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Densities, viscosities, and excess properties for binary mixtures of ethylene glycol with amides at 308.15 K

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Abstract The densities, ρ, and viscosities, η, of binary mixtures of ethylene glycol with formamide, *N*,*N*-dimethyl formamide and *N*,*N*-dimethyl acetamide, have been measured over the entire composition range at 308.15 K. From this experimental data, excess molar volume, $V_{\mathrm{m}}^{\mathrm{E}}$, deviation in viscosity, $\Delta\eta$, and excess Gibbs free energy of activation of viscous flow, $\Delta G^{*\mathrm{E}}$, have been determined. Negative values of $V_{\mathrm{m}}^{\mathrm{E}}$, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ are observed over the entire composition range in the mixtures studied. The observed negative values of various excess and deviation parameters are attributed to the existence of strong interactions, like dipole–dipole interactions, H-bonding between the carbonyl group of amide molecules, and hydroxyl group of glycol molecules, geometrical fitting of smaller molecules into the voids created by larger molecules in the liquid mixtures. The excess properties have been fitted to Redlich–Kister-type polynomial, and the corresponding standard deviations have been calculated. The derived partial molar volumes and excess partial molar volumes also support the $V_{\mathrm{m}}^{\mathrm{E}}$ results. The experimental viscosity data of all of these liquid mixtures have been correlated with four viscosity models.

Keywords Density · Viscosity · Redlich–Kister-type polynomial · Excess molar volume · Partial molar volume · Theoretical viscosity model

Introduction

The volumetric and viscometric study of liquid mixtures enables the determination of some useful thermodynamic and other properties that are highly sensitive to molecular interactions [1–4]. Binary liquid mixtures containing glycols are used in the pharmaceutical, cosmetic, and food industries [5]. Amides, relevant liquid systems for the study of molecular interactions, are among the most common solvents used in chemical reactions and in many industrial processes, and are important model systems for the investigation of peptide and protein interactions in biological systems. The present work focuses on the study of volumetric and viscometric behavior of binary mixtures of ethylene glycol (EG) with formamide (FA), *N*,*N*-dimethyl formamide (DMF), and *N*,*N*-dimethyl acetamide (DMA) over the entire composition range at 308.15 K.

In the earlier years, so many researchers carried out the ultrasonic, volumetric, and viscometric studies on binary mixtures, glycol as one component and +2-methoxy ethanol [6], +formamide [7], +2-butoxy ethanol [8], +water [9, 10] as other components. This literature survey shows that the mixing properties of EG+FA/DMF/DMA binary mixtures have not been studied previously. In the present investigation, we report data related to densities, ρ, and viscosities, η, of binary liquid mixtures containing EG with FA/DMF/DMA over the entire composition range at

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308.15 K. The experimental data of ρ and η were used to calculate the excess molar volume, V_m^E, deviation in viscosity, $\Delta\eta$, and excess Gibbs free energy of activation of viscous flow, ΔG^{*E}. The variation of these properties with composition has been discussed in terms of molecular interactions.

Experimental

High purity and analytical reagent (AR) grade compounds of ethylene glycol, formamide, *N*,*N*-dimethyl formamide, and *N*,*N*-dimethyl acetamide were obtained from LOBA chemicals, India. The above chemicals used in the present investigation were further purified by standard methods [11]. The mass fraction purity of liquids obtained is >0.995. Binary mixtures of EG with FA/DMF/DMA were prepared so that the entire composition range is covered (i.e., 0–100 % of EG). The mixtures were prepared by mass in air-tight bottles. The mass measurements were performed with a METTLER TOLEDO (Switzerland) ABB5-S/FACT digital balance with an accuracy ±0.01 mg. The uncertainty in the mole fraction is 10^{-4}. The density and viscosity measurements of liquid mixtures have been measured using a two-stem double-walled Parker and Parker-type pycnometer [12] and Ostwald viscometer, respectively. The detailed descriptions of measurements of density and viscosity were presented in our previous papers [13–17]. The reproducibilities in the measured parameters of density and viscosity are 3 in 10^5parts and ±0.2 %, respectively. The units of density and viscosity measurements are kg m^{-3} and N s m^{-2}, respectively. The experimentally determined values of ρ and η at 308.15 K of all the pure liquids have been compared with the literature data [18–22] in Table 1.

