

Effect of temperature on excess molar volumes and viscosities of binary mixtures of ethylenediamine and water

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Abstract

Molar excess volumes (V^E) and viscosities have been evaluated for binary mixtures of ethylenediamine and water in the temperature range from 303.15 to 318.15 K at an interval of 5 K. Excess molar volumes V^E have been computed from density while excess Gibbs free energy of activation ΔG^{*E} is calculated from viscosity deviation $\Delta\eta$. The results were applied to Redlich–Kister equation. It is observed that all mixtures show negative values of V^E obviously due to increased interactions between amino and hydroxyl groups of the components.

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1. Introduction

Thermodynamic and transport properties of binary liquid mixtures are important in engineering, process industry and also in developing theoretical models. The more quantitative idea about the nature of molecular interactions in liquid systems is given by calculating deviation from ideal behaviour and this deviation can be best expressed in terms of excess thermodynamic functions.

Studies of thermodynamic and transport properties of binary mixtures have been extensively carried out. In our attempt to study these properties earlier we have reported experimental data and theoretical explanation for binary mixtures of systems ethanediol + water and ethanolamine + water [1,2].

In the present paper, we report excess molar volumes and viscosities of binary mixtures of ethylenediamine and water covering the whole composition range and at wide range of temperatures to assess the effect of variation in temperature.

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2. Experiments

2.1. Method

Densities of the pure components and their compositions were measured on a vibrating tube densimeter, which was reproducible to $1 \times 10^{-5} \text{ g cm}^{-3}$ (Anton Paar model DMA 5000). This unit offered high temperature accuracy ($\pm 0.001 \text{ K}$) in a wide temperature range. Calibration of the densimeter was done with triple distilled water, showing density $0.998212 \text{ g cm}^{-3}$ at 20°C which is close to literature value [3]. The mixtures were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimise evaporation losses. All measurements of mass were performed on an electronic balance with an accuracy of 0.1 mg .

Measurements of the dynamic viscosity η were carried out using a modified suspended level Ubbelohde viscometer. The viscometer was submerged in a thermostatic bath maintained at 303.15, 308.15, 315.15 and 318.15 K with a resolution of $\pm 0.05 \text{ K}$. The time given to attain thermal equilibrium for the content of viscometer was 15 min. The flow time was measured with a stopwatch to an accuracy of 0.01 s . The viscometer was calibrated separately with benzene and toluene. The observed viscosity of benzene and toluene (high performance liquid chromatography grade) was 0.6432 and 0.5863 mPa s at 20°C , respectively, which is indeed close to literature value [4]. Four to five sets of readings for the flow times were taken for each pure liquid or liquid mixture and arithmetic mean was used for the calculations. The reproducibility in the viscosity measurements was 0.004 mPa s .

2.2. Source and purity of samples

Ethylenediamine (analytical reagent grade, S.D. Fine-Chem Limited, India) was kept over potassium hydroxide and calcium oxide for about 24 h and then distilled. The first and the last fractions were discarded and only the middle fraction was collected. The density of the ethylenediamine was found to be 0.8997 g cm^{-3} at 20°C (literature value 0.8977 g cm^{-3}) [3]. Triple distilled water (specific conductance less than 10 S cm^{-1}) was used for preparation of various compositions.

3. Results

Excess molar volume V^E were calculated from the density measurement [5,6] by the relationship:

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - (x_1 V_1 + x_2 V_2) \quad (1)$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 the molecular weights, V_1 and V_2 the molar volumes of ethylenediamine (1) and water (2), respectively, and ρ the density of the mixture. The experimental densities, excess molar volumes, apparent molar volumes, viscosities and deviation in viscosity of binary mixtures of ethylenediamine (1) + water (2) at 303.15, 308.15, 313.15 and 318.15 K are listed in Table 1.

The excess molar volume were correlated by Redlich–Kister equation [7]:

$$V^E = x_1 x_2 \sum a_i (x_1 - x_2)^i \quad (2)$$

Deviation and the coefficients in the above equation were calculated by the least squares fit method (Table 2).

