

ASSOCIATION PHENOMENA IN QUATERNIZED POLYSULFONES/SOLVENT/NONSOLVENT SYSTEMS

Filimon A. *, Albu R.M., Avram E. and Ioan S.
Department of Physical Chemistry,
“Petru Poni” Institute of Macromolecular Chemistry,
Iasi, 700487,
Romania
E-mail: afilimon@icmpp.ro

ABSTRACT

Theoretical and experimental aspects on association phenomena generated by hydrogen bonding, dispersive and electrostatic interactions in ternary systems consisting of a proton-donor solvent (N,N-dimethylformamide or methanol), a proton-acceptor solvent (water), and a proton-acceptor polymer (polysulfone with different alkyl side chains), are investigated. In this context, binary and ternary thermodynamic interaction parameters are corrected on the basis of different association constants. Numerical values for these constants were evaluated as a function of the system composition, by mathematical simulations. As a result, mathematical simulations allow a good theoretical description of the preferential adsorption in agreement with experimental data.

INTRODUCTION

Polysulfones (PSF) and their derivatives were widely used as new functional materials in biochemical, industrial and medical fields, due to their structure and physical characteristics, such as good optical properties, high thermal and chemical stability, mechanical strength, resistance to extreme pH values and low creep [1]. These are noncrystalline polymers; their chain rigidity is derived from the relatively inflexible and immobile phenyl and SO₂ groups, whereas their toughness is derived from the connecting ether oxygen [2].

The polysulfone can be modified, to improve its performance for specific applications [3], by chloromethylation, a reaction of considerable interest from both theoretical and practical points of view, such as obtaining of precursors for functional membranes, coatings, ion exchange resins, ion exchange fibers and selectively permeable membranes [2]. Also, quaternization of chloromethylene groups with tertiary amines is an efficient method for obtaining charged polysulfones, which can be used in various applications, e.g., as biomaterials and semipermeable membranes. Their properties in solvent mixtures are strongly affected by the charge density of the ammonium groups. The polyelectrolyte effect is detected when charge density per

macromolecule reaches a critical value in terms of quaternization degree or molar mass [4].

The theoretical treatment of the excluded volume parameters and of preferential adsorption of one solvent component in polymer/solvent/solvent systems is performed according to the thermodynamic theory [5-7]. Generally, the theoretical values of the preferential adsorption coefficient in systems with specific interactions, such as hydrogen bonding, differ from the experimental data. The last researches [8,9] underlined the importance of association phenomena in theoretical evaluation of interaction parameters and elaborated the mathematical correction of preferential adsorption by means of a theory based on multiple association equilibria. In this context, some previous publications [10-12] studied the association phenomena between polar groups in ternary systems quaternized polysulfones with N,N-dimethylethanolamine (PSFQ)/N,N-dimethylformamide (DMF)/water, and PSFQ/methanol (MeOH)/water, with characteristics of proton-acceptor/proton-donor/proton-acceptor. Introduction of the association constants in the excess functions of binary interaction parameters led to a good agreement between the theoretical and experimental data of preferential adsorption.

The present study evaluates the influence of quaternized polysulfones with N,N-dimethylethylamine (PSF-DMEA) or N,N-dimethyloctylamine (PSF-DMOA), having proton-acceptor characteristics, and of mixed solvents, DMF (proton-donor solvent)/MeOH (proton-donor solvent) or DMF (proton-donor solvent)/water (proton-acceptor solvent), on the binary and ternary thermodynamic interaction parameters. Thus, the mathematical evaluation of preferential adsorption was based on the association equilibria theory developed for neutral polymers [8,9]. This investigation represents a new trend to understanding the behaviour of polyelectrolyte compounds.

