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THE PREDICTION OF VAPOR–LIQUID EQUILIBRIUM FROM HEAT OF MIXING DATA FOR BINARY HYDROCARBON–KETONE MIXTURES

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ABSTRACT

The method of Hanks et al. for predicting vapor–liquid equilibrium (VLE) from heat of mixing (h^E) data was successfully applied to binary hydrocarbon–ketone mixtures. The LEMF model for the excess free energy was found to be the most adequate to correlate experimental g^E and h^E data simultaneously for these mixtures. The predicted vapor–liquid equilibrium values were compared to experimental values and good agreement was found. The dependence of the accuracy of the VLE data predictions on the experimental uncertainties of heat of mixing data and on the set of parameters obtained by fitting these data to the algebraic equation for h^E is discussed.

INTRODUCTION

The usual approach used to correlate vapor–liquid equilibrium (VLE) data for non-ideal mixtures is to measure total pressure composition or vapor–liquid composition data from which liquid-phase activity coefficients may be calculated. The excess free energy is then computed from the activity coefficients and the resulting values are curve fitted to some semi-empirical model, g^E $(x_j, A_1, A_2 \ldots A_k)$ where x_j is the liquid mole fraction and A_k are adjustable parameters which are usually assumed to be temperature independent [1,2].

The correlation or prediction of other thermodynamic excess properties simultaneously with g^E is frequently attempted [3,4]. In order to predict excess enthalpies (h^E) from g^E data, for instance, the semi-empirical equa-

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tion for g^E has to be introduced in the Gibbs–Helmholtz relation

$$h^E = -T^2 \frac{\partial(g^E/T)}{\partial T} \tag{1}$$

Results of such a prediction are usually poor unless the parameters of the g^E model are assumed to be temperature dependent [5] an approach which renders the equations so complex as to be of little practical use. When the model is able to simultaneously correlate g^E and h^E, an extremely accurate description of g^E is required due to the error magnification inherent in the differentiation process.

Hanks et al. proposed a method (here called the HGC method) [6] which provides the simultaneous description of the excess free energy and excess enthalpy. The parameters A_k of the g^E model are evaluated by curve-fitting experimental, binary, isothermal h^E data to the algebraic equation h^E $(x_j, A_1, A_2 \ldots A_k)$ derived from the g^E model by application of eqn. (1). These A_k values are then used in the g^E model to calculate the activity coefficients from which the x–y data may be predicted. The HGC method requires no experimental VLE data, only excess enthalpies and pure component vapor pressure data. Generally predictions can be made with an error of less than 10% in the vapor phase mole fraction. This method has been shown to be successful in the calculation of both isothermal and isobaric VLE data for a variety of non-associating binary hydrocarbon mixtures [6–10] and for associating alcohol–hydrocarbon [11], ether–hydrocarbon [12], aldehyde–hydrocarbon [12] and alcohol–alcohol [13] mixtures. Some multi-component mixtures have also been studied [7,8]. The method has also been shown to be capable of predicting VLE data at a higher temperature from lower temperature heat-of-mixing data, both when at least two sets of h^E data measured at different temperatures are available [8,10], and when only one set of heat of mixing data is available [12].

The purpose of the present paper is to extend the application of the HGC method to binary hydrocarbon–ketone mixtures. These mixtures show in most cases large endothermic values of h^E and considerable deviations from ideality in the VLE data.

PREDICTION METHOD

We have found that the Local Effective Mole Fraction [14], LEMF, equation used in the HGC method adequately predicts VLE data from h^E data for non-associating binary hydrocarbon mixtures [6–10]. For associating systems such as alcohol–hydrocarbon, ether–hydrocarbon, and aldehyde–hydrocarbon, the Continuous Linear Association Model [15], CLAM, should be used in the HGC method [11,12]. Since association processes are not important in hydrocarbon–ketone mixtures, it would be expected that the LEMF model should be used in the HGC method for this system. We have, however, also evaluated the use of the CLAM and the Non-Random Two Liquid, NRTL [16], equations in the method for comparison. Using the CLAM equation to derive an algebraic equation for h^E, it was found for some systems that the h^E data could not be fitted by the equation and for other systems that the standard deviation of the fits were high. This could be expected since association processes on which the CLAM model is based are not important in the hydrocarbon–ketone systems. When the NRTL equation was used to derive an equation for h^E, it was found that the h^E data could be represented by the derived equation. Best results were obtained when the parameter α was allowed to be freely adjustable instead of being set to a constant value of 0.3 as recommended by Renon and Prausnitz [16]. However, predictions of VLE data made using the NRTL model were often poor. This could also be expected since Hanks et al. [9] had already pointed out that when $h^E_{\max} > 800$ J mole^{-1}, the NRTL equation approaches ideal solution behavior and cannot be used to predict VLE data from h^E data. With the exception of systems containing an aromatic, the hydrocarbon–ketone mixtures investigated here all show endothermic excess enthalpies larger than 800 J mole^{-1}, reaching maximum values of 1000–1500 J mole^{-1} at a mole fraction value close to 0.5. The LEMF model which is essentially the NRTL equation with $\alpha = -1$ was found to correlate simultaneously the VLE and h^E data.