Theory and calculation

The experimental values of density have been used to calculate the molar volume and excess molar volume data with the following equations:

Table 1 Comparison of densities, ρ/kg m^{-3} and viscosities, $\eta/10^{-3}$ N s m^{-2} of pure liquids with literature data at 308.15 K

Liquid	ρ/kg m^{-3}		$\eta/10^{-3}$ N s m^{-2}	
	Present work	Literature	Present work	Literature
Ethylene glycol	1102.6	1102.9 [18]	10.968	10.590 [18]
Formamide	1120.2	1121.0 [19]	2.653	2.6531 [20]
N,*N*-dimethyl formamide	935.6	935.7 [19]	0.707	0.710 [21]
N,*N*-dimethyl acetamide	927.5	927.6 [19]	0.806	0.8056 [22]

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho}, \tag{1}$$

where M_1 and M_2 are the molar masses of the pure components 1 (EG), 2 (FA or DMF or DMA), respectively, and ρ is the density of the mixture.

The deviation/excess parameters are computed with the following equations:

Excess molar volume

$$V_m^E = V_m - \left(x_1 V_1^* + x_2 V_2^*\right) \tag{2}$$

Deviation in viscosity

$$\Delta\eta = \eta - \left(x_1 \eta_1^* + x_2 \eta_2^*\right) \tag{3}$$

Excess Gibbs free energy of activation for viscous flow

$$\Delta G^{*E} = RT\left[\ln(\eta V) - x_1 \ln\left(\eta_1^* V_1^*\right) - x_2 \ln\left(\eta_2^* V_2^*\right)\right], \tag{4}$$

where η_1^* and $V_1^*$are the viscosities and molar volumes of pure component 1 (EG) and η_2^* and V_2^* are the viscosities and molar volumes of pure component 2 (FA or DMF or DMA), respectively; and x_i represents the mole fraction of the component '*i*' in the mixture. The reproducibility in the excess molar volumes is twice the reproducibility in the molar volume (reproducibility in the molar volume is 3 in 10^5 parts).

The detailed calculations of excess/deviation properties have been described in our previous papers [13, 16]. The experimentally measured values of ρ, η, and evaluated values of V_m, $\Delta\eta$, and ΔG^{*E} for all the systems have been presented in Table 2. The excess molar volumes V_m^E are presented in Table 3. The values of deviation in viscosity, excess molar volume, and excess Gibbs free energy of activation of viscous flow have been fitted to a Redlich–Kister [23]-type polynomial equation.

$$Y^E = x(1-x)\sum A_i(1-2x)^i, \tag{5}$$

where Y^E is V_m^E, $\Delta\eta$, and ΔG^{*E}. The subscript '*i*' in the summation of the above equation takes values from 0 to 4. The values of coefficients A_i in the above equation have been determined using the least square method and are compiled in Table 4 along with the standard deviations $\sigma(Y^E)$ calculated using the expression

$$\sigma(Y^E) = \left[\sum\left(Y_{\text{exp}}^E - Y_{\text{cal}}^E\right)^2/(m-n)\right]^{1/2}, \tag{6}$$

where '*m*' is the total number of experimental points and '*n*' is the number of coefficients in Eq. (5). The value of '*n*' in the present study is 5.

Results and discussion

From Table 2, the density is found to decrease in EG+FA system, and it is observed to increase monotonically in EG+DMF/DMA systems, whereas the viscosity is found to

Table 2 Experimental values of densities, ρ, viscosities, η, molar volumes, V_m, deviation in viscosities, $\Delta\eta$ and excess Gibbs free energy of activation of viscous flow, $\Delta G^{*\mathrm{E}}$ for all the systems at 308.15 K