NOMENCLATURE

Cl_i	[%]	Ionic chlorine content
Cl_t	[%]	Total ionic chlorine content
$(dn/dc)_u$	[cm ³ /g]	Refractive index increment of the polymer in

$(dn/dc)_\mu$	[cm ³ /g]	solvent mixture before establishing dialysis equilibrium
$dn_0/d\phi_1$	[-]	Refractive index increment of the polymer in solvent mixture after establishing dialysis equilibrium
g_{12}	[-]	Variation of the refractive index increment of the solvent mixture
g_{13}	[-]	Solvent (1) - solvent (2) interaction parameter
g_{23}	[-]	Polymer (3) - solvent (1) interaction parameter
g_T	[-]	Polymer (3) - solvent (2) interaction parameter
m_0	[-]	Ternary interaction parameter
M_n	[g/mol]	Molecular weight of the structural unit
n_0	[-]	Number-average molecular weight
R	[kJ/mol·K]	Refractive index of the solvent mixture
s	[-]	Gas constant
T	[K]	Molar volume ratio of solvents
v_3	[cm ³]	Temperature
V_1	[cm ³]	Partial specific volume of polymer
$x_{1,2}$	[-]	Molar volumes of solvent (1)
		Mole fraction of the solvent mixtures
Special characters		
χ_{12}	[-]	Solvent (1) - solvent (2) interaction parameter
χ_{13}	[-]	Polymer (3) - solvent (1) interaction parameter
χ_{23}	[-]	Polymer (3) - solvent (2) interaction parameter
χ_T	[-]	Ternary interaction parameter
$\delta_{1,2}$	[(J/cm ³) ^{1/2}]	Solubility parameters of solvents
δ_3	[(J/cm ³) ^{1/2}]	Solubility parameters of polymers
ϕ_1, ϕ_2	[-]	Volume fraction of solvent (1) and (2)
λ_1	[-]	Preferential adsorption coefficient

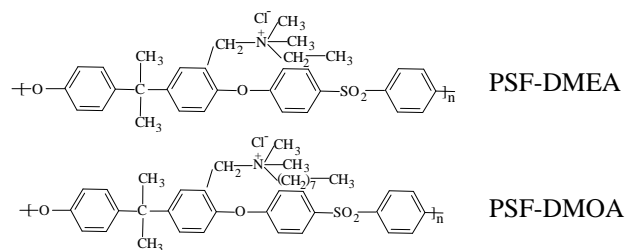
EXPERIMENTAL

Polysulfones with different alkyl side groups, PSF-DMEA and PSF-DMOA, were synthesized by reacting chloromethylated polysulfone (CMPSF) with different tertiary amines - N,N-dimethylethylamine (DMEA) and N,N-dimethyloctylamine (DMOA), respectively. The quaternization reaction was performed in DMF, at a CMPSF/tertiary amine molar ratio of 1:1.5, for 24 h. The quaternary polymers were isolated from the reaction medium by precipitation in diethylether, washed three times with diethylether, and dried for 48 h under vacuum, at room temperature. The characteristics of the obtained quaternized polysulfones are listed in Table 1. The general chemical structures of the quaternized polysulfones are presented in Scheme 1.

The preferential adsorption coefficients, λ_1 , were directly accessible from the experiments through interferometry (on a Zeiss interferometer) at 25°C and dialysis equilibrium. Equilibrium dialysis experiments of PSF-DMEA (3) or PSF-DMOA (3) in DMF (1)/MeOH (2) and DMF (1)/water (2) solvent mixtures were carried out in a dialyser with a total volume of about 15 mL. Before use, the semipermeable cellophane membranes (ZelluTrans/Roth V-Series with MWCO (molecular weight cutoffs) of 5000 and of 25 lm thick) were conditioned in each solvent mixture. Dialysis equilibrium was attained within 6 h, after which the refractive index increments of the dialyzed solution remained constant. The preferential adsorption coefficients were also determined from theoretical approximations.

