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Cellulose molecular properties in 1-alkyl-3-methylimidazolium-based ionic liquid mixtures with pyridine

Jürgen Vitz[a,b,c], Natalia P. Yevlampieva[d,*], Evgeny Rjumtsev[d], Ulrich S. Schubert[a,b,c,**]

[a] Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, D-07743 Jena, Germany
[b] Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands
[c] Dutch Polymer Institute (DPI), P.O. Box 902, NL-5600 AX Eindhoven, The Netherlands
[d] V.A. Fock Institute of Physics, Saint Petersburg State University, Ulianovskaya st. 1, 198504 Saint Petersburg, Russia

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ABSTRACT

A study of the viscometric and dynamooptical (flow birefringence) properties of cellulose samples in mixtures of 1-alkyl-3-methylimidazolium-based ionic liquids with pyridine was carried out. It was established that the mixtures provide stable molecular dispersed cellulose solutions which are suitable for the determination of the characteristics of the dissolved macromolecules. The viscous and dynamooptical properties of cellulose in ionic liquid/pyridine mixtures, cadoxen (CdO/ethylenediamine), and in cadoxen/water at low solute concentrations were compared, and the behavior of cellulose in these solvents was discussed. It was found that the values of the refractive index of 1-alkyl-3-methylimidazolium-based ionic liquid/pyridine mixtures are close to the refractive index of cellulose in their media. The extremely low refractive index increment ($|dn/dc| = (0.004 \pm 0.001)\,\mathrm{cm}^3\,\mathrm{g}^{-1}$) for cellulose in 1-ethyl-3-methylimidazolium diethylphosphate and pyridine ([EMIM]Et_2PO_4/pyridine (1:1)) allowed to confirm that the cellulose monomer unit is not optically isotropic and is characterized by a small in value and positive in sign anisotropy of polarizability ($\Delta a = +1.0 \times 10^{-25}\,\mathrm{cm}^3$).

1. Introduction

Cellulose is a renewable and biodegradable biopolymer consisting of β-1,4-glycosidically linked glucose units. It can be extracted from wood or cotton and is the starting material for a variety of products, including cellophane, rayon, cellulose acetate, carboxymethyl cellulose, and many more which are produced in tons every year.

Cellulose can be dissolved, e.g., by homogeneous or heterogeneous derivatization (Kolb, Finn, & Sharpless, 2001; Hafrén, Zou, & Córdova, 2006). One commonly applied industrial process to obtain regenerated, processible cellulose by derivatization is the xanthogenate route (Cross & Spruance, 1904; Green, 1906; Lyncke, 1908). Other derivatizing solvents are trifluoro acetic acid, formic acid, as well as *N*,*N*-dimethyl-formamide/N_2O_4. Examples for non-derivatizing solvents are aqueous inorganic complexes, e.g., cuprammonium hydroxide (Cuoxam, Cuam), cupriethylene diamine (Cuen) and CdO/ethylenediamine (cadoxen), or organic solvents together with inorganic salts or gases, e.g., DMA/LiCl, DMSO/SO_2, or DMSO/TBAF. The use of molten salts, *N*-alkylpyridinium halogenides or oxides of tertiary amines like *N*-methylmorpholine *N*-oxide (Lyocell® process) are further possibilities (for details see: Heinze & Liebert, 2001; Heinze et al., 2000; Köhler & Heinze, 2007; Horvath, 2006; Ohno & Fukaya, 2009; Riedel, Taeger, Eilers, & Kramer, 2001).

To circumvent disadvantages of the above mentioned processes, e.g., the long dissolution times and a degradation of the cellulose backbone, the use of ionic liquids (ILs) was re-invented in the last years. Although the ability of ILs to dissolve cellulose was already recognized in 1934 (Graenacher, 1934), the importance was not fully noticed at that time. Later, it was shown that also ionic liquids with lower melting temperatures can be used as non-derivatizing solvents for cellulose of different degree of polymerization (Swatloski, Rogers, & Holbrey, 2003; Swatloski, Spear, Holbrey, & Rogers, 2002; Wu et al., 2004).

However, the utilization of ionic liquids (ILs) as solvents for cellulose requires advanced conditions. Because of their high dynamic viscosity (see Table 1), ionic liquids themselves cannot be considered as suitable media for the analysis of the solute in general, but the viscosity value of the ILs and, in particular, the IL/cellulose mixtures can be essentially decreased by diluting them with an

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* Corresponding author.
Tel.: +7 812 428 4365; fax: +7 812 428 7240.
** Corresponding author at: Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, D-07743 Jena, Germany.
Tel.: +49 3641 9482 00; fax: +49 3641 9482 02.
E-mail addresses: yevlam@paloma.spbu.ru (N.P. Yevlampieva), ulrich.schubert@uni-jena.de (U.S. Schubert).

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Table 1
Melting temperatures of 1-alkyl-3-methylimidazolium-based ILs, density ρ_o, dynamic viscosity η_o and refractive index n_o of initial ILs and their mixtures with pyridine at 21 °C.

Substance	Ratio (v/v)	Melting point (°C)	ρ_o (g cm^{-3})	η_o (cP)	n_o
[EMIM]OAc		<−20[a]	1.05	180	1.4932
[EMIM]Et_2PO_4		19–21[b]	1.16	460	1.4743
[BMIM]Cl		70[a]	–	Solid at r.t.	–
[EMIM]OAc/pyridine	1:1		1.03	4.9	1.4975
[EMIM]OAc/pyridine	2:1		–	6.4	–
[EMIM]Et_2PO_4/pyridine	1:1		1.07	8.6	1.4749
[EMIM]Et_2PO_4/pyridine	1.5:1		–	10.0	–
[BMIM]Cl/pyridine	1.4:1		1.08	5.0	1.5090
[BMIM]Cl/pyridine	2:1		–	6.0	1.5093
Cadoxen			1.06	4.4	1.3969
Pyridine			0.982	0.974	1.5095

[a] (BASF, http://www.basionics.com/en/ionic-liquids/cellionic/).
[b] (Aldrich, http://www.sigmaaldrich.com).

organic solvent. In this process, a possible precipitation of the cellulose must be avoided. Therefore, different organic solvents were investigated to identify stable IL/cellulose/solvent mixtures wherein cellulose does not degrade and wherein cellulose stays molecular-dispersed.

