Excess Properties for Water + Ethylene Glycol at 288.15, 293.15, 298.15 and 303.15 K

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Abstract

Densities and viscosities of the binary systems water + ethylene glycol have been measured at 288.15, 293.15, 298.15, 303.15 K and atmospheric pressure, over the whole composition range. The excess values of molar volume, viscosity, and Gibbs free energy of activation of viscous flow were calculated from experimental measurements. Based on the variations of the excess functions with composition, conclusions about the molecular interactions in these kinds of mixtures were obtained.

Keywords: *excess properties, binary mixtures, water, ethylene glycol.*

Introduction

Viscosities and densities of liquid mixtures are needed for many engineering applications. Viscometer and volumetric data pertaining to water + ethylene glycol mixtures are relatively scarce in the literature [1–3].

The aim of this work is to provide information on the molecular interactions between water and ethylene glycol. In this work, which represents one part of a continuing program in our laboratory [4-6], we are reporting the viscosities and densities at atmospheric pressure, over the entire composition range, of the binary systems water + ethylene glycol at 288.15, 293.15, 298.15 and 303.15 K. We are also reporting the following excess properties: molar volumes (V^E), viscosity (η^E) and molar free energy of activation of viscous flow (G^{*E}) for the same binary solutions.

Experimental

Ethylene glycol was obtained from Merck with a specified purity of 99.5 % mass and was used without further purification. The water was doubly distilled; the purities of the components were verified by comparing their densities, viscosities and refractive indices with the literature values (Table 1).

Viscosities of binary mixtures were determined with an Ubbelohde kinematic viscometer that was always kept in a vertical position in a water thermostat. A thermostatically controlled bath (constant to ± 0.05 K) was used.

Table 1. Comparison of experimental physical properties of the pure liquids with literature values

Component	Temp. °C	Density g.cm^{-3}		Viscosity mPa.s		Refractive indices	
		This work	Literature data	This work	Literature data	This work	Literature data
Water	288.15	0.9991	0.999099[7]	1.1691	-	1.3337	1.3333[7]
	293.15	0.9982	0.99821[7]	1.0023	1.00209[7]	1.3332	1.3330[1]
	298.15	0.9970	0.9973[3]	0.8805	0.891[3]	1.3325	1.3325[1]
	303.15	0.9956	0.99565[7]	0.7984	0.7977[7]	1.3318	1.3320[1]
Ethylene glycol	288.15	1.1136	-	27.9164	-	1.4326	-
	293.15	1.1101	1.1132[1]	20.5990	20.8064[1]	1.4311	1.4318[7]
	298.15	1.1068	1.1095[7]	18.3335	18.6826[1]	1.4305	1.4310[1]
	303.15	1.1031	1.1055[1]	14.0673	13.8678[1]	1.4281	1.4287[1]

The kinematic viscosity was calculated using the relation:

$$\nu = At - B/t \tag{1}$$

where t is the flowing time of a constant volume liquid through the viscometer capillary correct to ± 0.1 s; A and B are characteristic constants of the used viscometer, which were determined by taking n-octane and benzene as the calibrating liquids for correction of kinetic energy (Hagen-Poiseuille) deviations.

The dynamic viscosity was determined from the equation:

$$\eta = \nu\rho \tag{2}$$

where ρ is the density of liquid. The accuracy of the viscosity measurement was estimated to be 0.0008 mPa.s.

The densities were determined by hydrostatic weighing method of Kohlrausch [8]. The experimental technique has been previously described [5]. Trough weighing, mole fractions were determined. The precision of the densities was ± 0.00005 g/cm^3 and of the mole fraction was ± 0.0001.

The refractive indices (sodium D line) of the pure liquids were measured using a thermostatically controlled Abbe refractometer.

In all determinations, triplicate experiments were performed for each composition and temperature, and the arithmetic mean was taken for the calculations of the density and viscosity.

Results and Discussion

Experimental values of viscosities and densities of the binary mixtures at 288.15, 293.15, 298.15 and 303.15 K are listed as a function of mole fraction of ethylene glycol in Tables 2. The results in this study are in close agreement with the work of Tsierkezo and Molinou [1] with regard to these systems at 293.15 and 313.15 K. Our results at 298.15 K are also in agreement with the work reported by Aminhabavi and Gopalakrishna [3]. No experimental data were found for the studied mixtures at 288.15 K with which a comparison of the present values could be made.

The excess functions were calculated with the following equations:

$$V^E = V - \left(x_1V_1 + x_2V_2\right) \tag{3}$$

$$\eta^E = \eta_{exp} - \left[x_1\eta_1 + x_2\eta_2\right] \tag{4}$$

$$G^{*E} = RT\left[\ln \eta V - \left(x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2\right)\right] \tag{5}$$

where V and η are the molar volumes and the viscosities of the mixture; V_1, V_2, η_1, η_2, x_1 and x_2 are the molar volumes, viscosities and the molar fractions of the pure components, respectively.

