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Calculations of thermodynamic derivative properties from the NRTL and UNIQUAC models

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Abstract

The local composition models NRTL and UNIQUAC with temperature-dependent parameters have been employed to calculate the surfaces of excess heat capacity, C_p^E, excess enthalpy, h^E and thermodynamic factor, Γ for binary liquid mixtures. These thermodynamic properties represent the derivatives of the models with respect to temperature, C_p^E, h^E and composition, Γ. The parameters used in evaluating C_p^E and h^E are directly obtained from separate C_p^E and h^E data at different isotherms. Experimental g^E and h^E data at more than one different isotherm are used simultaneously to estimate the parameters in the evaluation of Γ. The following mixtures are considered: methanol(1)–methyl acetate(2); 2-propanol(2)–*n*-heptane(2); methanol(1)–water(2); benzene(1)–*n*-heptane(2) and ethanol(1)–water(2). These mixtures show close deviations between experimental and calculated values obtained from both models and also include associating mixtures. Performances of the models based on different types of experimental data have been compared. The models show considerable regional discrepancies of the same thermodynamic property over the entire composition and temperature ranges for the mixtures that show small overall deviations between the calculated and experimental data. © 1997 Elsevier Science B.V.

Keywords: Binary liquid mixtures; NRTL and UNIQUAC models; Surfaces of derivative properties

1. Introduction

Deiters [1] has recently suggested that the thermodynamic models based on excess Gibbs energy have been the preferred method for the calculation of thermodynamic properties of various mixtures including associating liquids at low pressures. Capabilities of the models often depend upon the care taken in the parameter estimation stage [2,3]. The industry widely recognized the practical advantages of local composition models of NRTL [4,5] and UNIQUAC [6]. Renon [5] has pointed out that these model lead to a consistent representation of fluid-phase equilibria and excess thermodynamic properties by assuming all the parameters that are temperature-dependent. Previously, excess Gibbs energy, g^E, excess enthalpy, h^E, and excess heat capacity, C_p^E data were correlated at more than one different isotherm, and adjustable temperature-dependent parameters of the models were estimated [3,7–9]. The actual experimental data, utilized in estimating the parameters is taken from the published chemical literature.

This study shows the performances of the models in representing different types of thermodynamic data, and their ability in interpolating and extrapolating the

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thermodynamic property over the composition and temperature. The regional discrepancies between the models are determined and displayed in a qualitative and quantitative manner with respect to composition and temperature for the binary liquid mixtures.

2. Thermodynamic properties

Excess heat of mixing h^E is given by the Gibbs–Helmholtz equation.

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

C_p^E may be calculated by differentiating h^E with respect to temperature.

$$C_p^E = \frac{\partial h^E}{\partial T} \tag{2}$$

Analytical expressions for h^E and C_p^E derived from g^E are given elsewhere for both the models NRTL and UNIQUAC [8,9].

Higher derivative properties can be obtained by differentiating an expression for g^E with respect to mole fraction and temperature. They are particularly important in understanding the structural changes in the mixtures and testing the thermodynamic models [10–13]. The partial molar excess enthalpy, h_i^E, provides direct information on the solute–solvent interactions. The partial molar properties are calculated as

$$h_i^E = h^E + (1 - x_i)(\partial h^E/\partial x_i) \tag{3}$$

$$C_{p,i}^E = C_p^E + (1 - x_i)[\partial(C_p^E)/\partial x_i] \tag{4}$$

For a binary mixture the thermodynamic factor that describes diffusion in multicomponent systems is given as [14]

$$\Gamma = 1 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1} \tag{5}$$

and it is associated with the second derivative of g^E with respect to composition.

