Viscosities, excess molar volume of binary mixtures of ethanolamine with water at 303.15, 308.15, 313.15 and 318.15 K

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Abstract

The density and viscosity values of binary mixtures of ethanolamine with water were measured at 303.15, 308.15, 313.15 and 318.15 K, using this data excess molar volume V^E, viscosity deviation $\Delta \eta$ and excess Gibbs free energy of activation ΔG^{E*} of viscous flow have been calculated. The results were fitted by Redlich–Kister equation. All mixtures show negative values of V^E due to increased interactions between unlike molecules or very large differences in the molar volumes of pure components at relatively low temperature.
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1. Introduction

The thermodynamic properties of binary mixtures of ethanolamine with water have been extensively studied with the aim of investigating the interactions in the solution phase.

We have studied systematically the excess properties of the binary mixtures containing diols, as the latter are industrially important organic compounds and reported the findings in the previous paper [1,2]. We have reported for the first time the viscosities and excess molar volumes for binary mixtures of ethanediol and propane 1,2 diol with water. It was observed that there exists specific interactions in water rich region and its magnitude increases at low temperatures.

The diol and water have both a proton donor and a proton acceptor group. Therefore, there will be a significant degree of H-bonding [3], leading to self-association in pure state and in addition to mutual association in their binaries.

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2. Experiments

2.1. Method

Densities of the pure components and their compositions were measured on a vibrating tube density-meter, reproducible to 1×10^{-5} g cm^{-3} (Anton Paar Model DMA 5000) measuring with high temperature accuracy (± 0.001 K) in a wide temperature range. The density-meter was calibrated with triple distilled water, the observed density was 0.99821 g cm^{-3} at 20 °C, which is close to the literature value [4]. The mixtures were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimize the 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 obtained with a modified suspended level Ubbelohde viscometer. The viscometer was submerged in a thermostatic bath at 303.15, 308.15, 315.15 and 318.15 K with a resolution of ± 0.05 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 close to the literature value [5]. The reproducibility in the viscosity measurements was 0.004 mPa s. Four–five sets of readings for the flow times were taken for each pure liquid or liquid mixture and arithmetic mean was considered for the calculations.

2.2. Source and purity of samples

Ethanolamine (analytical reagent grade, S.D. Fine -Chem. Limited, India) was distilled under reduced pressure on short path distillation unit ('UIC', USA). The density of the ethanolamine was found to be 1.01223 g cm^{-3} at 25 °C (literature value, 1.0117 g cm^{-3}) [4]. Triple distilled water (specific conductance <10 S cm^{-1}) was used for preparation of various compositions.

3. Results

Excess molar volume V^{E} were calculated from the density measurement [6,7] by the relationship as follows:

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

where x_1 and x_2 are mole fractions, M_1 and M_2 the molecular weights, and V_1 and V_2 the molar volumes of ethanolamine (1) and water (2), respectively. The experimental densities, excess molar volumes, viscosities and deviation in viscosity of binary mixtures of ethanolamine (1) + water (2) at four different temperatures are listed as shown in Table 1.

The excess molar volume were correlated by Redlich–Kister [8] as shown in Eq. (2):

$$V^{\mathrm{E}} = x_1 x_2 \sum a_i (x_1 - x_2)^i \tag{2}$$

The coefficient in Eq. (2) was estimated by the least squares fit method. The standard deviation (Table 2)

