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Excess Molar Enthalpies of (Water + Monoalkanolamine) Mixtures at 298.15 K and 308.15 K

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Excess enthalpies for (water + monoethylethanolamine), (water + diethylethanolamine), and (water + *n*-propylethanolamine) have been measured at $T = 298.15$ K and for (water + 2-amino-2-methyl-1-propanol) at 308.15 K. Results of these measurements show some structure dependence on the excess molar enthalpies of these aqueous binary mixtures and also on the partial excess enthalpies of alkanolamines at infinite dilution in water.

Introduction

Alkanolamines and their mixtures with water are used in different chemical industries as described by Astarita et al. (1983) and Kirk-Othmer (1992). Physical properties of these compounds and their mixtures with water are needed. Volumetric properties of these aqueous solutions have been studied by Maham et al. (1994, 1995) and Zhang et al. (1995), and transport properties have been measured by Teng et al. (1994). Heat capacities of fourteen pure alkanolamines have been reported by Maham et al. (1997). Excess molar enthalpies and volumes of (water + monoethanolamine) have been given by Touhara et al. (1982); Maham et al. (1997) have also reported excess molar enthalpies of (water + polyethanolamine).

This is a continuation of our investigation on the physical and thermodynamic properties of (water + alkanolamine) mixtures. Here we report excess molar enthalpies of (water + monoethylethanolamine), (water + diethylethanolamine), and (water + *n*-propylethanolamine) at 298.15 K and (water + 2-amino-2-methyl-1-propanol) at 308.15 K.

Experimental Procedure and Technique

The alkanolamines used were as follows: monoethylethanolamine, $(C_2H_5)(NH)C_2H_4OH$, (MEEA), is from Aldrich Chemical Company with a purity of 99%; diethylethanolamine, $(C_2H_5)_2(N)C_2H_4OH$, (DEEA), is from Fluka Chemical Company, with a purity of >99%; *n*-propylethanolamine, $(C_3H_7)(NH)C_2H_4OH$, (*n*-PEA), is from Aldrich Chemical Company, with a purity of 97.0%, and 2-amino-2-methyl-1-propanol, $(CH_3)_2C(NH_2)CH_2OH$, (AMP) is from Fluka Chemical Company with a purity of >99%. Each of these was used as received, after confirmatory analysis by titration with standard hydrochloric acid. Water was nanopure water. All the mole fractions are determined by weighing (an accuracy of 1×10^{-4}), with care being taken to minimize exposure to air (carbon dioxide). The melting point of AMP is 30 to 31 °C. For this reason, the excess enthalpies of (H_2O + AMP) mixtures were studied at 35 °C (308.15 K).

Table 1. Excess Enthalpies of (Water + MEEA) and (Water + DEEA) at 298.15 K[a]

x_{MEEA}	$H^E/J\cdot mol^{-1}$	x_{DEEA}	$H^E/J\cdot mol^{-1}$
0.0296	−557	0.0472	−966
0.0430	−784	0.0681	−1309
0.0763	−1228	0.0982	−1654
0.1020	−1393	0.1339	−1924
0.1408	−1797	0.1393	−1978
0.2107	−2123	0.2272	−2382
0.2590	−2260	0.2648	−2520
0.3543	−2350	0.3069	−2540
0.4227	−2429	0.3672	−2650
0.5116	−2314	0.4554	−2615
0.5854	−2087	0.4986	−2554
0.6533	−1908	0.5515	−2398
0.7002	−1543	0.6089	−2191
0.8021	−1185	0.6928	−1828
0.8533	−793	0.7544	−1463
0.9022	−598	0.8006	−1208
		0.8500	−895
		0.9011	−530

[a] Compositions are specified by mole fractions x_{MEEA} and x_{DEEA}, where MEEA and DEEA represent monoethylethanolamine and diethylethanolamine, respectively.

All calorimetric measurements were made with a Setaram C-80, which is a heat-flow calorimeter of the Tian-Calvet type (Setaram, France). The experimental procedures are given by Maham et al. (1997). The uncertainties in the reported molar excess enthalpies (H^E) are approximately 2%. The actual temperature of each measurement was within ±0.08 K of the stated temperature (298.15 and 308.15 K).

Results

Results of our calorimetric measurements of excess molar enthalpies for (H_2O + MEEA) and (H_2O + DEEA) mixtures are reported in Table 1 and (H_2O + *n*-PEA) and (H_2O + AMP) mixtures in Table 2. The excess molar enthalpies of (H_2O + AMP) systems are at 308.15 K. The (H_2O + *n*-PEA) mixtures are not completely miscible (*n*-PEA is immiscible at ($0.037 < x_2 < 0.1228$). The composition dependence of the excess molar enthalpies of monoalkyl derivatives (MMEA+H_2O) (Touhara et al., 1982), (MEEA + H_2O), and (*n*-PEA+H_2O) with (MEA+H_2O) (Touhara et

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Table 2. Excess Enthalpies of (Water + *n*-PEA) at 298.15 K and (Water + AMP) at 308.15 K[a]

