

Olga Kuzmina,
*Elena Sashina,
*Svetlana Troshenkowa,
Dariusz Wawro

Institute of Polymers and Chemical Fibers,
ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland

*St.-Petersburg State University
of Technology and Design,
ul. B. Morskaja 18, St.-Petersburg, Russia
Olgakuzmina.chem@gmail.com

Dissolved State of Cellulose in Ionic Liquids - the Impact of Water

Abstract

The aggregate size of cellulose dissolved in 1-ethyl-3-methylimidazolium acetate (EMIMAc) and 1-butyl-3-methylimidazolium chloride (BMIMCl) was measured by static and dynamic light scattering. Examined were cellulose solutions containing various amounts of water. The impact of water on the size of cellulose particles in the solutions tested has been defined based upon the measurement results

Key words: cellulose, particle size, ionic liquids, light scattering.

(viscose fibres, cuprammonium fibres, Lyocell etc.).

Derivatives of cellulose [3, 4] or volumetric metallo-complexes [5, 6] are formed by an interaction that proceeds between the cellulose and the solvent used. In such solutions the macromolecules of cellulose are, as a rule, completely separated from each other, and the size of their aggregates is defined by the gyration radius R_g or hydrodynamical radius R_h , which are close to the size of a single macromolecule [7, 8].

Completely derivatised cellulose is molecularly dispersed in its solutions [7, 9]. Direct solvents of cellulose do not form either complexes or derivatives of cellulose. Direct solvents transfer polymer into the solution by the mechanism of physical solvation. Different values of the aggregate size are obtained for cellulose solutions in direct solvents such as ionic liquids. Diluted solutions of cellulose of various origin and polymerisation degree in N-methylmorpholine-N-oxide (NMMO) show a gyration radius of $R_g = 136-204$ nm [10 - 13], a value which considerably exceeds that of isolated macromolecules. For comparison, cellulose with a degree of polymerisation of DP = 486 when dissolved in NMMO reveals R_g values up to 204 nm, while in the cadmium complexing Cd-tren

(tren = tris(2-aminoethyl)amine) solution, the size of cellulose particles with the same DP value is equal to 20 nm [8]. Thus, it may be assumed that with direct solvents the condition of the real solution of cellulose cannot be achieved.

Known dissolution procedures of cellulose, including cuprum-ammonium and xanthate processes, are burdensome and expensive [14 - 18].

Increasing industrial pollution and ever more stringent governmental regulations are a challenge to implement 'green' processes capable of preventing pollution as well as waste and of using renewable resources.

Investigations devoted to cellulose dissolution in ionic liquids (ILs) began about ten years ago. In 2001 Swatłowski and Rogers patented ionic liquids as new kinds of direct solvents for cellulose [19, 20], opening a new division in the history of cellulose dissolution. ILs have the big advantage of negligible vapour pressure, and of being non-explosive and recyclable [21]. The dissolution of cellulose in ILs proceeds by the mechanism of direct solvation [14] without derivatisation [22]. It is hoped that ILs will pave the way for entirely new technologies in the processing of cellulose [23]. So far, in scientific works little attention has been given to the dis-

Introduction

To elaborate a technology for the manufacture of fibres and films from cellulose solutions, profound knowledge is needed of the dissolution process, and of the physical and chemical features of the cellulose solution obtained. [1, 2]. The most important characteristic is the particle (aggregates) size of the polymer in the spinning solution. Knowing it, one can judge whether a real solution is obtainable, in which all of the macromolecules have been separated from each other or, alternatively, whether a bi-phase (disperse) system with the rest of the original structure of the polymer has been formed. As is well known [3 - 13], the size of cellulose aggregates in solutions depends on the nature of the solvent and on the polymer dissolution mechanism.

Many cellulose solvents are well known, some of which are used in the manufacture of commercial cellulose products

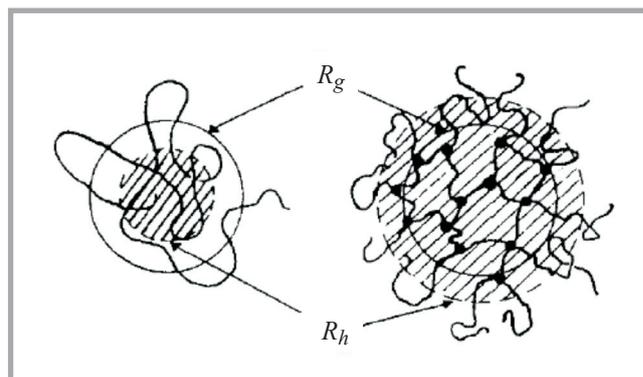


Figure 1. Schematic demonstration of the difference between R_h and R_g of the linear chain of cellulose (left) and microgel (right) [7].

solved state of cellulose in ILs and the role of water in the solution. Therefore it is the purpose of this work to study the problem using the methods of static and dynamic light scattering. In this work, the hydrodynamic radius R_h and radius of gyration R_g of the particles were measured (**Figure 1**).