Table 1
Densities, viscosities, excess molar volume, excess viscosities and Gibbs energy of activation of viscous flow for ethanolamine (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})	$\Delta\eta$ (mPa s)	ΔG^{E*} (J mol^{-1})
303.15 K					
0.0000	0.99565	0.797			
0.1122	1.00810	2.062	−0.1973	−0.352	3397
0.2278	1.01765	4.543	−0.4292	0.465	5779
0.3067	1.02106	6.862	−0.5448	1.647	6720
0.4076	1.02237	9.966	−0.6205	3.298	7117
0.5412	1.02076	13.275	−0.6052	4.683	6557
0.6257	1.01897	14.592	−0.5527	4.770	5736
0.7264	1.01621	15.408	−0.4434	4.148	4449
0.8486	1.01283	15.638	−0.2774	2.619	2589
1.0000	1.00828	15.200			
308.15 K					
0.0000	0.99401	0.719			
0.1122	1.00572	1.780	−0.1969	−0.201	3291
0.2278	1.01462	3.788	−0.4250	0.507	5604
0.3067	1.01774	5.579	−0.5390	1.411	6484
0.4076	1.01882	7.974	−0.6143	2.671	6873
0.5412	1.01704	10.502	−0.6000	3.697	6340
0.6257	1.01517	11.518	−0.5484	3.762	5560
0.7264	1.01235	12.095	−0.4404	3.207	4297
0.8486	1.00892	12.374	−0.2761	2.111	2538
1.0000	1.00431	11.966			
313.15 K					
0.0000	0.99206	0.653			
0.1122	1.00321	1.573	−0.1998	−0.095	3252
0.2278	1.01151	3.228	−0.4233	0.514	5474
0.3067	1.01437	4.673	−0.5358	1.245	6321
0.4076	1.01523	6.564	−0.6105	2.223	6684
0.5412	1.01328	8.588	−0.5964	3.038	6186
0.6257	1.01135	9.367	−0.5457	3.052	5419
0.7264	1.00847	9.850	−0.4385	2.624	4207
0.8486	1.00499	10.002	−0.2751	1.670	2462
1.0000	1.00034	9.702			
318.15 K					
0.0000	0.99013	0.597			
0.1122	1.00058	1.373	−0.2033	−0.045	3113
0.2278	1.00834	2.732	−0.4309	0.468	5269
0.3067	1.01094	3.886	−0.5459	1.044	6081
0.4076	1.01160	5.389	−0.6252	1.810	6441
0.5412	1.00949	6.936	−0.6184	2.379	5934
0.6257	1.00751	7.567	−0.5730	2.392	5209
0.7264	1.00457	7.970	−0.4717	2.058	4051
0.8486	1.00104	8.127	−0.3156	1.321	2380
1.0000	0.99635	7.914			

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

T (K)	a_0	a_1	a_2	σ (cm^3 mol^{-1})
303.15	−2.4199	0.2848	1.1228	0.037
308.15	−2.3996	0.2879	1.0996	0.036
313.15	−2.3879	0.3041	1.0712	0.035
318.15	−2.5102	0.3025	1.1980	0.043

was calculated by Eq. (3):

$$\sigma(V^E) = \left[\sum \frac{(V^E_{Experimental} - V^E_{Calculated})^2}{D - N} \right]^{0.5} \tag{3}$$

where D and N are the numbers of data points and parameters, respectively.

Dynamic viscosities (η) of ethanolamine (1) + water (2) mixtures at different temperatures were calculated by the measuring density and flow time of the mixture (Table 1). The viscosity deviation was calculated [9,10] by the Eq. (4):

$$\Delta\eta = \eta - \{x_1\eta_1 + x_2\eta_2\} \tag{4}$$

The experimental values of $\Delta\eta$ are also reported in Table 1.

On the basis of the theory of absolute reaction rates, the excess Gibbs energies (ΔG^{E*}) of activation of viscous flow were calculated [7,11] from Eq. (5):

$$\frac{\Delta G^{E*}}{RT} = \left\{ \ln\left(\frac{\eta V}{\eta_2 V_2}\right) - x_1 \ln\left(\frac{\eta_1 V_1}{\eta_2 V_2}\right) \right\} \tag{5}$$

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

Table 3
The activation parameters ΔG^*, ΔH^* and ΔS^* of ethanolamine (1) + water (2) mixtures at various temperatures

x_1	$\Delta G^* \times 10^{-3}$ (J mol^{-1})	$\Delta H^* \times 10^{-3}$ (J mol^{-1})	$-\Delta S^*$ (J K^{-1} mol^{-1})
0.0000	2.6807	1.357	4.3680
0.1122	2.7036	1.368	4.4052
0.2278	2.7225	1.378	4.4360
0.3067	2.7326	1.383	4.4524
0.4076	2.7423	1.383	4.4683
0.5412	2.7501	1.392	4.4824
0.6257	2.7546	1.394	4.4883
0.7264	2.7575	1.395	4.4931
0.8486	2.7601	1.397	4.4972
1.0000	0.4449	0.613	−0.5563

