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Measurement and Correlation of Phase Equilibria for Poly(ethylene glycol) Methacrylate + Alcohol Systems at 298.15 K

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The activities of methanol, ethanol, 2-propanol, and 1-butanol in poly(ethylene glycol) methacrylate (M_n = 360) solutions have been measured by the isopiestic method at 298.15 K. Sodium iodide and calcium chloride were used as the isopiestic standards for the calculation of activities. The original equation of Flory−Huggins and the modified Flory−Huggins equation with concentration-dependent interaction parameters have been used for the correlation of the experimental solvent activity data. The strength of interaction between different alcohols and the polymer was discussed on the basis of the obtained Flory−Huggins interaction parameters. The reliability of the two local-composition models, NRTL and NRF, were also assessed by fitting the experimental activity data to these models. All of these models satisfactorily present the obtained experimental activity data.

Introduction

An understanding of the thermodynamics of the polymer solutions is important in practical applications such as polymerizations, devolatilization, and the incorporation of plasticizers and other additives. Diffusion phenomena in polymer melts and solutions are strongly affected by nonideal solution behavior because the chemical potential rather than the concentration provides the driving force for diffusion. Proper design and engineering of many polymer processes depend greatly upon accurate modeling of thermodynamic parameters such as solvent activities.

VLE data for some polymer solutions have been compiled in ref 1. Here, in regard to poly(ethylene glycol) methacrylate (PEGMA) solutions, however, no data have been given. Although there is some VLE data for alcohol solutions of poly(ethylene glycol)[1,2] and poly(propylene glycol)[3,4] and a few other polymer solutions[1,5] in the literature, for alcohol solutions of PEGMA there are no activity data in the literature. This work is the continuation of our study[4,5] on the thermodynamics of polymer + solvent systems. In the present report, activities of methanol, ethanol, 2-propanol, and 1-butanol in solutions of PEGMA having a molar mass of M_n = 360 are measured by the improved isopiestic method at 298.15 K. The results were correlated with the Flory−Huggins (FH)[6] and the modified FH equations. [7] To obtain the performance of well-known NRTL model[8,9] and the NRF model developed recently by Zafarani-Moattar et al.,[10] the experimental activity data for the investigated systems were also correlated with these models.

Experimental Procedure

All chemicals were obtained from Merck, except PEGMA360, which was obtained from Aldrich. Sodium iodide (GR, minimum 99.5% by mass) and calcium chloride (GR, minimum. 99.5% by mass) were dried in an electrical oven at about 110 °C for 24 h prior to use. Methanol (GR, minimum 99.8% by mass), ethanol (GR, minimum 99.8% by mass), and 2-propanol (GR, minimum 99.7% by mass) were dehydrated according to Vogel.[11] 1-Butanol (GR, minimum 99.5% by mass) and PEGMA 360 were used without further purification. The density and refractive index of the alcohols have been measured in previous work[4] and compared with literature values. The number-average molar mass M_n of this polymer was determined by a cryoscopic osmometer (Osmomat model 030). For this purpose, freezing-point depression measurements on PEGMA + H_2O were carried out at different concentrations and $\Delta T/K_s$ versus C curves were plotted (ΔT, C, and K_s are the freezing-point depression, concentration of samples, and cryoscopic constant, respectively). The intercept of this curve is $1/M_n$, from which M_n for this polymer was found to be 361 g·mol^{-1}.

The isopiestic apparatus employed is essentially similar to the one used previously.[12] Recently, this technique has been used to measure the activity of the four mentioned alcohols in alcohol + poly(vinylpyrolidone)[5] and alcohol + poly(propylene glycol)[4] and 2-propanol in 2-propanol + poly(ethylene glycol)[2] systems with different molar masses of the polymer. This apparatus consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard NaI or $CaCl_2$ solutions, two flasks contained PEGMA solutions, and the central flask was used as an alcohol reservoir. The apparatus was held in a constant-temperature bath for at least 120 h for equilibration at (298.15± 0.005) K. The temperature was controlled to within ±0.005 °C by a Heto temperature controller (Hetotherm PF, Heto Lab Equipment, Denmark). After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with a precision (10^{-7} kg) analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan). It was assumed that the equilibrium condition was reached when the differences between the mass fractions of each duplicate were less than 1%. In all cases, the averages of the duplicate are reported as the total isopiestic mass fraction. The uncertainty in the measurement of solvent activity was estimated to be ±0.0002.

