

## Studies of viscosity and excess molar volume of binary mixtures of propane-1,2 diol with water at various temperatures

U.R. Kapadi<sup>a,\*</sup>, D.G. Hundiwale<sup>a</sup>, N.B. Patil<sup>a</sup>, M.K. Lande<sup>a</sup>, P.R. Patil<sup>b</sup>

<sup>a</sup> School of Chemical Sciences, North Maharashtra University, Jalgaon 425001, India

<sup>b</sup> School of Environmental and Earth Sciences, North Maharashtra University, Jalgaon 425001, India

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### Abstract

The excess molar volume  $V^E$ , viscosity deviation  $\Delta\eta$  and excess Gibbs free energy of activation  $\Delta G^{*E}$  of viscous flow have been investigated from the density and viscosity measurements of propane-1,2 diol (1) + water (2) over the entire range of mole fractions at 303.15, 308.15, 313.15 and 318.15 K. The results were fitted by Redlich–Kister equation. The system exhibited very large negative values of  $V^E$  due to increased interactions between unlike molecules or very large differences in the molar volumes of pure components at low temperature. © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

We have been engaged in a systematic study of the thermodynamic and transport properties of binary mixtures containing diols, as the latter are industrially important organic compounds. In the previous paper [1], we have reported viscosities and excess molar volumes for binary mixtures ethanediol with water. It was observed that there exist specific interactions in water rich region and its magnitude increases at low temperatures.

The diol and water have both a proton donor and proton acceptor group. Therefore, there will be a significant degree [2] of H-bonding, leading to self-association in pure state and in addition to mutual association in their binaries.

\* Corresponding author. Tel.: +91-257-252187; fax: +91-257-252183.

E-mail address: nmunjial@vsnl.net.in (U.R. Kapadi).

## 2. Experiments

### 2.1. Method

Densities of the pure components and their compositions were measured on a vibrating tube densimeter, reproducible to  $1 \times 10^{-5} \text{ g cm}^{-3}$  (Anton Paar model DMA 5000) measuring with high temperature accuracy ( $\pm 0.001^\circ\text{C}$ ) in a wide temperature range. The densimeter was calibrated with triple distilled water, the observed density was  $0.998212 \text{ g cm}^{-3}$  at  $20^\circ\text{C}$ , which is close to literature [3]. 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 accurate to 0.1 mg.

Measurements of the dynamic viscosity  $\eta$  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  $\pm 0.05 \text{ K}$ . The time given to attain thermal equilibrium for the content of viscometer was 15 min. The flow time was measured with an accurate 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  $20^\circ\text{C}$ , respectively, which is close to literature [4]. The reproducibility in the viscosity measurements was 0.004 mPa s. Four to 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

Propane-1,2 diol (analytical reagent grade, S.D. Fine-Chem Ltd., India) was kept over anhydrous sodium sulfate for about 24 h and then distilled under reduced pressure. The first and the last fractions were discarded and only middle fraction was collected. The density of the propane-1,2 diol was found to be  $1.036325 \text{ g cm}^{-3}$  at  $20^\circ\text{C}$  (literature value  $1.0364 \text{ g cm}^{-3}$ ) [3]. Triple distilled water (specific conductance  $< 10 \text{ S cm}^{-1}$ ) was used for preparation of various compositions.

## 3. Results

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

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

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 propane-1,2 diol (1) + water (2), respectively. The experimental densities, excess molar volumes, viscosities and deviation in viscosity of binary mixtures of propane-1,2 diol (1) + water (2) at four different temperatures are listed in Table 1.

