

## Excess molar volumes and viscosities of the binary mixtures of ethylene glycol monoisopropyl ether with water at 298.15, 308.15 and 318.15K

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Excess molar volumes ( $V_m^E$ ) and viscosities ( $\eta$ ) have been measured for ethylene glycol monoisopropyl ether + water from 298.15 to 318.15 K at 10 K intervals. The excess volumes are negative while viscosities are positive over the entire composition range for the system studied, and temperature has no appreciable influence on excess volumes. The observed negative  $V_m^E$  values are compared with the available published results at 298.15 K. Densities ( $\rho$ ) and deviations in viscosity ( $\Delta\eta$ ) of the mixtures have been calculated from the results. The deviations in viscosity values are positive over the entire range of mole fractions and temperatures. The results of excess molar volume and deviations in viscosity are fitted to the Redlich-Kister relation to estimate the adjustable parameters and standard deviations.

In recent years there has been considerable upsurge<sup>1-4</sup> in the theoretical and experimental investigations of the excess thermodynamic properties of binary liquid mixtures in view of their importance in engineering, process industry and also in developing theoretical models.

Our earlier work focused upon the study of the changes in excess volumes and viscosities of aqueous polyethylene glycol monoether solutions arising from the variation of the alkyl chain length for species with a common polar group and from the variation of the polar head group size for species with a common alkyl chain<sup>5-10</sup>. The present note deals with the study of the changes arising from the branching in the alkyl group for isomeric species during mixing. We report herein the excess molar volumes ( $V_m^E$ ) and viscosities ( $\eta$ ) for ethylene glycol monoisopropyl ether + water over the whole concentration range from 298.15 to 318.15 K at 10 K intervals.

### Experimental

Ethylene glycol monoisopropyl ether (E. Merck,

zur Synthese, GC > 98%) was dried over 4A molecular sieves before being fractionally distilled. The density of the purified sample of ethylene glycol monoisopropyl ether at 298.15 K was found to be 0.8999 g cm<sup>-3</sup>, in good agreement with the literature data<sup>11</sup>. Gas chromatographic analysis showed solvent purities to be 99.5 mol %. Karl-Fischer titration gave water contents of < 0.01 wt %. Water was deionized and distilled in glass. Its conductivity was always below 1.0 × 10<sup>-6</sup> Ω<sup>-1</sup> cm<sup>-1</sup>. Prior to the experimental measurements, all liquids were partially degassed under vacuum.

Excess volumes were measured using a continuous-dilution dilatometer as described by Dickinson *et al.*<sup>12</sup> Details of calibration, experimental set up, and operational procedure have been described previously<sup>5,13</sup>. The mercury meniscus as well as reference mark were measured with the help of a cathetometer which could read correct to ± 0.001 cm. Excess molar volumes were reproducible within ± 0.003 cm<sup>3</sup> mol<sup>-1</sup>. The mole fraction of each mixture was obtained with an accuracy of 0.0001 from the measured masses of the pure components. All the mass measurements were performed on an electric balance (Dhona 200D, India) accurate to 0.05 mg. Buoyancy corrections were made. A thermostatically controlled, well-stirred water bath with temperature controlled to ± 0.01 K using Beckmann thermometer was used for all the measurements. The measurements over the full mole fraction range were completed by two runs, i.e. one for the aqueous rich regions starting from pure water and the other for the organic rich regions starting from pure ethylene glycol monoisopropyl ether up to the composition of about 50 wt%.

The kinematic viscosities of the pure liquids and the mixtures were measured using an Ubbelohde suspended-level viscometer. The viscometer was calibrated using high-purity benzene, toluene, *n*-hexane and water at the working temperatures<sup>14,15</sup>. The average of four or five sets of flow time for each fluid was taken for the purpose of the calculation of viscosity. After multiplication by the density, the dynamic viscosity  $\eta$  is deduced with a relative error of ± 0.003 mPa s. The flow time measurements were made with an electronic stopwatch having a precision of 0.01s. The performance of the viscometer was assessed by mea-

suring and comparing the viscosities of the pure components with the values reported in literature<sup>15,16</sup>. Densities of the pure components were measured with a double-armed pycnometer<sup>10</sup> having a total volume of approximately 15 cm<sup>3</sup> and the relative error in densities at 298.15 ± 0.01 K is estimated to be ≤ 0.0003 g cm<sup>-3</sup>. From the measured values of excess molar volumes, densities of mixtures were computed as:

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

where  $M_1$  and  $M_2$  are molar masses,  $x_i$  is the mole fraction and  $V_i$  is the molar volume. The density and viscosity of water at all the three temperatures were taken as reported by Riddick *et al.*<sup>15</sup> and Kel<sup>17</sup>.

