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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Molecular Solutions of Cellulose in Mixtures of Ionic Liquids with Pyridine

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Abstract—New systems suitable for determination of molecular characteristics of cellulose, mixtures of ionic liquids based on 1-*n*-alkyl-3-methylimidazolium with pyridine, were found. In ionic liquid–pyridine mixtures, cellulose is dispersed on the molecular level. The cellulose–ionic liquid–pyridine systems with 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium diethyl phosphate are stable in time. The dynamic viscosity and refractive index of the mixtures can be controlled by varying the ionic liquid to pyridine ratio. The viscometric and dynamooptical properties of cellulose in these mixtures were compared with those in Cadoxen.

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Researchers working in various fields of chemistry and materials science display steadily growing interest in cation–anion compounds with relatively low melting points conventionally termed ionic liquids (ILs) [1–4]. This is primarily due to possible applications of ILs as so-called "green" solvents combining high solvency with low vapor pressure and infinite miscibility with water. These properties allow ILs to be considered as environmentally safer liquid media for industrial use, compared to common organic solvents.

Ionic liquids used in place of volatile, dangerously explosive, environmentally harmful, and carcinogenic solvents can be a versatile medium for performing chemical, biochemical, and electrochemical reactions [3, 4]. They can also be used as catalysts [5] and as stationary phases in chromatography [6]. Wide application prospects stimulate synthesis of new ILs [1, 2]. Today the number of published procedures for IL synthesis apparently exceeds the number of papers concerning determination of the main chemical and physical characteristics of ILs (such as melting and decomposition points, miscibility with other solvents, density) and of their stability and solvency, which certainly hinders introduction of ILs into practice.

Recently low-melting (room-temperature, RTILs) ionic liquids with the melting point close to or below 20°C have been of particular interest [7]. One of the causes of increased interest in RTILs is their capability to dissolve native cellulose. The capability of high-melting ILs (at temperatures of about 180°C) to dissolve cellulose was demonstrated as early as the middle 1930s [8], and up to the beginning of the XXI century ILs were considered only as exotic, having no practical significance, solvents of polyglucans. However, with the development of RTILs and of processes for their regeneration [9, 10], these compounds came to be considered as promising cellulose solvents for industrial use.

It is well known that cellulose is difficultly soluble to the molecular level because of the high degree of crystallinity, caused by inter- and intramolecular hydrogen bonds [11]. Complex organometallic systems dissolving cellulose without degradation such as copper–ammonia and cadmium–ethylenediamine (Cadoxen) complexes or systems containing aggressive salts such as dimethylacetamide–LiCl and dimethyl sulfoxide–tetrabutylammonium fluoride cannot be used on the commercial scale because of high toxicity and lack of feasible regeneration procedures [11]. This fact strongly restricts the use of cellulose as renewable natural polymer.

Table 1. Melting point of ILs based on 1-*n*-alkyl-3-methylimidazolium; density ρ_0, viscosity η_0, and refractive index n_0 of the initial ILs, their mixtures with pyridine with various weight ratios of components, Cadoxen, and pyridine at 21°C

Ionic liquid	T_m, °C	ρ_0, g cm^{-3}	η_0, cP	n_0
[EMIM]OAc	17[a]	1.05	180	1.4932
[EMIM]Et_2PO_4	19–20 [a]	1.16	460	1.4743
[BMIM]C1	70	–	–	–
[EMIM]O Ac/ pyridine:				
1:1	–	1.03	4.9	1.4975
2:1	–	–	6.4	–
[EMIM]Et_2PO_4/ pyridine:				
1:1	–	1.10	8.6	1.4749
1.5:1	–	–	10.0	–
[BMIM]C1/ pyridine:				
1.4:1	–	1.06	5.0	1.5093
2:1	–	–	6.5	
Cadoxen	–	1.06	4.40	1.3969
Pyridine	–	0.982	0.974	1.5095

[a] The melting points of the ILs are taken from Sigma–Aldrich data, and the other characteristics of the solvents have been determined in this study.

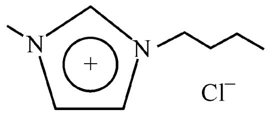
As compared to organometallic complexes, ILs are considerably safer for the environment. Therefore, they deserved the reputation of "green" solvents [12].