3. Results and discussion

Surfaces of derivative properties h^E, C_p^E and Γ, together with the partial molar quantities have been evaluated for the mixtures methanol(1)–methyl acetate(2), 2-propanol(1)–n-heptane(2), methanol(1)–water(2), benzene(1)–n-heptane(2), and ethanol(1)–water(2) for the entire composition and specified temperature ranges using the NRTL and UNIQUAC models. The temperature-dependent parameters and the type of data regressed in estimating them are given in Table 1(a) and (b) and Table 2. Estimations of the adjustable parameters are explained in detail elsewhere [3,8,9]. Table 1(a) and (b) show the linear and non-linear temperature dependencies of adjustable parameters that are employed in the NRTL model. Table 3 shows the average deviations in the predictions of g^E, $D(g^E)$, h^E, $D(h^E)$, and C_p^E, $D(C_p^E)$ which are expressed as [23]

$$D(f) = \frac{1}{m}\left[\sum_{i=1}^{m} |f_{i,\exp tl} - f_{i,\mathrm{calc}}| \Big/ f_{i,\exp tl}\right] \times 100 \tag{6}$$

where f represents g^E, h^E or C_p^E, while m is the number of data points at each isotherm. Table 3 indicates that for the mixtures considered the overall deviations for the NRTL and UNIQUAC, related to total number of data points, are similar or very close. Temperature intervals used in the surface evaluations are: 295–320 K for methanol(1)-methyl acetate(2); 300–335 K for 2-propanol(1)-n-heptane(2); 280–325 K for methanol(1)-water(2); 295–325 K for benzene(1)-n-heptane(2) and 290–310 K for ethanol(1)-water(2). These intervals are taken slightly outside the isotherms of experimental data to make extrapolation.

Fig. 1 shows the surfaces of h^E and h_1^E in terms of the composition and temperature obtained from UNIQUAC, while Fig. 2 shows the ratio of these obtained from NRTL, h^E(N), UNIQUAC, h^E(U), for the mixture methanol(1)–water(2). For this mixture, Table 3 gives the overall deviations as 6.3% for NRTL and 5.5% for UNIQUAC. Fig. 2 shows that in methanol dilute region predictions of the models differ from each other, and the effect of temperature on these differences is more apparent in the water-rich region.

The surfaces of h^E, h_1^E, and their ratios obtained from the NRTL and UNIQUAC for the mixture benzene(1)–n-heptane(2) are shown in Figs. 3 and 4. This mixture shows the overall deviations of 0.8 and 1.0 for NRTL and UNIQUAC, respectively, and is nearly ideal. At low temperatures, and at midpoint composi-

Table 1

(a) Temperature-dependent parameters of the NRTL model estimated using g^E and h^E data simultaneously [3]$(g_{21} - g_{11}) = c_1 + c_2(T - 273.15)$; $(g_{12} - g_{22}) = c_3 + c_4(T - 273.15)$; $\alpha_{21} = \alpha_{12} = c_5 + c_6(T - 273.15)$

System (Reference)	c_1 (J mol^{-1})	c_2 (J mol^{-1} K^{-1})	c_3 (J mol^{-1})	c_4 (J mol^{-1} K^{-1})	c_5	c_6 10^4 (K^{-1})	T_{min}–T_{max} (°C)
Methanol(1)–methyl acetate(2) [15]	1857.82	−12.30	1940.87	2.87	0.5928	3.566	25–45
2-Propanol(1)–*n*-heptane(2) [16]	7655.88	−34.93	3616.44	−2.88	0.4874	9.453	30–60

(b) Temperature-dependent parameters of the NRTL model [8,9] $(g_{21} - g_{11}) = c_1 + c_2/(T - 273.15)$; $(g_{12} - g_{22}) = c_3 + c_4/(T - 273.15)$; $\alpha_{21} = \alpha_{12} = c_5 + c_6/(T - 273.15)$

System (Reference)	c_1 (J mol^{-1})	c_2 (J K mol^{-1})	c_3 (J mol^{-1})	c_4 (J K mol^{-1})	c_5	c_6 (K)	T_{min}–T_{max} (°C)	Data reduced
Methanol(1)–water(2) [17]	−2538.0	2159.9	807.7	−2636.9	0.4505	1.1850	5–50	h^E
Benzene(1)–*n*-heptane(2) [18–20]	349.2	8266.9	4159.7	−6108.6	0.1831	0.8838	25–40	h^E
Ethanol(1)–water(2) [21,22]	29453.0	−340.7	16333.0	−62.8	0.1794	0.0001	15–35	C_p^E

Table 2
Temperature-dependent parameters of the UNIQUAC model estimated using g^E and h^E data simultaneously [7,3,9]: $a_{21} = d_1 + d_2/T$; $a_{12} = d_3 + d_4/T$