Table 1 Ionic chlorine content, total ionic chlorine content, molecular weight of the structural units, and number-average molecular weight, of polysulfones with different alkyl side groups

Sample	Cl_i	Cl_t	m_0	M_n
PSF-DMEA	2.89	3.10	551.7	49,000
PSF-DMOA	3.23	3.29	627.3	55,800



Scheme 1 General chemical structures of polysulfones with quaternary ammonium groups

RESULTS AND DISCUSSION

Experimental results of the preferential adsorption coefficients

Figure 1 illustrates the variation of the preferential adsorption coefficient, λ_1 , with the DMF content, for PSF-DMEA and PSF-DMOA in DMF (1)/MeOH (2) and DMF (1)/water (2) binary mixtures, respectively, as experimentally determined from refractive index increments, both before $(dn/dc)_u$ and after $(dn/dc)_\mu$ establishing dialysis equilibrium (Table 2), from equation (1).

$$\lambda_1 = \frac{(dn/dc)_\mu - (dn/dc)_u}{dn_0/d\phi_1} \quad (1)$$

The values of $dn_0/d\phi_1$ for DMF/MeOH and DMF/water systems, obtained from the derivatives of the linear dependencies expressed by equations (2) and (3) [13], are also listed in Table 2.

$$n_0 = 1.328 + 0.101\phi_1 \quad (2)$$

$$n_0 = 1.333 + 0.096\phi_1 \quad (3)$$

In these systems, the experimental results indicate that preferential adsorption is influenced by the alkyl chain length of the charged groups attached to the polymer backbone, as well as by the solvent mixture. Thus, for PSF-DMEA with a low number of carbon atoms, the “synergistic effect” appears in the DMF/MeOH solvent mixture [14]. According to the presented data, negative values of the preferential adsorption coefficient over the composition range indicate the preferential adsorption of MeOH (Figure 1a).

Table 2 Specific refractive index increments prior to and after attainment of dialysis equilibrium for polysulfones with quaternary groups in binary solvent mixtures DMF (1)/MeOH (2) and DMF (1)/water (2), as a function of the DMF content, and refractive index increments of the solvent mixtures

System	ϕ_1	$(dn/dc)_u$	$(dn/dc)_\mu$	$dn_0/d\phi_1$
PSF-DMEA/ DMF/MeOH	0.75	0.106	0.096	0.101
	0.25	0.199	0.253	0.101
PSF-DMEA/ DMF/water	0.75	0.143	0.161	0.096
	0.25	0.217	0.206	0.096
PSF-DMOA/ DMF/MeOH	0.75	0.194	0.162	0.101
	0.25	0.157	0.064	0.101
PSF-DMOA/ DMF/water	0.75	0.077	0.067	0.096
	0.60	0.189	0.163	0.096
	0.50	0.199	0.138	0.096

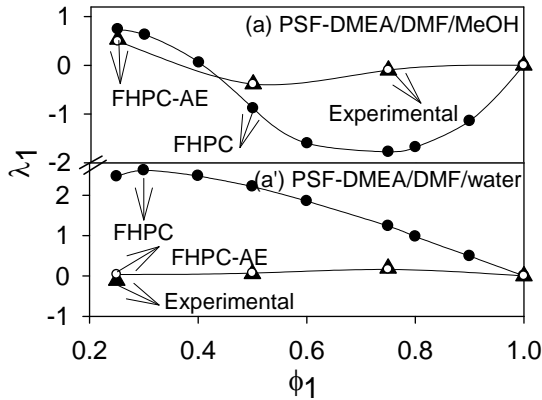


Figure 1 Influence of the DMF volume fraction on the theoretical (FHPC and FHPC-AE models) and experimental values of the preferential adsorption coefficient: (a) – PSF-DMEA/DMF/MeOH; (a') – PSF-DMEA/DMF/water at 25 °C

In addition, for PSF-DMEA in the DMF/water solvent mixture, λ_1 presents positive values, meaning the preferential adsorption of DMF over the 0.5 – 1 composition domain (Figure 1a'); the preferential adsorption of water (non-solvent) appears only at a minimum content of DMF.

