Viscometric studies of interactions between ionic liquid 1-octyl-3-methyl-imidazolium bromide and polyvinyl pyrrolidone in aqueous solutions

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ABSTRACT

Ionic liquids are investigated as solvents for polymerization processes, as plasticizers of various kinds of polymers and as components of the polymeric matrixes. In this research, viscosity of polyvinyl pyrrolidone in aqueous solution of ionic liquid, 1-octyl-3-methyl imidazolium bromide are measured at various temperatures. The flow activation energies are calculated and correlated in terms of polymer concentration. From sign of the initial slope of the activation energy versus polymer concentration at zero concentration, it is concluded that thermodynamic quality of ionic liquid aqueous solutions are reduced by increasing temperature. The value of the intrinsic viscosity of polyvinyl pyrrolidone was determined using Huggins equation and thermodynamic parameters of this polymer were calculated on the basis of intrinsic viscosity. Also the effect of ionic liquid, 1-octyl-3-methyl imidazolium bromide on the thermodynamic parameters of dilute aqueous polyvinyl pyrrolidone solutions, such as (polymer + solvent) interaction parameter, theta temperature, the heat of dilution parameter and the entropy of dilution parameter was investigated. Results suggest that the thermodynamic quality of water was increased slightly by the addition of ionic liquid in aqueous solution of polyvinyl pyrrolidone.

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1. Introduction

Investigation of the effect of solvent's nature on the viscosity of polymer solutions leads to a better understanding of the fundamental properties of polymer solutions. The polymers miscibility can be affected by addition of another solvent in a polymer solution. Polymers dissolved in mixtures of water with polar organic solvents are widely used in applications such as coatings, paints and inks, pharmaceutics, personal care products, and protein processing [1–3]. The hydrodynamic volume occupied by a given polymer mass is the intrinsic viscosity which is a parameter that depends on the interactions of the molecular structure with the solution [4]. In this work, intrinsic viscosity measurements were used to obtain the thermodynamic parameters and discussion of these parameters in terms of the quality of the mixed solvent. Thermodynamic properties of polymer solutions are important for understanding (solute + solvent) and (solute + solute) interactions. The intrinsic viscosity method is simple and available to get precise values indirectly from viscosity measurements of polymer dilute solutions.

Polyvinyl pyrrolidone, PVP, an amorphous polymer, are used by a wide variety of industries, such as cosmetics, textile, adhesives, coatings, and ceramics. It is also one of the most commonly used polymers in medicine because of its solubility in water and its extremely low cytotoxicity [5–8]. A considerable number of experimental researches have been conducted regarding PVP solutions. The previous findings indicate that addition of ionic and nonionic solutes to aqueous PVP solutions disrupts hydrogen bonds and/or molecular association of polymers [9–15]. Ionic liquids, IL, are organic salts that are liquid at ambient temperatures. In recent years ionic liquids have emerged as a new class of solvents for practical applications due to their unique properties such as low volatility, ability to dissolve organic, inorganic and polymeric compounds, good thermal stability and high conductivity. The use of ionic liquids in polymer science is not limited to their application as solvents. Ionic liquids are used as additives to polymers (plasticizers, components of polymer electrolytes, porogenic agents) [16–18]. In recent years the rheological behavior of some polymers in ILs has been studied [19–22]. In previous work we have also studied the viscosity behavior of polyvinyl pyrrolidone in the presence of 1-hexyl-3-methyl-imidazolium bromide ionic liquid in aqueous solutions. The obtained results indicated that addition of IL to PVP aqueous solution increases thermodynamic quality of water for

PVP [23]. In this research, the properties of solutions of PVP in binary mixtures of water and ionic liquid, 1-octyl-3-methyl imidazolium bromide, [OMIm]Br were investigated at different temperatures.

In polymer science, reduced viscosity, η_{red}, is defined as follows:

$$\eta_{red} = \frac{\eta - \eta_0}{\eta_0 C}, \qquad (1)$$

where η and η_0 are the viscosities of the polymer solution and the solvent and C is the polymer concentration. The intrinsic viscosity, $[\eta]$, of PVP are determined using the Huggins equation by plotting reduced viscosity against the polymer concentration and subsequently extrapolating to zero polymer concentration [24,25].

$$\eta_{red} = [\eta] + b_H C, \qquad (2)$$

where $b_H = k_H [\eta]^2$ is the interaction parameter of Huggins and k_H is Huggins constant.