System	d_1 (K)	d_2 (K^2)	d_3 (K)	d_4 (K^2)	T_{min}–T_{max} (°C)	Data reduced
Methanol(1)–methyl acetate(2)	233.02	69416.0	−145.54	24272.0	25–45	$g^E + h^E$
2-Propanol(1)–*n*-heptane(2)	−407.50	545930.0	−400.33	72080.0	30–60	$g^E + h^E$
Methanol(1)–water(2)	−221.52	−36272.0	713.03	79796.0	5–50	h^E
Benzene(1)–*n*-heptane(2)	−14.64	18254.0	35.57	1217.0	25–40	h^E
Ethanol(1)–water(2)	−970.20	605870.0	1114.70	285610.0	15–35	C_p^E

Table 3
Correlation of thermodynamic data by the NRTL and UNIQUAC models

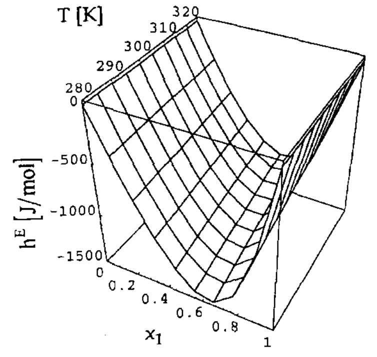
System							Deviations					
	g^E		h^E		C_p^E		NRTL			UNIQUAC		
	T (°C)	m	T (°C)	m	T (°C)	m	$D(g^E)$	$D(h^E)$	$D(C_p^E)$	$D(g^E)$	$D(h^E)$	$D(C_p^E)$
Methanol(1)–methyl acetate(2)	25	13	25	14			4.9	1.5		4.9	3.6	
	45	13	35	16			4.1	0.9		4.1	1.2	
			45	10				1.9			4.0	
							4.5[a]	1.4[a]		4.5[a]	2.9[a]	
2-propanol(1)–*n*-heptane(2)	30	17	30	24			2.6	14.7		3.2	11.9	
	45	17	45	22			2.2	11.6		3.2	9.1	
	60	17	60	21			1.9	10.6		2.9	13.8	
							2.2[a]	12.3[a]		3.1[a]	11.6[a]	
Methanol(1)–water(2)			5	6				2.0			7.0	
			15	6				8.3			5.9	
			25	6				7.4			5.1	
			40	6				5.7			3.9	
			50	6				7.9			5.4	
								6.3[a]			5.5[a]	
Benzene(1)–*n*-heptane(2)			25	14				1.0			0.8	
			45	8				0.5			1.3	
			50	4				1.0			0.8	
								0.8[a]			1.0[a]	
Ethanol(1)–water(2)					15	15			10.5			7.9
					25	17			7.9			6.0
					35	22			7.4			8.7
									8.6[a]			7.5[a]

[a] Overall deviation.

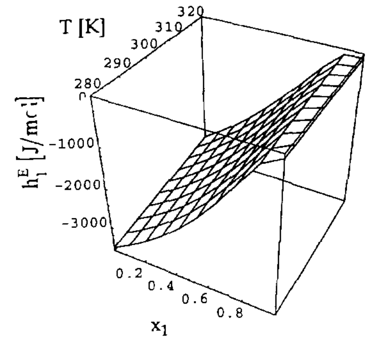
tions there is a slight difference between the model predictions of h^E and h_l^E.

Surfaces of C_p^E and $C_{p,l}^E$, obtained from the NRTL model are shown for the mixture ethanol(1)–water(2) in Fig. 5, while Fig. 6 shows the ratio of surfaces of C_p^E and $C_{p,l}^E$, by NRTL $C_p^E(N)$ and UNIQUAC $C_p^E(U)$. Although Table 3 gives the close overall deviations of 8.6% for NRTL and 7.5% for UNIQUAC, Fig. 6 shows considerable differences between the regional performances of the models through the entire composition and temperature intervals. This reveals that the sensitivity to accuracy of experimental data regressed varies from one model to another.