In the present contribution we suggest mixtures of imidazolium-based ILs (Fig. 1) with pyridine as new IL-based media suitable for the investigation of the molecular parameters of cellulose. The solution stability in time, viscometric and dynamooptical properties (Maxwell effect (Tsvetkov, 1989)) of the cellulose in different mixtures of ILs/pyridine were studied and compared to the data obtained in cadoxen – which is a well-known metal–organic-complex for dissolving cellulose without destruction (Bikales & Segal, 1971).

Three ILs with 1-*N*-alkyl-3-methyl-imidazolium as cation and with different anions (Fig. 1) were selected for the study. Their ability to dissolve cellulose was shown previously (Swatloski et al., 2003).

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) was donated by Solvent Innovation (Art.-No. 99,002-1) and 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) was bought from Aldrich (BASIONIC® BC 01, Art.-No. 51053). The purity of these ionic liquids was checked by NMR and the water content by Karl–Fischer titration, an additional purification was not necessary. 1-Ethyl-3-methylimidazolium diethylphosphate ([EMIM]Et_2PO_4) was synthesized according to the literature (Kuhlmann, Himmler, Giebelhaus, & Wasserscheid, 2007) using a flat flange reaction vessel (250 mL) with thermostatic jacket. Pyridine was received from Merck and distilled before utilization.

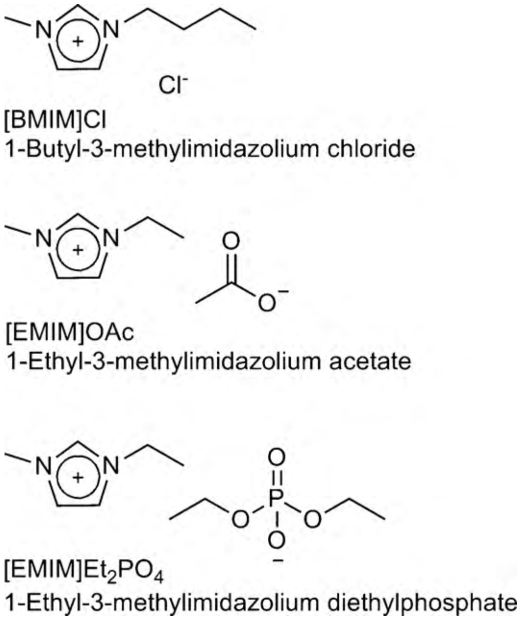

Fig. 1. Schematic representation of the chemical structures of the used 1-alkyl-3-methylimidazolium-based ILs.

The refractive index n_o of pyridine, ILs and their mixtures with pyridine were determined using an Abbe-type refractometer (Table 1) using the standard wavelength. Densities ρ_o of mixtures IL/pyridine were determined using a pyknometer of 5 cm^3 volume graduated by water and benzene.

Cadoxen was prepared according to a standard method with concentrations of Cd 4.65% and ethylenediamine 25.8% in bidistilled water (Bikales & Segal, 1971). Physical properties of cadoxen determined at 21 °C are listed in Table 1.

Two cellulose samples of different degree of polymerization (DP) have been used for the present study. The majority of measurements have been performed with sample N1 (DP 247, Avicel PH-101, high purity cellulose powder for partition chromatography, Fluka, art.-No. 11363). The high molar mass sample N2 (DP 5000, cotton linters, Academy of Plant Polymers, St. Petersburg, Russia) was tested with the purpose to confirm the conclusions made mainly based on the results received for the microcrystalline, relatively low molar mass sample N1. Cellulose samples were dried for 12 h at 100 °C under reduced pressure (10 mbar) before the study. The DP of the samples have been determined using their experimental intrinsic viscosity [η] in cadoxen and the Mark–Kuhn-equation $[\eta] = 4.5 \times 10^{-4} M^{0.74}$ for cellulose in cadoxen (Ljubina et al., 1977). The values $[\eta] = 1.13 \times 10^2$ cm^3 g^{-1} and $[\eta] = 10.9 \times 10^2$ cm^3 g^{-1} were received for samples N1 and N2 in cadoxen, correspondently.

For the dissolution process, the cellulose sample was added to the IL under permanent stirring and heated up to 80–100 °C. The maximal temperature was used for [BMIM]Cl, the minimal for [EMIM]OAc. Visually, the cellulose sample N1 dissolves in selected ILs very fast, during 5–7 min. However, sample N2 required more time for dissolving in the IL. Afterwards, the IL–cellulose solution was cooled to room temperature, and droplets of pyridine were added to the solution under stirring. In general, the total procedure took about 20–30 min for sample N1 and nearly 1 h for sample N2.

The measurements of the intrinsic viscosity and the Maxwell effect were performed during 1–2 h just after the preparation of the solutions. For the study of the concentration dependencies of the molecular properties, the initial solution of cellulose in mixtures of IL/pyridine was dissolved by the separately prepared mixture of IL and pyridine with the component's ratio corresponding to the initial cellulose solution.

2.2. Dynamic and intrinsic viscosity

Dynamic viscosities of pure ILs and cellulose/IL/pyridine mixtures were measured using an Anton Paar AMVn microviscometer which is based on the approved and acknowledged rolling/falling ball principle according to DIN 53015 and ISO 12058. The system allows a variable inclination angle of the measurement capillary and, therefore, both the variation of shear stress and the shear rate as well as the easy repetition of measurements on a wide viscosity range (0.3–2500 cP). A Peltier thermostat allows to measure over a large temperature range (+5 to 135 °C).

An Ostwald type capillary viscometer graduated with distilled water, benzene and toluene has been used for the viscometric measurements of cellulose/IL/pyridine (henceforward cellulose solution) and IL/pyridine (henceforward solvent) mixtures. The dynamic viscosity of solvents η_o and the reduced viscosity of cellulose solutions $(\eta-\eta_o)/\eta_o c$ or $(t/t_o-1)/c$ (simplified, neglecting the solute and solution densities) were determined by measuring the effusion time of solution/solvent through a viscometer capillary tube (c is the solute concentration; η is the solution viscosity, t and t_o are the effusion times of the solution and solvent, respectively).

