Correlation of measured excess enthalpies of binary systems composed of n-alkane+1-alkanol

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Abstract−The excess enthalpies of the binary mixture composed of n-alkane (n-octane, n-nonane, n-decane) and 1-alkanol (ethanol, 1-propanol, 1-butanol) have been measured by using a flow-type isothermal microcalorimeter (model CSC 4400, Calorimetry Science Corp., USA) at 313.15 K under atmospheric pressure. The measured excess enthalpy data were correlated by the Redlich-Kister equation and the nonrandom lattice fluid with hydrogen bonding (NLF-HB) equation of state. Hydrogen bonding type specific parameters were introduced in the NLF-HB equation of state framework, and the effects of those parameters were investigated for excess enthalpy calculations. With two adjustable temperature-dependent interaction parameters, the NLF-HB equation represents the excess enthalpies for nine binary systems qualitatively.

Key words: Excess Enthalpy, Isothermal Microcalorimeter, Equation of State, N-Alkane, 1-Alkanol, Redlich-Kister Equation

INTRODUCTION

Excess enthalpy is an important thermophysical property for understanding the nature of interactions between the molecules of a mixture. It is well known that hydrogen bonding interactions are difficult to understand but are the most important factors for modeling biomolecules and engineering polymers with hydrogen bonding sites. Vapor liquid equilibrium and excess enthalpy data can be used to verify the theoretical soundness of a specific model. Several attempts have been made to correlate the vapor-liquid equilibrium and excess enthalpy simultaneously [1,2], but correlations within an equation of state framework still lack the desired accuracies. Kang and coworkers [3] first attempted to correlate vapor liquid equilibrium (VLE) and excess enthalpy (H^E) using the lattice fluid equation of state (NLF EoS). The calculation results were not satisfactory, especially for mixtures with associated species. Recently, the NLF EoS [4,5] has been combined with hydrogen bonding statistics proposed by Veytzman [6] and proven to be an efficient method for vapor-liquid equilibrium calculations, including associated species [9-11].

In this paper, we measured the excess enthalpy data of n-alkane (n-octane, n-nonane and n-decane)+1-alkanol (ethanol, 1-propanol and 1-butanol) system at 313.15 K and attempted to correlate using the Relich-Kister equation and the nonrandom lattice fluid with hydrogen bonding equation of state (NLF-HB EoS). The effect of hydrogen bonding parameters will be reviewed.

MATERIALS AND METHODS

1. Materials

All chemicals used were HPLC grade reagents and used without further purification. All chemicals were first placed in an ultrasonic vibrator for 10-20 minutes to remove dissolved gases in solution. Sources and properties of the chemicals used in this study are summarized in Table 1. The densities of the pure compounds at 298.15 K were measured with an Anton Paar DMA 5000 density meter with an uncertainty of $\pm 1.0 \times 10^{-5}$ (g/cm^3). The measured densities agree reasonably well with the literature values at 298.15 K within the range of specified purities of the components, as shown in Table 1.

2. Apparatus

An isothermal calorimeter (model CSC 4400, Calorimetry Science Corp., USA) was used to measure excess enthalpy. The overall configuration of the isothermal microcalorimeter is shown in Fig. 1. A similar configuration was used by other researchers [12]. The system is composed of two sets of HPLC pumps (model Acuflow series II, the uncertainty of $\pm 2\%$), a flow-mixing cell and a computer for data collection. The temperature of calorimeter was kept within ± 0.01 K. The uncertainty in mole fraction was estimated to be $\pm 1.3 \times 10^{-3}$ and the average uncertainty in excess enthalpy measurement was estimated to be $\pm 2\%$. The uncertainty in the mole fractions was calculated by using the uncertainty in the pump flowrates, and the uncertainty of the enthalpy was calculated from the uncertainty in the heat value measurements.