### Results and discussion

The experimental excess volume and viscosity for water + ethylene glycol monoisopropyl ether at 298.15, 308.15 and 318.15 K as a function of mole fraction of organic solvent are reported in Tables 1 and 2. The  $V_m^E$  results of the binary mix-

tures at different temperatures are shown in Fig. 1. The viscosity deviations,  $\Delta\eta$ , are obtained by

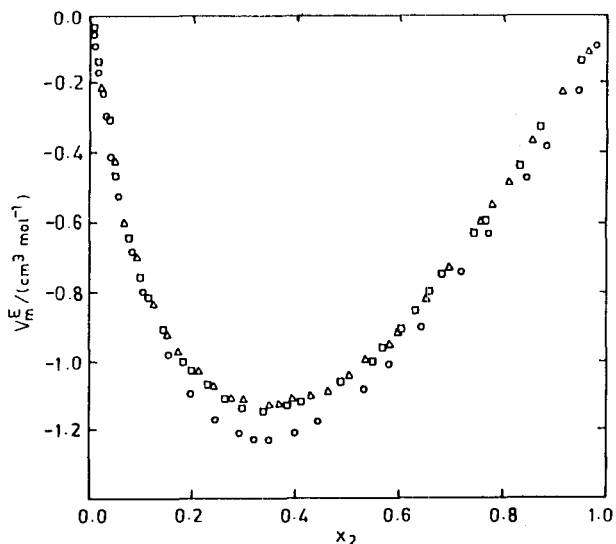


Fig. 1—Excess molar volume ( $V_m^E$ ) of water (1)+ethylene glycol monoisopropyl ether (2); ○, T=298.15 K; □, T=308.15 K; △, T=318.15 K

Table 1—Excess molar volumes ( $V_m^E$ ) for water (1)+ethylene glycol monoisopropyl ether (2)

$x_2$	$V_m^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$x_2$	$V_m^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$x_2$	$V_m^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$x_2$	$V_m^E$ (cm <sup>3</sup> mol <sup>-1</sup> )
T=298.15 K							
0.0067	-0.065	0.0851	-0.681	0.3516	-1.232	0.7756	-0.633
0.0092	-0.095	0.1048	-0.790	0.4013	-1.212	0.8467	-0.473
0.0167	-0.171	0.1561	-0.979	0.4445	-1.175	0.8845	-0.382
0.0235	-0.237	0.1972	-1.092	0.5342	-1.075	0.9465	-0.227
0.0319	-0.303	0.2478	-1.171	0.5822	-1.009	0.9812	-0.092
0.0456	-0.415	0.2935	-1.211	0.6432	-0.900		
0.0587	-0.529	0.3521	-1.229	0.7225	-0.741		
T=308.15 K							
0.0038	-0.037	0.1712	-0.974	0.3839	-1.132	0.6881	-0.749
0.0133	-0.144	0.1820	-1.002	0.4185	-1.122	0.7462	-0.634
0.0366	-0.359	0.1992	-1.021	0.4807	-1.059	0.7675	-0.600
0.0524	-0.472	0.2299	-1.065	0.5456	-1.001	0.8349	-0.439
0.0774	-0.649	0.2697	-1.112	0.5700	-0.960	0.8763	-0.333
0.1008	-0.755	0.2975	-1.136	0.6060	-0.909	0.9509	-0.141
0.1153	-0.817	0.3428	-1.148	0.6307	-0.851		
T=318.15 K							
0.1431	-0.906	0.3487	-1.144	0.6639	-0.796		
0.0065	-0.066	0.2110	-1.033	0.4652	-1.085	0.7829	-0.545
0.0216	-0.220	0.2425	-1.074	0.5044	-1.051	0.8100	-0.488
0.0431	-0.423	0.2733	-1.105	0.5395	-1.015	0.8158	-0.476
0.0693	-0.601	0.3028	-1.116	0.5829	-0.957	0.8594	-0.371
0.0872	-0.699	0.3519	-1.130	0.6002	-0.929	0.9166	-0.242
0.1241	-0.837	0.3721	-1.129	0.6534	-0.822	0.9644	-0.122
0.1525	-0.921	0.3954	-1.114	0.6990	-0.726		
0.1768	-0.979	0.4318	-1.103	0.7616	-0.595		