The intrinsic viscosity values $[\eta]$ of cellulose in different solvents were determined at infinite dilution as (Yamakawa, 1971).

$$[\eta] = \lim_{c\to o} \frac{\eta-\eta_o}{\eta_o c} \tag{1}$$

2.3. Flow birefringence

The flow birefringence (FB) is a not well-known method for studying polymers in solution (Tsvetkov, 1989). FB (also called dynamooptical Maxwell effect) is an optical phenomenon connected with the orientation and the deformation of macromolecular chains under mechanical forces of the flow. The optical birefringence appears in the polymer solution owing to ordering of the long axis of optically anisotropic molecules in the flow. The FB value is determined by the chemical structure, the optical anisotropy of polarizability, geometrical and conformational properties of the solute. This method is useful for the analysis of structural and conformation specificities of polymers in multicomponent solutions when spectral methods are not informative for any reasons.

The optical birefringence is the value $\Delta n = n_{\|} - n_{\perp}$, where $n_{\|}$ is the refractive index of the solution in direction parallel to the optical axis and $n_{\perp}$ is the refractive index in perpendicular direction; the optical axis of the solution is connected with the primary direction of the macromolecules orientation under the flow velocity gradient g, which, in general, does not coincide with the main axis of these macromolecules. Experimentally, the values $\Delta n/g$ are determined as the slopes of the dependencies $\Delta n = f(g)$ for several solute concentrations c. Finally, the intrinsic FB value is determined as $[n] = \lim_{c\to o}(\Delta n/g\eta_o c)$ at the infinite dilution for the polymer characterization.

The theories of FB in polymer solutions are operating with the reduced FB value $[n]/[\eta]$ (Tsvetkov, 1989). The latter parameter, as a ratio of capacities both relying on the hydrodynamic interactions in the polymer chain, is less sensitive to the thermodynamic conditions for the polymers in solution. Therefore, the reduced FB value is more independent for conclusions made on the molecular properties of polymers based on the FB data.

Due to a difference of the optical properties of polymer chains and solvent molecules included into the polymer coil in solution as well as due to interactions between the polymer chain units and solute–solvent interaction, the FB of macromolecules depends not only on its initial optical anisotropy of the polarizability determined by the chemical structure, but also on the degree of correlation between the monomer units in the chain, which are called short- and long-distance interactions. These lead to a strong dependence of the dynamooptical properties of polymers on the refractive index increment dn/dc in solute/solvent system and on the chain rigidity. Traditionally, the polymer chain rigidity is characterized by a statistical segment length, for instance, the Kuhn segment length A of the simplest model of freely jointed linear segments for polymer chain modeling (Yamakawa, 1971).

According to the theory of random polymer coils in dilute solution (Tsvetkov, 1989) the reduced FB value of polymers is determined by Eq. (2).

$$\frac{[n]}{[\eta]} = \frac{4\pi(n_o^2+2)^2}{45kT} \times \left\{ s\Delta a_{\mathrm{i}} + \frac{(dn/dc)^2 M_0 s}{2\pi\nu N_A} + \frac{2.61\Phi(dn/dc)^2}{\pi^2 N_A^2}\frac{M}{[\eta]} \right\} \tag{2}$$

Here, $4\pi(n_o{}^2+2)^2/45\ kT$ is the optical coefficient, n_o is the solvent refractive index, k is the Boltzmann constant, T is the absolute temperature, $s = A/l$ is a number of monomer units in the statistical segment equal to the ratio of its length A to l – its projection of monomer unit on the direction of chain expansion; N_A is the Avogadro's number, ν is the partial specific volume of the polymer, M_o is the molar mass of the monomer unit, and $\Phi = 2.87\times10^{23}\ \mathrm{mol}^{-1}$ is the Flory viscous hydrodynamic parameter (Tsvetkov, 1989).

The FB of cellulose solutions was measured using a photoelectric recording technique based on the principle of compensation (Tsvetkov, 1989). A thin mica plate with a phase difference of $(0.04\pm0.004)2\pi$ was used as an elliptical compensator. A laser module (Al-ArGa) operating at the wavelength $\lambda = 6500\times10^{-8}$ cm was used as the light source. A titanium device composed of two coaxial cylinders (or dynamooptimeter (Tsvetkov, 1989)) with an inner rotor having a diameter of 3.76 cm and 3.38 cm in length along the path of the light beam was used for creating a laminar flow with a constant velocity gradient g between the cylinders in radial direction. The gap between the stator and the rotor of the dynamooptimeter (ΔR) was 2×10^{-2} cm. The FB was observed in the middle of the gap in the direction perpendicular to the direction of the flow velocity gradient. All measurements were performed at non-turbulence conditions when the flow velocity gradient value was below its critical value g_{cr} provided by Taylor's formula $g_{cr} = \pi^2\eta_o R^{1/2}/(0.057\rho_o\Delta R^{5/2})$, where R is the radius of the rotor (Tsvetkov, 1989). The thermostatting was carried out at 25 °C with an accuracy of 0.1 °C.

2.4. Refractive index increments

The refractive index increments dn/dc of cellulose in solution were determined by means of a differential refractometer based on Lebedev's interferometer which is widely applied now in analytical ultracentrifugation techniques (Scott, Harding, & Rowe, 2005). The refractometer–interferometer of this type permits to determine dn/dc values with an accuracy of 0.001/0.0005 $\mathrm{cm}^3\,\mathrm{g}^{-1}$ and also allows to determine the sign of dn/dc. The differential refractometer was characterized by the following parameters: the splitting value of pare of Iceland spars, having three cm in length, was 0.3 cm; Babinet's compensator constant determining a distance between the interference bandwidths, was 0.75 cm; The light source wavelength was 5460 Å. Two-sections cell of 1.085 cm in length was used for the measurements. A shift of the interference bandwidths was determined for the light beam passed through only one section and the beam passed through both sections. The solute concentration range for the study was selected so that it was possible to detect a zero-bandwidth replacement. The refractive index increment was calculated according to formula (3).

$$\frac{\mathrm{d}n}{\mathrm{d}c} = \left(\frac{H}{c}\right)\left(\frac{\lambda}{b_\lambda h}\right) \qquad (3)$$

Here (H/c) is the slope of the concentration dependence of the interference bandwidths' shift H, λ is the light source wavelength, b_λ is Babinet's compensator constant and h is the cell length.

2.5. Partial specific volume

The partial specific volume ν of cellulose in [EMIM]OAc/pyridine mixtures with ratio 1:1 have been determined by means of a standard glass pyknometer of 5 cm^3 volume. The partial specific volume ν of cellulose in [EMIM]Et_2PO_4/pyridine mixtures with a ratio of 1:1 were determined using an Anton Paar DMA 4100 density meter. The system is based on a patented reference oscillator (AT399051) and allows an accuracy of 0.0001 g/cm^3 for density and 0.05 °C for temperature with a repeatability of 0.00005 g/cm^3. The measurements were performed at 25 °C.

