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Calculation of Excess Entropy for Binary Liquid Mixtures by the NRTL and UNIQUAC Models

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Isothermal excess entropy data for 23 binary liquid mixtures were calculated using the excess Gibbs energy and excess enthalpy correlations obtained from the local composition models of NRTL and UNIQUAC. The mixtures include highly nonideal, associating, and partially miscible systems. Temperature-dependent parameters of the models were used in the calculations. The experimental data of excess Gibbs energy and excess enthalpy, which were base of excess entropy data, covers the temperature range of 288.15−358.15 K. The average absolute relative deviations of the excess entropy data calculations were obtained as 7.34 and 8.51% for the NRTL and UNIQUAC models, respectively. Excess entropy data at isobaric conditions were also calculated using excess heat capacity data for eight binary liquid mixtures in the range of 238.15−318.15 K. Temperature-dependent parameters estimated directly from excess heat capacity data were used in the calculations which gave the average absolute relative deviations of 10.91 and 12.76% for the NRTL and UNIQUAC models, respectively.

Introduction

Excess entropy, Ts^E, is essential for thermodynamic analysis of mixtures and separation processes in chemical engineering (Perry et al., 1984; Hayashi and Kojima, 1993). The excess entropies are also helpful in understanding the mode of mixing in terms of entropy (Koga et al., 1990; Prausnitz et al., 1986).

Recently Hayashi and Kojima (1993) predicted the excess entropy for binary liquid mixtures by the ASOG group contribution method. In the previous work by Demirel and Gecegormez (1989, 1991) data for excess Gibbs energy, g^E, and excess enthalpy, h^E, at more than one different isotherm, were correlated simultaneously, and the temperature-dependent parameters of the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) models were estimated. In a separate work, the temperature-dependent parameters of the models were also estimated directly from the excess heat capacity data (Demirel and Paksoy, 1992). Since a systematic predictive method for excess entropy has not yet been established, in this work an attempt is made to evaluate the accuracy of the excess entropy predictions by the local composition models of NRTL and UNIQUAC with temperature-dependent parameters.

Determination of Excess Entropy

The excess entropy (Ts^E) can be calculated from the fundamental thermodynamic relation

$$Ts^E = h^E - g^E \qquad (1)$$

by using experimental data for h^E and g^E at isothermal

conditions. The NRTL and UNIQUAC models are widely used to correlate the excess Gibbs energy. The rate of change of excess Gibbs energy with respect to temperature is proportional to the excess enthalpy and is given by the Gibbs−Helmholtz equation

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

Interaction energy parameters $(g_{21} - g_{11})$, $(g_{12} - g_{22})$ and the nonrandomness parameter, α_{12}, of the NRTL model may be assumed to change with temperature in a linear way (Nagata and Yamada, 1973; Renon and Prausnitz, 1968; Demirel and Gecegormez, 1991).

$$g_{21} - g_{11} = c_1 + c_2\,(T - 273.15) \qquad (3)$$

$$g_{12} - g_{11} = c_3 + c_4\,(T - 273.15) \qquad (4)$$

$$\alpha_{12} = \alpha_{21} = c_5 + c_6\,(T - 273.15) \qquad (5)$$

The effect of temperature on the characteristic energies, a_{ij}, of the UNIQUAC model may be expressed as (Anderson and Prausnitz, 1978; Demirel and Gecegormez, 1989, 1991)

$$a_{21} = d_1 + d_2/T \qquad (6)$$

$$a_{12} = d_3 + d_4/T \qquad (7)$$

The UNIQUAC model contains pure component structural parameters. Anderson and Prausnitz (1978) modified the UNIQUAC model slightly and introduced new values of surface parameters for alcohols and water to be used in the residual part of the model equation for g^E.

The excess entropy at isobaric conditions can be calculated by the expression

$$\left(\frac{\partial s^E}{\partial T}\right)_{p,x} = \frac{c_p^E}{T} \tag{8}$$

or

$$\Delta s^E = \int \frac{c_p^E}{T}\, dT \tag{9}$$

where c_p^E shows the excess heat capacity. Differentiating the expression for h^E with respect to temperature gives an expression for c_p^E

$$c_p^E = \left(\frac{\partial h^E}{\partial T}\right)_{p,x} \tag{10}$$

Previously excess heat capacities were calculated by the differentiation of the equations of excess enthalpy obtained from the NRTL and UNIQUAC models, but the results were unsatisfactory (Demirel et al., 1992a,b), because, mainly, these calculations were performed by using the temperature-dependent parameters of the models estimated by the simultaneous regression of h^E and g^E data. In order to predict c_p^E data accurately from this indirect method, the accuracy of the measurement of h^E must be very high over a narrow temperature range. Therefore we decided to correlate experimental data for c_p^E directly with the NRTL and UNIQUAC models (Demirel and Paksoy, 1992).

