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Determination of Solubility of Starch in Selected Ionic Liquids by Turbidimetry

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A novel method was investigated to determine the solubility of starch in ionic liquids based on the turbidity of the solution. This method was used to monitor the dissolving capability of 1-butyl-3-methylimidazolium chloride ([C_4C_1im][Cl]) and 1-butyl-3-methyl-imidazolium acetate ([C_4C_1im][Ac]). Quantitative solubility of three starches (normal maize starch, waxy maize starch and high-amylose maize starch) in two selected ionic liquids (ILs) was studied. The solubilities of normal maize, waxy maize and high-amylose maize starches measured by turbidimetry were 10.750, 10.252 and 11.003 g/100 g of [C_4C_1im][Cl] at 100 °C, respectively. In [C_4C_1im][Ac], the solubility measured was 9.501, 9.250 and 9.752 g/100 g of ionic liquid at 100 °C, respectively. The influence of water content on the real dissolution of starch in these two ionic liquids was investigated. The theoretical amount of anhydrous starch dissolved in ionic liquid at different temperatures was also determined by extrapolation methodology.

Keywords: Starch dissolution, Ionic liquids, Turbidimetric measurements.

INTRODUCTION

As one of the most abundant natural polymers, starch has generated a wide interest in manufacturing value-added products [1-4]. Native starch granules tend to contain a semi-crystalline structure and normally have both amylase and amylopectin. However, their low solubility in most conventional solvents has created drawbacks in reaction processes such as low reaction efficiency and low degree of functionalization. Hence, complete dissolution of starch during some physico-chemical processes is of great importance to enhance its process ability and increase its compatibility with thermoplastics, mechanical properties and resistance to decay.

With unique properties, such as low melting temperature (< 100 °C), high thermal stability, low vapour pressure and recyclability [5,6], ionic liquids (ILs) are regarded as a green solvent and have the potential of replacing volatile organic solvents [7-9]. During the last few years, research efforts in dissolving starch with ionic liquids have increased. Biswas *et al.* [10] reported that homogeneous solution of 10 wt % of maize starch in [C_4C_1im][Cl] at 80 °C and 10 wt % of maize starch in 1-butyl-3-methylimidazolium dicyanamide at 90 °C. Xu *et al.* [11,12] found that maize starch could be soluble up to 20 wt % in 1-allyl-3-methylimidazolium chloride at 80 °C and even to 50 wt % at 100 °C.

With concentric patterns of semi-crystalline layers, native starch granules show birefringence under polarized light [13]. The loss of birefringence in starch granules can potentially be used as an assessment for starch dissolution [14]. In all these studies, the assessment of starch dissolution in ionic liquid media was done by polarized light microscopes or by visual methods where the evaluation of starch dissolution was to observe the transparency of starch solution with observers' own eyes [10-12]. Polarized light microscopes are usually applied to provide qualitative assessment in determining starch dissolution in ionic liquids [15,16]. Moreover, the evaluation process is based on a small quantities of samples, which increases the risk of inaccuracy. Visual method may cause more inaccuracy due to the limitation of sensory evaluation.

In this study, an alternative method to assess the real solubility of starch in ionic liquid was proposed. Turbidimetry was selected as a simple technique with high accuracy and reproducibility, which could also evaluate the quantitative solubility of starch in solvents. Turbidity is the cloudiness of a fluid caused by particles in suspension [17]. When turbidity of solution is measured by a nephelometer, which generally consists of light source, a transmission detector facing the light beam and a scattering light detector perpendicular to the light beam, light generated goes through the testing sample and is collected by the transmitted and scattered detector. As non-dissolved particles that exist in the solution can cause source beam to be scattered rather than transmit in straight lines through the sample, the wavelength of the incident light (860 nm) and the correlation between transmitted and scattered light constitute a precise evaluation parameter if non-dissolved particles are present in a solution. When there are more solid particles scattering the source beam, more light reaches the scattering detector. Therefore, turbidity will keep constant when native starch granules are perfectly soluble. However, when the solubility is reached, the newly added starch granules will remain solid and turbidity of the solution will increase sharply. Meanwhile, a polarized light microscope was used to investigate the granular structure of starch heated in ionic liquid and the turbidimetric measurement calculates the total number of starch granules emerged in the visual field.