On the other hand, the PSF-DMOA, with a higher number of carbon atoms, addition of MeOH or of water as non-solvents leads to a continuous decrease of λ_1 (Figures 2a and a'). Therefore, the polymer chains exhibit the tendency to surround themselves with the thermodynamically most efficient solvent, at a given composition of the solvent mixture. This behavior is perturbed by the weak polyelectrolyte character of the studied polysulfones with quaternary groups and by the specific interactions established among the components of the complex polymeric systems.

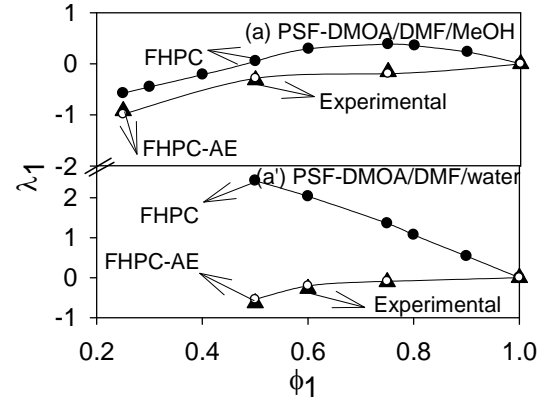


Figure 2 Influence of the DMF volume fraction on the theoretical (FHPC and FHPC-AE models) and experimental values of the preferential adsorption coefficient: (a) – PSF-DMOA/DMF/MeOH; (a') – PSF-DMOA/DMF/water at 25 °C

Theoretical interpretation of the preferential adsorption coefficients

For understanding and knowledge the all interactions from polyelectrolyte systems in solution, the theoretical values of the preferential adsorption coefficients (Figures 1 and 2) were calculated according to the Flory-Huggins-Pouchly model (FHPC) from equations (4)-(6):

$$\lambda_1 = -v_3 \frac{M_{13}}{M_{11}} \quad (4)$$

$$M_{11} = \frac{RT}{V_1} \left(\frac{1}{\phi_1} + \frac{s}{\phi_2} + \frac{\partial^2(\phi_1\phi_2g_{12})}{\partial\phi_1^2} \right) \quad (5)$$

$$M_{13} = \frac{RT}{V_1} \left(s - I + g_{13} - sg_{23} - \frac{\partial(\phi_1\phi_2(g_{12} - g_T))}{\partial\phi_1} \right) \quad (6)$$

To determine the theoretical preferential adsorption coefficients, evaluation of the solvent-solvent interaction parameters, g_{12} , of the polymer-solvent interaction parameters, g_{i3} , and χ_{i3} , (where subscript $i = 1$ refers to DMF, while subscript $i = 2$ refers to MeOH or water, and subscript 3 refers to the polymer), and of the ternary interaction parameters, g_T and χ_T , is necessary.

The solvent-solvent interaction parameters, g_{12} , were determined by Flory-Huggins equation (7) [15] and quaternized polysulfone-solvent interaction parameters, χ_{i3} , were calculated considering the entropic and enthalpic contributions (equation (8)) [16].

$$g_{12} = \left(\frac{G^E}{RT} + x_1 \ln \left(\frac{x_1}{\phi_1} \right) + x_2 \left(\frac{x_2}{\phi_2} \right) \right) \frac{1}{x_1\phi_2} \quad (7)$$

$$\chi_{i3} = \frac{V_1}{RT} (\delta_{1,2} - \delta_3)^2 + 0.34 \quad (8)$$

Also, the quaternized polysulfone-solvent interaction parameters, g_{i3} , was calculated from equation (9), with the coordination number of lattice $z = 8$:

$$\chi_{i3} = \left(1 - \frac{2}{z}\right) g_{i3} \quad (9)$$

Thus, the values obtained for the polymer-solvent interaction parameters are presented in Table 3.