Diffusion calculations can be quite sensitive to the model used to compute the thermodynamic factor Γ, [14,24]. The several models may provide estimates of activity coefficients, $\ln\gamma$, that give equally good fits of the vapor–liquid equilibrium data. However, this does

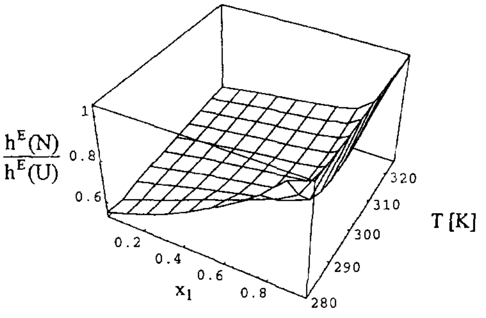


methanol(1)-water(1), 275-325 K a

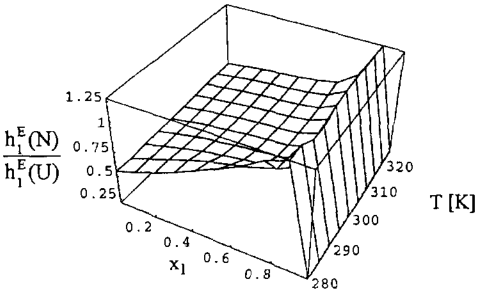


methanol(1)-water(2), 275-325 b

Fig. 1. (a) Surface of excess enthalpy, h^E; (b) Surface of partial molar excess enthalpy, h_1^E by UNIQUAC for the mixture methanol(1)–water(2) at temperature interval 280–325 K.



methanol(1)-water(1), 280-325 a



methanol(1)-water(2), 280-325 b

Fig. 2. (a) Ratio of surfaces of h^E, $h^E(N)/h^E(U)$; (b) Ratio of surfaces of h_1^E by NRTL and UNIQUAC, $h_1^E(N)/h_1^E(U)$, for the mixture methanol(1)–water(2) at temperature interval 280–325 K.

not mean that the values of Γ from different models will be close to one another [14]. Fig. 7 shows the surfaces of Γ for the mixture methanol(1)–methyl acetate(2) obtained from NRTL, and the ratio of Γ obtained by NRTL, Γ(N), and UNIQUAC, Γ(U). Similar sets of plots are given for the mixture 2-propanol(1)–*n*-heptane(2) in Fig. 8 that shows considerable performance differences between the models that are mainly due to rather high overall deviations between the calculated and the experimental data. The surfaces of derivative properties are sensitive to the interpolation ability and the adjustable parameters. The ratio of surfaces produces qualitative and quantitative information on regions of composition and temperature in which the local discrepancies between the models are considerable. Greater discrepancies are observed for the properties of higher derivatives (partial molar properties), especially for the mixtures with high overall deviations shown in Table 3.

The empirical advantages and shortcomings of NRTL and UNIQUAC were reviewed by Renon [5]. The UNIQUAC model requires information on size and shape of molecules, through the term combinatorial part, which is assumed to be independent of temperature. This aspect of the model was investigated by Sayegh and Vera [25].

4. Conclusions

The surfaces of Γ, C_p^E, h^E and the partial molar properties have been calculated by the NRTL and

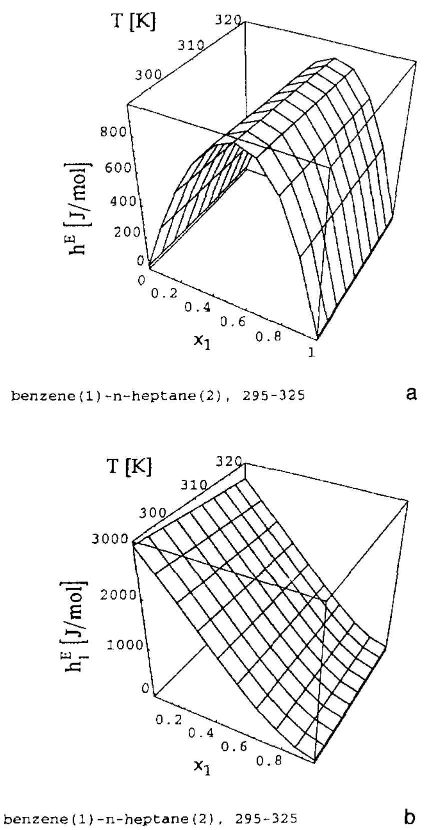


Fig. 3. (a) Surface of excess enthalpy, h^E; (b) Surface of partial molar excess enthalpy, h_1^E by UNIQUAC for the mixture benzene(1)–*n*-heptane(2) at temperature interval 295–325 K.

