Volumetric, viscosimetric and surface properties of aqueous solutions of triethylene glycol, tetraethylene glycol, and tetraethylene glycol dimethyl ether

Syeda K. Begum [a,*], Ronald J. Clarke [b], M. Shamsuddin Ahmed [a], Shahanara Begum [a], Mohammad A. Saleh [a,1]

[a] Professor M. A. Saleh Research Laboratory, Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh
[b] School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

ABSTRACT

Densities (ρ) and viscosities (η) for water (W) + triethylene glycol (TrEG), W + tetraethylene glycol (TeEG), and W + tetraethylene glycol dimethyl ether (TeEGDME) were measured for the whole range of composition at five different temperatures ranging from 303.15 K to 323.15 K. Surface tensions for these systems were measured at 303.15 K for different mole fractions. The excess molar volumes, V_m^E, and excess viscosities, (η^E), were calculated from measured parameters. Derived volumetric and viscosimetric properties were fitted to Redlich–Kister type equation. The properties were found to change significantly with increasing the number of glycol units and to be greatly affected by methyl substitution within the glycol unit. For unsubstituted glycols a gradual increase in density and viscosity was observed on increasing the concentration, whereas for the methyl-substituted glycol TeEGDME sharp maxima were apparent in the density–composition and viscosity–composition curves. The surface tensions of aqueous solutions of methyl-substituted glycol TeEGDME were found to be significantly lower than other aqueous glycols.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Recently we reported both volumetric and viscosimetric properties of aqueous solutions of alcohols [1], diols [2], dimethoxyethane [3], and diamines [4]. Considering the versatile applications of glycols and their aqueous solutions, very recently we reported density, viscosity and surface tensions of aqueous solutions of diethylene glycol [5]. From a similar point of view, in this work we report the properties for aqueous solutions of triethylene glycol (TrEG), tetraethylene glycol (TeEG) and tetraethylene glycol dimethyl ether (TeEGDME). A literature survey reveals that although volumetric and viscosimetric data on these systems are available [6–10], most of the works has been done at limited mole fractions or temperatures. For instance, densities and viscosities for aqueous solutions of TrEG were studied only at three mole fractions by Sun et al. [6]. The same properties for aqueous TrEG and TeEG were studied by Pal et al. [7] only at two temperatures. Furthermore, in spite of the importance of surface tension data in mass transfer processes [11], no data are available in the literature on the surface tensions of these systems.

In this study we aim to extend the experimental information on volumetric and viscosimetric properties of aqueous TrEG, TeEG and TeEGDME, provide new data on surface tensions for these systems and determine the effect of temperature, number of glycol units and methyl-substitution within the glycol on their volumetric, viscosimetric and surface properties.

2. Experimental section

Triethylene glycol, tetraethylene glycol and tetraethylene glycol dimethyl ether were obtained from Merck Schuchardt with a purity of 0.99 mass fraction. Prior to use the samples were kept over molecular sieves (0.4 nm) to reduce water content and to protect from moisture and CO_2. The purity of the glycols and ether was confirmed by comparing the experimental densities and viscosities of the samples with corresponding literature values in the temperature range (298.15 to 308.15) K. There was a good agreement between our measured values and the literature values [9,10,12–18], as shown in Table 1. Doubly distilled water was used for all solution preparation.

Solutions were prepared by mixing known weights of pure components. An electronic analytical balance (Mettler Toledo) with an accuracy of $\pm 1 \times 10^{-5}$ g was used for weighing. To avoid evaporation and contamination, solutions were kept in air-tight glass stoppered bottles. The accuracy of the mole fraction of each mixture was calculated from the measured masses of the pure liquids and was found to be $\pm 2 \times 10^{-5}$. For the measurement of density and viscosity at temperatures 293.15 to 323.15 K, a thermostatic water bath with an accuracy of ± 0.05 K was used. The densities of pure components and mixtures were measured by a 10 cm^3 bicapillary pycnometer which had been calibrated using redistilled water. Our density values for pure TrEG are within 0.008 % of available literature values [12,13,15] at 298.15 K and 0.06% of literature values [7,13–16] at 303.15 K and

* Corresponding author. Tel.: +880 1830034350.
   E-mail address: syedacu@gmail.com (S.K. Begum).
[1] Deceased.

Table 1
Experimental densities, ρ (g·cm^{-3}), and viscosities, η (mPa s), of TrEG, TeEG and TeEGDME at $T =$ (303.15, 308.15, 313.15, 318.15, 323.15) K and literature values at $T =$ (298.15, 303.15, 308.15) K.

T/K	ρ this work	ρ lit.	η this work	η lit.
TrEG				
298.15	1.1199	1.1198[13]	3.682	
		1.1198[12]		
		1.1198[15]		
303.15	1.1158	1.1164[7]	2.919	2.926[7]
308.15	1.1119	1.1126[13]	2.336	2.284[7]
		1.1120[14]		
		1.1126[15]		
		1.1127[7]		
		1.1120[16]		
313.15	1.1084		1.898	
318.15	1.1040		1.559	
323.15	1.1000		1.299	
TeEG				
298.15	1.1211	1.1201[13]	4.463	
		1.1201[12]		
		1.1201[15]		
303.15	1.1166	1.1170[7]	3.497	3.458[7]
		1.1168[16]		3.569[15]
308.15	1.1126	1.1123[13]	2.789	2.692[7]
		1.1131[7]		2.793[15]
		1.1128[15]		
313.15	1.1087		2.248	
318.15	1.1045		1.842	
323.15	1.1005		1.532	
TeEGDME				
298.15	1.0070	1.0066[18]	3.334	3.380[10]
		1.0060[12]		3.294[9]
				3.394[15]
				3.313[17]
303.15	1.0020		2.955	
308.15	0.9972		2.646	
313.15	0.99256		2.388	
318.15	0.9878		2.169	
323.15	0.9830		1.976	