Table 3 Polymer-solvent binary interaction parameters

Ternary system	χ_{13}	χ_{23}	g_{13}	g_{23}
PSF-DMEA(3)/ DMF(1)/MeOH(2)	0.661	1.395	0.881	1.860
PSF-DMEA(3)/ DMF(1)/water(2)	0.661	5.459	0.881	7.279
PSF-DMOA(3)/ DMF(1)/MeOH(2)	0.783	1.547	1.044	2.063
PSF-DMOA(3)/ DMF(1)/water(2)	0.783	5.685	1.044	7.580

In equations (4)-(6), there appears the ternary interaction parameters defined as:

$$g_T(\varphi_1) = a_g g_{12}(\varphi_1) \quad (10)$$

$$\chi_T(\varphi_1) = a_\chi g_{12}(\varphi_1) \quad (11)$$

$$a_g = \frac{g_{13}g_{23}}{1-D} \quad (12)$$

$$a_\chi = \frac{2g_{13}g_{23} - D}{2(1-D)} \quad (13)$$

$$D = g_{13}(g_{23} - \chi_{23}) + g_{23}(g_{13} - \chi_{13}) \quad (14)$$

The values of the ternary interaction parameters were calculated from equations (10) and (11), with a_g and a_χ coefficients from equations (12)-(14), according to FHPC model. The obtained results are listed in Table 4.

According to Figures 1 and 2, the experimental results are not fitted by the FHPC model. Important deviations appear in the theoretical data, due to the electrostatic interactions which are neglected in the calculation of the binary interaction parameters, g_{i3} , and χ_{i3} , and also due to some association phenomena, which influence the interaction parameters g_{12} .

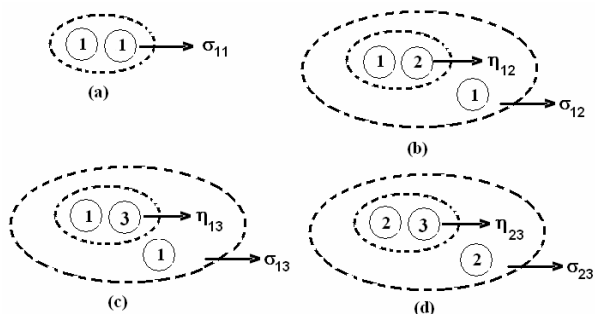
Table 4 Theoretical values of ternary interaction parameters according to the FHPC model

System	φ_1	g_T	χ_T
PSF-DMEA/ DMF/MeOH	0.2	0.719	0.629
	0.5	0.609	0.533
	0.7	0.165	0.144
PSF-DMEA/ DMF/water	1	-0.828	-0.725
	0.2	-2.225	-1.668
	0.5	-1.806	-1.354
PSF-DMEA/ DMF/water	0.7	-1.622	-1.282
	1	-1.453	-1.090
	0.2	0.944	0.826
PSF-DMOA/ DMF/MeOH	0.5	0.800	0.700
	0.7	0.215	0.189
	1	-1.088	-0.952
PSF-DMOA/ DMF/water	0.5	-1.663	-1.247
	0.6	-1.574	-1.181
	0.7	-1.494	-1.120
	1	-1.338	-1.004

From this reason, below is considered a new approximation concerning the theoretical evaluation of preferential adsorption on the basis of multiple association equilibria (FHPC-AE), applied in literature only for neutral polymers [8,9]. In this context, was established that the possible specific interactions, such as hydrogen bonding and dispersive interactions from ternary systems, and also the electrostatic interactions induced by the ionic groups from polymeric structure, generate association phenomena. Consequently, the different association constants were considered for the correction of g_{12} , g_{13} , g_{23} and g_T :