Mole fraction of ethylene glycol	ρ/kg m^{-3}	$\eta/10^{-3}$ N s m^{-2}	$\Delta\eta/10^{-3}$ N s m^{-2}	$V_\mathrm{m}/10^{-6}$ m^3 mol^{-1}	$\Delta G^{*\mathrm{E}}$/kJ mol^{-1}
EG+FA					
0.0000	1120.2	2.653	0.000	40.21	0.00
0.0761	1118.9	2.392	−0.894	41.41	−0.53
0.1538	1117.6	2.439	−1.493	42.64	−0.76
0.2311	1116.7	2.487	−2.088	43.86	−0.98
0.3245	1115.2	2.636	−2.715	45.34	−1.17
0.4125	1114.3	2.996	−3.087	46.72	−1.16
0.5236	1113.7	4.026	−2.981	48.45	−0.81
0.6337	1113.0	5.164	−2.758	50.16	−0.58
0.7468	1111.2	6.594	−2.269	51.98	−0.37
0.8596	1108.6	8.193	−1.608	53.83	−0.23
1.0000	1102.6	10.968	0.000	56.29	0.00
EG+DMF					
0.0000	935.6	0.707	0.000	78.12	0.00
0.1399	953.8	0.956	−1.187	75.02	−0.20
0.2568	970.2	1.132	−2.210	72.42	−0.58
0.3715	987.7	1.288	−3.231	69.86	−1.05
0.4762	1004.6	1.898	−3.695	67.54	−0.79
0.5807	1022.8	2.801	−3.865	65.21	−0.53
0.6745	1040.6	3.878	−3.750	63.10	−0.36
0.7677	1059.4	5.167	−3.417	61.01	−0.29
0.8456	1074.2	6.582	−2.802	59.37	−0.22
0.9229	1088.3	8.355	−1.822	57.82	−0.15
1.0000	1102.6	10.968	0.000	56.29	0.00
EG+DMA					
0.0000	927.5	0.806	0.000	93.93	0.00
0.1632	947.4	1.166	−1.298	87.64	−0.11
0.2752	962.3	1.388	−2.215	83.37	−0.39
0.4068	981.8	1.611	−3.329	78.36	−0.88
0.5162	1000.3	2.416	−3.636	74.17	−0.57
0.6269	1021.8	3.622	−3.555	69.89	−0.28
0.7125	1039.6	4.662	−3.384	66.63	−0.21
0.7974	1056.3	5.882	−3.027	63.57	−0.20
0.8652	1071.4	7.289	−2.309	61.08	−0.11
0.9339	1087.5	8.916	−1.380	58.60	−0.07
1.0000	1102.6	10.968	0.000	56.29	0.00

increase monotonically and non-linearly in all the binary systems with increase in concentration of EG. This non-linear variation which is a deviation from ideal behavior suggests that interactions exist between molecules of component liquids of the mixtures.

The variations of excess molar volume, V_m^E, with the mole fraction of EG for the binary systems are shown in Fig. 1. The deviation of physical and chemical properties of the liquid mixture from the ideal behavior is a measure of the interaction between molecules of the components of liquid mixtures, and such a type of deviation is generally attributed to dipole–dipole interactions and hydrogen bond between unlike molecules [24], respectively. The factors that are mainly responsible for the expansion of volume, that is, positive values of V_m^E are (i) breaking one or both of the components in a solution, that is, loss of dipolar association between the molecules (dispersion forces); (ii) the geometry of molecular structures which does not favor the fitting of molecules of one component into the voids created by the molecules of other component; (iii) steric

Table 3 Excess molar volumes, V_m^E, Partial molar volumes, $\overline{V}_{m,1}$, $\overline{V}_{m,2}$, and excess partial molar volumes, $\overline{V}_{m,1}^E$, $\overline{V}_{m,2}^E$ of all binary systems at 308.15 K