The absolute size of cellulose aggregates in direct solvents depends not only on its molecular weight [7, 10] but also on the preliminary activation [10] and on the presence of low-molecular liquids [11, 24]. In general, all these factors exert an impact upon the quality of the final product, such as films and fibres. Water accompanies cellulose-containing plants during vegetation and all stages of processing. The aim of this study was to learn the influence of water on the size of cellulose aggregates in ILs solutions and find the theoretical limit of water content in the solutions up to which dramatic effects would not occur in the course of cellulose dissolution.

Materials

- Cellulose pulp: Alicell-Super (Western Pulp Inc, Canada) with DP 494 and molecular weight = $8 \cdot 10^4$ g/mol
- Ionic liquids:
 - 1-butyl-3-methylimidazolium chloride (BMIMCl) from Merck KgaA, Germany;
 - 1-ethyl-3-methylimidazolium acetate (EMIMAc) from Sigma Aldrich, Germany.

Both ionic liquids were used without any pretreatment.

Methods

Preparation of cellulose solution in ionic liquids

Cellulose pulp was dissolved for 2 h in ILs at 110 °C using an oil-bath (to evacuate moisture).

The particle size was measured after complete dissolution of the cellulose. The turbidity as an indicator of dissolution completeness was measured at a microscopic zoom of 20×.

Procedure for adjusting the water content

Cellulose pulp was either dried with UV-lamps at 105 °C to reduce the water content (drying time 1 – 6 hours depending

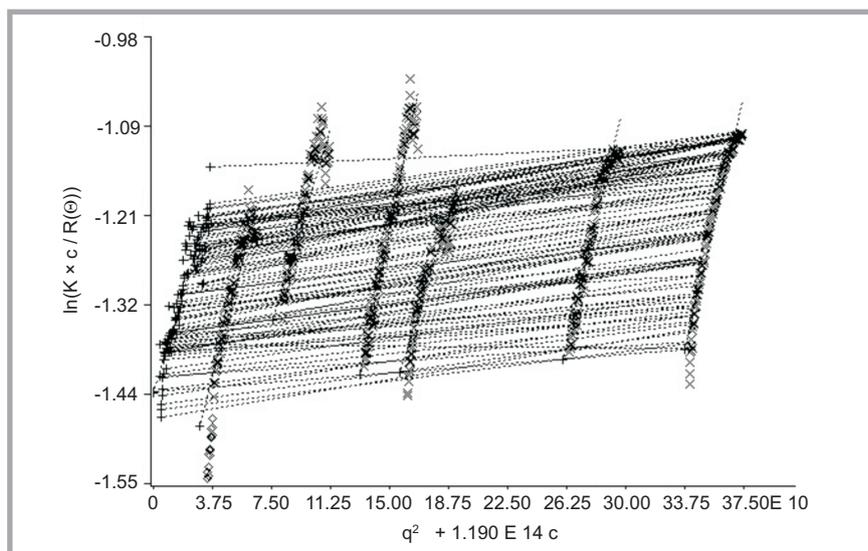


Figure 2. Guinier plot of SLS-data for cellulose /EMIMAc solutions.

on the water content required) or mixed with water to obtain the content required.

Estimation of water content in cellulose pulp

WPE 30S apparatus (moisture analyzer) was used for cellulose pulps with more than 1% of water. The Karl Fisher titration with a DL39 coulometer and DO307 drying oven (Mettler Toledo, GmbH) was employed for more precise data if the moisture expected was less than 1%. The temperature of drying was 100 °C.