The LEMF model is described by the equations [14]

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{G_1}{x_1 + x_2\tau_1} + \frac{G_2}{x_2 + x_1\tau_2} \right] \tag{2}$$

$$\frac{h^E}{RT} = \frac{g^E}{RT} + x_1 x_2 \left[\frac{x_1\tau_2 G_2^2}{(x_2 + x_1\tau_2)^2} + \frac{x_2\tau_1 G_1^2}{(x_1 + x_2\tau_1)^2} \right] \tag{3}$$

$$\ln\gamma_1 = x_2^2 \left[\frac{G_2}{(x_2 + \tau_2 x_1)^2} + \frac{G_1\tau_1}{(x_1 + x_2\tau_1)^2} \right] \tag{4}$$

$$\ln\gamma_2 = x_1^2 \left[\frac{G_1}{(x_1 + x_2\tau_1)^2} + \frac{G_2\tau_2}{(x_2 + x_1\tau_2)^2} \right] \tag{5}$$

where $G_1 = (g_{12} - g_{22})/RT$, $G_2 = (g_{21} - g_{11})/\mathrm{RT}$, $\tau_1 = \exp(-G_1)$ and $\tau_2 = \exp(-G_2)$. $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$ are adjusted to fit the data. We will refer to the parameters $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$ as Δg_{12} and Δg_{21}, respectively. Subscript 1 refers to the hydrocarbon, while subscript 2 refers to the ketone. γ_1 and γ_2 are the activity coefficients of the hydrocarbon and ketone, respectively. The HGC method consists of fitting eqn. (3) to a set of experimental h^E data at a given temperature by a non-linear regression technique [17]. The values of Δg_{12} and Δg_{21} obtained are used to compute to activity coefficients. The activity coefficients are in turn used to calculate VLE data, y/x, according to the equation

$$\frac{y_i}{x_i} = \frac{\gamma_i f_i^{0L}}{P\phi_i^{0L}} \tag{6}$$

where P is the total pressure of the system, x_i is the liquid-phase mole fraction, y_i is the vapor-phase mole fraction, ϕ_i^{0L} the vapor-phase fugacity coefficient, and f_i^{0L} is the pure liquid fugacity of component i in the equilibrium mixture. The Wilson formulation [18] of the Redlich–Kwong equation of state was used to take into account the non-ideality of the vapor.

RESULTS AND DISCUSSION

A survey of the literature [19,20] revealed eighteen binary hydrocarbon–ketone systems for which VLE data and h^E data are available simultaneously. Of these only four [n-pentane(1) + 2-propanone(2), n-hexane(1) + 2-propanone(2), n-heptane(1) + 2-butanone(2), and cyclohexane(1) + 2-butanone(2)] had h^E data available at three or more temperatures. Two more systems [benzene(1) + 2-propanone(2) and benzene(1) + 2-butanone(2)] had h^E data available at two temperatures. Table 1 lists the components of the systems, the temperature at which h^E data have been measured, the number of data points, the values obtained for the parameters Δg_{12} and Δg_{21}, the standard deviation, σ, of the fits, the ratio of the standard deviation and the maximum value of h^E and the source of data. Sometimes h^E data measured at a certain temperature by several authors are in excellent agreement and there are many data points to be fitted to eqn. (3). For instance, this is the case of the n-hexane(1) + 2-propanone(2) system at several temperatures, as shown in Fig. 1a. In most cases, h^E data for a system at a particular temperature were measured by only one author. In some cases only a few data points are available. Figures 2a, 3a and 4a give examples of this situation.

