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Prediction of excess enthalpies for 1-alkanol + *n*-alkane systems from infinite dilution activity coefficients

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Abstract

The previously developed approach [16] to predicting excess enthalpies of binary mixtures from infinite dilution activity coefficients has been applied to 1-alkanol + *n*-alkane systems. The predicted results of excess enthalpies for 49 1-alkanol + *n*-alkane systems are in good agreement with the literature experimental data; the considered systems include a wide range of molecular sizes for both 1-alkanol (from methanol) and *n*-alkane (from pentane to hexadecane).

Keywords: *n*-Alkane; 1-Alkanol; Binary system; Excess enthalpy; Infinite dilution activity coefficient

List of symbols

aa	parameter in MOSCED model
$\Delta E_{21}, \Delta E_{12}$	binary parameters as defined by Eq. (7)
G^E	excess molar Gibbs free energy
H^E	excess molar enthalpy
NC_H	number of skeletal carbon atoms for *n*-alkane component
NC_A	number of skeletal carbon atoms for 1-alkanol component
(No)	Avogadro constant
q_i	molecular surface area parameter of component *i*
r_i	molecular volume parameter of component *i*

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R	universal gas constant
T	absolute temperature
v_i	saturated liquid volume of component i at 20°C
v_{ji}	volume defined in Eq. (9)
x_i	liquid mole fraction of component i
Z	lattice coordination number

Greek letters

α	parameter in MOSCED model
α	non-random parameter in the model of Shen et al. [18]
β	parameter in MOSCED model
γ_i	activity coefficient of component i
γ_i^∞	infinite dilution activity coefficient of component i
θ_i	area fraction of component i
ε	minimum potential energy
ζ	parameter in MOSCED model
τ	parameter in MOSCED model
τ_{21}, τ_{12}	binary parameters as defined by Eq. (8)
ϕ_i	segment fraction of component i
ϕ_i'	modified segment fraction of component i
ψ	parameter in MOSCED model

1. Introduction

1-Alkanol + n-alkane systems are the most important systems in theoretical and experimental investigations, and are also often involved in many chemical engineering processes. Due to the strong association existing in this kind of system, their thermodynamic behaviour and properties are very complicated. The original local composition models (Wilson [1], NRTL [2], UNIQUAC [3]) and group contribution models (ASOG [4], UNIFAC [5]) are only suitable for describing vapour–liquid equilibrium (VLE) data of this type of system. They cannot be used for simultaneous correlations and cross predictions between excess Gibbs free energy (G^E) data and excess enthalpy (H^E) data of these systems owing to their limited ability to represent large numerical values of H^E and very asymmetric shapes [6, 7]. The accuracy of simultaneously representing G^E and H^E data for 1-alkanol + n-alkane systems with these models can be much improved by increasing adjustable temperature dependent parameters [7–11] and by incorporating chemical association models, e.g. the Mecke–Kempter or Kretschmer–Wiebe, into these models [12–15]. However, the increase in the adjustable temperature dependent parameters is no more than increasing the ability of these models to represent H^E data and simultaneously correlate G^E and H^E data. It does not improve the cross predictions between G^E and H^E data by these models [16]. Incorporating a chemical association model into the original physical model will make the combined model more complicated. Also, it is difficult to draw a distinct border between chemical and physical interactions [17].

Recently, Shen et al. [18, 19] have developed a unified model with only three adjustable parameters which is capable of simultaneously representing H^E and VLE data for many different mixtures. Based on this model, Shen and Nagata [16] have also developed a new approach to predicting excess enthalpies from infinite dilution activity coefficients (γ_i^∞). This approach does not have any uncertainty for predicted results due to using infinite dilution activity coefficients. It has been successfully used for predicting excess enthalpy data of 23 ketone + n-alkane systems. In this work, we will extend this approach to the prediction of excess enthalpy data of 49 1-alkanol + n-alkane systems.

2. Thermodynamic models

The expressions for the excess molar enthalpy, excess molar Gibbs free energy, activity coefficient and infinite dilution activity coefficient of the unified model of Shen et al. [18, 19] for a binary system can be written as

$$H^E = \frac{Z}{2}x_1x_2\left(\frac{\Delta E_{21}\tau_{21}}{x_1 + x_2\tau_{21}} + \frac{\Delta E_{12}\tau_{12}}{x_2 + x_1\tau_{12}}\right) \tag{1}$$

$$\frac{G^E}{RT} = x_1 \ln\frac{\phi'_1}{x_1} + x_2 \ln\frac{\phi'_2}{x_2} + \frac{Z}{2}\left(x_1q_1\ln\frac{\theta_1}{\phi_1} + x_2q_2\ln\frac{\theta_2}{\phi_2}\right)$$
$$-\frac{Z}{2\alpha}(x_1\ln(x_1 + x_2\tau_{21}) + x_2\ln(x_2 + x_1\tau_{12})) \tag{2}$$

