

## Excess thermodynamic properties of the binary mixtures of ethylenediamine with isomeric butanols

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**Abstract.** Isothermal vapour-liquid equilibrium data at 333·15 K and excess molar volumes of mixing at 298·15 K for the binary mixtures of ethylenediamine with isomeric butanols were measured over the entire mole fraction range. The values of molar excess free energy,  $G_m^E$ , and excess volumes,  $V_m^E$ , are negative for all the four systems, indicating strong specific interactions between two unlike molecules. The branching of the alkyl chain of alcohol also affects the excess properties considerably.

**Keywords.** Excess thermodynamic properties; binary mixtures; amine-alcohol interactions; dilution dilatometer; excess volumes; excess free energy.

### 1. Introduction

In continuation of the earlier studies (Datta Choudhary 1976; Pradhan 1979, 1981) in this laboratory on the excess thermodynamic properties of the binary mixtures of associated liquids viz. alcohol-amine systems, the present work was undertaken to understand the diamine-alcohol interactions.

In this communication, the isothermal vapour-liquid equilibrium data at 333·15 K and the excess molar volumes,  $V_m^E$ , at 298·15 K for the four binary systems of ethylenediamine (EDA) with *n*-, *iso*-, *sec*-, and *t*-butanol ( $V_m^E$  of EDA-*t*-butanol at 299·15 K) have been reported.

Vapour liquid equilibrium data is not available for any of the above systems, whereas excess volumes at 303·15 K for ethylenediamine with *n*-, *iso*- and *sec*-butanol have been reported by Rao *et al* (1981, 1982). In the present studies, a continuous dilution dilatometer has been used to obtain  $V_m^E$  data at 298·15 K. This method is better and more accurate than the batch method (Kumaran and McGlashan (1977)).

### 2. Experimental

#### 2.1 Materials

Analytical reagent grade butanols were fractionally distilled twice over a NaOH-AgNO<sub>3</sub> mixture using a meter long column packed with glass helices. Ethylenediamine was similarly purified over metallic sodium. All the compounds were stored over activated molecular sieves (4A). The purity of the compounds was checked by comparing the densities with literature values (Reddick and Bunger 1970; Timmermans 1950).

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## 2.2 Apparatus and procedure

**2.2a Vapour-liquid equilibrium:** The vapour-liquid equilibrium data at 333.15 K were obtained using a modified Jones-Colburn recirculating still (Ammer *et al* 1956). The values of system pressures determined were accurate to within  $\pm 0.01$  mm. Barometric and gravitational corrections were applied to the measured values of system pressures. The liquid and vapour compositions of the solutions were determined by densitometric analysis.

The liquid phase activity coefficients ( $\gamma$ ) were calculated by means of the relations (Datta Choudhary 1976):

$$\gamma_i = (P y_i / P_i^s x_i) \exp \{ [(V_i - B_{ii})(P_i^s - P) + \delta_{12}(1 - y_i)^2 P] / RT \}, \quad (1)$$

where  $i = 1, 2$  (1 = ethylenediamine and 2 = butanol);  $\delta_{12} = 2B_{12} - B_{11} - B_{22}$ ;  $x$ ,  $y$  are the liquid and vapour mole fractions respectively;  $P$  is the solution pressure,  $P^s$  is vapour pressure of pure component (atm);  $V$  is liquid molar volume ( $\text{cm}^3 \text{mol}^{-1}$ );  $B$  is the second virial coefficient ( $\text{cm}^3 \text{mol}^{-1}$ );  $R$  = gas constant and  $T$  is the temperature. Here  $\delta_{12}$  was taken as zero.

The second virial coefficients ( $B$ ) for alcohols were calculated using Tsonopoulos equation (Tsonopoulos 1974) and for ethylenediamine by the Pitzer Curl equation (Pitzer and Curl 1957). The values of  $B$  are listed in table 1 along with the liquid molar volumes ( $V$ ) at 333.15 K. The values of  $B$  do not affect the  $\gamma$  values much at lower pressures.

The molar excess free energy,  $G_m^E$ , was calculated by the relation.

$$G_m^E (\text{J. mol}^{-1}) = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2). \quad (2)$$

**2.2b Excess molar volumes:** The excess volumes,  $V_m^E$ , at 298.15 K were measured by a dilution dilatometer based on the design of Kumaran and McGlashan (1977). The necessary calibrations were done at 298.15 K, before the dilatometer was assembled. The proper working of the apparatus was tested by measuring  $V_m^E$  of a benzene-cyclohexane system at 298.15 K.