Determination of particle size

An SLS-2 goniometer, Systemtechnik Hansen, Germany with a helium-neon laser ($\lambda_0 = 632.6 \mu\text{m}$) was used for static light scattering. The Guinier plot method and Kratky models are described in literature [25 - 27]. The temperature of the experiment was 25 °C. The particle size of cellulose in the solution was measured by light scattering for some concentrations of the solution and angles of light incidence. The graph in **Figure 2** represents the amount of Rayleigh scattering R as a complex function of the angle θ . The Zimm equation is mostly used to calculate the average molecular weight, M_w :

$$K c/R(\theta, c) = 1/M_w (1 + q^2 (R g^2/3)) + 2 A_2 c,$$

where

$$K = 4 \pi^2 n_0^2 (dn/dc) 2 / N_A \lambda^4$$

n_0 – the refractive index of the solvent

λ – the wave length of the light source

N_A – the Avogadro's number
(6.023×10^{23})

R – Rayleigh scatter, cm^{-1}

Few equations relate light scattering data with the angle of $R(\theta)$ [28]. In this work R_g was calculated using the Guinier approximation. Firstly, there was drawn a double extrapolation of the concentration to $c = 0$ for points relating to each particular angle θ , and $\theta = 0$ for points relating to each particular concentration. The zero point of the coordinate system is determined by the intersection of these extrapolated lines. The mass of particles and second virial coefficient A_2 are calculated from the angle of slope $\text{tg } \theta = 0$.

A Zetasizer Nano (Malvern Instruments Ltd., UK) was used for dynamic light scattering. The size range measured by this apparatus is 2 nm - 3 μm . Instead of standard polystyrene, quartz square cuvettes were used due to the fact that the measurements were conducted at 85 °C.

Method of cellulose recovering from the solution

Film is the easiest and simplest cellulose product made by the recovering of cellulose from its solutions. Cellulose solutions with a 2% concentration were cast onto a warm glass pad (85 °C) to form a 1mm thick film, which was then rinsed with distilled water at 20 °C to remove the solvent. All the ILs used are absolutely miscible with water.

EWNN-analysis

The determination of the polymerisation degree (DP) of the cellulose film was undertaken using the standard method in iron (III) sodium tartarate complex (EWNN_{mod NaCl}) solution (ISO 5351/2-1982).

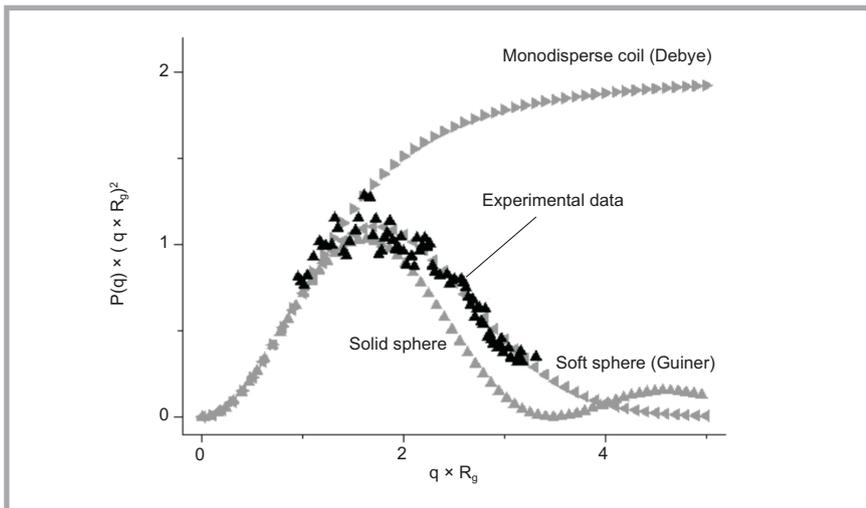


Figure 3. Normalised Kratky plot of SLS-data obtained in cellulose/EMIMAc solutions.

The time of efflux of the diluted solvent and solution of cellulose was measured by a capillary-tube viscometer at 25 °C.

FTIR spectroscopy

Fourier transform infrared spectroscopy measurements were made with Genesis Series FTIR™ apparatus (Unicam Ltd.) in the mid-infrared region, approximately 4000–500 cm⁻¹. The samples were ground with specially purified salt (potassium bromide). From the mixture, pellets were formed translucent to the light beam of the spectrometer.

Results and discussion

Measurements of the size of cellulose aggregates in the ILs solutions

The indices of the solvent's refraction of n_0 and the increment of the index of the

solution's refraction dn/dc were found for data processing. The index of refraction at 25 °C for EMIMAc is 1.5022, and the increment of the index of the solution's refraction dn/dc is 0.060 cm³/g. The value of the increment of the refraction index obtained for cellulose solution in EMIMAc is similar to that of solutions of cellulose in NMMO and is equal to 0.061 ± 0.007 cm³/g, [12].

