3.24	5.18	0.0991
19. n-pentanol 3-methyl penane Sayegh (1976), Nguyen (1975)	25	1318.2 514.76	25	9	25	9	-416.2 62049	1046.1 -32005	2.58	4.89	0.0906
20. n-pentanol 2,2-dimethyl butane Sayegh (1976), Nguyen (1975)	25	1406.7 505.9	25	9	25	9	-389.93 58392	1144.6 -34930	2.55	4.02	0.0743
21. acetonitrile benzene Palmer (1972)	45	1490.7 490.7	45	8	45	13	-227.55 62703	559.09 -102250	8.87	2.11	0.1537
22. benzene n-heptane Palmer (1972)	45	2368.4 891.1	45	11	45	14	312.55 -70745	-300.29 65439	8.96	0.92	0.1307
23. acetonitrile n-heptane Palmer (1972)	45	1974.3 964.7	45	8	45	12	-195.34 65383	390.38 38508	7.31	2.28	0.1330
24. ethanol cyclohexane Scatchard (1964)	65	1253.1 928.2	5 20 35 60 65	8 10 9 8 8	5 20 35 50 65	10 10 8 8 8	-46.33 33265	892.82 -87599	5.35 4.35 3.84 4.03 4.74	12.73 7.65 7.32 7.77 2.11	0.1697

n, m : number of experimental g^E and h^E data points respectively, at a specified temperature

S : average absolute error

σ : variance of the fit

α_{ij}, β_{ij} : constants of the energy parameter of the UNIQUAC equation ($a_{ij} = \alpha_{ij} + \beta_{ij}/T$)

*: the system for which the experimental value of h^E is higher than that of the predicted value by the original UNIQUAC equation.

The estimated variance of the fit, σ , provides a measure of how well g^E and h^E data are represented simultaneously by the UNIQUAC equation. Except for some of the systems, such as methyl acetate-benzene and 2-propanol-ethyl acetate, the obtained values S and σ are satisfactory. The value of S for either g^E or h^E is rather poor for these systems. The minimum and maximum values for $S(g^E)$ and $S(h^E)$ are 1.23-20.05 and 0.92-13.86 respectively, while they are 0.0678 and 0.249 for the variance of the fit. These indicate that Equation (7) provides also a reliable representation of temperature dependency of the energy parameters a_{21} and a_{12} for mixtures other than the ones containing alcohols. Table 1 also shows that the limitations on the UNIQUAC equation, for estimating h^E data, can be overcome by treating the energy parameters as functions of temperature, as indicated by Equation (9).

The MINUIT program also performs the error analysis. The error matrix, also called the covariance matrix, is the inverse of the second derivative matrix of the function with respect to its free parameters. When the matrix is inverted, the diagonal elements of the inverse contain contributions from all the elements of the covariance matrix, where the correlations come from. Using the error matrix the off-diagonal elements of the correlation coefficient matrix is

calculated as

$$\mu_{ij} = c_{ij} / (c_{ii} \cdot c_{jj})^{1/2}; \mu_{ii} = 1; \mu_{ij} = \mu_{ji} \dots \dots \dots (14)$$

where c_{ij} represents the elements of the error matrix. If c is positive definite, $|\mu| < 1$ for all elements. If $\mu = 0$, then the parameters are uncorrelated and if $|\mu| = 1$, the parameters are completely correlated. The global correlation coefficient is given by

$$\mu_k^2 = 1 - [c_{kk}(c^{-1})_{kk}]^{-1} \dots \dots \dots (15)$$

and is the correlation between it and that linear combination of the other parameters most highly correlated with it. All such coefficients should be between zero and one for a positive definite error matrix. The values of error matrix correlation coefficients and global correlation coefficients for some of the systems are given in Table 2 and 3. As seen from the tables, the parameters for some of the systems are highly correlated. For such highly correlated parameters it is not possible to specify unique values from a given set of data. As discussed by Abrams and Prausnitz (1975) and Anderson and Prausnitz (1978), non-uniqueness is a common difficulty

TABLE 2
Elements of Correlation Coefficient Matrix
($\mu_{ii} = 1$; $\mu_{ij} = \mu_{ji}$)