UNIQUAC models for the binary liquid mixtures, using the adjustable parameters estimated directly from the relevant experimental data. The study reveals that the models with similar performances based on conventionally defined deviations (Eq. (6)) in representing a derivative property may still display considerable regional discrepancies with respect to composition and temperature.

5. List of symbols

a_{ij}	UNIQUAC binary interaction parameters
c_1, c_3	values of $(g_{21}-g_{11})$ and $(g_{12}-g_{22})$ at 0°C (J mol^{-1})
c_2, c_4	coefficients of temperature change of $(g_{21}-g_{11})$ and $(g_{12}-g_{22})$ (J mol^{-1} K^{-1})
c_5	value of α_{21} at 0°C
c_6	coefficient of temperature change of α_{21} (K^{-1})
d_1, d_3	UNIQUAC parameters related to a_{ij}, (K)
d_2, d_4	UNIQUAC parameters related to a_{ij}, (K^2)
C_p^E	excess heat capacity (J mol^{-1} K^{-1})
$C_{p,1}^E$	partial molar excess heat capacity (J mol^{-1} K^{-1})
D	deviation (Eq. (6))
f	function representing either of g^E, h^E or C_p^E
g^E	excess Gibbs energy (J mol^{-1})
h^E	excess enthalpy (J mol^{-1})
h_1^E	partial molar excess enthalpy (J mol^{-1})
m	number of data points at each isotherm
P	pressure (Pa)
T	temperature (K)
x_i	liquid-phase mole fraction of component i

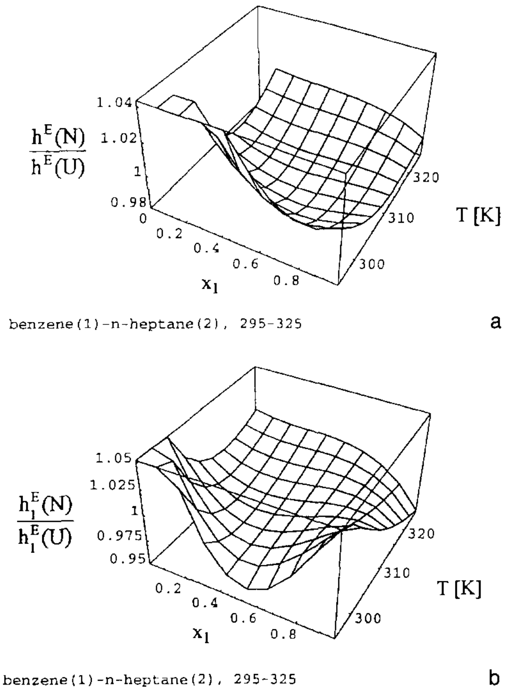


Fig. 4. (a) Ratio of surfaces of h^E, $h^E(\mathrm{N})/h^E(\mathrm{U})$; (b) Ratios of surfaces of h_1^E by NRTL and UNIQUAC, $h_1^E(\mathrm{N})/h_1^E(\mathrm{U})$, for the mixture benzene(1)–*n*-heptane(2) at temperature interval 295–325 K.