Table 1

Density, viscosity, excess molar volume, apparent molar volume, viscosity deviation and Gibbs energy of activation of viscous flow for ethylenediamine (1) + water (2) at 303.15, 308.15, 313.15 and 318.15 K

x_1	ρ (g cm ⁻³)	η (mPa s)	V^E (cm ³ mol ⁻¹)	$V_{\phi,1}$ (cm ³ mol ⁻¹)	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol ⁻¹)
303.15 K						
0.0000	0.995645	0.797				
0.1138	0.989519	2.607	-0.6708	61.61	1.753	5,855
0.2306	0.990933	6.369	-1.5142	60.94	5.458	10,058
0.3102	0.984486	7.766	-1.8613	61.50	6.815	10,900
0.4116	0.970266	6.837	-2.0107	62.62	5.860	10,102
0.5452	0.948611	4.416	-1.8533	64.10	3.351	7,674
0.6294	0.935776	3.321	-1.6346	64.91	2.214	6,045
0.7296	0.921457	2.434	-1.2700	65.76	1.277	4,200
0.8507	0.906904	1.789	-0.7854	66.58	0.573	2,237
1.0000	0.890325	1.290		67.05		
308.15 K						
0.0000	0.994013	0.719				
0.1138	0.986502	2.203	-0.6675	62.00	1.433	5,596
0.2306	0.98704	5.069	-1.5095	61.32	4.246	9,544
0.3102	0.980162	6.072	-1.8539	61.89	5.214	10,308
0.4116	0.965724	5.411	-2.0047	62.99	4.508	9,561
0.5452	0.944023	3.639	-1.8527	64.46	2.676	7,301
0.6294	0.931182	2.793	-1.6369	65.26	1.792	5,756
0.7296	0.916844	2.010	-1.2740	66.12	1.054	4,015
0.8507	0.902261	1.574	-0.7899	66.93	0.432	2,124
1.0000	0.885616	1.167		67.86		
313.15 K						
0.0000	0.992060	0.653				
0.1138	0.983768	1.911	-0.6763	62.28	1.212	5,423
0.2306	0.983094	4.122	-1.5081	61.69	3.375	9,096
0.3102	0.975803	4.906	-1.8497	62.26	4.127	9,835
0.4116	0.961156	4.410	-2.0014	63.36	3.589	9,123
0.5452	0.939410	3.070	-1.8541	64.83	2.196	7,011
0.6294	0.926564	2.402	-1.6408	65.62	1.493	5,544
0.7296	0.912212	1.842	-1.2791	66.47	0.892	3,884
0.8507	0.897597	1.416	-0.7946	67.29	0.417	2,098
1.0000	0.880896	1.060		68.23		
318.15 K						
0.0000	0.990132	0.597				
0.1138	0.981470	1.652	-0.6953	62.49	1.013	5,193
0.2306	0.979094	3.388	-1.5052	62.07	2.706	8,656
0.3102	0.971405	3.963	-1.8445	62.67	3.251	9,318
0.4116	0.956560	3.585	-1.9975	63.74	2.836	8,632
0.5452	0.934772	2.574	-1.8551	65.19	1.775	6,654
0.6294	0.921922	2.066	-1.6445	65.98	1.236	5,300
0.7296	0.907556	1.613	-1.2841	66.84	0.746	3,714
0.8507	0.892912	1.258	-0.7995	67.66	0.346	1,987
1.0000	0.876153	0.967		68.60		

Table 2

Regression results for the excess volumes of ethylenediamine (1) + water (2) mixtures at various temperatures

T (K)	a_0	a_1	a_2	σ (cm ³ mol ⁻¹)
303.15	-7.6772	2.3880	5.1522	0.1840
308.15	-7.6609	2.1639	4.8674	0.1733
313.15	-7.6567	2.0205	4.5117	0.1613
318.15	-7.6647	2.1525	4.3866	0.1569

Apparent molar volume ($V_{\phi,1}$) of ethylenediamine in water was calculated from density measurement [8] using the Eq. (3):

$$V_{\phi,1} = \frac{x_2 M_2 (\rho_2 - \rho_{\text{mix}})}{x_1 \rho_2 \rho_{\text{mix}}} + \frac{M_1}{\rho_{\text{mix}}} \quad (3)$$

where x_1 and x_2 are the mole fractions of ethylenediamine (1) and water (2), ρ_2 and ρ_{mix} the densities of water and mixtures, and M_1 and M_2 the molecular weights of ethylenediamine (1) and water (2). $V_{\phi,1}$ values of ethylenediamine at temperatures 303.15–318.15 K are listed in Table 1 as a function of mole fraction.