Figure 2 presents data of static light scattering (SLS) for solutions of cellulose in EMIMAc.

To calculate the radius of gyration R_g of cellulose aggregates in the solution, the Guinier plot was used:

$$\ln \Delta R(\theta) = 1 - (R_g/3) q^2,$$

where: the scattering vector for vertically polarised light $q = 4 \pi n_0 \lambda \sin(\theta/2)$.

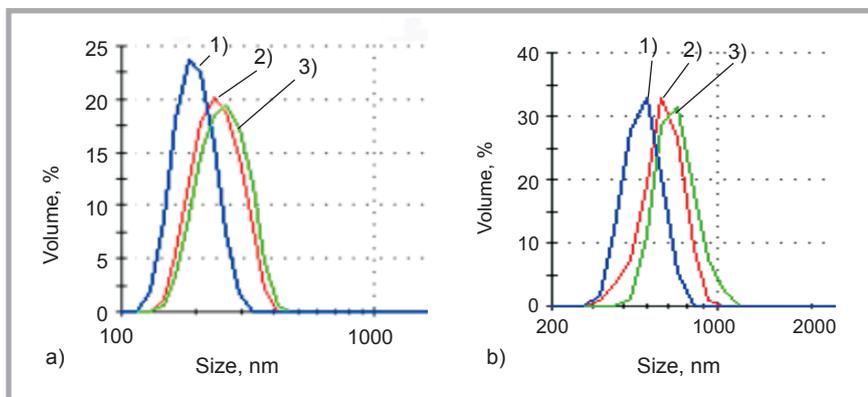


Figure 4. Size distribution by volume for cellulose solution in BMIMCl with a) a water content of 0.1%. 1) 0.5% of cellulose in the solution (average volume being 183.4 nm), 2) 1% of cellulose in the solution (average volume being 238.2 nm), 3) 2% of cellulose in the solution (average volume being 260.9 nm), b) a water content of 0.8%. 1) 0.5% of cellulose in the solution (average volume being 663 nm), 2) 1% of cellulose in the solution (average volume being 789 nm), 3) 2% of cellulose in the solution (average volume being 863 nm).

Experimental data for solutions of cellulose in EMIMAc for the calculation of aggregate size values using the equation above are presented in the form of a Guinier plot (**Figure 2**), which represents the dependence of $\ln(Kc)/R(\theta)$ on the scattering vector for vertically polarised light, Kc chosen in such a way that $Kc_{max} = 1$. Information provided in the form of a Guinier plot allows to obtain the value sought for by simple graphical techniques.

The wide spread of experimental data from which curves of the first or second order can be drawn suggest a large variation of the aggregate size. The molecular mass of the particle and the second virial coefficient were calculated by the double extrapolation of the R_g -values (for infinite dilution) and of the slope determined by the angle of $\tan \theta$ to the intersection with Y-axis.

The average molecular weight M_w of cellulose aggregates in the solution was found to be $1.67 \cdot 10^6$ g/mol, which is much more than the real molecular weight ($8 \cdot 10^4$ g/mol). The gyration radius R_g amounts to 101 nm and the second virially coefficient $A_2 = 2.83 \cdot 10^{-5}$ mol·ml/g². Large units of cellulose are found in its solutions in EMIMAc, although the latter is a good solvent for cellulose (the second virially coefficient is of the order of $\sim 10^{-5}$). These are probably persisting the rest of the original polymer structure. The forming of units can be clearly described by means of a 'soft spheres' model (**Figure 3**).

In **Figure 3** experimental curve is compared with theoretical ones for the soft sphere Guinier, solid spheres, and monodisperse coil Debye. The theoretical model of 'soft spheres', unlike the one for 'solid' spheres, implies the less elasticity and ability to deform in a collision of the aggregates. The experimental curve for cellulose solutions in EMIMAc corresponds with the theoretical curve of Guinier soft spheres. Thus, cellulose in EMIMAc solutions appears in the form of soft spherical particles.