Table 2—Viscosities ( $\eta$ ), and deviations in viscosities ( $\Delta\eta$ ) for water (1) + ethylene glycol monoisopropyl ether (2)

$x_2$	$\frac{\eta}{\text{mPa s}}$	$\frac{\Delta\eta}{\text{mPa s}}$	$x_2$	$\frac{\eta}{\text{mPa s}}$	$\frac{\Delta\eta}{\text{mPa s}}$	$x_2$	$\frac{\eta}{\text{mPa s}}$	$\frac{\Delta\eta}{\text{mPa s}}$
T = 298.15 K								
0.0109	1.267	0.362	0.3221	4.357	3.031	0.6778	3.200	1.394
0.0413	2.063	1.117	0.3521	4.306	2.951	0.7202	3.048	1.185
0.0765	2.814	1.821	0.4030	4.163	2.728	0.7746	2.877	0.940
0.1205	3.576	2.523	0.4524	4.010	2.509	0.7995	2.787	0.817
0.1674	4.049	2.933	0.4994	3.837	2.272	0.8831	2.544	0.461
0.2045	4.256	3.090	0.5800	3.542	1.869	0.9744	2.301	0.094
0.2644	4.376	3.129	0.6181	3.408	1.683			
T = 308.15 K								
0.0117	0.873	0.145	0.2791	2.670	1.726	0.6795	2.059	0.791
0.0243	1.048	0.310	0.3362	2.653	1.663	0.7299	1.963	0.654
0.0480	1.393	0.636	0.3613	2.624	1.613	0.7669	1.898	0.560
0.0818	1.805	1.020	0.4016	2.568	1.525	0.8478	1.756	0.352
0.1081	2.078	1.272	0.4861	2.440	1.328	0.9015	1.680	0.233
0.1452	2.343	1.507	0.5552	2.303	1.136	0.9345	1.622	0.147
0.1739	2.480	1.621	0.5964	2.222	1.021	0.9761	1.563	0.055
0.2237	2.615	1.716	0.6229	2.168	0.946			
T = 318.15 K								
0.0064	0.660	0.059	0.2840	2.123	1.322	0.6549	1.746	0.678
0.0205	0.828	0.217	0.3278	2.125	1.293	0.7115	1.649	0.541
0.0505	1.117	0.544	0.3659	2.102	1.242	0.7651	1.586	0.440
0.0838	1.468	0.811	0.4119	2.062	1.169	0.8252	1.515	0.325
0.1271	1.756	1.068	0.4724	1.994	1.058	0.8743	1.454	0.230
0.1717	1.950	1.230	0.5277	1.898	0.922	0.9506	1.367	0.088
0.2346	2.088	1.322	0.5697	1.854	0.538			

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad \dots (2)$$

where  $\eta$  is viscosity of the mixture and  $x_1$ ,  $\eta_1$  and  $x_2$ ,  $\eta_2$  are the mole fraction and viscosity of pure components 1 and 2, respectively. The plot of  $\Delta\eta$  as a function of  $x_2$  at different temperatures are presented in Fig. 2.

Each set of values of  $V_m^E$  and  $\Delta\eta$  at various temperatures have been fitted to the Redlich-Kister-type Eq. (3):

$$(V_m^E \text{ or } \Delta\eta) = x_1 x_2 \sum_{j=1}^n a_j (x_2 - x_1)^{j-1} \quad \dots (3)$$

In each case, the optimum number of coefficients  $a_j$  was ascertained from an examination of the variation of the standard deviation with  $n$ :

$$\sigma = (\sum (V^E \text{ or } \Delta\eta_{\text{exptl}} - V^E \text{ or } \Delta\eta_{\text{calcd}})^2 / (n - p))^{1/2} \quad \dots (4)$$

where  $n$  is the total number of experimental points,  $p$  is the number of parameters. The values adopted for the coefficients  $a_j$  and standard deviation