$$\ln\gamma_1 = \ln\frac{\phi'_1}{x_1} + 1 - \frac{\phi'_1}{x_1} - \frac{Z}{2}q_1\left(\ln\frac{\phi_1}{\theta_1} + 1 - \frac{\phi_1}{\theta_1}\right)$$
$$+\frac{Z}{2\alpha}\left(-\ln(x_1 + x_2\tau_{21}) + x_2\left(\frac{\tau_{21}}{x_1 + x_2\tau_{21}} - \frac{\tau_{12}}{x_2 + x_1\tau_{12}}\right)\right) \tag{3}$$

$$\ln\gamma_2 = \ln\frac{\phi'_2}{x_2} + 1 - \frac{\phi'_2}{x_2} - \frac{Z}{2}q_2\left(\ln\frac{\phi_2}{\theta_2} + 1 - \frac{\phi_2}{\theta_2}\right)$$
$$+\frac{Z}{2\alpha}\left(-\ln(x_2 + x_1\tau_{12}) + x_1\left(\frac{\tau_{12}}{x_2 + x_1\tau_{12}} - \frac{\tau_{21}}{x_1 + x_2\tau_{21}}\right)\right) \tag{4}$$

$$\ln\gamma_1^\infty = 1 - \left(\frac{r_1}{r_2}\right)^{3/4} + \ln\left(\frac{r_1}{r_2}\right)^{3/4} - \frac{Z}{2}q_1\left(1 - \frac{r_1q_2}{r_2q_1} + \ln\frac{r_1q_2}{r_2q_1}\right)$$
$$+\frac{Z}{2\alpha}[1 - \ln\tau_{21} - \tau_{12}] \tag{5}$$

$$\ln\gamma_2^\infty = 1 - \left(\frac{r_2}{r_1}\right)^{3/4} + \ln\left(\frac{r_2}{r_1}\right)^{3/4} - \frac{Z}{2}q_2\left(1 - \frac{r_2q_1}{r_1q_2} + \ln\frac{r_2q_1}{r_1q_2}\right)$$
$$+\frac{Z}{2\alpha}[1 - \ln\tau_{12} - \tau_{21}] \tag{6}$$

where

$$\Delta E_{ji} = (\mathrm{No})(\varepsilon_{ii} - \varepsilon_{ji}) \tag{7}$$

$$\tau_{ji} = \frac{v_{ji}}{v_j} \exp(-\alpha \Delta E_{ji}/RT) \tag{8}$$

$$v_{ji} = (v_j + v_i)/2 \tag{9}$$

$$\theta_j = \frac{x_j q_j}{\Sigma_k x_k q_k} \tag{10}$$

$$\phi_j = \frac{x_j r_j}{\Sigma_k x_k r_k} \tag{11}$$

$$\phi'_j = \frac{x_j r_j^{3/4}}{\Sigma_k x_k r_k^{3/4}} \tag{12}$$

(No) is the Avogadro constant, and v_j, q_j and r_j are the saturated liquid volume at 293.15 K, the molecular surface area parameter and molecular volume parameter of component j, respectively; they are all taken from the literature [20]; Z is the coordination number and its value is taken as 10 in this work; ε_{ji} denotes the minimum potential energy which characterizes the molecular interaction between a central molecule j and a surrounding molecule i. Like the NRTL model, the parameter α is used to characterize the tendency of the components to mix a non-random fashion.

Following the same approach as our previous work [16], we firstly predetermine the parameter α, then we can easily find the other two parameters (ΔE_{21} and ΔE_{12}) by simultaneously solving Eqs. (5) and (6) with γ_1^∞ and γ_2^∞. Finally, H^E data of the considered system can be definitely predicted by these parameters and Eq. (1). For 1-alkanol + n-alkane mixtures, α can be estimated by the following simple equation

$$\alpha = \begin{cases} 4.38 - 0.8(NC_H - 5.0) & \text{if} \quad NC_A < 6 \\ 4.40 + 0.2(NC_A - 6.0) - 0.05(NC_H - 5.0) & \text{if} \quad NC_A \geq 6 \end{cases} \tag{13}$$

where NC_H denotes the number of skeletal carbon atoms for the n-alkane component, e.g. for pentane, $NC_H = 5$, for hexadecane $NC_H = 16$, and NC_A is the number of skeletal carbon atoms for the 1-alkanol component, e.g. for methanol, $NC_A = 1$, for decanol $NC_A = 10$.

