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Effect of 1–butyl–4–methylpyridinium and 1–butyl–3–methylimidazolium halide ionic liquids on the interactions of lactic acid in the aqueous solutions of polyethylene glycol

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ABSTRACT

In this study, effect of some ionic liquids on the thermodynamic and transport properties of L(+)–lactic acid in aqueous polyethylene glycol solutions have been investigated. Density, speed of sound, and viscosity of L(+)–lactic acid in the aqueous solutions of polyethylene glycol, polyethylene glycol +1–butyl–3–methylimidazolium bromide, polyethylene glycol +1–butyl–3–methylimidazolium chloride, polyethylene glycol +1–butyl–4–methylpyridinium bromide, and polyethylene glycol +1–butyl–4–methylpyridinium chloride were measured at $T/\mathrm{K} = (288.15, 298.15, 308.15 \text{ and } 318.15)$. Infinite dilution apparent molar volumes, transfer apparent molar volume, infinite dilution apparent molar isentropic compressibility and viscosity *B*–coefficient of L(+)–lactic acid were calculated using experimental data and were discussed in terms of solute–solute and solute–solvent interactions. The results reveal that solute–solvent interactions were decreased with increasing temperature, size of halide anion. Also solute–solvent interactions in the presence pyridinium ionic liquids are stronger than those of imidazolium ionic liquids. The obtained results from spectroscopic reveal that λ_{max} of imidazolium based ionic liquids were red shifted in the presence of lactic acid and this behaviour confirmed existence hydrogen bound between lactic acid and imidazolium based ionic liquids.

1. Introduction

L(+)–lactic acid (LaH), as one of important carboxylic acids in chemical industries, has widespread applications in the pharmaceutical industry [1], food industry [2], in environmentally favourable solvents and in the manufacture of biodegradable polymers [3]. LaH can be produced either by chemical synthesis or fermentation processes. To recover the lactic acid from fermentation broths, several techniques have been developed including ion exchange resins, direct distillation, adsorption, electrodialysis, and liquid–liquid extraction [4–6]. Among the various methods for recovery of lactic acid, Liquid–liquid extraction based on aqueous biphasic systems (ABS) is a useful technique for separation, extraction, and enrichment both in industry and academia [7,8]. Recently, a new type of ABS based on ionic liquids–polymer has been reported [9–13]. Ionic liquids has been widely used for many processes as green solvent due to their interesting physical and chemical properties such as low vapor pressure, high thermal stability, non–flammability under ambient conditions, high electrical conductivity and strong solubility power [14–18]. Hence, these properties caused ionic liquids to have many attractive applications in biotechnology for separation and purification of organic acids. The mechanism of ABS formation is almost uncertain at the molecular level. There are some reports in the literatures about the extraction of lactic acid using the ionic liquids in recent years [19–26]. One method to the clarification of the mechanism of phase separation in the ILs–polymer ABS is investigation of the thermodynamic and transfer properties of polymer–ILs aqueous mixtures. Although the thermodynamic and transfer properties of aqueous IL–polymer solutions give useful information on the interactions exist in these systems. However information on the thermodynamic properties of IL–polymer aqueous solutions is scarce. The knowledge of volumetric, viscometric and spectroscopic properties is useful to evaluating the solute–solute and solute–solvent interactions which occur in these solutions. In the present work, volumetric and transport properties of lactic acid in aqueous solution of (PEG + IL) were investigated at different temperatures to provide the information about the nature of interactions LaH in aqueous solutions of (PEG + IL). The infinite dilution apparent molar volumes (V°_{φ}), transfer volume ($\Delta_{tr}V^{\circ}_{\varphi}$), the infinite dilution apparent molar isentropic compressibility (κ°_{φ}) and the viscosity

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B–coefficient were used to interpret the solute–solute and solute-solvent interactions of LaH in the aqueous solutions of (PEG + IL).

2. Experimental

2.1. Chemicals

The names, CAS numbers, abbreviations, purity in mass fraction of the used chemicals and analysis method are listed in Table 1. The double distilled water was used for preparation of the solutions.

2.2. Synthesis of ionic liquids

2.2.1. 1–Butyl–3–methylimidazolium halide

The ionic liquids, 1–butyl–3–methylimidazolium halides, [BMIm]X where X = Cl and Br, were synthesized as described in the literatures by direct alkylation of *N*-methylimidazole with an excess amount of 1-halobutane in a round bottom flask about at *T*/K = 353 for 72 h under an nitrogen atmosphere [27,28]. The product was dried in high vacuum at *T*/K = 353 using a rotary evaporator for at least 4 h under reduced pressure. The ionic liquids were used after vacuum desiccated for at least 48 h to remove trace amount of moisture. The water content of the ionic liquids was determined using a Karl–Fischer titrator (720-KSS-Metrohm Herisau, Switzerland) about 0.015 mass fractions. The ionic liquids were analysis by ^{1}HNMR (Bruker Av 400) spectra to confirm the absence of any major impurities and were found to be in good agreement with those reported in the literature [29,30]. ^{1}H NMR spectrum of [BMIm]Br and [BMIm]Cl are shown in Figs. S1 and S2 (Supporting Information). Purity of synthesized ionic liquids was calculated by considering the area of peaks from H-containing impurities. The purity of synthesized ionic liquids were >0.96 and >0.97 for [BMIm]Br and [BMIm]Cl, respectively.