The physico-chemical properties of ionic liquids have been shown to be very sensitive to water content [18]. It is thought that water interacts strongly with the imidazolium ring of the cation in imidazolium-based ionic liquids [19,20]. Hydrogen bonding between some ionic liquids and water has been observed [21]. Therefore, dissolution of starch in ionic liquids can be strongly influenced by moisture content. In the present case, water can come from the hygroscopicity of ionic liquid, the initial starch water content and the process. We quantified the negative influence of water when dissolving starch in ionic liquid in this study. Extrapolation methodology was applied to determine the theoretical amount of dissolved anhydrous starch in the ionic liquid at different temperatures.

EXPERIMENTAL

Normal maize starch and waxy maize starch were obtained from Chang Chun DaCheng Corn Products Co. (Chang Chun, China). High-amylose maize (Hylon VII) starch was purchased from National Starch LLC (Bridgewater, NJ, USA). 1-butyl-3-methylimidazolium chloride ([C_4C_1im][Cl], > 99 %) and 1-butyl-3-methyl-imidazolium acetate ([C_4C_1im][Ac], > 99 %) were provided from Lanzhou Institute of Chemical Physics (Lanzhou, China). Starches were oven dried at 105 °C for 6 h prior to use. Other chemicals and solvents were commercially available and of analytical grade.

Determining the dissolution of an ionic compound, a polymer in water and starch in ionic liquids by turbidimetry: Dissolution of the three chemicals was conducted using similar method. A precise quantity of solvent (100.0 ± 0.1 g) was added into turbidimetric clear glass vials with a magnetic stirrer. Then the vials were heated in a heating oil bath at constant temperature. Small precise amounts of solutes (0.025 ± 0.001 g) were added into the vials. The turbidity of the solution was measured with a nephelometer (2100AN, Hach Company, Loveland, CO, U.S.A) until a stable nephelometric turbidity units (NTU) value was reached. Dissolution of an ionic compound (NaCl) in water was conducted at 30 ± 1 °C. Dissolution of a polymer (soluble maize starch) in water and starch in ionic liquids were performed at 95 ± 1 °C and 100 ± 1 °C, respectively, with continuous stirring. In between each addition, 30 min was allowed for dissolution.

Determining the dissolution of starch in ionic liquids by polarized light microscopy: For the dissolution of starch in ionic liquids, a polarized light microscope (Olympus BX51, Tokyo, Japan) was also used to investigate the structure of starch heated in ionic liquid during the turbidity measurement. When determining solubility of the starch samples with optical microscopy, ten different visual fields were observed per sample. The total number of starch granules emerged in each of the ten visual fields was calculated.

Influence of the water content: Starch dispersions with different concentrations (0.5, 1 and 2 g in 100 g of ionic liquid) were first prepared at 120 °C to eliminate the ambient moisture. Then the solutions were put into vials with a magnetic stirrer and placed in an oil bath at a controlled temperature (100 or 110 °C). Small precise amounts of water were added discretely into the vials. Turbidity of solutions was measured every 15 min until constant values were reached. The water content in each vial could be calculated based on the quantity of added water.

Statistical analysis: All determinations were replicated three times and mean values and standard deviations were reported. Analysis of variance (ANOVA) was performed and the mean separations were performed by Tukey's HSD test ($p < 0.05$) using SigmaStat Version 2.0 (Jandel Scientific/SPSS Science, Chicago, IL, USA). The correlation between the turbidity of solutions and the number of existed starch granules was analyzed using Data Analysis Toolbox for MATLAB® mathematical software [22].