- σ_{11} - obtained by self-association of solvent (1) molecules (Scheme 2a);
- η_{12} - obtained by inter-association of solvent (1) molecules with solvent (2) molecules, leading to 1-2 complex (Scheme 2b);
- σ_{12} - obtained by association of the free molecules of solvent (1) to the 1-2 afore-mentioned complex (Scheme 2b);
- η_{13} - obtained by inter-association of solvent (1) molecules with segments of the polymer chain (3), leading to 1-3 complex (Scheme 2c);
- σ_{13} - obtained by association of the free molecules of solvent (1) to the 1-3 afore-mentioned complex (Scheme 2c);
- η_{23} - obtained by inter-association of solvent (2) molecules with polymer chain segment (3), leading to 2-3 complex (Scheme 2d);
- σ_{23} - obtained by association of the free molecules of solvent (2) to the 2-3 afore-mentioned complex (Scheme 2d).

Thus, Gibbs free energy (ΔG) of the total process, and, implicitly, preferential adsorption coefficients (λ_i) are corrected on the basis of these association constants.



Scheme 2 Graphical representation of molecular associations defined by association constants, where 1 is solvent (1) (DMF), 2 is solvent (2) (MeOH or water) and 3 is polymer (3) (PSF-DMEA or PSF-DMOA)

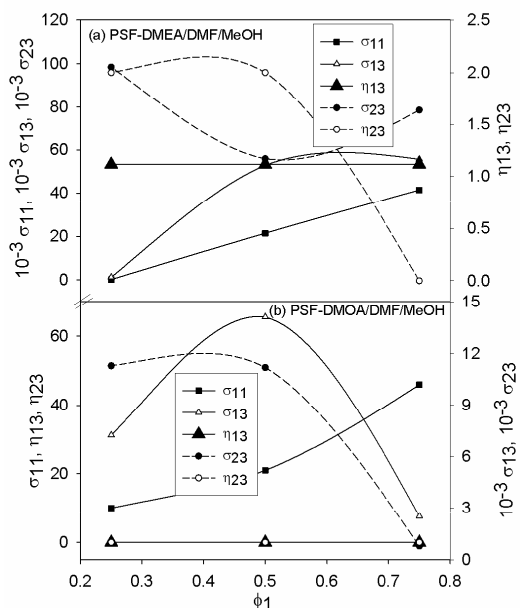


Figure 3 Association constants giving the minimum deviation between the theoretical and experimental values for the preferential adsorption coefficient, calculated according to the association equilibria theory for:

- (a) PSF-DMEA (proton-acceptor)/DMF (proton-donor)/MeOH (proton-donor) and
 (b) PSF-DMOA (proton-acceptor)/DMF (proton-donor)/MeOH (proton-donor) systems

Figures 3 and 4 present association constants determined by mathematical simulation, as best adjusted parameters to the predicted values of preferential adsorption from the FHPC model. Thus, Figures 3a and b illustrate the association phenomena, generated by hydrogen bonding, dispersive interactions and electrostatic interactions, from PSF-DMEA/DMF/MeOH and PSF-DMOA/DMF/MeOH ternary systems by the σ_{11} , σ_{13} , σ_{23} , η_{13} , η_{23} constants, as a function of the composition of solvent mixtures. Examination of Figures 3a and b reveals that:

- $\sigma_{12} = 0$ and $\eta_{12} = 0$, because both solvents are proton-donor species;
- addition of DMF to MeOH leads to self-association and to an increased hydrogen bonding between (1)-(1) components (Figure 3a and b). In addition, dispersive interactions occur due to the association of molecules from solvent (1);