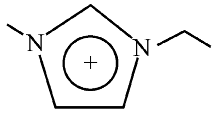
A series of recent studies convincingly demonstrated the high solvency of ILs toward cellulose of various origins and molecular weights [9, 10, 13, 14]. Recent success in the development of processes for large-scale synthesis of ILs by microwave methods [15] and for complete regeneration of ILs by distillation [16] open real prospects for the development of new environmentally safe and cheap technologies for processing of cellulose raw materials using ILs. Therefore, it becomes topical to study the behavior of cellulose macromolecules in these new solvents. However, aggressive properties and relatively high dynamic viscosity η_0 of ILs (Table 1) strongly restrict the use of many traditional methods for studying macromolecules in ILs.

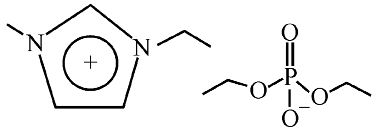
The goal of this study was to find systems free of these drawbacks and suitable for controlling the state and studying the properties of cellulose dissolved in ILs. We took advantage of such an important property of ILs as miscibility with organic solvents and experimentally chose organic additives that would not significantly impair the thermodynamic conditions and cause precipitation of the polysaccharide.

EXPERIMENTAL

Preliminary tests showed that, on adding pyridine to solutions of cellulose in ILs based on 1-*n*-alkyl-3-methylimidazolium as cation and various anions, the solutions remain stable and suitable for studying the molecular properties of the polysaccharide. Furthermore, by varying the composition of mixtures, it was possible to control the viscosity and optical properties of the medium containing dissolved cellulose. To determine the molecular characteristics of cellulose by methods of viscometry and dynamooptical Maxwell effect in mixed solvents, we chose as ILs 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), and 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM]Et_2PO_4), dissolving cellulose at 80–100°C [9, 13, 14]:


[BMIM]Cl


[EMIM]OAc


[EMIM]Et_2PO_4

We took a sample of microcrystalline cellulose (Avicel RN-101 no. 11363, Sigma–Aldrich, Germany). [EMIM]OAc and [EMIM]Et_2PO_4 were purchased from Sigma–Aldrich (nos. 51053 and 671541, respectively). The compound [BMIM]Cl was synthesized at the Technological University of Eindhoven (the Netherlands) by the procedure described in [15]. Pyridine (Merck) was used without additional purification. The characteristics of the solvents used, determined at 21°C, are given in Table 1.

Solutions of cellulose in IL–pyridine mixtures were prepared by the following procedure: Powdered cellulose was added to a heated ILs with continuous stirring.

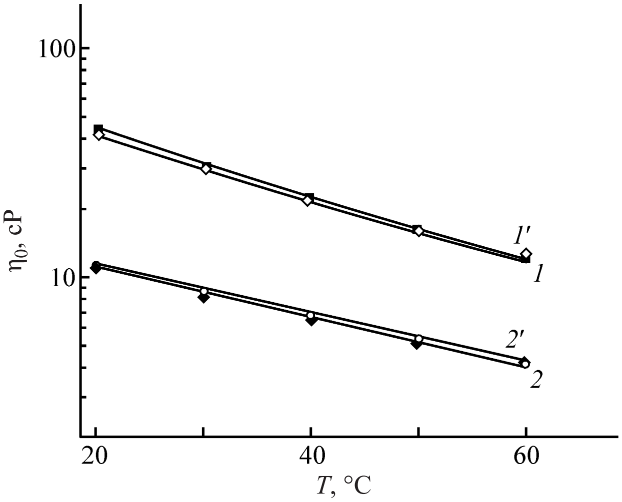


Fig. 1. Two measurements of the temperature dependence of the dynamic viscosity η_0 of 2×10^{-2} g cm^{-3} cellulose solutions in (*1, 1*′) [EMIM]Et$_2$PO$_4$–pyridine (1 : 1) and (*2, 2*′) [EMIM]OAc–pyridine (1 : 1) mixtures, made at an interval of 3 months.

After the crystals disappeared (visual monitoring) and transparent solution was obtained, it was cooled to room temperature, and pyridine was added dropwise at room temperature. Cellulose dissolved in the heated IL within 5–7 min, and the whole process for preparing a solution of cellulose in an IL–pyridine mixture took 20–25 min. The intrinsic viscosity and birefringence of solutions of cellulose in the mixed solvents were measured immediately after preparation (within 1–2 h).

