Liquid Viscosities, Surface Tension and Viscous Flow Thermodynamics of Ethylene Glycol + Water Mixtures at 308.15, 313.15, 318.15 and 323.15 K

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This paper reports the measurements of viscosities and surface tension for the binary mixtures of ethylene glycol + water as a function of composition at T = (308.15, 313.15, 318.15 and 323.15) K. Viscosities were determined with an Ubbelohde capillary viscometer. The experimental results are compared with data published in the literatures. From the experimental data, viscosity, surface tension and viscosity deviations $\Delta\eta$ were calcualted. The calculated results were fitted to a Redlich-Kister equation to obtain the coefficients and estimate the standard deviations between the experimental and calculated quantities. The values of $\Delta\eta$ are negative over the whole concentration range. From the kinematic viscosity data, enthalpy of activation for viscous flow (ΔH^*) and entropy of activation for the viscous flow (ΔS^*) were calculated.

Key Words: Ethylene glycol, Viscosity, Surface tension, Viscous flow thermodynamics.

INTRODUCTION

Sulfur dioxide (SO_2) is one of the most significant atmospheric pollutants and its emission is directly related to combustion processes, such as the consumption of fossil fuels and burning of biomass[1]. It is known to have crucial effects on human health and environment and as a consequence, receives more and more attention. Presently, there are several ways of reducing SO_2 emissions from flue gases[2-4]. Limestone-based wet flue gas desulfurization technology has been seen as the most effective method for the control of SO_2 from coal fired boilers[5]. However, wet flue gas desulfurization produces the dry product of gypsum, which is difficult to recycle, so that a preferable method has been developed. Recently, more and more organic solvents are used in gas sweetening absorption processes[6,7]. Among numerous organic solvents, alcohols show favourable absorption and desorption properties for acid gases in industrial processes[8,9], for this reason, the alcohol + water systems for SO_2 scrubbing had been paid particular attention in previous works[10-15].

Ethylene glycol and its similar compounds of various molecular weights showed important chemical uses in the removal of SO_2 from flue gas[4] due to their low vapour pressure, low toxicity, high chemical stability and low melting point. The primary advantages of ethylene glycol may also be related with high solubility and desorption capability for SO_2. The knowledge of physicochemical properties of ethylene glycol + water mixtures (EGW) over a wide range of temperatures is important for practical applications in flue gas desulfurization[16]; however, the previous literatures[17-19] show that only the partly mixing properties of ethylene glycol + water mixtures have been reported. Therefore, we have to carry out the measurements for densities and viscosities of ethylene glycol + water mixtures.

This paper is a part of the systematic studies on the physico-chemical properties of binary mixtures of ethylene glycol and its similar compounds[9-15,20,21]. In this work, the viscosities and surface tensions of ethylene glycol + water mixtures are reported in the temperatures range of (308.15 to 323.15) K, over the entire mole fraction range of ethylene glycol under atmospheric pressure. From these results, viscosity deviations ($\Delta\eta$), enthalpy of activation for viscous flow (ΔH^*) and entropy of activation for the viscous flow (ΔS^*) were calculated.

EXPERIMENTAL

The analytical grade ethylene glycol was purchased from Beijing Reagent company. It was used after drying over molecular sieves (type 4A) and decompression filtration before measurements. The purity of the sample was checked by density determination at 298.15 K. The density of ethylene glycol + water mixtures at 308.15 K was found to be 1.1030 g cm^{-3}, in good agreement with the literatures[18,19]. Bidistilled water was used in this work.

Measurements: Solvent mixtures were prepared by mass using an electronic analytical balance with a precision of ± 0.0001 g (Sartorius BS 224S). The uncertainty in the mole fraction for each binary mixture was estimated to be ± 0.0001.

The kinematic viscosity in both the pure components and their mixtures was made with a commercial capillary viscometer of the ubbelohde type, which was calibrated with bi-distilled water and ethanol (HPLC grade) at T = (308.15 to 323.15) K. A thermostatically controlled and well-stirred water bath, which was controlled to ± 0.01 K, was used for all the viscosity and surface tension measurements. The flow time was determined with a hand-held digital stopwatch capable of measuring time within ± 0.01 s. The average of sixteen flow times for each fluid was taken for the purpose of the calculation of viscosities.