2.2.2. 1–Butyl–4–methylpyridinium halide

The ionic liquids, 1–butyl–4–methylpyridinium halides, [BMPyr]X where X = Cl and Br were prepared using the procedure described in the literature [31]. To direct alkylation, 1-halobutane was slowly added to 4–methylpyridin at ambient temperature then the mixture was refluxed at *T*/K = 323 for 72 h under an argon atmosphere. To enhance the reaction, toluene was added as co–solvent. Solvent was removed by a rotary evaporator in reduced pressure. The obtained solid was washed several times with ethyl acetate. The volatile compound in product were eliminated at *T*/K = 353 by rotary evaporator. The purification procedure is same as described previously [32]. The moisture of ionic liquids was measured by Karl Fischer method using a Karl-Fischer titrator and it was found to be mass fraction 0.01 for [BMPyr]X. The synthesized ionic liquids were analysis by ^{1}HNMR (Bruker Av-400) to confirm the absence of any major impurities. The purity of the synthesized ionic liquids was determined using the procedure described in the literature [33]. ^{1}H NMR spectrum of [BMPyr]Br and [BMPyr]Cl are shown in Figs. S3 and S4 (Supporting Information). The purity of synthesized ionic liquids was >0.98.

2.3. Apparatus and procedure

LaH solutions were prepared in the aqueous solutions of (PEG + IL) ($w_{\mathrm{PEG}} = 0.020$ and $w_{\mathrm{IL}} = 0.020$). The solutions were prepared in glass vials using an analytical balance (CP224 S Sartorius Co.) with precision of 1×10^{-7} kg. The water content of materials is considered in preparation of the solutions. The experimental density and speed of sound were measured by a density and sound velocity analyzer (DSA5000, Anton Paar). The apparatus was calibrated with doubly distilled and degassed water and dry air at atmospheric pressure. Temperature was kept constant within $\pm 1.0 \times 10^{-3}$ K using the Peltier device built in densimeter. The experimental uncertainty of density and speed of sound measurements were 0.15 $\mathrm{kg\,m^{-3}}$ and 0.5 $\mathrm{m\,s^{-1}}$, respectively. Viscosity of the solutions was measured by digital viscometer (Lovis 2000 M, Anton Paar). An average time is automatically recorded for the desired number of successive runs. The temperature of the capillary is controlled by a Peltier device within a precision of 0.01 K. The relative uncertainty of the viscosity measurements was 1%.

For UV–Vis analysis, ionic liquids spectra of ionic liquids were recorded in water and aqueous solutions of LaH using UV–Vis spectrophotometer (T80, PG Instrument Ltd.). In this study weight fraction of ILs and LaH adjusted as 0.001.

3. Results and discussion

3.1. Apparent molar volume

The experimental density (ρ) and speed of sound (u) for LaH in the aqueous solutions of PEG and in the aqueous solutions of (PEG + IL) ($w_{PEG} = 0.020$ and $w_{IL} = 0.020$) at *T*/K = (288.15, 298.15,

Table 1
Table of the materials used in this study.

Chemical Name	CAS No.	Abbreviation	Supplier	Purity (Mass Fraction)	Purification Method	Analysis Method	Water content (Mass Fraction)
L(+)-Lactic acid	79-33-4	LaH	Sigmaaldrich	≥0.98	None	Karl Fischer titration	0.015
Polyethylene glycol[a]	25,322-68-3	PEG	Merck		None		
N –Methylimidazole	616-47-7		Merck	>0.99	None		
4 –Methylpyridine	108-89-4		Merck	>0.99	None		
1–Bromobutane	109-65-9		Merck	>0.99	None		
1–Chlorobutane	109-69-3		Merck	>0.99	None		
Ethyl acetate	141-78-6		Merck	>0.99	None		
Toluene	108-88-3		Merck	>0.99	None		
1-Butyl-3-methyl imidazolium bromide	85,100-77-2	[BMIm]Br	Synthesized	>0.96	Rotary/evaporator and vacuum	Karl Fischer titration and ^{1}H NMR	0.015
1-Butyl-3-methyl imidazolium chloride	79,917-90-1	[BMIm]Cl	Synthesized	>0.97	Rotary/evaporator and vacuum	Karl Fischer titration and ^{1}H NMR	0.015
1-Butyl-4-methyl pyridinium bromide	65,350-59-6	[BMPyr]Br	Synthesized	>0.98	Rotary/evaporator and vacuum	Karl Fischer titration and ^{1}H NMR	0.010
1-Butyl-4-methyl pyridinium chloride	112,400-86-9	[BMPyr]Cl	Synthesized	>0.98	Rotary/evaporator and vacuum	Karl Fischer titration and ^{1}H NMR	0.010

[a] The average molar mass was 20 $\mathrm{kg \cdot mol^{-1}}$.