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EXCESS MOLAR ENTHALPIES FOR THE PROPAN-2-OL + METHYLACETATE + DICHLOROMETHANE SYSTEM AT 298.15 K

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Heat of mixing data for the ternary liquid system propan-2-ol + methylacetate + dichloromethane at 298.15 K are reported along with data for the constituent binary systems. Different expressions published in the literature were used to calculate excess enthalpies from the corresponding binary data. The empirical correlation of Tanaka and Tamura gives the best prediction for this system. The UNIFAC group contribution is applied to predict enthalpies, in this case only for binary systems and compared with experimental data.

KEY WORDS: Enthalpies, binary and ternary systems, prediction by UNIFAC group contribution.

1 INTRODUCTION

Data of excess molar enthalpies of mixtures of ternary system are rare in the literature. It is therefore interesting to estimate excess molar enthalpies of mixtures from binary data and compared with experimental values. In previous papers, we have published densities, viscosities, enthalpies and excess Gibbs energies for the 2-propanol (2-PR) + methylacetate (MA)¹ system; densities, viscosities, enthalpies and excess molar Gibbs free energies for the 2-propanol (2-PR) + dichloromethane (DCM)² and the same parameters for the MA + DCM³ system at 298.15 K.

For the ternary 2-PR(1) + MA(2) + DCM(3) system it has been published excess molar volumes, viscosities⁴ and vapor-liquid equilibrium⁵. Now, in this paper, we determined the excess molar enthalpies H_{123}^E for the ternary system in order to consider some methods for empirical correlations, assuming that interactions in a ternary mixture, are closely dependent on the interaction of the constituent in binary mixtures.

The group contribution method are widely used in fluid phase equilibrium calculations. In this work, the UNIFAC contribution method will be applied to predict only binary excess enthalpies because for the ternary systems, interaction parameters are not available.

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2 EXPERIMENTAL SECTION

The methods used in our laboratory have been described previously⁶. Densities were measured with a digital densimeter AP, model DMA 45. All weighings were made on a H315 Mettler balance. The adiabatic calorimeter described by Loiseleur *et al.*⁷ was used with some modifications to determine the enthalpy changes. The appreciation in densities was $\pm 0.1 \text{ kg m}^{-3}$ and for enthalpies the error is $\pm 5 \text{ J mol}^{-1}$.

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 mixture was prepared by mixing $(1 - x_3)$ of the initial binary mixture and x_3 of the component 3. The ternary H_{123}^E is given by:

$$\Delta H_{123}^E = \Delta H_m + (1 - x_3) H_{12}^E \quad (1)$$

where ΔH_m is the observed molar excess enthalpy for the pseudobinary mixture and H_{12}^E is the excess molar enthalpy of the 2-PR(1) + MA(2) system. The same procedure was followed with 2-PR(1) + DCM(3) and MA(2) + DCM(3).

3 RESULTS AND DISCUSSION

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

$$H_{ij}^E = x_i x_j \sum_{k=0}^n a_k (x_i - x_j)^k \quad (2)$$

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 coefficients was ascertained from an estimation of the variation of the standard error estimate with n :

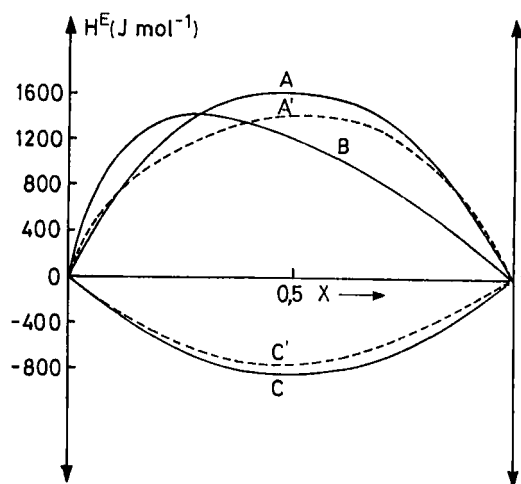
$$\sigma = \left[\frac{\sum (H_{ij}^E(\text{obs}) - H_{ij}^E(\text{cal}))^2}{(n_{\text{obs}} - n)} \right]^{1/2} \quad (3)$$

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

Figure 1 shows values of H_{ij}^E for the three binary systems. The continuous curves were calculated from Eqn. (2) using the coefficients of Table 1. Table 2 shows the experimental values of H_{123}^E for the 2-PR(1) + MA(2) + DCM(3) system at 298.15 K. Figure 2 shows curves of constant excess molar enthalpies for the ternary system.