Values of $\sigma/h^E_{\mathrm{max}}$ in Table 1 indicate that the fits are good except for those systems containing an aromatic (benzene, toluene or ethyl-benzene) + 2-butanone. This could be related to the fact that h^E data for these systems do not follow the same pattern as that of the n-alkane + ketone or cyclohexane + ketone systems (which show large endothermic values with a maximum at a mole fraction close to 0.5). Instead, h^E data for the aromatic + 2-butanone systems either show both an endothermic and an exothermic section, or are moderately endothermic (100 J mole^{-1}) with a maximum in the hydrocarbon rich region. h^E data are less endothermic than the alkane + ketone systems for the aromatic + 2-propanone systems and exothermic for the toluene (1) + cyclohexanone(2) system and the maximum or minimum for these systems appears at a mole fraction close to 0.5 (see Figs. 2a and 4a).

The variation of the values of the parameters, Δg_{12} and Δg_{21}, with temperature is linear for the *n*-pentane(1) + 2-propanone(2) system and for the *n*-hexane(1) + 2-propanone(2) system up to 293 K. These linear variations correspond to moderate increases with temperature in the values adopted by the excess enthalpy. An example of such a variation of h^E with temperature may be seen in Fig. 1a which illustrates results for the *n*-pentane(1) + 2-propanone(2) system. When the values of h^E decrease or remain almost constant with temperature, as is the case in the *n*-heptane(1) + 2-butanone(2) system (see Fig. 3a), linear variations of the values of the parameters are not observed. This could be due to experimental errors in the sets of h^E data which have been measured by different authors, and/or lack of capability of the g^E model to adopt the variations of the excess enthalpy with temperature different from that of a moderate increase.

Table 2 gives the results of VLE predictions. The conditions of the VLE data are indicated. When the data are isothermal, both the temperature and the range of total pressures are indicated. When the data are isobaric, the pressure and the temperature interval are stated. If h^E data for a system were taken at only one temperature, there is only one set of parameters available

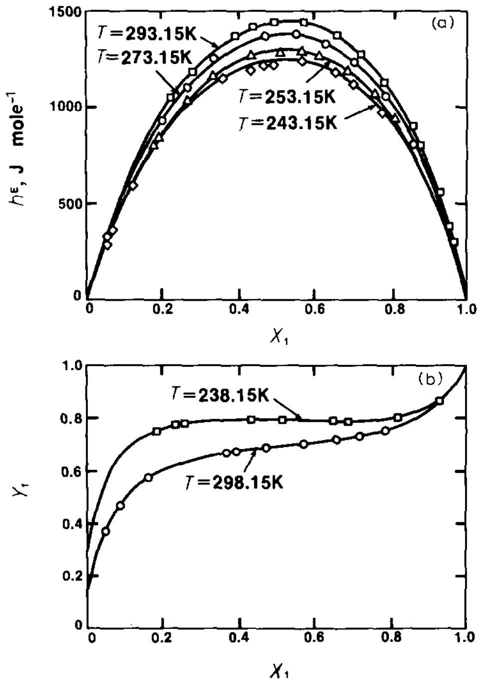

Fig. 1. Comparison of calculated and experimental data for the system *n*-pentane(1)–2-propanone(2). (a), h^E: □, ○, △, ◇, experimental; ———, calculated. (b), VLE: □, ○, experimental; ———, calculated. Solid curves are calculated from the LEMF equation. VLE data were evaluated using the 273.15 K set of parameters.

TABLE 1

Parameters for the LEMF equation determined from h^E data, statistical measures of fits of h^E and source of data

System	T (K)	Number of points	Δg_{12} (J mole^{-1})	Δg_{21} (J mole^{-1})	σ [a] (J mole^{-1})	σ/h^E_{max} (%)	Ref.
n-Pentane (1)+ 2-propanone(2)	243.15	15	1390.2	1589.4	26	2.2	21, 22
	253.15	13	1441.0	1647.4	22	1.7	21, 22
	273.15	14	1520.3	1784.3	18	1.3	21, 22
	293.15	13	1608.8	1886.1	20	1.4	21, 22
n-Hexane(1)+ 2-propanone(2)	243.15	25	1499.0	1571.5	30	2.3	23
	253.15	27	1555.2	1664.6	30	2.2	23
	273.15	26	1662.7	1795.0	21	1.4	23
	293.15	25	1750.5	1913.6	18	1.2	23
	298.15	9	1715.0	1940.1	59	3.7	24
	303.15	7	1753.6	2028.2	59	3.7	25
	313.15	6	2039.8	2156.4	151	8.1	25
n-Heptane(1)+ 2-propanone(2)	298.15	6	1922.7	1998.2	39	2.3	26
n-Decane(1)+ 2-propanone(2)	298.15	10	2088.9	2291.5	66	3.4	27
Cyclohexane(1)+ 2-propanone(2)	298.15	8	1719.5	1976.6	26	1.2	28
Benzene(1)+ 2-propanone(2)	303.15	6	54.60	480.9	9.9	6.8	29
	318.15	8	− 138.4	634.8	10	6.3	30
Toluene(1)+ 2-propanone(2)	318.15	9	454.4	396.0	6.9	2.7	31
n-Hexane(1)+ 2-butanone(2)	298.15	19	1378.5	1731.2	14	1.1	32