The activation parameters ΔG^*, ΔH^* and ΔS^* were determined [13] using Eyring and John's equation [12] Eq. (6):

$$\eta = \frac{hN}{V} \exp\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \right) \tag{6}$$

where η is viscosity of binary mixture in 0.1 Pa s and h, N, and V are Planck's constant, Avogadros number and molar volume, respectively. When $\ln(\eta V/hN)$ is plotted against $1/T$, the slope is equal to $\Delta H^*/R$ and the intercept is equal to $-\Delta S^*/R$. Using both graphical and least-squares method, the activation parameters ΔH^* and ΔS^* were obtained and ΔG^* was obtained using the equation $\Delta G^* = \Delta H^* - T \Delta S^*$ values obtained are presented in Table 3.

4. Discussion

The graphical presentation of the V^E of ethanolamine(1) + water (2) are as 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. Positive V^E indicates the weak interaction, whereas, large negative values of V^E are found, when these interactions are strong [14–18]. In the present study, the values of excess molar volume are found to be negative indicating strong hydrogen-bonding interaction for the entire mole fraction. Maximum deviation in excess molar volume occurs at 0.5 mole fraction. The large negative value of V^E can be
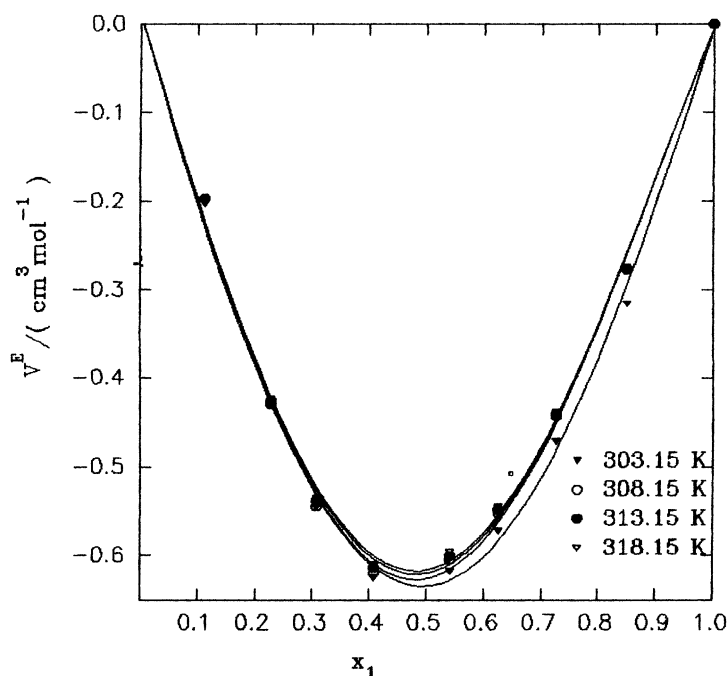