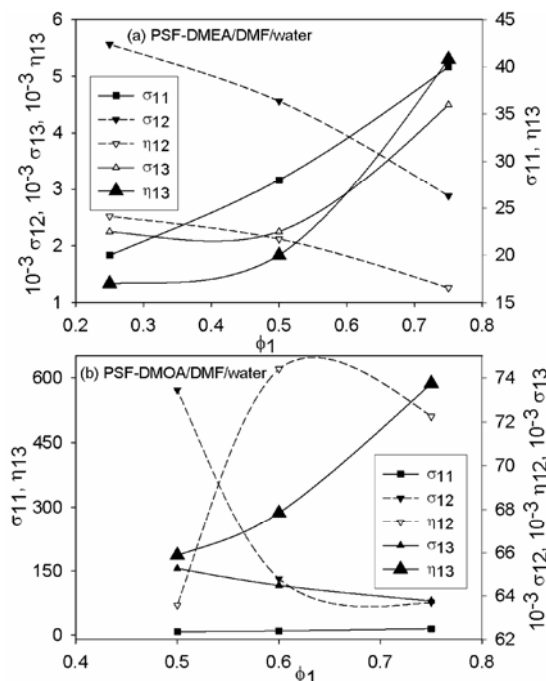


Figure 4 Association constants giving the minimum deviation between the theoretical and experimental values for the preferential adsorption coefficient, calculated according to the association equilibria theory for:

- (a) PSF-DMEA (proton-acceptor)/DMF (proton-donor)/water (proton-acceptor) and
 (b) PSF-DMOA (proton-acceptor)/DMF (proton-donor)/water (proton-acceptor) systems

- for the PSF-DMEA/DMF/MeOH system, the electrostatic interactions influenced significantly σ_{13} , σ_{23} , η_{23} constants and insignificantly the η_{13} constant (Figure 3a), while for the PSF-DMOA/DMF/MeOH system, the influence is significant for σ_{13} , σ_{23} and insignificant for the η_{13} , η_{23} constants (Figure 3b).

Figures 4a and b depict the association constants from PSF-DMEA/DMF/water and PSF-DMOA/DMF/water systems, where:

- in the absence of polymer, the DMF molecules may exhibit hydrogen bonding interactions with the coexistent water associations, and dispersive interactions. These interactions are caused by charge fluctuations that occur throughout a molecule through electron/nuclei vibrations. For a low DMF content, isolated associations, represented by DMF-water associations, and self-associations of water appear, while for a higher DMF

content, the association structure is obviously reorganized, and DMF self-association is remarkably promoted;

- σ_{13} and η_{13} increase with increasing the DMF content (Figures 4a and b), being influenced by the presence of the polymer;

- $\eta_{23} = 0$ and $\sigma_{23} = 0$ due to the weak dispersive and electrostatic interactions, without the hydrogen bonding between components (2) and (3).

In finally, Figures 1a, a', and 2a, a' show that the preferential adsorption coefficients calculated with these evaluations satisfactorily verified the experimental data.

CONCLUSION

Modification of the preferential adsorption coefficients in ternary systems formed of PSF-DMEA or PSF-DMOA (with a different number of carbon atoms present in the alkyl groups) and DMF/MeOH or DMF/water solvent mixtures, characterized by proton-acceptor (polymer), proton-donor (solvent) and proton-acceptor (solvent), was investigated. The occurrence of association phenomena was quantified by insertion of some association constants, which modified the Gibbs free energy of the total process, and implicitly, the binary and ternary interaction parameters from the system. The association phenomena are caused by the dispersive, electrostatic and hydrogen bonding interactions.

For the studied systems, the results reveal that:

- the experimental data of preferential adsorption are different from the theoretical values determined by the FHPC model. Deviations of the theoretical data are caused by neglect of electrostatic interactions and association phenomena, in the calculation of the interaction parameters;
- the FHPC-AE model, which introduces the association phenomena in theoretical approximation of interaction parameters, predicts well the preferential adsorption coefficient of a polymer with ionic groups in mixed solvents.

This investigation represents a new contribution to understanding the behaviour of polyelectrolyte solutions, in order to obtain the membranes from solutions with different applications.

