J. Chem. Thermodynamics 58 (2013) 340–350

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Investigation on some thermophysical properties of poly(ethylene glycol) binary mixtures at different temperatures

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ARTICLE INFO

Article history:
Received 14 June 2012
Received in revised form 24 October 2012
Accepted 17 November 2012
Available online 7 December 2012

Keywords:
Viscosity
Density
Excess properties
Binary mixtures
Poly(ethylene glycol)

ABSTRACT

Densities ρ and viscosities η for the binary mixtures of poly(ethylene glycol) + water, + 1,2-ethanediol, + 1,3-propanediol, + 1,4-butanediol over the entire concentration range were determined at temperatures (298.15 to 308.15) K with 5 K interval. The experimental data were used to calculate the excess molar volume V_m^E, coefficient of thermal expansion α, excess coefficient of thermal expansion α^E, excess Gibbs free energy of activation ΔG^{*E}, and other activation parameters (*i.e.*, $\Delta G^*, \Delta H^*, \Delta S^*$). The values of excess properties were fitted to Redlich–Kister polynomial equation to estimate the binary coefficients. The excess refractive index n^E and electronic polarizability α_e of PEG + water binary mixtures were also determined from the experimental values of refractive indices. The viscosity data were correlated with Grunberg–Nissan and Tamura–Kurata equations. Moreover, the Prigogine–Flory–Patterson theory has been used to correlate the excess molar volumes of the studied mixtures.

1. Introduction

In recent years with advances in industry, the accurate values of thermodynamic and transport properties of solutions are required for engineering design and subsequent operations concerning heat transport, mass transport, fluid flow and pipeline systems [1–3]. In comparison to gas and solid, liquids are much more complicated state of the matter in nature because a diverse kind of interactions can be influenced in solution behavior [4]. Hence, study on the physical properties of liquids plays a crucial role in understanding of intermolecular interactions. Furthermore, with the use of these physical data, scientist can make diverse molecular models or theories of solutions to extend our knowledge about the molecular interactions between components [5–9]. In this paper, some thermodynamic and transport properties of poly(ethylene glycol) 200 + water, + 1,2-ethanediol, + 1,3-propanediol, + 1,4-butanediol were measured for two main points; first, investigation on the effect of carbon chain length in viscometric and volumetric properties and second, the important role of these materials in industry that below we note to some of their properties and applications. Poly(ethylene glycol) (PEG) is a nonionic and synthetic polymer which is produced by polymerization of ethylene oxide [10,11]. Owing to some special properties such as neutrality, low toxicity, solubility in aqueous and organic media, and excellent biocompatibility, PEG has found widespread applications in food, pharmaceutical, biomedical, cosmetic, membrane, and chemical industry as solvent, carrier, humectant, lubricant, binder, and coupling agent [12,13]. 1,2-ethanediol or ethylene glycol (EG), which is produced by the vapor-phase oxidation of ethylene, has two major commercial uses as an antifreeze and for polyester fiber production [14,15]. Good ability for removal of SO_2 from industrial gas has been found on the use of PEG and EG solution along with their water mixture [16–20]. Similar to PEG and EG, another glycol family including 1,3-propanediol (PD) and 1,4-butanediol (BD) have diverse industrial applications. The main uses of these materials are in the manufacture of commercial polymers including polyesters and polyurethanes [21,22]. Although various methods have been used for production of 1,3-propanediol and 1,4-butanediol [23–25], but they are mostly produced by the catalytic solution phase hydration of acrolein followed by reduction [26,27] and by the formaldehyde ethynylation that commonly called the Rappe process, respectively [28,29]. The molecular structures of the studied glycols are shown in figure 1.

Many researchers have studied various binary solutions consisting of PEG and different alcohols. Yasmin *et al.* reported the viscosity and optical dielectric constant, as well as some excess properties and activation parameters of poly(ethylene glycol) 200 with ethanolamine, m-cresol and aniline within the temperature range (293.15 to 303.15) K [13]. Zafarani-Moattar and coworkers investigated the density, viscosity, speed of sound and related excess parameters of Poly(ethylene glycol) 400 with ethanol at different temperatures [30]. Yang *et al.* [14] measured density, viscosity, and heat capacity of ethylene glycol with water from 273.15 to 353.15 K. The George group studied the physical properties of some diols + water at various temperatures [31]. The temperature

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0021-9614/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jct.2012.11.016

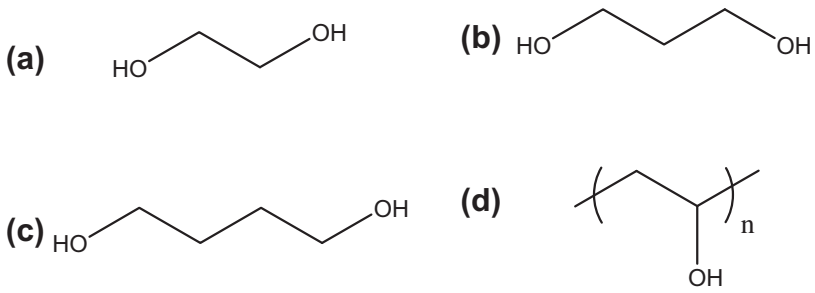

FIGURE 1. The structural formulas of (a) 1,2-ethanediol, (b) 1,3-propanediol, (c) 1,4-butanediol, and (d) poly(ethylene glycol).

dependence of density and excess properties of 1,4-butanediol with 1,2-ethanediol and 1,3-propanediol were studied by Li *et al.* [32]. Kirincic *et al.* [33] and also Bhanot *et al.* [34] measured the viscosity of PEG with different molecular weight at different temperatures. Moreover, Survey of the more literature shows that many thermophysical properties of the above-mentioned solutions have been reported [35–38].