Mole fraction of Ethylene glycol (x_1)	$V_m^E/10^{-6}$ m^3 mol^{-1}	$\overline{V}_{m,1}/10^{-6}$ m^3 mol^{-1}	$\overline{V}_{m,2}/10^{-6}$ m^3 mol^{-1}	$\overline{V}_{m,1}^E/10^{-6}$ m^3 mol^{-1}	$\overline{V}_{m,2}^E/10^{-6}$ m^3 mol^{-1}
EG+FA					
0.0000	0.00	56.04	40.21	−0.25	0.00
0.0761	−0.02	56.00	40.21	−0.29	0.00
0.1538	−0.04	56.02	40.20	−0.27	−0.01
0.2311	−0.07	56.02	40.20	−0.27	−0.01
0.3245	−0.09	55.97	40.20	−0.32	−0.01
0.4125	−0.12	55.91	40.22	−0.39	0.01
0.5236	−0.18	55.87	40.25	−0.42	0.04
0.6337	−0.24	55.92	40.19	−0.37	−0.02
0.7468	−0.24	56.07	39.96	−0.22	−0.25
0.8596	−0.20	56.22	39.56	−0.07	−0.65
1.0000	0.00	56.29	39.18	0.00	−1.03
EG+DMF					
0.0000	0.00	56.92	78.12	0.63	0.00
0.1399	−0.05	55.68	78.16	−0.61	0.04
0.2568	−0.09	55.90	78.07	−0.39	−0.05
0.3715	−0.15	55.96	78.00	−0.33	−0.12
0.4762	−0.19	55.83	78.06	−0.46	−0.06
0.5807	−0.24	55.74	78.19	−0.55	0.07
0.6745	−0.30	55.80	78.19	−0.49	0.07
0.7677	−0.35	55.99	77.95	−0.30	−0.17
0.8456	−0.29	56.17	77.60	−0.12	−0.52
0.9229	−0.16	56.27	77.39	−0.02	−0.73
1.0000	0.00	56.29	77.93	0.00	−0.19
EG+DMA					
0.0000	0.00	54.16	93.93	−2.13	0.00
0.1632	−0.15	55.88	93.82	−0.41	−0.11
0.2752	−0.20	55.85	93.81	−0.44	−0.12
0.4068	−0.26	55.58	93.92	−0.71	−0.01
0.5162	−0.33	55.52	93.95	−0.77	0.02
0.6269	−0.44	55.69	93.75	−0.60	−0.18
0.7125	−0.48	55.91	93.39	−0.38	−0.54
0.7974	−0.35	56.12	92.90	−0.17	−1.03
0.8652	−0.28	56.24	92.55	−0.05	−1.38
0.9339	−0.18	56.29	92.43	0.00	−1.50
1.0000	0.00	56.29	92.81	0.00	−1.12

hindrance of the molecules, where the negative values of V_m^E are due to strong specific interactions such as (iv) association of molecules through the formation of hydrogen bonds, association due to dipole–dipole interactions, or association due to induced dipole–dipole interactions; and (v) accommodation of molecules due to larger differences in molar volumes. The variation of excess molar volume in the present investigation is negative over the entire mole fraction range. The molar volumes of EG, FA, DMF, and DMA are 56.29, 40.21, 78.12, and 93.93 cm^3 mol^{-1} at 308.15 K, respectively.

EG molecules are self-associated through inter- as well as intra-molecular hydrogen bonding [25], whereas FA molecules are strongly associated through hydrogen bonding due to the presence of strong proton-acceptor group (>C=O) and proton-donor group (–NH_2) in their molecules in pure state [1], and this association decreases with increase in the number of methyl groups in the

Table 4 Coefficients A_i of Redlich–Kister-type polynomial equation Eq. 5 and the corresponding standard deviation $\sigma(Y^E)$ of all the systems

	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
EG+FA						
$\Delta\eta/10^{-3}$ N s m^{-2}	−12.349	−1.43	3.796	5.097	−8.354	0.054
$V_m^E/10^{-6}$m^3 mol^{-1}	−0.67	1.02	−0.81	−0.23	0.44	0.008
ΔG^{*E}/kJ mol^{-1}	−3.78	−4.79	1.47	3.66	−4.32	0.053
EG+DMF						
$\Delta\eta/10^{-3}$N s m^{-2}	−15.118	5.131	1.487	6.844	−6.037	0.034
$V_m^E/10^{-6}$ m^3 mol^{-1}	−0.78	1.17	−2.07	0.27	2.04	0.015
ΔG^{*E}/kJ mol^{-1}	−3.08	−4.49	1.84	9.30	2.19	0.077
EG+DMA						
$\Delta\eta/10^{-3}$N s m^{-2}	−14.384	4.517	1.814	6.318	−3.146	0.074
$V_m^E/10^{-6}$ m^3 mol^{-1}	−1.35	1.74	−1.14	−1.68	0.30	0.029
ΔG^{*E}/kJ mol^{-1}	−2.56	−3.64	3.87	8.78	0.68	0.097