6. Greek symbols

α	non randomness parameter in the NRTL model

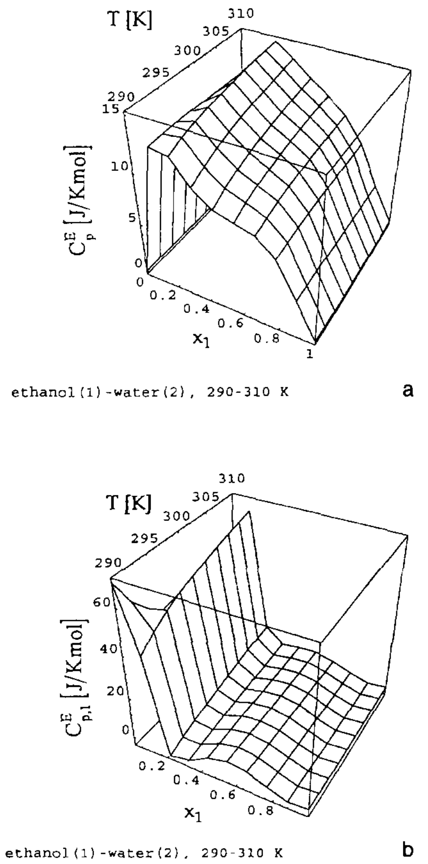


Fig. 5. (a) Surface of excess heat capacity, C_p^E; (b) Surface of partial molar excess heat capacity, $C_{p,1}^E$, by NRTL for the mixture ethanol(1)–water(2) at temperature interval 285–310 K.

γ	activity coefficient
Γ	thermodynamic factor

7. Subscripts

calc	calculated
exp	experimental
max	maximum
min	minimum
i,j	component

8. Superscript

E	excess

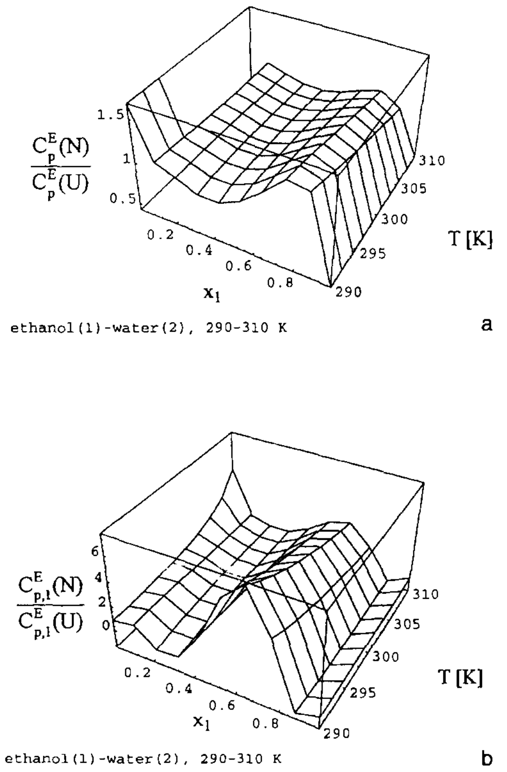


Fig. 6. (a) Ratio of surfaces of C_p^E, $C_p^E(N)/C_p^E(U)$; (b) Ratio of surfaces of $C_{p,1}^E$ by NRTL and UNIQUAC, $C_{p,1}^E(N)/C_{p,1}^E(U)$, for the mixture ethanol(1)–water(2) at temperature interval 285–310 K.

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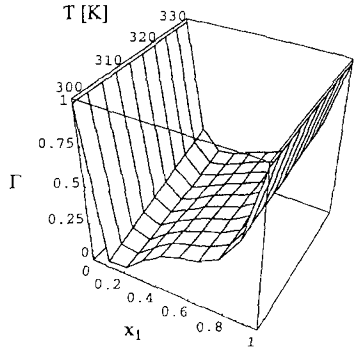
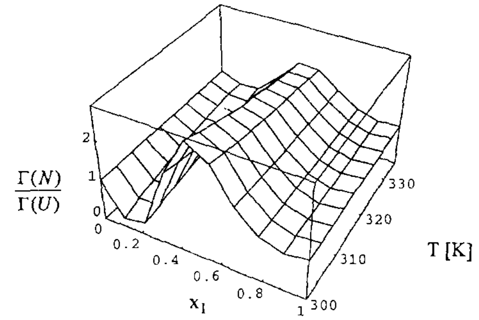
References

[1] U.K. Deiters, Fluid Phase Equilibria, 89 (1993) 229.
[2] J.M. Prausnitz, R.N. Lichtenthaler and E.G. Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd edn., Prentice Hall, Englewood Clifs, N.J., 1986.
[3] Y. Demirel, H. Gecegormez, Fluid Phase Equilibria, 65 (1991) 111.
[4] H. Renon, J.M. Prausnitz, AIChE J., 14 (1968) 135.
[5] H. Renon, Fluid Phase Equilibria, 24 (1985) 87.
[6] D.S. Abrams, J.M. Prausnitz, AIChE J., 21 (1975) 116.
[7] Y. Demirel, H. Gecegormez, Can. J. Chem. Eng., 67 (1989) 455.