3. Methods

The measurement of excess enthalpy is very sensitive to the temperature of the surroundings. The room temperature was kept within ± 2 K to avoid unnecessary disturbance of the measurements. Before measurements began, the calorimeter was calibrated and stabilized at least for 3 days. After the stabilization period, base line measurements were made for each pure component. The total flow rates to mixing cell were chosen as 0.70 ml/min. The optimum flow rates were determined by repeated measurement of mixing enthalpy. The mixing enthalpy was measured after the baseline determination. The total flow rate was kept constant (0.7 ml/min) while the flow rates of each component in the binary systems were varied. The consistency of the measurements was verified by comparing with literature


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Table 1. Purities and densities of the measured components

Component	Supplier	Purity	ρ (g/cm^3) at 298.15 K	
			This work	Literature data [16]
n-Octane	Fluka Chemie	>99.5%	0.69854	0.699
n-Nonane	Aldrich Chemical Co.	>99.0%	0.71394	0.715
n-Decane	Fluka Chemie	>99.0%	0.72614	0.728
Ethanol	Aldrich Chemical Co.	>99.5+%	0.78513	0.787
1-Propanol	Fluka Chemie	>99.9%	0.80034	0.802
1-Butanol	Junsei Chemical Co.	>99.0%	0.80590	0.806
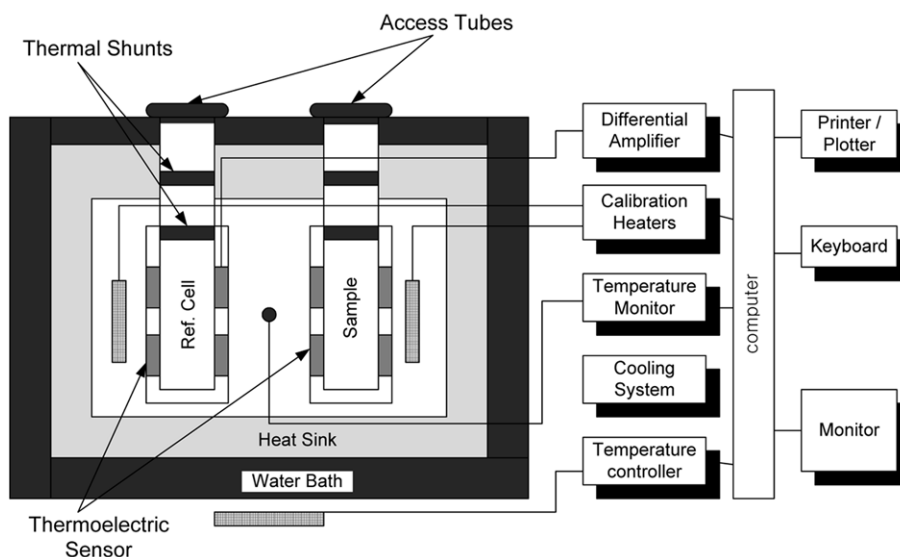
Fig. 1. Isothermal microcalorimeter (model CSC 4400, Calorimetry Science Corp., USA).
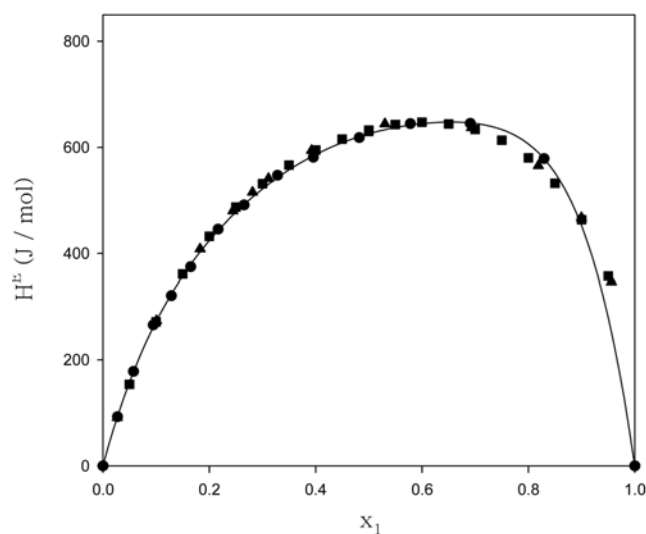
Fig. 2. Comparison experimental data H^E and reported literature values for n-octane+ethanol at 298.15 K. ●, This work; ▲, data from Ref. [12]; ■, Data from Ref [13]; Curve based on calculation from the application of Eq. (1).

data for n-octane+ethanol system at 298.15 K [13,14]. The measured data were compared and they showed fair agreement with litera-

ture data as shown in Fig. 2. The measured results were correlated by Redlich-Kister correlation [15] and the standard deviation was 2.62% .The standard deviation was slightly higher than the experimental uncertainty in the excess enthalpy data measurement (2%).

RESULTS AND DISCUSSION

1. Experimental Data

The excess enthalpies for n-alkane+1-alkanol systems (total 9 systems) were measured with an isothermal microcalorimeter at 313.15 K and atmospheric pressure. The measured values of excess enthalpy are summarized in Table 2.