For comparison, we performed measurements for solutions of cellulose in Cadoxen of the following composition, %: Cd 4.65 and ethylenediamine 25.8. The physical characteristics of the Cadoxen used are given in Table 1 together with those of the other solvents.

The molecular weight M = 40×10^3 of the initial cellulose sample was determined from its intrinsic viscosity in Cadoxen and the Mark–Kuhn–Houwink relationship known for the cellulose–Cadoxen system: $[\eta] = 4.5 \times 10^{-4} M^{0.74}$ [17].

The densities of mixtures ρ_0 were determined in a 5 cm^3 pycnometer. The dynamic viscosity η_0 of ILs and 2 wt % solutions of cellulose in ILs and IL–pyridine mixtures was determined with an AMVn Anton Paar microviscometer (the Netherlands) in which the viscosity is determined from the time of sphere travel under the action of gravity in a capillary filled with a liquid. To evaluate the stability of cellulose in the new solvents, the temperature dependences of the dynamic viscosity were recorded during a period of 3 months.

The refractive indices n_0 of liquids were determined with an Abbe refractometer.

The intrinsic viscosity [η] of solutions of cellulose in IL–pyridine mixtures and Cadoxen was measured with an Ostwald capillary viscometer calibrated using water, benzene, and toluene. The viscometer constant at 25°C was 0.140 ± 0.0008 cP cm^3 g^{-1} s^{-1}. When measuring [η], solutions prepared by the above-described procedure were diluted with a separately prepared IL–pyridine mixture with the same component ratio. The intrinsic viscosity of the polymer [η] was determined by extrapolation to infinite dilution, i.e., at $c \to 0$, of the quantity $(\eta - \eta_0)/\eta_0 c = (1 - \tau/\tau_0)/c$, where η and η_0 are viscosities of the solution of concentration c and of the solvent, respectively; τ and τ_0 are the flow times of the solution and solvent through the viscometer capillary.

The flow birefringence (FBR, Maxwell effect) was measured on a compensation-type installation with photoelectric recording and modulation of polarized light [18]. As light source we used a laser unit with the wavelength $\lambda = 6500$ Å, and as elliptic compensator, a thin mica film with the intrinsic birefringence $\Delta\lambda/\lambda = 0.04$. To create a dynamic flow with a constant velocity gradient, we used a titanium dynamooptimeter with an internal rotor, having a height of 3.38 cm in the direction of the light beam. The clearance between the stator and rotor was 0.02 cm. The rotor rotation rate was measured with a frequency meter with an accuracy of 0.005 s^{-1}.

The birefringence in cellulose solutions was characterized by the quantity $[n] = \lim_{c \to 0} \Delta n / g \eta_0 c_0$, where Δn is the difference between the refractive indices of the ordinary and extraordinary beams and g is the rate gradient, and also by the reduced FBR [n]/[η] and optical shift coefficients $\Delta n/\Delta\tau = \Delta n/g(\eta - \eta_0) = \Delta n/g\eta_0(\tau/\tau_0 - 1)$, related by $[n]/[\eta] = \lim_{c \to 0} \Delta n/g(\eta - \eta_0)$ [18].

The choice of pyridine as an additive for decreasing the viscosity of cellulose solutions in IL was governed by the structural similarity of IL cations and pyridine ring. The stability of IL–cellulose–pyridine mixtures was confirmed by measurements of their dynamic viscosity in time (Fig. 1). The dynamic viscosity usually rapidly decreases if cellulose starts to degrade in IL solution; in the process, the solution becomes colored. Such phenomena were not observed in solutions of cellulose in pure ILs chosen for this study. The measurements in cellulose–IL–pyridine solutions at a polymer concentration of 2 wt % and IL to pyridine weight ratios of 1 : 1, 1 : 2, and 1 : 3 showed that, after storage of the mixtures for 3 months, the dynamic