As eq 9 indicates, the expression for c_p^E requires the second degree differentiation of excess Gibbs energy with respect to temperature. Previously used linear temperature dependency, given by eqs 3–5, for the NRTL model is not satisfactory in such differentiation. Therefore in the direct correlation of excess heat capacity data by the NRTL model, the temperature dependence of the energy interaction parameters were assumed as (Demirel and Paksoy, 1992)

$$g_{21} - g_{11} = c_1{}^* + c_2{}^*/(T - 273.15) \tag{11}$$

$$g_{12} - g_{22} = c_3{}^* + c_4{}^*/(T - 273.15) \tag{12}$$

$$\alpha_{21} = \alpha_{12} = c_5{}^* + c_6{}^*/(T - 273.15) \tag{13}$$

The effect of the nature of the temperature dependence of the parameters of the NRTL model was investigated in a separate study. The interaction energy parameters of linear and nonlinear type were estimated using h^E data alone for 55 binary liquid mixtures of various kinds including highly nonideal, associating, and partially miscible systems. It was found that the effect of the type of temperature dependence on the performance of the NRTL model was marginal, although the performance of the model with nonlinear temperature dependence was slightly better (Demirel, 1993).

Results and Discussion

The excess entropy was calculated by the local composition models of NRTL and UNIQUAC for 34 data sets of the 23 binary mixtures at isothermal conditions. The same sets of temperature-dependent parameters for excess Gibbs energy and excess enthalpy were used to calculate the excess entropy by eq 1. Six parameters, c_1–c_6, for the NRTL model and four parameters, d_1–

Table 1. Deviation of Excess Entropy at Isothermal Conditions

no.	system reference	T, °C	deviation NRTL	deviation UNIQUAC
1	methyl acetate + cyclohexane Nagata (1973)	35	0.84	4.30
2	ethyl formate + methanol Nagata et al. (1976)	45	2.08	8.00
3	ethyl formate + ethanol Nagata et al. (1976)	45	2.74	8.26
4	ethyl formate + 2-propanol Nagata et al. (1976)	45	5.02	9.60
5	methyl acetate + methanol Nagata et al. (1972)	35	4.98	5.09
		45	4.57	5.72
6	methyl acetate + ethanol Nagata et al. (1972)	45	9.42	11.07
7	ethanol + toluene Van Ness et al. (1967)	45	6.02	6.65
		60	5.15	8.63
8	2-propanol + n-heptane Van Ness et al. (1967)	30	14.89	12.38
		45	11.86	9.67
		60	10.79	14.17
9	n-pentanol + n-hexane Nguyen (1975); Sayegh (1976)	25	15.46	3.93
10	n-pentanol + 2,2-dimethylbutane Nguyen (1975); Sayegh (1976)	25	8.21	4.76
11	n-pentanol + 2,3-dimethylbutane Nguyen (1975); Sayegh (1976)	25	3.89	4.99
12	n-pentanol + 2-methylpentane Nguyen (1975); Sayegh (1976)	25	4.77	5.30
13	n-pentanol + 3-methylpentane Nguyen (1975); Sayegh (1976)	25	7.59	5.53
14	isopentanol + n-hexane Nguyen (1975); Sayegh (1976)	25	7.98	6.11
15	acetonitrile + benzene Palmer (1972); Monfort (1983)	45	7.60	7.93
16	benzene + n-heptane Palmer (1972); Lundberg (1964)	45	9.25	8.81
17	acetonitrile + n-heptane Palmer (1972)	45	7.58	7.66
18	ethanol + cyclohexane Scatchard and Satkiewitcz (1964)	5	9.68	13.80
		20	4.19	8.80
		35	4.32	8.26
		50	4.88	8.75
		65	5.26	5.18
19	water + butyl glycol Scatchard and Wilson (1964)	5	nc[a]	15.26
		25	nc	15.75
		45	nc	15.87
		65	nc	13.62
		85	nc	15.50
20	1,4-dioxane + acetonitrile Francesconi (1988)	40	11.82	17.66
21	carbon tetrachloride + diethyl sulfide Gray et al. (1988a, b)	25	16.08	16.61
22	chloroform + diethyl sulfide Gray et al. (1988a, b)	25	6.57	6.60
23	1,3-dioxalene + methylcyclohexane Castellari et al. (1988)	40	6.69	11.14

[a] Not calculated.

d_4, for the UNIQUAC model were estimated by the simultaneous regression of g^E and h^E data at more than one different isotherm, and are given elsewhere in detail together with the UNIQUAC structural parameters (Demirel and Gecegormez, 1989, 1991).

