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Enthalpies of mixing for the *n*-pentane + methylacetate + dichloromethane system at 298.15 K and their prediction with the UNIFAC model [1]

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Abstract

New experimental data of the excess molar enthalpies at 298.15 K for the ternary system *n*-pentane + methylacetate + dichloromethane, together with corresponding data for the constituent binary mixtures, are presented. Different expressions from the literature are used to predict excess enthalpies from the corresponding binary data. The empirical correlation of Nagata and Tamura (J. Chem. Eng. Data, 33 (1988) 283) gives the best results for this system. The UNIFAC group contribution is applied to predict ternary excess molar enthalpies which are compared with the experimental data.

INTRODUCTION

Excess molar enthalpy H^E data are known for a number of binary liquid mixtures of non-electrolytes and can be found in several articles. However, experimental data on excess molar enthalpies of multicomponent mixtures are rare in the literature. It is, therefore, interesting to estimate H^E values of ternary systems from binary data. In this case, we have used only the correlations of Radojkovic et al. [1], Jacob and Fitzner [2], Cibulka [3], Singh et al. [4] and Nagata and Tamura [5].

In previous papers, we have published experimental data of H^E_{ij} at 298.15 K for the binary systems *n*-pentane + methylacetate [6], methylacetate + dichloromethane [7] and *n*-pentane + dichloromethane [8]. In the present work, we have determined H^E_{123} at 298.15 K for the *n*-pentane (P) + methylacetate (MA) + dichloromethane (DCM) ternary system in order to consider some empirical correlation methods, assuming that interactions in a ternary mixture are closely dependent on the interaction of the constituents in binary mixtures.

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Group contribution methods are widely used in fluid phase equilibrium calculations. In this article, the UNIFAC contribution method will be applied to predict H^E_{123} for the ternary system and for the three binary systems, respectively. Values for the parameters have been taken from the literature.

EXPERIMENTAL

The methods used in our laboratory have been described previously [9]. Densities were measured with a digital densimeter AP, model DMA 45. All weighings were made on an H315 Mettler balance. The adiabatic calorimeter described by Loiseleur et al. [10] was used with some modifications to determine the enthalpy changes. The estimated error was $\pm 0.1\ \mathrm{kg\,m^{-3}}$ in densities and $\pm 5\ \mathrm{J\,mol^{-1}}$ in enthalpies.

The substances were purified as described in the references. Caution was taken to prevent evaporation. Each experimental run was performed by adding the third component to a binary mixture of the other two. A ternary system was regarded as a pseudo-binary system made up of one binary mixture and the third component. One mole of the ternary system was prepared by mixing $(1 - x_3)$ of the initial binary mixture and x_3 of component 3.

The ternary excess molar enthalpy is given by

$$H^E_{123} = \Delta H_m + (1 - x_3)H^E_{12} \tag{1}$$

where ΔH_m is the observed molar excess enthalpy for the pseudo-binary mixture and H^E_{12} is the excess molar enthalpy of the P(1) + MA(2) system. The same procedure was followed with P(1) + DCM(3) and MA(2) + DCM(3).

The values of H^E_{ij} for the binary systems can be calculated from the experimental data (the mole fraction being known) by using a Redlich–Kister polynomial expression

$$H^E_{ij} = x_i x_j \sum_{k=0}^{n} a_k (x_i - x_j)^k \tag{2}$$

where a_k are polynomial coefficients. The method of least squares was used to determine the values of the coefficients. In each case, the optimum number of the coefficients was ascertained from an estimation of the variation of the standard error estimate with n

$$\sigma = \left[\sum (H^E_{ij(\mathrm{obs})} - H^E_{ij(\mathrm{cal})})^2 / (n_{\mathrm{obs}} - n) \right]^{1/2} \tag{3}$$

The values adopted for the coefficients and the standard error of the estimate associated with the use of eqn. (3) are summarized in Table 1.

Figure 1 shows the experimental values of H^E_{ij} for the three binary systems. The continuous curves were calculated from eqn. (2) using these values for the coefficients.