2-propanol(1)-n-heptane(2), 300–335 K a



2-propanol(1)-n-heptane(2), 300–335 K b

Fig. 7. Surfaces of thermodynamic factor, Γ; (a) By NRTL; (b) Ratio of surfaces of Γ by NRTL and UNIQUAC; Γ(N)/Γ(U) for the mixture methanol(1)–methyl acetate(2) at temperature interval 295–320 K.

[8] Y. Demirel, H. Gecegormez and H.O. Paksoy, Thermochim. Acta, 194 (1992a) 329.

[9] Y. Demirel, H.O. Paksoy, Thermochim. Acta, 198 (1992) 329.

[10] K.P. Shukla, A.A. Chialvo, J.M. Haile, Ind. Eng. Chem. Res., 27 (1988) 664.

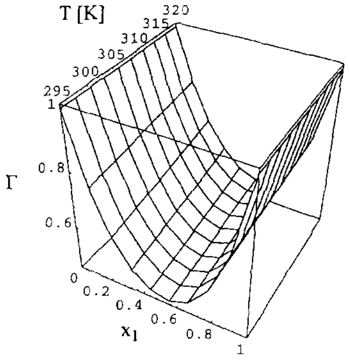
[11] Y. Koga, W.W. Siu, T. Wong, J. Phys. Chem., 94 (1990) 7700.

[12] A.H. Roux, G. Roux-Desgranges, J-P.E. Grolier, Fluid Phase Equilibria, 89 (1993) 57.

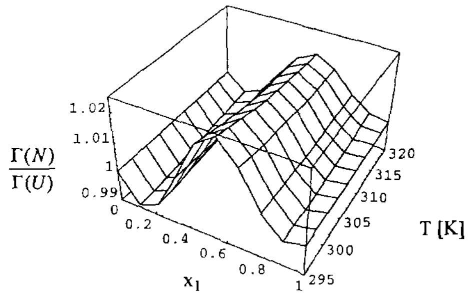
[13] M. Page, J-Y. Huot, C.A. Jolicoeur, J. Chem. Thermodyn., 25 (1993) 139.

[14] R. Taylor, H.A. Kooijman, Chem. Eng. Comm., 102 (1991) 87.

[15] I. Nagata, T. Ohta, T. Takahashi, J. Chem. Eng. Data, 5 (1972) 227.



methanol(1)-methyl acetate(2), 295–320 K a



methanol(1)-methyl acetate(2), 295–320 K b

Fig. 8. Surfaces of thermodynamic factor, Γ; (a) By NRTL; (b) Ratio of surface of Γ by NRTL and UNIQUAC; Γ(N)/Γ(U) for the mixture 2-propanol(1)–*n*-heptane(2) at temperature interval 300–355 K.

[16] H.C. Van Ness, C.A. Soczek, G.L. Peloguin, R.L. Mashed, J. Chem. Eng. Data, 12 (1967) 217.

[17] A.J. Easteal, L.A. Woolf, J. Chem. Eng. Thermodyn., 17 (1985) 69.

[18] D.A. Palmer, B.D. Smith, J. Chem. Eng. Data, 17 (1972) 71.

[19] T.M. Letcher, J.W. Bayles, J. Chem. Eng. Data, 16 (1971) 266.

[20] G.W. Lundberg, J. Chem. Eng. Data, 9 (1964) 193.

[21] G.C. Benson, P.J.D. D'Arcy, J. Chem. Eng. Data, 27 (1982) 439.

[22] H. Ogawa, S. Murakami, Thermochim. Acta, 109 (1986) 145.

[23] Y. Demirel, H.O. Paksoy and H. Gecegormez, Thermochim. Acta, 194 (1992b) 343.

[24] Y. Demirel, Chim. Acta Turc., 14 (1986) 114.

[25] S.G. Sayegh, J.H. Vera, Chem. Eng. J, 19 (1980) 1.