Excess Molar Enthalpies for Butylamine + 1,4-Dioxane + Carbon Tetrachloride at 298.15 K

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Excess molar enthalpies for the ternary system butylamine + 1,4-dioxane + carbon tetrachloride at 298.15 K are reported along with corresponding data for two constituent binary mixtures. Different expressions are used to predict excess enthalpies for the ternary system from the corresponding binary results.

Introduction

In recent papers (Ruiz Holgado et al., 1992; Acevedo et al., 1991) from our laboratory, we have described measurements of excess properties of some ternary systems.

This paper reports the excess molar enthalpies of the butylamine (1) + 1,4-dioxane (2) + carbon tetrachloride (3) system at 298.15 K. In a previous paper, we have published excess molar enthalpy (H^E) values for the binary system butylamine (1) + 1,4-idoxane (2) which were modified by new measurements (Acevedo et al., 1991). The 1,4-dioxane (2) + carbon tetrachloride (3) system was studied by Murakami and Benson (1969). In this paper, we include the values obtained for butylamine (1) + 1,4-idoxane (2) and butylamine (1) + carbon tetrachloride (3), and they are shown in Table 1.

Assuming that interactions in a ternary mixture are closely dependent on the interactions in binary systems, we consider the application of empirical correlations.

Experimental Section

The methods used in our laboratory have been previously described (Acevedo et al., 1991). The adiabatic calorimeter described by Loiseleur (1965) was used with some modifications such as the use of one dewar in a isopor block. Temperatures were measured with a Beckmann thermometer with an error of ±0.001 °C. The error in enthalpies was generally within ±7 J mol^{-1}. The performance of the calorimeter was checked by measuring H^E of the test mixture benzene + cyclohexane. All weighings were made on a H315 Mettler balance with an error of ±10^{-7} kg.

The substances were purified as follows: butylamine (Fluka, puriss) was dried over potassium hydroxide for three days, refluxed for 2 h, and distilled and the middle colorless fraction collected. 1,4-Dioxane (Baker, puriss) was distilled over sodium metal under reduced pressure and the middle colorless fraction collected. Carbon tetrachloride (Merck, puriss) was used without further purification. Caution was taken to prevent evaporation.

Each run was performed by adding one component to a binary mixture of the other two. A ternary system was regarded as a pseudobinary system made up of one binary mixture and the third component. One mole of the ternary system was prepared by mixing, for example, $1 - x_3$ of the initial binary mixture (1 + 2) and x_3 of component (3), by mass. Then, the values of H^E_{123} are given by (Nagata and Tamura, 1988)

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

where H_m is the observed molar excess enthalpy for the pseudobinary mixture (1 + 2) + component 3 and H^E_{12} is the the excess molar enthalpy of the butylamine (1) + 1,4-dioxane (2) system at x_1' and x_2' compositions. The same procedure was followed with 1,4-dioxane (2) + carbon tetrachloride (3) at compositions x_2' and x_3' and butylamine (1) + carbon tetrachloride (3) at compositions x_1' and x_3', respectively.

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Table 1. Excess Enthalpies for Binary Mixtures at 298.15 K

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
Butylamine (1) + 1,4-Dioxane (2)			
0.1002	190	0.5962	502
0.1987	320	0.6963	425
0.2937	408	0.7949	304
0.3970	488	0.8980	200
0.4967	520		
Butylamine (1) + Carbon Tetrachloride (3)			
0.0805	−233	0.6357	−3600
0.1473	−503	0.7099	−4232
0.2518	−1020	0.7762	−4616
0.3385	−1445	0.8544	−4460
0.4099	−1880	0.9151	−3590
0.4707	−2208	0.9521	−2500
0.5418	−2792		

Results and Discussion

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

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

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

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

The values adopted for the coefficients and the standard

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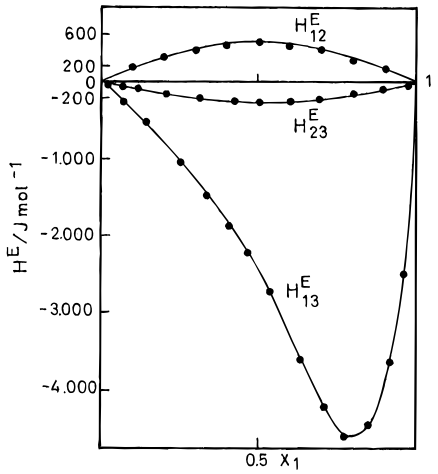

Figure 1. Excess enthalpy of binary mixtures. Continuous curves were calculated from eq 2. Key: H^E_{12}, butylamine (1) + 1,4-dioxane (2); H^E_{13}, butylamine (1) + carbon tetrachloride (3); H^E_{23}, 1,4-dioxane (2) + carbon tetrachloride (3) (all at 298.15 K).