2. Correlation using Redlich-Kister Equation

The experimental data were first correlated by using the Redlich-Kister correlation.

$$H^E/J\cdot mol^{-1} = x(1-x)\sum_{i=1}^{k}A_i(1-2x)^{i-1} \tag{1}$$

The measured excess enthalpy data and correlation results are shown in Figs. 3-5, and the values of the five parameters (A$_i$) and standard deviation (S.D) are reported in Table 3.

3. Correlation using NLF-HB Equation of States

Derivations and various aspects of NLF-HB EoS are given in the literature [4,5,9-11]. In this paper, we will give only the final form of the expressions. The equation of state is given as,

Table 2. Experimental fraction, x_1, and excess enthalpies, H^E for N-alkane+1-alkanol systems at 313.15 K

x_1	H^E (J/mol)	x_1	H^E (J/mol)	x_1	H^E (J/mol)	x_1	H^E (J/mol)	x_1	H^E (J/mol)
				n-Octane+Ethanol					
0.027	108	0.058	181	0.095	322	0.129	402	0.165	473
0.216	571	0.265	637	0.328	719	0.396	776	0.482	836
0.578	880	0.691	859	0.829	756				
				n-Octane+1-Propanol					
0.034	106	0.072	208	0.117	323	0.157	410	0.200	495
0.259	609	0.313	693	0.382	797	0.453	854	0.540	918
0.634	961	0.738	948	0.860	818				
				n-Octane+1-Butanol					
0.042	109	0.086	168	0.139	335	0.185	432	0.233	523
0.298	642	0.357	725	0.429	823	0.502	872	0.5898	917
0.678	931	0.775	884	0.882	748				
				n-Nonane+Ethanol					
0.025	114	0.053	186	0.088	331	0.119	409	0.154	478
0.203	575	0.249	639	0.310	721	0.376	779	0.461	843
0.557	895	0.672	874	0.817	814				
				n-Nonane+1-Propanol					
0.032	109	0.066	214	0.108	332	0.146	419	0.186	502
0.242	620	0.295	706	0.361	806	0.431	873	0.518	942
0.613	992	0.721	989	0.849	869				
				n-Nonane+1-Butanol					
0.038	112	0.079	184	0.128	346	0.172	444	0.218	533
0.280	650	0.337	734	0.408	831	0.480	896	0.567	948
0.659	971	0.759	932	0.873	797				
				n-Decane+Ethanol					
0.023	126	0.049	230	0.080	339	0.110	412	0.142	478
0.188	575	0.232	640	0.290	727	0.354	789	0.438	862
0.534	923	0.652	947	0.803	830				
				n-Decane+1-Propanol					
0.029	114	0.060	223	0.099	344.	0.135	432	0.172	516
0.226	632	0.276	715	0.340	820	0.408	896	0.495	973
0.591	1034	0.702	1043	0.837	938				
				n-Decane+1-Butanol					
0.035	115	0.073	179	0.118	358	0.159	456	0.202	550
0.262	672	0.317	759	0.385	860	0.457	931	0.544	990
0.638	1025	0.741	999	0.862	871				

$$\frac{PV_H}{RT} = \frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - \ln(1-\rho) + \rho\frac{l_M}{r_M} - v_{HB}\rho - \frac{z\beta}{2}\varepsilon_M\theta^2 \quad (2)$$

The expression for the chemical potential is given as follows:

$$\mu_i/RT = (r_i+l_i)\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - r_i\ln(1-\rho) + \ln\left(\frac{\theta_i}{q_{l'}}\right) + \left(\frac{z\beta}{2}\right)q_i\varepsilon_M\theta^2$$
$$\times\left[1 - \frac{r_i}{q_i}\frac{2\sum\theta_k\varepsilon_{ik}+\beta\sum\sum\sum\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+2\varepsilon_{kl}-2\varepsilon_{jk}-\varepsilon_{ik})}{\varepsilon_M\theta^2}\right]$$
$$-\sum_k d_k^i\ln\frac{N_d^k}{N_{k0}} - \sum_l a_i^l\ln\frac{N_a^l}{N_{l0}} \quad (3)$$