TABLE 1

Coefficients a_k from eqn. (2) and standard deviations for the binary systems at 298.15 K

System	a_0	a_1	a_2	a_3	a_4	a_5	σ
P(1) + MA(2) [a]	6090	360	−800	900	1200	–	7
MA(2) + DCM(3) [b]	−3398	320	−890	−2100	1800	2400	11
P(1) + DCM(3) [c]	5590	−2390		5000	1900	−6300	17

[a] Ref. 11. [b] Ref. 7. [c] Ref. 8.

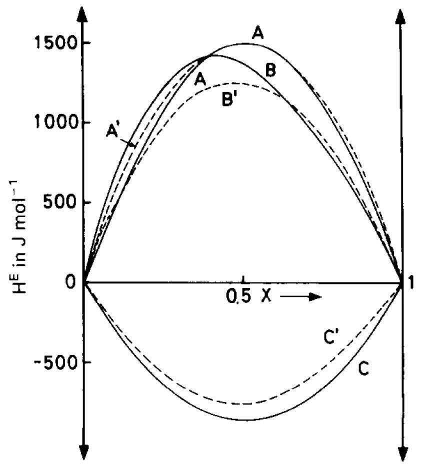

Fig. 1. Excess molar enthalpies of binary mixtures at 298.15 K: curves A and A′, *n*-pentane(1) + methylacetate(2); curves B and B′, *n*-pentane(1) + dichloromethane(3); curves C and C′, methylacetate(2) + dichloromethane(3): —— experimental data; – – – calculated by the UNIFAC method.

RESULTS AND DISCUSSION

Table 2 shows the experimental values of H^E_{123} for the P(1) + MA(2) + DCM(3) system at 298.15 K, following eqn. (1).

Figure 2 shows curves of constant excess molar enthalpies for the ternary system.

If interpretation in a ternary system $i + j + k$ is assumed to be closely dependent on the interaction of the constituent mixtures $i + j$, $j + k$ and $i + k$, it should be possible to evaluate the H^E_{123} values of non-electrolytes considering that the corresponding enthalpies for the binary systems are known.

Radojkovic et al. [1] considered an expression proposed by Redlich and Kister of the form

$$H^E_{123} = H^E_{12*} + H^E_{23*} + H^E_{13*} \qquad (4)$$

TABLE 2

Experimental excess molar enthalpies for the *n*-pentane(1) + methylacetate(2) + dichloromethane(3) system at 298.15 K

x_1	x_2	$\Delta H^E_m/(\mathrm{J\ mol^{-1}})$	$H^E_{123}/(\mathrm{J\ mol^{-1}})$
$x'_2/x'_3 = 0.3998$; $x'_2 = 0.2856$; $H^E_{23} = -716\ \mathrm{J\ mol^{-1}}$			
0.1309	0.2482	546	−76
0.2266	0.2208	792	238
0.3741	0.1787	1088	640
0.5477	0.1292	1036	712
0.6612	0.0988	903	660
0.7876	0.0607	662	510
$x'_2/x'_3 = 1.0328$; $x'_2 = 0.5081$; $H^E_{23} = -848\ \mathrm{J\ mol^{-1}}$			
0.1475	0.4332	491	−231
0.3084	0.3514	918	332
0.4401	0.2845	1111	637
0.6061	0.2002	1104	770
0.7356	0.1343	882	658
0.8476	0.0744	521	392
$x'_2/x'_3 = 3.2502$; $x'_2 = 0.7647$; $H^E_{23} = -639\ \mathrm{J\ mol^{-1}}$			
0.0985	0.6894	591	15
0.1896	0.6198	924	407
0.3605	0.4891	1203	795
0.4733	0.4028	1403	1067
0.7129	0.2195	1016	888
0.8360	0.1254	588	483
$x'_1/x'_2 = 0.2200$; $x'_1 = 0.1803$; $H^E_{12} = 813\ \mathrm{J\ mol^{-1}}$			
0.1604	0.7291	−221	502
0.1372	0.6235	−529	89
0.1109	0.5043	−785	−285
0.0883	0.4011	−830	−432
0.0570	0.2590	−655	−398
0.0189	0.0859	−263	−178
$x'_1/x'_2 = 1.2251$; $x'_1 = 0.5506$; $H^E_{12} = 1514\ \mathrm{J\ mol^{-1}}$			
0.4891	0.3993	−165	1180
0.4102	0.3348	−482	646
0.3334	0.2722	−496	421
0.2444	0.1995	−428	305
0.1544	0.1260	−181	244
0.0604	0.0493	−13	153
$x'_1/x'_3 = 0.8179$; $x'_1 = 0.4499$; $H^E_{13} = 1441\ \mathrm{J\ mol^{-1}}$			
0.4056	0.0986	−326	973
0.3328	0.2603	−652	414
0.2693	0.4015	−521	341
0.1980	0.5600	−353	281
0.1339	0.7025	−196	233
0.0466	0.9008	−18	125