Table 1 Coefficients a_k from Eqn. (2) and standard deviations σ for the binary system at 298.15 K.

System	a_0	a_1	a_2	a_3	a_4	a_5	σ
2-PR(1) + MA(2)	6456	-240	3040	-30	-4480	-1000	5
2-PR(1) + DCM(3)	4900	-3000	3600	-3000	-	-	47
MA(2) + DCM(3)	-3398	320	-890	-2100	1800	2400	11

**Figure 1** Excess molar enthalpies at 298.15 K. Curves A and A' propan-2-ol(1)+ methylacetate(2); curve B, propan-2-ol(1)+ dichloromethane(3); curves C and C'; methylacetate(2)+ dichloromethane(3); — experimental data; - - - calculated by the UNIFAC method.

Development of reliable methods for representing the behavior of a ternary system depend on the availability of appropriate experimental data. In this work we considered to be possible to evaluate H_{123}^E of non-electrolytes when the corresponding enthalpies of the binary systems are known. This approach has led to the development of several empirical relations to calculate H_{123}^E .

Tsao and Smith⁸ proposed an equation who has the following expressions:

$$H_{123}^E = \left(\frac{x_2}{1-x_1} \right) H_{12}^E + \left(\frac{x_3}{1-x_1} \right) H_{13}^E + (1-x_1) H_{23}^E \quad (4)$$

in which H_{ij}^E refers to the excess enthalpy for the binary mixtures at compositions x_i^0 and x_j^0 such that $x_i^0 = x_i$ for the 1-2 and 2-3 systems and $x_2^0 = x_2/(x_2 + x_3)$ for the 2-3 binary system.

Table 2 Experimental excess molar enthalpies for the propan-2-ol(1) + methylacetate(2) + dichloromethane (3) system at 298.15 K.

x_1	x_2	$\Delta H_m(\text{J mol}^{-1})$	$H_{123}^E(\text{J mol}^{-1})$
$x'_1/x'_2 = 0.9985; x'_1 = 0.4996; H_{12}^E = 1614 (\text{J mol}^{-1})$			
0.4449	0.4456	990	1167
0.3841	0.3847	543	916
0.3248	0.3254	287	852
0.2494	0.2497	-28	781
0.1843	0.1846	-379	640
0.1148	0.1149	-788	455
0.0493	0.0494	-1203	252
$x'_2/x'_3 = 0.2738; x'_2 = 0.2150; H_{23}^E = -580 (\text{J mol}^{-1})$			
0.0966	0.1943	747	223
0.1720	0.1779	1102	622
0.2979	0.1509	1363	956
0.4595	0.1161	1276	962
0.6398	0.0774	1022	813
0.7752	0.0483	678	548
0.9005	0.0214	312	25
$x'_2/x'_3 = 1.0263; x'_2 = 0.5243; H_{23}^E = -848 (\text{J mol}^{-1})$			
0.1690	0.4209	1125	420
0.3150	0.3469	1001	850
0.4671	0.2699	1410	958
0.5698	0.2179	1228	863
0.6026	0.2013	1177	840
0.8089	0.0968	623	461
0.8685	0.0668	422	310
$x'_2/x'_3 = 2.9897; x'_2 = 0.7494; H_{23}^E = -664 (\text{J mol}^{-1})$			
0.1210	0.6587	890	306
0.2617	0.5533	1330	840
0.4503	0.4119	1385	1020
0.5623	0.3280	1299	1008
0.7004	0.2245	967	768
0.7993	0.1504	718	585
0.8927	0.0804	392	321
$x'_1/x'_3 = 0.5363; x'_1 = 0.3491; H_{13}^E = 1415 (\text{J mol}^{-1})$			
0.3146	0.0984	-184	1092
0.2953	0.1543	-216	981
0.2448	0.2988	-262	730
0.1848	0.4706	-196	553
0.1193	0.6581	-208	325
0.1106	0.5831	-311	279
0.0647	0.8148	-66	196