System	μ_{21}	μ_{31}	μ_{32}	μ_{41}	μ_{42}	μ_{43}
ethanol cyclohexane	-0.925	-0.873	0.822	0.869	-0.912	-0.946
2-propanol <i>n</i> -heptane	-0.979	0.145	-0.269	-0.106	0.255	-0.958
acetonitrile benzene	-0.981	-0.982	0.981	0.929	-0.978	-0.964
methyl acetate cyclohexane	-0.988	-0.994	0.977	0.990	-0.994	-0.991

TABLE 3
Global Correlation Coefficients

System	μ_k^2				σ
	α_{21}	β_{21}	α_{12}	β_{12}	
ethanol cyclohexane	0.932	0.953	0.954	0.968	0.1697
2-propanol <i>n</i> -heptane	0.985	0.985	0.936	0.953	0.1529
acetonitrile benzene	0.998	0.998	0.996	0.997	0.1537
methyl acetate cyclohexane	0.998	0.998	0.998	0.998	0.0678

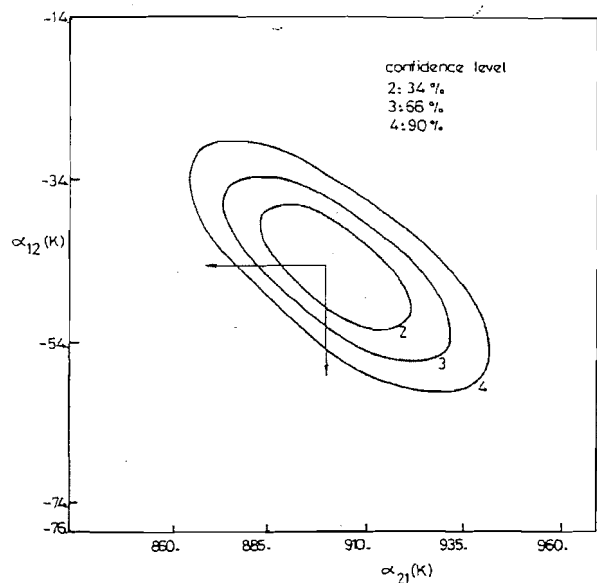


Figure 1 — Binary parameters, α_{12} and α_{21} , and their approximate confidence regions for the ethanol-cyclohexane system.

for models that have only two parameters representing energy differences, as in the case for the UNIQUAC equation. Such problems have arisen when the same free energy function is used for two of the phases, as in liquid-liquid equilibria, at points where the mole fractions in two phases are identical.

Estimated confidence regions for some of the systems are shown in Figures 1-4. These are estimated from the eigenvalues and eigenvectors of the second derivative matrix. The

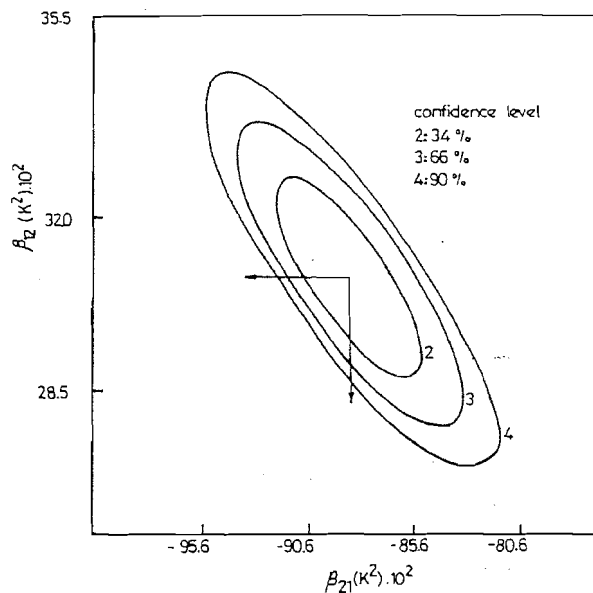


Figure 2 — Binary parameters, β_{12} and β_{21} , and their approximate confidence regions for the ethanol-cyclohexane system.