n-Heptane(1)+ 2-butanone(2)	293.15	12	1554.8	1199.4	11	1.0	33
	298.15	45	1526.4	1746.3	20	1.5	26, 34 35, 36
	313.15	5	1615.3	1250.8	4.8	0.4	33
n-Octane(1)+ 2-butanone(2)	298.15	20	1631.3	1762.8	20	1.4	36
Cyclohexane(1)+ 2-butanone(2)	291.15	9	1319.5	1848.9	30	2.3	40
	298.15	9	1828.6	1338.6	30	2.3	41
	318.15	9	1779.5	1456.3	49	3.7	41
Benzene(1)+ 2-butanone(2)	293.15	9	539.7	−1349.0	18	36	37
	298.15	25	375.4	−939.8	8.8	16	32
Toluene(1)+ 2-butanone(2)	298.15	8	827.4	−1537.7	16	14	38
Ethyl-benzene(1)+ 2-butanone(2)	298.15	23	820.7	−1418.2	9.6	9.0	39
n-Heptane(1)+ 2-pentanone(2)	298.15	30	1251.4	1628.1	14	1.2	35, 36
n-Hexane(1)+ 3-pentanone(2)	298.15	20	1042.0	1572.3	5.6	0.6	32
Cyclohexane(1)+ cyclohexanone(2)	298.15	5	1575.0	907.6	15	1.6	42
Toluene(1)+ cyclohexanone(2)	298.15	5	−301.9	−424.6	18	11	42

[a] $\sigma = \sum_j (h^E_{j_{\text{calcd.}}} - h^E_{j_{\text{exp.}}})^2/(N-3)^{1/2}$

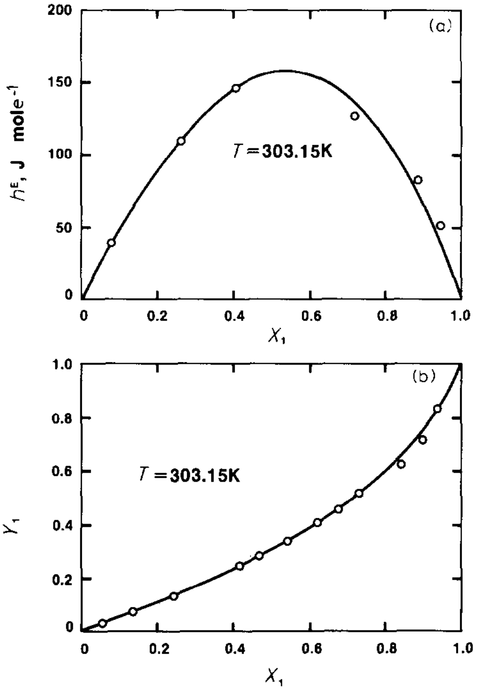

Fig. 2. Comparison of calculated and experimental data for the system benzene(1)–2-propanone(2), (a), h^E: ○, exp.; ———, calcd. (b), VLE: ○, exp.; ———, calcd. Solid curves are calculated from the LEMF equation using the 318.15 K set of parameters.