Dynamic viscosities (η) of ethylenediamine (1) + water (2) mixtures at different temperatures were calculated by the measured densities and flow times of several compositions of the mixture (Table 1).

The viscosity deviation was calculated [9,10] by Eq. (4):

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (4)$$

The experimental values of $\Delta\eta$ are also reported in Table 1. Viscosity deviation was correlated by Redlich–Kister equation (5):

$$Q = x_1 x_2 \sum H_i (x_1 - x_2)^i \quad (5)$$

where $Q = \Delta\eta$ (mPa s). The coefficients in Eq. (5) are regressed by employing the least square fit method. The optimal parameters in correlating the deviation of viscosity are listed in Table 3.

On the basis of the theory of absolute reaction rates, the excess Gibbs energies (ΔG^{*E}) of activation of viscous flow were calculated [6,11] as follows:

$$\frac{\Delta G^{*E}}{RT} = \ln \left(\frac{\eta V}{\eta_2 V_2} \right) - x_1 \ln \left(\frac{\eta_1 V_1}{\eta_2 V_2} \right) \quad (6)$$

where V , V_1 and V_2 are the molar volumes of the binary mixture and pure components. The calculated values of ΔG^{*E} are shown in Table 1.

Table 3

Regression results for the deviation of viscosity of ethylenediamine (1) + water (2) mixtures at various temperatures

T (K)	a_0	a_1	a_2	σ (mPa s)
303.15	17.5104	-5.7566	-9.7328	1.7014
308.15	13.6542	-4.8554	-6.9978	1.2459
313.15	11.0620	-4.2281	-5.1998	0.9282
318.15	8.8771	-3.5849	-3.7778	0.6990

Table 4

The activation parameters ΔG^* , ΔH^* and ΔS^* of ethylenediamine (1) + water (2) mixtures at various temperatures

x_1	ΔG^* ($\times 10^{-3}$ J mol $^{-1}$)	ΔH^* ($\times 10^{-3}$ J mol $^{-1}$)	$-\Delta S^*$ (J K $^{-1}$ mol $^{-1}$)
0.0000	1.361	1.357	4.368
0.1138	1.375	1.370	4.413
0.2306	1.385	1.381	4.446
0.3102	1.388	1.384	4.456
0.4116	1.389	1.384	4.457
0.5452	1.387	1.382	4.450
0.6294	1.385	1.380	4.445
0.7296	1.383	1.379	4.439
0.8507	1.381	1.377	4.434
1.0000	0.603	0.604	−0.547

The activation parameters ΔG^* , ΔH^* and ΔS^* were determined using Eyring equation (7) [12,13]:

$$\eta = \frac{hN}{V} \exp \left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \right) \quad (7)$$

where, η is the viscosity of binary mixture expressed in 0.1 Pa s, and h , N and V the Planck constant, Avogadro constant and molar volume, respectively. It is obvious that $\Delta H^*/R$ and $-\Delta S^*/R$ can be obtained graphically. Using this the activation parameters ΔH^* and ΔS^* were obtained and ΔG^* was obtained using the Gibbs equation. The values obtained are presented in Table 4.

4. Discussion

The graphical presentation of the excess molar volumes (V^E) of ethylenediamine (1) + water (2) are shown in Fig. 1. The sign and magnitude of V^E gives a good estimate of the strength of unlike molecular interactions in the solution phase. It is explicit that when large negative values of V^E are found, then interactions are strong [14–18]. Maximum deviation in excess molar volume occurs at 0.4116 mole fraction.

In the present study the values of excess molar volume are found to be indeed negative indicating strong hydrogen bonding interaction for the entire mole fraction range. In this binary system molecular association of ethylenediamine and water take place. The hydrogen bond in the association of ethylenediamine and water is of N–H \cdots O type, the strength of which is determined by the substituents of ethane moiety.