It may be concluded that in direct solvents, an ionic liquid inclusive NMMO, cellulose is not dispersed up to single macromolecules. However, unlike unstable solutions of low-molecular substances, suspensions of cellulose, with its large particle size, are stable (equilibrium) because of high viscosity and slow dif-

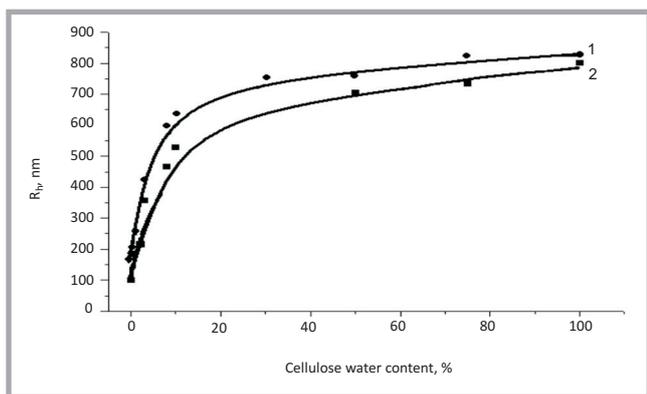


Figure 5. Relation between the hydrodynamical radius of cellulose aggregates in diluted solutions of EMIMAc (1) and BMIMCl (2) and the content of water in cellulose at dissolution at 85 °C (calculated for infinitive dilution).

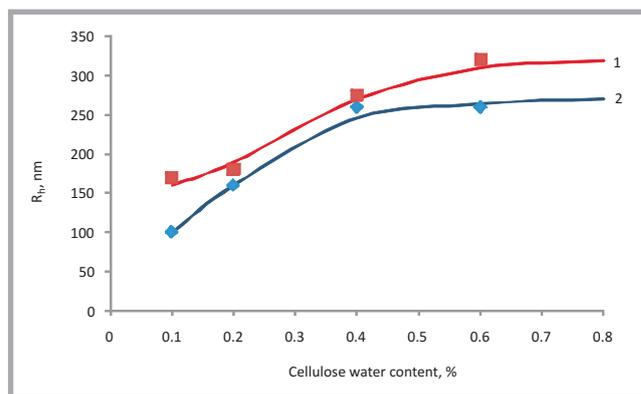


Figure 6. Effect of the water content of cellulose on the hydrodynamical radius of cellulose aggregates in diluted solutions of EMIMAc (1) and BMIMCl (2) at 85 °C (calculated for infinitive dilution).

fusion. The suspensions are suitable for processing and producing good film. It is worth noting that the size of cellulose aggregates in EMIMAc solutions is about half of that with the same DP in NMMO [10, 13].

Influence of water on the size of particles in solutions of cellulose in ionic liquids

In the first part of the work it was shown that cellulose in an IL's solution appears rather in the form of aggregates than as single macromolecules. Therefore the definition of the hydrodynamical radius R_h seems to provide better information concerning the characterisation of the size of cellulose aggregates in a solution.

It can be seen from the scheme in **Figure 1** that the static radius of rotation for a single chain and microgel remains identical, while the hydrodynamical radius changes, giving more exact information on the size of a particle. Comparison of the R_h and R_g values provides further information. From **Figure 1** it appears that for isolated macromolecules the radius of gyration R_g exceeds the hydrodynamical radius R_h , while for microgels it is the reverse situation.

R_h values were defined for cellulose solutions with different contents of water. The concentration of cellulose in the solution was changed from 0.5 - 2 wt%. The refraction index of BMIMCl at 85 °C is equal to that of EMIMAc at the same temperature and corresponds to 1.503.

The size distribution of R_h – values of cellulose aggregates in IL solutions is presented in **Figure 4**. Examples are given for BMIMCl solutions with a 0.5, 1 &

2 wt% cellulose concentration and 0.1% & 8% water content. The size distribution of cellulose aggregates in the EMIMAc solutions looks identical.

As can be seen from **Figure 4**, the size of cellulose aggregates increases with a rising cellulose concentration in the solution as result of agglomeration. At infinitive dilution, the size of polymer particles reaches the minimum, which depends solely on polymer-solvent interaction. With an increasing polymer concentration, macromolecules are more inclined to interact with each other, resulting in an increase in particle size. The water content also has an influence on the size of cellulose aggregates. The deterioration of solvent quality is the supposed reason for the progressive changes in aggregation. The dependence of the hydrodynamical radius of cellulose aggregates in BMIMCl and EMIMAc solutions (calculated for infinitive dilution) on the relative content of water in cellulose is presented in **Figure 5**.

The size of cellulose particles increases with a rising water content in the solution. With an equal water content, cellulose particles are larger in EMIMAc than in BMIMCl solutions.