$x_{n-\mathrm{PEA}}$	H^E/J·mol^{-1}	x_{AMP}	H^E/J·mol^{-1}
0.0146	−263	0.0514	−658
0.0201	−336	0.0939	−1154
0.0249	−425	0.1486	−1463
0.0292	−488	0.1967	−1667
0.2008	−1542	0.2502	−1761
0.2365	−1661	0.3157	−1858
0.3487	−1907	0.3300	−1861
0.4002	−1969	0.4157	−1922
0.4543	−1965	0.4254	−1916
0.4943	−1940	0.5183	−1783
0.5781	−1821	0.6017	−1632
0.6521	−1602	0.6135	−1614
0.7028	−1436	0.7258	−1305
0.8004	−1027	0.8032	−1008
0.8518	−787	0.8518	−765
0.9014	−516	0.9039	−501
0.9499	−255		

[a] Compositions are specified by mole fractions $x_{n-\mathrm{PEA}}$ and x_{AMP}, where *n*-PEA and AMP represent *n*-propylethanolamine and 2-amino-2-methyl-1-propanol, respectively.

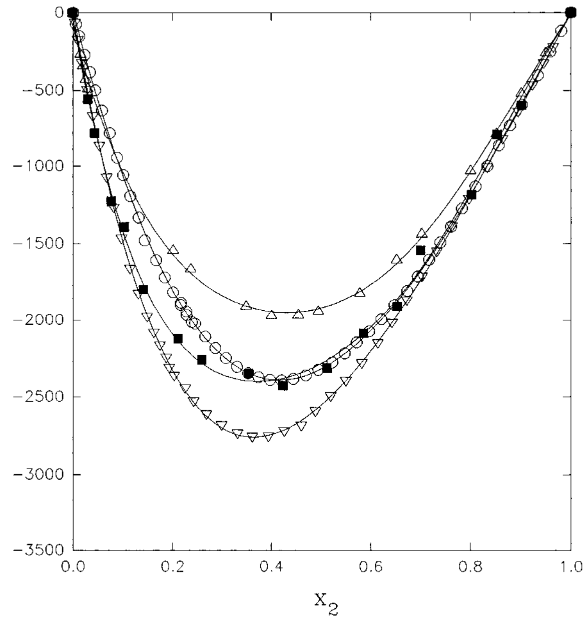

Figure 1. Excess molar enthalpies of (○) (H_2O + MEA) and (▽) (H_2O + MMEA), both studied by Touhara et al. (1982), and (■) [H_2O (1) + MEEA (2)] and (△) [H_2O (1) + *n*-PEA (2)] in this work at 298.15 K.

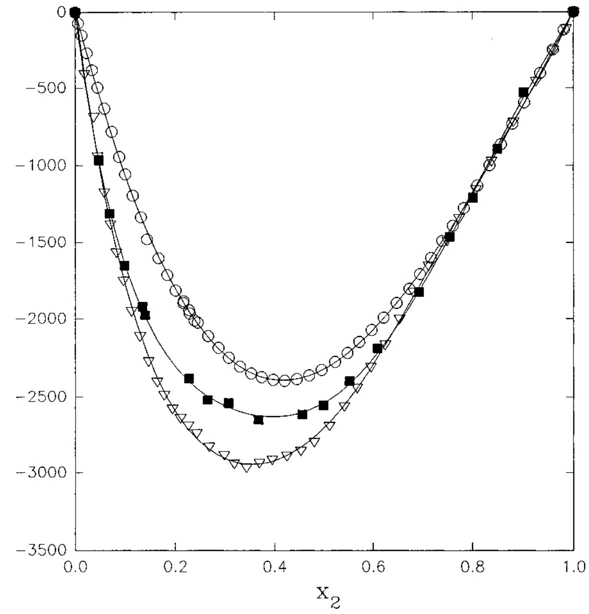

Figure 2. Excess molar enthalpies of (○) [H_2O (1) + MEA (2)], (▽) [H_2O (1) + DMEA (2)], both studied by Touhara et al. (1982), and (■) [H_2O (1) + DEEA (2)] in this work at 298.15 K.

al., 1982) mixtures is given in Figure 1. The same composition dependence for dialkyl derivatives (DMEA + H_2O) (Touhara et al., 1981) and (DEEA + H_2O) with (MEA + H_2O) (Touhara et al., 1982) mixtures is given in Figure 2. In both Figures 1 and 2, the position of the minimum becomes more negative by adding one or two methyl group to the nitrogen atom but its position rises for ethyl and propyl groups. Figure 3 shows this composition dependence of the minimum of excess molar enthalpies for mono and dialkyl derivatives of alkanolamines with water at 298.15 K. The excess molar enthalpy was correlated by the Redlich−Kister equation:

$$H^E = x_2(1 - x_2) \sum A_n (1 - 2x_2)^{n-1} \quad (1)$$

A_n values for all four binary systems are given in Table 3. Another technique for fitting is given by Davis (1983) where the whole range of concentrations is divided into three or four different zones (fragmental fitting).

