# Excess Molar Enthalpies of (Water + Alkanolamine) Systems and Some Thermodynamic Calculations

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We have made calorimetric measurements of enthalpies of mixing of (water + monoethanolamine), (water + diethanolamine), and (water + triethanolamine) at $T = 298.15$ K and of (water + methyldiethanolamine) at $T = 298.15$ and 313.15 K. Results of these measurements have been used in some thermodynamic calculations to illustrate general principles that are applicable to many systems of mixed liquids.

## Introduction

Several (water + alkanolamine) systems are used for removal of acidic gases such as carbon dioxide and hydrogen sulfide from gas streams in the natural gas and petroleum industries and are of increasing importance in treating streams in the chemical production industries. Knowledge of various properties (enthalpies, heat capacities, viscosities, ionization constants) is required for engineering design and subsequent operations, as summarized by Astarita et al. (1983) and Kirk-Othmer (1992).

In addition to the well-established industrial uses of experimental data for these completely miscible (water + alkanolamine) systems, there is general scientific interest in using some of these same kinds of experimental data in combination with theories or mathematical models to improve our understanding of molecular interactions in nonideal liquid systems.

The purpose of the research described here has been to obtain useful enthalpies on mixing (excess enthalpies) of some (water + alkanolamine) systems and to use these enthalpies for thermodynamic calculations that illustrate some general principles.

Reports of earlier research that provide background for the research to be described here include the following:

Touhara et al. (1982) have measured vapor pressures (leading to excess Gibbs energies), densities (leading to excess volumes), and enthalpies of mixing for three (water + alkanolamine) systems; their excellent results provide the basis for some of our thermodynamic calculations.

De Oliveira et al. (1980) reported excess Gibbs energies for three aqueous solutions of mono, di, and triethanolamines and also for binary mixtures of ethanolamines.

Zhang et al. (1995) have measured densities leading to the excess molar volumes of (water + dimethylethanolamine) and (water + diethylethanolamine) mixtures from 20 to 40 °C.

Maham et al. (1994, 1995) have measured densities (25−80 °C) for several (water + alkanolamine) systems and have reported thermodynamic calculations that are related to some of the calculations that are reported later in this paper.

Kim et al. (1987) have measured enthalpies of solution of small amounts of several alkanolamines in relatively large amounts of water containing dilute sodium hydroxide to prevent hydrolysis and reported $\Delta H°$ values for dissolving several alkanolamines in water, as represented by

$$\mathrm{Am(pure)} = \mathrm{Am(aq)} \qquad (1)$$

As part of this same research program, Kim et al. (1987) also measured enthalpies of solution of these same alkanolamines into dilute aqueous acid, which permitted evaluation of $\Delta H°$ values for ionization represented by

$$\mathrm{AmH^+(aq)} = \mathrm{Am(aq)} + \mathrm{H^+(aq)} \qquad (2)$$

Teng et al. (1994) have also measured viscosities of some (water + alkanolamine) systems at several temperatures.

Pagé et al. (1993) have made very accurate measurements of densities, heat capacities, and compressibilities of (water + monoethanolamine) systems at 10, 25, and 40 °C.

Chang et al. (1993) have made measurements leading to activity coefficients for several (water + alkanolamine) systems.

## Experimental Section

The alkanolamines used were as follows: monoethanolamine, $H_2N(C_2H_4OH)$ (MEA) (Fisher Scientific with a purity of 99%); diethanolamine, $HN(C_2H_4OH)_2$ (DEA) (Fisher Scientific, with a purity of 99%); triethanolamine, $N(C_2H_4OH)_3$ (TEA) (Fisher Scientific with a purity of 99.8%); methyldiethanolamine, $CH_3N(C_2H_4OH)_2$ (MDEA) (Aldrich, 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 were determined by weighing, (an accuracy of $1 \times 10^{-4}$) with care being taken to minimize exposure to air (carbon dioxide).