3. Results and discussion

Besides their promising dissolution properties, ionic liquids sometimes also show a degradation of cellulose, which can be monitored by measuring the DP values by capillary viscometry in Cuen. Heinze, Schwikal, and Barthel, 2005 found that in particular 3-methyl-*N*-butylpyridinium chloride ([C4mpy]Cl) leads to a significant degradation of the microcrystalline cellulose (Avicel PH-101), whereby [BMIM]Cl shows only a slight degradation for spruce sulfite pulp and cotton linters. In addition, we observed in previous experiments with [BMIM]Cl, [EMIM]Cl and [EMIM]Et_2PO_4, that a degradation of the Avicel cellulose appeared in [BMIM]Cl and less degradation could be observed in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), whereby for [EMIM]Et_2PO_4 only a slight DP change was observed while heating all three samples for 2 h at 100 °C (Vitz, Erdmenger, Haensch, & Schubert, 2009). For shorter reaction/dissolution times, the magnitude of degradation can be minimized significantly.

In case of a depolymerization of the polysaccharide backbone, the dynamic viscosity of the cellulose solution in IL decreases with time duration and temperature elevation. Therefore, the viscosities of solutions of cellulose in IL/pyridine were measured on an automated microviscometer based on the rolling/falling ball principle. The following Figs. 2 and 3 show the plots of the dynamic viscosity *versus* temperature for different measuring angles. Because the viscosity is independent from the measuring angle, it can be deducted that the ionic liquids used behave like a Newtonian liquid (Kuhlmann et al., 2007). As a rule of thumb, the viscosity is reduced to approximately the half of its starting value only by heating up for 10 °C. Since water can influence the viscosity of ionic liquids significantly, it is essential that the ionic liquids are severely dried before its use. Furthermore, the solutions were stored at room temperature and the dynamic viscosities of selected solutions were measured again after 3 months. The viscosities did not change significantly and it can be concluded that the cellulose is stable in these solvent mixtures at room temperature over a long period of time.

3.1. Intrinsic viscosity

Fig. 4 demonstrates the results on the intrinsic viscosity [η] of cellulose sample N1 determined in cadoxen and mixtures of IL/pyridine at a 1:1 ratio according to relation (1). Thereby, identical dependencies of $(\eta-\eta_o)/\eta_o c = f(c)$ and [η] values were received in cadoxen, [EMIM]OAc/pyridine and [BMIM]Cl/pyridine. A twice higher [η] value characterizes the same cellulose sample in [EMIM]Et_2PO_4/pyridine. The observed variation of the [η]

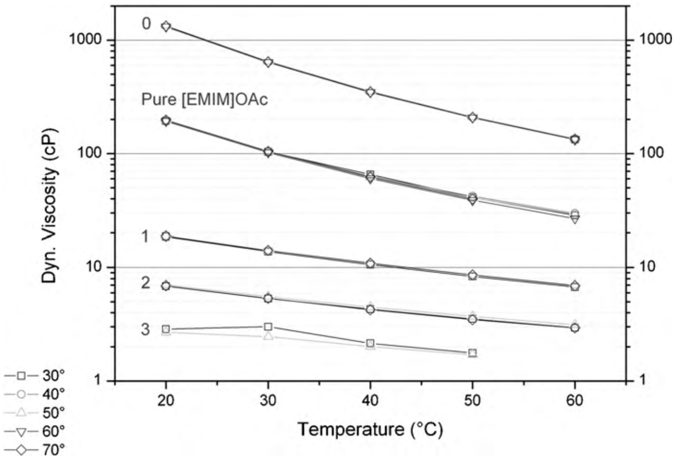

Fig. 2. The dependence of dynamic viscosity of pure [EMIM]OAc, [EMIM]OAc/cellulose (0) and three mixed solutions [EMIM]OAc/cellulose/pyridine (1–3) on temperature measured at different angles. Cellulose concentrations in mixed solvents were 2.25 g cm^{-3} (0), 0.97 g cm^{-3} (1), 0.64 g cm^{-3} (2), and 0.48 × 10^{-2} g cm^{-3} (3).

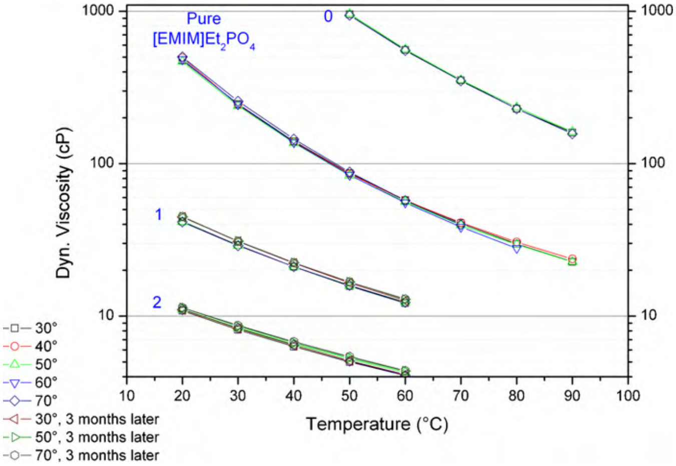

Fig. 3. The dynamic viscosity measurements of pure [EMIM]Et_2PO_4, [EMIM]Et_2PO_4/cellulose (0) and [EMIM]Et_2PO_4/cellulose/pyridine solutions (1–2) within an interval of 3-month. Cellulose concentrations in mixed solvents were 2.36 g cm^{-3} (0), 1.08 g cm^{-3} (1), and 0.69 × 10^{-2} g cm^{-3} (2).

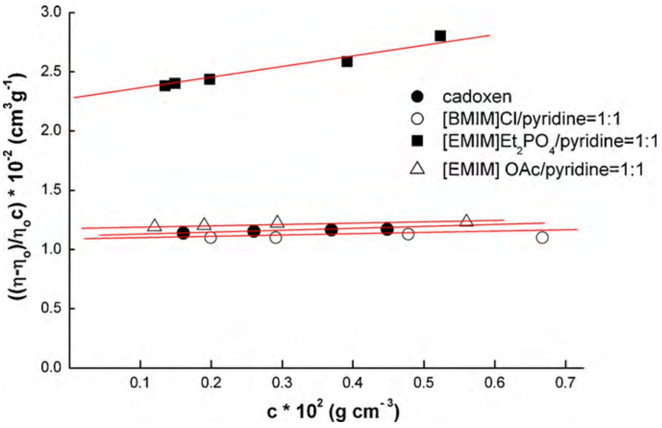

Fig. 4. Concentration dependence of viscosity value $(\eta-\eta_o)/\eta_o c$ for sample N1 in cadoxen and IL/pyridine mixtures.