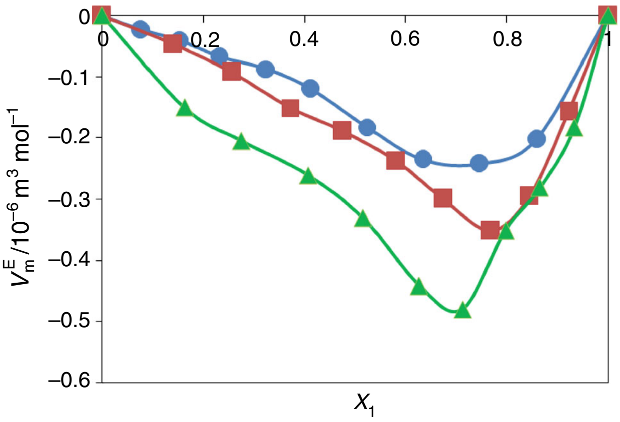

Fig. 1 Plots of excess molar volume, V_m^E against mole fraction, x_1 of EG for binary mixtures of EG with FA (*filled circle*), DMF (*filled square*), and DMA (*filled triangle*)

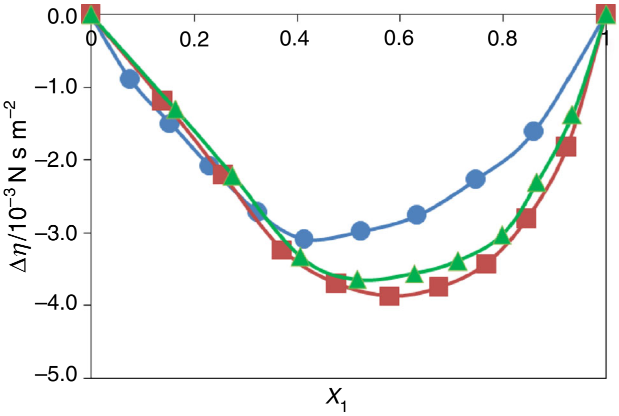

Fig. 2 Plots of deviation in viscosity, $\Delta\eta$, against mole fraction, x_1, of EG for binary mixtures of EG with FA (*filled circle*), DMF (*filled square*), and DMA (*filled triangle*)

molecule. Thus, DMF and DMA are practically unassociated [26, 27]. FA molecules having hydrogen atoms bonded to nitrogen have both hydrogen-bond donating and hydrogen-bond accepting abilities; on the other hand, DMF and DMA contain only a hydrogen-bond accepting carbonyl group. The addition of amide molecules causes breaking of the hydrogen bonds between EG molecules and the subsequent formation of strong hydrogen bonds between the hydrogen atom of –OH group of glycol molecules and oxygen molecule of >C=O group of amide molecules.

The V_m^E values are more negative for EG+DMA than that of EG+DMF. This is due to that the electron density at oxygen atom of carbon atom of DMA is greater than that of DMF [28, 29] due to the presence of –CH$_3$ group at the carbon atom of carbonyl group in DMA resulting strong interactions in EG+DMA system. In general, the interactions are more in EG+FA system due to the presence of strong proton-acceptor group (>C=O) and proton-donor group (–NH$_2$), and the interactions are expected to decrease with increase of –CH$_3$ group attached to nitrogen atom. But in the present study, the interaction is strong in EG+DMA system, and it follows the order EG+DMA > EG+DMF > EG+FA. This is due to one of the favorable effects of fitting of smaller molecules into the voids created by the bigger molecules. This geometrical fitting of smaller molecules into the bigger molecules was also reported by the others for interpreting negative V_m^E vales [28, 30, 31]. Similar type of studies were also reported by other researchers as alcohol one of the component [32, 33].