The melting point of diethanolamine is 301 K, which means that the solid is the stable form at 298.15 K. But diethanolamine is readily supercooled, and all of our calorimetric measurements were made with the liquid. Each of the other alkanolamines discussed here melts/freezes at $T < 298.15$ K and is a stable liquid at 298.15 K.

All calorimetric measurements were made with a Setaram C-80, which is a heat-flow calorimeter of the Tian-Calvet type (Setaram, France). Electrical calibration and testing of this calorimeter have been described by Xu (1990) and Xu and Hepler (1993). The cells are also from Setaram (mixing cells). These cells do have vapor spaces; however, the ethanolamines and water have much higher boiling points relative to the measurement temperatures. The two

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**Table 1. Excess Molar Enthalpies ($H^E$) (Water + DEA) and (Water + TEA) at 298.15 K[a]**

| $x_{DEA}$ | $H^E$/(J·mol$^{-1}$) | $x_{TEA}$ | $H^E$/(J·mol$^{-1}$) |
|---|---|---|---|
| 0.0529 | −678 | 0.0628 | −690 |
| 0.0609 | −768 | 0.0903 | −884 |
| 0.0947 | −1099 | 0.1494 | −1193 |
| 0.3009 | −2041 | 0.2347 | −1362 |
| 0.3388 | −2086 | 0.2989 | −1453 |
| 0.3703 | −2070 | 0.3480 | −1445 |
| 0.3971 | −2077 | 0.4284 | −1390 |
| 0.4962 | −1920 | 0.5009 | −1277 |
| 0.5869 | −1629 | 0.6053 | −1071 |
| 0.6615 | −1372 | 0.6909 | −895 |
| 0.7425 | −1097 | 0.7311 | −794 |
| 0.8362 | −712 | 0.7697 | −672 |
| 0.9180 | −355 | 0.7784 | −643 |
| | | 0.7802 | −610 |
| | | 0.8267 | −433 |
| | | 0.8393 | −383 |
| | | 0.8726 | −316 |

[a] Compositions are specified by mole fractions $x_{DEA}$ and $x_{TEA}$, where DEA and TEA represent diethanolamine and triethanolamine, respectively.

**Table 2. Excess Molar Enthalpies ($H^E$) of (Water + MDEA) at 298.15 K and 313.15 K[a]**

| 298.15 K | | 313.5 K | |
|---|---|---|---|
| $x_{MDEA}$ | $H^E$/(J·mol$^{-1}$) | $x_{MDEA}$ | $H^E$/(J·mol$^{-1}$) |
| 0.0310 | −559 | 0.0964 | −1379 |
| 0.0481 | −863 | 0.1413 | −1762 |
| 0.0916 | −1427 | 0.2238 | −2178 |
| 0.1475 | −1936 | 0.2703 | −2327 |
| 0.2082 | −2267 | 0.3468 | −2326 |
| 0.3105 | −2493 | 0.4274 | −2252 |
| 0.3794 | −2463 | 0.5151 | −1942 |
| 0.4792 | −2291 | 0.6360 | −1609 |
| 0.5349 | −2098 | 0.7412 | −1143 |
| 0.6377 | −1750 | 0.8177 | −838 |
| 0.6668 | −1471 | | |
| 0.7375 | −1226 | | |
| 0.7953 | −1022 | | |
| 0.8676 | −665 | | |
| 0.9009 | −432 | | |
| 0.9328 | −357 | | |

[a] Compositions are specified by the mole fractions ($x_{MDEA}$) of methyldiethanolamine.

compounds (water and alkanolamine) are kept inside the calorimeter before mixing until thermal equilibrium is established. Uncertainties for the molar excess enthalpies ($H^E$) are approximately 2% over the whole range of composition. The disadvantage of these cells is that the mole fraction cannot be accurately determined in the regions of $x_2 < 0.025$ and $x_2 > 0.975$. Actual temperatures of each measurement were within ±0.08 K of the stated temperatures (298.15 and 313.15 K).