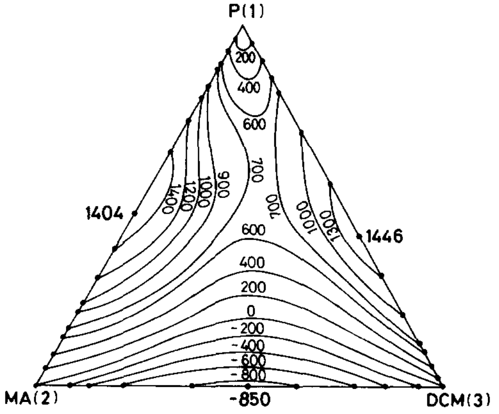

Fig. 2. Lines of constant excess molar enthalpies for the *n*-pentane(1) + methylacetate(2) + dichloromethane(3) system at 298.15 K.

where $H^{\mathrm{E}}_{12^*}$, $H^{\mathrm{E}}_{23^*}$ and $H^{\mathrm{E}}_{13^*}$ represent the excess molar enthalpies and x_1, x_2 and x_3 (mole fractions of the ternary system) were calculated from eqn. (2) using the coefficients in Table 1.

Jacob and Fitzner [2] suggested an expression for estimating the properties of a ternary mixture of the form

$$H^{\mathrm{E}}_{123} = \frac{x_1 x_2 H^{\mathrm{E}}_{12}}{\left(x_1 + \frac{x_3}{2}\right)\left(x_2 + \frac{x_3}{2}\right)} + \frac{x_1 x_3 H^{\mathrm{E}}_{13}}{\left(x_1 + \frac{x_2}{2}\right)\left(x_3 + \frac{x_2}{2}\right)} + \frac{x_2 x_3 H^{\mathrm{E}}_{23}}{\left(x_2 + \frac{x_1}{2}\right)\left(x_3 + \frac{x_1}{2}\right)} \qquad (5)$$

The H^{E}_{ij} is the excess enthalpy of the binary mixture at compositions (x_i^0, x_j^0) such that $x_i^0 - x_j^0 = x_i - x_j$.

Cibulka [3] proposed the equation

$$H^{\mathrm{E}}_{123} = H^{\mathrm{E}}_{12^*} + H^{\mathrm{E}}_{23^*} + H^{\mathrm{E}}_{13^*} + x_1 x_2 x_3 (A + Bx_1 + Cx_2) \qquad (6)$$

where A, B and C are parameters characteristic of the mixture which are evaluated by fitting this equation by the least-squares method, with a standard deviation defined as in eqn. (3) where $n = 1$.

The parameters obtained are $A = 19741$, $B = 9247$ and $C = 28793$. Singh et al. [4] proposed an equation of the form

$$H^{\mathrm{E}}_{123} = H^{\mathrm{E}}_{12^*} + H^{\mathrm{E}}_{23^*} + H^{\mathrm{E}}_{13^*} + x_1 x_2 x_3 (A + B(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2) \qquad (7)$$

The parameters obtained are $A = -13134$, $B = 46264$ and $C = 45884$. These two equations are modifications of eqn. (4). Nagata and Tamura [5] proposed the equation

$$H^{\mathrm{E}}_{123} = H^{\mathrm{E}}_{12^*} + H^{\mathrm{E}}_{23^*} + H^{\mathrm{E}}_{13^*} + x_1 x_2 x_3 \Delta_{123} \qquad (8)$$

where

$$\Delta_{123}/RT = \sum_{j=1}^{6} b_j (1 - 2x_3)^{j-1} \qquad (9)$$

TABLE 3

Standard deviations for the *n*-pentane(1) + methylacetate(2) + dichloromethane(3) system at 298.15 K

Equation	SD(H^{E}_{123})/(J mol^{-1})	Equation	SD(H^{E}_{123})/(J mol^{-1})
(4)	326	(7)	126
(5)	326	(8)	7
(6)	88		

Equation (8) was used by Van Ness and his coworkers [12, 13] in correlating their excess molar enthalpy results. The coefficients of eqn. (9) are $b_1 = -5.3546$, $b_2 = -6.5195$, $b_3 = 2.3841$, $b_4 = 61.4659$, $b_5 = -22.61811$ and $b_6 = -56.4352$.