RESULTS AND DISCUSSION

Dissolution of an ionic compound and a polymer in water: First, the turbidimetric principle was validated by using an ionic compound (NaCl) and a polymer (soluble maize starch) dissolved in water. Turbidity is expected to keep constant when the solute is perfectly soluble and when the solubility is reached, the addition of solid will cause a sharp increase in the turbidity.

The turbidity behaviour of the dissolution of sodium chloride in water at 30 °C and the dissolution of soluble maize starch in water at 95 °C are depicted in Figs. 1 and 2, respectively. Turbidity of the solution kept constant in the beginning of the addition of NaCl and then increased sharply when the concentration of NaCl was higher than 36 g/100 g water (Fig. 1). According to the Handbook of Chemistry and Physics [23], the solubility value of NaCl is 36.1 g in 100 cm^3 of water at 30 °C, which is consistent with the result obtained from the proposed turbidimetry method [24]. Hence, the perfect dissolution of a salt in water could not cause turbidity within the solubility. The predicted behaviour of turbidity was confirmed with the study of the dissolution of NaCl in water.

As for a polymer, the dissolution of soluble maize starch in water at 95 °C depicted a linear trend with a small slope instead of constant value (Fig. 2). Its turbidity could be regarded as almost constant in the entire scale of turbidity (1-1,000 NTU). However, the saturation could not be reached because the solution became too viscous to be stirred with the addition of soluble maize starch, which prevented the homogenization of sample. Nevertheless, the dissolution trend of NaCl and soluble maize starch in water illustrated that the main turbidimetric principle could be confirmed by ionic compound and polymer.

Dissolution of starch in ionic liquids: Solubility of normal maize starch, waxy maize starch and high-amylose maize starch dissolved in [C_4C_1im][Cl] and [C_4C_1im][Ac] were