In our earlier work [1,2], it was found that the maximum deviation in excess molar volume occurred at 0.4037 and 0.4076 mole fraction for ethanediol + water and ethanolamine + water, respectively. It is observed that changes in excess molar volume (V^E) values are nearly same in the temperature region 303.15–318.15 K. In the systems studied earlier (i.e. ethanolamine + water), there was noticeable but decreasing magnitudes of V^E at the temperature ranges studied. This decreasing trend can be justified as the number of total –OH groups went on decreasing from system ethanediol + water, ethanolamine + water and ethylenediamine + water.

Graphical presentation of apparent molar volume ($V_{\phi,1}$) of ethylenediamine (1) + water (2) is shown in Fig. 2. It is found that the calculated values of $V_{\phi,1}$ are positive over entire range of mole fraction. The

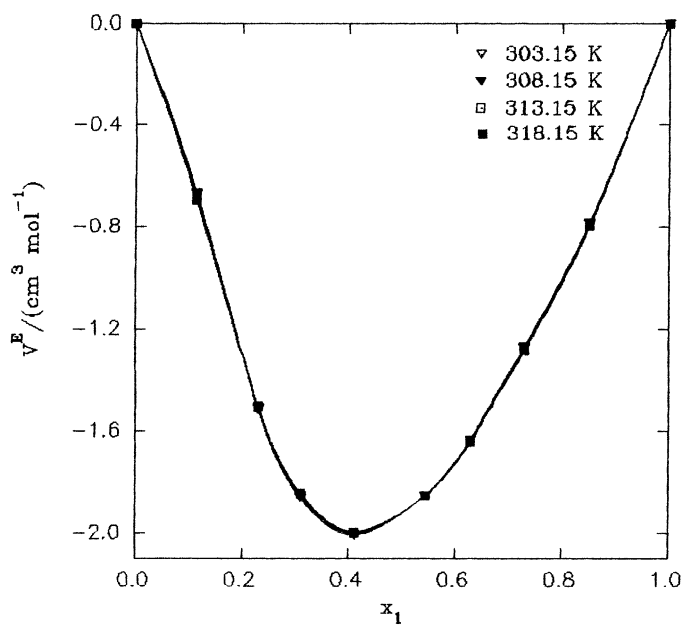


Fig. 1. Excess molar volumes (V^E) for the system ethylenediamine (1) + water (2) from 303.15 to 318.15 K.

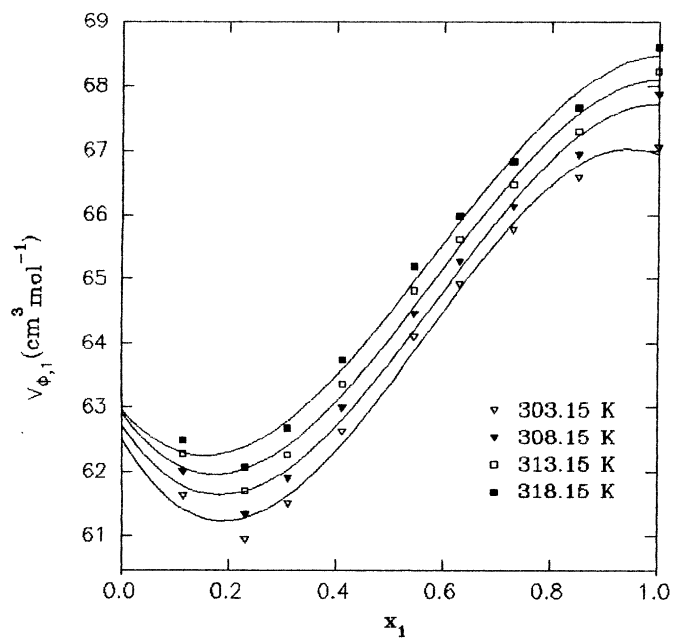


Fig. 2. Apparent molar volume ($V_{\phi,1}$) for the system ethylenediamine (1) + water (2) from 303.15 to 318.15 K.

