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Influence of Copolymer Molar Mass on the Thermodynamic Properties of Aqueous Solution of an Amphiphilic Copolymer

Masumeh Foroutan* and Marmar Haghighi Khomami

Department of Physical Chemistry, Faculty of Chemistry, College of Science, University of Tehran, Tehran, Iran

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The osmotic coefficients and water activities in binary solutions of water-soluble DMAM−TBAM copolymer (the abbreviation for *N*,*N*-dimethylacrylamide and *t*-butylacrylamide copolymer) with different molar masses were determined by isopiestic method using NaCl(aq) as the reference standard at 308.15 K. From these measurements, values of the vapor pressure of solutions were determined, and the effect of molar mass on the vapor−liquid equilibrium of DMAM−TBAM copolymer has been studied. The experimental water activities data have been correlated using the Flory−Huggins equation, the modified Flory−Huggins equation, and the Freed Flory−Huggins equation + the nonrandom two-liquid model (NRTL). Better agreement with the experimental data was obtained using the Freed Flory−Huggins equation + NRTL model.

Introduction

Hydrophobic associating polymers are synthetic water-soluble polymers that contain a small proportion of hydrophobic groups, usually in the form of pendent side chains or terminal groups, which are of increasing interest for a wide variety of industrial applications such as flocculants, thickening agents in oil recovery, latex paints, and cosmetics because of the advantage of both the polyelectrolyte and hydrophobic groups effect.[1−6]

It has been shown that changing the chemical structure of a copolymer may bring about considerable attention to their thermodynamics properties. Recently, Csaki et al. studied the effect of the chain composition on the water activity of binary polymer solution.[7] They regulated the hydrophilic/hydrophobic character of the polyvinyl alcohol-based macromolecules by changing the chemical structure of copolymers (acetal content, length of side chains, or both). They have investigated how the alterations in the chemical structure of the dissolved copolymers are reflected in the relevant pair interaction parameters and in the compatibility of chemically different polymers in solution. Recently, ionic interactions in aqueous ionic solution with hydrophobic species have been described by Kumar et al.[8] They have estimated the binary, ternary, and quaternary interactions in aqueous ionic mixtures with uncommon ions with hydrophobic character including NaCl with four guanidinium salts using the isopiestic osmotic coefficient.

In the present work, at first, a series of DMAM−TBAM copolymers with the same hydrophobic/hydrophilic character but different molar mass were synthesized, and then, the isopiestic method was used to obtain activities of water for aqueous solutions of DMAM−TBAM copolymer. DMAM−TBAM copolymer contains two parts: a water-soluble hydrophilic monomer, *N*,*N*-dimmethylacrylamide (DMAM), and a water-insoluble hydrophobic monomer, *t*-butylacrylamide (TBAM). It has been shown that DMAM−TBAM copolymer is a hydrophobic associating water-soluble copolymer and because of this importance, it has been chosen. A detailed description of this copolymer is given elsewhere.[9]

Table 1. Copolymerization Condition for DMAM−TBAM Copolymers

copolymer	DMAM mL	TBAM g	solvent mL	AIBN g	time h
A	18.54	7.90	500	0.20	20.00
B	21.63	8.90	583	0.30	48.00
C	16.72	6.90	450	0.16	36.00

From the obtained water activity data, the vapor pressures and osmotic coefficients of solutions have been determined. Furthermore, the Flory−Huggins equation, the modified Flory−Huggins equation, and the Freed Flory−Huggins equation + NRTL have been used for correlation of the experimental water activity data.

Experimental Section

Material. *N*,*N*-Dimethylacrylamide (DMAM, 99 %) and *t*-butylacrylamide (TBAM, 97 %) were products of Aldrich and were used as received. Analytical grade tetrahydrofuran (THF, 98 %) and azobisisobutyrnitrile (AIBN, 98 %) from Fluka was purified by recrystallization from ethanol. Also, analytical grade THF (98 %) was from Fluka. Sodium chloride was obtained from Merck and dried in an oven at about 120 °C for 24 h. All chemicals were used without further purification.

