



Investigation of interaction between polyethylene oxide and ionic liquid 1-octyl-3-methyl-imidazolium bromide in aqueous solutions by spectroscopic and viscometric methods



Abbas Mehrdad*, Zahra Niknam

Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

ARTICLE INFO

Article history:

Received 9 July 2016

Received in revised form 8 August 2016

Accepted 9 August 2016

Available online 10 August 2016

Keywords:

Polyethylene oxide

Ionic liquid

Spectroscopy

Viscosity

Interaction

ABSTRACT

The effect of ionic liquid, 1-octyl-3-methyl imidazolium bromide on the thermodynamic quality of water for polyethylene oxide was studied at the temperature range of 288.15–313 K by viscometric method. The obtained data reveal that thermodynamic quality of water for polyethylene oxide is increased by addition of 1-octyl-3-methyl imidazolium bromide. The flow activation energy was determined and correlated in terms of polymer concentration. The sign of initial slope of the activation energy versus polymer concentration at zero concentration indicates that the thermodynamic quality of ionic liquid aqueous solutions is reduced by increasing temperature. Also, the type of interaction between polyethylene oxide and 1-octyl-3-methyl imidazolium bromide was investigated by FT-IR and UV-Vis spectroscopy methods. The results of FT-IR and UV-Vis spectroscopy confirmed the existence of hydrogen bonding between imidazolium cation and oxygen atom of polyethylene oxide.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The mixture of polymer and ionic liquid suggests a wide spectrum of applications in processing and the research of new products; therefore significant attention is being given to study of their interactions and analyze the fundamental thermodynamic parameters. Investigation of the viscosity of polymer solution is fundamental in the design of processes. Parameters derived from measurements of dilute solution viscosity can be related to interaction between polymer and solvent [1].

Over the last decade, ionic liquids as green and designer solvents have found interest. These compounds have a large organic cation (e. g., 1,3-dialkyl imidazolium) and an organic or inorganic anion (e. g., acetate, chloride) [2]. Ionic liquids, a new class of solvents, have attracted considerable attention due to their unique combination of nonflammability, negligible volatility, high ion conductivity, thermal and chemical stability and ability to dissolve organic and inorganic solutes and gases [3–7]. Over the last few years, the rheological properties of some polymers in ionic liquids have been investigated [8–10]. Recently, combination of polymers and ionic liquids were used in various areas. For

example, polyethylene glycol along with ionic liquids in aqueous biphasic systems for extraction of biomolecules [11–15], mixture of polyethylene glycol and ionic liquid as gel compound in solar cells [16,17], as electrolyte in electrochemical systems [18], as lubricant [19–21] and antioxidant in steel-steel contact [22,23], as catalyst [24–26] and as absorbant in extraction of CO₂ were used [27,28]. Moreover our research group is interested in studying the role of imidazolium based ionic liquid as compatibilizer for polyvinyl pyrrolidone and polyethylene glycol, so a systematic study carried out on (polyvinyl pyrrolidone + ionic liquid) and (polyethylene glycol + ionic liquid) systems because in studying the compatibility of polymers by viscometric methods, specific data of each polymer with ionic liquid is necessary. In the previous works, the interactions of polyvinyl pyrrolidone with imidazolium based ionic liquid in aqueous solution were investigated [29–31]. Also in the previous works, the viscosity behavior of polyethylene oxide in the presence of ionic liquids, 1-butyl-3-methyl-imidazolium bromide, [BMIm]Br, and 1-hexyl-3-methyl-imidazolium bromide, [HMIm]Br, in aqueous solutions has been studied [32,33]. Polyethylene oxide (PEO), a linear and nontoxic homopolymer, is water soluble due to hydrogen bonding [34,35]. In this paper, thermodynamic quality of solvent was investigated using viscometric method at different temperatures. In addition, interaction of PEO and 1-octyl-3-methyl-imidazolium bromide was investigated by FT-IR, UV-Vis spectroscopy and viscometric methods.

The relationship of the reduced viscosity, η_{red} , with concentration, C , is indicated by Huggins equation. This well-known relationship is used

* Corresponding author.

E-mail address: a_mehrdad@tabrizu.ac.ir (A. Mehrdad).

for calculation of intrinsic viscosity by extrapolating η_{red} linearly to $C = 0$ [36,37].

$$\eta_{red} = \frac{\eta - \eta_0}{\eta_0 C} = [\eta] + b_H C \quad (1)$$

where η and η_0 are viscosity of the given polymer solution and solvent, respectively, C is solution concentration and b_H is the interaction parameter of Huggins.

The expansion factor, α , which describes the excluded volume effect, is given by [38,39]:

$$\alpha = \left(\frac{[\eta]M}{\Phi} \right)^{\frac{1}{3}} \left(Nl^2 \frac{1 - \cos\phi}{1 + \cos\phi} + 2l^2 \cos\phi \frac{1 + (\cos\phi)^N}{(1 + \cos\phi)^2} \right)^{-\frac{1}{2}} \quad (2)$$

where M , N , l , ϕ and Φ are molecular weight of polymer, the number of bonds existing in polymer chain, the bond length, bond angles and the Flory constant respectively. Flory and Fox further suggested that the temperature dependence of the expansion factor is as follows [40]:

$$\alpha^5 - \alpha^3 = \left(\frac{27}{2^{1.5} \pi^{1.5}} \right) \left(\frac{\bar{v}^2}{N_A V_s} \right) \left(\frac{\langle R^2 \rangle_0}{M} \right)^{-1.5} M^{0.5} (0.5 - \chi) \quad (3)$$

where V_s , \bar{v} , N_A and χ are the molar volume of solvent, the partial specific volume of the polymer, Avogadro's number and polymer-solvent interaction parameter respectively. The temperature dependence of the polymer-solvent interaction parameter can be expressed as [41]:

$$\chi = \chi_s + \frac{\chi_h}{T} \quad (4)$$

where χ_s and χ_h are the entropic and enthalpic contribution of polymer-solvent interaction parameter, respectively.