The kinematic viscosity (ν) was calculated from the following equation:

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

where, ν denotes the kinematic viscosity; t denotes flow time of liquids; and A and B denote viscometer constants, respectively. A and B are calculated from measurements with the calibration fluids. The absolute viscosity (η) was obtained by the equation of $\eta = \nu\rho$ and the ρ values were shown in the previous work[22]. The uncertainty of the viscosity measurement was estimated to be lower than ± 0.3 %.

The experimental viscosities and surface tensions of pure ethylene glycol at the various temperatures are compared with the reported literature values and listed in Table-1.

TABLE-1
COMPARISON OF VISCOSITIES (η), SURFACE TENSION (γ) OF ETHYLENE GLYCOL WITH LITERATURE VALUES

T (K)	η/mPa s		γ/(mN m⁻¹)	
	Exp.	Lit.	Exp.	Lit.
308.15	9.2122	10.473[19]	50.114	
313.15	7.9605		48.732	48.07[17]
318.15	6.2933		47.254	
323.15	5.4468	6.992[18]	46.406	

The surface tension of pure liquids and their mixtures were determined using the drop volume method and the diameter of the dropper is 4.451 mm. A capillary, which was recreated from a pipette, was put into the glass tube with liquid. The appliance was kept in the water bath vertically until the temperature kept at a constant. The volume of the liquid drop could be read out from the capillary. The average of five times for each fluid was taken.

The surface tension (γ) was calculated from the following equation:

$$\gamma = \frac{V\rho g}{r} F \tag{2}$$

where, γ denotes the surface tension, V denotes the volume of the liquid drop, ρ denotes the density of the liquid, g denotes the acceleration of gravity, r denotes the semi-diameter of the dropper, F denotes the correction factor.

RESULTS AND DISCUSSION

Experimentally measured viscosities (η) of ethylene glycol + water mixtures at T = (308.15, 313.15, 318.15 and 323.15) K are shown in Table-2 and Fig. 1. In all cases, the viscosities (η) increase with the increasing ethylene glycol concentration in ethylene glycol + water mixtures and decrease with the increasing temperature.

TABLE-2
EXPERIMENTAL KINEMATIC VISCOSITIES (ν) OF ETHYLENE GLYCOL (1) + WATER (2)

x_1	ν/(m²s)			
	Temperature (K)			
	308.15	313.15	318.15	323.15
0.0000	0.725	0.658	0.596	0.556
0.0145	0.754	0.705	0.636	0.591
0.0312	0.831	0.760	0.677	0.632
0.0484	0.911	0.828	0.736	0.684
0.0686	0.999	0.909	0.788	0.734
0.0883	1.10	0.993	0.857	0.799
0.1107	1.23	1.09	0.933	0.865
0.1621	1.50	1.35	1.14	1.05
0.2247	1.92	1.68	1.41	1.28
0.3032	2.49	2.16	1.78	1.59
0.4035	3.25	2.80	2.30	2.04
0.5366	4.32	3.73	3.03	2.67
1.000	8.94	7.24	5.73	4.99

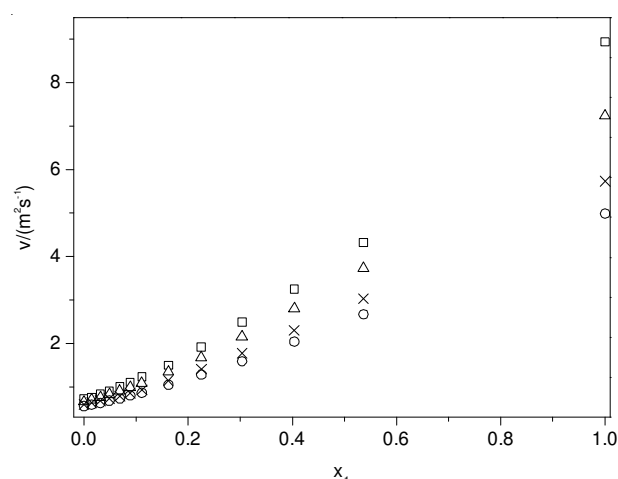
Fig. 1. Experimental kinematic viscosities with mole fraction for ethylene glycol (1) + water (2): □, 308.15 K; △, 313.15 K; ×, 318.15 K; O, 323.15 K