Copolymerization Condition. DMAM−TBAM copolymer was synthesized through the following method. In dried two-necked flask, 18.54 mL of DMAM and 7.9 g of TBAM were added. THF was added through a septum under a nitrogen atmosphere. When the monomers were dissolved, 0.2 g AIBN was added to initiate copolymerization, and the reaction mixture was heated to 338.15 K. The copolymerization proceeded under a nitrogen atmosphere for 20 h. The product was recovered by precipitation in diethyl ether and dried under vacuum at 313.15 K for 8 h and cooled to room temperature. TO obtain three samples with different molar masses, DMAM and TBAM were copolymerized in THF with different ratios of DMAM and TBAM (monomer's ratios are 3 to 1, respectively) and initiator at different times at 338.15 K.

Table 1 shows the copolymerization condition for the synthesis of copolymers. The average molar masses of synthe-

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* Corresponding author. E-mail: foroutan@khayam.ut.ac.ir. Fax: +98 21 66495291.

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sized copolymers were measured by a GPC (Agilent, 1100 series vacuum Degasser) device, and they were equal to 1350 $g\cdot mol^{-1}$ (copolymer A), 1700 $g\cdot mol^{-1}$ (copolymer B), and 2520 $g\cdot mol^{-1}$ (copolymer C).

Apparatus and Procedures. The isopiestic method was used to obtain the activity of water in DMAM−TBAM copolymer solutions. It is based on the equilibrium between two phases, vapor and liquid. At equilibrium, the chemical potentials of the solvent in each of the solutions in the closed system are identical. The equality of the solvent chemical potential implies the equality of the solvent activity.

The isopiestic apparatus consisted of a five-legged manifold attached to round-bottomed flasks. Two flasks contained the standard NaCl(aq), two flasks contained DMAM−TBAM copolymer solution, and the central flask was used as a distilled water reservoir. Full details of isopiestic method have been previously reported.[10] The apparatus was held in a constant temperature bath for at least 120 h at 308.15 K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with a high precision (± 0.00001 g) analytical balance (Sartorius, TE1245). It was assumed that the equilibrium condition was reached when the differences between the mass fractions of the duplicates were less than 1 %. In all cases, averages of the duplicates are reported as the total isopiestic mass fraction.

Thermodynamic Models

There are several models that describe the vapor−liquid equilibrium of polymer solutions. For the correlation of solvent activity data for polymer solutions, there are theoretical models such as Wilson,[11] Flory−Huggins[12,13] and nonrandom two liquid (NRTL).[14,15] In this work, the solvent activities for the investigated systems were correlated with the Flory−Huggins, the modified Flory−Huggins, and the Freed Flory−Huggins−NRTL.

Flory−Huggins Model. The model of Flory−Huggins is an important lattice model that has the form

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \varphi_1) + \chi_{12}(1 - \varphi_1)^2 \tag{1}$$

where a_1 and φ_1 are the activity and the volume fraction of solvent, respectively, r_2 is the number of segments of polymer defined as the molar volume of polymer divided by the molar volume of solvent, and χ_{12} is the interaction parameter between polymer and solvent.

Modified Flory−Huggins Model. In the modified Flory−Huggins model, χ_{12} has been considered to be dependent on concentration and temperature. For the concentration and temperature dependency of χ_{12}, Bae et al.[13] have suggested the following relation

$$\chi_{12}(T, \varphi) = D(T)F(\varphi_2) \tag{2}$$

with

$$D(T) = d_0 + \frac{d_1}{T} + d_2 \ln T \tag{3}$$

and

$$F(\varphi_2) = \frac{1}{1 - f\varphi_2} \tag{4}$$

where d_0, d_1, d_2, and f are adjustable parameters and φ_2 is the polymer volume fraction. χ_{12} can be expressed in terms of the solvent volume fraction, φ_1, at constant temperature using the above equations as

$$\chi_{12} = \frac{d}{1 - f(1 - \varphi_1)} \tag{5}$$

where $d = D(T)$ at a constant T.