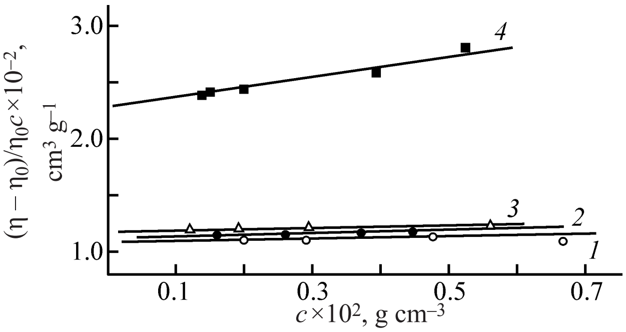


Fig. 2. Specific viscosity $(\eta - \eta_0)/\eta_0 c$ of cellulose sample in (*1*) 1 : 1 [EMIM]OAc–pyridine mixture, (*2*) Cadoxen, (*3*) 4 : 1 [BMIM]Cl–pyridine mixture, and (*4*) 1 : 1 [EMIM]Et_2PO_4–pyridine mixture as functions of the cellulose concentration in solution *c*.

viscosity remained unchanged within the measurement error. Thus, the cellulose–[EMIM]OAc–pyridine and cellulose–[EMIM]Et_2PO_4–pyridine systems are highly stable in time. The cellulose–[BMIM]Cl–pyridine system appeared to be less stable, and at an IL to pyridine ratio of 1 : 2 cellulose started to precipitate within 1 month. However, at an IL to pyridine ratio of 2 : 1, this system also remained stable for 3 months.

The characteristics of the solvents used in this study (Table 1) show that addition of pyridine to [EMIM]OAc and [BMIM]Cl to 1 : 1 weight ratio decreases their viscosity to the level of Cadoxen of standard composition [11], which stimulated us to make a comparative study of the molecular properties of the same cellulose sample in Cadoxen and in the new solvents.

The results of measuring the intrinsic viscosity [η] of the cellulose sample in various solvents are given in Fig. 2 and Table 2. As seen from Fig. 2, the concentration dependences of the specific viscosity $(\eta - \eta_0)/\eta_0 C$ of cellulose in Cadoxen and in 1 : 1 [EMIM]OAc–pyridine and 1.4 : 1 [BMIM]Cl–pyridine mixtures are similar, but differ from that in the more viscous 1 : 1 [EMIM]Et_2PO_4 mixture.

The close values of [η] obtained for cellulose in solvents that are different in nature but have similar physical characteristics suggest the similarity of the size, shape, and hence conformation of the polymer molecules in Cadoxen and the new media, 1 : 1 [EMIM]OAc–pyridine and 1.4 : 1 [BMIM]Cl–pyridine. This fact also suggests that interaction of IL with cellulose is similar to interaction of Cadoxen with cellulose.

The different [η] of cellulose in 1 : 1 [EMIM]Et_2PO_4–pyridine mixture (by a factor of 2 compared to Cadoxen) is fully consistent with differences in the dynamic viscosity η_0 of these solvents (Table 1).

The similarity of the behavior of cellulose in IL–pyridine mixtures and Cadoxen is also manifested when varying the mixture composition. The intrinsic viscosity [η] only slightly changes with a change in the content of pyridine in the mixtures by a factor of 1.5–2. Similar behavior of [η] of cellulose was noted when diluting solutions of cellulose in Cadoxen with water [17], which can also be considered as analogy in the mechanism of interaction of Cadoxen and the ILs chosen for the study with hydrogen bonds of cellulose. Apparently, solvation of the cellulose chain at first contact with solvents breaking its hydrogen bonds can be preserved upon subsequent dilution of the initial solution with another solvent and upon variation of the solution composition

Table 2. Intrinsic viscosity [η], intrinsic FBR [*n*], optical shift coefficient Δn/Δτ, reduced FBR [n]/[η], and optical anisotropy β [calculated by formula (2)] of cellulose in Cadoxen and in IL–pyridine mixtures at 25°C

Solvent	$[\eta] \times 10^{-2}$, cm^3 g^{-1}	$[n] \times 10^8$, cm^4 g^{-2} s^{-2}	$(\Delta n/\Delta\tau) \times 10^{10}$, cm g^{-1} s^{-2}	$([n]/[\eta]) \times 10^{10}$, cm g^{-1} s^{-2}	$\beta \times 10^{17}$, cm^2
Cadoxen	1.12	22	20.0	19.7	2.5
[EM1M]OAc:pyridine :					
1:1	1.14	4.1	3.5	3.6	0.46
2:1	1.18	–	–	–	
EMIM]Et_2PO_4: pyridine:					
1:1	2.23	3.8	2.0	1.7	0.22
1.5:1	2.26	–	–	–	
[BMIM]C1: pyridine:					
1.4:1	1.10	4.1	3.5	3.7	0.48
2:1	1.25	–	–	–	

within certain limits.