For a better understanding of the changes in cellulose particle size at a low water content, data for the beginning area of **Figure 5** are presented in **Figure 6**, showing particle size in a solution with a low content of water.

Figures 5 & 6 show that the size of cellulose aggregates in BMIMCl and EMIMAc solutions increases with a rise in the water content of cellulose. This phenom-

enon can be explained by possible competition between water and ILs molecules in their drift towards interacting with the active centers of the polymer. As soon as sufficient water molecules are available to occupy all accessible active centers of the polymer, the “effect of competition” on particle size becomes less noticeable, and the increase in aggregate size takes a moderate course compared with the vehement change at a low water content in the cellulose. Molecules of water strongly associated with the cellulose chains contribute to an additional increase in aggregate volume. With a more than 8% water content in cellulose, the size of aggregates in the solutions investigated reached several hundred nm, making the dispersion visible to the eye.

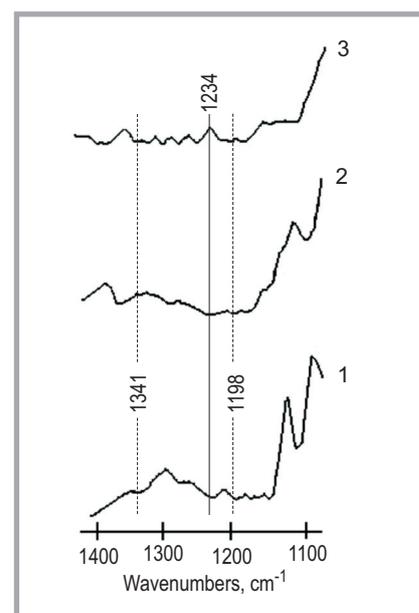


Figure 7. FTIR spectrum of a native cellulose (2) and film obtained from the solution in BMIMCl (1) and EMIMAc (3).

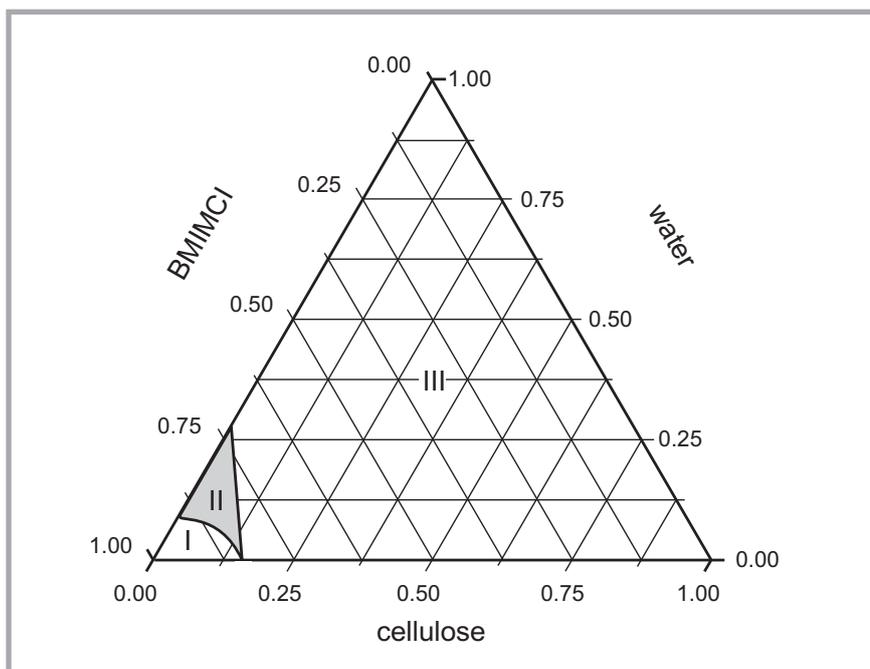


Figure 8. Solubility diagram of cellulose-water-BMIMCl mixtures. I – area of colloid solution, II – area of suspension, III – area of bi-phase system (large-size dispersion).

For identical samples, the value of the hydrodynamical radius R_h is bigger than the radius of rotation R_g . For dissolved, practically dry cellulose, the values are $R_g = 101$ nm and $R_h = 160$ nm, indicating the absence of individual macromolecules and the presence of micro-gel - units with a possible inclusion of solvent molecules.

The film samples obtained from ILs solutions of cellulose with equilibrium water moisture were also examined by the FTIR method (**Figure 7**, see page 35).