Table 2
Intrinsic viscosity [η], intrinsic FB value [n], reduced FB value [n]/[η], refractive index increment d*n*/d*c* and partial specific volume *ν* for cellulose samples in cadoxen and 1-alkyl-3-methylimidazolium-based IL/pyridine mixtures at 25 °C.

Solvent	$[\eta] \times 10^{-2}$ ($cm^3 g^{-1}$)	$[n] \times 10^8$ ($cm^4 g^{-2} s^2$)	$([n]/[\eta]) \times 10^{10}$ ($cm g^{-1} s^2$)	$(dn/dc) \times 10^{10}$ ($cm^3 g^{-1}$)	ν ($cm^3 g^{-1}$)
Sample N1					
Cadoxen	1.12 ± 0.05	22 ± 3	20 ± 4	+0.138 ± 0.001	0.62 ± 0.01
[EMIM]OAc/pyridine					
1:1	1.14	4.1 ± 0.5	3.7 ± 0.5	−0.011	0.67
2:1	1.18	–	–	–	–
[EMIM]Et_2PO_4/pyridine					
1:1	2.23	3.8 ± 0.5	1.7 ± 0.5	−0.004	0.70
1.5:1	2.26	–	–	–	–
[BMIM]Cl/pyridine					
1:1	1.10	–	–	–	–
1.4:1	1.10	4.1 ± 0.5	3.7 ± 0.5	−0.02	–
2:1	1.25	–	–	–	–
Sample N2					
Cadoxen	10.9 ± 0.2	272 ± 3	25 ± 5		
[EMIM]OAc/pyridine					
1:1	8.9 ± 0.2	31.2 ± 0.5	3.5 ± 0.5		

value for sample N1 in IL/pyridine mixtures may be connected with the difference of the solute/solvent thermodynamic conditions for cellulose (Yamakawa, 1971). The difference of the slopes of the dependencies in Fig. 4, where the slope for [EMIM]Et_2PO_4/pyridine mixture 1:1 is larger than others, also may be considered as an evidence for a stronger interaction between the cellulose macromolecules in this solvent (Yamakawa, 1971). But besides of this, another possible reason may be mentioned. Because the [η] value depends on the size and shape of the polymer macromolecules, it may be assumed that the anions of the ILs influence the molecular dimension of cellulose in solution being involved into the IL/cellulose interaction. The anion $Et_2PO_4^-$ has the maximal size in comparison to the other two anions presented in Fig. 1. If the interaction scheme of a cellulose chain with the 1-*N*-alkyl-3-methyl-imidazolium cation is similar for all tested ILs it could be assumed from the data of Fig. 4 that the increasing anion size/volume could lead to a chain expansion of the cellulose in the corresponding IL. However, this explanation requires a more in-depth investigation in the future because of both reasons mentioned above. They may be linked with each other and have an influence on the cellulose behavior in IL/pyridine mixtures.

The intrinsic viscosity values of sample N1, received at the infinite dilution ($c \to o$) for another ratio of mixtures and [η] for sample N2 in cadoxen and [EMIM]OAc/pyridine = 1:1, are presented in Table 2.

It is possible to draw conclusions for the cellulose behavior in IL-based solvents assuming the well studied molecular behavior of cellulose in cadoxen and cadoxen-water mixtures (Ljubina et al., 1977). Due to the experimentally detected coincidence in viscous properties for cellulose in cadoxen and in the mixtures [EMIM]OAc/pyridine and [BMIM]Cl/pyridine (Table 2), it may be supposed that the conformation of cellulose molecules is very similar in these solvents. In other words, the destruction of intermolecular H-bonds of the cellulose by ILs leads to the same final conformation of the cellulose molecules as induced by cadoxen. In spite of structural differences, these different solvents dissolve cellulose by means of the same or an identical mechanism. We did not detect a strong change of the [η] value of cellulose solutions with increasing IL fraction in the mixture with pyridine (see Table 2). A similar behavior of [η] was observed for cellulose in cadoxen-water mixtures, when water was added to cellulose solution in cadoxen (Ljubina et al., 1977). Hence, it can be concluded that the dilution of the IL–cellulose solution by pyridine at ratios IL/pyridine = 2:1, 1.4:1, 1:1 weakly influence the polyglucan chains' dimensions and conformations because the cellulose macromolecules continue to be solvated by the IL.

Additionally, a dependence of [η] *versus* temperature was tested, and fully identical temperature dependences of the intrinsic viscosity for cellulose sample N1 in [BMIM]Cl/pyridine = 1.4:1 and in cadoxen were detected in the range from 21 °C to 31 °C. For both solvents the coefficient $d\ln[\eta]/dT = -0.01 \pm 0.005$ was received. Thus, a small, but detectable decreasing of the [η] value took place with increasing temperature in these solvents.

The negative in sign $d\ln[\eta]/dT$ coefficient is typical for polymer chains with strong interactions between the molecular units (Tsvetkov, 1989; Yamakawa, 1971), to whom cellulose can be related because of its own chain rigidity (or Kuhn segment length A), estimated from the hydrodynamic investigations in cadoxen, varying from 90 Å to 100 Å (Ljubina et al., 1977). This means that 18–20 monomer units are involved into the correlation interactions along the cellulose chain compared to a typical flexible polymer (as polyethylene) where the correlation length is not longer than 4–6 monomer units (Yamakawa, 1971). A coincidence of viscous properties of cellulose in cadoxen and IL/pyridine mixtures may be considered as evidence that cellulose macromolecules do not became more flexible in new solvents.

Table 2 also contains the viscosity data of the high molar mass cellulose sample N2 measured in cadoxen and in a [EMIM]OAc/pyridine mixture 1:1. The [η] values for this sample in different solvents are also similar, but do not correlate as well as it was found for sample N1. However, this is reasonable taking into account that an industrial cotton linter was used. As a whole, the viscous cellulose behavior in IL/pyridine mixtures corresponds to a solution behavior of a molecular dispersed rigid chain polymer.