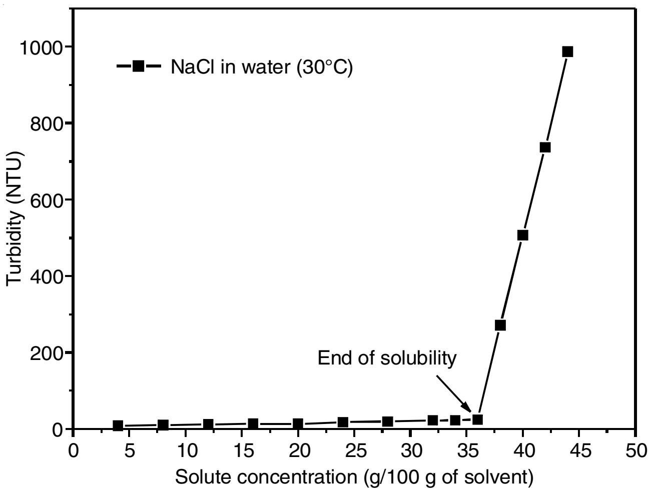

Fig. 1. Turbidity *versus* solute concentration: NaCl in water

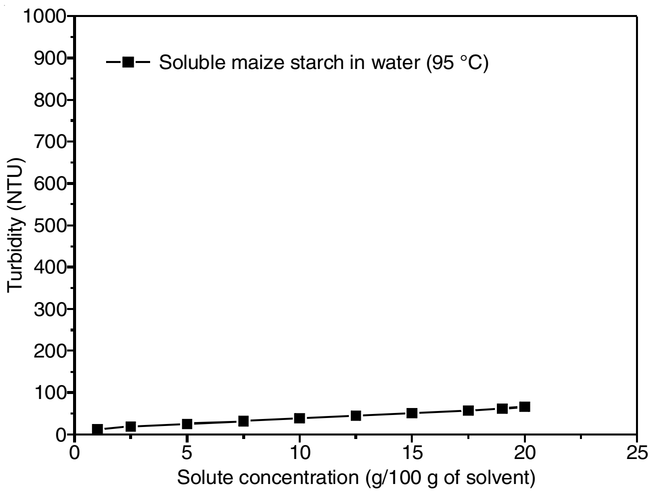

Fig. 2. Turbidity *versus* solute concentration: soluble maize starch in water

determined by measuring the turbidity. The solubility of starch in the above ionic liquids was also observed by an optical microscopy to further validate the principle of solubility evaluation by turbidimetry. Turbidity results of starches dissolved in [C_4C_1im][Cl] and [C_4C_1im][Ac] at 100 °C, which is the total number of starch granules that emerged in every visual field for each sample and the corresponding photographs are presented in Fig. 3. During the dissolution process, the turbidity curves of three starches dissolved in [C_4C_1im][Cl] and [C_4C_1im][Ac] gave a linear trend with a small slope, which could be considered almost constant with regard to the entire scale of turbidity (1-1,000 NTU). An abrupt change of the turbidity could be observed with the increase of starch concentration, which indicated that the solubility of starch in ionic liquids had been reached. At this time, the newly addition of starch could lead to sharp increase in turbidity. The result from polarized light microscope measurement showed the similar tendency. When the turbidity of starch/[C_4C_1im][Cl] and starch/[C_4C_1im][Ac] solutions was near constant, there was almost no starch granules with birefringence in the optical photographs. Then the number of starch granules seen from polarized light microscope increased rapidly when the turbidity rose dramatically. This clearly revealed that the optical microscopy test gave the similar results to turbidity measurement when dissolving starch. Furthermore, the correlation between the turbidity of solutions and the number of existed starch granules was assessed by MATLAB®, which showed high determination coefficient (> 0.99). Therefore, based on the results of the turbidity test from NaCl and soluble maize starch as well as the polarized light microscope measurement, it could be concluded that turbidity measurements are an effective method in determining quantitative solubility of starch in ionic liquids. The solubility of starch in ionic liquids was the breaking point of turbidity curve.

Based on observations from turbidity measurements, the solubilities of normal maize, waxy maize and high-amylose maize starches were 10.750, 10.252 and 11.003 g/100 g of [C_4C_1im][Cl] at 100 °C, respectively. For three starches in [C_4C_1im][Ac], they were 9.501, 9.250 and 9.752 g/100 g of ionic liquid at 100 °C, respectively. Biswas *et al.* [10] reported that starch can be soluble in [C_4C_1im][Cl] up to 15 % at 80 °C. They assessed the dissolution of starch by observing the transparency of starch solutions with eyes when starch was dispersed in ionic liquid and water after heating. It is highly probably that the higher solubility in their experiment may be due to the inaccuracy of their assessment method.

Influence of the water content: Ionic liquids that have potential to dissolve starch are polar and hygroscopic organic solvents. They act as powerful hydrogen bond acceptors and break associative bonds between starch molecules [25,26]. It was reported that heat was produced when mixing ionic liquid and water, indicating that interactions occurred between the components [27]. Hydrogen bonding between some ionic liquids and water has been observed using NMR and IR experiments [21,28]. Therefore, when starch is perfectly dissolved in one ionic liquid system, the addition of water will disturb the solution of starch. Turbidity is expected to keep constant as long as starch is still soluble in the solvent. However, when the maximum water content in the solution is reached, starch will start to precipitate, which will result in an abrupt increase of the turbidity.

Influence of water content on the turbidity of starch solutions is depicted in Fig. 4. The expected behaviour was verified in the case of the [C_4C_1im][Cl]/starch and [C_4C_1im][Ac]/starch solutions. With the addition of water, turbidity was nearly constant in the first stage. When the maximum water content in the solution was reached, a sharp increase of the turbidity was observed at the beginning of precipitation. As a result, little starch remained in solution and amounts of starches precipitated in suspension.