The data on excess volumes were obtained at 298.15 K for all the systems except for EDA-*t*-butanol at 299.15 K. The thermostat temperature was controlled to  $\pm 0.01$  K and the excess volumes were reproducible to  $\pm 0.002 \text{ cm}^3 \text{mol}^{-1}$ . Compression corrections were taken into account.

**Table 1.** Second virial coefficients ( $B$ ) and liquid molar volume ( $V$ ) of pure compounds at 333.15 K.

Compounds	$B$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$V$ ( $\text{cm}^3 \text{mol}^{-1}$ )
<i>n</i> -Butanol	-2360	95.2
<i>iso</i> -Butanol	-2634	96.4
<i>sec</i> -Butanol	-2288	96.0
<i>t</i> -Butanol	-1740	99.7
Ethylenediamine	-1485	70.0

### 3. Results and discussions

#### 3.1 Excess free energy of mixing

The values of  $G_m^E$  are plotted against  $x_1$ , the liquid mole fraction of EDA, in figure 1. The thermodynamic consistency of the experimental data was checked by the equal area method (Herington 1952). All the systems were found to be thermodynamically consistent within 4–5%. The higher deviations may be due to the imperfect nature of the vapour phase.

The  $G_m^E$  vs  $x_1$  plot shows that the excess free energy is negative throughout the concentration range, indicating strong specific interactions due to the hydrogen bonding between unlike molecules. The  $G_m^E$  values decrease with the branching of alcohol. They are in the order:

$$iso > n > sec \geq t\text{-butanol.}$$

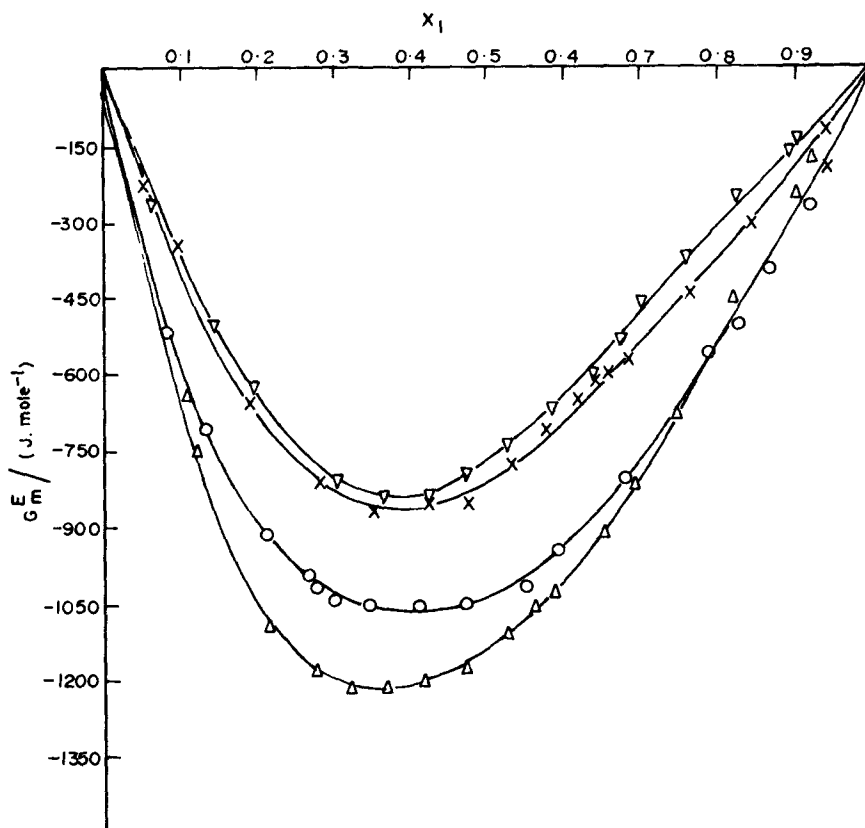


Figure 1. The  $G_m^E$  versus  $x_1$  curves for (○) ethylenediamine (1) + *n*-butanol (2); (△) ethylenediamine (1) + *iso*-butanol (2); (×) ethylenediamine (1) + *sec*-butanol (2); (▽) ethylenediamine (1) + *t*-butanol (2) at 333.15 K; (—) values calculated from (3).