Therefore, at a constant temperature, the modified Flory−Huggins equation proposed by Bae et al.[13] takes the following form

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \varphi_1) + \frac{d(1 - \varphi_1)^2}{1 - f(1 - \varphi_1)} \tag{6}$$

Freed Flory−Huggins Model + Nonrandom Two-Liquid Model. The activity coefficient models are often expressed as a sum of two terms: a combinatorial and a residual term.

$$\ln \gamma_k = \ln \gamma_k^{\mathrm{com}} + \gamma_k^{\mathrm{res}} \tag{7}$$

The combinatorial (com) part accounts for the entropic effects, whereas the residual (res) part accounts for the energetic interactions that exist between the solvent and the polymer. The Freed Flory−Huggins model[16] can be used as the combinatorial part. This model is the exact solution for the Flory−Huggins lattice theory.

$$\ln \gamma_1^{\mathrm{com}} = \ln \frac{\varphi_1}{x_1} + \left(1 - \frac{r_1}{r_2}\right)\varphi_2 + \alpha\left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 \varphi_2^2 \tag{8}$$

Recently, different residual terms have been studied such as UNIQUAC[17] and NRF.[18] Wu et al. proposed a modification of the NRTL model with the following form[15]

$$\ln \gamma_{\mathrm{s}}^{\mathrm{res}} = q_{\mathrm{s}} x_{\mathrm{p}}^2 \left\{ \frac{\tau_{\mathrm{ps}}(\exp(-2\alpha\tau_{\mathrm{ps}}))^2}{x_{\mathrm{s}} + x_{\mathrm{p}} \exp(-\alpha\tau_{\mathrm{ps}})^2} + \frac{\tau_{\mathrm{sp}} \exp(\alpha\tau_{\mathrm{sp}})}{[x_{\mathrm{p}} + x_{\mathrm{s}} \exp(\alpha\tau_{\mathrm{sp}})]^2} \right\} \tag{9}$$

where

$$X_i = \frac{N_i q_i}{N_q} \tag{10}$$

$$N_q = \sum\nolimits_i N_i q_i \tag{11}$$

where N_i is the number of molecules of component i and N_q is the total number of segments present in the solution mixture. q_i is the actual number of segments for species i and is usually related to r_i by

$$q_i = r_i\left(1 - 2\alpha\left(1 - \frac{1}{r_i}\right)\right) \tag{12}$$

where α is the nonrandomness factor defined in the same way as that in the original NRTL model. The value of r_i is taken as unity for the solvent, and for the polymer, it is obtained from the ratio between the polymer and solvent molar volumes.[19] Also, in this equation, there are two fitting parameters, τ_{sp} and $\tau_{\mathrm{ps.}}$ The obtained interaction parameters for the studied systems based on three equations have been presented in Tables 5 and 6.

Results and Discussion

Evaluation of Parameters of Pitzer Model for NaCl as Reference Salt at 308.15 K. The solvent activity of polymer solution (a_1) can be calculated by the following equation

$$\ln a_1 = -\nu m_{\mathrm{NaCl}} \Phi_{\mathrm{NaCl}} M_s \tag{13}$$

where ν is the sum of the stoichiometric numbers of anions and cations in the reference solutions and m_{NaCl} and M_{s} are, respectively, the substance concentration of NaCl and the relative molar mass of solvent. We need to mention that NaCl served as an isopiestic reference for this solution. Φ_{NaCl} is the osmotic coefficient of the isopiestic reference standard. It is well known that if the thermodynamics properties of a given solution are ideal, then the osmotic coefficient is unity and the difference $(\Phi - 1)$ yields an immediate indication of the extent to which the properties of a given solution are not ideal.