In Table 1 the calculated values of excess entropy are compared with the ones determined from experimental data of g^E and h^E at isothermal conditions. The average absolute relative deviation, $\Delta_{av}(Ts^E)$, of the calculated excess entropy is calculated by the expression (Hayashi and Kojima, 1993)

$$\Delta_{av}(Ts^E) = [\Delta_{av}(g^E)^2 + \Delta_{av}(h^E)^2]^{1/2} \tag{14}$$

where average absolute relative deviation, Δ_{av}, is given as

Table 2. Deviation of Excess Entropy Data at Temperature Range of T_1-T_2, °C

no.	system reference	T_1-T_2, °C	deviation NRTL	deviation UNIQUAC
1	ethanol + heptane Brown (1979)	(−20)−(15)	nc^a	11.25
		25−45	11.87	14.61
2	2-propanol + n-heptane Brown (1979)	(−35)−(−5)	nc	27.55
		5−15	17.40	26.35
3	1-propanol + n-hexene Kalinowska (1985)	(−8)−(7)	nc	9.79
		12−22	10.00	9.44
4	1-hexanol + n-hexane Kalinowska (1984)	(−8)−(17)	nc.	15.58
5	water + methanol Ogawa (1986), Benson (1982)	15−35	11.41	10.16
6	water + ethanol Ogawa (1986), Benson (1982)	15−35	8.61	7.53
7	water + 1-propanol Ogawa (1986), Benson (1982)	15−30	12.90	7.02
8	benzene + n-heptane Tanaka (1987)	20−35	4.13	1.27

^{a} Not calculated.

$$\Delta_{av} = \frac{\sum_{i=1}^{n}[(f_{exptl} - f_{calcd})/f_{exptl}]_i}{n} \times 100 \quad (15)$$

where n shows the number of data points, while f indicates g^E, h^E, or, c_p^E. Table 1 shows deviations of the correlated excess entropy calculated from eq 1 for 23 binary mixtures at isothermal conditions. The average relative deviations are 7.34 and 9.46% for NRTL and UNIQUAC models, respectively. If the results for the system water + butyl glycol are excluded, then the average relative deviation for the model UNIQUAC becomes 8.51%. At isobaric conditions, the absolute relative deviations are based on similar deviations obtained for excess heat capacity correlations, which are given in Table 2 for eight binary mixtures. Absolute relative deviations are 10.91 and 12.76% for the NRTL and UNIQUAC models respectively. Both models perform satisfactorily compared with the ASOG method (Hayashi and Kojima, 1993).

Conclusion

Excess entropy data at isothermal and isobaric conditions were determined in order to establish the best predictive model for the excess entropy by using the NRTL and UNIQUAC local composition models. A comparison with the determined excess entropy data yielded 9.1 and 11.1% in overall average relative deviations for the NRTL and UNIQUAC models respectively. The level of deviations indicates that both models are capable of correlating excess entropy satisfactorily for various type of mixtures, although the performance of the NRTL model is slightly better than that of the UNIQUAC model for the mixtures considered.

Acknowledgment

Nomenclature

a_{ij} = UNIQUAC binary characteristic parameters between components of i and j [K]

c_1, c_3 = values of $(g_{21} - g_{11})$, $(g_{12} - g_{22})$ at 273.15 K [J/mol]

c_2, c_4 = coefficients of temperature change of $(g_{21} - g_{11})$, $(g_{12} - g_{22})$ [J/(mol K)]

c_5 = value of α_{12} at 273.15 K

c_6 = coefficient of temperature change of α_{12} [1/K]

c_1^*, c_3^* = NRTL interaction parameters [J/mol]

c_2^*, c_4^* = coefficients of temperature change of $(g_{21} - g_{11})$, $(g_{12} - g_{22})$ [J K/mol]

c_5^* = parameter of α_{12}

c_6^* = coefficient of temperature change of α_{12} [K]

c_p^E = excess heat capacity [J/(mol K)]

d_1, d_3 = UNIQUAC parameters related to a_{ij} [K]

d_2, d_4 = UNIQUAC parameters related to a_{ij} [K^2]

f = function indicating g^E, h^E, or c_p^E

g^E = excess Gibbs energy [J/mol]

h^E = excess enthalpy [J/mol]

n = number of data points

P = pressure [Pa]

Ts^E = excess entropy [J/mol]

T = absolute temperature [K]

x = liquid mole fraction

Greek Symbols

α_{ij} = nonrandomness parameter for component i and j of the NRTL model

Indexes

av = average

calcd = calculated quantity

exptl = experimental quantity

E = excess quantity

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