Also, following the previous work [16], we use the MOSCED model of Thomas and Eckert [21] to provide the values of both γ_1^∞ and γ_2^∞ at a specific temperature for the considered mixture. The MOSCED model can be expressed as

$$\ln \gamma_2^\infty = \frac{v_2}{RT}\left((\lambda_1 - \lambda_2)^2 + \frac{q_1^2 q_2^2(\tau_1 - \tau_2)^2}{\psi_1} + \frac{(\alpha_1 - \alpha_2)(\beta_1 - \beta_2)}{\zeta_1}\right) + (\ln (v_2/v_1)^{aa} + 1 - (v_2/v_1)^{aa}) \tag{14}$$

where v_2 is the liquid molar volume at 20°C; γ_1^∞ is obtained by interchanging the subscripts. The MOSCED parameters $\tau, \alpha, \beta, \psi, \zeta$ and aa are temperature dependent

Table 1
Results of predicted excess enthalpies for 1-alkanol(1) + *n*-alkane(2) systems with estimated values of γ_1^∞ amd γ_2^∞ from the MOSCED model

System (1 + 2)	T_h^a/K	γ_1^∞	γ_2^∞	α	ΔE_{21}/J mol^{-1}	ΔE_{12}/J mol^{-1}	No. of data points	Abs. arith. mean deviations			Ref. of data
								H^E_{max} ^{b}/J mol^{-1}	$\Delta H^{E\,c}$/J mol^{-1}	$\delta H^{E\,d}$%	
Methanol + pentane	298.15	58.60	19.75	4.3800	1986.46	809.586	26	538.53	22.91	4.26	[22]
Methanol + hexane	306.85	43.27	25.21	4.3000	1950.45	980.483	17	640.00	22.89	3.58	[23]
	313.15	35.46	23.94	4.3000	1889.09	982.589	17	717.00	33.55	4.68	[23]
	318.15	30.57	22.93	4.3000	1842.79	982.924	17	781.00	52.79	6.76	[23]
	318.15	30.57	22.93	4.3000	1842.79	982.924	10	761.00	26.60	3.50	[24]
	323.15	26.56	21.90	4.3000	1798.43	982.118	17	850.00	75.52	8.88	[23]
Methanol + heptane	333.15	20.23	26.05	4.2200	1772.82	1148.93	28	1061.00	136.90	12.90	[25]
Ethanol + pentane	298.15	44.07	8.88	4.3800	1765.84	425.971	24	526.11	48.68	9.25	[22]
Ethanol + hexane	298.15	43.08	10.96	4.3000	1783.68	525.147	14	584.10	39.19	6.71	[26]
	298.15	43.08	10.96	4.3000	1783.68	525.147	11	575.70	38.75	6.73	[27]
	298.15	43.08	10.96	4.3000	1783.68	525.147	14	573.00	45.40	7.92	[23]
	303.15	36.58	10.76	4.3000	1731.97	531.178	18	628.80	43.46	6.91	[23]
	308.15	31.34	10.54	4.3000	1682.34	536.341	9	688.00	35.85	5.21	[24]
	318.15	23.60	10.04	4.3000	1589.73	544.219	8	833.00	64.89	7.79	[24]
Ethanol + heptane	228.15	2027.	10.84	4.2200	2884.94	363.394	5	285.00	35.27	12.38	[28]
	258.15	245.0	13.82	4.2200	2325.84	523.158	5	333.00	30.52	9.17	[28]
	298.15	42.26	13.56	4.2200	1808.24	631.908	5	610.00	37.04	6.07	[28]
	303.15	35.85	13.29	4.2200	1756.41	639.190	26	666.60	40.85	6.13	[29]
	313.15	26.50	12.64	4.2200	1659.46	650.688	5	812.00	48.92	6.02	[28]
	323.15	20.24	11.92	4.2200	1570.63	658.797	33	985.90	74.81	7.59	[29]
	333.15	15.89	11.15	4.2200	1489.12	664.072	20	1204.00	237.24	19.70	[25]
Ethanol + octane	293.15	49.44	17.08	4.1400	1891.39	732.218	12	587.00	48.01	8.18	[30]
	298.15	41.48	16.74	4.1400	1837.02	742.038	12	644.00	41.39	6.43	[30]
	303.15	35.16	16.36	4.1400	1785.19	750.531	15	708.00	41.91	5.92	[30]
Ethanol + nonane	303.15	34.53	20.14	4.0600	1814.40	866.063	18	746.40	48.37	6.48	[23]
	318.15	22.12	18.27	4.0600	1672.15	887.699	18	991.20	128.87	13.00	[23]
Ethanol + hexadecane	325.15	16.04	61.66	3.5000	1874.65	1727.78	52	1461.40	166.31	11.38	[31]