Table 3 shows the standard deviations using the above-mentioned equations for H^{E}_{23}. Equation (8) shows the best agreement with the experimental data. Obviously, the models using ternary parameters are superior to the predictive one not containing ternary parameters.

Prediction of H^{E}_{123} *using* UNIFAC

The enthalpy of mixing can be calculated from the excess Gibbs free energy G^{E} by

$$\frac{\partial}{\partial T}\left(\frac{G^{E}_{123}}{T}\right) = -\frac{H^{E}_{123}}{T^2} \tag{10}$$

Equation (10), in conjunction with the UNIFAC model [14], yields the following expression for the enthalpy of mixing

$$H^{E}_{123} = \sum_i x_i \overline{\Delta H_i} \tag{11}$$

where

$$\overline{\Delta H_i} = \sum_k \nu_k^{(i)}(H_k - H_k^{(i)}) \tag{12}$$

where $\nu_k^{(i)}$ is the number of groups of type k in component i, H_k is the excess enthalpy of group k, and $H_k^{(i)}$ is the same as H_k but in a reference solution containing only molecules of type i. The final expression is

$$\frac{H_k}{RT^2} = Q_k \frac{\sum\limits_m \Theta_m \psi'_{mk}}{\sum\limits_m \Theta_m \psi_{mk}} + \sum_m \left(\frac{\Theta_m \psi'_{km}}{\sum\limits_n \Theta_n \psi_{nm}} - \frac{\Theta_m \psi_{km} \sum\limits_n \Theta_n \psi'_{nm}}{(\sum\limits_n \Theta_n \psi_{nm})^2} \right) \tag{13}$$

where Θ_m is the area fraction of group m in the mixtures

$$\Theta_m = Q_m X_m \Big/ \sum_n Q_n X_n \tag{14}$$

TABLE 4

Group interaction parameters and Q_k values

m	Q_k	CH_3	CH_2	COOC	CH_2Cl_2
CH_3	0.848	0	0	44.98	26.60
CH_2	0.540	0	0	44.98	26.60
COOC	1.728	114.11	114.1	0	1315.1
CH_2Cl_2	1.988	−0.39	−0.39	−5.53	0

Q_k is the area parameter of group k, and X_m is the mole fraction of group m in the mixture, which can be calculated with the expression

$$X_m = \sum_i x_i \nu_{mi} \Big/ \sum_i x_i \sum_k \nu_{ki} \tag{15}$$

and ψ_{mn} is

$$\psi_{mn} = \exp(-Za_{mn}/2T) \tag{16}$$

$$\psi'_{mn} = \frac{\partial}{\partial T}(\psi_{mn}) \tag{17}$$

and

$$Z = Z(T) = 35.2 - 0.12772T + 0.00014T^2 \tag{18}$$

where Z is the temperature-dependent coordination number and a_{mn} the temperature-independent interaction parameters between groups m and n.

The parameters used [14] are summarized in Table 4.

The values for H_{ij}^{E} for the three binary systems are shown in Fig. 1.

For the ternary system, the obtained values show an average error defined as

$$\mathrm{AE} = \frac{1}{n} \sum \left| \frac{(H_{\mathrm{exp}}^{E} - H_{\mathrm{cal}}^{E})}{H_{\mathrm{cal}}^{E}} \right| \times 100 \tag{19}$$

The AE for this system is 151%. The UNIFAC model for calculating H_{ij}^{E} for binary systems agrees quite well with the experimental data as shown in Fig. 1, with AE = 6% for P(1) + MA(2), 14% for MA(2) + DCM(3), and 15% for P(1) + DCM(3) systems.

For this ternary system, the AE is not good. Probably because one of the systems shows negative H^E values and the other two show positive H^E values.

Using other parameters, as shown by Larsen et al. [15], which use a modified UNIFAC group-contribution model, the values obtained for H_{123}^{E} are no better.

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