The Maxwell effect, being optical, is sensitive to the presence of aggregates or associates in the polymer solutions [18]. All the obtained dependences of the birefringence Δn (FBR) (Figs. 3a, 3b) and orientation angles $\chi = 45° - \varphi$, where φ is the direction of the optical axis of the solution (Fig. 4), on the flow velocity gradient g were linear, suggesting the molecular level of dispersion of cellulose in the examined IL–pyridine mixtures. This level of dispersion is also indicated by the coincidence, within 10–15% error, of the optical coefficient $\Delta n/\Delta\tau$ and reduced FBR $[n]/[\eta]$, averaged over the concentrations.

The molecular properties of celluloses of various origins and molecular weights varying in a wide range in Cadoxen solutions were studied previously by hydrodynamic and FBR methods [17]. Hydrodynamic studies showed that the equilibrium rigidity A of cellulose in Cadoxen of the above-given composition and in 1 : 1 Cadoxen–water mixtures was 95 Å, suggesting the occurrence of correlation interactions between approximately 19–20 glucopyranose rings in cellulose chains. Measurements of FBR in cellulose solutions in Cadoxen showed that the reduced birefringence $[n]/[\eta] = 20 \times 10^{-10}$ cm g^{-1} s^{-2} was independent of the molecular weight of the sample and was determined by the contribution of the microform effect due to high increment of the refractive index, $dn/dc = 0.18$, for this system. The intrinsic anisotropy of the polarizability of the cellulose chain was not determined in [17].

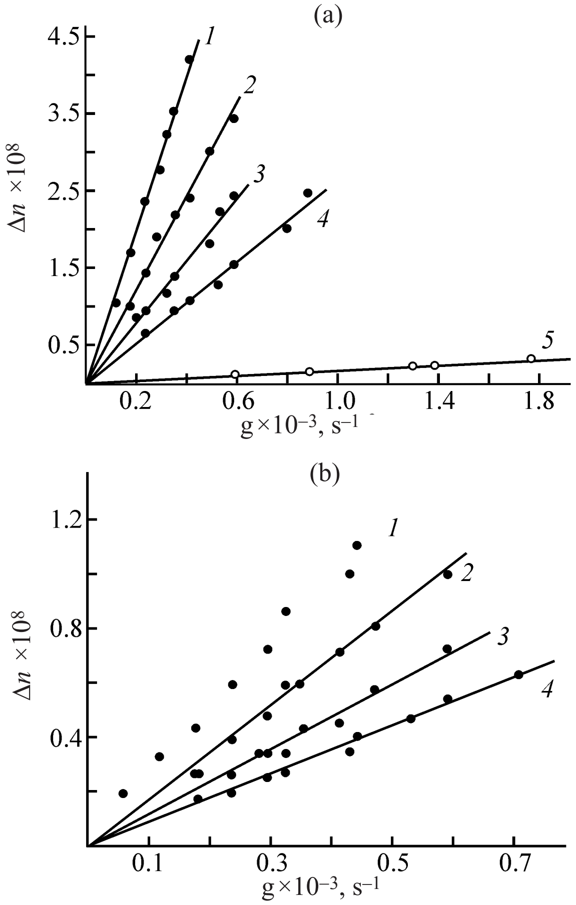


Fig. 3. Birefringence Δn as a function of the flow velocity gradient g for cellulose in (a) Cadoxen and (b) 1 : 1 [EMIM]OAc–pyridine mixture. (a) Polymer, g cm^{-3}: (*1*) 1.042, (*2*) 0.581, (*3*) 0.317, and (*4*) 0.223 × 10^{-2}. (*5*) Solvent contribution to the total dynamooptical effect, subtracted in determination of the parameters given in Table 2. (b) Polymer concentration, g cm^{-3}: (*1*) 1.195, (*2*) 0.844, (*3*) 0.465, and (*4*) 0.389 × 10^{-2}. In this case, as for the other mixtures of ILs with pyridine, the solvent contribution to Δn was low, being within the determination error, and therefore was neglected.