Table 1 *(Continued)*

System (1 + 2)	T_h^a/K	γ_1^∞	γ_2^∞	α	ΔE_{21}/J mol^{-1}	ΔE_{12}/J mol^{-1}	No. of data points	Abs. arith. mean deviations			Ref. of data
								H^E_{max} ^{b}/J mol^{-1}	$\Delta H^{E\,c}$/J mol^{-1}	$\delta H^{E\,d}$%	
Propanol + hexane	298.15	34.17	6.83	4.3000	1644.78	305.737	8	612.00	25.88	4.22	[24]
	308.15	25.48	6.61	4.30000	1551.01	312.679	9	707.50	69.53	9.83	[32]
Propanol + heptane	293.15	39.45	8.33	4.2200	1700.73	379.914	12	585.00	36.56	6.25	[30]
	298.15	33.58	8.21	4.2200	1650.25	385.451	13	643.00	37.88	5.90	[30]
	303.15	28.85	8.06	4.2200	1602.09	390.273	13	704.00	45.20	6.42	[33]
	303.15	28.85	8.06	4.2200	1602.09	390.273	20	712.30	57.42	8.06	[34]
Propanol + octane	293.15	38.77	10.00	4.1400	1712.03	462.658	12	624.00	41.49	6.65	[30]
	298.15	32.98	9.82	4.1400	1661.41	469.368	13	683.00	41.09	6.02	[30]
	303.15	28.32	9.63	4.1400	1613.11	475.277	14	752.00	47.75	6.35	[30]
Propanol + nonane	298.15	32.43	11.75	4.0600	1674.46	558.032	27	745.60	29.24	3.92	[35]
Propanol + decane	308.15	23.64	13.30	3.9800	1599.52	662.003	9	917.40	74.61	8.13	[32]
Propanol + tetradecane	293.15	35.16	28.39	3.6600	1840.91	995.571	14	809.00	61.46	7.60	[33]
	298.15	29.80	27.53	3.6600	1790.71	1009.43	14	891.00	50.34	5.65	[33]
	303.15	25.49	26.59	3.6600	1742.72	1021.97	15	970.00	48.91	5.04	[33]
Butanol + pentane	298.15	29.43	4.48	4.3800	1565.98	155.308	17	516.57	42.47	8.22	[22]
Butanol + hexane	288.15	38.53	5.26	4.3000	1643.71	189.004	10	450.30	23.53	5.23	[36]
	298.15	28.29	5.13	4.3000	1548.79	193.764	11	565.70	29.91	5.29	[37]
	298.15	28.29	5.13	4.3000	1548.79	193.764	14	599.00	50.73	8.47	[38]
	298.15	28.29	5.13	4.3000	1548.79	193.764	8	573.00	31.40	5.48	[24]
	308.15	21.52	4.97	4.3000	1462.47	196.846	9	700.00	92.82	13.26	[24]
Butanol + heptane	288.15	37.38	6.07	4.2200	1635.80	235.662	10	480.30	44.03	9.17	[36]
	303.15	23.83	5.80	4.2200	1495.60	244.975	21	692.30	69.38	10.02	[39]
Butanol + octane	288.15	36.41	7.00	4.1400	1633.94	288.415	10	535.40	41.75	7.80	[36]
Butanol + nonane	298.15	26.05	7.76	4.0600	1537.87	356.716	28	742.40	30.51	4.11	[35]
Butanol + decane	288.15	34.71	9.22	3.9800	1643.41	403.482	10	596.70	69.51	11.65	[36]
	298.15	25.43	8.87	3.9800	1546.58	416.404	48	784.10	23.43	2.99	[40]
Butanol + dodecane	328.15	11.50	9.51	3.8200	1324.01	577.915	10	1440.20	301.15	20.91	[36]