Table 2. Coefficients a_k from Eq 2 and Standard Deviations for the Binary Systems at 298.15 K

a_1	a_2	a_3	a_4	a_5	a_6	$\sigma(H^E)$/(J mol^{-1})
Butylamine (1) + 1,4-Dioxane (2)						
2093	230	−1000	−1740	1680	2300	5
Butylamine (1) + Carbon Tetrachloride (3)						
−9780	−15040	−18200	−12400	−4900	−5200	36
1,4-Dioxane (2) + Carbon Tetrachloride (3)						
−1002	−62	156	−42			0.3

error of the estimate associated with the use of eq 3 are summarized in Table 2.

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

Table 3 shows the experimental values of H^E_{123} for the butylamine (1) + 1,4-dioxane (2) + carbon tetrachloride (3) system at 298.15 K.

Figure 2 shows curves of constant excess molar enthalpies for the ternary system. The curves are obtained by plotting H^E_{123} as a function of the molar fraction of the added component. Each one of the curves corresponds to a constant relation of the molar fractions of the other two. With these graphics it is possible to determine the values of H^E_{123} of selected ternary mixtures.

Figure 1 shows positive values of H^E for the butylamine (1) + 1,4-idoxane (2) system with a maximum of approximately 520 J mol^{-1} at $x_1 = 0.4967$. The other two systems are exothermic. For 1,4-dioxane (2) + carbon tetrachloride (3) the maximum is −250 J mol^{-1} at $x_2 = 0.5098$, and for butylamine (1) + carbon tetrachloride (3) it is −4616 J mol^{-1} at $x_1 = 0.7762$. These large values of H^E in this system indicate specific interactions, which is corroborated by the negative values of excess molar volumes (Acevedo et al., 1988). This implies a possible complex formation between both chemical species.

Figure 2 shows exothermic effects, except with solutions with a small molar fraction of carbon tetrachloride, where there is an influence of the endothermic effect of the butylamine (1) + 1,4-dioxane (2) system.

If the behavior of a ternary system is assumed to be closely dependent on the interaction of the constituent binary mixtures, it should be possible to evaluate H^E_{123} of nonelectrolytes considering the corresponding enthalpies for the binary systems.

Table 3. Experimental Excess Molar Enthalpies for the Butylamine (1) + 1,4-Dioxane (2) + Carbon Tetrachloride (3) System at 298.15 K

x_1	x_2	H^E_m/(J mol^{-1})	H^E_{123}/(J mol^{-1})
$x_1'/x_2' = 0.1151$; $x_1' = 0.1032$; $H^E_{12} = 148$ J mol^{-1}			
0.0914	0.7951	−430	−299
0.0795	0.6909	−614	−500
0.0712	0.6192	−653	−551
0.0575	0.4994	−655	−573
0.0438	0.3807	−592	−520
0.0329	0.2860	−488	−441
0.0197	0.1711	−320	−292
$x_1'/x_2' = 0.5337$; $x_1' = 0.3480$; $H^E_{12} = 356$ J mol^{-1}			
0.3102	0.5808	−1022	−705
0.2640	0.4945	−1606	−1336
0.2213	0.4144	−1879	−1653
0.1702	0.3186	−1764	−1590
0.1147	0.2149	−1159	−1042
0.0703	0.1327	−578	−506
0.0322	0.0602	−180	−147
$x_1'/x_2' = 1.4691$; $x_1' = 0.5950$; $H^E_{12} = 381$ J mol^{-1}			
0.5235	0.3562	−1700	−1365
0.4430	0.3015	−2588	−2304
0.3797	0.2585	−2926	−2683
0.2854	0.1943	−2542	−2350
0.1977	0.1346	−1537	−1410
0.1305	0.0889	−844	−760
0.0596	0.0405	−272	−234
$x_1'/x_2' = 9.1729$; $x_1' = 0.9017$; $H^E_{12} = 134$ J mol^{-1}			
0.7797	0.0850	−3636	−3520
0.7014	0.0765	−3852	−3748
0.5513	0.0601	−3578	−3496
0.4954	0.0540	−3236	−3162
0.3792	0.0414	−2231	−2175
0.2694	0.0294	−1346	−1306
0.1718	0.0187	−774	−748
$x_2'/x_3' = 0.3583$; $x_2' = 0.2638$; $H^E_{23} = -181$ J mol^{-1}			
0.1299	0.2296	−1041	−1198
0.2943	0.1862	−2228	−2356
0.4313	0.1500	−3067	−3170
0.4980	0.1323	−3311	−3402
0.6663	0.0880	−3590	−3650
0.7760	0.0591	−3484	−3525
0.8884	0.0294	−2996	−3016
$x_2'/x_3' = 0.9940$; $x_2' = 0.4985$; $H^E_{23} = -250$ J mol^{-1}			
0.1252	0.4361	−777	−996
0.3100	0.3440	−1794	−1966
0.4434	0.2775	−2500	−2639
0.5012	0.2481	−2778	−2903
0.6897	0.1547	−3328	−3406
0.6430	0.0782	−2826	−2865
0.9099	0.0448	−2074	−2097
$x_2'/x_3' = 3.0225$; $x_2' = 0.7514$; $H^E_{23} = -187$ J mol^{-1}			
0.1298	0.6539	−535	−698
0.3346	0.5000	−1220	−1344
0.4261	0.4312	−1463	−1570
0.5103	0.3680	−1661	−1753
0.6288	0.2789	−1849	−1918
0.7840	0.1623	−1586	−1626
0.9005	0.0748	−976	−995