The expression for excess enthalpy requires derivatives with respect to temperature:

$$\frac{H^c}{RT} = \frac{Pv}{RT} - \frac{z}{z-2}q_M'\left(\frac{Pv_H}{RT}+v_{HB}\rho\right)$$

$$+\sum\sum\left[\frac{U_{ij}^{HB}}{kT}v_{ij}r_M\right] + \frac{zq_M'}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]$$
$$+\frac{z\beta q_M}{2\theta}\left[\sum\sum\theta_i\theta_j\varepsilon_{ij}\left(\frac{q_i'}{q_i}+\frac{q_j'}{q_j}-\frac{q_M'}{q_M}\theta+\frac{\varepsilon_{ij}'}{\varepsilon_{ij}}-1\right)\right]$$
$$+\frac{\beta}{2}\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}\times\{(\varepsilon_{ij}+\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk})$$
$$\left(\frac{q_i'}{q_i}+\frac{q_j'}{q_j}+\frac{q_M'}{q_M}\theta+\frac{\varepsilon_{ij}'}{\varepsilon_{ij}}-2\right) - \frac{q_M'}{q_M}\theta(2\varepsilon_{ij}+4\varepsilon_{kl}-3\varepsilon_{ik}-3\varepsilon_{jk})$$
$$+\varepsilon_{ij}'+\varepsilon_{kl}'-\varepsilon_{ik}'-\varepsilon_{jk}'+\frac{q_k'}{q_k}(\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk})+\frac{q_l'}{q_l}\varepsilon_{kl}\}\right] \quad (4)$$

where primed quantities mean derivatives of parameters with respect to ln T.

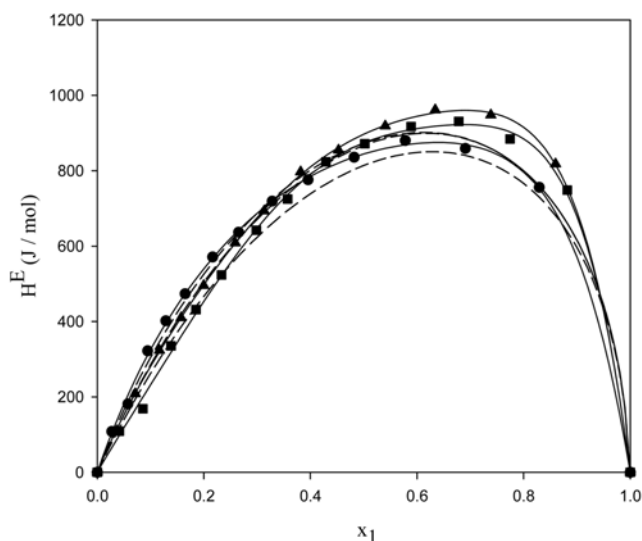If associated components are present in the mixture, the following nonlinear equations have to be solved.

Fig. 3. Excess enthalpy H^E at 313.15 K for alkane (1)+alkanol (2). Experimental data; ●, octane+ethanol; ▲, octane+1-propanol; ■, octane+1-butanol. (—), calculated from the Redlich-Kister equation; (---), calculated from the NLF-HB equation of state
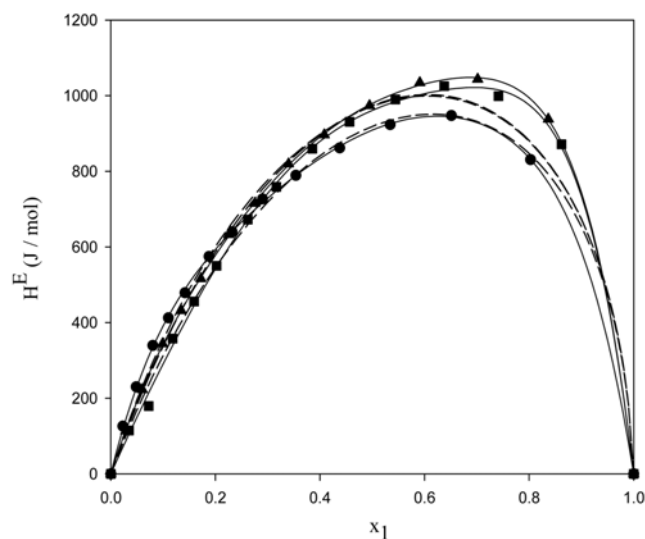