Parameter values for NaCl(aq) at 308.15 K and 0.1 MPa were calculated from the temperature/pressure coefficients and equations reported by Archer.[20] Archer's extended ion-interaction equation for the molality-based osmotic coefficient of a binary solution of an electrolyte may be written as

$$\phi - 1 = \left|Z_+Z_-\right| f^{\phi} + m[(2v_+v_-)/v]B^{\phi} + m^2[(2v_+v_-)^{1.5}/v]C^{\phi} \tag{14}$$

$$f^{\phi} = -A_{\phi}I^{0.5}/(1 + bI^{0.5}) \tag{15}$$

$$B^{\phi} = \beta^0 + \beta^1 \exp(-\alpha_1 I^{0.5}) \tag{16}$$

$$C^{\phi} = C^0 + C^1 \exp(-\alpha_1 I^{0.5}) \tag{17}$$

$$A_{\phi} = (1/3)(2\pi N_A d_0)^{0.5}(e^2/4\pi\varepsilon_0 D k_B T)^{1.5} \tag{18}$$

Here β^0, β^1, C^0 and C^1 are Pitzer's ion-interaction parameters obtained by fitting of experimental data. α_1, α_2, and b are adjustable parameters, and A_{ϕ} is the Debye−Hückel constant for the osmotic coefficient. Z_+ and Z_- are positive and negative ionic charges. In eq 18, N_A is Avogadro's number, e is the proton charge, ε_0 is the permittivity of vacuum, and k_B is the Boltzmann constant. The ionic strength, I, is on the molal scale. For aqueous electrolyte solutions, $b = 1.2\ \text{kg}^{0.5}\cdot\text{mol}^{-0.5}$ is used, and the quantities α_1 and α_2 are usually assigned values of 2.0 $\text{kg}^{0.5}\cdot\text{mol}^{-0.5}$ and 2.5 $\text{kg}^{0.5}\cdot\text{mol}^{-0.5}$, respectively. Four ion-interaction parameters, $\beta^0 = -28.357$, $\beta^1 = 203.58$, $C^0 = 1.779$, and $C^1 = -8.557$, were obtained for NaCl solution at 308.15 K. At the isopiestic equilibrium, the osmotic coefficient of DMAM−TBAM copolymer solutions can be obtained from the relation

$$\Phi = -\ln \frac{a_1}{x_2/x_1} \tag{19}$$

where x_1 and x_2 are the molar fraction of water and polymer, respectively. The vapor pressure of the investigated solution, p (kPa), was determined with the help of the following relation[21,22]

$$\ln a_1 = \ln \frac{P}{P^0} + [(B - V^0)(P - P^0)]/RT \tag{20}$$

where B is the second virial coefficient of water vapor,[23] V^0 is the molar volume of liquid water, and P^0 is the vapor pressure of pure water.

Experimental Results. The isopiestic equilibrium mass fractions of the reference standard solution of NaCl and aqueous solutions of DMAM−TBAM copolymers with different molar masses have been investigated at $T = 308.15$ K. It is reminded that the isopiestic equilibrium of this system can be carried out at any other temperature below its cloud point, 343.15 K. The data for the osmotic coefficients, vapor pressure, and water activity are collected in Tables 2, 3, and 4.

Figure 1 shows the measured water activity versus mass fraction of copolymer for the binary DMAM−TBAM−H_2O system at 308.15 K. As shown in this Figure, the water activity of the DMAM−TBAM−H_2O system increases with increasing the molar mass of copolymer. This means with increasing molar mass, the interaction between DMAM−TBAM copolymer and solvent decreases.

Table 2. Experimental Isopiestic Mass Fractions of Polymer (W_p) and salt (W_s), Osmotic Coefficients (Φ), Vapor Pressure, and Activities of Water for DMAM−TBAM Copolymer A at $T = 308.15$ K

W_P	W_S	a_w	p/kPa	Φ
0.45	0.16	0.82	5.59	0.001
0.47	0.18	0.74	5.58	0.20
0.49	0.21	0.72	5.57	0.31
0.51	0.23	0.62	5.56	0.53
0.53	0.26	0.54	5.55	0.74
0.54	0.31	0.51	5.51	0.83
0.57	0.32	0.38	5.51	1.25
0.58	0.34	0.32	5.49	1.48
0.60	0.38	0.24	5.45	1.83
0.62	0.41	0.17	5.41	2.26
0.64	0.43	0.15	5.38	2.48
0.67	0.46	0.11	5.33	2.88