## 3.2 Excess molar volumes

Excess volumes are obtained at 298.15 K for all the systems and the results are plotted in figure 2, as a function of  $x_1$ . The excess volumes are negative over the entire mole fraction range, indicating complex formation between two unlike molecules. The results can be explained in terms of bond breaking and making, and structural effects. Both the ethylenediamine and the butanols are self-associated due to the formation of N-H . . . N and O-H . . . O type hydrogen bonds in their pure state (Vinogradov and Linnel 1971). The experimental  $V_m^E$  values being negative indicate that O-H . . . N bonds result from stronger specific interactions between compounds with dissimilar molecules than those between similar molecules. This is in agreement with views

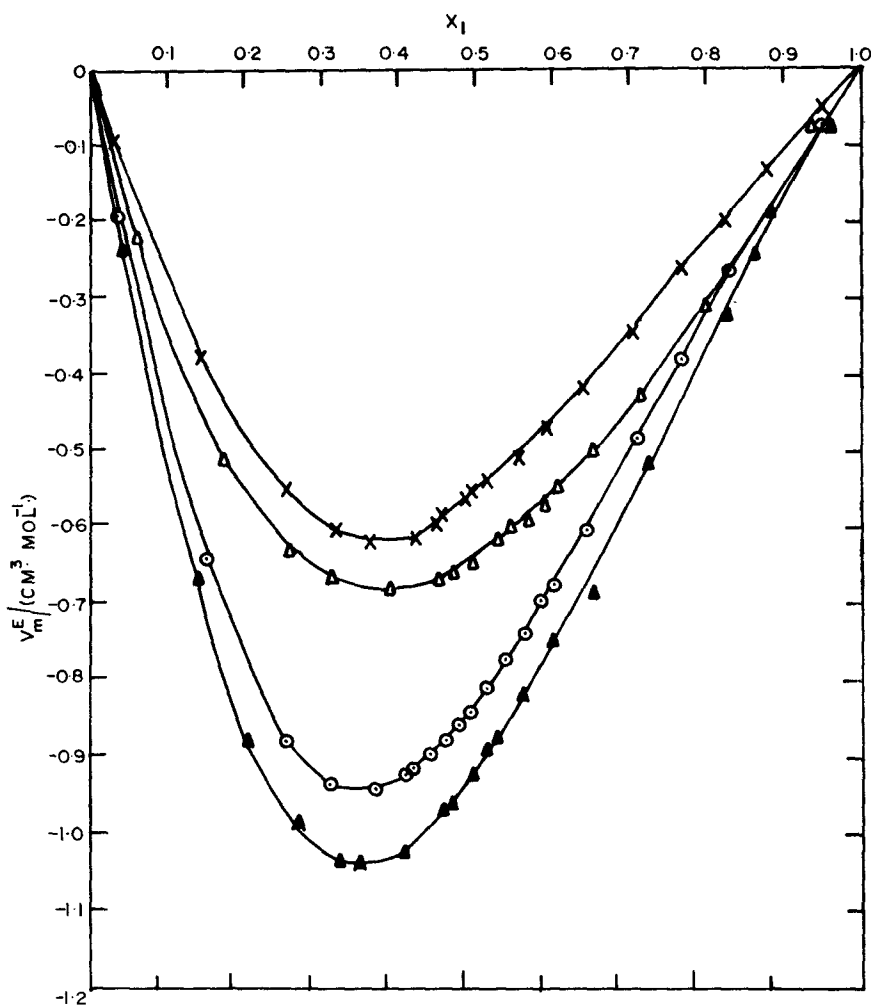


Figure 2. The  $V_m^E$  versus  $x_1$  curves for (O) ethylenediamine (1) + iso-butanol (2); (▲) ethylenediamine (1) + iso-butanol (2); (x) ethylenediamine (1) + sec-butanol (2) at 298.15 K; (△) ethylenediamine (1) + t-butanol (2) at 299.15 K; (—) values calculated from (3).