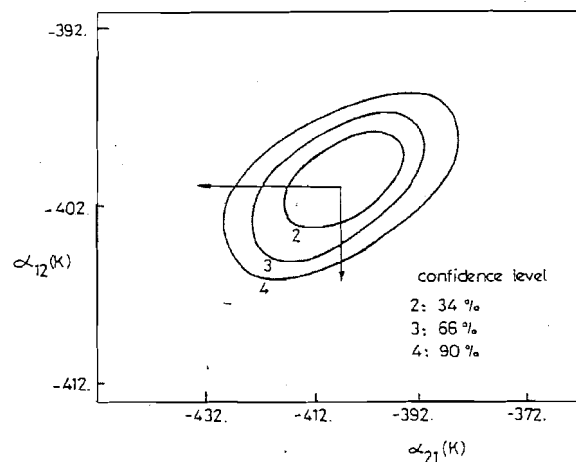


Figure 3 — UNIQUAC parameters, α_{12} and α_{21} , and their approximate confidence regions for the 2-propanol-*n*-heptane system.

regions shown represent areas within which the parameter values can be expected to lie at a confidence level associated with the contours. The probability content of the confidence regions become very small as the number of parameters

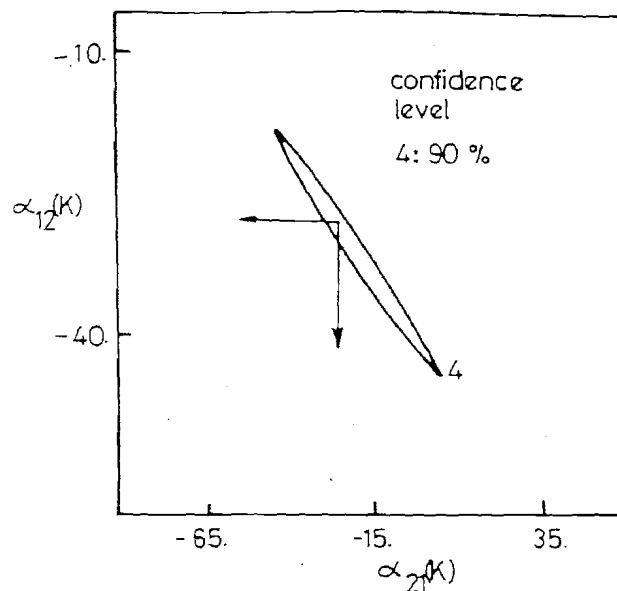


Figure 4 — UNIQAC parameters, α_{12} and α_{21} , and their approximate confidence region for the methyl acetate-cyclohexane system.

increases. The probability statement is the probability that all parameters take on values within the two standard deviation contour is 34%, three standard deviation contour is 66% and four standard deviation contour is 90%. In the Figures 1-4 confidence regions for the systems ethanol-cyclohexane, 2-propanol-*n*-heptane, and methyl acetate-cyclohexane are given. The figures show that the confidence regions become small and narrow as the estimated variance of the fit decreases. The confidence regions for the parameters β_{21} and β_{12} are large. This is seen in Figure 2 for the system ethanol-cyclohexane.

Conclusions

A simultaneous fit of excess Gibbs free energy and heat of mixing data for 24 binary systems are well made with the UNIQAC equation whose parameters are assumed to be temperature dependent. Treating the parameters as temperature dependent, the UNIQAC equation is able to represent larger values of h^E data, and the effect of temperature on h^E data and activity coefficient. This property is especially important in process calculations such as bubble point and distillation.

The MINUIT program performs satisfactorily in estimating the temperature dependent parameters. Since it does not need the partial derivatives of an objective function with respect to parameters, it is easy to use. However the convergence is not rapid.

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Nomenclature

- a_{ij} = UNIQAC binary interaction parameter related to Δu_{ij} and τ_{ij} [K]
 c_{ij} = elements of covariance matrix

- g^E = excess molar Gibbs energy [J/mol]
 h^E = excess enthalpy of mixing [J/mol]
 q_i' = molecular interaction area parameter for component *i*
 P = pressure [Pa]
 R = gas constant [J/mol K]
 T = absolute temperature [K]
 S = average absolute error (Equations 11 and 12)
 Δu_{ij} = UNIQAC binary interaction parameter [J/mol]
 x_i = liquid phase mole fraction of component *i*

Greek letters

- α_{ij} = parameter of UNIQAC equation related to a_{ij} [K] (Equation 7)
 β_{ij} = parameter of UNIQAC equation related to a_{ij} [K] (Equation 7)
 γ_i = activity coefficient for component *i*
 Θ_i' = area fraction for component *i* in residual contribution to the activity coefficient
 μ_{ij} = elements of correlation coefficient matrix (Equation 14)
 μ_k = elements of global correlation vector (Equation 15)
 τ_{ij} = UNIQAC binary parameter
 σ = variance of the fit (Equation 13)

Subscripts

- exp* = experimental
 $calc$ = calculated
 i, j = component
 max = maximum

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