This equation is assymetrical and needs some specification to identify component 1. Kohler⁹ proposed an equation for a ternary system of the following form:

$$H_{123}^E = (x_1 + x_2)^2 H_{12}^E + (x_1 + x_3)^2 H_{13}^E + (x_2 + x_3)^2 H_{23}^E \quad (5)$$

which is symmetrical in that all three binary systems are treated identically. In this

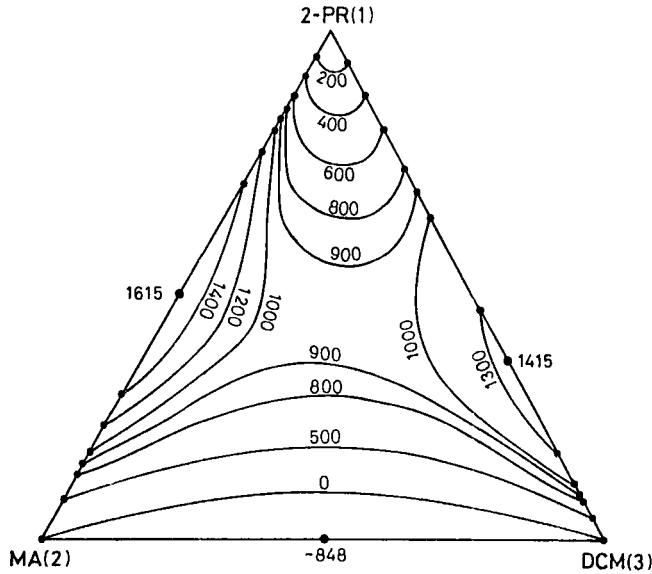


Figure 2 Lines of constant excess molar enthalpies for the propan-2-ol(1) + methylacetate(2) + dichloromethane(3) system at 298.15 K.

equation H_{ij}^E refers to the excess molar enthalpies of x_i^0 , x_j^0 where $x_i^0 = 1 - x_j^0 = x_i/(x_i + x_j)$.

Radojkovic *et al.*¹⁰ considered an expression of the form:

$$H_{123}^E = H_{12}^E + H_{13}^E + H_{23}^E \quad (6)$$

where H_{12}^E , H_{13}^E and H_{23}^E represents the excess enthalpies with x_1 , and x_2 and x_3 mole fractions of the ternary systems calculated from Eqn. [2] using the coefficients of Table 1.

Cibulka¹¹ proposed the equation:

$$H_{123}^E = H_{12}^E + H_{13}^E + H_{23}^E + x_1 x_2 x_3 (A + Bx_1 + Cx_2) \quad (7)$$

where A , B and C are parameters characteristic of the mixtures evaluated by fitting this equation by the least squares method with a standard deviation defined as in Eqn. (3). The parameters obtained are $A = 10662$, $B = -44018$ and $C = 4745$.

Singh *et al.*¹² proposed an equation of the following form

$$H_{123}^E = H_{12}^E + H_{13}^E + H_{23}^E + x_1 x_2 x_3 [A + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)] \quad (8)$$

The parameters obtained are $A = -807$, $B = -22957$ and $C = -323282$. These two equations are modifications of the equation of Radojkovic *et al.*¹⁰ like Nagata

and Tamura equation¹³:

$$H_{123}^E = H_{12}^E + H_{13}^E + H_{23}^E + x_1 x_2 x_3 \Delta_{123} \quad (9)$$

where

$$\frac{\Delta_{123}}{RT} = \sum_{j=1}^{\sigma} b_j (1 - 2x_j)^{j-1} \quad (10)$$