It is important to mention that the dissolution of the high molar mass sample N2 in a 1:1 [EMIM]OAc/pyridine mixture took less than 1 h compared to days in cadoxen. Thus, it is obvious that IL/pyridine mixtures can be considered as the more favorable solvents for the fast characterization of cellulose in dilute solutions.

3.2. Flow birefringence

A study of flow birefringence (FB) of cellulose in mixtures IL/pyridine further supported our conclusion on the molecular dispersity of these solutions. As an optical method the FB method is highly sensitive to aggregations or associations of macromolecules in solutions (Tsvetkov, 1989). A presence of aggregates normally leads to deviations from Maxwell's law according to which the opti-

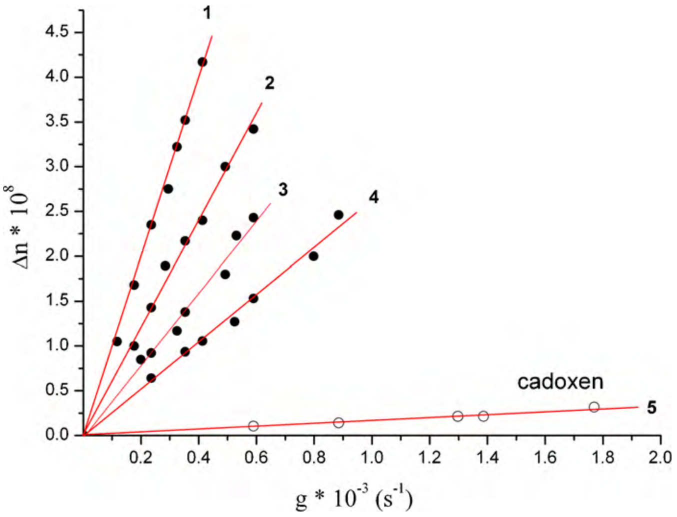

Fig. 5. The dependence of the FB value Δn on the flow velocity gradient g for cellulose solutions in cadoxen at solute concentrations of 1.042 g cm^{-3} (1), 0.581 g cm^{-3} (2), 0.317 g cm^{-3} (3) and 0.223×10^{-2} g cm^{-3} (4). The input of solvent (5), shown at the bottom of the figure, was excluded when the dynamooptical parameters of cellulose, presented in Table 2, were determined.

cal birefringence value Δn of a truly molecular liquid is directly proportional to the flow velocity gradient value g.

A positive FB value Δn strongly proportional to the flow velocity gradient g has been observed in cellulose solutions in cadoxen and in mixtures IL/pyridine (Figs. 5 and 6). A concentration dependence of $\Delta n/g\eta_o c$ for cellulose in IL/pyridine mixtures was not observed (see Fig. 7). Therefore, the intrinsic FB values [n] for cellulose were calculated as an averaged value through the different concentrations in the same solvent. The full set of experimental data on FB of cellulose solutions is presented in Table 2.

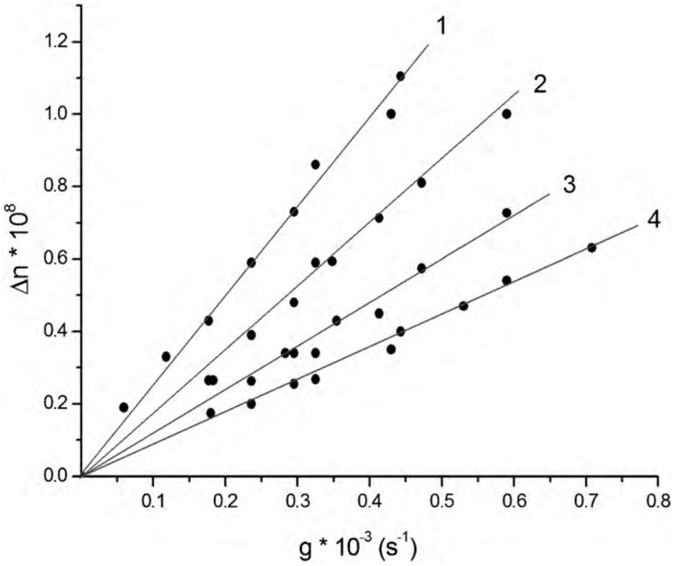

Fig. 6. The dependence of FB value Δn on the flow velocity gradient g for cellulose N1 solutions in the mixture [EMIM]OAc/pyridine = 1:1 at solute concentrations of 1.195 g cm^{-3} (1), 0.844 g cm^{-3} (2), 0.465 g cm^{-3} (3) and 0.389×10^{-2} g cm^{-3} (4). The input of the solvent here was negligible in value (for all IL/pyridine mixtures themselves $\Delta n/g < 10^{-13}$ s have been received, which is less than experimental error) and not taken into consideration.

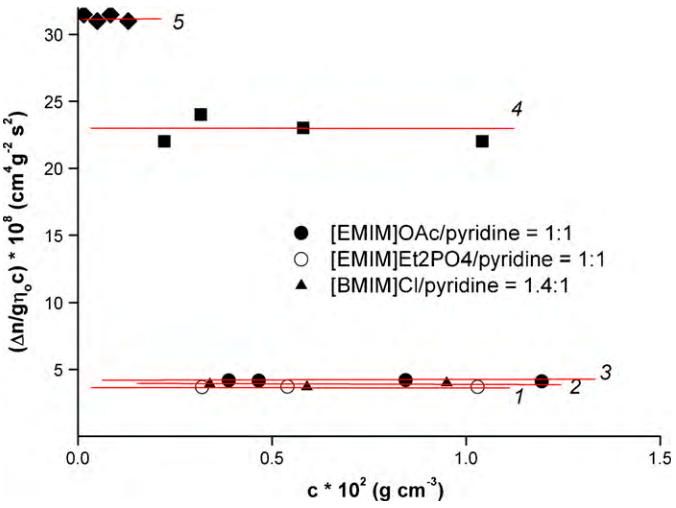

Fig. 7. Concentration dependences of $\Delta n/g\eta_o c$ for cellulose sample N1 in different solvents (*1–4*), and for sample N2 in mixture [EMIM]OAc/pyridine 1:1 (*5*).