Table 2. Experimental Densities (ρ) and Viscosities (η) of binary mixtures of Ethylene Glycol (x)+ Water (1-x) at different temperatures

x	ρ g·cm^{-3}	η mPa·s	x	ρ g·cm^{-3}	η mPa·s
		288.15 K			
0.0000	0.9991	1.1691	0.6015	1.1039	15.1937
0.0910	1.0341	2.1272	0.7014	1.1075	19.6608
0.2003	1.0613	3.5838	0.7983	1.1099	22.1477
0.2992	1.0787	5.3408	0.9046	1.1117	24.9999
0.3971	1.0896	7.9792	1.0000	1.1136	27.9164
0.4982	1.0957	11.4080			
		293.15 K			
0.0000	0.9982	1.0023	0.6015	1.1007	11.1732
0.0910	1.0323	2.0120	0.7014	1.1040	13.9524
0.2003	1.0589	3.3536	0.7983	1.1065	16.0057
0.2992	1.0755	5.2949	0.9046	1.1086	18.6807
0.3971	1.0860	6.8349	1.0000	1.1101	20.5990
0.4982	1.0923	8.7434			
		298.15 K			
0.0000	0.9970	0.8805	0.6015	1.0975	9.8818
0.0910	1.0303	1.8512	0.7014	1.1003	11.4931
0.2003	1.0562	3.0235	0.7983	1.1029	13.2666
0.2992	1.0723	5.2361	0.9046	1.1051	15.2725
0.3971	1.0824	6.1749	1.0000	1.1068	18.3335
0.4982	1.0889	8.1795			
		303.15 K			
0.0000	0.9956	0.7984	0.6015	1.0942	7.4752
0.0910	1.0286	1.8272	0.7014	1.0969	8.7184
0.2003	1.0539	2.9848	0.7983	1.0996	10.2356
0.2992	1.0691	5.2200	0.9046	1.1022	12.3520
0.3971	1.0788	5.4974	1.0000	1.1031	14.0673
0.4982	1.0855	6.2697			

The excess molar volumes calculated at 288.15, 293.15, 298.15 and 303.15 K are plotted against composition in fig. 1. We note that negative values are obtained for all cases. The negative values of excess molar volumes for water + ethylene glycol systems show that hydrogen-bonding interactions prevail in these systems. These negative values are the result of a more efficiency packing in the mixture than in pure liquids. This effect can be attributed to the heteroassociation, which exceeds the positive contribution to V^E arising from the breaking up of the self-associated-like molecules, of ethylene glycol or water.

The excess viscosity for all binary mixtures of water + ethylene glycol are presented in Figure 2. The values of η^E are negative over the whole composition range that is in complete agreement with the conclusions reached for the V^E behaviour.

Figure 3 presents the dependence of G^{*E} values with composition for all four temperatures. According to previous reports [9,10] this parameter can be considered as a valid measure of molecular interaction. In our case, the positive G^{*E} values lead us to conclude that cohesive

forces are dominant for water + ethylene glycol mixtures. It is known that the strength of molecular interactions increases as G^{*E} decreases. In particular, for the above systems the interactions decrease as the temperature increase.
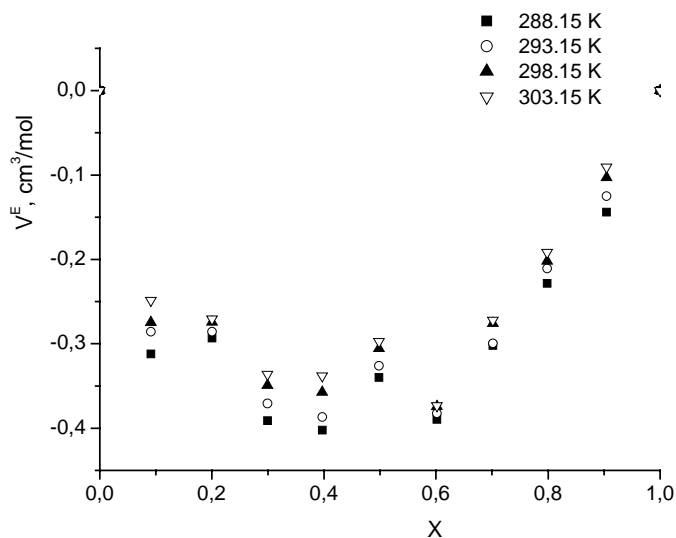

Fig. 1. Excess molar volumes of Ethylene Glycol (x) + Water (1-x)
mixtures at different temperatures
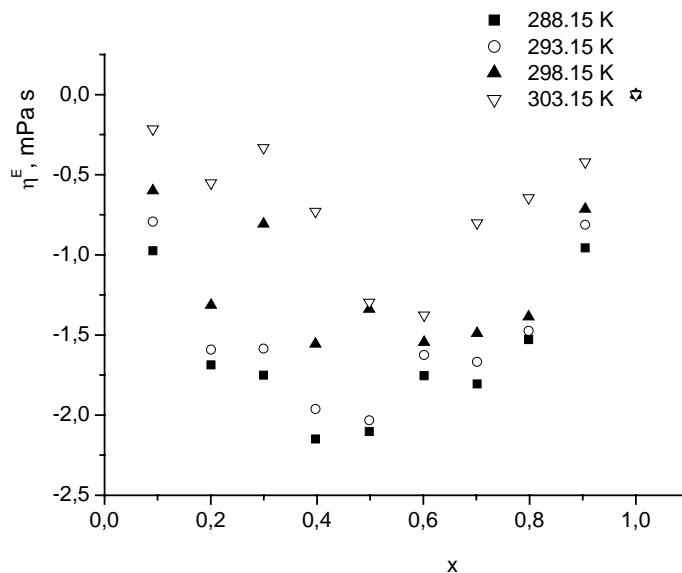