## Results and Thermodynamic Calculations

Results of our calorimetric measurements of the excess enthalpies for (water + liquid alkanolamine) are reported in Table 1 for (water + diethanolamine) and (water + triethanolamine) at $T = 298.15$ K and in Table 2 for (water + methyldiethanolamine) at both $T = 298.15$ and $T = 313.15$ K. Posey (1996) has measured the excess molar enthalpy of (water + diethanolamine) and (water + methyldiethanolamine) at 25 and 69.4 °C and (water + monoethanolamine) at 69.4 °C. The results for the (water + methyldiethanolamine) system at 298.15 K have been compared with our results in Figure 1. His results show a large amount of scatter at concentrations near equimolar.

As mentioned earlier, Touhara et al. (1982) have made calorimetric measurements leading to $H^E$ values for (water + monoethanolamine) at $T = 298.15$ K. Because their $H^E$ values (for 52 mole fractions) are at least as accurate as our values, we do not report our results (for 13 mole fractions) for this system but emphasize that there is good (within 1%) agreement between the two sets of $H^E$ results.

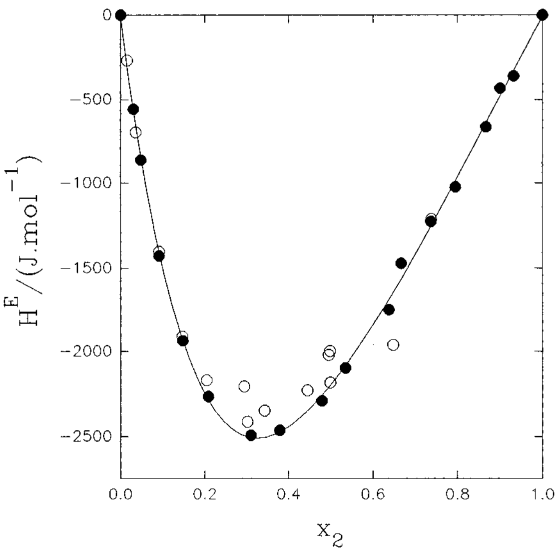

**Figure 1.** Excess enthalpies of binary mixtures of methyldiethanolamine and water at 298.15 K: (○) Posey, (●) this work.

Background for the following thermodynamic calculations is provided in three books by Van Ness and Abbott (1982), Acree (1984), and Wood and Battino (1990) and a review by Davis (1993). To start, we note that differentiation of $H^E$ with respect to $x_2$ and considerable algebraic manipulation leads to the following:

$$H_2 - H_2{}^* = H^E + (1 - x_2)(\partial H^E/\partial x_2)_{P,T} \tag{3}$$

$$H_1 - H_1{}^* = H^E - x_2(\partial H^E/\partial x_2)_{P,T} \tag{4}$$

In these equations $H_2$ and $H_1$ represent the partial molar enthalpies of compounds 2 and 1 while $H_2{}^*$ and $H_1{}^*$ represent the molar enthalpies of pure components 2 and 1.

A common approach to carrying out the differentiations required for use of eqs 3 and 4 is to fit the Redlich−Kister equation

$$H^E/\mathrm{J{\cdot}mol^{-1}} = x_2(1 - x_2)\sum A_n(1 - 2x_2)^{n-1} \tag{5}$$

to the experimental results ($H^E$, $x_2$). Redlich−Kister coefficients (eq 5) are given in Table 3. We have recalculated also Redlich−Kister coefficients for the (water + ethanolamine), (water + monomethylethanolamine), and (water + dimethylethanolamine) mixtures from Touhara et al. (1982). All the fitting polynomials were examined by the $F$-test [Shoemaker et al. (1989) and Bevington (1969)]. This is a test of goodness of fitting of the power of a polynomial.