Pentanol + pentane	298.15	24.93	3.77	4.3800	1494.21	116.511	22	495.98	31.28	6.31	[22]
Pentanol + hexane	298.15	23.89	4.27	4.3000	1467.29	140.449	10	528.00	29.70	5.62	[36]
	303.15	20.93	4.20	4.3000	1426.83	140.514	18	592.70	72.35	12.21	[41]
Pentanol + heptane	288.15	30.93	5.01	4.2200	1537.58	172.839	10	459.60	30.67	6.68	[36]
	293.15	26.64	4.93	4.2200	1492.52	174.282	13	519.00	20.95	4.04	[33]
	298.15	23.15	4.85	4.2200	1449.59	175.358	14	579.00	37.07	6.40	[30]
	298.15	23.15	4.85	4.2200	1449.59	175.358	25	593.50	50.92	8.58	[42]
	303.15	20.28	4.76	4.2200	1408.65	176.110	15	633.00	55.25	8.73	[30]
Pentanol + octane	293.15	25.94	5.61	4.1400	1468.88	102.070	12	590.00	76.75	13.17	[30]
	298.15	22.54	5.50	4.1400	1425.46	102.141	13	629.00	91.49	14.55	[30]
Pentanol + nonane	298.15	21.97	6.23	4.0600	1430.64	264.528	22	695.00	30.33	4.36	[35]
Pentanol + decane	288.15	28.68	7.33	3.9800	1521.21	304.574	10	580.50	61.77	10.64	[36]
	298.15	21.45	7.03	3.9800	1431.34	312.114	36	747.20	21.11	2.82	[40]
Pentanol + tetradecane	293.15	22.61	11.38	3.6600	1498.29	514.371	14	851.00	43.16	5.07	[30]
	298.15	19.62	11.05	3.6600	1453.96	521.581	13	898.00	40.11	4.47	[30]
	303.15	17.16	10.70	3.6600	1411.59	528.228	13	949.00	48.54	5.12	[30]
Hexanol + pentane	298.15	21.70	3.35	4.4000	1432.96	106.964	22	437.78	20.39	4.66	[22]
Hexanol + hexane	298.15	20.77	3.77	4.3500	1394.69	125.465	9	494.00	31.85	6.45	[24]
	298.15	20.77	3.77	4.3500	1394.69	125.465	20	507.42	28.65	5.65	[43]
	308.15	16.28	3.63	4.3500	1322.23	122.566	9	604.00	95.86	15.87	[24]
Hexanol + heptane	288.15	26.47	4.41	4.3000	1449.79	155.297	10	432.20	37.91	8.77	[36]
	308.15	15.79	4.08	4.3000	1295.40	152.110	9	671.10	58.98	8.79	[44]
Hexanol + octane	288.15	25.81	5.00	4.2500	1413.04	95.3299	10	467.90	20.91	4.47	[36]
Hexanol + nonane	298.15	19.16	5.40	4.2000	1333.88	235.053	24	650.70	32.95	5.06	[35]
	298.15	19.16	5.40	4.2000	1333.88	235.053	9	664.00	33.30	5.02	[45]
	298.15	19.16	5.40	4.2000	1333.88	235.053	47	694.20	57.06	8.22	[40]
Octanol + pentane	303.15	14.46	2.72	4.8000	1260.02	133.874	34	402.24	29.48	7.33	[22]
Octanol + hexane	288.15	19.86	3.23	4.7500	1307.81	151.804	10	352.70	52.60	14.91	[36]
	298.15	15.52	3.09	4.7500	1241.09	144.704	10	466.70	25.86	5.54	[46]
	298.15	15.52	3.09	4.7500	1241.09	144.704	8	435.00	15.88	3.65	[24]
	308.15	12.47	2.96	4.7500	1180.90	137.260	10	565.80	66.75	11.80	[46]
	308.15	12.47	2.96	4.7500	1180.90	137.260	7	539.00	75.36	13.98	[24]

Table 1 *(Continued)*

System (1 + 2)	T_h^a/K	γ_1^∞	γ_2^∞	α	ΔE_{21}/J mol^{-1}	ΔE_{12}/J mol^{-1}	No. of data points	Abs. arith. mean deviations			Ref. of data
								H^E_{max} ^{b}/J mol^{-1}	$\Delta H^{E\,c}$/J mol^{-1}	$\delta H^{E\,d}$%	
Octanol + heptane	288.15	19.30	3.63	4.7000	1272.64	171.169	10	391.60	47.65	12.17	[36]
	293.15	17.01	3.55	4.7000	1237.91	167.738	12	435.00	35.61	8.19	[30]
	298.15	15.10	3.47	4.7000	1204.93	164.174	20	486.20	17.33	3.56	[47]
	298.15	15.10	3.47	4.7000	1204.93	164.174	13	487.00	35.50	7.29	[33]
	303.15	13.50	3.39	4.7000	1173.55	160.584	9	542.00	27.48	5.07	[33]
Octanol + octane	288.15	18.91	4.10	4.6500	1246.39	199.115	10	418.30	57.94	13.85	[36]
	293.15	16.67	4.00	4.6500	1211.19	195.790	12	485.00	34.71	7.16	[33]
	298.15	14.81	3.90	4.6500	1177.73	192.317	14	523.00	30.54	5.84	[33]
	303.15	13.24	3.80	4.6500	1145.90	188.804	13	558.00	50.05	8.97	[33]
Octanol + nonane	298.15	14.52	4.35	4.6000	1154.94	226.116	20	573.90	27.41	4.78	[35]
	303.15	12.99	4.23	4.6000	1122.64	222.747	18	623.70	92.03	14.76	[23]
Octanol + decane	293.15	16.04	5.00	4.5500	1175.00	264.262	22	536.20	49.45	9.22	[48]
	298.15	14.25	4.86	4.5500	1140.65	261.113	49	613.50	25.96	4.23	[40]
	298.15	14.25	4.86	4.5500	1140.65	261.113	26	578.10	39.21	6.78	[48]
	308.15	11.48	4.57	4.5500	1076.82	254.501	23	702.80	58.20	8.28	[48]
	313.15	10.40	4.44	4.5500	1047.10	251.093	21	792.00	108.85	13.74	[48]
Octanol + tetradecane	293.15	14.92	7.56	4.3500	1146.54	428.252	14	677.00	50.66	7.48	[33]
	298.15	13.25	7.27	4.3500	1111.06	425.872	14	747.00	53.17	7.12	[33]
	303.15	11.85	6.99	4.3500	1077.17	423.350	13	821.00	79.01	9.62	[33]
Decanol + pentane	298.15	12.88	2.38	5.2000	1198.46	165.485	40	390.40	25.41	6.51	[22]
	298.15	12.88	2.33	5.2000	1198.46	165.485	17	375.40	33.03	8.80	[42]
Decanol + hexane	298.15	12.36	2.64	5.1500	1139.60	166.108	19	422.40	24.93	5.90	[42]
Decanol + heptane	293.15	13.50	3.03	5.1000	1125.04	184.639	13	437.00	34.63	7.92	[30]
	298.15	12.10	2.95	5.1000	1096.73	179.248	14	459.00	38.52	8.39	[33]
	298.15	12.10	2.95	5.1000	1096.73	179.248	19	458.90	26.38	5.75	[49]