It is evident that cellulose N1 displays a very similar value of the Maxwell effect in all IL/pyridine mixtures. Fig. 7 demonstrates that the intrinsic FB values [n] of sample N1 in IL/pyridine mixtures are close to each other but differ from the value found for cadoxen. The same is true for the reduced FB value [n]/[η] (see, please, data for both samples in Table 2), which also confirms the difference of the dynamooptical properties of cellulose in different solvents. Based on the data of Table 2, it can be concluded that the values [n]/[η] for samples N1 and N2 coincide in the same solvent. Latter is true for all molecular dispersed polymers in the Gaussian region of the molar masses where statistical laws are valid (Tsvetkov, 1989).

To gain a deeper insight into the experimental results on the FB data, the optical properties of the solvents, in particular the refractive index value n_o and the refractive index increment dn/dc of cellulose in solution need to be taken into consideration. Eq. (2) inserted at the experimental part may be rewritten in another form (4) (Tsvetkov, 1989).

$$\frac{[\mathrm{n}]}{[\eta]} = B\Delta a\, s + \left(\frac{[\mathrm{n}]}{[\eta]}\right)_{\mathrm{fs}} + \left(\frac{[\mathrm{n}]}{[\eta]}\right)_{\mathrm{f}} \tag{4}$$

where $B = 4\pi\ (n_o{}^2+2)^2/45\,kT$, $([\mathrm{n}]/[\eta])_{\mathrm{fs}} = B\ (((\mathrm{d}n/\mathrm{d}c)^2 M_o s)/2\pi\nu N_A)$ is the so called microform's effect contribution to the total [n]/[η] value corresponding to second item of Eq. (2), and $([\mathrm{n}]/[\eta])_{\mathrm{f}} = B((2.61\Phi(dn/dc)^2)/(\pi^2 N_A^2))([M]/[\eta])$ is the macroform's effect contribution corresponding to the last item of Eq. (2).

Eq. (4) shows how the reduced FB value [n]/[η] depends on the optical and the conformation properties of the polymer and on the solvent/solute system properties. It is clear that for polymers with a slightly anisotropic monomer unit, having a small Δa value, the input of the second and third terms in Eq. (4) to the experimentally determined [n]/[η] value may be significant. Cellulose itself is one of those types of polymers because its monomer unit is often considered as optically isotropic. But the latter opinion is mainly based on quantum chemical calculation data (Bikales & Segal, 1971). Attempts to confirm the absence of optical anisotropy of glucose- or pyranose-cycles from FB investigation in solutions of polyglucan derivatives till now were not successful due to a strong dependence of the Δa value of cellulose derivatives on the structure and the optical anisotropy of its side-chain groups, as well as on the dn/dc of the solute/solvent system (Tsvetkov, 1989). The latter parameter, as easy to see from Eq. (4), plays a crucial role if $\Delta a \sim 0$. Therefore, a special attention had to be paid for the dn/dc determination in the present work.

Fig. 8 presents the results of the study of cellulose solutions in IL/pyridine mixtures and in cadoxen by means of a differential refractometer. The slopes of the straight lines in Fig. 8 are proportional to the dn/dc of cellulose in different solvents. Values of dn/dc calculated with Eq. (3) are presented in Table 2. The opposite

Table 3
Comparative data on $[n]/[\eta]$, $([n]/[\eta])_{fs}$ and $([n]/[\eta])_f$ values for cellulose sample N1 in different solvents, and optical anisotropy of polarizability Δa per monomer unit of polyglucans calculated using Eq. (4).

Sample	Solvent	$([n]/[\eta]) \times 10^{10}$	$([n]/[\eta])_{fs} \times 10^{10}$	$([n]/[\eta])_f \times 10^{10}$	$\Delta a \times 10^{25}$ cm^3	Ref.
Cellulose N1	Cadoxen	20	25	1.5	–	
	[EMIM]OAc/pyridine 1:1	3.6	0.2	0.01	2	
	[EMIM]Et$_2$PO$_4$/pyridine 1:1	1.7	0.017	0.0007	1	
	[BMIM]Cl/pyridine 1.4:1	3.7	0.7	0.04	–	
Triacetate Methylcellulose	DMF $n_o = 1.427$, dn/dc = 0.03	–	–	–	2	[a]
Cellulose nitrate (DS[b] = 7.5%)	DMA + 6% LiCl $n_o = 1.456$, dn/dc = 0.055	–	–	–	−1[c]	[d]

[a] (Pogodina, Yevlampieva, Lazareva, Zakharov, & Tsvetkov, 1989).
[b] DS, degree of substitution.
[c] Negative sign of Δa is connected with the negative sign of FB in cellulose nitrate solutions.
[d] (Yevlampieva, 1990).

signs and the significant difference in values of dn/dc for cellulose in cadoxen and IL/pyridine mixtures may be pointed out as an interesting experimental fact. With a negative refractive index increment (dn/dc) samples can show also negative signals in a RI detector system often used in SEC setups (Held & Kilz, 2008; Wyatt, 1990). However, the sign of dn/dc does not play any role for the FB observations in solution, as it follows from Eq. (4) due to FB dependence on the squared value of $(\mathrm{d}n/\mathrm{d}c)^2$.

Using Eq. (4), data on dn/dc (Fig. 8, Table 2) and the partial specific volume values ν (Table 2) for cellulose in IL/pyridine allows to calculate own Δa values for the monomer unit of the 1–4 polyglucan. In Table 3, the calculated values of micro- and macroform terms of Eq. (4) for cellulose sample N1 in different solvents are presented showing that a high FB value for cellulose in cadoxen is connected with the microform effect mainly when in IL/pyridine mixtures the own optical anisotropy of polyglucan chain is displaying. The data of Table 3 explains well why the solvents with a large refractive index increment cannot be used for the determination of the optical properties of cellulose. In this case, the experimental error will increase the error on the determination of the macro- and microform terms through macromolecular parameters (see Eq. (4)). As a consequence, it is not possible to estimate correctly the Δa of a cellulose monomer unit from the FB data in cadoxen. In contrast, IL/pyridine mixtures having low dn/dc values allow the estimation due to a negligible influence of the macro- and microform on the experimental data. Using experimentally reduced FB values for sample N1 in the [EMIM] Et$_2$PO$_4$/pyridine mixture = 1:1, which was characterized as a system with minimal dn/dc (Table 2), a Δa value of 1×10^{-25} cm^3 was observed for the cellulose monomer unit. This value corresponds well to the Δa estimation from the FB data for the cellulose derivatives with slightly anisotropic side-chain groups or with a low degree of substitution using organic solvents with a small refractive index increment of the solvent–solute system shown in the last two lines of Table 3.

