Solubility Behaviour of Cellulose Acetate Butyrate in Mixture of Solvents

ANCA GIORGIANA GRIGORAS*, NICULAE OLARU
Petru Poni Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, 41A, 700487, Iasi, Romania

In order to identify the proper solvent mixture for future processing from solution of cellulose derivatives, the laser light scattering method was used. The multiangle laser light scattering parameters of macromolecular chains in solution (weight-average molecular weigh $\overline{M}_w$ *, radius of gyration* R_g *and second virial coefficient* A_2*) were correlated with the values of dielectric constant of solvent mixture (2-methoxyethanol + N,N-dimethylformamide). The experimental results revealed that the protic solvent favored the extended conformation of the macromolecules in solution, necessary condition to obtaine nanofibers by electrospinning.*

Keywords: cellulose acetate butyrate, 2-methoxyethanol, N,N-dimethylformamide, laser light scattering

Cellulose acetate butyrate (CAB) is a biocompatible, semi-crystalline, thermoplastic, UV resistant polymer that can be used in different forms (film, membrane, fibers, microspheres) both alone and in combination with others substances. Due to the hydroxyl groups of CAB, it is expected to it provides hydrogen bond interactions. Also, the presence of acetyl and butyryl substituents allows to CAB to interact with hydrophobic moiety of solvents. Generally, the suitable solvents recommended by ASTM to dissolve CAB with variable composition (D.S. (acetate) = 0.8-2.1 and D.S. (butyrate) = 0.7-2.35) are chloroform, tetrachloroethane, dioxane, acetone and nitroethane [1].

To merge the biodegradability and biocompatibility of the natural polymers with the processability of the synthetic polymers in order to design new implants, tissue scaffolds or drug delivery systems, some authors studied the modifications in physical properties of CAB in blends with miscible partners. Thus, it was found that cellulose acetate butyrate was miscible with poly(butylene succinate) in chloroform [2], poly(vinylidene fluoride) in *N,N*-dimethylformamide [3], poly(methylmethacrylate) in *N,N*-dimethylformamide [4], poly(vinylpyrrolidone) in *N,N*-dimethylformamide [5] or poly(caprolactonetriol) in acetone [6]. Usually, their miscibility was based on intermolecular H-bonds or electrostatic interactions.

As others cellulose esters, CAB received a great deal of attention in the pharmaceutical, food and waste water industries. It was exploited as ultrafine membrane for osmotic drug delivery [7], hyperfiltration of sodium chloride and urea feed solution [8], filtration of uranyl ions from contaminated waters [9]. CAB microspheres were used for controlled release of theophylline [10] or paracetamol [11], while poly(vinylalcohol)/cellulose acetate butyrate electrospun core/shell nanofibers were tested for oxytetracycline [12]. Some researchers appealed to the electrospinning of CAB to design fibers with desired sizes and various applications. Beside the process and environmental variables, the polymer solution variables (polymer molecular weight, and solvents used for preparation of initial polymer solution) influenced the morphological or mechanical characteristics of the resulted micro-/nano-fibers, too [13-16]. In case of a binary solvent mixture, the composition was varied in order to control the dielectric constant of the electrospinning solvent.

This work studied the influence of polarity of solvent binary system (2-methoxyethanol + *N,N*-dimethylformamide) on the conformation of CAB chains in solution. The results obtained on dilute solutions by the laser light scattering could be extrapolated to the more concentrated solutions used for electrospinning.

Experimental part

Material and methods

The cellulose acetate butyrate (CAB from Eastman with M_n = 30 000 g mol^{-1}, 2 wt % acetyl content, 52 wt % butyryl content, and 1.8 wt % hydroxyl content), *N,N*-dimethylformamide (DMF, from Fluka), 2-methoxyethanol (MEt, from Sigma-Aldrich), poly(ethylene oxide) (PEO, M_n = 3930 g mol^{-1}, from Polymer Laboratories, Stretton, UK; standard for GPC), poly(styrene) (PS, M_n = 4490 g mol^{-1}, from Polymer Laboratories, Stretton, UK; standard for GPC) and HPLC-grade toluene (from Sigma Aldrich) were used as received. The CAB solutions in pure solvent (MEt or DMF), and solvent mixture with different volumetric ratio were prepared as follows: after 24 h of CAB swelling in solvent at room temperature, the stock polymer solutions were homogenized with a magnetic stirrer about 3 h, and then filtered through 0.2 mm Whatman syringe filters with PTFE membrane. From these homogeneous solutions, dilutions with concentration range from 1x 10^{-3} to 1.2x10^{-4} g mL^{-1} were gravimetrically prepared for refractometric and laser light scattering measurements. The resulted solutions were deposited for 72 h in capped quartz scintillation vials (Quartz SUPRASIL, provided by Hellma GmbH & Co. KG, Germany) to allow the solution degassing (necesary condition for proper laser light scattering measurements).