REFERENCES

[1] Barikani, M., and Mehdipour-Ataei S., Synthesis, characterization and thermal properties of novel arylene sulfone ether polyimides and polyamides, *Journal of Polymer Science, Part A: Polymer Chemistry*, 2000, Vol. 38, pp. 1487-1492

[2] Tomaszewska, M., Jarosiewicz, A., and Karakulski, K., Physical and chemical characteristics of polymer coatings in CRF Formulation, *Desalination*, 2002, Vol. 146, pp. 319-323

[3] Khang, G., Lee, H.B., and Park, J.B., Biocompatibility of polysulfone. I. Surface modifications and characterizations, *Bio-Medical Materials and Engineering*, 1995, Vol. 5, pp. 245-258

[4] Ydens, I., Moins, S., Degée, P., and Dubois, P., Solution properties of well-defined 2-(dimethylamino)ethyl methacrylate-based (co)polymers: A viscometric approach, *European Polymer Journal*, Vol. 41, 2005, pp.1502-1509

[5] Campos, A., Gavara, R., Tejero, R., Gomez, C., and Celda, B., A Flory-Huggins thermodynamic approach for predicting sorption equilibrium in ternary polymer system, *Journal of Polymer Science Polymer Physics Edition*, 1989, Vol. 27, pp. 1559-1597

[6] Celda, B., Campos, A., Gavara, R., and Figueruelo, J.E., Quantitative relationship between total and preferential sorption coefficients in polymer cosolvent systems, *Polymer*, 1986, Vol. 27, pp. 1247-1253

[7] Campos, A., Gavara, R., Tejero, R., Gomez, C., and Celda, B., A procedure for predicting sorption equilibrium in ternary polymer systems from Flory-Huggins binary interaction parameters and the inversion point of preferential solvation, *Journal of Polymer Science Polymer Physics Edition*, 1989, Vol. 27, pp. 1599-1610

[8] Soria, V., Figueruelo, J.E., Abad, C., and Campos, A., Association equilibria theory for polymers in mixed solvents with specific interactions, *Macromolecular Theory and Simulations* 2004, Vol. 13, pp. 441-452

[9] Garcia-Lopera, R., Monzo, I.S., Abad, C., and Campos, A., A thermodynamic approach to study hydrogen-bonding interactions in solvent/solvent/polymer ternary systems, *European Polymer Journal*, 2007, Vol. 43, pp. 231-242

[10] Filimon, A., Avram, E., and Ioan, S., Influence of mixed solvents and temperature on the solution properties of quaternized polysulfones, *Journal of Macromolecular Science, Part B: Physics*, 2007, Vol. 46, pp. 503-520

[11] Ioan, S., Filimon, A., and Avram, E., Conformation and viscometric behavior of quaternized polysulfone in dilute solution, *Polymer Engineering Science*, 2006, Vol. 46, pp. 827-836

[12] Filimon, A., Avram, E., and Ioan, S., Specific interactions in ternary system quaternized polysulfone/mixed solvent, *Polymer Engineering Science*, 2009, Vol. 49, pp. 17-25

[13] Gooda, S.R., and Huglin M.B., Preferential adsorption and viscometric behaviour of poly(2-acrylamido-2-methyl propane sulphonamide) in formamide/water mixtures, *European Polymer Journal*, 1993, Vol. 29, pp. 365-369

[14] Simionescu, C.I., Ioan, S., Bercea, M., Mitu, N., and Simionescu, B.C., High molecular weight polystyrene in solvent mixtures. Preferential and total adsorption, *European Polymer Journal*, 1993 Vol. 29, pp. 183-191

[15] Horta, A., Radic, D., and Gargallo, L., Association equilibria theory of preferential adsorption in systems with solvent-solvent and solvent-polymer interactions, *Macromolecules*, 1989, Vol. 22, pp. 4267-4272

[16] Grulke, E.A., Solubility parameter value. In: *Polymer Handbook*, 4th edition, Brandrup, J., and Immergut E. H., editors, New York: J Wiley & Sons, 1999, VII, pp. 675