The excess molar volume were correlated by Redlich and Kister [6] equation:

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

Table 1

Densities, viscosities, excess molar volume, excess viscosities and Gibbs energy of activation of viscous flow for propane-1,2 diol (1) + water (2) at 303.15, 308.15, 313.15 and 318.15 K

$x_1$	$\rho$ (g cm <sup>-3</sup> )	$\eta$ (mPa s)	$V^E$ (cm mol <sup>-1</sup> )	$\Delta\eta$	$\Delta G^{*E}$ (J mol <sup>-1</sup> )
303.15 K					
0.0000	0.995645	0.797			
0.0256	1.002633	1.078	-0.0731	-0.567	610
0.0559	1.010467	1.507	-0.175	-1.141	1258
0.0921	1.018478	2.137	-0.2983	-1.710	1886
0.1363	1.026158	3.025	-0.4374	-2.285	2431
0.1914	1.031540	4.280	-0.5448	-2.853	2870
0.2620	1.035242	5.795	-0.6287	-3.676	3038
0.3558	1.036721	8.282	-0.6593	-4.294	3098
0.4863	1.036096	12.922	-0.6113	-3.974	2975
0.6806	1.033513	20.318	-0.4345	-3.010	2147
1.0000	1.028939	33.902			
308.15 K					
0.0000	0.994013	0.719			
0.0256	1.000764	0.971	-0.0727	-0.376	629
0.0559	1.008358	1.315	-0.1742	-0.774	1223
0.0921	1.015820	1.823	-0.2902	-1.152	1823
0.1363	1.023104	2.526	-0.4245	-1.532	2344
0.1914	1.028161	3.520	-0.5278	-1.889	2778
0.2620	1.031627	4.918	-0.6090	-2.220	3066
0.3558	1.032983	6.955	-0.6397	-2.481	3145
0.4863	1.032311	10.159	-0.5945	-2.474	2915
0.6806	1.029731	15.526	-0.4237	-1.867	2095
1.0000	1.025188	25.218			
313.15 K					
0.0000	0.992060	0.653			
0.0256	0.998683	0.862	-0.0739	-0.272	593
0.0559	1.006012	1.160	-0.1741	-0.545	1192
0.0921	1.013054	1.588	-0.2851	-0.798	1785
0.1363	1.019948	2.163	-0.4144	-1.055	2290
0.1914	1.024706	2.965	-0.5138	-1.290	2713
0.2620	1.027956	4.074	-0.5925	-1.509	2991
0.3558	1.029195	5.677	-0.6229	-1.672	3073
0.4863	1.028480	8.165	-0.5798	-1.640	2853
0.6806	1.025905	12.35	-0.4141	-1.114	2073
1.0000	1.021399	19.47			
318.15 K					
0.0000	0.990152	0.597			
0.0256	0.996476	0.772	-0.0723	-0.066	555
0.0559	1.003514	1.025	-0.1705	-0.397	1142
0.0921	1.010213	1.377	-0.2782	-0.580	1708
0.1363	1.016697	1.851	-0.4018	-0.758	2206
0.1914	1.021176	2.501	-0.4977	-0.921	2619
0.2620	1.024221	3.400	-0.5741	-1.065	2901
0.3558	1.025353	4.680	-0.6045	-1.1700	2988
0.4863	1.024602	6.641	-0.5639	-1.135	2780
0.6806	1.022037	9.800	-0.4037	-0.844	1999
1.0000	1.017573	15.36			

Table 2

Regression results for the excess volumes of propane-1,2 diol (1) + water (2) mixtures at various temperatures

$T$ (K)	$a_0$	$a_1$	$a_2$	$\sigma$ (cm <sup>3</sup> mol <sup>-1</sup> )
303.15	-3.1624	1.0009	1.4505	0.095
308.15	-3.0720	0.9894	1.3674	0.092
313.15	-2.9971	1.0078	1.2650	0.089
318.15	-2.9109	0.9870	1.2129	0.086

The coefficient in Eq. (2) was estimated by the least-square fit method. The standard deviation was calculated by Eq. (3):

$$\sigma(V^E) = \left[ \frac{\sum (V_{\text{expt}}^E - V_{\text{cal}}^E)^2}{D - N} \right]^{0.5} \quad (3)$$