308.15 K. For TeEG it is within 0.09% of literature values [12,13,15] at 298.15 K. In the case of tetraethylene glycol dimethyl ether it was found to be within 0.09% of literature values [12,18] at 298.15 K. The uncertainty in density measurements was estimated to be $\pm 1.5 \times 10^{-4}$ g cm^{-3}.

The coefficient of viscosity, η, of pure glycols and their aqueous solutions were measured using an A-type Ostwald U-tube viscometer (British Standard Institution) with sufficiently long efflux time, which had been calibrated with redistilled water. The flow time was determined using a digital stopwatch with an accuracy of ± 0.01 s. The uncertainty in viscosity measurements was estimated to be ± 0.04 mPa s.

The excess molar volumes were calculated using the following relation:

$$V_m^E = (x_1 M_1 + x_2 M_2)/\rho - (x_1 M_1/\rho_1 + x_2 M_2/\rho_2)$$ (1)

where ρ, ρ_1, and ρ_2 represent the densities of the solution, water (1) and organic solutes (2) respectively. M_1, M_2, and x_1, x_2 represent the molar masses and mole fractions of the corresponding components. Here the word 'excess' means 'deviation from additivity'.

The excess viscosity η^E was calculated from the following equation [19–21]:

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2)$$ (2)

where η is the experimental viscosity of the solution. η_1 and η_2 are the viscosities of water and the organic solute, respectively.

The apparatus used to measure the surface tension, γ, of the solutions was a Langmuir trough (type 601) from Nima Technology (Coventry, UK). The surface tension was determined via the Wilhelmy paper plate method as discussed in our earlier report [5]. At each temperature measurement was repeated for six times and then average was taken. Based on the measurements and comparing the values of water with literature value [22] the uncertainty in surface tension measurement was estimated to be ± 0.51 mN.m^{-1}.

3. Results and discussion

The densities and excess molar volumes for aqueous solutions of TrEG, TeEG and TeEGDME in the whole range of composition at different temperatures ranges from 303.15 to 323.15 K are listed in Table 2. The densities for the systems are plotted in Fig. 1. The excess molar volumes are plotted in Fig. 2. The viscosities and excess viscosities of the systems at the same compositions and temperatures are listed in Table 3. The viscosity values are plotted in Fig. 3 and excess viscosities are plotted in Fig. 4. All the values are plotted at two different temperatures, 303.15 K and 323.15 K, to see the effect of temperature. Densities, excess molar volumes, viscosities and excess viscosities of aqueous solutions of diethylene glycol (DEG), at 323.15 K, from the literature [5] are shown in Figs. 1, 2, 3 and 4 respectively for comparison purposes.

The excess molar volumes, V_m^E, and excess viscosities, η^E, were fitted to the following form of the Redlich–Kister equation:

$$Y^E = x_2(1 - x_2)\sum_{i=0}^{n} A_i(2x_2 - 1)^i$$ (3)

where x_2 is the mole fraction of the organic solute and A_i is the ith coefficient of the equation. The coefficients of this equation and the standard deviations, σ, for excess molar volumes and excess viscosities are listed in Tables 4 and 5 respectively.

It has been found that, at 303.15 K, the densities of the pure glycols, DEG (1.1095 g cm^{-3}) , TrEG (1.1150 g cm^{-3}) and TeEG (1.1166 g cm^{-3}) are considerably higher than those of the methyl-substituted glycol TeEGDME (1.002 g cm^{-3}). This observation clearly suggests that glycols, owing to their terminal —OH groups, are highly associated through intermolecular H-bonds but, due to the lack of a terminal —OH group, such strong association is not possible in the methyl-substituted glycol TeEGDME.

Fig. 1 shows that for the systems W + TrEG and W + TeEG, the density rises sharply in the water-rich region, followed by a consistently slower increase as the solution becomes richer and richer in glycol. This is similar to the behavior observed in the system W + DEG [5]. The sharpness of the initial increase of density with composition increases with an increase in the number of glycol units. The magnitude of the initial sharp increase of density with composition also increases with increasing number of glycol units. The densities for these systems follow the order W + TeEG > W + TrEG > W + DEG. The density profile of the system consisting of water and TeEGDME is completely different from those of other aqueous glycols. Although initially the density of the W + TeEGDME system rises very rapidly (as also observed for three other aqueous glycols), after showing a well-defined maxima at ~0.08 mole fraction of TeEGDME the density then declines sharply with increasing mole fraction of TeEGDME. Although this density–composition curve for the glycol ether TeEGDME is different from those of the unsubstituted glycols, it is similar to those found for some other glycol ethers [23,24]. Similar observations were also reported by Li et al. [25] for aqueous diethylene glycol monomethyl ether (DEGMME), triethylene glycol monomethyl ether (TrEGMME), diethylene glycol monoethyl ether (DEGMEE), and triethylene glycol monoethyl ether (TrEGMEE).