Partial molar enthalpies are obtained by differentiation of eq 1

$$H_1 = x_2^{\,2}\sum A_n(1 - 2x_2)^{n-1} + 2x_2^{\,2}(1 - x_2)\sum A_n(n - 1)(1 - 2x_2)^{n-2} \quad (2)$$

and

$$H_2 = (1 - x_2)^2\sum A_n(1 - 2x_2)^{n-1} - 2x_2(1 - x_2)^2\sum (n - 1)A_n(1 - 2x_2)^{n-2} \quad (3)$$

The partial molar enthalpies of water at infinite dilution ($x_1 = 0$) in alkanolamine (H_1^∞), and the partial molar enthalpies of alkanolamine at infinite dilution ($x_2 = 0$) in water (H_2^∞) are given by:

$$H_1^\infty = \sum A_n(-1)^{n-1} \quad (4)$$

and

$$H_2^\infty = \sum A_n \quad (5)$$

in which H_1^∞ and H_2^∞ are used to emphasize that these equations represent the molar enthalpy of solution of alkanolamine (at infinite dilution) in water and the molar enthalpy of solution of water (at infinite dilution) in alkanolamine, respectively. Maham et al. (1997) obtained the partial molar enthalpies at infinite dilution in water for monoethanolamine, diethanolamine, methyldiethanolamine, and triethanolamine in water by using eq 5. Here we have used the same equation to obtain the partial molar enthalpies of monomethylethanolamine, diethylethanolamine, *n*-propylethanolamine, and 2-amino-2-methyl-1-propanol at infinite dilution in water, and they are given in Table 4.

Conclusions

From the results of Maham et al. (1997) and Touhara et al. (1982) and the present work, we conclude that the presence of an alkyl group (on the nitrogen atom of alkanolamine) is an important factor affecting the excess molar properties (enthalpy and volume) of (water + al-

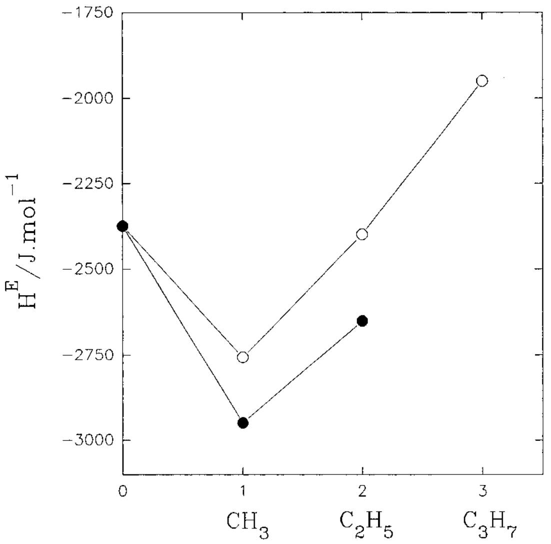

Figure 3. Variation of the minimum of the excess enthalpy with the size of alkyl groups (methyl, ethyl, and *n*-propyl) for (alkanolamine + H_2O) mixtures at 298.15 K: ○, (monoalkylethanolamine + H_2O); ●, (dialkylethanolamine + H_2O) mixtures.

Table 3. Redlich−Kister Coefficients for (H_2O + MEEA), (H_2O + DEEA), and (H_2O + *n*-PEA) at 298.15 K and (H_2O + AMP) at 308.15 K

A_1 A_6	A_2	A_3	A_4	A_5
		H_2O + MEEA		
−9302.0	−3634.0	−26.1	−3504.7	−4977.4
		H_2O + DEEA		
−10116.2 −3535.4	−3946.5	−1052.6	−3634	−3510.5
		H_2O + *n*-PEA[a]		
−7778.4 −5472.1	−2030.7	1068.5	26.1	−5295.7
		H_2O + AMP (at 308.15 K)		
−7271.6	−2472.5	−2975.3	−2650.7	

[a] These values are for the miscible area of ($0.2008 < x_{n-\mathrm{PEA}} < 0.9499$).

kanolamine) mixtures. From Touhara et al. (1982), one may observe the effect of methyl group of V^E and H^E values of (water + alkanolamine) mixtures. Both excess quantities increase with the presence of one or two methyl groups on the nitrogen atom of alkanolamine. In the case of ethyl derivatives, this effect is less important compared with methyl derivatives. This could be related to the size of the alkyl groups. We have seen this in the case of the excess molar volume of (water + diethanolamine) mixtures where V^E increases with increasing size of the alkyl group. We are continuing to study the V^E and H^E of (water + alkanolamine) mixtures with higher alkyl groups. This will give us a better understanding of the effect of the alkyl groups on the excess properties and on the partial molar volume and enthalpy.

Table 4. Enthalpies of Water in Infinite Dilution in Alkanolamines (H_1^∞) and Enthalpies of Alkanolamines at Infinite Dilution in Water (H_2^∞) at 298.15 K[a]

alkanolamines	H_1^∞/kJ·mol^{-1}	H_2^∞/kJ·mol^{-1}
AMP	−5.1	−15.4
MEEA	−7.2	−21.4
DEEA	−6.2	−25.8
n-PEA	−5.4	−19.5

[a] AMP values are at 308.15 K.

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