The experimental values of ν for the various mixtures have been used to calculate the viscosity deviation ($\Delta\eta$), which is defined by the following equations:

$$\Delta h = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

where, η denote the viscosity of the mixtures, η_1 and η_2 denote viscosities of pure ethylene glycol and pure water and x_1 and x_2 denote the mole fractions of the pure components. The results of the viscosity deviation are showed in Table-3 and Fig. 2.

Fig. 2 shows that the $\Delta\eta$ values are positive over the main composition range for all mixtures. The $\Delta\eta$ versus x_1 curves shift toward the water-rich region. The viscosity deviations, $\Delta\eta$, decrease with the increasing temperatures.

The viscosity deviations, $\Delta\eta$, were also represented by the Redlich-Kister equation as follows:

$$\Delta\nu / m^2 \cdot s = x_1 x_2 \sum_{i=0}^{4} C_i (2x_i - 1)^i \tag{4}$$

TABLE-3
KINEMATIC VISCOSITY DEVIATIONS
($\Delta\nu$) FOR ETHYLENE GLYCOL (1) + WATER (2)

| x_1	$\Delta\nu/(m^2s)$			
	Temperature (K)			
	308.15	313.15	318.15	323.15
0.0000	0.000	0.000	0.000	0.000
0.0145	-0.091	-0.049	-0.035	-0.029
0.0312	-0.150	-0.103	-0.079	-0.063
0.0484	-0.212	-0.149	-0.109	-0.087
0.0686	-0.290	-0.200	-0.161	-0.126
0.0883	-0.349	-0.246	-0.192	-0.149
0.1107	-0.410	-0.293	-0.232	-0.182
0.1621	-0.553	-0.378	-0.290	-0.230
0.2247	-0.648	-0.461	-0.342	-0.274
0.3032	-0.727	-0.498	-0.377	-0.313
0.4035	-0.788	-0.510	-0.369	-0.306
0.5366	-0.819	-0.454	-0.321	-0.269
1.0000	0.000	0.000	0.000	0.000
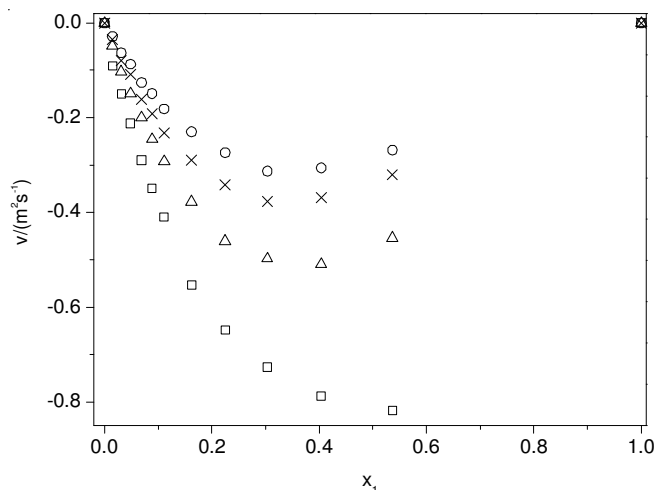
Fig. 2. Kinematic viscosity deviations with mole fraction for ethylene glycol (1) + water (2): □, 308.15 K; △, 313.15 K; ×, 318.15 K; O, 323.15 K

The coefficients C_i and the standard deviation s are presented in Table-4.