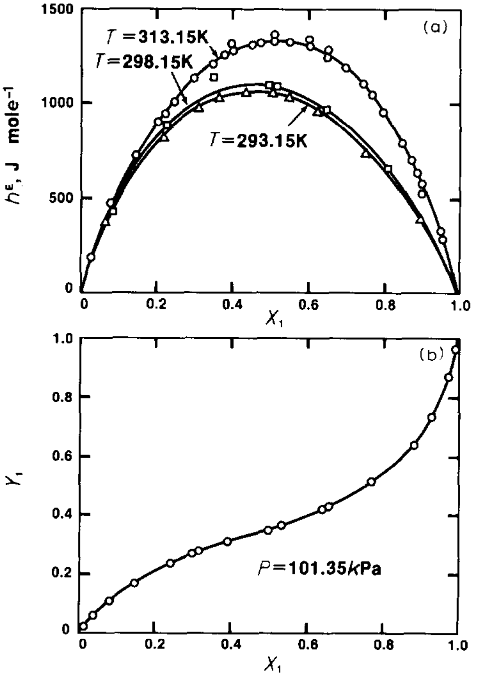

Fig. 3. Comparison of calculated and experimental data for the system *n*-heptane(1)–2-butanone(2), (a), h^E: ○, □, △, exp.; ———, calcd. (b), VLE: ○, exp.; ———, calcd. Solid curves are calculated from the LEMF equation. VLE data were evaluated using the 313.15 K set of parameters.

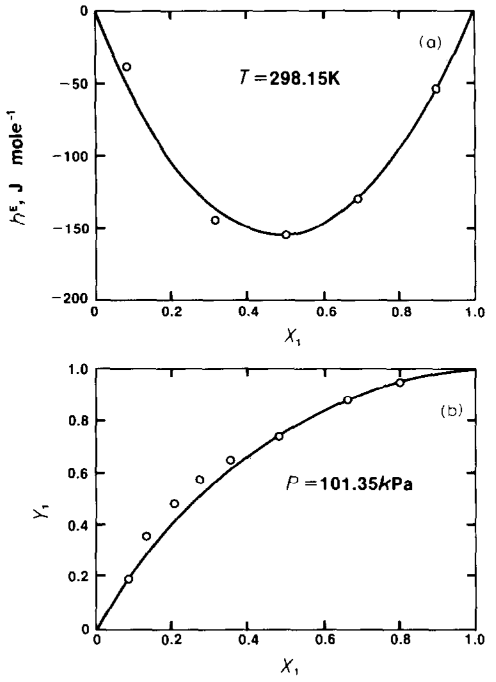

Fig. 4. Comparison of calculated and experimental data for the system toluene(1)–cyclohexanone(2). (a), h^E: ○, exp.; ———, calcd. (b), VLE: ○, exp.; ———, calcd. Solid curves are calculated from the LEMF equation.

to predict VLE data at any conditions. In this case, the temperature of the h^E data is indicated in Table 2 under the heading "Set of parameters".

The mean deviation of y_1 has been chosen as the criterion to examine the accuracy of the VLE predictions and is given in Table 2. Values for the maximum deviation are also reported in order to complement the information provided by the mean deviation. When experimental values of y_1 were not available, the mean deviations of the total pressure were calculated and expressed in kPa. The source of VLE data are indicated in the last column of Table 2. Values for the molar volumes were taken from Timmermans [84] and from the Handbook for Chemistry and Physics [85]. Some molar volumes used in the calculation of isobaric VLE data had to be estimated using the method of Gunn and Yamada [86]. Application of Wilson's formulation of the Redlich–Kwong equation [18] requires knowledge of the critical constants and accentric factors for pure components. Values for these parameters have been taken from Reid et al. [87]. Values for the pure components vapor pressures were also taken from Reid et al. [87] except for the cases in which these values were reported together with total pressure measurements of the mixtures.

Values of the y_1 mean deviation for most systems are low and of similar

TABLE 2

Summary of VLE predictions from h^E data using LEMF equation and source of VLE data

System	Experimental VLE data	Set of parameters	Vapour composition y_1		Ref.
			Mean dev.	Max. dev.	
n-Pentane(1)+ 2-propanone(2)	238.15 K (3–5 kPa)	a(243K)	0.0118	−0.0237	43
		b(273K)	0.0126	−0.0194	
		c(238K)	0.0143	−0.0294	
	258.15 K (8–13 kPa)	a(253K)	0.0111	0.0194	43
		b(273K)	0.0094	−0.0197	
		c(258K)	0.0083	−0.0117	
	298.15 K (34–75 kPa)	a(293K)	0.0211	−0.0487	43
		b(273K)	0.0088	−0.0194	
		c(298K)	0.0247	−0.0568	
	101.35 K kPa (307–322 K)	a(293K)	0.0506	−0.1007	44
		b(273K)	0.0359	−0.0776	
n-Hexane(1)+ 2-propanone(2)	253.15 K (3–4 kPa)	a(253K)	0.0064	0.0137	45
		b(293K)	0.0420	0.1051	
	268.15 K (7–10 kPa)	a(273K)	0.0123	0.0477	43
		b(293K)	0.0267	0.0885	
		c(268K)	0.0073	0.0333	
	293.15 K (25–32 kPa)	a,b(293K)	0.0292	0.0767	43
	308.15 K (44–60 kPa)	a(303K)	0.0416	0.1375	46
		b(293K)	0.0327	0.1132	
		c(308K)	0.0451	0.1431	
	318.15 K (59–85 kPa)	a(313K)	0.0682	0.1679	45
		a(303K)	0.0420	0.1120	
		b(293K)	0.0336	0.0868	
		c(318K)	0.0534	0.1360	
	318.14 K (64–86 kPa)	a(313K)	0.0584	0.1674	46
		a(303K)	0.0364	0.1155	

