Journal of Molecular Liquids 216 (2016) 12–17

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Interaction between polyethylene oxide and ionic liquid 1-hexyl-3-methyl-imidazolium bromide: Spectroscopic and viscometric methods

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ARTICLE INFO

Article history:
Received 13 August 2015
Received in revised form 13 December 2015
Accepted 5 January 2016
Available online xxxx

Keywords:
Polyethylene oxide
Ionic liquid
Spectroscopy
Viscosity

ABSTRACT

In this research, the type of interactions between polyethylene oxide and 1-hexyl-3-methyl imidazolium bromide was studied by FT-IR and UV–Vis methods. The results of FT-IR and UV–Vis spectroscopy confirmed existence of hydrogen bonding between imidazolium cation and oxygen atom of polyethylene oxide. Also, the solution properties of polyethylene oxide in binary mixtures of water and ionic liquid, 1-hexyl-3-methyl imidazolium bromide, were studied at the temperature range of 288.15–313.15 K. The effect of ionic liquid, 1-hexyl-3-methyl imidazolium bromide on the thermodynamic quality of water for polyethylene oxide was investigated by viscometric method. The results indicate that thermodynamic quality of water for polyethylene oxide is reduced by addition of 1-hexyl-3-methyl imidazolium bromide and increasing temperature. The flow activation energy was calculated and correlated in terms of polymer concentration. The sign of initial slope of the activation energy versus polymer concentration at zero concentration reveals that thermodynamic quality of ionic liquid aqueous solutions is reduced by increasing temperature.

1. Introduction

Properties of polymer solutions are affected by the type of solvent with altering thermodynamic affinities [1]. The effect of solvent's nature on the viscosity of polymer solutions is significant in the practical aspects of processing and synthesizing polymers [2]. Addition of another solvent in a polymer solution can improve or reduce the polymer miscibility. This is particularly the case when the main solvent is water. Polymers dissolved in mixtures of water with polar organic solvents are widely used in applications such as pharmaceutics, personal care products, protein processing, coatings and paints [3]. Ionic liquids are used as solvents for polymerization processes and as components of polymeric materials. Room temperature ionic liquids (RTILs) have emerged as a new class of solvents for practical applications due to their unique properties such as negligible volatility, thermal and chemical stability, nonflammability, and high ion conductivity. Ionic liquids are composed of large organic cations and small inorganic or organic anions [4]. The use of ionic liquids in polymer science has rapidly promoted from use as solvents and has become focused on using ionic liquids as functional additives to polymer chains or to hybrid materials [5].

Over the last few years, the rheological properties of some polymers in ILs have been investigated [6–9]. In previous works we have also studied the viscosity behavior of polyvinyl pyrrolidone in the presence of ionic liquids, 1-butyl-3-methyl-imidazolium bromide [BMIm]Br, 1-hexyl-3-methyl-imidazolium bromide [HMIm]Br and 1-octyl-3-methyl-imidazolium bromide [OMIm]Br in aqueous solutions [10–12]. Our previous researches revealed that addition of ionic liquid in aqueous solution of polyvinyl pyrrolidone increases thermodynamic quality of water for polyvinyl pyrrolidone.

Polyethylene oxide (PEO), a linear and nontoxic homopolymer, is water soluble due to hydrogen bonding with ethylene oxide groups [13,14]. In this paper, thermodynamic quality of the solvent was investigated using viscometric method at different temperatures. Also, the interaction of PEO and 1-hexyl-3-methyl-imidazolium bromide was investigated by FTIR, UV–Vis spectroscopy and viscometric method.

The reduced viscosity of polymer solutions, η_{red}, was calculated by the following equation:

$$\eta_{red} = \frac{\eta - \eta_0}{\eta_0 C} \tag{1}$$

where η and η_0 are the viscosities of the polymer solution and the solvent and C is the polymer concentration. In order to study the conformation of a polymer chain by viscometric method, the intrinsic viscosity data, $[\eta]$, are used. The relationship of the reduced viscosity η_{red} with concentration C, is indicated by the Huggins equation [15,16]:

$$\eta_{red} = [\eta] + b_H C \tag{2}$$

where $b_H = k_H[\eta]^2$ is the interaction parameter of Huggins and k_H is the Huggins constant. The intrinsic viscosity is calculated by extrapolating η_{red} linearly to $C = 0$.

http://dx.doi.org/10.1016/j.molliq.2016.01.014

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-Bromohexane	Merck	None	>0.99	–
Ethylacetate	Merck	None	>0.99	–
Acetonitrile	Merck	None	>0.99	
1-Hexyl-3-methyl imidazolium bromide	Synthesis	Rotary and vacuum pump	>0.98	NMR

In Newtonian fluids the temperature dependence of the viscosity is usually expressed in the form of Arrhenius relationship [17,18]:

$$\eta = Ae^{E_v/_{RT}} \tag{3}$$

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 $Ln\eta$ as a function of reciprocal temperature $(1/T)$. The flow activation energy and pre-exponential factor are determined from the slope and intercept of these diagrams.