Fig. 1. Excess molar volumes (V^E) for the system ethanolamine (1) + water (2) from 303.15 to 318.15 K.
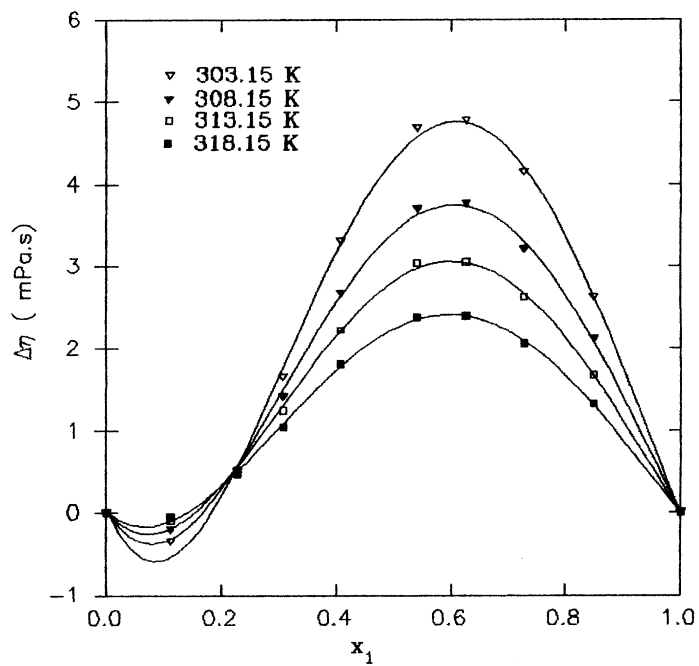
Fig. 2. Viscosity deviation for ethanolamine (1) + water (2) from 303.15 to 318.15 K.
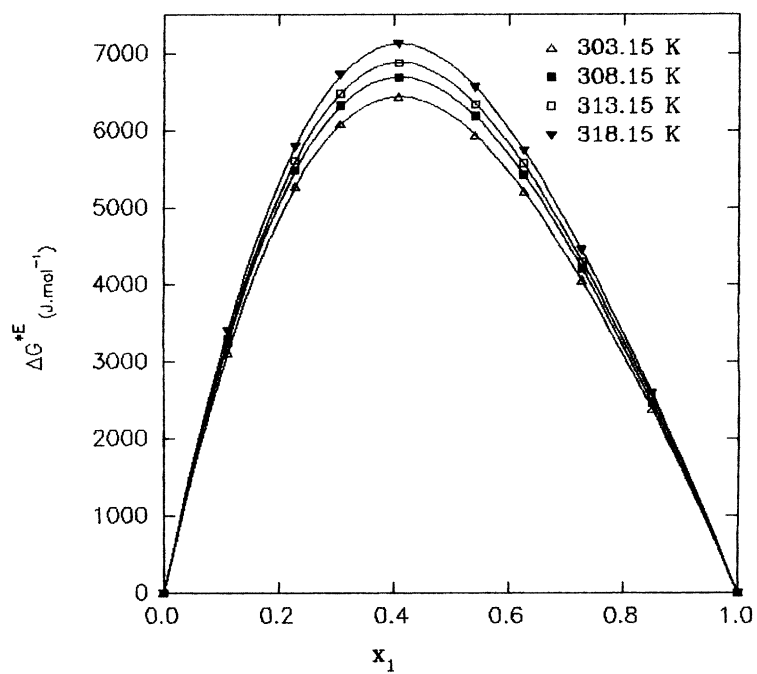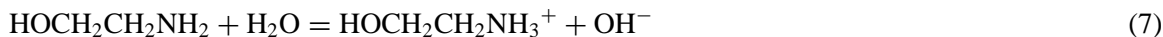

Fig. 3. Excess Gibbs energy of activation, ΔG^{E*} for ethanolamine (1) + water (2) from 303.15 to 318 K.

interpreted by following equation:

$$HOCH_2CH_2NH_2 + H_2O = HOCH_2CH_2NH_3^+ + OH^- \tag{7}$$

$$HOCH_2CH_2NH_2 + HOCH_2CH_2NH_2 = HOCH_2CH_2NH_3^+ +^- OCH_2CH_2NH_2 \tag{8}$$

It is observed that change in V^E values are nearly same with the temperature region 303.15–318.15. The change in values of V^E in this temperature range is $0.0049\,cm^3\,mol^{-1}$.

Graphical presentation of the experimental $\Delta\eta$ values plotted against the fitted equation are as shown in Fig. 2. The $\Delta\eta$ is only negative to mole fraction 0.1122 of ethanolamine and near about constant to mole fraction 0.2277 and increases steadily and attempt maximum positive [19] values at mole fraction 0.6257. The positive deviation indicates the predominance of specific hydrogen bonding interaction between the unlike molecules (to form adducts between them) over the dissociation effects in the system [19].

Excess energy of activation for viscous flow is as shown in Fig. 3. The observed ΔG^{E*} values are positive [1,2] for the entire mole fraction of ethanolamine (1) + water (2). Large positive values indicate the specific interaction leading to complex formation through intermolecular hydrogen bonding interaction between unlike molecules compared to like molecules.

The observed values of ΔH^* and ΔG^* for the binary mixture are positive as shown in Table 3. The ΔG^* and ΔH^* values steadily increases with concentration of ethanolamine upto 0.3 mole fraction and then attains nearly constant values.

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