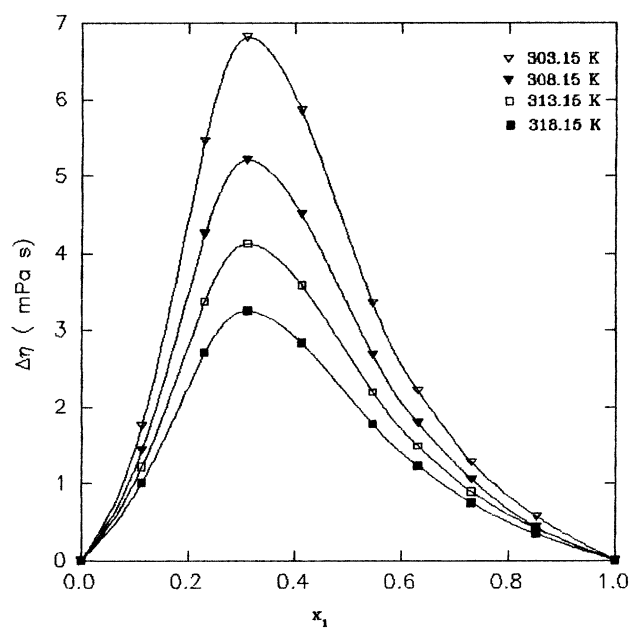


Fig. 3. Viscosity deviation for ethylenediamine (1) + water (2) from 303.15 to 318.15 K.

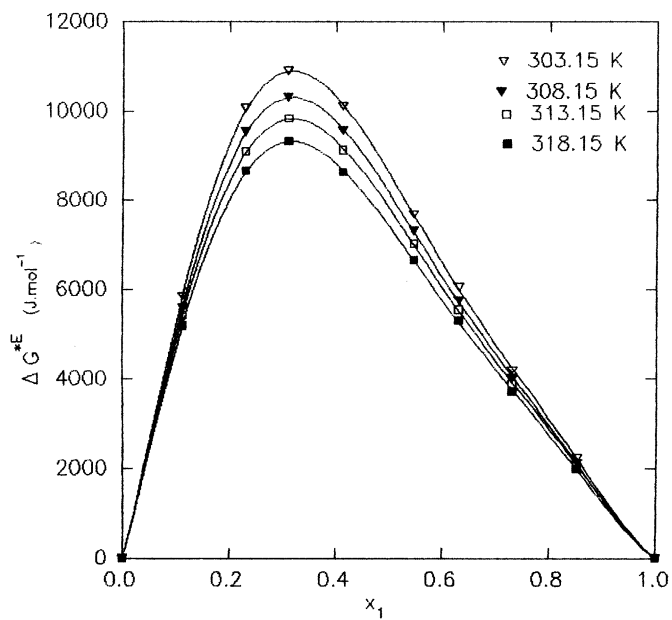


Fig. 4. Excess Gibbs energy of activation ΔG^{*E} for ethylenediamine (1) + water (2) from 303.15 to 318.15 K.

apparent molar volume decreases initially up to 0.2 mole fraction (x_1) and then increases linearly up to 0.8 mole fraction (x_1). It is further to be noted that $V_{\phi,1}$ values increase with increasing temperature [19]. Graphical presentation of the experimental $\Delta\eta$ values plotted against the fitted curve (Fig. 3) implies a positive trend over entire range of mole fractions. A similar trend was also observed regarding viscosity behaviour.

In the system [1] ethanediol + water, the values of $\Delta\eta$ are negative in which dispersion forces are dominant. The values of $\Delta\eta$ become less negative and then increasingly positive as the strength of the interaction increases in the system ethanolamine + water [2]. In the present system the trend was positive throughout probably due to association between ethylenediamine + water through hydrogen bonding.

Excess energy of activation (ΔG^{*E}) for viscous flow is shown in Fig. 4. ΔG^{*E} may be considered a reliable measure to detect the presence of interaction between molecules [9]. Positive values of ΔG^{*E} for the entire mole fraction of ethylenediamine (1) + water (2) indicate specific interactions (hydrogen-bonding and dipole–dipole) between the molecules [2,20].

The observed values of ΔH^* and ΔG^* are positive and ΔS^* are negative for the present binary system of ethylenediamine + water suggesting a strong specific interaction between constituent molecules. The observed values of ΔH^* , ΔG^* and ΔS^* are as shown in Table 4. The ΔG^* and ΔH^* values slightly increase with concentration of ethylenediamine up to 0.4 mole fraction and then slightly decrease with increasing concentration of ethylenediamine.

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