In this study, tangent methods were applied to determine the start of starch precipitation and the maximum water content that the homogeneous starch/ionic liquid system could contain. For an initial solution of 1 g starch/100 g [C_4C_1im][Cl] at 110 °C, precipitation started at 0.1824 g water/g [C_4C_1im][Cl] (Fig. 4A). For [C_4C_1im][Ac], the value was 0.1503 g water/g [C_4C_1im][Ac] (Fig. 4B). Clearly, the maximum water content in a homogeneous starch/ionic liquid system relies on the concentration of starch, the types of ionic liquids and the temperature. The values based on different conditions are presented in Table-1.

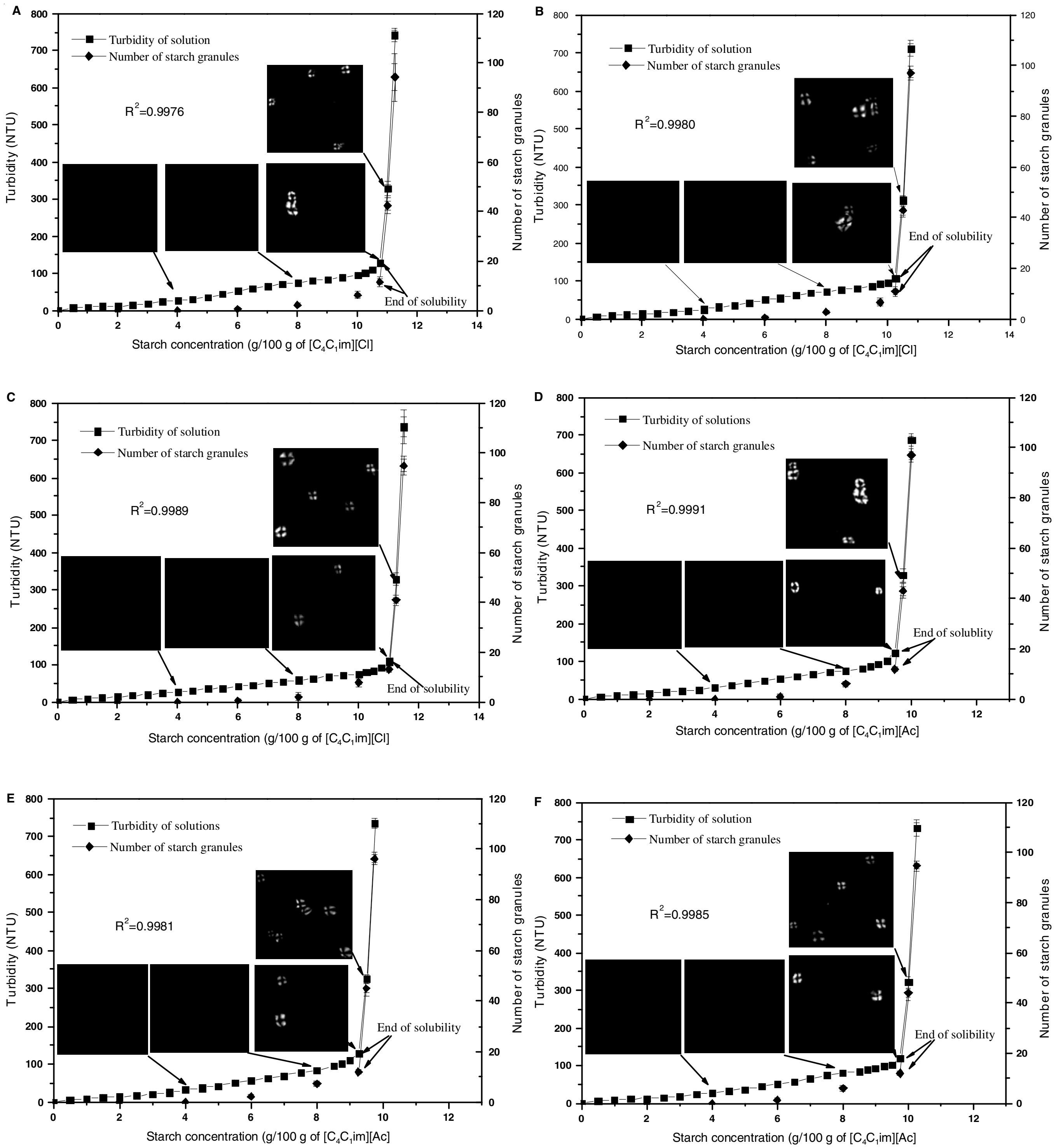

Fig. 3. Turbidity and polarized micrographs of starch dissolved in [C_4C_1im][Cl] and [C_4C_1im][Ac] at 100 °C. A, D. normal maize; B, E. waxy maize; C, F. high-amylose maize