The unfractionated samples were analyzed by differential refractometry and multiangle laser light scattering methods following a well known protocol [17, 18]. An Optilab-rEX differential refractometer (Wyatt Tech. Co., Santa Barbara CA, USA), used in off-line mode, allowed the determination of the refractive index increments (*dn/dc*) of the polymer solutions at 25°C. The accurate measurement of these values it is an important preliminary step for the laser light scattering determinations considering that *dn/dc* is a specific parameter for every polymer-solvent pair, which is dependent on temperature and wavelenght of mesurement, too [19].

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* *email:angrig@icmpp.ro; Phone: +40 232 217 454*

The multiangle laser light scattering (MALLS) measurements were realized with a DAWN DSP laser photometer (Wyatt Technology) at 25 °C, in batch mode. The incident light has come from the laser with wavelength of 633 nm and power of 5 mW, and the scattered light intensities were measured at $\theta = 14^{\circ} \div 152^{\circ}$ by a group of photodiodes, arranged in a circle around the scintillation vial containing the polymer solution (fig. 1).

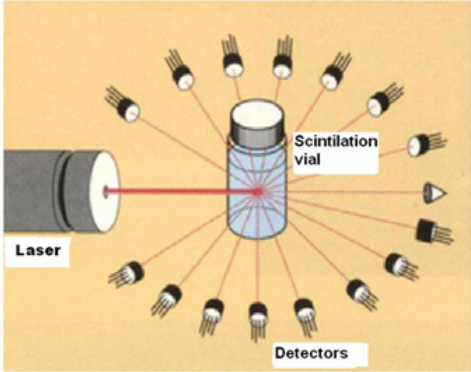

Fig. 1 MALLS setting up (Adapted from ASTRA for Windows, User's Guide, Wyatt Tech. Corp.)

The calibration of photometer was realized with toluene. In case of CAB solutions with MEt, the signals from photodiodes were normalized with PEO 3930, whereas in case of solutions in DMF and DMF mixed with MEt, the normalization was made with PS 4490. After the laser light scattering data processing by Astra 4.90.07 software, the important parameters of the macromolecules in solution (weight-average molecular weight $\overline{M}_w$ and radius of gyration R_g and second virial coefficient A_2) were determined based on Zimm plots and Debye formalism. Astra 4.90.07 software operated with Zimm equation (eq.1) which, in addition, relate the following physical quantities: the optical constant for vertical polarized incident light (K), the concentration of the scattering species (c in g mL^{-1}), the Rayleigh ratio between incident and scattered lights (R_θ), the scattered intensity angle (θ), the wavelength of the incident light on sample (λ_0), the radius of gyration of the macromolecular chain (R_g), the refractive index of the macromolecular solution (n), and the Avogadro number (N):

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + 2A_2c + \frac{16\pi^2}{3\lambda_0}\frac{R_g^{\;2}}{\overline{M}_w}\sin^2\frac{\theta}{2} + \ldots \qquad (1)$$

where:

$$K = \frac{4\pi^2 (dn/dc)^2 n^2}{N\lambda_0^{\;4}} \qquad (2)$$

Then, the Zimm plots were computed using the Berry formalism (eq. 3):

$$\left(\frac{K \cdot c}{R_\theta}\right)^{0.5} \textit{versus} \ \sin^2\left(\frac{\theta}{2}\right) \qquad (3)$$

The second virial coefficient A_2 defines the thermodynamic interactions between molecules in solution at a specific temperature. In case of dominantion of the polymer-solvent interactions compared with polymer-polymer interactions, the second virial coefficient is positive and the solvent is considered *good* from thermodynamically point of view. If $A_2 = 0$, the both interactions are energetically equivalent (specific case for a *theta* solvent). In case of a *poor* solvent, $A_2 < 0$ and the polymer-polymer contacts are more probable instead of polymer-solvent ones [20].

Results and discussion

The interactions present in a polymer-solvent system are important for engineering application, even more if the system contains two solvents. Obviously, the chemical nature and polarity of each ones represent some factors that will influence the interactions between partners in solution such that, finally, the intermolecular associations will affect the solution rheology and electrospinning performance.

Refractometric and laser light scattering data

The refractometric and multiangle laser light scattering measurements of the dilute solutions of CAB in all solvent (pure and mixed) generated the data shown in Table 1.