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Table 1. Experimental Isopiestic Mass Fraction *w*, Osmotic Coefficients Φ, and Activity of Methanol (1) + PEGMA 360 (2) at 298.15 K

w_{NaI}	$w_2{}^a$	Φ_{NaI}	$a_1{}^{exptl}$	p^{exptl}/kPa
0.0279	0.1239	0.834	0.9898	16.785
0.0445	0.1649	0.847	0.9833	16.674
0.0475	0.1761	0.851	0.9820	16.653
0.0584	0.2010	0.865	0.9773	16.573
0.0646	0.2256	0.874	0.9745	16.526
0.0708	0.2389	0.884	0.9716	16.476
0.0732	0.2483	0.888	0.9704	16.456
0.0816	0.2645	0.903	0.9663	16.386
0.0853	0.2883	0.909	0.9644	16.354
0.0960	0.3312	0.930	0.9587	16.257
0.1028	0.3621	0.943	0.9549	16.192
0.1101	0.3714	0.959	0.9506	16.119
0.1210	0.3954	0.982	0.9438	16.005
0.1310	0.4192	1.005	0.9373	15.894
0.1397	0.4370	1.026	0.9313	15.792
0.1486	0.4589	1.047	0.9248	15.683
0.1853	0.5440	1.144	0.8948	15.173
0.2051	0.5865	1.201	0.8759	14.854
0.2213	0.6208	1.249	0.8592	14.570
0.2228	0.6231	1.254	0.8576	14.543
0.2356	0.6463	1.294	0.8433	14.301
0.2641	0.6945	1.387	0.8083	13.707
0.2664	0.6991	1.394	0.8054	13.658
0.2829	0.7227	1.451	0.7830	13.278
0.3190	0.7748	1.580	0.7288	12.359
0.3774	0.8445	1.802	0.6269	10.630
0.3789	0.8505	1.807	0.6242	10.586

[a] Polymer mass fraction.

Table 2. Experimental Isopiestic Mass Fraction *w*, Osmotic Coefficients Φ, and Activity of Ethanol (1) + PEGMA 360 (2) at 298.15 K

w_{NaI}	$w_2{}^a$	Φ_{NaI}	$a_1{}^{exptl}$	p^{exptl}/kPa
0.0253	0.0888	0.736	0.9884	7.779
0.0341	0.1184	0.729	0.9843	7.747
0.0499	0.1661	0.727	0.9768	7.688
0.0572	0.1954	0.729	0.9732	7.659
0.0610	0.2073	0.731	0.9713	7.644
0.0680	0.2244	0.736	0.9676	7.615
0.0731	0.2464	0.740	0.9648	7.593
0.0775	0.2563	0.745	0.9623	7.574
0.0796	0.2595	0.747	0.9611	7.564
0.0931	0.3145	0.765	0.9529	7.500
0.0982	0.3228	0.773	0.9496	7.474
0.1078	0.3633	0.790	0.9431	7.422
0.1115	0.3685	0.797	0.9404	7.401
0.1183	0.3823	0.811	0.9354	7.362
0.1252	0.4177	0.826	0.9299	7.319
0.1274	0.4218	0.831	0.9282	7.305
0.1323	0.4328	0.843	0.9241	7.273
0.1371	0.4523	0.855	0.9199	7.240
0.1545	0.5030	0.902	0.9037	7.113
0.1681	0.5371	0.943	0.8894	7.000
0.1709	0.5521	0.952	0.8865	6.977
0.1907	0.6026	1.017	0.8631	6.793
0.1978	0.6164	1.041	0.8541	6.722
0.2013	0.6231	1.053	0.8495	6.686
0.2064	0.6387	1.072	0.8427	6.632
0.2093	0.6441	1.082	0.8386	6.600
0.2142	0.6529	1.099	0.8319	6.548

Table 3. Experimental Isopiestic Mass Fraction *w*, Osmotic Coefficients Φ, and Activity of 2-Propanol (1) + PEGMA 360 (2) at 298.15 K

w_{NaI}	$w_2{}^a$	Φ_{NaI}	$a_1{}^{exptl}$	p^{exptl}/kPa
0.0759	0.2063	0.743	0.9650	5.574
0.0794	0.2089	0.747	0.9632	5.563
0.0944	0.2585	0.767	0.9552	5.517
0.0949	0.2681	0.768	0.9548	5.514
0.1076	0.2941	0.789	0.9474	5.471
0.1134	0.3153	0.801	0.9437	5.450
0.1137	0.3167	0.801	0.9435	5.448
0.1185	0.3325	0.811	0.9403	5.430
0.1223	0.3487	0.820	0.9376	5.414
0.1387	0.3852	0.835	0.9234	5.331
0.1408	0.4199	0.865	0.9208	5.316
0.1439	0.4210	0.873	0.9116	5.263
0.1539	0.4468	0.901	0.9067	5.234
0.1588	0.4628	0.915	0.9006	5.199