The variation of deviation in viscosity, $\Delta\eta$, with the mole fraction of EG is shown in Fig. 2. Generally, negative values of $\Delta\eta$ indicate the presence of dispersion forces or mutual loss of specific interactions in molecules operating in the systems arising due to weak intermolecular interactions, and positive values of deviation in viscosity indicate strong specific interactions [34, 35]. The sign and magnitude of $\Delta\eta$ depend on the combined effect of factors such as molecular size, shape, and intermolecular forces. The molecules of FA, DMF, and DMA are highly polar $\mu = 3.37$, 3.86, and 3.72 D, respectively, at $T = 298.15$ K [36], and dipole–dipole interactions between the unlike molecules are also expected to play an important role in determining liquid structure. The observed negative $\Delta\eta$ values are due to the dipole–dipole interactions between the unlike molecules which lead to strong interactions in the liquid mixtures. This type of behavior (both V_m^E and $\Delta\eta$ negative) is observed by the several researchers [9, 21, 37].

The variation in excess Gibbs free energy of activation of viscous flow, ΔG^{*E} with the mole fraction of secondary alcohols, is shown in Fig. 3. The excess Gibbs free energy of activation of viscous flow is negative over the entire composition range studied [38]. The less negative ΔG^{*E} values for EG+DMA system indicate that the interactions are predominant compared to EG+FA and EG+DMF systems. Such type of behavior was also observed by Pikkarainen [37]. This supports the conclusions drawn from V_m^E and $\Delta\eta$.

The existing molecular interactions in the systems are well reflected in the properties of partial molar volumes. The partial molar volumes $\overline{V}_{m,1}$ of component 1 (EG) and $\overline{V}_{m,2}$ of component 2 (amides) in the mixtures over the entire composition range have been calculated using the following relations:

$$\overline{V}_{m,1} = V_m^E + V_1^* + x_2\left(\frac{\partial V_m^E}{\partial x}\right)_{T,P} \tag{7}$$

$$\overline{V}_{m,2} = V_m^E + V_2^* - x_1\left(\frac{\partial V_m^E}{\partial x}\right)_{T,P}, \tag{8}$$

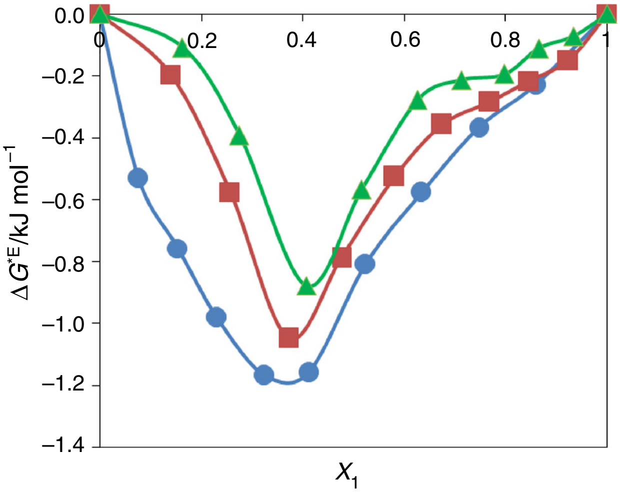

Fig. 3 Plots of excess Gibbs free energy of activation of viscous flow, ΔG^{*E} against mole fraction, x_1, of EG for binary mixtures of EG with FA (*filled circle*), DMF (*filled square*), and DMA (*filled triangle*)

where V_1^* and V_2^* are the molar volumes of pure components of EG and amides, respectively. The derivates $\left(\frac{\partial V_m^E}{\partial x}\right)_{T,P}$ in Eqs. (7) and (8) are obtained by differentiating Eq. (5) which lead to the following equations for $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$:

$$\overline{V}_{m,1} = V_1^* + x_2^2\sum_{i=0}^{j} A_i(x_2 - x_1)^i - 2x_1x_2^2\sum_{i=1}^{j} A_i(x_2 - x_1)^{i-1} \tag{9}$$

$$\overline{V}_{m,2} = V_2^* + x_1^2\sum_{i=0}^{j} A_i(x_2 - x_1)^i + 2x_2x_1^2\sum_{i=1}^{j} A_i(x_2 - x_1)^{i-1}. \tag{10}$$