TABLE-4
COEFFICIENTS AND STANDARD DEVIATIONS OF VISCOSITY
DEVIATIONS ($\Delta\nu$) FOR ETHYLENE GLYCOL (1) + WATER (2)

T (K)	B_4	B_3	B_2	B_1	B_0	$\sigma/(m^2 \cdot s)$
308.15	-2.40	-3.86	-3.84	-0.47	-3.24	0.010
313.15	-0.77	-1.14	-0.94	0.99	-1.89	0.004
318.15	0.04	-0.01	-0.51	0.87	-1.35	0.004
323.15	-2.57	-3.93	-1.87	0.61	-1.11	0.003

The thermodynamic parameters of activation of viscous flow of the binary mixtures, such as Gibbs energies of activation of viscous flow (ΔG^*), enthalpy of activation for viscous flow (ΔH^*) and entropy of activation for the viscous flow (ΔS^*), have been evaluated on the basis of Eyring's approach to Andrade's theory[23] with the viscosity expressed in the form:

$$\nu = \frac{hN_A}{M} exp\left(\frac{\Delta G^*}{RT}\right) \qquad (5)$$

where, $M = \sum_i X_i M_i$ is the average molar mass, h is Planck's constant, N_A is the Avogadro number, R is the gas constant and T is the absolute temperature.

By applying the standard thermodynamic equation

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (6)$$

which is possible to write

$$R \ln\left(\nu \frac{M}{hN_A}\right) = \frac{\Delta H^*}{T} - \Delta S^* \qquad (7)$$

According to the Eyring theory, the enthalpy and entropy of activation for the viscous flow can be calculated from eqn. 6.

Plots of the term on the left-hand side of eqn. 7[23] against 1/T for each binary mixture are nearly linear, in Fig. 3. The ΔH^* values were calculated from the slopes of the curves. The ΔH^* values so obtained, together with the ΔG^* values calculate from eqn. 5[23], were used to calculate the corresponding ΔS^* values by using eqn. 6[23]. The ΔH^* and ΔS^* values are listed in Table-5. The positive ΔH^* values reveal that the binding force of ethylene glycol-ethylene glycol molecules is weaker than ethylene glycol-water or water-water. On the other hand, the generally negative ΔS^* data show that the viscous flow is an ordered process involving contiguous liquid layers which should retain their structural configuration even moving in a stationary steady state.
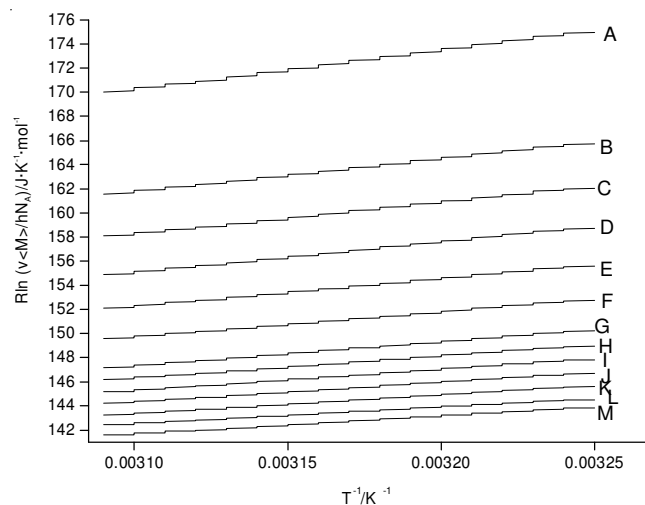

Fig. 3. Plots of Rln ($\nu<M>/hN_A$) against 1/T for ethylene glycol (1) + water (2) at various temperatures, the molar fractions corresponding to lines as follows: A, 0.0000; B, 0.0145; C, 0.0312; D, 0.0484; E, 0.0686; F, 0.0883; G, 0.1107; H, 0.1621; I, 0.2247; J, 0.3032; K, 0.4035; L, 0.5366; M, 1.000

Experimental surface tension of ethylene glycol + water mixtures at T = (308.15, 313.15, 318.15 and 323.15) K throughout the whole concentration range are summarized in Table-6. The measured surface tension values at different temperatures are plotted in Fig. 4.

Table-6 and Fig. 4 show that the surface tension values decrease with the increasing ethylene glycol concentration in ethylene glycol + water mixtures over the whole concentration range. Meanwhile, the surface tension values decrease with the temperature rise.