The quantity $[n]/[\eta]$ obtained for cellulose in Cadoxen (Table 2) fully agrees with data of [17], and the conclusion made previously on the basis of viscometric data that the conformational properties of cellulose in Cadoxen and in the new solvents are similar suggests that the equilibrium rigidity of cellulose in IL–pyridine mixtures is also close to 95 Å.

The data given in Fig. 5 and Table 2 indicate that the dynamooptical properties (Table 2, $[n]$, $[n]/[\eta]$) of the examined cellulose sample in IL–pyridine mixtures are very close, but at the same time they differ essentially from those in Cadoxen. This is associated with the difference in the optical characteristics of the solvents, because it is known [18] that, along with the contribution of the intrinsic optical anisotropy of the polymer β_i to FBR, at strong difference between the refractive indices of the polymer and solvent it is necessary to take into

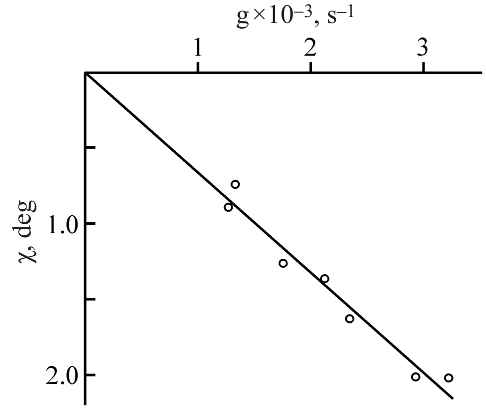


Fig. 4. Orientation angle χ as a function of the flow velocity gradient g for cellulose in 1 : 1 [EMIM]Et$_2$PO$_4$–pyridine mixture at a polymer concentration of 1.05 × 10^{-2} g cm^{-3}.

account the contribution of the microform [second term in braces in relationship (1)] and macroform (last term in braces) effects:

$$[n]/[\eta] = \frac{4\pi(n_0^2+2)^2}{45kT}\left\{A\beta_i + \frac{(\mathrm{d}n/\mathrm{d}c)^2 M_s}{2\pi\nu N_A} + \frac{2.61\Phi(\mathrm{d}n/\mathrm{d}c)^2}{\pi^2 N_A^2}\frac{M}{[\eta]}\right\},$$

where k is the Boltzmann constant; T, absolute temperature; N_A, Avogadro number; $\beta_i = \Delta a/\lambda$, optical anisotropy of unit length of polymer chain; A, equilibrium rigidity of the polymer chain; Δa and λ, optical anisotropy of the monomeric unit (glucopyranose ring in our case) and its projection onto the direction of chain propagation; ν, specific partial volume of the polymer in solution; M_s, molecular weight of the statistical segment; and $\Phi = 2.87 \times 10^{23}$ mol^{-1}, Flory parameter.

For the same reason, to determine β_i of a polymer from FBR data, it is necessary to choose a solvent with as low dn/dc as possible.

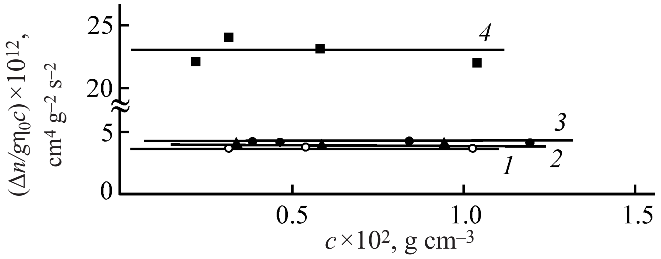


Fig. 5. Plots of $\Delta n/g\eta_0 c$ for the examined cellulose samples in (*1*) 1 : 1 [EMIM]Et_2PO_4–pyridine mixture, (*2*) 1.4 : 1 [BMIM]Cl–pyridine mixture, (*3*) 1 : 1 [EMIM]OAc–pyridine mixture, and (*4*) Cadoxen vs. cellulose concentration c.