Equation (9) was used by Van Ness and his coworkers^{14,15} in correlating their excess molar enthalpy results. The coefficients of Eqn. (10) together with the standard deviations are:

$$b_1 = -0.021226; \quad b_2 = -10.3954; \quad b_3 = 0.620608; \quad b_4 = 81.2468;$$

$$b_5 = -44.4992; \quad b_6 = -78.2714 \text{ and } \sigma = 142.$$

Table 3 shows the standard deviation calculated by using all the above mentioned equations for H_{123}^E . This standard deviation *SD* is defined as:

$$SD = \left(\sum \frac{(H_{\text{exp}}^E - H_{\text{cal}}^E)^2}{n} \right)^{1/2} \quad (11)$$

Eqn. (9) shows the best agreement with the experimental data.

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

$$\frac{\partial}{\partial T} \left(\frac{G_{ij}^E}{T} \right) = - \frac{H_{ij}^E}{T^2} \quad (12)$$

Equation (12) in conjunction with the UNIFAC model¹⁴ yields the following expression for the enthalpy of mixing:

$$H_{ij}^E = \sum x_i \Delta \bar{H}_i \quad (13)$$

Table 3 Standard deviations for the propan-2-ol(1) + methylacetate (2) + dichloromethane(3) system at 298.15 K.

Equation	$SD(H_{123}^E) (J \text{ mol}^{-1})$	Equation	$SD(H_{123}^E) (J \text{ mol}^{-1})$
(4)	125	(7)	90
(5)	173	(8)	164
(6)	181	(9)	5

where

$$\Delta \bar{H}_i = \sum v_k^{(i)} (H_k - H_k^{(i)}) \quad (14)$$

Here, $v_k^{(i)}$ 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 derivatives of Γ_k respect to temperature is:

$$\frac{H_k}{RT^2} = Q_k \left[\frac{\sum_m \vartheta_m \psi'_{mk}}{\sum_m \vartheta_m \psi_{mk}} + \sum_m \left(\frac{\vartheta_m \psi'_{km}}{\sum_n \vartheta_n \psi_{nm}} - \frac{\vartheta_m \psi_{km} \sum_n \vartheta_n \psi'_{nm}}{(\sum_n \vartheta_n \psi_{nm})^2} \right) \right] \quad (15)$$

where θ_m is the area fraction of group m in the mixtures:

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (16)$$

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

$$X_m = \frac{\sum_i x_i v_{mi}}{\sum_k x_i \sum_k v_{ki}} \quad (17)$$

and ψ_{mn} is:

$$\psi_{mn} = \exp(Z a_{mn} / 2T) \quad (18)$$

$$\psi'_{mn} = \frac{\partial}{\partial T} (\psi_{mn}) \quad (19)$$

and

$$Z = Z(T) = 35.2 - 0.12772T + 0.00014T^2 \quad (20)$$

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

The parameters used¹⁶ are summarized in Table 4. The values for H_{12}^E and H_{23}^E are shown in Figure 1 with an average absolute error defined as:

$$AAE = \frac{1}{n} \sum \left| \frac{(H_{\text{exp}}^E - H_{\text{cal}}^E)}{H_{\text{exp}}^E} \right| \times 100 \quad (21)$$

with 12% for 2-PR(1) + MA(2) system and 16% for MA(2) + DCM(3) system. The interaction parameters between OH and CH_2Cl_2 are not available. Using parameters from Larsen *et al.*¹⁷, the values obtained for our systems including ternary systems presents great errors.

Table 4 Group interaction parameters and Q_k values.

$m \setminus n$	Q_k	CH_3	CH_2	OH	$COOC$	CH_2Cl_2
CH_3	0.848	0.0	0.0	545.77	44.98	26.60
CH_2	0.540	0.0	0.0	545.77	44.98	26.60
OH	1.200	99.57	99.57	0.0	249.07	na
$COOC$	1.728	114.1	114.1	291.46	0.0	1315.1
CH_2Cl_2	1.988	-0.39	-0.39	na	-5.53	0.0

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