	303.15	10.91	2.88	5.1000	1069.88	173.849	13	437.00	35.58	8.14	[33]
	318.15	8.28	2.68	5.1000	997.208	157.968	9	630.00	91.85	14.58	[44]
Decanol + octane	293.15	13.32	3.40	5.0500	1093.28	206.947	13	454.00	48.42	10.67	[30]
	298.15	11.95	3.31	5.0500	1064.44	201.366	20	497.80	29.85	6.00	[49]
	303.15	10.79	3.22	5.0500	1037.13	195.795	14	514.00	61.40	11.95	[30]
Decanol + nonane	298.15	11.79	3.68	5.0000	1037.10	229.006	20	519.70	37.50	7.22	[49]
Decanol + decane	298.15	11.65	4.10	4.9500	1018.37	258.088	22	549.30	47.27	8.60	[49]
Decanal + tetradecane	293.15	12.28	6.31	4.7500	1004.56	406.173	14	638.00	61.84	9.69	[30]
	298.15	11.02	6.04	4.7500	973.426	399.998	14	688.00	69.07	10.04	[30]
	303.15	9.96	5.79	4.7500	943.771	393.877	14	743.00	81.50	10.97	[30]

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[a] T_h denotes the temperature of the excess enthalpy data.

[b] H^E_{max} is the maximum value in one set of excess enthalpy data.

[c] $\Delta H^E = \frac{1}{N_p}\sum_i |H^E_{exp} - H^E_{cal}|_i$.

[d] $\delta H^E = \frac{1}{N_p}\sum_i |(H^E_{exp} - H^E_{cal})/H^E_{max}|_i \times 100\%$.

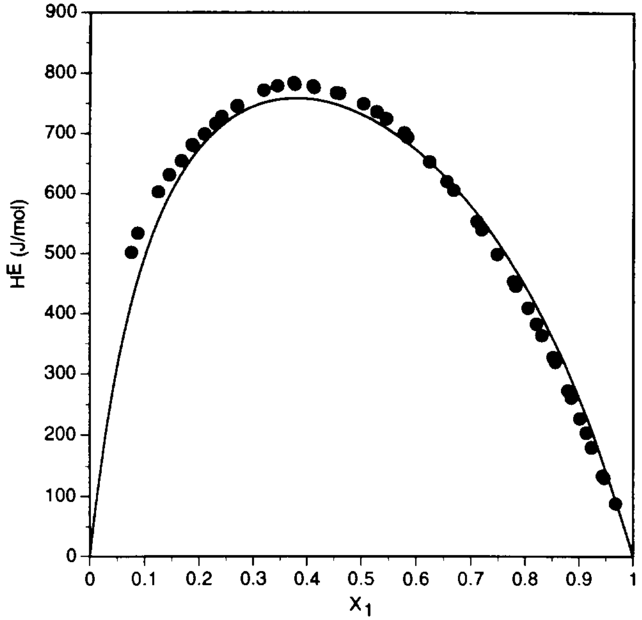

Fig. 1. Excess enthalpies of butanol(1) + decane(2) at 298.15 K: ●, experimental [40]; ——, predicted.