TABLE-5
ENTHALPY OF ACTIVATION (ΔH^*/J mol^{-1}) AND ENTROPY OF ACTIVATION (ΔS^*/JK mol^{-1}) FOR THE VISCOUS FLOW ABOUT ETHYLENE GLYCOL + WATER

x_1	ΔS^*	ΔH^*
0.0000	-95.7 ± 2.2	14.84 ± 0.70
0.0145	-99.8 ± 2.6	13.77 ± 0.83
0.0312	-95.0 ± 3.0	15.59 ± 0.95
0.0484	-94.0 ± 2.8	16.21 ± 0.90
0.0686	-90.4 ± 4.8	17.69 ± 1.52
0.0883	-89.0 ± 5.0	18.45 ± 1.57
0.1107	-85.5 ± 5.4	19.94 ± 1.71
0.1621	-85.0 ± 5.4	20.89 ± 1.72
0.2247	-80.4 ± 5.1	23.17 ± 1.61
0.3032	-75.8 ± 5.2	25.54 ± 1.63
0.4035	-76.2 ± 5.0	26.46 ± 1.57
0.5366	-77.0 ± 5.4	27.36 ± 1.70
1.0000	-68.3 ± 6.7	32.85 ± 2.10

TABLE-6
EXPERIMENTAL SURFACE TENSION (γ) FOR ETHYLENE GLYCOL (1) + WATER (2)

| x_1	γ/(mN·m^{-1}) at the following temperatures of T/K			
	308.15	313.15	318.15	323.15
0.0000	71.023	69.657	67.676	66.125
0.0145	69.732	66.552	65.925	63.244
0.0312	67.829	65.577	63.916	60.584
0.0484	66.131	64.095	62.244	59.621
0.0686	64.568	62.512	60.569	57.964
0.0883	63.274	61.325	59.211	56.767
0.1107	62.145	60.324	58.412	55.754
0.1621	60.017	58.103	56.253	54.153
0.2247	57.515	55.923	54.356	52.152
0.3032	56.034	54.446	52.663	50.524
0.4035	54.026	52.412	50.648	49.124
0.5366	52.470	50.701	49.336	47.875
1.0000	50.114	48.732	47.254	46.406
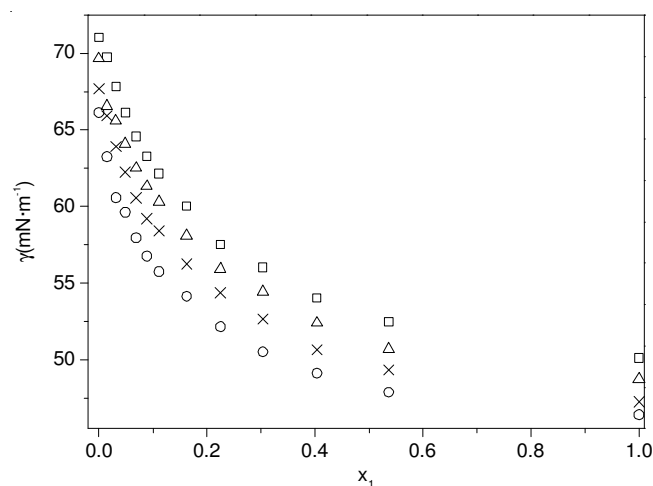
Fig. 4. Surface tension with mole fraction for ethylene glycol (1) + water (2): □, 308.15 K; Δ, 313.15 K; ×, 318.15 K; O, 323.15 K

Conclusion

This paper reports experimental data for the surface tension, viscosities and viscous flow thermodynamics of the aqueous ethylene glycol solutions at T = (308.15 to 323.15) K. These data have been used to compute excess properties of the system. The viscosity deviations for the ethylene glycol + water system were positive in the whole concentration range at all the temperatures. The enthalpy of activation for viscous flow (ΔH^*) and entropy of activation for the viscous flow (ΔS^*) were calculated. The results show that the ΔH^* are all positive, while the ΔS^* values are negative. The surface tension values decrease with the increasing ethylene glycol concentration in ethylene glycol + water mixtures. Meanwhile, the surface tension values decrease with the temperature rise over the whole concentration range.

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