Table 3. Experimental Isopiestic Mass Fractions of Polymer (W_p) and Salt (W_s), Osmotic Coefficients (Φ), Vapor Pressure, and Activities of Water for DMAM−TBAM Copolymer B at $T = 308.15$ K

W_P	W_S	a_w	p/kPa	Φ
0.47	0.18	0.84	5.58	0.07
0.49	0.23	0.77	5.56	0.23
0.52	0.27	0.69	5.54	0.42
0.53	0.28	0.70	5.53	0.45
0.54	0.32	0.69	5.50	0.54
0.56	0.34	0.63	5.49	0.70
0.58	0.35	0.58	5.48	0.87
0.61	0.39	0.55	5.47	1.03
0.62	0.40	0.51	5.43	1.16
0.63	0.44	0.39	5.37	1.47
0.65	0.45	0.30	5.36	1.81
0.69	0.51	0.22	5.33	2.28

Table 4. Experimental Isopiestic Mass Fractions of Polymer (W_p) and Salt (W_s), Osmotic Coefficients, Φ, Vapor Pressure, and Activities of Water for DMAM−TBAM Copolymer C at $T = 308.15$ K

W_P	W_S	a_w	p/kPa	Φ
0.48	0.36	0.89	5.60	0.05
0.51	0.39	0.83	5.59	0.22
0.53	0.43	0.78	5.57	0.38
0.56	0.45	0.75	5.56	0.55
0.59	0.47	0.71	5.55	0.69
0.61	0.49	0.65	5.53	0.89
0.63	0.52	0.58	5.51	1.07
0.65	0.54	0.53	5.49	1.25
0.67	0.57	0.45	5.45	1.50
0.69	0.60	0.38	5.41	1.78
0.72	0.62	0.35	5.39	1.92
0.74	0.64	0.30	5.36	2.28

Table 5. Parameters of Flory−Huggins Model and Modified Flory−Huggins Models for DMAM−TBAM Copolymer Solutions at $T = 308.15$ K

copolymer	modified Flory−Huggins model			Flory−Huggins model	
	f	d	ard[a]	χ_{12}	ard[a]
A	1.00	− 1.84	0.42	− 1.18	0.11
B	1.09	− 0.01	0.64	− 0.68	0.23
C	1.06	−0.02	0.56	− 0.70	0.11

[a] ard $= \sum_{j=1}^{n} |(a_1^{\text{calcd}} - a_1^{\text{exptl}})/a_1^{\text{exptl}}|/n$, where n is the number of experimental data points.

As shown in Figure 2, the vapor pressure of DMAM−TBAM copolymer solution also increases with increasing molar mass. It demonstrates that water becomes a poorer solvent for the copolymers with greater molar mass. This increase in vapor pressure is a consequence of the decrease in the copolymer−solvent

Table 6. Freed Flory Huggins + NRTL Parameters of DMAM−TBAM Copolymer Solutions at $T = 308.15$ K

	Freed Flory−Huggins + NRTL model		
copolymer	τ_{sp}	τ_{ps}	ard[a]
A	− 871.550	− 13.505	0.104
B	− 1017.250	− 13.110	0.083
C	786.050	− 13.854	0.051

[a] ard $= \sum_{i=1}^{n} |(a_1^{\text{calcd}} - a_1^{\text{exptl}})/a_1^{\text{exptl}}|/n$, where n is the number of experimental data points.