Table 4. Experimental Isopiestic Mass Fraction *w* and Activity of 1-Butanol (1) + PEGMA 360 (2) at 298.15 K

w_{CaCl_2}	$w_2{}^a$	$a_1{}^{exptl}$	p^{exptl}/kPa
0.0298	0.1091	0.966	0.80
0.0385	0.1383	0.955	0.79
0.0390	0.1414	0.954	0.79
0.0702	0.2611	0.908	0.75
0.0944	0.3627	0.863	0.71
0.1143	0.4293	0.819	0.67
0.1146	0.4318	0.818	0.67
0.1215	0.4557	0.801	0.66
0.1248	0.4639	0.793	0.65
0.1256	0.4677	0.791	0.65
0.1343	0.5006	0.767	0.63
0.1435	0.5351	0.740	0.61
0.1463	0.5377	0.731	0.60
0.1474	0.5444	0.728	0.60
0.1517	0.5603	0.714	0.59
0.1773	0.6268	0.623	0.51

Results and Discussions

Experimental Results. At isopiestic equilibrium, the activity of the solvent in the reference and PEGMA solutions must be the same. Therefore, the isopiestic equilibrium mass fractions with reference standard solutions as reported in Tables 1−4 enabled the calculation of the solvent activity, a_1, in the solutions of alcohol (1) + PEGMA (2) from that of reference solutions. NaI served as an isopiestic reference for each of the solutions of methanol, ethanol, or 2-propanol because very accurate vapor pressure data are available for solutions of this salt in these solvents.[13−15] Similarly, because reliable activity data are available for solutions of $CaCl_2$ in 1-butanol,[16] this salt was chosen as an isopiestic reference for 1-butanol solutions. To calculate solvent activity for methanol, ethanol, and 2-propanol solutions, the following relations were used:

$$\ln(a_1) = -\nu m_{NaI}\Phi_{NaI}M_s \tag{1a}$$

$$m_{NaI} = \frac{w_{NaI}}{M_{NaI}(1 - w_{NaI})} \tag{1b}$$

where v is the sum of the stoichiometric number of anions and cations in the reference solutions, m_{NaI} and w_{NaI} are, respectively, the concentration and mass fraction of NaI that is in isopiestic equilibrium with the polymer solutions. M_s and M_{NaI} are, respectively, the relative molar mass of the solvent and NaI, and Φ_{NaI} is the osmotic coefficient of the isopiestic reference standard, calculated at m_{NaI}. For methanol, ethanol, and 2-propanol solutions, the necessary Φ_{NaI} values at any m_{NaI} were obtained from the fitted Pitzer and Mayorga equation,[17] including the $\beta^{(2)}$ term as described in the previous papers.[18−20] For solutions of NaI in each of these solvents, it was shown that,[18−20] using the obtained Pitzer parameters, the osmotic coefficients, Φ_{NaI}, are reproducible with a standard deviation of 0.005. In the case of 1-butanol + PEGMA solutions, the activities for the isopiestic reference $CaCl_2$ in 1-butanol solutions were calculated using the polynomial equation presented in our previous work[4] with a standard deviation of about 0.001.

Table 5. Parameters of Flory−Huggins and Modified Flory−Huggins Equations along with the Corresponding Absolute Relative Percentage Deviations

solvent	concentration range (w_2)	Flory−Huggins χ_{12}	Flory−Huggins dev %	modified Flory−Huggins d	modified Flory−Huggins f	modified Flory−Huggins dev %
methanol	0. 1239−0.8505	0.6034	1.55	0.3424	0.6229	0.25
ethanol	0.0888−0.6529	0.5836	0.35	0.4641	0.4014	0.08
2-propanol	0.2063−0.4628	0.5815	0.17	0.6397	−0.3073	0.14
1-butanol	0.1091−0.6268	−0.1337	0.61	−0.0397	1.4568	0.54