Tsao and Smith (Acree, 1984) suggested an expression which takes the following form:

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

H^E_{ij} is the enthalpy for binary systems at compositions x_i^o, x_j^o where $x_i^o = x_i$ for the systems 1 + 2 and 1 + 3, while $x_2^o = x_2/(x_2 + x_3)$ for the 2 + 3 system.

The symmetric Kohler equation (Acree, 1984) is

$$H^E = (x_1 + x_2)^2 H^E_{12} + (x_1 + x_3)^2 H^E_{12} + (x_2 + x_3)^2 H^E_{23} \quad (5)$$

where H^E_{ij} refers to the excess enthalpies of the binary

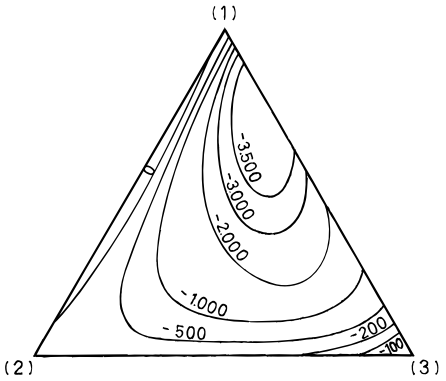

Figure 2. Lines of constant excess enthalpy for the butylamine (1) + 1,4-dioxane (2) + carbon tetrachloride (3) system at 298.15 K.

mixtures at a composition x_i^o, x_j^o such that, $x_i^o = 1 - x_j^o = x_i/(x_i + x_j)$.

Radojkovič et al. (1977) considered an expression proposed by Redlich and Kister of the form

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

where H_{12}^E*, H_{23}^E*, and H_{13}^E* represent the excess molar enthalpies and x_1, x_2, and x_3 (mole fractions of the ternary system) were calculated from eq 2 by using the coefficients of Table 2.

Jacob and Fitzner (Acree, 1984) suggested an expression for estimating properties of a ternary mixture of the form

$$H_{123}^E = \frac{x_1x_2H_{12}^E}{(x_1 + x_3/2)(x_2 + x_3/2)} + \frac{x_1x_3H_{13}^E}{(x_1 + x_2/2)(x_3 + x_2/2)} + \frac{x_2x_3H_{23}^E}{(x_2 + x_1/2)(x_3 + x_1/2)} \quad (7)$$

H_{ij}^E is the excess enthalpy of the binary mixture at compositions x_i^o, x_j^o such that $x_i^o - x_j^o = x_i - x_j$.

Cibulka (1982) proposed the following equation:

$$H_{123}^E = H_{12}^E* + H_{23}^E* + H_{13}^E* + x_1x_2x_3(A + Bx_1 + Cx_2) \quad (8)$$

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 eq 3 where $n = 1$. The parameters obtained are $A = -48\,055$, $B = 5145$, and $C = 36\,438$.

Singh et al. (1984) proposed an equation of the following form:

$$H_{123}^E = H_{12}^E* + H_{23}^E* + H_{13}^E* + x_1x_2x_3(A + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2) \quad (9)$$

The parameters obtained are $A = -32\,009$, $B = 51\,398$, and $C = -409\,865$.

These two equations are modifications of eq 6. Nagata and Tamura (1988) proposed the equation

$$H_{123}^E = H_{12}^E* + H_{23}^E + H_{13}^E* + x_1x_2x_3\Delta_{123} \quad (10)$$

where

$$\Delta_{123}/RT = \sum_{j=1}^{6} b_j(1 - 2x_3)^{j-1} \quad (11)$$

Equation 10 was used by Van Ness and his co-workers (Morris et al., 1975; Shatas et al., 1975) in correlating their excess molar enthalpy results. The coefficients of eq 11 are $b_1 = -14.989$, $b_2 = 1.313$, and $b_3 = 6.903$.

Table 4. Enthalpy Standard Deviations for the Butylamine (1) + 1,4-Dioxane (2) + Carbon Tetrachloride (3) System at 298.15 K

eq	DM	eq	DM
4	976	8	213
5	671	9	208
6	726	10	232
7	726		

Table 4 shows the standard deviations by using the above-mentioned equations for H_{123}^E. Equation 9 shows the best agreement with the experimental data. Obviously, the models using ternary parameters are superior to the predictive one (not containing ternary parameters). The standard deviation is defined as

$$DM = \left[\frac{\sum(H_{exp}^E - H_{cal}^E)^2}{n}\right]^{1/2} \quad (12)$$

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