		b(293K)	0.0280	0.0931	
		c(318K)	0.0458	0.1381	
	328.15 K (89–121 kPa)	a(313K)	0.0537	0.1514	46
		a(303K)	0.0321	0.1025	
		b(293K)	0.0241	0.0819	
		c(328K)	0.0482	0.1414	
	101.35 kPa (322–332 K)	a(313K)	0.0595	0.1446	46
		a(303K)	0.0463	0.1013	
		b(293K)	0.0319	0.0773	
	101.35 kPa (322–331 K)	a(313K)	0.0558	0.1143	47
		a(303K)	0.0415	0.0714	
		b(293K)	0.0272	0.0475	
n-Heptane(1)+ 2-propanone(2)	323.15 K (35–81 kPa)	a(298K)	0.0426	0.1390	48
	323.15 K (19–82 kPa)	a(298K)	0.0853	0.2013	49
	338.15 K (77–137 kPa)	a(298K)	0.0303	0.0916	50
	101.35 kPa (329–360 K)	a(298K)	0.0389	0.1323	51
n-Decane(1)+ 2-propanone(2)	313.15 K (31–56 kPa)	a(298K)	0.0027	−0.0034	52
	333.15 K (69–100 kPa)	a(298K)	0.0043	−0.0069	52
Cyclohexane(1)+ 2-propanone(2)	298.15 K (15–33 kPa)	a(298K)	0.0290	0.0616	53
	298.15 K (31–34 kPa)	a(298K)	0.0166	0.0355	54
	308.15 K (38–50 kPa)	a(298K)	0.0249	0.0882	55
	318.15 K (53–73 kPa)	a(298K)	0.0243	0.0835	55
	328.15 K (74–105 kPa)	a(298K)	0.0251	0.0792	55
	101.35 kPa (327–338 K)	a(298K)	0.0343	0.0733	55
	101.35 kPa (328–347 K)	a(298K)	0.0468	0.1591	56
Benzene(1)+ 2-propanone(2)	298.15 K (17–30 kPa)	a(303K)	0.0335	−0.0771	57
		b(318K)	0.0330	−0.0758	
	298.15 K (15–30 kPa)	a(303K)	0.0141	−0.0386	53
		b(318K)	0.0140	−0.0371	
	303.15 K (18–37 kPa)	a(303K)	0.0115	−0.0270	58
		b(318K)	0.0113	−0.0259	
	308.15 K (26–45 kPa)	a(303K)	0.0272	−0.0650	57
		b(318K)	0.0268	−0.0638	

System	Experimental VLE data	Set of parameters	Vapour composition y_1		Ref.
			Mean dev.	Max. dev.	
	313.15 K (28–54 kPa)	a,b(318K)	0.0158	−0.0354	58
	318.15 K (33–67 kPa)	a,b(318K)	0.0130	−0.0313	59
	323.15 K (39–80 kPa)	a,b(318K)	0.0145	−0.0341	58
	98.39 kPa (329–351 K)	a,b(318K)	0.0093	−0.0217	60
	98.66 kPa (329–348 K)	a,b(318K)	1.05 ^{a}	2.83 ^{a}	61
	99.99 kPa (329–347 K)	a,b(318K)	0.0150	−0.0403	62
	101.35 kPa (329–349 K)	a,b(318K)	0.0168	−0.0297	63
	101.35 kPa (330–350 K)	a,b(318K)	0.0119	−0.0307	64
	101.35 kPa (337–352 K)	a,b(318K)	0.0139	−0.0277	65
	101.35 kPa (331–353 K)	a,b(318K)	0.0152	−0.0266	66
	101.35 kPa (329–353 K)	a,b(318K)	0.0105	−0.0353	67
Toluene(1)+ 2-propanone(2)	308.15 K (15–43 kPa)	a(318K)	0.0085	−0.0228	58
	318.15 K (13–64 kPa)	a(318K)	0.0135	−0.0488	58
	318.15 K (11–67 kPa)	a(318K)	2.83 ^{a}	4.69 ^{a}	68
	328.15 K (20–92 kPa)	a(318K)	0.0154	−0.0583	58
	100.17 kPa (331–362 K)	a(318K)	0.0151	−0.0390	69
	101.35 kPa (329–381 K)	a(318K)	0.0382	−0.0814	70
n-Hexane(1)+ 2-butanone(2)	333.15 K (67–88 kPa)	a(298K)	0.0270	−0.0406	71
	338.15 K (69–102 kPa)	a(298K)	0.0277	−0.0481	72
n-Heptane(1)+ 2-butanone(2)	323.15 K (29–39 kPa)	a,b(313K)	0.0283	0.0569	73
	101.35 kPa (350–369 K)	a,b(313K)	0.0091	−0.0427	74
	101.35 kPa (350–367 K)	a,b(313K)	0.0069	−0.0183	73
n-Octane(1)+ 2-butanone(2)	338.15 K (22–61 kPa)	a(298K)	0.0228	−0.0865	72
Cyclohexane(1)+ 2-butanone(2)	101.35 kPa (344–352 K)	a(291K)	0.0526	−0.1009	56
		a(298K)	0.0280	−0.0523	