Table 6. Parameters of the NRF, Chen's NRTL, and Wu's NRTL Equations along with the Corresponding Absolute Relative Percentage Deviations

solvent	concentration range (w_2)	α	polymer NRF model λ_S	polymer NRF model λ_P	polymer NRF model dev %	Wu-NRTL model τ_{12}	Wu-NRTL model τ_{21}	Wu-NRTL model dev %	Chen-NRTL model τ_{12}	Chen-NRTL model τ_{21}	Chen-NRTL model dev%
methanol	0. 1239−0.8505	0.2	−0.2213	−0.3093	0.22	−0.1945	0.9479	0.25	−0.5930	1.5047	0.33
		0.4	−0.1997	−0.1505	0.21	0.6218	0.2380	0.17	−0.1492	1.0077	0.32
ethanol	0.0888−0.6529	0.2	−0.2946	−0.3759	0.08	0.5105	0.1784	0.08	−0.2068	0.9643	0.08
		0.4	−0.2644	−0.2329	0.08	1.2364	−0.2625	0.08	0.0593	0.7054	0.08
2-propanol	0.2063−0.4628	0.2	0.0699	−0.5398	0.14	1.6612	−0.8779	0.14	0.6250	−0.0677	0.14
		0.4	0.0952	−0.4167	0.14	1.9971	−0.9046	0.14	0.4464	0.1170	0.14
1-butanol	0.1091−0.6268	0.2	0.3595	0.1450	0.59	2.2931	−1.8293	0.60	−0.7280	0.6757	0.59
		0.4	0.3956	0.2652	0.59	1.7688	−1.4714	0.60	−0.5364	0.4799	0.59

Hence, the solvent activity data reported in Table 4 for 1-butanol + PEGMA solutions are also given to three decimal places.

From the calculated solvent activity data, vapor pressures of the investigated solutions, p, were determined with the help of the following relation:

$$\ln(a_1) = \ln\left(\frac{p}{p^*}\right) + \frac{(B - V^*_s)(p - p^*)}{RT} \qquad (2)$$

where B, V^*_s, and p^* are the second virial coefficient, molar volume, and vapor pressure of pure alcohol, respectively. Values of the physical properties of the solvents have been given in our previous work.[4] The experimental vapor pressure data are also given in Tables 1−4. In Table 4, the calculated vapor pressure data for 1-butanol + $CaCl_2$ solutions are given to two decimal places because the corresponding activity data are meaningful to only three decimal places.

Correlation of Data. There are several models describing the VLE of polymer solutions. Some authors use empirical equations. For the correlation of solvent activity data for polymer solutions, there are theoretical models such as Flory−Huggins,[6,7] which belongs to the lattice model, and local composition models such as the NRTL[8,9] and NRF[10] models. In this work to examine the reliability of these models, we fit the the solvent activity data for the investigated systems to the FH equation,[6] the modified FH[7] with concentration-dependent interaction parameters, and the NRTL and NRF models.

The solvent activity data were fit to the model of Flory−Huggins,[6] which has the form

$$\ln(a_1) = \ln(\varphi_1) + \left(1 - \frac{1}{r_2}\right)(1 - \varphi_1) + \chi_{12}(1 - \varphi_1)^2 \quad (3)$$

where φ_1 is the volume fraction of solvent and r_2 is the number of segments of polymer defined as the molar volume of polymer divided by the molar volume of solvent. χ_{12} is the interaction parameter of the system. The density of PEGMA was measured to be 1.091106 g·cm^{-3}, from which the required molar volume of the polymer was calculated. The obtained interaction parameters, χ_{12}, for the studied systems are presented in Table 5 along with the corresponding absolute relative percentage deviations (ARD%) of the fit. On the basis of the obtained ARD%, we conclude that the FH equation[6] is a suitable model to represent our solvent activity data. Table 5 shows that the χ_{12} value decreases when the alcohol compound contains more and more of the methylene group. This can be explained as follows: Methanol is the alcohol that has the strongest hydrogen bonding. This prevents PEGMA from establishing strong intermolecular interactions with methanol, leading to high values of the FH parameter. Then, with the addition of a nonpolar methylene group, the self-association of the alcohol (ethanol, 2-propanol, and 1-butanol) will decrease, leading to a stronger interaction between the solvent and PEGMA. This is represented by lower values of the FH parameter. This trend was also observed for solutions of these alcohols with poly(propylene glycol)[4] and poly(vinylpyrolidone).[5]