Fig. 2. Excess viscosities of Ethylene Glycol (x) + Water (1-x)
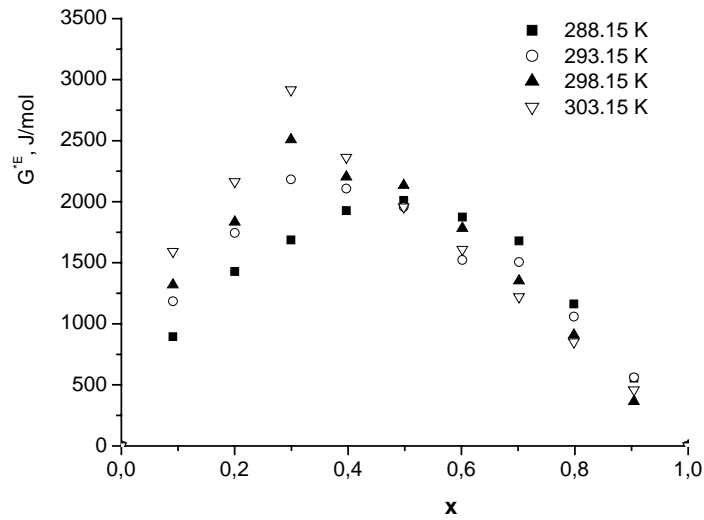mixtures at different temperatures

Fig. 3. Molar excess free energies of activation of viscous flow for
Ethylene Glycol (x) + Water (1-x) mixtures at different temperatures

The excess functions for these binary systems were computed by using the following Redlich – Kister equation [11]:

$$X^E = x(1-x) \sum_{i=0}^{i=3} A_i (2x-1)^i \qquad (6)$$

where X^E represents any of the following properties: V^E, η^E, G^{*E}; x and (1-x), respectively, represent the molar fractions of the components; A_i denote the polynomial equation coefficients. The values of A_i coefficients for the excess functions of the binary systems and their standard deviation (σ) are shown in Table 3.

Table 3. Coefficients A_i from eq. (6) and standard deviations σ or the binary systems

Temp., K	Coefficients	V^E, cm^3/mol	η^E, mPa s	G^{*E}, J/mol
	A_0	-1.47444	-8.00596	7939.32
	A_1	0.07184	1.27095	314.35
288.15	A_2	-1.1559	-5.02639	633.87
	A_3	1.49949	-1.66367	-4541.85
	σ	0.0411	0.1117	31.03
	A_0	-1.44089	-7.55394	7695.74
	A_1	-0.00012	0.99285	-4300.33
293.15	A_2	-0.93298	-3.76412	3869.80
	A_3	1.62169	-1.57876	297.71
	σ	0.0356	0.1305	95.12
	A_0	-1.36338	-5.71909	8455.29
	A_1	-0.09693	-2.74627	-5271.409
298.15	A_2	-0.8488	-4.49624	1705.97
	A_3	1.89252	3.84481	-1826.64
	σ	0.0339	0.2100	117.97
	A_0	-1.33906	-4.33304	8163.01
	A_1	-0.15455	-3.90135	-8861.55
303.15	A_2	-0.67868	2.58957	5612.21
	A_3	1.93925	5.85268	1898.27
	σ	0.0295	0.2052	159.38

The standard deviation has been calculated with the following equation:

$$\sigma = \left[\frac{\sum (X_{exp.}^{E} - X_{calc.}^{E})^2}{m - n} \right]^{1/2} \qquad (7)$$

where m is the number of experimental points; n - the number of A_i estimated coefficients.

Conclusions

Density and viscosity for binary mixtures of water with ethylene glycol are reported as a function of mixture composition at four temperatures.

These experimental data were used to calculate excess molar volumes, excess viscosities and excess molar Gibbs free energy of activation of viscous flow. The results were interpreted in terms of specific interactions between the molecules.

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Proprietăţi de exces pentru apă + etilenglicol la 288.15, 293.15, 298.15 and 303.15 K

Rezumat

Au fost determinate densităţile şi viscozităţile sistemelor binare de apă + etilenglicol la 288.15, 293.15, 298.15, 303.15 K şi presiune atmosferică, pe întreg domeniul de concentraţie. Din măsurătorile experimentale s-au calculat valorile de exces ale volumului molar, viscozităţii şi energiei libere Gibbs de activare a curgerii. Pe baza variaţiei funcţiilor de exces cu compoziţia s-au obţinut concluzii despre interacţiunile moleculare din aceste amestecuri.