	101.35 kPa (344–348 K)	a(291K)	0.0592	−0.0980	80
		a(298K)	0.0318	0.0505	
Benzene(1)+ 2-butanone(2)	313.15 K (23–25 kPa)	a,b(298K)	0.0201	0.0284	58
	323.15 K (35–38 kPa)	a,b(298K)	0.0200	0.0300	58
	323.15 K (35–38 kPa)	a,b(298K)	0.0223	0.0313	75
	333.15 K (52–55 kPa)	a,b(298K)	0.0201	0.0306	58
	101.35 kPa (351–352 K)	a,b(298K)	0.0166	−0.0304	76
	101.35 kPa (351–354 K)	a,b(298K)	0.0135	−0.0264	74
	101.35 kPa (351–353 K)	a,b(298K)	0.0121	−0.0223	77
	101.35 kPa (351–353 K)	a,b(298K)	0.0165	−0.0284	75
	298.12 kPa (389–393 K)	a,b(298K)	0.0141	0.0219	78
	431.49 kPa (405–409 K)	a,b(298K)	0.0123	0.0185	78
	564.86 kPa (418–422 K)	a,b(298K)	0.0120	−0.0173	78
Toluene(1)+ 2-butanone(2)	323.15 K (13–35 kPa)	a(298K)	0.0218	−0.0544	79
	328.15 K (17–41 kPa)	a(298K)	0.0230	−0.0548	58
	338.15 K (25–60 kPa)	a(298K)	0.0220	−0.0567	58
	348.15 K (43–84 kPa)	a(298K)	0.0204	−0.0546	58
	101.35 kPa (352–384 K)	a(298K)	0.0171	−0.0600	74
Ethyl benzene(1)+ 2-butanone(2)	298.15 K (2–12 kPa)	a(298K)	0.63 [a]	0.90 [a]	38
	328.15 K (6–41 kPa)	a(298K)	0.0302	−0.0864	58
	338.15 K (10–60 kPa)	a(298K)	0.0334	−0.0767	58
	348.15 K (15–84 kPa)	a(298K)	0.0313	−0.0845	58
n-Heptane(1)+ 2-pentanone(2)	363.15 K (87–90 kPa)	a(298K)	0.0113	0.0249	81
n-Hexane(1)+ 3-pentanone(2)	338.15 K (42–92 kPa)	a(298K)	0.0250	−0.0618	72
Cyclohexane(1)+ cyclohexanone(2)	323.15 K (10–35 kPa)	a(298K)	0.0081	0.0203	82
	348.15 K (18–83 kPa)	a(298K)	0.0110	−0.0286	82
Toluene(1)+ cyclohexanone(2)	101.35 kPa (389–423 K)	a(298K)	0.0255	0.0606	83

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[a] Deviations in the total pressure expressed in kPa.

magnitude to those obtained when VLE data are directly fitted to an expression for g^E such as the Wilson, NRTL, UNIQUAC, etc. equations [20]. Thus, even when only a few h^E data points are available, values of y_1 predicted by the HGC method are essentially as accurate as experimental data. In order to examine the accuracy of the predictions when experimental values of y_1 are not reported, values for the total pressure mean deviation should be compared with the corresponding pressure interval.