Following methods already described by Van Ness and Abbott (1982), Acree (1984), Wood and Battino (1990), and Davis (1993), differentiation of eq 5 and insertion of the result in eqs 3 and 4 lead to a long equation for ($H_2 - H_2{}^*$) and another long equation for ($H_1 - H_1{}^*$). We do not write these equations here, since the same long equations (for volumes instead of enthalpies) have been provided elsewhere by Maham et al. (1994, 1995). Our focus here will be on the values of these quantities at $x_2 = 1$ (infinitely dilute water in alkanolamine). Setting $x_2 = 0$ in one equation and then $x_2 = 1$ in the other equation referred to above leads to

**Table 3. Redlich−Kister Coefficients for (Water + Alkanolamine) Systems at 298.15 K**[a]

| $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ |
|---|---|---|---|---|
| | | MEA + $H_2O$[b] | | |
| −9260.7 | −3395.8 | −601.3 | 491.0 | 977.6 |
| | | MMEA + $H_2O$[b] | | |
| −10170.7 | −5803.9 | −2813.2 | −438.2 | 832.7 |
| | | DMEA + $H_2O_b$ | | |
| −10684.1 | −6605.9 | −2907.1 | −2314.7 | −1579.4 |
| | | DEA + $H_2O$ | | |
| −7556.2 | −4717.3 | −1912.9 | −343.0 | |
| | | TEA + $H_2O$ | | |
| −5158.2 | −2746.8 | −2026.1 | −3772.8 | |
| | | MDEA + $H_2O$ | | |
| −8735.8 | −6219.9 | −3950.1 | −1111.0 | |
| | | MDEA + $H_2O$ (313.15 K) | | |
| −8172.8 | −6140.1 | −3377.5 | | |

[a] MEA, DEA, TEA, and MDEA represent monoethanolamine, diethanolamine, triethanolamine, and methyldiethanolamine, respectively. [b] These values were obtained by fitting the data of Touhara et al. (1982).

$$(H_2 - H_2^*) = \Delta H_2^{\infty} = \sum A_n \tag{6}$$

and

$$(H_1 - H_1^*) = \Delta H_1^{\infty} = \sum A_n (-1)^{n-1} \tag{7}$$

in which we have used $\Delta H_2^{\infty}$ and $\Delta H_1^{\infty}$ 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. Equations 6 and 7 show that it is possible to calculate enthalpies of solution at infinite dilution by appropriate summing of the Redlich−Kister coefficients represented by $A_n$.

Enthalpies at infinite dilution for alkanolamines and water are given in parts a and b of Table 4, respectively. Our results calculated from eqs 6 and 7 are compared with direct measurements done by Kim et al. (1987) and by Touhara et al. (1982). These comparisons show that our method is as good as other techniques with the advantage that one can obtain the partial molar enthalpy at infinite dilution with the same precision as the others without measurement at very low concentrations. The protonation of ethanolamines becomes important only at high dilution in water, (Pagé et al., 1993). We did not make any measurement in this range of concentration because of the limitations of the calorimetric cells.

**Table 4. Enthalpies of Ethanolamines and Water at Infinite Dilution at 298.15 K**

(a) Ethanolamines

| compounds | $\Delta H_2^{\infty}$ (literature), kJ·mol$^{-1}$ | $\Delta H_2^{\infty}$(this work), kJ·mol$^{-1}$ |
|---|---|---|
| MEA | −11.4[a]<br>−12.6[b] | −12.8 |
| MMEA | −18.5[b] | −18.4 |
| DMEA | −25.4[b] | −24.1 |
| DEA | −14.5[a] | −14.5 |
| TEA | −14.4[a] | −13.7 |
| MDEA | −20.5[a] | −20.0<br>−17.7 (at 313.15K) |

(b) Water

| compounds | $\Delta H_1^{\infty}$,[b] kJ·mol$^{-1}$ | $\Delta H_1^{\infty}$(this work), kJ·mol$^{-1}$ |
|---|---|---|
| MEA | −6.7 | −6.0 |
| MMEA | −6.2 | −5.9 |
| DMEA | −6.3 | −6.3 |
| DEA | | −4.4 |
| TEA | | −0.7 |
| MDEA | | −5.4<br>−5.4 (at 313.15K) |

[a] Kim et al. (1987). [b] Touhara et al. (1982).