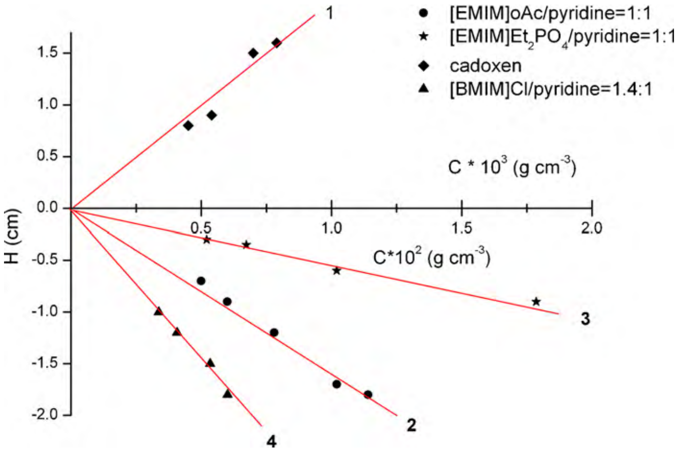

Fig. 8. The dependence of interference bandwidth shift H *versus* cellulose sample N1 concentration in cadoxen (*1*) and in mixtures IL/pyridine (*2*–*4*).

4. Conclusion

The study has shown the stability of cellulose in 1-alkyl-3-methylimidazolium-based ILs mixtures with pyridine at different solute concentrations and at different ratios of IL/pyridine. The data of the Maxwell effect and the viscometry data have confirmed the molecular dispersity of these solutions and demonstrated the possibility to study molecular parameters of cellulose chains in mixtures of ILs with pyridine.

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References

Bikales, N. M., & Segal, L. (1971). *Cellulose and cellulose derivatives*. New York: Wiley-Interscience.
Cross, C. F., & Spruance, D. C. (1904). Process of purifying viscose. *US Patent Office*, Pat. No. 763266.
Graenacher, C. (1934). Cellulose solution. *US Patent Office*, Pat. No. 1943176.
Green, P. (1906). Constitution of cellulose. *Journal of the Chemical Society, Transactions*, *89*, 811–813.
Hafrén, J., Zou, W., & Córdova, A. (2006). Heterogeneous organoclick derivatization of polysaccharides. *Macromolecular Rapid Communications*, *27*, 1362–1366.
Heinze, T., Dicke, R., Koschella, A., Klohr, E.-A., Koch, W., & Kull, A. H. (2000). Effective preparation of cellulose derivatives in a new simple cellulose solvent. *Macromolecular Chemistry and Physics*, *201*, 627–631.
Heinze, T., & Liebert, T. (2001). Unconventional methods in cellulose functionalization. *Progress in Polymer Science*, *26*, 1689–1762.
Heinze, T., Schwikal, K., & Barthel, S. (2005). Ionic liquids as reaction medium in cellulose functionalization. *Macromolecular Bioscience*, *5*, 520–525.
Held, D., & Kilz, P. (2008). Understanding positive and negative detector signals. *The Column, October*, 17–20.
Horvath, A. L. (2006). Solubility of structurally complicated materials. I. Wood. *Journal of Physical Chemistry, Reference Data*, *35*, 77–92.
Köhler, S., & Heinze, T. (2007). New solvents for cellulose: dimethyl sulfoxide/ammonium fluorides. *Macromolecular Bioscience*, *7*, 307–314.

Kolb, H. C., Finn, M. G., & Sharpless, K. B. (2001). Click chemistry: diverse chemical function from a few good reactions. *Angewandte Chemie (International Ed.)*, *40*, 2004–2021.

Kuhlmann, E., Himmler, S., Giebelhaus, H., & Wasserscheid, P. (2007). Imidazolium dialkylphosphates – a class of versatile, halogen-free and hydrolytically stable ionic liquids. *Green Chemistry*, *9*, 233–242.

Ljubina, S., Klenin, S., Strelina, I., Troitskya, A., Chripunov, A., & Urinov, E. (1977). *Polymer Science, Series A*, *19*, 244–249.

Lyncke, H. (1908). Improvements relating to the production or preparation of powdered soluble alkali-cellulose xanthate. *GB Patent Office*, Pat. No. 190808023.

Ohno, H., & Fukaya, Y. (2009). Task specific ionic liquids for cellulose technology. *Chemistry Letters*, *38*, 2–7.

Pavlov, G. M. (1988). Differential refractometer based on the principle of Lebedev's polarization interferometer. In *Proceeding of Leningrad. University, Series Physics and Chemistry, vol. N18* (pp. 89–91).

Pogodina, N. V., Yevlampieva, N. P., Lazareva, M. A., Zakharov, V. I., & Tsvetkov, V. N. (1989). Conformational and optical characteristics of triacetate-methylol cellulose molecules according to the flow birefringence data. *The Polymer Science, Series A*, *31*, 1070–1075.

Riedel, B., Taeger, E., Eilers, M., & Kramer, H. (2001). Method for producing and processing a cellulose solution. *WO Patent Office*, Pat. No. 0158960A1.

Scott, D. J., Harding, S. E., & Rowe, A. J. (2005). *Analytical ultracentrifugation. Techniques and methods*. Cambridge, UK: RSC Publishing.

Swatloski, R. P., Rogers, R. D., & Holbrey, J. D. (2003). Dissolution and processing of cellulose using ionic liquids. *WO Patent Office*, Pat. No. 03029329.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *Journal of the American Chemical Society*, *124*, 4974–4975.

Tsvetkov, V. N. (1989). *Rigid-chain polymers*. Plenum, New York: Consultants Bureau.

Vitz, J., Erdmenger, T., Haensch, C., & Schubert, U. S. (2009). Extended dissolution studies of cellulose in imidazolium based ionic liquids. *Green Chemistry*, *11*, 417–424.

Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q., & Guo, M. (2004). Homogeneous acetylation of cellulose in a new ionic liquid. *Biomacromolecules*, *5*, 266–268.

Wyatt P. J. (1990). Differential refractometer. *US Patent Office*, Pat. No. 4952055.

Yamakawa, H. (1971). *Modern theory of polymer solutions*. New York: Harper and Row.

Yevlampieva, N. P. (1990). *PhD Thesis*. Leningrad.