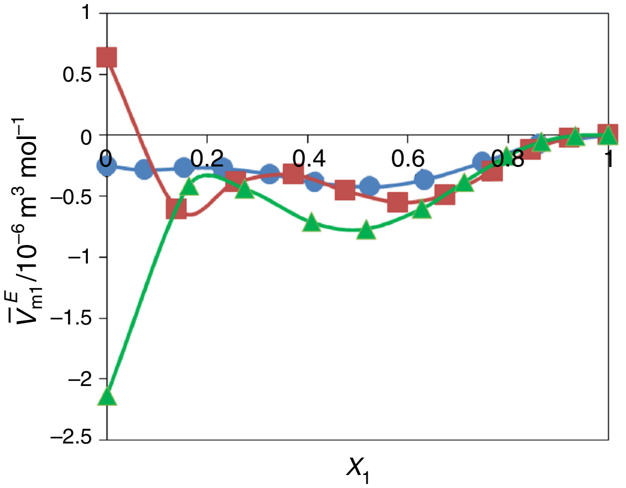

Fig. 4 Plots of excess partial molar volumes of EG for the binary mixtures of EG with FA (*filled circle*), DMF (*filled square*), and DMA (*filled triangle*)

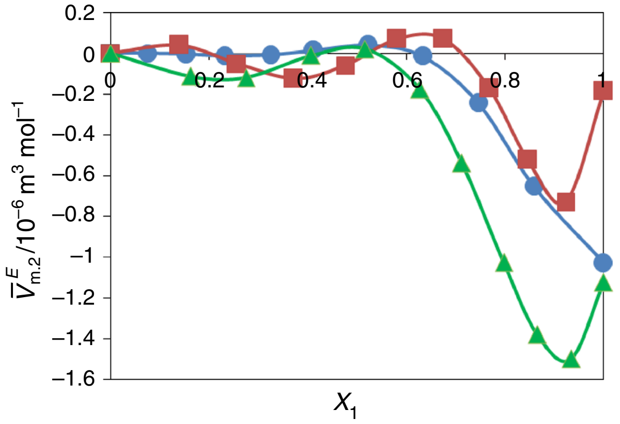

Fig. 5 Plots of excess partial molar volumes of FA, DMF, and DMA for the binary mixtures of EG with FA (*filled circle*), DMF (*filled square*), and DMA (*filled triangle*)

Table 5 Calculated values of the viscosity, $\eta/10^{-3}$N s m^{-2} of all the systems from viscosity models

Mole fraction of ethylene glycol (x_1)	Grunberg and Nissan	Hind and Ubbelohde	Katti and Chaudari	Heric and Brewer
EG+FA				
0.0000	2.653	2.653	2.653	2.653
0.0761	2.619	2.425	2.617	2.619
0.1538	2.639	2.338	2.635	2.638
0.2311	2.714	2.399	2.710	2.713
0.3245	2.886	2.667	2.881	2.885
0.4125	3.142	3.115	3.139	3.142
0.5236	3.634	3.952	3.636	3.635
0.6337	4.377	5.080	4.386	4.380
0.7468	5.534	6.547	5.548	5.537
0.8596	7.304	8.323	7.323	7.308
1.0000	10.968	10.968	10.968	10.968
EG+DMF				
0.0000	0.707	0.707	0.707	0.707
0.1399	0.924	0.146	0.923	0.924
0.2568	1.189	0.175	1.187	1.189
0.3715	1.562	0.644	1.559	1.562
0.4762	2.050	1.454	2.046	2.050
0.5807	2.746	2.625	2.743	2.746
0.6745	3.634	3.985	3.635	3.634
0.7677	4.883	5.625	4.892	4.883
0.8456	6.331	7.217	6.343	6.331
0.9229	8.288	8.996	8.296	8.288
1.0000	10.968	10.968	10.968	10.968
EG+DMA				
0.0000	0.806	0.806	0.806	0.806
0.1632	1.118	0.316	1.118	1.118
0.2752	1.430	0.464	1.430	1.431
0.4068	1.956	1.143	1.954	1.957
0.5162	2.587	2.122	2.584	2.588
0.6269	3.494	3.496	3.493	3.494
0.7125	4.462	4.823	4.465	4.461
0.7974	5.747	6.367	5.745	5.744
0.8652	7.088	7.763	7.087	7.084
0.9339	8.825	9.325	8.828	8.822
1.0000	10.968	10.968	10.968	10.968