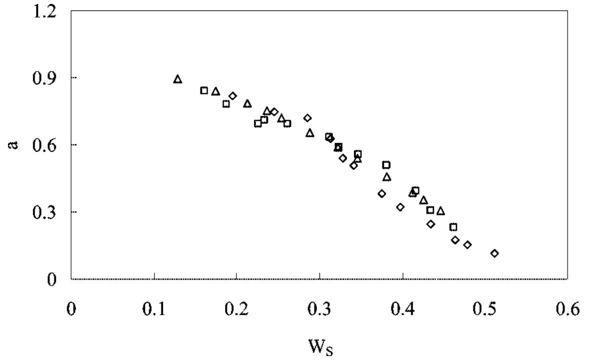

Figure 1. Plot of water activity data against mass fraction of DMAM−TBAM copolymer with different molar masses at $T = 308.15$ K: △, copolymer C; □, copolymer B; ◇, copolymer A.

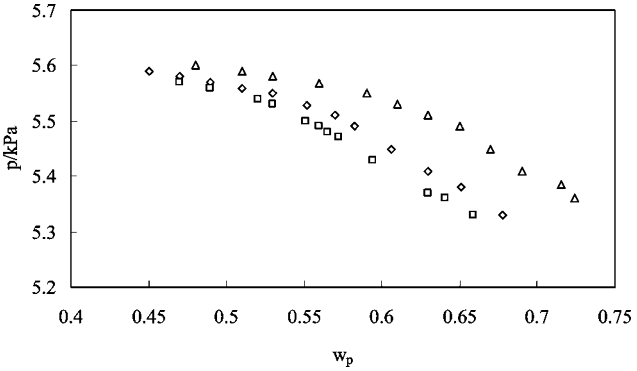

Figure 2. Plot of vapor pressure data against mass fraction of DMAM−TBAM copolymer with different molar masses at $T = 308.15$ K: △, copolymer C; □, copolymer B; ◇, copolymer A.

interaction. As shown by Table 5, with increasing molar mass, χ_{12}, became less negative, or in others words, the interaction decreases.

Figure 3 compares the measured osmotic coefficients of the DMAM−TBAM copolymers with different molar mass as a function of the square root of the molality copolymer. As this Figure shows, as molar mass increases, the osmotic coefficient increases.

The obtained interaction parameters of each model for the studied systems are presented in Tables 5 and 6 along with the corresponding absolute relative deviations (ard). As these Tables show, the values of interaction parameters depend on the molar mass of copolymers. As shown in Table 5, the Flory−Huggins equation is more suitable than the modified Flory−Huggins equation. Therefore, as shown in the results, the modified Flory−Huggins equation with concentration-dependent interaction parameters is not useful for the correlation of the experimental solvent activity data, and there is no concentration dependency in the investigated systems. With increasing molar mass, the error of extended Flory−Huggins will be greater; therefore, it should not be used anymore.

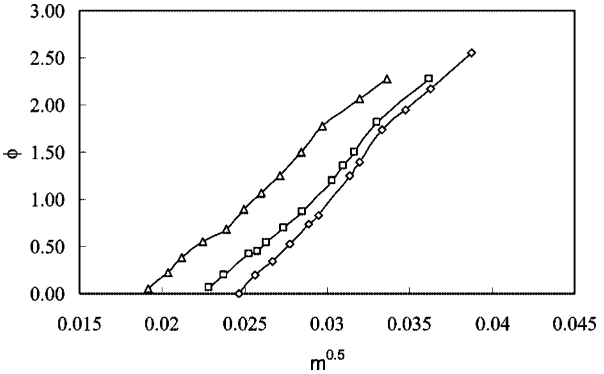

Figure 3. Measured osmotic coefficient data against the square root of the copolymer molality for aqueous solutions of DMAM−TBAM copolymers with different molar masses at $T = 308.15$ K: △, copolymer C; □, copolymer B; ◇, copolymer A.

The Freed Flory−Huggins equation + NRTL equation is more suitable than the other equations for representing our solvent activity data.

Conclusions

The accurate water activity of DMAM−TBAM copolymer solutions has been measured by the isopiestic technique at $T = 308.15$ K. The changing molar mass of copolymers was well reflected in the pressure and water activity of copolymer solutions. The results have been correlated to Flory−Huggins, modified Flory−Huggins, and Freed Flory−Huggins + NRTL equations. The best equation for describing the behavior of VLE in the system has been determined.

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