At previous works we showed that there is a power law function between the flow activation energy and polymer concentration based on viscosity of polyvinyl pyrrolidone/imidazolium-based ionic liquid aqueous solutions [10,12].

$$\Delta E_v \eta_r = A_0 C + A_1 C^2 \tag{4}$$

The parameters A_0 and A_1 in Eq. (4) are expressed as:

$$A_0 = R\left([\eta]\left(\frac{\partial \ln[\eta]}{\partial 1/T}\right)_P + [\eta]\left(\frac{\partial \ln d}{\partial 1/T}\right)_P\right)$$

$$A_1 = R\left(k_H[\eta]^2\left(\frac{\partial \ln k_H}{\partial 1/T}\right)_P + 2k_H[\eta]^2\left(\frac{\partial \ln[\eta]}{\partial 1/T}\right)_P + 2k_H[\eta]^2\left(\frac{\partial \ln d}{\partial 1/T}\right)_P\right)$$

where η_r is the relative viscosity and d is the density of solution.

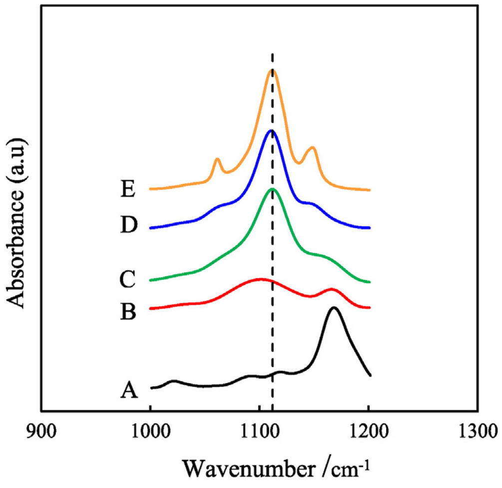


Fig. 1. FT-IR spectra of ionic liquid, PEO and IL/PEO blends in the region 1000–1200 cm^{-1}: (A) pure IL; (B) 75 IL/25 PEO (C) 50 IL/50 PEO (D) 25 IL/75 PEO (E) pure PEO.

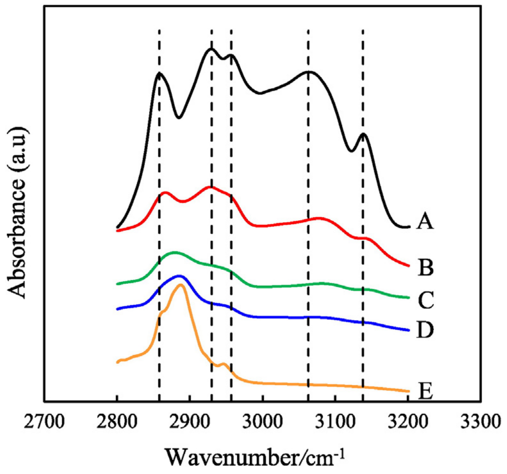
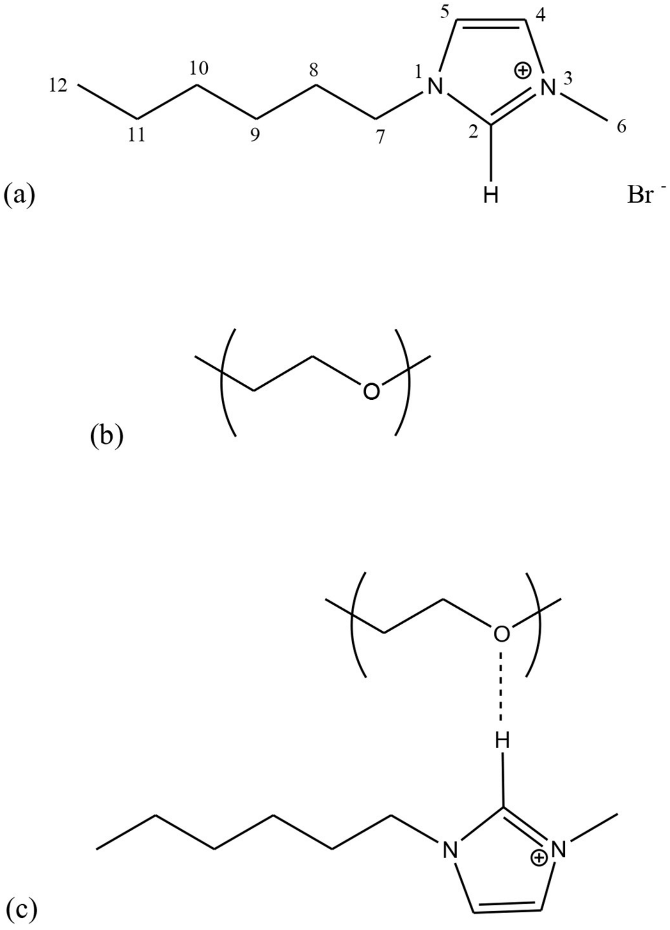


Fig. 2. FT-IR spectra of ionic liquid, PEO and IL/PEO blends in the region of 2800–3200 cm^{-1}: (A) pure IL; (B) 75 IL/25 PEO (C) 50 IL/50 PEO (D) 25 IL/75 PEO (E) pure PEO.

The initial slope of the ΔE_v versus C at zero concentration is given by:

$$(\partial \Delta E/\partial C)_{C=0} = R\left([\eta]\left(\frac{\partial \ln[\eta]}{\partial 1/T}\right)_P + [\eta]\left(\frac{\partial \ln d}{\partial 1/T}\right)_P\right). \tag{5}$$

The sign of initial slope of the ΔE_v versus C at zero concentration is related to the thermodynamic quality of the solvent. The negative initial slope indicates that thermodynamic quality of the solvent is improved



Scheme 1. Chemical structure of ionic liquid (a) and polyethylene oxide (b) and hydrogen bond interaction between imidazolium cation and polyethylene oxide (c).