Comparison of the refractive indices n_0 of 1 : 1 IL–pyridine mixtures (Table 1) with those of solvents of other polysaccharides and cellulose derivatives for which the refractive index increments di/dc are known and are low (Table 3) shows that n_0 of the 1 : 1 [EMIM]Et_2PO_4–pyridine mixture is close to that of polyglucans and their derivatives in organic solvents. This means that, in the [EMIM]Et_2PO_4–pyridine mixture, the contribution of the microform effect to the measured FBR value should be minimal. If the increment of the refractive index of the polymer–solvent system is low, relationship (1) transforms into

$$[n]/[\eta] = \frac{4\pi(n_0^2+2)^2}{45kT}A\beta.$$

The optical anisotropy of cellulose chain in the 1 : 1 [EMIM]Et_2PO_4–pyridine mixture, evaluated from FBR data, according to (2) should be determined only by the intrinsic optical anisotropy of the glucopyranose chain.

The parameters β for the cellulose chain in IL–pyridine mixtures, obtained using relationship (2) at A = 95 Å, are given in Table 2. As can be seen, in the 1 : 1 [EMIM]Et_2PO_4–pyridine mixture $\beta = +0.22 \times 10^{-17}$ cm^2 is, indeed, minimal compared to the other solvents. As known, the consequence of the small value of the intrinsic polarizability anisotropy of the glucopyranose unit is strong dependence of β_i of polysaccharide derivatives on the structure of side substituents (Table 3).

CONCLUSIONS

(1) On dilution of solutions of cellulose in ionic liquids based on 1-*n*-alkyl-3-methylimidazolium with pyridine, the polysaccharide does not precipitate. Systems

Table 3. Optical anisotropy of unit length of the chain β (β_i) of polysaccharides and cellulose derivatives according to FBR data in polymer–solvent systems with the refractive index increment dn/dc ≤ 0.06

Polymer	Solvent	n_0	dn/dc	$\beta^a \times 10^{17}$,	$\beta^b \times 10^{17}$,	References
				cm^2		
Methylol cellulose triacetate	DMF	1.427	0.03	0.7	+0.4	[19]
Methyl cellulose	DMSO	1.478	0.02	1.4	–	[20]
Pullulan (1,6-glucan)	DMSO	1.477	0.04	1.7	–	[21]
Dextran	DMSO	1.477	0.04	2.4	–	[21]
Nitrochitin	DMF	1.427	0.06	–2.3	–3	[22]
Nitrocellulose (DS^c 12.5%)	CH	1.451	0.04	–1.3	–2	[22]
Nitrocellulose (DS 7.5%)	DMAA+6% LiCl	1.456	0.055	0.3	–0.2	[22]

^{a} Calculation by formula (1). ^{b} Calculation by formula (2). ^{c} Degree of substitution.

cellulose–1-ethyl-3-methylimidazolium acetate–pyridine and cellulose–1-ethyl-3-methylimidazolium diethyl phosphate–pyridine at ionic liquid to pyridine ratios of 1 : 1, 1 : 2, and 1 : 3 are stable in time in the temperature interval 20–60°C and are characterized by molecular dispersion. Monitoring of their dynamic viscosity for 3 months revealed no signs of cellulose degradation in these systems. The cellulose–1-butyl-3-methylimidazolium chloride–pyridine system is stable at ionic liquid to pyridine ratios of 2 : 1 and 1.4 : 1.

(2) The dynamic viscosity and refractive index of the medium containing cellulose dispersed on the molecular level can be controlled by varying the ionic liquid to pyridine ratio.

(3) 1-Ethyl-3-methylimidazolium diethyl phosphate is a unique cellulose solvent with respect to optical properties, as its refractive index is close to that of the polyglucan itself. The previously unknown optical anisotropy of cellulose polarizability per unit chain length, $+0.22 \times 10^{-17}$ cm^2, was determined in the 1 : 1 1-ethyl-3-methylimidazolium diethyl phosphate–pyridine mixture.

(4) Mixtures of ionic liquids based on 1-*n*-alkyl-3-methylimidazolium with pyridine allow direct determination of the molecular characteristics of cellulose without using a traditional procedure for preliminary chemical modification and subsequent study of properties of cellulose derivatives.

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