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

Dynamic viscosities ( $\eta$ ) of propane-1,2 diol (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 [7,8] by the 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 Tables 1 and 2. Viscosity deviation were correlated by Redlich–Kister Eq. (5):

$$Q = x_1x_2 \sum H_i(x_1 - x_2)^i \quad (5)$$

where  $Q = \Delta\eta$  mPa s. The coefficient in Eq. (5) are regressed by employing the least-square fit method. Standard deviations for the viscosity calculations were determined by Eq. (6), similar to Eq. (3):

$$\sigma(\Delta\eta) = \left[ \frac{\sum (\Delta\eta_{\text{expt}} - \Delta\eta_{\text{cal}})^2}{D - N} \right]^{0.5} \quad (6)$$

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 energy ( $\Delta G^{*E}$ ) of activation of viscous flow were calculated [9] as follows:

$$\frac{\Delta G^{*E}}{RT} = \left\{ \ln \left( \frac{\eta V}{\eta_2 V_2} \right) - x_1 \ln \left( \frac{\eta_1 V_1}{\eta_2 V_2} \right) \right\} \quad (7)$$

Table 3

Regression results for the deviation of viscosity of propane-1,2 diol (1) + water (2) mixtures at various temperatures

$T$ (K)	$a_0$	$a_1$	$a_2$	$\sigma$ (cm <sup>3</sup> mol <sup>-1</sup> )
303.15	-18.6187	7.8751	5.8575	0.378
308.15	-11.7764	5.2542	3.1134	0.314
313.15	-7.8926	3.8466	1.5806	0.242
318.15	-5.7970	0.5530	3.6902	0.227

Table 4

The activation parameters  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  of propane-1,2 diol (1) + water (2) mixtures at various temperatures

$x_1$	$\Delta G^* \times 10^{-3} \text{ (J mol}^{-1}\text{)}$	$\Delta H^* \times 10^{-3} \text{ (J mol}^{-1}\text{)}$	$-\Delta S^* \text{ (J mol}^{-1}\text{)}$
0.0000	49.7	15.2	113.8
0.0256	50.6	17.7	108.8
0.0559	51.7	20.2	103.8
0.0921	52.7	23.0	98.3
0.1363	53.9	25.6	93.1
0.1914	55.0	28.1	88.9
0.2620	56.1	28.1	93.0
0.3558	57.4	30.1	90.0
0.4863	59.0	35.0	79.2
0.6806	60.6	38.2	74.2
1.0000	62.1	41.2	69.2

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

The activation parameters  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  were determined using Eq. (8) by Eyring and John [10] and Ali et al. [11]:

$$\eta = \frac{hN}{V} \exp \left( \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \right) \quad (8)$$

where  $\eta$  is the viscosity of binary mixture in 0.1 Pa s,  $h$ ,  $N$ , and  $V$  are Planck's constant, Avogadro's 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-square fit method, the activation parameters  $\Delta H^*$  and  $\Delta S^*$  were obtained and  $\Delta G^*$  was obtained using the equation:  $\Delta G^* = \Delta H^* - T \Delta S^*$ . Values obtained are presented in Table 4.

#### 4. Discussion

The graphical presentation of the excess molar volumes ( $V^E$ ) is shown in Fig. 1. Propane-1,2 diol is polar and extensively self-associated through hydrogen bonding. The large negative  $V^E$  can be interpreted qualitatively [2] considering following effect: (i) expansion due to de-polymerization of propane-1,2 diol (1) + water (2) by one another, (ii) contraction due to free volume difference of unlike molecules, and (iii) contraction due to hydrogen bond formation between propane-1,2 diol (1) + water (2) through OH–OH bonding.

Thus, the large negative [12–15] values of  $V^E$  over the free volume contribution indicates the predominance of formation of hydrogen bonds between propane-1,2 diol (1) + water (2) over rupture of hydrogen bonding in propane-1,2 diol–propane-1,2 diol and water–water.

