Intermolecular interactions in mixtures of poly (ethylene glycol) with methoxybenzene and ethoxybenzene: Volumetric and viscometric studies

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ABSTRACT

The density and viscosity values of the binary mixtures of {poly (ethylene glycol) (PEG400) + methoxybenzene, or + ethoxybenzene} have been measured at $T = (298.15, 308.15,$ and $318.15)$ K. From these experimental values, the excess molar volume, apparent specific volume, partial specific volume of solute, partial specific volume of solvent and excess Gibbs free energy of activation have been computed over the entire range of composition at three temperatures. From the experimental data, the thermodynamic functions of activation have been estimated for each binary mixture. The obtained results have been interpreted in light of polymer–solvent interactions and packing effects. The signs of excess molar volume and deviations of excess Gibbs free energy of activation have been used to obtain some information in regard to existence of specific interactions between PEG400 and solvents molecules. The changes in entropy and enthalpy of activation from the initial state to the transition state were also calculated in order to see which one of these functions controls viscous flow process in the studied polymer solutions. The excess molar volume and excess Gibbs free energy of activation values have been adequately fitted to the Redlich–Kister polynomial. Apparent specific volume values were correlated with the suitable equation. The different models proposed for correlating the viscosity of polymer solutions or liquid mixtures (segment-based-Eyring–NRTL, segment-based-Eyring–Wilson, Grunbreg–Nissan, Frenkel, Hind *et al.*, Katti–Chauddhri, Tamura–Kurata, Auslander and McAllister) have also been used to fit the viscosity values.

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1. Introduction

Thermodynamic and transport property data are of great interest in process design and operation. Viscosity and density data are required in many chemical engineering calculations involving fluid flow, heat and mass transfer. Moreover, knowledge of the dependence of viscosity and density on mixture composition is of considerable interest in understanding the intermolecular interactions [1–3].

In recent years, numerous studies have been carried out on mixtures containing poly(ethylene glycols), PEGs. PEG, an industrially important polymer, has numerous uses in biotechnology [4,5], in chemical partitioning [6–8], in extractive crystallization of inorganic salt [9], and its low toxicity and non-irritating nature led to a wide range of applications in the pharmaceutical, petroleum, cosmetic and food industry [10]. Moreover, solubility of PEG in water and in a large number of organic solvents make a valuable property in the development of environmental friendly processes, like the

design of water soluble catalyst, and the purification of biological substances [11–13].

Solution properties of binary mixtures of PEG with some monoethers, diethers and aliphatic–aromatic ethers have previously been investigated. The excess molar volume, viscosity deviation, deviation in molar refraction and excess molar enthalpy of PEG with linear diethers, dimethoxymethane or 1,2-dimethoxyethane have been measured by Comelli *et al.* [14]. The forenamed properties of binary solutions of {PEG + cyclic ethers, +1,3-dioxolane, +1,4-dioxane, +oxolane or +oxane}, have been reported by Ottani *et al.* [15,16]. Comelli *et al.* [17] have also reported the excess molar enthalpies of PEG in methoxybenzene.

As far as we know, there is no density, d, and viscosity, η, data for {poly(ethylene glycol) 400 + methoxybenzene or + ethoxybenzene} systems at different temperatures in the literature. Methoxybenzene and ethoxybenzene are well-known electron-pair donor aliphatic–aromatic ethers. Methoxybenzene is a solvent widely used in the perfume industry and in organic syntheses. Ethoxybenzene is used in the preparation of a lot of pharmaceutical substances. In present report density and dynamic viscosity values of {poly (ethylene glycol) 400 + methoxybenzene or + ethoxyben-

zene} solutions have been measured over the entire composition range of polymer at T = (298.15, 308.15, and 318.15) K and at atmospheric pressure, from which the excess molar volume, apparent specific volume, partial specific volume of solute, partial specific volume of solvent, and excess Gibbs free energy of activation have been calculated. The excess molar volume, excess Gibbs free energy of activation and apparent specific volume values have been adequately fitted with the suitable equations.

The viscosity values of the investigated systems have also been correlated with models proposed for polymer solutions and liquid mixtures.

2. Experimental

2.1. Material

Poly (ethylene glycol) 400 (PEG 400) and methoxybenzene (minimum mass fraction purity 0.99) were obtained from Merck. Ethoxybenzene (minimum mass fraction purity 0.99) was obtained from Aldrich. Number-average molar mass of PEG 400 is 380 g · mol^{-1} as determined by the manufacture. Therefore, in our calculation, we used the value of 380 for molar mass of PEG400. The specifications of the compounds are given in table 1. The water content of the used compounds were also determined using a microprocessor based automatic Karl–Fischer Titrated with the results reported in table 1.

