THERMODYNAMIC PROPERTIES IN QUATERNIZED POLYSULFONES/NEUTRAL POLYMER/SOLVENT COMPLEX SYSTEMS

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Abstract
Theoretical and experimental aspects concerning the interactions generated via electrostatic interactions and hydrogen-bonding in quaternized polysulfones/neutral polymer/solvent complex ternary systems are investigated. The experimental results related to the intrinsic viscosity and hydrodynamic parameters have been obtained by viscometric measurements, using new Wolf model, and discussed in terms of the chemical structure of compounds, density of charged groups, solution concentrations, and mixing ratio of the two polymers. The conformational changes of the polymer chains in dilute solution as well as the effect of electrostatic interactions, hydrogen bonding or association phenomena are reflected in variations of viscosity function on polysulfone content. Moreover, through the perspective of the new theories approached, this work analyzes the thermodynamic and hydrodynamic functions, making possible choosing of the suitable polymer blends for obtaining membranes with certain applications.

Introduction
Analysis of polyelectrolyte solution dynamics is of great interest in many tehnological processes implying a good control of the flow properties of the fluids [1]. Due to the variety of specific physicochemical properties, the ionic polymers have started to be studied, especially in terms of their viscometric behavior in dilute solution. One of these polymers, having polyelectrolyte characteristics, is polysulfone containing quaternary ammonium side groups (PSFQ). Good solubility [2], hydrophilicity [3], biocompatibility [4], and water permeability [5] make them proper for applications from various fields. Moreover, these properties can be improved and tailored by blending with other compounds for further applications in biotechnology as membrane for separation or ultrafiltration [6]. In this context, neutral polymers, as polyvinyl alcohol (PVA) and cellulose acetate phthalate (CAP), were used in blends with PSFQ. Their selection is based on excellent physical properties (*i.e.,* hydrophilicity, flexibility, tensile strength), and on the emulsifying capacity, dispersing power and ability to form films [7].

Knowledge of the thermodynamics and kinetics of the ternary systems in solution is necessary for understand the membrane formation mechanisms, changing of the preparation conditions, and for prediction of the membranes final structure [8]. The presence of the specific interactions in the multicomponent polymer systems namely, nanostructures, polyelectrolytes, polymers in the presence of surfactants, complicates the structural and thermodynamic assessments. Therefore, is necessary to specify all possible interactions between the components system that can lead to the formation of multicomponent complexes in accord with different processes of equilibrium characterized by association/interaction constants. The

specific intermolecular interactions established between the polar groups are also, important in the formation of the hydrogen bonding that must be taken into account in interpreting of the thermodynamic properties.

In this context, the quaternized polysulfones/neutral polymer/solvent multicomponent systems were investigated by viscometric studies to establish the specific interactions developed by electrostatic interactions, hydogen bonding, and association phenomenan that occur in system. Also, specific interactions of the studied multicomponent systems were theoretical evaluated by means of a theory based on multiple association equilibria. Consequently, the results of this study represent the basis for future researches concerning the good compatibilization of polymers from blends in order to design membranes for bioapplications.

Experimental

Quaternized polysulfone, with average molecular weight of about $\overline{M}_w = 28,000$ g/mol, degree of substitution $DS \cong 1$, and ionic chloride content of 5.44%, was synthesized starting from commercial polysulfone in powder form (PSF) (UDEL-3500) following the synthesis reactions previously mentioned [9]. Polyvinyl alcohol (PVA) having average molecular weight of $\overline{M}_w = 23,000$ g/mol and hydrolysis degree of about 98.8% was purchased from Celanese Corporation (Texas). Cellulose acetate phthalate (CAP) with number average molecular weight $\overline{M}_n = 2,534$ g/mol, a substitution degree for acetyl and phthaloyl groups of 1.07 and 0.77 was purchased from Sigma-Aldrich.

Viscosity measurements were carried out with a Schott AVS 350 computerized apparatus provided with an Ubbelohde suspended-level viscometer at $25 \pm 0.01°C$. The flow volume of the viscometer was higher than 5mL and flow times were obtained with an accuracy of 0.035%, for different measurements. The homogeneous solutions of PSFQ, PVA, CAP, prepared by dissolution in in N-methyl-2-pyrrolidone (NMP), and their blends (PSFQ/PVA and PSFQ/CAP in different mixing ratios) whose obtaining protocol was presented in previous studies [9] have concentrations between $0.01 \div 0.99$ g/dL. For determination of intrinsic viscosities, the Huggins equation was used (Equation 1) [10]:

$$\eta_{sp} / c = [\eta]_{Huggins} + k_H [\eta]_{Huggins}^2 c \tag{1}$$

where: η_{sp} - specific viscosity, k_H - Huggins constant, c - polymer solution concentration, $[\eta]$ - intrinsic viscosity.