Fig. 5. Excess enthalpy H^E at 313.15 K for alkane (1)+alkanol (2). Experimental data; ●, decane+ethanol; ■, decane+1-propanol; ■, decane+1-butanol. (—), calculated from the Redlich-Kister equation; (---), calculated from the NLF-HB equation of state.
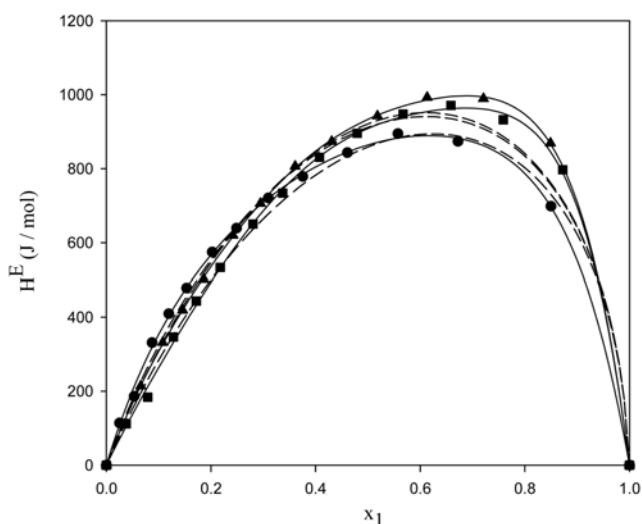
and vapor pressure data.

$$\varepsilon_{ii}/k=\varepsilon_a+\varepsilon_b(T-T_0)+\varepsilon_c[Tln(T_0/T)+(T-T_0)] \tag{6}$$

$$r_i=r_a+r_b(T-T_0)+r_c[Tln(T_0/T)+(T-T_0)] \tag{7}$$

where the reference temperature T_0 is 298.15 K. The parameters for components considered in this study are summarized in Table 4. For interactions between segments of different species, a binary interaction parameter is required.

$$\varepsilon_{ij}=(\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1-k_{ij}) \tag{8}$$

The binary interaction parameters are assumed to be temperature-dependent as,

$$k_{ij}=A+B/T. \tag{9}$$

As discussed in the previous work [3], excess enthalpy cannot be successfully represented without introducing the temperature dependencies in the binary interaction parameters. The experimental values in Table 2 were used for the estimation of coefficients (A and B) for binary interaction parameters. The optimized values of binary interaction parameters are listed in Table 5. The hydrogen bonding parameters were slightly adjusted to give better representation of excess enthalpy data. The adjusted hydrogen-bonding energy and entropy were −36,016 J/mol and −24.8 J/mol-K, respectively. The correlation results are compared with the experimental data in Fig. 3, 4 and 5. A fair description (less than 8%) was obtained for correlating excess enthalpy values of the studied systems. As discussed in the previous work [3], the excess enthalpy cannot be represented within 20% of errors for systems composed of alcohols and alkanes without the introduction of hydrogen bonding consideration. Although there is still a moderate discrepancy (<8%) with experimental data, the NLF-HB can qualitatively represent excess enthalpy data reasonably. This fact reflects the soundness of the theory.

Fig. 4. Excess enthalpy H^E at 313.15 K for alkane (1)+alkanol (2). Experimental data; ●, nonane+ethanol; ▲, nonane+1-propanol; ■, nonane+1-butanol. (—), calculated from the Redlich-Kister equation; (---), calculated from the NLF-HB equation of state.

$$N_{kl}^{HB}N_r=N_{k0}N_{l0}exp(-\beta A_{kl}) \tag{5}$$

When there is a single type of hydrogen bonding in the mixture, this equation becomes quadratic and can be solved analytically. If there is more than one type of hydrogen bonding, a successive substitution method starting from reasonable initial guess can be used for solving the set of nonlinear equations.

The NLF-HB EoS requires the segment chain length and interaction energy parameters. The parameters can be represented as functions of temperature and fitted by using saturated liquid volume

Table 3. Coefficients, A_i for Redlich-Kister equation and standard deviation, S.D., for the representation of H^E by Eq. (1) for the binary systems at 313.15 K