The absorbance spectra of the film are compared with the spectrum of cellulose pulp. Very interesting peaks appear in the IR-spectra of cellulose film obtained from the BMIMCl solution at wave numbers of $\sim 1198 - 1334$ cm^{-1} and in the IR-spectrum of cellulose film obtained from the solution in EMIMAc at wave numbers of $\sim 1201 - 1341$ cm^{-1} . There is a symmetric stretching of the C-N group. The peak of the acetyl group stretching (1234 cm^{-1}) is also present in the spectrum of the film obtained from the EMIMAc solution. The appearance of these groups is evidence of the presence of solvent in the film. Macromolecules of cellulose strongly absorb the molecules of the ionic liquid, traces of which remain in the pulp, sustaining careful washing. The results call for further investigation.

For a better understanding of the influence of water on cellulose dissolution in ILs, the relation between aggregate size and the mass ratio of components in the solution is presented in **Figure 8**.

In the diagram drawn for a temperature of 85 $^{\circ}\text{C}$ and atmospheric pressure, three areas of state are found: I – area of colloid solution with the size of aggregates less than 10^{-7} m, II – area of suspension with the size of aggregates more than 10^{-7} m and less than 10^{-5} m, III – area of bi-phase system, characterised by a large size of polymer particles - above 10^{-5} m.

A solution with a possibly small particle size is a prerequisite to obtain a good quality product (fibres or film). Solutions from area I in **Figure 8** are in line with the requirement. From area II the maximum component ratio can be found to obtain a solution suitable for technological processing into fibre or film. If the component ratio in the mix corresponds to area III, the cellulose aggregates in this area are large enough to be observed by the naked eye and it is not possible to produce a homogeneous and good-quality product from this system.

Conclusion

Solutions of cellulose in ionic liquids BMIMCl and EMIMAc represent stable disperse systems containing the remains of the undissolved structure of the poly-

mer, with a diameter of gyration approximately up to 5 times higher than that of a single macromolecule of cellulose of the same molecular weight. Molecules in the solutions are aggregates in the form of soft spheres. The hydrodynamical radius of particles of cellulose in EMIMAc slightly exceeds those in BMIMCl, with other conditions being equal (humidity of cellulose, concentration of the solution, and the temperature). The size of cellulose aggregates in BMIMCl and EMIMAc solutions grows with an increase in the water content of cellulose and its concentration in the solutions, which may be interpreted in terms of both the deterioration of the solvent and the swelling of particles in the presence of water. A colloid solution useful for technical purposes could be obtained only at a water content in the solution below 8%. Molecules of the ionic solvent in the solution are presumably linked with cellulose chains. Strong adherence to the polymer makes the solvent resistant to washing.

Acknowledgments

- The research presented received funding from the European Community's Seventh Framework Program [FP7/2007-2013] under grant agreement No. PITN-GA-2008-214015.
- This work was supported by the Ministry of Education and Science of the Russian Federation.
- Analysis of the size of the cellulose particle in a solution was performed with equipment provided by the Institute of Polymer and Dye Technology of the Technical University of Lodz, Poland.

References

1. Kuzmina O. G., Sashina E. S., Novoselov N. P., Zaborski M.; *Fibres and Textiles in Eastern Europe*, 2009, V 17, №6, pp. 36-39.
2. Wendler F., Meister F., Wawro D., Wesolowska E., Ciechańska D., Saake B., Puls J., Le Moigne N., Navard P.; *Fibres and Textiles in Eastern Europe*, 2010, V 19, №2 (in press).
3. Sutter W., Burchard W.; *Macromol. Chem.* 1978. V. 179. P. 1961-1980.
4. Hunt M. L., Newman S., Scheraga H. A., Flory P. J.; *J. Phys. Chem.* 1956. V. 60. № 8. pp. 1278-1290.
5. Burchard W., Klüfers P.; *Angewandte Chemie*. 1994. H. 106. № 8. pp. 936-939.
6. Schulz L., Burchard W.; *Papier*. 1993. № 47. pp. 1-10.
7. Schulz L., Seger B., Burchard W.; *Macromol. Chem. Phys.* 2000. 201. № 15. pp. 2008-2022.