using the above equations $\overline{V}^{\mathrm{E}}_{\mathrm{m},1}$,$\overline{V}^{\mathrm{E}}_{\mathrm{m},2}$ have been calculated using

$$\overline{V}^{\mathrm{E}}_{\mathrm{m},1} = \overline{V}_{\mathrm{m},1} - V^{*}_{1} \tag{11}$$

$$\overline{V}^{\mathrm{E}}_{\mathrm{m},2} = \overline{V}_{\mathrm{m},2} - V^{*}_{2}. \tag{12}$$

The values of $\overline{V}_{\mathrm{m},1}$, $\overline{V}_{\mathrm{m},2}$, $\overline{V}^{\mathrm{E}}_{\mathrm{m},1}$, and $\overline{V}^{\mathrm{E}}_{\mathrm{m},2}$ are furnished in Table 3. From this table, the values of $\overline{V}_{\mathrm{m},1}$ and $\overline{V}_{\mathrm{m},2}$ for both the components in the mixtures are less than their respective molar volumes in the pure state i.e., contraction of volume takes place on mixing EG with amides. These data are also supporting the observed negative values of $V^{\mathrm{E}}_{\mathrm{m}}$ in all the binary systems. Figures 4 and 5 represent the variation of excess partial molar volumes of EG and FA/DMF/DMA in the binary mixtures, respectively. Examination of Figs. 4 and 5 reveals that indicating strong interactions exist between the unlike molecules. These figures support the conclusions drawn from $V^{\mathrm{E}}_{\mathrm{m}}$ values.

The dynamic viscosities of the binary liquid mixtures have been calculated using various empirical relations like Grunberg and Nissan, Ubbelohde et al., Katti and Chaudari and Heric and Brewer, and the corresponding interaction parameters are also evaluated. The detailed description of the above empirical relations is already reported in our previous papers [13, 15]. Theoretical values of viscosity of the liquid mixtures calculated using the above equations are given in Table 5. Table 6 presents the values of interaction parameters along with the standard deviations, σ. The estimated values of σ are found to be smaller, which indicate that experimental values of viscosities are well correlated with that obtained from different viscosity models.

Conclusions

The densities, ρ, and viscosities, η, of binary mixtures of EG with formamide, DMF, and DMA have been measured over the entire composition range at 308.15 K. From this experimental data, excess molar volume, $V^{\mathrm{E}}_{\mathrm{m}}$, deviation in viscosity, $\Delta\eta$, and excess Gibbs free energy of activation of

Table 6 Various interaction parameters calculated from viscosity models and the corresponding standard deviations $\sigma/10^{-3}$ N s m^{-2}

G_{12}	σ	H_{12}	σ	W_{vis}/RT	σ	Δ_{12}	σ
EG+FA							
−1.717	0.697	0.001	0.105	0.686	−1.675	−1.665	0.694
EG+DMF							
−0.966	0.228	−0.002	0.736	0.223	−0.932	−0.953	0.228
EG+DMA							
−0.727	0.214	−0.002	0.652	0.213	−0.619	−0.668	0.216

viscous flow, ΔG^{*E} have been determined. These deviation/excess properties have been fitted to Redlich–Kister-type polynomial. The observed negative values of deviation/excess properties are due to the addition of amide molecules causes breaking of the hydrogen bonds between EG molecules and the subsequent formation of strong hydrogen bonds between the hydrogen atom of –OH group of glycol molecules and oxygen molecule of >C=O group of amide molecules and fitting of smaller molecules into the voids created by the bigger molecules and also due to the dipole–dipole interactions between the unlike molecules causes the strong specific interactions exist between the unlike molecules. The strength of interactions follows the order EG+DMA > EG+DMF > EG+FA. The experimental viscosity values are compared with the viscosity values obtained from different empirical relations, and these are in good agreement with the experimental values.

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