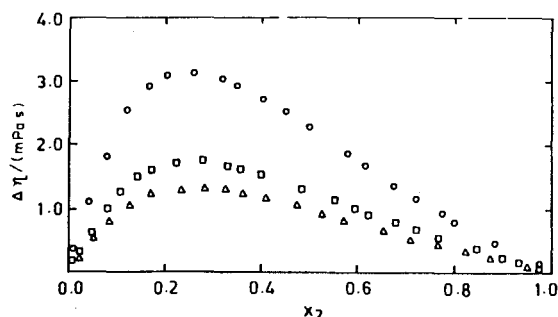


Fig. 2—Deviations in viscosity ( $\Delta\eta$ ) for water (1) + ethylene glycol monoisopropyl ether (2):  $\circ$ , T = 298.15 K;  $\square$ , T = 308.15 K;  $\triangle$ , T = 318.15 K

associated with the use of Eq. (4) are recorded in Table 3.

The  $V_m^E$  values for water + ethylene glycol monoisopropyl ether reported by Davis and Chacon<sup>11</sup> at 298.15 K from density values obtained using flow vibrating-tube densimeter are in agreement with the  $V_m^E$  values at 298.15 K obtained in this laboratory over the whole mole fraction range. The equimolar values of  $V_m^E$  at 298.15 K is

Table 3—Values of the parameters of Eq. (3) and standard deviations

	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	$\sigma$
T = 298.15 K							
$V_m^E(\text{cm}^3\text{mol}^{-1})$	-4.505	2.404	-1.252	1.076	-2.171	-0.596	0.007
$\Delta\eta$ (mPa s)	9.064	-9.798	8.586	-6.490	0.011	2.836	0.019
T = 308.15 K							
$V_m^E(\text{cm}^3\text{mol}^{-1})$	-4.213	2.265	-1.029	0.473	-2.028	1.752	0.006
$\Delta\eta$ (mPa s)	5.094	-5.073	4.995	-5.459	-1.142	4.773	0.017
T = 318.15 K							
$V_m^E(\text{cm}^3\text{mol}^{-1})$	-4.236	1.982	-0.399	1.817	-3.075	0.262	0.006
$\Delta\eta$ (mPa s)	3.966	-4.060	3.450	-2.576	-0.196	1.512	0.012

-1.120  $\text{cm}^3\text{mol}^{-3}$  compared with -1.130  $\text{cm}^3\text{mol}^{-1}$  reported by Davis and Chacon<sup>11</sup>.

The deviations in viscosity ( $\Delta\eta$ ) are positive whereas the excess molar volumes ( $V_m^E$ ) are negative over the entire range of composition at all the temperatures studied. Excess volumes become less negative with the rise in temperature; however, the effect of temperature on excess volume is not appreciable. Both  $\eta$  and  $\Delta\eta$  decrease with an increase in temperature. No experimental data of  $V_m^E$  and  $\eta$  for this system are available in the literature at higher temperature with which the present results can be compared. Negative excess volumes and rather large positive  $\Delta\eta$  indicate specific interactions leading to complex formation through intermolecular hydrogen-bonding interactions between unlike molecules compared to like molecules. This may be comparable where the linear chain ether molecules<sup>8</sup>, show strong intramolecular hydrogen bonding as compared to a branched chain ether. Again, the presence of the etheric oxygen enhances the ability of the -OH group of the glycol molecules to form hydrogen bonds with water molecules and hence result in a contraction in volume. The sharp changes of these properties at low mole fraction of glycol would imply more order and hence more structure or clustering in an aqueous environment<sup>18</sup>. This leads to substantial increases in the viscosities of the mixtures and corresponding decreases in their excess molar volumes. Considering the differences of the molar volumes of pure components ( $V_1 = 18.07\text{ cm}^3\text{mol}^{-1}$ ,  $V_2 = 115.73\text{ cm}^3\text{mol}^{-1}$  at 298.15 K), it appears that such clustering might also arise from interstitial accommodation of water into the amphiphile structure without any significant change in the latter's scheme of self-aggregation<sup>19</sup> thereby giving rise to marked changes in their properties at water-rich region. Further, the variation of these pro-

erties with temperature indicates that an increase in temperature effects the molecular organisation in this system so as to decrease the interaction between glycol and water molecules.

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