In this work, we reported the experimental values of densities ρ and viscosities η of Poly(ethylene glycol) 200 + water, + 1,2-ethanediol, + 1,3-propanediol, + 1,4-butanediol binary mixtures over the entire concentration range and temperatures of (298.15 to 308.15) K. The excess molar volume V_m^E, thermal expansion coefficient α and its excess value α^E, excess Gibbs free energy of activation ΔG^{*E}, and other activation parameters (*i.e.*, $\Delta G^*, \Delta H^*, \Delta S^*$) were calculated from the obtained experimental results. Moreover, excess refractive indices and electronic polarizabilities were calculated from the refractive index measurements at different temperatures for PEG + water binary system. The values of V_m^E and ΔG^{*E} have been fitted to the Redlich–Kister polynomial equation to drive binary coefficients and estimate the standard deviation between experimental and calculated results. Furthermore, the viscosities of these binary mixtures were calculated theoretically using various semi-empirical relations and the results were compared with the experimental data. Finally, the Prigogine–Flory–Patterson theory has been examined to estimate the excess molar values of the mixtures.

2. Experimental

2.1. Chemicals

Poly(ethylene glycol) 200 with the molecular weight of (190–210) $g \cdot mol^{-1}$ was purchased from Merck. The 1,3-propanediol was also obtained from Merck. 1,2-ethanediol and 1,4-butanediol were supplied by Fluka. The purity of these chemicals was higher than 98% and their water content was around 0.2%. All these compounds were used without further purification as received. Table 1 shows the specifications of the used chemicals in detail. Double-distilled water was used for the preparation of aqueous solutions.

The experimental densities ρ, viscosities η, and refractive indices n of pure liquids are compared with the available literature values at T = (298.15–303.15) K and given in table 2. As it can be seen, there is a good agreement between the experimental and literature values.

2.2. Apparatus and procedure

All binary solutions were prepared by mass using a single pan Matter balance with an accuracy of ±0.1 mg. The mixtures were freshly prepared and retained at desired temperature for some hours to ensure complete miscibility.

Densities of pure liquids and their mixtures were determined using an Anton Paar oscillation U-tube densitometer (model: DMA 500) with the accuracy of $\pm 10^{-4}$ $g \cdot cm^{-3}$ calibrated with double-distilled water and air. The temperature was regulated using a circulating bath (model: Heto DBT) with precision of 0.01 K.

The kinematic viscosities of liquids were measured with Ubbelohde glass capillary tube viscometer with a Schott-Grate automatic measuring unit (model: AVS 400) immersed in a transparent thermostat water bath, which allows temperatures stabilization with an uncertainty of 0.01 K and the bath filled with distilled pure water. Different capillaries having various diameters were used depending on the sample viscosity. The kinematic viscosity ν and dynamic viscosity η were computed using equations:

$$\nu = k \cdot t, \tag{1}$$

$$\eta = \upsilon \cdot \rho, \tag{2}$$

where k is the capillary constant of viscosimeter and t is the flow time. The viscosities were averaged from three measurements. The accuracy of viscosity measurements was estimated to be ±0.001 mPa · s.

Refractive indices n measurements of pure components and mixtures were carried out using a digital Abb.type refractometer. The uncertainty of refractive indices measurement was estimated to be less than ±0.0001 units.

The water content of the chemicals was measured with Kyoto mks-210 Karl Fischer instrument in order to be aware of the nature of impurities and their effect on temperature control.

3. Results and discussion

The results of densities ρ, viscosities η, excess molar volume V_m^E, thermal expansion coefficient α, and excess Gibbs free energy of activation ΔG^{*E} Δ, for binary mixtures of PEG + water, + 1, 2-ethanediol, + 1,3-propandiol, + 1,4-butanediol as a function of poly(ethylene glycol) mole fraction (X_1) at temperatures (298.15 to 308.15) K are presented in tables 3–6, respectively.

TABLE 1
The specifications of the used chemicals.

Compound	CAS number	Supplier	Purity (GC assay, supplier)	Water content (Supplier)	Water content (K.F.)
1,2-Ethanediol	107-21-1	Fluka AG	⩾98.0%	⩾0.2%	0.25%
1,3-Propanediol	504-63-2	Merck	⩾98.0%	⩾0.2%	0.30%
1,4-Butanediol	110-63-4	Fluka	⩾98.0%		0.28%
PEG 200	25322-68-3	Merck			0.21%