2.2. Apparatus and procedures

Densities of the pure components and their mixtures were measured using a single-arm capillary pycnometer having a bulb volume of approximately 10 cm^3 and a capillary bore with an internal diameter of 1 mm. The pycnometer filled with the liquid was placed in glass-sided water thermostat (HAAKE-DC3-Germany) with temperature stability of ±0.01 K. The uncertainty in the density measurements was found to be 1 · 10^{-4} g · cm^{-3}. Solutions were prepared gravimetrically with an analytical balance (ADAM, AFA-12OLC) with an uncertainty of 1 · 10^{-4} g.

The viscosity of the binary liquid mixtures was measured using three Ubbelohde micro-viscometers calibrated by water and toluene. The thoroughly cleaned and dried viscometer, filled with the liquid, was placed vertically in glass-sided water thermostat (HAAKE-DC3-Germany) with temperature stability of ±0.01 K. After attaining thermal equilibrium the flow time measurements were performed by a digital stopwatch with uncertainty of 0.01 s. The dynamic viscosity of solution, η, was calculated with the equation:

$$\eta = dK(t - \gamma),\tag{1}$$

where t is the flow time, K is the viscometer constants, γ is the Hagenbach correction factor, and d is the density. The uncertainty for the dynamic viscosity determination was estimated to be ±0.001 mPa · s.

Density and viscosity values of the pure components are given in table 2 at different temperatures and compared with the literature values.

TABLE 2
Density (d) and viscosity (η) of pure components at different temperatures.

Component	$d/(\text{g} \cdot \text{cm}^{-3})$		$\eta/(\text{mPa} \cdot \text{s})$	
	Experimental	Literature	Experimental	Literature
		T = 298.15 K		
Methoxybenzene	0.9889	0.98918 [41]	0.989	1.008 [41]
Ethoxybenzene	0.9602	0.96018 [42]	1.223	1.2235 [43]
PEG400	1.1220	1.12308 [21]	84.113	
		T = 308.15 K		
Methoxybenzene	0.9795	0.97978 [17]	0.906	0.861 [41]
Ethoxybenzene	0.9534	0.95220 [43]	0.982	0.9842 [43]
PEG400	1.1139	1.11487 [21]	51.917	
		T = 318.15 K		
Methoxybenzene	0.9705		0.840	
Ethoxybenzene	0.9425	0.94304 [43]	0.823	0.8284 [43]
PEG400	1.1058	1.10669 [21]	34.079	

3. Results and discussion

3.1. Volumetric properties

The experimental density, excess molar volume data for (methoxybenzene + PEG400) and (ethoxybenzene + PEG400) systems as a function of mass fraction of polymer at T = (298.15, 308.15, and 318.15) K are collected in tables 3 and 4, respectively.

Values of the excess molar volumes, V_m^E, were calculated by the following equation

$$V_m^E = \sum_{i=1}^{2} x_i M_i \left[\frac{1}{d} - \frac{1}{d_i} \right],\tag{2}$$

where x_i and M_i, are the mole fraction and the molar mass of component i, respectively. The subscripts 1 and 2 stand for solvent and solute, respectively.

The V_m^E values of (methoxybenzene + PEG400) and (ethoxybenzene + PEG400) at T = (298.15, 308.15, and 318.15) K are plotted vs. the mole fraction of polymer, x_2, in figure 1. As can be seen from tables 3 and 4 and figure 1, the V_m^E values are negative and become more negative when temperature increases.

The negative V_m^E value can be explained in terms of positive contributions due to breaking of like interactions of the pure liquids and negative contributions due to the formation of unlike (polymer–solvent) interactions and also accommodation of methoxybenzene or ethoxybenzene molecules in the voids provided by the PEG400 (packing effect). The interaction between the hydrogen atom of the hydroxyl group of PEG400 and the oxygen atoms of the methoxybenzene and ethoxybenzene as well as the packing effect are responsible for the negative V_m^E values obtained for the systems investigated. It was found that the —O—CH$_3$ group of methoxybenzene and —O—CH$_2$—CH$_3$ group of ethoxybenzene can give some degrees of intermolecular interaction by weak H-bonds [18]. The negative values of V_m^E indicate that the packing degree in these mixed liquids is higher than in the pure species and in their "idealized" mixtures, suggesting that there are specific intermolecular interactions such as hydrogen bonding and dipolar interactions. The excess molar volume values reported for

TABLE 1
Provenance and mass fraction purity of the compounds studied.

Compound	CAS number	Supplier	Mass fraction purity	Water content [a] mass fraction	Molar mass (g · mol^{-1})
Poly(ethylene glycol)	25322-68-3	Merck	0.99	0.0005	400
Methoxybenzene	100-66-3	Merck	0.99 (GC)	0.0004	108.14
Ethoxybenzene	103-73-1	Aldrich	0.99 (GC)	0.0003	122.16

[a] Determined by a microprocessor based automatic Karl–Fischer Titrated.