As the volume fraction (φ1) of MEt in mixture with DMF increased, the value of radius of gyration of macromolecular chain in solution (*Rg*) increased, meaning that the average size of macromolecular chain was higher in MEt (177.2 nm) than in DMF (85.1 nm). This phenomenon was due to the maximizing of the polymer-solvent contacts followed by the chain expansion, so that the most *swollen* chain existed in pure MEt.

The apparent value of weight-average molecular weigh $\overline{M}_w$ was a mean for all types of the associations in solution. In case of the systems with more DMF, the hydrophobic interactions between CAB substituents increased so that the CAB-CAB *intramolecular* interactions were dominant. As the volume fraction of MEt in solvent mixture increased, more *intermolecular* interactions by hydrogen bonds between different CAB chains and solvent molecules (CAB-MEt-CAB and CAB-CAB) appeared, and coexisted with CAB autoasociations such that $\overline{M}_w$ values increased.

It was expected that the hydroxyl groups of CAB to provide a good solubilization of the cellulose derivative in MEt. In addition, the large size and low polarity of the butyryl groups on the CAB spaced the macromolecular chains and lowered the attraction between them and thus facilitated the access of the solvent molecules, especially of MEt ones. Regarding to CAB, generally, as the butyryl content of the

Volume fraction of MEt in mixture with DMF (φ1)	*dn/dc* (mL g^{-1})	R_g (nm)	M_w (g mol^{-1})	A_2 (mol mL g^{-2})
0	0.106	85.1	65870	2.10 E-3
0.1	0.101	60.5	55750	1.02 E-2
0.5	0.093	64.4	63264	5.66 E-3
0.8	0.085	91.4	264500	1.67 E-3
0.9	0.081	163.7	705800	4.32 E-3
1	0.073	177.2	558400	1.43 E-4

Table 1
REFRACTOMETRIC AND LASER LIGHT SCATTERING DATA FOR CELLULOE ACETATE BUTYRATE IN DIFFERENT SOLVENTS (25oC)

ester increases, solubility increases and viscosity decreases. The positive values of A_2 for all CAB solutions suggested that all solvent combinations were *goods* from thermodynamically point of view and polymer-solvent interactions were favored as the content of MEt increased.

Conformational analysis

The linearity of Debye plots corresponding to detector placed at $\theta = 90^0$ indicated that the probes were quasimonodisperse in each solvent. The power law relation between molecular size and molecular weight ($R_g \sim \overline{M}_w{}^a$) represented the basic relation for the conformational plots log (R_g) *vs.* log $\overline{M}_w$. These plots for CAB in each solvent were constructed based on equation 4, where C was an arbitrary constant:

$$\log (R_g) = a \log (\overline{M}_w) + C \qquad (4)$$

The scientific literature associated the theoretical values of the power law exponent *a* (e.g. 0.33, 0.5, 0.55 - 0.6 and 1.0) with a specific conformation of macromolecular chain in solution: compact/hard sphere, random coil at theta conditions, random coil in a thermodynamically good solvent, and rigid rod, respectively [21, 22]; the intermediary values were due to the transitions from an extreme conformation to another. Generally, in this study, CAB adopted the compact sphere conformation in solution as figure 2 shown.

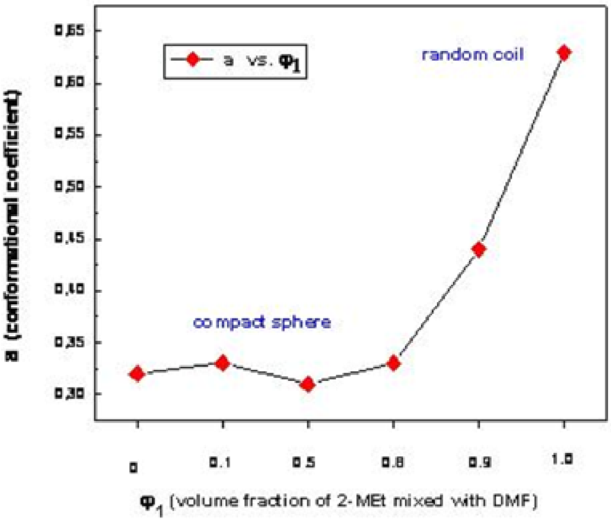

Fig.2. Variation of power law exponent *a* with volume fraction of MEt (φ_1) in mixture of solvents

Only after that the volume fraction of MEt in solvent mixture (φ_1) was high enough, the conformation of macromolecules in solution was changed to the random coil ones. After the inflection point corresponding to the 8:1 volume ratio of solvents, the macromolecules recorded a transition between the two conformational states (for 9:1 volume ratio of solvents), and finally in pure MEt, the CAB chains adopted the random coil conformation in solution.