The observed values of  $V^E$  are negative over the entire range of compositions, which indicates the presence of strong specific interactions in the binary mixtures of propane-1,2 diol (1) + water (2). The

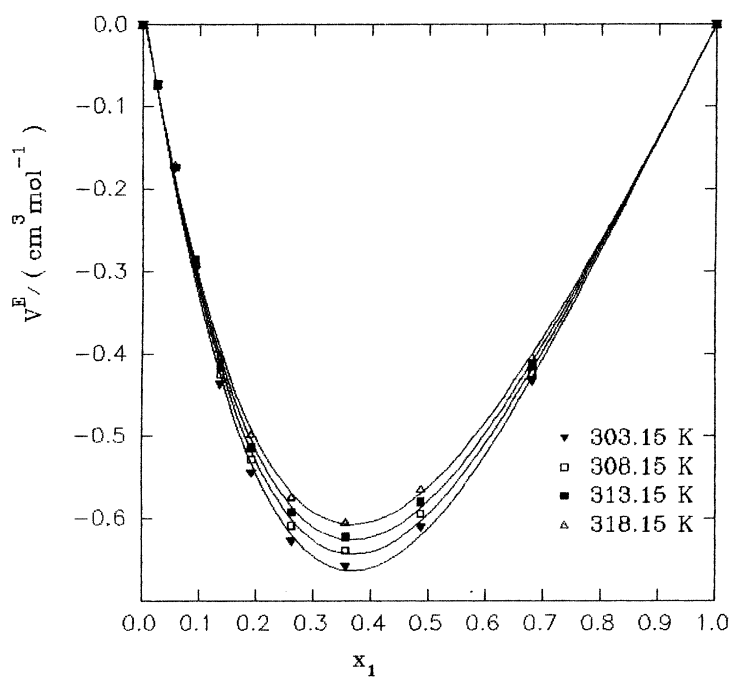


Fig. 1. Excess molar volumes ( $V^E$ ) for the system of propane-1,2 diol (1) + water (2) from 303.15 to 318.15 K.

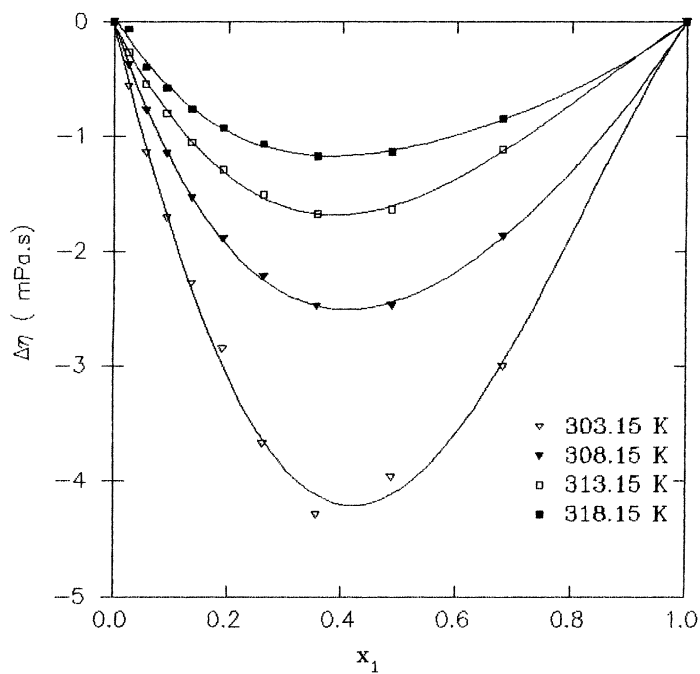


Fig. 2. Viscosity deviation for propane-1,2 diol (1) + water (2) from 303.15 to 318.15 K.

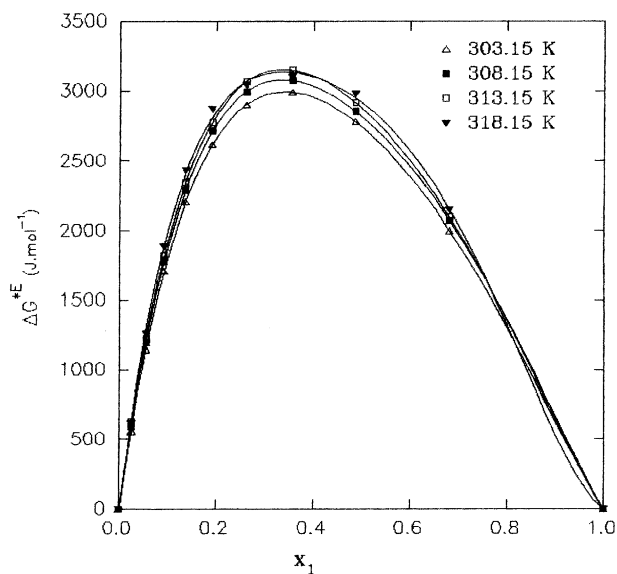


Fig. 3. Excess Gibbs energy of activation,  $\Delta G^{*E}$  for propane-1,2 diol (1) + water (2) from 303.15 to 318.15 K.