TABLE-1
MAXIMUM WATER CONTENT BEFORE PRECIPITATION FOR DIFFERENT STARCH CONCENTRATIONS IN [C_4C_1im][Cl] AND [C_4C_1im][Ac] AT DIFFERENT TEMPERATURES

Temperature (°C)	[C_4C_1im][Cl]			[C_4C_1im][Ac]		
	0.5 g of starch in 100 g of ionic liquid	1 g of starch in 100 g of ionic liquid	2 g of starch in 100 g of ionic liquid	0.5 g of starch in 100 g of ionic liquid	1 g of starch in 100 g of ionic liquid	2 g of starch in 100 g of ionic liquid
100	0.2201	0.2097	0.1872	0.1844	0.1731	0.1528
110	0.1911	0.1824	0.1634	0.1605	0.1503	0.1337

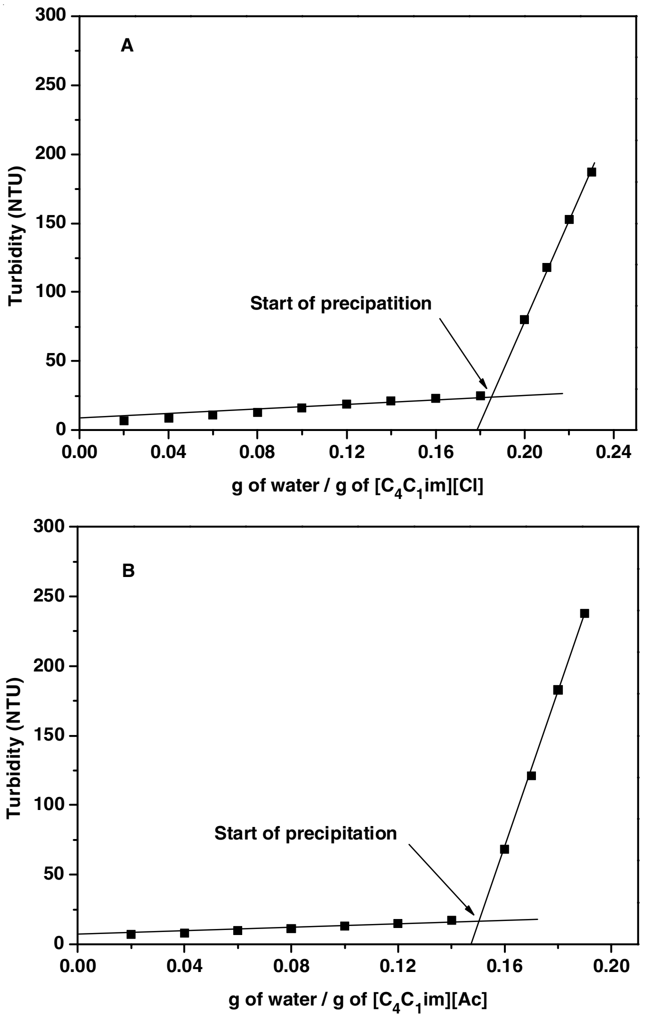

Fig. 4. Influence of water content in the turbidity of starch solutions. (A) 1 g of starch in 100 g of [C_4C_1im][Cl] at 110 °C; (B) 1 g of starch in 100 g of [C_4C_1im][Ac] at 110 °C