It may be observed that the accuracy of the predictions depends to a great extent on the goodness of the fit of experimental h^E data by eqn. (3). The only exceptions are the predictions for the benzene(1) + 2-butanone(2) system which are very good although the fit of h^E data to eqn. (3) is poor. This could be due to the ideal behavior of this system and the similar vapor pressure of both pure components which lead to values of y very close to those of x. Figures 1b–5b show some typical examples of the VLE predictions obtained. These figures correspond to systems comprised of an n-alkane, cyclohexane or aromatic and a ketone. The VLE data for these systems are either isothermal or isobaric.

When two or more sets of h^E data taken at different temperatures are available for a system, VLE data at a certain temperature can be predicted using: (a) the set of parameters obtained from h^E data taken at the closest

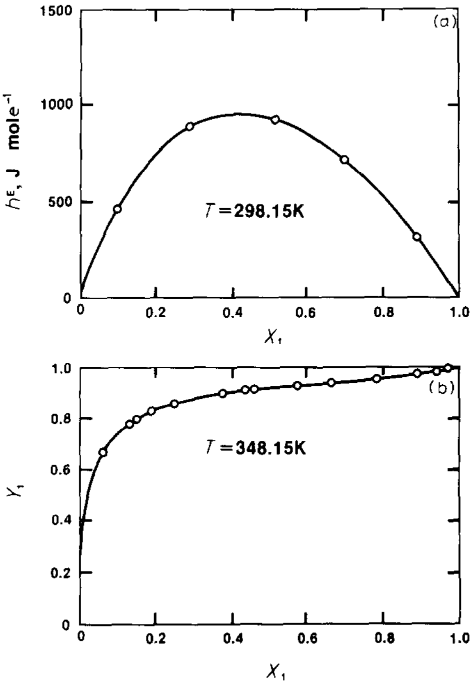

Fig. 5. Comparison of calculated and experimental data for the system cyclohexane(1)–cyclohexanone(2), (a), h^E: ○, exp.; ———, calcd. (b), VLE: ○, exp.; ———, calcd. Solid curves are calculated from the LEMF equation.

temperature to that of the VLE data; (b) the set of parameters obtained from the best fit of h^E data to eqn. (3) for this particular system; or (c) the set of extrapolated or interpolated parameters if values of the parameters show a linear variation with temperature for the system studied. The set of parameters used in each prediction of VLE data is indicated in Table 2 under the heading "Set of parameters". In cases (a) and (b) the temperature of h^E data is listed. For six systems having h^E data at more than one temperature, two or more sets of parameters are available and it may be noted how the accuracy of the VLE predictions depends on the parameters used. For a majority of the VLE data, the set of parameters obtained by method (b) leads to the most accurate predictions regardless of the temperature difference between the VLE data predicted and the h^E data from which the parameters were calculated. This is the case of the *n*-pentane(1) + 2-propanone(2), *n*-hexane(1) + 2-propanone(2) and benzene(1) + 2-propanone(2) systems.

The best fits for the *n*-heptane(1) + 2-butanone(2) and benzene(1) + 2-butanone(2) systems were obtained using method (a) described earlier. Consequently, the reported results correspond to only one set of parameters. Results for the other sets of parameters were worse even though the temperatures of their h^E data were close to the temperatures of the best fits.

As to the cyclohexane(1) + 2-butanone(2) system, there are two sets of parameters obtained from h^E data at 291.15 and 298.15 K which have the same values of σ/h^E_{max}. However, the 298.15 K set of parameters leads to more precise VLE predictions and is in better agreement with a third set of parameters available at 318.15 K. As has been already pointed out, these discrepancies could be due to experimental errors in the h^E data. Values of h^E at these three temperatures are very close even though those at 291.15 K were taken by a different author from the one who took those at 298.15 and 318.15 K.

CONCLUSIONS

The results of this study suggest that VLE data for the hydrocarbon–ketone systems can be successfully predicted using the parameters of the LEMF model determined from heat of mixing data (HGC method). The accuracy of the predictions depends to a great extent on the goodness of the fit of the h^E data to the algebraic equation for the heat of mixing. The better this fit is the more precisely can the experimental VLE data be predicted. Parameters obtained from h^E data at lower temperature can be used to predict accurate VLE data at a higher temperature provided that the fit of h^E data is good. This seems to indicate that the HGC method used in conjunction with the LEMF model is able to account properly for the temperature dependence of VLE data.

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