8. Saalwachter K., Burchard W., Kettenbach G.; *Macromolecules* 2000, 33, pp. 4094-4107.
9. Michels Ch., Kosan B.; *Beitrag zum Lösungszustand von Cellulose und Cellosederivaten*. 6. Int. Symp. „Alternative Cellulose - Herstellen, Verformen, Eigenschaften“ 4-5 Sept. 2004. Deutschland, Rudolstadt. 2004.
10. Röder T., Morgenstern B.; *Polymer*. 1999. V. 40. № 14. pp. 4143-4147.
11. Drechsler U., Radosta S., Vorweg W.; *Macromol. Chem. Phys.* 2000. V. 201. № 15. pp. 2023-2030.
12. Arndt K-F., Morgenstern B., Röder T.; *Macromol. Symp.* 2002. 162. pp. 109-119.
13. Morgestern B., Roder T.; *Papier* 1998, 52, pp. 713-717.
14. Kennedy J. F., Phillips J. F., Kennedy G. O., Williams, P. A.; *Cellulosic pulps, fibres and materials*. Abington: Woodhead Publishing Limited, 2000. – p. 330.
15. Woodings C.; Woodings P.; *Regenerated cellulose fibres*. Abington: Woodhaed Publishing Ltd, 2001. – 336 p.
16. Rogovin Z. A., Galbrajikh L. S.; *Chimicheskiye prevrascheniya i modifikacija celljulosity*. Himija, 1979. – 206 p.
17. Bajjkiza H., Segala L. *Celljuloza i ee proizvodnye*. Moscow Mir, 1974. Vol. 1. p. 495, Vol 2. p. 510.
18. Young R. A., Rowell R. M.; *Cellulose, structure, modification and hydrolysis*. New York: John Willey and Sone, 1986. p. 286.
19. Swatoski, R.P, Spear, S.K., Holbrey, J.D., Rogers, R. D.; *J. Am. Chem. Soc.* 2002, Vol. 24, pp. 4974-4975
20. U.S. Patent No. 6,824,599 B2; *International Application PCT/US02/31404; International Publication Number WO 03/029329 A2, April 10, 2003*
21. Massonne K.; *Ionic liguids – an introduction [Text]* / K. Massonne, M. Maase, V. Stegmann, U. Vagt // *Mater. 7-th Int. Symp. "Alternative cellulose – manufacturing, forming, properties*. 6-7 Sept. 2006. Rudolstadt, Germany, 2006. – p. 32.
22. Sashina E. S., Novoselow N. P.; *Russian Journal of General Chemistry*. 2009. V. 79. № 6. pp. 885-890.
23. Mizumo T.; *Chemistry Letters*. 2004. V. 33. № 10. pp. 1360-1361.
24. Sasina E. S., Novoselow N. P., Kuzmina O.G., Troshenkowa S.V.; *Fibre Chemistry*. 2008. № 3. pp. 75-79.
25. Bocek A. M.; *Rastwory cellulosity i eje proizvodnyh w nevodnyh sredach i plenki na ich osnowe*. Diss. doc. chem. nauk. St-Petersburg, Institut chimii rastvorov RAN. 2002. p. 306.
26. Troshenkowa S. V., Sasina E. S., Novoselow N. P., Arndt K.-F.; *Russian Journal of General Chemistry*. 2010, № 3, pp. 479-484.
27. Eskin V. E. *Rassejaniye sveta rastvorami polimerow i swojstwa macromolecul*. Leningrad. Nauka. 1986.
28. *Kratky plot. IUPAC Compendium of Chemical Terminology, 2nd ed., 1997.*

UNIVERSITY OF BIELSKO-BIAŁA

Faculty of Materials and Environmental Sciences

The Faculty was founded in 1969 as the Faculty of Textile Engineering of the Technical University of Łódź, Branch in Bielsko-Biała. It offers several courses for a Bachelor of Science degree and a Master of Science degree in the field of Textile Engineering and Environmental Engineering and Protection. The Faculty considers modern trends in science and technology as well as the current needs of regional and national industries. At present, the Faculty consists of:

■ The Institute of Textile Engineering and Polymer Materials, divided into the following Departments:

- Physics and Structural Research
- Textiles and Composites
- Physical Chemistry of Polymers
- Chemistry and Technology of Chemical Fibres

■ The Institute of Engineering and Environmental Protection, divided into the following Departments:

- Biology and Environmental Chemistry
- Hydrology and Water Engineering
- Ecology and Applied Microbiology
- Sustainable Development of Rural Areas
- Processes and Environmental Technology



University of Bielsko-Biała
Faculty of Materials and Environmental Science

ul. Willowa 2, 43-309 Bielsko-Biała
tel. +48 33 8279 114, fax. +48 33 8279 100