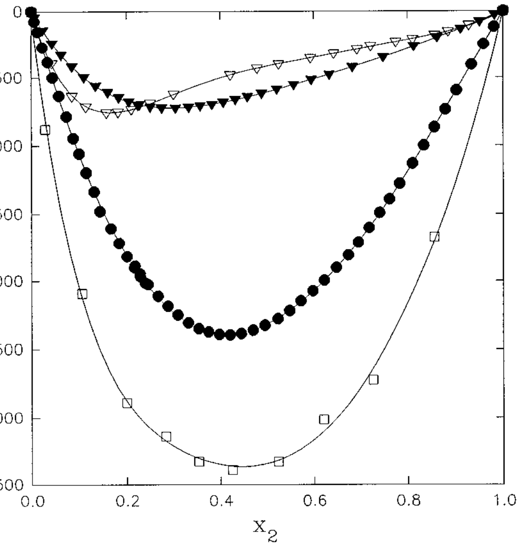

**Figure 2.** Excess enthalpies of binary mixtures of ethanol, ethylene glycol, monoethanolamine, and diethylamine and water at 298.15 K: ▽, (EtOH + $H_2O$), ▼, (EG + $H_2O$), ●, (MEA + $H_2O$), and □, (DEtA + $H_2O$).

Alkanolamines are multifunctional compounds with ethanol, amine, and alkyl groups. The effects of above groups on the excess molar enthalpies are shown in Figure 2, where the excess molar enthalpies of (ethanol + water) (Larkin, 1975), (glycol + water) (Matsumoto et al., 1977), (ethanolamine + water) (Touhara et al., 1982), and (diethylamine + water) (Copp and Everett, 1953) mixtures are plotted against mole fraction of organic compound at 298.15 K. One may also look at the structure of these compounds and compare ethanol (asymmetric, with −OH and $-C_2H_5$ groups) with glycol (symmetric with two $-C_2H_2$-OH groups). These two types of behavior are also shown in Figure 2. We may compare the magnitude of the excess molar enthalpies of (water + ethanol) and (water + diethylamine) systems. The excess molar enthalpies of (water + diethylamine) are seven times higher than of (water + ethanol) systems. This could mean that the interaction between water (−OH group) and diethylamine (−NH group) is more dominant that the interactions between −OH groups from water and ethanol molecules. Finally, we also have the excess molar enthalpies of (water + monoethanolamine) mixtures, which are situated between (water + ethanol) and (water + diethylamine) mixtures. This shows that ethanol and amine groups have the opposite effect on the excess enthalpies of aqueous binary mixtures. The excess enthalpies of mono-, di-, and triethanolamine with water are shown in Figure 3. We see here the effect of additional ethanol groups on the position of the minimum. The position of the minimum in the $H^E$ axis is inversely related to the number of the ethanol groups on the nitrogen atom, where the higher the number of ethanol groups, the less negative the excess molar enthalpy. This is comparable to the case of (water + diethylamine) and (water + monoethanolamine) mixtures in Figure 2. The methyl group effect is shown in Figure 4 for the excess molar enthalpies of (water + diethanolamine) and (water +methyldiethanolamine) mixtures. The difference between diethanolamine and meth-