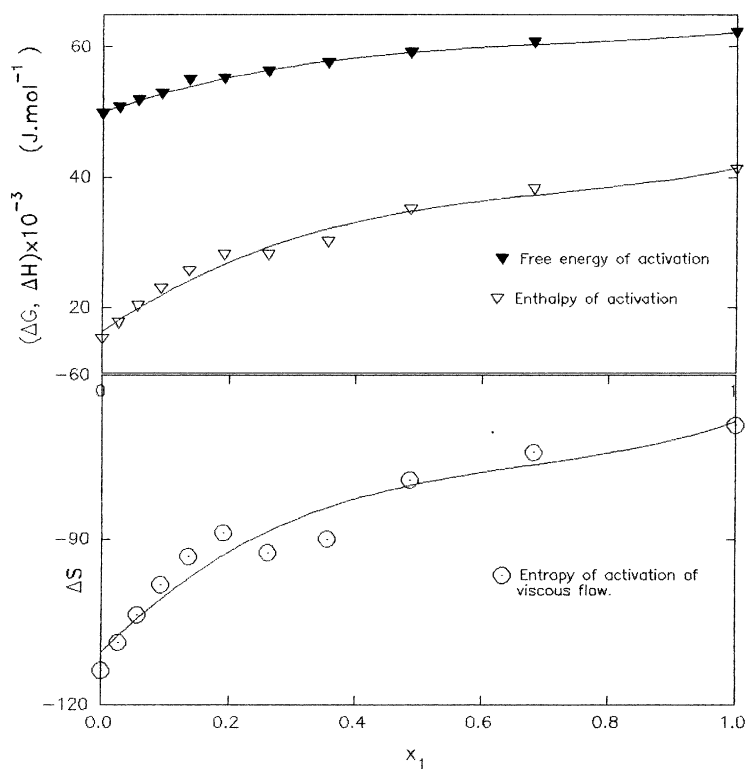


Fig. 4. Plot of free energy ( $\Delta G^*$ ), enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) of activation of viscous flow vs. mole fraction of propane-1,2 diol.

maximum deviation in the  $V^E$  occurs at 0.3558 mol fraction of propane-1,2 diol. The largest value of  $V^E$  is  $-0.6593 \text{ cm}^3 \text{ mol}^{-1}$  in the temperature range 303.15–318.15 K.

Excess molar volume becomes less negative as the temperature is raised, indicating volume expansion. The variation of excess molar volume with temperature points out the decrease in interaction between propane-1,2 diol (1) + water (2) molecules with increase in temperature.

Graphical presentation of viscosity deviation are shown in Fig. 2. Curves are found skewed [1] towards the water rich region. The values of  $\Delta\eta$  are negative over entire range of mole fractions. The values decrease with increasing temperature due to weakening of the interaction.

The large negative  $\Delta\eta$  can be interpreted qualitatively by considering the strength of intermolecular hydrogen bonding, molecular size and shapes of the components. The large negative values of  $\Delta\eta$  indicates the formation of cyclic structures of multimer [2,16] of propane-1,2 diol (1) + water (2) species.

Excess energy of activation for viscous flow are shown in Fig. 3. The observed  $\Delta G^{*E}$  values are positive for the entire mole fraction of propane-1,2 diol. 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  $\Delta H^*$  and  $\Delta G^*$  for the binary mixture are positive as shown in Fig. 4. The  $\Delta G^*$  values steadily increases with concentration of propane-1,2 diol. The  $\Delta H^*$  values exponentially increase is observed at 0.20 mol fraction and then increases steadily.

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