The expansion factor, α, which describes the excluded volume effect, is given by [26]:

$$\alpha = \left(\frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} \right)^{0.5}, \qquad (3)$$

where $\langle R^2 \rangle$ and $\langle R^2 \rangle_0$ are the mean square end-to-end distance of a polymer chain in expanded and in unperturbed chain, respectively. Flory and Fox suggested that the Mark–Houwink equation can be put in the form [27]:

$$[\eta] = K M^{0.5} \alpha^3, \qquad (4)$$

where M is molecular weight of polymer and K is given by:

$$K = \Phi \left(\frac{\langle R^2 \rangle_0}{M} \right)^{1.5}, \qquad (5)$$

where Φ is the Flory constant which equals to 2.8×10^{-20} [28]. In the "random walk chains" model with restricted bond angles, φ, rotations about the bonds not restricted, $\langle R^2 \rangle_0$ is given by [29]:

$$\langle R^2 \rangle_0 = Nl^2 \frac{1 - \cos \phi}{1 + \cos \phi} + 2l^2 \cos \phi \frac{1 + (\cos \phi)^N}{(1 + \cos \phi)^2}, \qquad (6)$$

where N and l are the number of bonds existing in polymer chain and the bond length, respectively. However, in the case of PVP, $\phi = 109.5°$ and the value of N is twofold of ratio molecular mass of polymer to mass of monomer, because there are two linkages in each monomer of PVP. The value of l in the case of PVP is equal bond length of (C—C). The used bond length is 0.153 nm [15]. Therefore substitute equations (5) and (6) in equation (4) yields:

$$\alpha^3 = \frac{[\eta]M}{\Phi} \left(Nl^2 \frac{1 - \cos \phi}{1 + \cos \phi} + 2l^2 \cos \phi \frac{1 + (\cos \phi)^N}{(1 + \cos \phi)^2} \right)^{-1.5}. \qquad (7)$$

Flory and Fox further suggested that the temperature dependence of the expansion factor is as follows [27]:

$$\alpha^5 - \alpha^3 = \left(\frac{27}{2^{1.5} \pi^{1.5}} \right) \left(\frac{\bar{v}^2}{N_A V_s} \right) \left(\frac{\langle R^2 \rangle_0}{M} \right)^{-1.5} \Psi M^{0.5} \left(1 - \frac{\theta}{T} \right), \qquad (8)$$

where V_s, $\bar{v}$ and N_A are the molar volume of solvent, the partial specific volume of the polymer and Avogadro's number, respectively. On the other hand, the relation of Ψ and κ is given by [30]:

$$\kappa = \frac{\theta \Psi}{T}. \qquad (9)$$

In this equation, thermodynamic parameters Ψ, κ and θ are the entropy of dilution parameter, the heat of dilution parameter and theta temperature, respectively. The (polymer + solvent) interaction parameter, χ, can be expressed in terms of entropy and heat of dilution parameter as [30]:

$$\chi = 0.5 + \kappa - \Psi. \qquad (10)$$

2. Experimental

2.1. Materials

Polyvinyl pyrrolidone with an average molecular weight of 1300 kg · mol^{-1} was used. The ionic liquid, 1-octyl-3-methylimidazolium bromide was prepared and purified using the procedure described in the literature [31]. N-methylimidazole, 1-bromooctane, and ethylacetate were used for synthesis of the ionic liquid. The moisture of ionic liquid is measured by Karl Fischer method using a Karl-Fischer titrator (720-KSS-Metrohm Herisau, Switzerland) and it was found that the mass fraction of water is about 0.02. Distilled water was used to prepare solutions. The source of all used compounds, purification methods, and purity of the substances are presented in table 1.

2.2. Synthesis of ionic liquid

1-octyl-3-methylimidazolium bromide was synthesized by direct alkylation of N-methylimidazole with an excess of 1-bromooctane in a round bottom flask at ambient temperature for 72 h under an argon inert atmosphere. The crude product was separated from reagents and then washed three times with ethylacetate. The volatile compounds in the ionic liquid were removed in high vacuum at about 333 K using a rotary evaporator for at least 4 h at reduced pressure. The ionic liquid was used after vacuum desiccated for at least 48 h to remove trace amount of moisture. Ionic liquid was analyzed by 1H NMR (Brucker Av-300) and FTIR (PerkinElmer, Spectrum RXI) to confirm the absence of any major impurities [31].

2.3. Apparatus and procedure

Aqueous ionic liquid solutions with different concentrations (0.0035, 0.0111, 0.0185) mol · kg^{-1} were prepared by using double distilled water. The polymer solutions were prepared in the concentration range from (1 to 7) kg · m^{-3} by using double distilled water and prepared ionic liquid aqueous solutions. The weightings were performed by Sartorius analytical balance (CP224 S) with an uncertainty of $\pm 1 \times 10^{-7}$ kg. The solutions were filtered before use by a filter with aperture 75 μm and their viscosities were measured by

TABLE 1
The source of all used compounds, purification methods, and purity of the substances.

Chemical name	Source	Purification method	Mass fraction purity	Analysis method
Polyvinyl pyrrolidone	Acros	None	–	–
N-methylimidazole	Merck	None	>0.99	–
1-bromooctane	Merck	None	>0.99	–
Ethylacetate	Merck	None	>0.99	–
1-octyl-3-methyl imidazolium bromide	Synthesis	Rotary and vacuum pump	>0.98	NMR