In addition, due to polyelectrolyte complicated behavior in dilute and semi-dilute domains, as a result of the combined action of electrostatic and hydrodynamic interactions, the new Wolf method (Equation 2) was used [11]:

$$\ln \eta_{rel} = \frac{c[\eta]_{Wolf} + Bc^2 [\eta]_{Wolf} [\eta]^{\bullet}}{1 + Bc[\eta]_{Wolf}} \tag{2}$$

The new parameters included in this equation are the hydrodynamic interaction parameter, (B) and specific hydrodynamic volume $[\eta]^{\bullet}$.

Additionaly, in order to evaluate all specific interactions for studied systems, the knowledge of the Gibbs free energy (Equation 3) [12] is necessary. The association constants (

$\sigma_{11}, \sigma_{12}, \eta_{12}, \sigma_{13}, \eta_{13}$) - evaluated by the mathematical simulations - correct the binary interaction parameters, g_{ij}'.

$$\left(\frac{\Delta G}{RT}\right)_{Ter} = \phi_1 \ln\left(\frac{Y + X - \left[X^2 + 2XY\right]^{1/2}}{\phi_1\left[2\sigma_{11} + 1 - \left(1 + 4\sigma_{11}\right)^{1/2}\right]}\right) + s\phi_2 \ln\left(\phi_2 \frac{1 - \sigma_{12}P_1}{1 - (\sigma_{12} - \eta_{12})P_1}\right) + \tag{3}$$

$$r\phi_3 \ln\left(\phi_3 \frac{1 - \sigma_{13}P_1}{1 - (\sigma_{13} - \eta_{13})P_1}\right)^m - \frac{P_1}{1 - \sigma_{11}P_1} +$$

$$\phi_1\left(\frac{2\sigma_{11} + 1 - (1 + 4\sigma_{11})^{1/2}}{\sigma_{11}(1 + 4\sigma_{11})^{1/2} - \sigma_{11}}\right) + \phi_1\phi_2 g_{12}' + \phi_1\phi_3 g_{13}' + \phi_2\phi_3 g_{23}'$$

Results and discussion

The obtained results from the dilute solution study (intrinsic viscosity, $\lfloor\eta\rfloor$, listed in Table 1) for the polyelectrolyte/neutral polymer/solvent multicomponent systems (PSFQ/PVA/NMP and PSFQ/CAP/NMP) indicate the balance between the forces acting in these polymeric complex systems, as well as the cumulative effects of the thermodynamic and/or hydrodynamic interactions between the polymers.

Table 1. Viscometer parameters evaluated for the multicomponent systems PSFQ/CAP/NMP and PSFQ/PVA/NMP at 25 °C

System	φ_1	$\lfloor\eta\rfloor$ (dL/g)	$\lfloor\eta\rfloor^\bullet$ (dL/g)	B
PSFQ/CAP/NMP	1	6.496	0.671	1.490
	0.75	2.473	0.204	0.655
	0.5	1.720	0.192	-1.049
	0.25	1.418	0.140	-0.138
	0	0.715	0	0.225
PSFQ/PVA/NMP	1	6.496	0.671	1.490
	0.75	1.758	0.141	0.774
	0.5	1.205	0	0.658
	0.25	0.961	0	0.611
	0	0.653	0	0.236

Higher values of the viscosity appear as results of the electrostatic repulsion between charge groups and/or intermolecular associations, while small values are determined by the intramolecular associations. Moreover, the structural characteristics of each of the polymer, their mixing ratio, as well as the nature of the used solvent have a major role in generating new type of interactions with impact on the viscometric behavior. Therefore, it can be concluded that the characteristics of the polymers are those that limit the range of solubility and therefore, the viscometric behavior.

Typically, the occurrence of any type of interaction involving hydrogen-bonding, ion-ion pairing, electron-donor, donor-acceptor, dipole-dipole etc., determines a suitable enthalpy which implies a good blending of the constituents. Particularly, the conformational aspects of the mixtures are determined by the hydrogen-bonding and electrostatic interactions presence in the system, and evaluated by the hydrodynamic interaction parameter, B. Thus, it is

observed from Table 1 that, value of B parameter attains a maximum for PSFQ and decrease with at addition of uncharged polymers, CAP and PVA. A poor interaction between the polymer coils and the solvent appears for 50/50 and 25/75 (v/v) PSFQ/CAP mixtures, where B corresponds to negative values. This condition suggests an aggregation tendency as a result of hydrogen bonding formation.