	A_1	A_2	A_3	A_4	A_5	S.D (J/mol)
n-Octane+Ethanol	3377.03	−857.84	1847.66	−1332.31	1028.53	8.62
n-Octane+1-Propanol	3587.15	−1304.61	1617.67	−2420.27	1896.63	4.13
n-Octane+1-Butanol	3494.17	−1143.36	1211.19	−3068.19	1931.68	12.58
n-Nonane+Ethanol	3456.40	−842.37	1754.16	−846.86	1107.78	9.15
n-Nonane+1-Propanol	3733.21	−1303.01	1850.12	−2333.66	1805.08	3.51
n-Nonane+1-Butanol	3635.14	−1200.29	1548.91	−2829.08	1732.21	11.19
n-Decane+Ethanol	3635.22	−1133.00	1659.25	−366.99	1802.66	5.10
n-Decane+1-Propanol	3917.27	−1373.34	2071.94	−2214.13	1933.90	3.28
n-Decane+1-Butanol	3844.24	−1192.97	1984.59	−2961.96	1422.91	12.97

$$\text{S.D. (J/mol)} = \frac{\sum_i^N \left| HE_i^{cal} - HE_i^{exp} \right|}{N-1}$$

Table 4. Pure parameters and temperature ranges for the NLF-HB equation of state

	ε_a	ε_b	ε_c	r_a	r_b	r_c	Range (K)
n-Octane	100.590	.0356	−.0243	14.594	−.0019	.0075	273-533
n-Nonane	101.279	.0480	.0081	16.171	−.0027	.0060	373-575
n-Decane	101.689	.0529	.0125	17.805	−.0034	.0057	368-598
Ethanol	84.918	.1791	.1674	4.945	.0019	−.0009	293-473
1-Propanol	90.291	.1362	.0827	6.523	.0001	−.0086	273-537
1-Butanol	89.946	.1917	.2471	7.810	.0061	.0104	275-545

Table 5. Binary interaction parameters for NLF-HB EOS

	A (dimensionless)	B (K^{-1})	AADH (%)
Octane+Ethanol	0.0267	9.9827	3.4988
Octane+1-Propanol	0.0210	9.9855	2.9523
Octane+1-Butanol	0.0281	9.9815	7.3946
Nonane+Ethanol	0.0279	9.9816	5.275
Nonane+1-Propanol	0.0213	9.9853	2.263
Nonane+1-Butanol	0.0282	9.9813	5.690
Decane+Ethanol	0.0267	9.9826	7.048
Decane+1-Propanol	0.0215	9.9852	2.621
Decane+1-Butanol	0.0272	9.9824	5.716

$$\text{AADH (\%)} = \left((1/N) \sum_i^N \left| HE_i^{cal} - HE_i^{exp} \right| / HE_i^{exp} \right) \times 100$$

CONCLUSION

The excess enthalpy data for nine systems composed of n-alkane and 1-alkanols were measured and correlated by using the Redlich-Kister correlation and the NLF-HB equation of state. All excess enthalpies have positive values and their graphical shapes are asymmetric. The enthalpy data have maximum values with respect to mole fraction between 0.6 and 0.80.

The measured excess enthalpy data can be correlated by using Redlich-Kister equation with five parameters within the uncertainty of the experiment (2%). The theoretical expression using NLF-HB EoS can represent the excess enthalpy data within 8% by using two adjustable interaction parameters.

ACKNOWLEDGMENTS

NOMENCLATURE

A^c : configurational Helmholtz free energy
g_R : number of non-degenerate states for the random distribution
g_{NR} : number of non-degenerate states for the nonrandom correction
N_a : Avogadro's number
N_i : number of molecular species i
N_{ij}^0 : number of i-j segment contacts for the random distribution
N_{ij} : number of i-j segment contacts for the nonrandom distribution
N_o : number of vacant sites or holes
N_r : defined by $N_r = N_o + \sum_{i=1}^c N_i r_i$
N_q : defined by $N_q = N_o + \sum_{i=1}^c N_i q_i$
P : pressure
q_i : surface area parameter
q_M : mole fraction average of q_i
r_i : segment number
r_M : mole fraction average of r_i
R : universal gas constant [J mol^{-1}K^{-1}]
T : temperature
V : molar volume [cm^{3}mol^{-1}]
V_H : volume of a unit cell [cm^3]
x_i : (liquid) mole fraction of component i
y_i : vapor mole fraction of component i
z : lattice coordination number

Greek Letters

β : reciprocal temperature [1/kT]
Ω^c : configurational lattice partition function
Γ_{ij} : nonrandomness correction factor for i-j segment contacts
ε_{ij} : interaction energy for i-j segment contacts
ρ : reduced density
ρ_{ij} : segment fraction of component i
μ_i : chemical potential for component i
λ_{ij} : binary interaction parameter for i-j contacts
θ : total surface area fraction
θ_i : surface area fraction of component i

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