Polarity of solvents

To establish a relationship between dielectric constant of mixed solvents and solvent composition, a method usually used by researchers was applied to calculate the dielectric constant of a binary mixture:

$$\varepsilon_m = \varphi_1\varepsilon_1 + \varphi_2\varepsilon_2 \qquad (5)$$

where ε_m, ε_1 and ε_2 are the dielectric constants of the mixture and solvents 1 and 2, respectively, φ_1 and φ_2 are the volume (weight or mole) fractions of solvents 1 and 2 in the mixture. Since φ_2 = 1- φ_1, equation 5 could be rearranged as:

$$\varepsilon_m = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2)\varphi_1 = M_0 + M_1\varphi_1 \qquad (6)$$

where M_0 and M_1 are the intercept and slope of the equation [23]. In this study the values for ε_1 and ε_2 were selected from literature data [24, 25]. The calculated dielectric constant of our binary mixture (MEt + DMF) took into account the volume fractions of each solvent in mixture.

Depending on their physical characteristics (e.g. polarity) the solvents are classified either polar or non-polar, as the dielectric constant indicated. Generally, the solvents with dielectric constants greater than about 5 are considered *polar* and those with dielectric constants less than 5 are considered *non-polar.* Even more, the polar solvents could be protic or aprotic, function of the capacity or incapacity of some functional groups (e.g. -OH or -NH) to participate to formation of a hydrogen bond, respectively. A hydrogen bond is an electrostatic attractive interaction between a hydrogen atom (H) from a molecule and a highly electronegative atom (N, O, F). The energy associated with hydrogen bonds (6-30 kJ/mol) is greater than the energy of van der Waals interactions, but lower than the energy of covalent or ionic bonds. Depending on the environmental conditions and geometry, the hydrogen-bond attractions can occur between different molecules (*intermolecular*) or within different parts of same molecule (*intramolecular*), both in case of the low molecular mass molecules and macromolecules.

In this study it could be observed that as the dielectric constant of the solvent mixture varied, the degree of association by hydrogen bonds between susceptible hydrogen bonding groups was tuned due to systematic screening of intermolecular interactions.

Table 2

CALCULATED AND EXPERIMENTAL DIELECTRIC CONSTANTS FOR BINARY SOLVENT MIXTURES

Volume fraction of MEt in mixture with DMF (φ_1)	**Calculated dielectric constant of binary mixture (ε_m)**	**Experimental dielectric constant (ε_0) of binary mixture at 25 °C and 2 MHz** [26]	**Experimental dielectric constant (ε_0) of binary mixture at 25 °C and 10 MHz** [27]
0	38.00	37.59	40.21
0.1	35.90	36.40	39.45
0.5	27.48	29.37	35.64
0.8	21.17	22.30	25.34
0.9	19.06	19.88	21.99
1	16.96	16.94	17.58

ε_1(MEt) = 16.96 [24], ε_2(DMF) = 38.00 [25]

Considering that DMF was a polar aprotic solvent (more polar than MEt; with dielectric constant 37.8 > 16.93) and it not participated to hydrogen bonds, the most probable H-bonding interactions were due to MEt and CAB. Both molecules possessed –OH groups capable to interact with H atom of hydroxyl groups of its partner (OH···OH). Thus, intermolecular (CAB-MEt) and intramolecular (CAB-CAB, MEt-MEt) H-bonds were possible. Because their weighting in part cannot be determined, it was just presumed that the number of CAB-MEt interactions became dominant to the extent that the volume fraction of MEt in solvent mixture increased.

Comparing the values calculated on the basis of equation (5) with the experimental values collected from literature, it was observed a similar behavior: the dielectric constant of solvent binary mixture decreased with the increasing of 2-methoxyethanol content in the binary mixture for all the systems because the polarity of MEt was lower than DMF (table 2).

Conclusions

This work showed that CAB in solution displayed a more extended conformation and raised apparent molecular weight in solvent mixture with dominant protic polar content (2-methoxyethanol). In addition, in these systems the significant hydrogen bonding associations appeared with decreasing of solvent dielectric constant. Thus, 9:1 volume ratio of MEt:DMF was the best solvent mixture to dissolve CAB. These results suggested that a solvent mixture reached in MEt will be more proper to obtain composites based on CAB electrospinned smoother nanofibers.

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