For complete description of the possible specific interactions esthablished in ternary systems, *i.e.,* the electrostatic interactions induced by the ionic groups of the PSFQ structure, disperse interaction, and hydrogen bonding that can generate the association phenomena - CAP or/and PVA, evaluation of the Gibbs free energy (Equation 3) is imposed. Based on the association constants, calculated function of system composition by mathematical simulation (Figure 1), the excess functions, corrected binary interaction parameters and implicitly, the Gibbs free energy were determined.
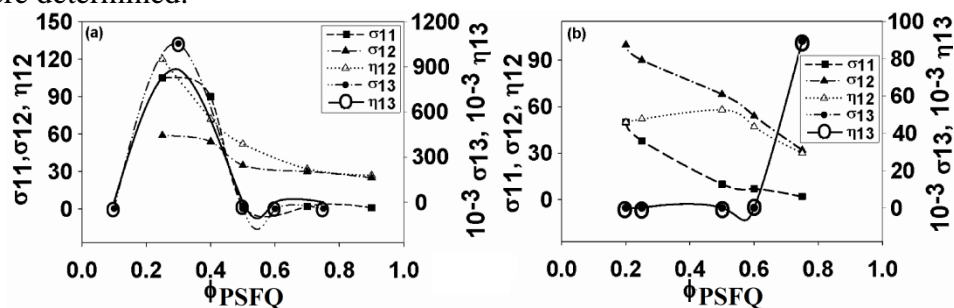

Figure 1. Interaction constants evaluated by mathematical simulations for: (a) PSFQ/CAP/NMP and (b) PSFQ/PVA/NMP multicomponents systems

The polyeletrolyte effect is due to the polyion chain expansion which leads to an progressive intensification of the ionizable groups dissociation. From this reason, the repulsive intermolecular interactions between the ionized groups (*i.e.* ammonium groups attached to the polymer chain) are enhanced. This effect, a result of electrostatic interactions and steric hindrance leads to an increase in long-distance interactions.

Conclusion

Thermodynamic and hydrodynamic properties of polysulfone/neutral polymer/solvent complex ternary systems have been discussed in terms of the chemical structure of compounds, charged groups density, and polymer mixtures composition, by viscometric measurements and Wolf method ($\left[\eta\right]$, B). Also, for a good understanding of the specific interactions from the systems, the Gibbs free energy with corresponding association constants specific to each equilibrium ($\sigma_{11}, \sigma_{12}, \eta_{12}, \sigma_{13}, \eta_{13}$) were evaluated. Consequently, this investigation represents a new contribution to understanding the behavior of polyelectrolyte solutions, which is needed in order to obtain membranes for different applications.

References
[1] J. Barzin, S. S. Madaeni, H. Mirzadeh, M. Mehrabzadeh, J. Appl. Polym. Sci. 92 (2004) 3804.
[2] A. Filimon, E. Avram, S. Ioan, J. Macromol. Sci.: Part B – Phys. 46 (2007) 503.
[3] R. Guan, H. Zou, D. Lu, C. Gong, Y. Liu, Eur. Polym. J. 41 (2005) 1554.
[4] A. Filimon, E. Avram, S. Dunca, I. Stoica, S. Ioan, J. Appl. Polym. Sci. 112 (2009) 1808.
[5] H. Yu, Y. Huang, H. Ying, C. Xiao, Carbohydr. Polym. 69 (2007) 29.

[6] S. Cheng, F. L. Beyer, B. D. Mather, R. B. Moore, T. E. Long, Macromolecules 44 (2011) 6509.

[7] A. Sabetghadam, T. Mohammadi, Polym. Eng. Sci. 50 (2010) 2392.

[8] M.Ö. Arsalan, Measurments and Modeling of Thermodynamic and Kinetic Data of Membrane-Forming Systems, Master Thesis, Izmir, 2007.

[9] A. Filimon, A.M. Dobos, E. Avram, S. Ioan, Pure Appl. Chem. 86 (2014) 1871.

[10] M.L. Huggins, J. Am. Chem. Soc. 64 (1942) 2716.

[11] B.A. Wolf, Macromol. Rapid Commun. 28 (2007) 164.

[12] R. Garcia-Lopera, I.S. Monzo, C. Abad, A. Campos, Eur. Polym. J. 43 (2007) 23.