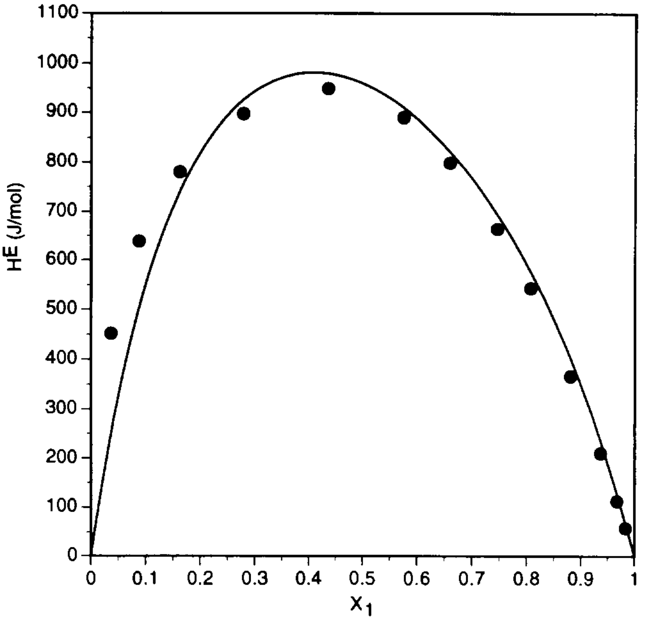

Fig. 2. Excess enthalpies of pentanol(1) + tetradecane(2) at 303.15 K: ●, experimental [30]; ——, predicted.

according to the following equations

$$\tau_T = \tau_{293}\left(\frac{293}{T}\right)^{0.4} \tag{15}$$

$$\alpha_T = \alpha_{293}\left(\frac{293}{T}\right)^{0.8} \tag{16}$$

$$\beta_T = \beta_{293}\left(\frac{293}{T}\right)^{0.8} \tag{17}$$

$$\psi = \mathrm{POL} + 0.011\alpha_T\beta_T \tag{18}$$

$$t = (293/T)^2 \tag{19}$$

$$\zeta = 0.68(\mathrm{POL} - 1) + \{3.4 - 2.4\exp[-0.023(\alpha_{293}\beta_{293})^{1.5}]\}^t \tag{20}$$

$$\mathrm{POL} = q^4[1.15 - 1.15\exp(0.020\tau_T^3)] + 1 \tag{21}$$

$$aa = 0.953 - 0.00968(\tau_2^2 + \alpha_2\beta_2) \tag{22}$$

The parameters $v, \lambda, \tau, q, \alpha, \beta, \psi, \zeta$ and aa are tabulated by Thomas and Eckert [21] for about 145 compounds. For other compounds, the parameters can be estimated from approximate relations valid for some classes of compounds [21].

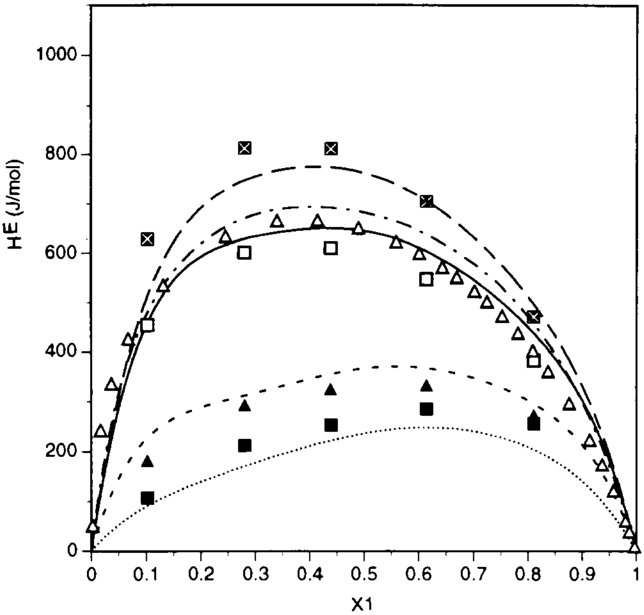

Fig. 3. Temperature dependence of excess enthalpies for ethanol(1) + heptane(2): ■, experimental [28]; ···, predicted at 228.15 K; ▲, experimental [28]; – – –, predicted at 258.15 K; □, experimental [28]; ——, predicted at 298.15 K; Δ, experimental [29]; —·—·, predicted at 303.15 K; ⊠, experimental [28]; — — —, predicted at 313.15 K.

Table 2
Results of predicted excess enthalpies for 1-alkanol(1) + *n*-alkane(2) systems with experimental γ_1^∞ and γ_2^∞ [a]