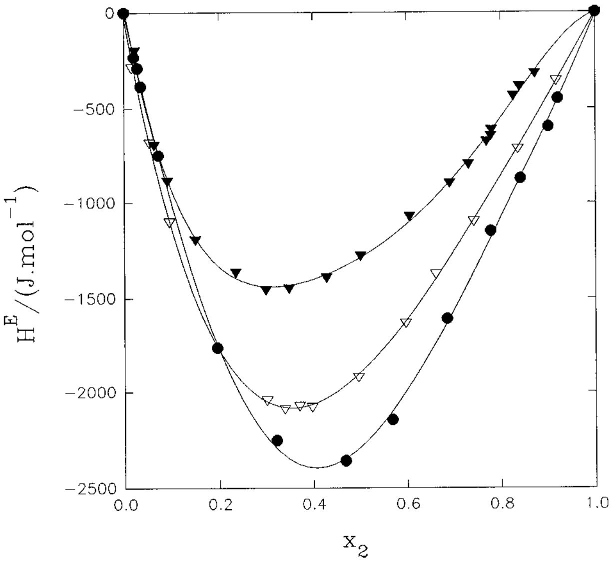

**Figure 3.** Excess enthalpies of binary mixtures of ethanolamine and water at 298.15 K: ▼, (TEA + $H_2O$), ▽, (DEA + $H_2O$), and ●, (MEA + $H_2O$).

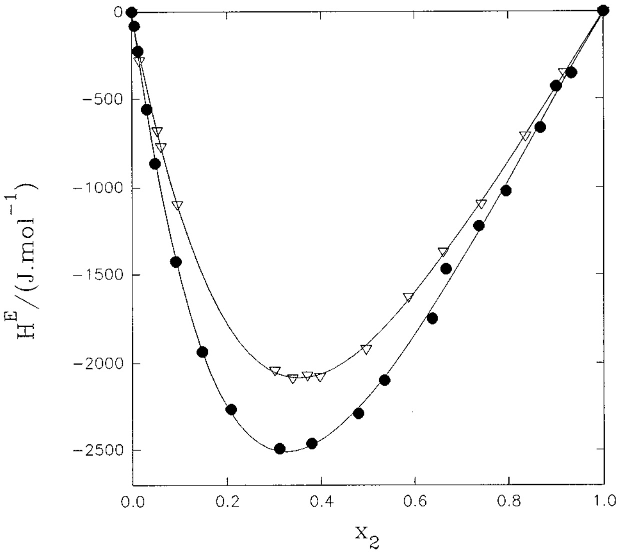

**Figure 4.** Excess enthalpies of binary mixtures of diethanolamine and methyldiethanolamine and water at 298.15 K: ▽, (DEA + $H_2O$) and ●, (MDEA + $H_2O$).

**Table 5. Excess Heat Capacity of (Water + MDEA) Mixtures**

| $X_2$ | $C_p^E$ ($J \cdot K^{-1} \cdot mol^{-1}$) |
|---|---|
| 0.1 | 6.3 |
| 0.2 | 9.6 |
| 0.3 | 11.0 |
| 0.4 | 11.2 |
| 0.5 | 10.5 |
| 0.6 | 8.9 |
| 0.7 | 6.3 |
| 0.8 | 3.2 |

yldiethanolamine is a methyl group that replaced the hydrogen atom of diethanolamine. This shows that the effect of the methyl group is to make the excess enthalpy more negative.

We have also obtained the excess heat capacities for (water + methyldiethanolamine) mixtures from our measurements at 298.15 K and 313.15 K and they are given in Table 5.

## Conclusions

As shown in Figure 2, the $-NH_2$ group has a much larger contribution to the excess enthalpies than the $-OH$ group in (water + alkanolamine) systems. Concerning the number of $-OH$ groups, there is an inverse relation to the excess enthalpies. They may be classified as:

$$\text{MEA} > \text{DEA} > \text{TEA}$$

The methyl group also contributes to the excess enthalpies, but opposite to the contribution of $-OH$. Also they may be classified as:

$$2(-CH_3) > -CH_3 > -H$$

This is true for mono and diethanolamines. For a general conclusion, one needs to study a few more alkanolamine (with bigger alkyl groups) and water mixtures. It will be of interest for biological systems to investigate the contribution of larger hydrophobic groups with a higher number of carbons in them.

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