The second osmotic virial coefficient, A_2 , in terms of the polymer-solvent interaction parameter can be expressed as [42]:

$$A_2 = \frac{\bar{v}^2}{V_s} (0.5 - \chi) F(\alpha) \quad (5)$$

where:

$$F(\alpha) = \sum_{n=0}^{\infty} \frac{(-2(\alpha^2 - 1))^2}{(n+1)!(n+1)^{1.5}} \quad (6)$$

In Newtonian fluids the temperature dependence of the viscosity is usually expressed in form of Arrhenius relationship [43,44]:

$$\eta = A e^{E_v / RT} \quad (7)$$

where η is the viscosity, E_v is the activation energy, A is pre-exponential factor, R is the gas constant, and T is the temperature in K. Viscosity-temperature data are on the basis of the above equations, usually presented in the form of $Lm\eta$ as a function of reciprocal temperature ($1/T$).

2. Experimental

2.1. Materials

Polyethylene oxide was purchased from Acros Chemical Co. The weight-average molecular weight was 900 kg mol^{-1} . The ionic liquid, 1-octyl-3-methylimidazolium bromide, which used in this research, was prepared and purified using the procedure described in the literature [45,46]. The chemicals used in this synthesis were N-methylimidazole, 1-bromooctane and ethylacetate. The moisture of ionic liquid was measured by Karl Fischer method using a Karl-Fischer titrator (720-KSS-Metrohm Herisau, Switzerland) and it was found to

Table 1
Table of the samples used in this study.

Chemical name	Source	Purification method	Mass fraction purity	Analysis method
Polyethylene oxide	Acros	None	–	–
N-methylimidazole	Merck	None	>0.99	–
1-bromooctane	Merck	None	>0.99	–
ethylacetate	Merck	None	>0.99	–
acetonitrile	Merck	None	>0.99	–
1-octyl-3-methylimidazolium bromide	Synthesis	Rotary and Vacuum pump	0.96	NMR

be mass fraction 0.013. Table 1 presents the studied chemicals, their suppliers, stated purities and purification procedure applied in each case. Double distilled water was used for preparation of solutions.

2.2. Synthesis of ionic liquid

To direct alkylation, 1-bromooctane was added to N-methylimidazole at $T = 313.15 \text{ K}$ for 48 h under an argon atmosphere. The purification procedure is same as described previously [31]. The synthesized ionic liquid was analyzed by $^1\text{H NMR}$ (Bruker Av-400) and FT-IR (Bruker, Tensor 27) to confirm the absence of any major impurities. $^1\text{H NMR}$ and FT-IR spectrums of synthesized ionic liquid are shown in Figs. S1 and S2 (supporting information). The purity of the synthesized ionic liquid was determined using the procedure described in the literature [2]. The content of 1-methylimidazole was determined by $^1\text{H NMR}$ spectroscopy. On the basis $^1\text{H NMR}$ analysis, the purity of synthesized ionic liquid was 96%.

2.3. Apparatus and procedure

In FT-IR analysis, PEO and [OMIm]Br were dissolved in acetonitrile, and the blends were casted onto the KBr pellets. PEO/ionic liquid solutions were prepared with varying compositions (25/75, 50/50, 75/25 w/w). Thin films of samples were dried under vacuum for 24 h then analyzed by FT-IR spectroscopy. FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer in the wave number range of $400\text{--}4000 \text{ cm}^{-1}$. For UV-Vis analysis, aqueous ionic liquid/PEO solutions were prepared at different compositions (1/0, 0.42/1, 1.2/1 and 2/1 w/w) using double distilled water. The UV-Vis spectra were recorded using a UV-Vis spectrophotometer (T80, PG Instrument Ltd).

In viscometric analysis, the ionic liquid aqueous solutions were prepared at various concentrations using double distilled water with a relative standard uncertainty of 4%. It is noted that the water content was considered in preparation of aqueous solution of ionic liquid. In order to preparation of polymer solutions, a stock solution was supplied with a relative standard uncertainty of 0.05%. Then the sample polymer solutions were prepared at various weight fractions of polymer by the stock solution of polymer. The relative standard uncertainty of final sample polymer solutions was 0.1%. The weighting was performed on a Sartorius analytical balance (CP224 S) with an uncertainty $1 \times 10^{-7} \text{ kg}$. The solutions were filtered before use by a filter with aperture $75 \mu\text{m}$ and their viscosity was measured using a jacketed Ubbelohde viscometer with 0.4 mm capillary at temperature range of $288.15\text{--}313.15 \text{ K}$. The flow time was determined from an average of several readings (at least 3 readings). The temperature of solutions was kept constant by a temperature controller (Lab. Companion, RW-0525G, Jeio tech Co.) with a precision of 0.05 K. The flow time of solutions was measured with an uncertainty of 0.2 s. The density of solutions was measured using a vibrating tube densimeter (Antoine Paar DSA-5000, Austria). The apparatus was calibrated with doubly distilled deionized and degassed water followed by dry air at atmospheric pressure. The absolute uncertainty of density was obtained as 0.05 kg m^{-3} .

Download English Version:

<https://daneshyari.com/en/article/5409501>

Download Persian Version:

<https://daneshyari.com/article/5409501>

[Daneshyari.com](https://daneshyari.com)