**Table 2.** Values of the parameters  $A_0, A_1, A_2, A_3$  of (3) along with standard deviations  $\sigma(G_m^E)$  and  $\sigma(V_m^E)$ .

System	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
For $G_m^E$ (at 333.15 K)					
EDA (1) + <i>n</i> -butanol (2)	-4038.9	1557.3	-1591.7	684.7	18.0
EDA (1) + <i>iso</i> -butanol (2)	-4644.1	2391.0	-329.4	610.3	19.0
EDA (1) + <i>sec</i> -butanol (2)	-3196.3	1778.0	-161.1	-697.3	15.0
EDA (1) + <i>t</i> -butanol (2)	-3071.9	1933.5	180.4	-171.8	12.0
For $V_m^E$ (at 298.15 K)					
EDA (1) + <i>n</i> -butanol (2)	-3.3161	2.5912	-0.2653	-0.4393	0.004
EDA (1) + <i>iso</i> -butanol (2)	-3.6822	2.7915	-0.2981	-0.5325	0.008
EDA (1) + <i>sec</i> -butanol (2)	-2.2300	1.5124	0.1391	-0.4235	0.004
EDA (1) + <i>t</i> -butanol (2)	-2.5414	1.2471	-0.3847	0.0680	0.004

expressed by other authors (Rao and Naidu 1981; Domonkos and Ratkovics 1982; Fernandez *et al* 1983).

The size, shape and symmetry of the molecules also affects the excess property. The values of  $V_m^E$  fall in the order:

$$iso > n > t > sec\text{-butanol.}$$

This trend is consistent with excess free energy results. It seems from the results that the interactions between unlike molecules are stronger at about 0.33 mole fraction of ethylenediamine. The ethylenediamine molecule contains two  $\text{NH}_2$  groups and can simultaneously bind with two molecules of alcohol.

This indicates the possibility of the formation of 1:2 complexes between ethylenediamine and alcohol molecules.

### 3.3 Correlation of data

The  $G_m^E$  and  $V_m^E$  data were least square fitted to a polynomial equation of the type:

$$X_m^E = x_1 x_2 \sum_{n=0}^3 A_n (x_1 - x_2)^n \quad (3)$$

where  $X_m^E = V_m^E$  or  $G_m^E$ ;  $x_1$  = mole fraction of ethylenediamine;  $A_n$  = least square constant.

The values of constants obtained by the least square method using an ICL-1904S computer, are reported in table 2, along with the standard deviation  $\sigma$ .

### References

- Ammer H H, Paxton R R and Van Winkle M 1956 *Ind. Eng. Chem.* **48** 142  
 Datta Choudhary M K 1976 *Indian J. Chem.* **A14** 553  
 Domonkos L and Ratkovics F 1982 *Monatsh. Chem.* **113** 1119  
 Fernandez J, Paz Andrade M I, Pintos M, Sarmiento F and Bravo R 1983 *J. Chem. Thermodyn.* **15** 581  
 Herington E F G 1952 *J. Appl. Chem.* (London) **2** 19

- Kumaran M K and McGlashan M L 1977 *J. Chem. Thermodyn.* **9** 259  
Mukherjee L M and Bruckenstein S 1966 *Pure Appl. Chem.* **13** 421  
Pitzer K S and Curl R F 1957 *J. Am. Chem. Soc.* **79** 2369  
Pradhan S D 1979 *Indian J. Technol.* **17** 324  
Pradhan S D 1981 *Proc. Indian Acad. Sci. (Chem. Sci.)* **90** 261  
Rao D N and Naidu P R 1981 *J. Chem. Thermodyn.* **13** 691  
Rao D N, Krishnaiah A and Naidu P R 1981 *J. Chem. Thermodyn.* **13** 367  
Rao D N, Krishnaiah A and Naidu P R 1982 *Indian J. Chem.* **A21** 606  
Riddick J A and Bunger W B 1970 *Organic solvents: (Techniques of chemistry Vol. II)* (ed.) A Weissberger (New York: Wiley Interscience) p. 152  
Timmermans J 1950 *Physicochemical constants of pure organic compounds* (New York: Elsevier) pp. 319, 321  
Tsonopoulos C 1974 *AIChE J.* **20** 263  
Vinogradov S N and Linnel R H 1971 *Hydrogen bonding* (New York: Van Nostrand Reinhold) p. 11