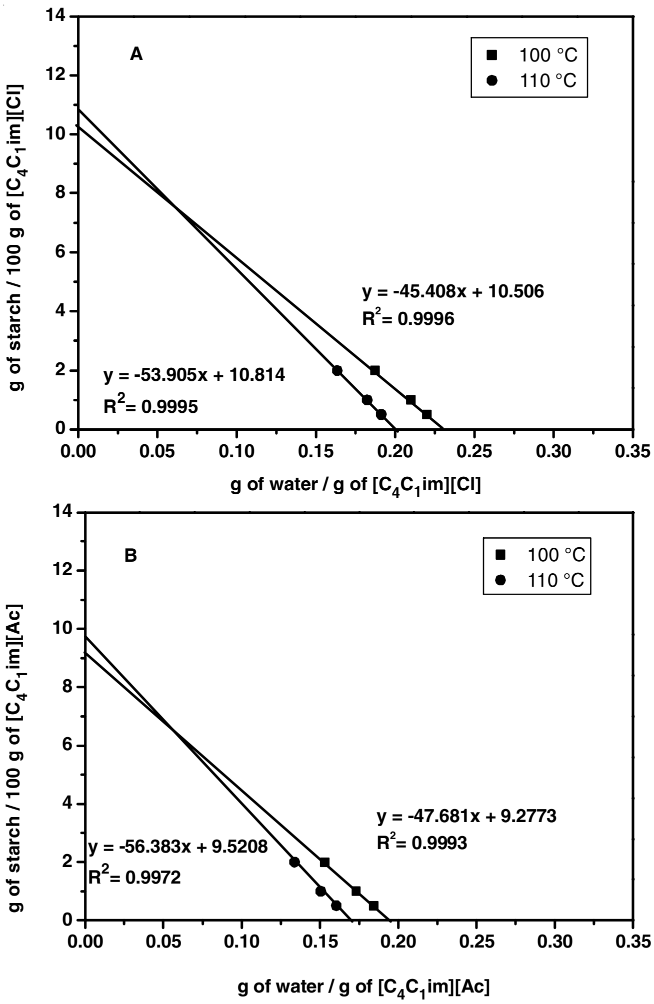

Fig. 5. Linear behaviour of starch in solution in ionic liquids as a function of maximum water content at constant temperature. (A) [C_4C_1im][Cl]; (B) [C_4C_1im][Ac]

The relationship between the maximum water content in a homogeneous starch/ionic liquid solution and the corresponding initial starch concentration at constant temperature is shown as a linear trend (Fig. 5). According to the figure, the theoretical solubility of starch dissolved in ionic liquids at the given temperature is the intersection of the straight line with the Y-axis when the water content in the solution is zero. At 110 °C, the values were 10.811 g/100 g of [C_4C_1im][Cl] and 9.522 g/100 g of [C_4C_1im][Ac], respectively. At 100 °C, the expected value decreased to 10.512 g/100 g of [C_4C_1im][Cl] and 9.280 g/100 g of [C_4C_1im][Ac]. These results were in agreement with the data obtained from turbidity experiment reported above (10.750 g/100 g [C_4C_1im][Cl] and 9.501 g/100 g [C_4C_1im][Ac] at 100 °C). The small difference could be justified by the uncertainty of the extrapolation.

Conclusion

The proposed turbidimetric measurement was demonstrated to be effective in measuring solubility of starch in ionic liquids. This analysis method had been used to evaluate the solubility of normal maize, waxy maize and high-amylose maize starches in [C_4C_1im][Cl] and [C_4C_1im][Ac]. Quantitative evaluation of the influence of water on the starch dissolving in ionic liquid was performed. Starch could be dissolved in [C_4C_1im][Cl] and [C_4C_1im][Ac] at different water contents. When more water existed in solution, lower concentrations of starch solubility were observed. The theoretical solubility of anhydrous starch in solution at 100 °C determined by extrapolation methodology were 10.512 g/100 g of [C_4C_1im][Cl] and 9.280 g/100 g of [C_4C_1im][Ac].

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