System (1 + 2)	$T_{\gamma 1}$ [b]/K	γ_1^∞	$T_{\gamma 2}$ [a]	γ_2^∞	α	ΔE_{21}/J mol^{-1}	ΔE_{12}/J mol^{-1}	T_h/K	Abs. arith. mean deviations			Ref. of data
									ΔH^E/J mol^{-1}	δH^E%	δH^{Ec}%	
Ethanol + pentane	309.65	47.00	299.65	8.90	4.3800	1873.98	423.225	298.15	30.47	5.79	9.25	[22]
Ethanol + hexane	297.35	58.20	293.15	12.00	4.3000	1920.21	549.909	298.15	32.01	5.48	6.71	[26]
	297.35	58.20	293.15	12.00	4.3000	1920.21	549.909	298.15	11.05	1.92	6.73	[27]
	297.35	58.20	293.15	12.00	4.3000	1920.21	549.909	298.15	25.89	4.52	7.92	[23]
	304.75	38.00	293.15	12.00	4.3000	1752.78	560.591	303.15	44.04	7.00	6.91	[23]
	304.75	38.00	293.15	12.00	4.3000	1752.78	560.591	308.15	41.27	6.00	5.21	[24]
	322.55	23.00	322.15	10.00	4.3000	1598.31	550.129	318.15	66.10	7.94	7.79	[24]
Ethanol + heptane	293.15	51.00	313.15	13.00	4.2200	1864.20	644.487	303.15	30.07	4.51	6.13	[29]
	313.45	36.30	313.15	13.00	4.2200	1825.82	647.858	313.15	82.79	10.20	6.02	[28]
	323.15	17.30	323.15	12.00	4.2200	1481.98	676.596	323.15	68.10	6.91	7.59	[29]
	333.15	16.00	333.15	11.00	4.2200	1495.17	655.070	333.15	238.71	19.83	19.70	[25]
Ethanol + octane	293.15	50.50	322.15	14.50	4.1400	1901.55	732.528	293.15	45.91	7.82	8.18	[30]
	293.15	50.50	322.15	14.50	4.1400	1901.55	732.528	298.15	27.51	4.27	6.43	[30]
	293.15	50.50	322.15	14.50	4.1400	1901.55	732.528	303.15	28.82	4.07	5.92	[30]
Ethanol + nonane	302.35	42.40	301.05	20.80	4.0600	1912.56	865.346	303.15	46.61	6.24	6.48	[23]
	323.65	24.20	320.85	19.80	4.0600	1744.95	929.516	318.15	139.05	14.03	13.00	[23]
Butanol + hexane	300.95	33.00	293.15	5.00	4.3000	1657.45	168.026	288.15	14.15	3.15	5.23	[36]
	300.95	33.00	293.15	5.00	4.3000	1657.45	168.026	298.15	49.92	8.83	5.29	[37]
	300.95	33.00	293.15	5.00	4.3000	1657.45	168.026	298.15	86.10	14.37	8.47	[38]
	300.95	33.00	293.15	5.00	4.3000	1657.45	168.026	298.15	66.13	11.54	5.48	[24]
	315.25	22.50	293.15	5.00	4.3000	1534.84	176.964	308.15	119.43	17.06	13.26	[24]

[a] Experimental values of γ_1^∞ and γ_2^∞ are taken from the literature [50].

[b] $T_{\gamma i}$ denotes the temperature of the experimental infinite dilution activity coefficient γ_i^∞.

[c] Obtained from the values of γ_1^∞ and γ_2^∞ estimated by the MOSCED model (Table 1).

3. Predicted results and discussions

122 sets of excess enthalpy data for 49 binary 1-alkanol + *n*-alkane systems have been predicted in this work. The predicted results are summarized in Table 1. Typical predicted results are shown in Figs. 1–3.

From Table 1 and Figs. 1–3, it can be seen that the predicted results are very satisfactory. The average relative deviation of predicted results for 1985 data points is only 7.54%. Like previous work [16] on ketone + *n*-alkane systems, our predicted results for 1-alkanol + *n*-alkane systems are also comparable with the calculated results of modified UNIFAC models [10, 11, 15], which usually have six adjustable parameters, while our approach is quite simple. Moreover, the 1-alkanol + *n*-alkane mixtures considered in this work include a wide range of molecular sizes for both 1-alkanol (from methanol to decanol) and *n*- alkane (from pentane to hexadecane). Fig. 3 shows the change of excess enthalpies with temperature for the ethanol + heptane system. It can be seen that the excess enthalpies for this system are more asymmetric in composition than other systems shown in Figs. 1 and 2, especially at low temperatures (228.15 and 258.15 K). Also, the mole fraction of ethanol at maximum H^E value is decreased with the increase in temperature. From 228.15 to 313.15 K, this mole fraction is changed from 0.690 to 0.355. However, our predicted results for this dramatically asymmetric system are still in good agreement with the experimental data, and can describe quite well the change of the mole fraction at maximum H^E value with temperature.

The additional predicted results for six systems by experimental infinite dilution activity coefficients [50] are summarized in Table 2. From Table 2, it can be seen that these predicted results are also very good. Comparing these results with those from the MOSCED model for the same set of excess enthalpy data, the average relative deviation of the predicted results from the MOSCED model for 309 data points is 8.33%, while that of results from experimental γ_1^∞ and γ_2^∞ is 8.04%. The latter is only slightly better than the former.

4. Conclusion

A simple expression of the parameter α in the model of Shen et al. [18, 19] for 1-alkanol + *n*-alkane systems has been provided in this work. Using this expression and our previously proposed approach [16], 1985 data points of excess enthalpies for 49 1-alkanol + *n*-alkane systems have been predicted. The average relative deviation is 7.54%.

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