The experimental activity data were also fit to the modified FH equation given by Bae et al.[7] in which the concentration dependency of χ_{12} was considered. As shown previously,[4] at constant temperature (here, 298.15 K), the Bae et al.[7] equation can be written as

$$\ln(a_1) = \ln(\varphi_1) + \left(1 - \frac{1}{r_2}\right)(1 - \varphi_1) + \frac{d(1 - \varphi_1)^2}{1 - f(1 - \varphi_1)} \qquad (4)$$

where d and f are adjustable parameters of the modified FH equation.[7] The results of fitting to eq 5 are also given in Table 5. From the reported low ARD% with eq 6, we conclude that the quality of fitting with the modified FH equation[7] is better than with the original FH equation.

Among the local composition models, the NRF[10] and two versions of the NRTL (Chen's NRTL[8] and Wu's NRTL[9]) model were found to be reliable in representing the solvent activity of some polymer + solvent systems. To determine the performance of each of these models, we also fit our data to these local composition models.

Omitting details in the local composition models, we may express the excess Gibbs energy of a polymer solution as the sum of the local composition contribution, $g^{\mathrm{ex,LC}}$, and the configurational entropy of mixing, $g^{\mathrm{ex,config}}$:

$$g^{\mathrm{ex}} = g^{\mathrm{ex,config}} + g^{\mathrm{ex,LC}} \qquad (5)$$

According to eq 6, the expression for the activity coefficient of the solvent in a polymer solution can also be considered as the sum of two contributions:

$$\ln(\gamma_s) = \ln(\gamma_s^{\mathrm{LC}}) + \ln(\gamma_s^{\mathrm{config}}) \qquad (6)$$

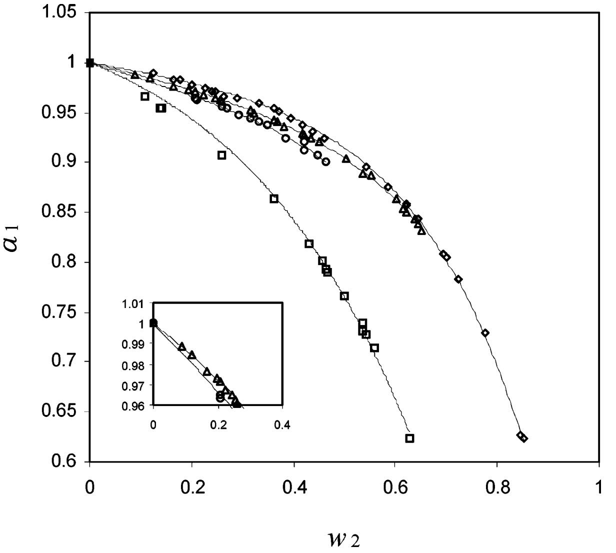

Figure 1. Solvent activity data for alcohol (1) + PEGMA 360 (2) at 298.15 K: ◊, methanol; Δ, ethanol; ○, 2-propanol; □×ff, 1-butanol. Lines were generated from fitting the experimental activity data to the NRF model.

Because the necessary expressions for the activity coefficient of solvent due to the enthalpic (ln γ_s^{LC}) and configurational entropy of mixing (ln γ_s^{config}) for Chen's NRTL,[8] Wu's NRTL,[9] and the NRF models[10] are rather lengthy, they are not given here. Using the appropriate expressions from the literature[8−10] for each model, we may easily obtain the necessary fitting equation for $\ln(a_s)$ and hence $\ln(a_s) = \ln(\gamma_s) + \ln(x_s)$. Here x_s is the mole fraction of water. In fitting the activity data to these local composition models, we may use different values for the nonrandomness factor (α). As stated by Chen,[8] Chen's NRTL model is not very sensitive to α values; however, the values in the range of 0.1−0.4 may be used. We also found that the NRF model is not very sensitive to the chosen α values in the range of 0.1−0.4 for the investigated systems in this work. However, the model of Wu et al.'s NRTL is very sensitive to the chosen α values in the case of PEGMA + methanol solutions. Therefore, the fitting of our experimental water activity data to these local composition models was carried out for two different values of α (0.2 and 0.4) with the results reported in Table 6. On the basis of obtained ARD% values, we note that two versions of the NRTL model and the NRF model satisfactorily represent the VLE data of investigated polymer solutions, especially when the value of $\alpha = 0.4$ is used. Also, from the comparison of ARD% values presented in Tables 5 and 6, we conclude that the quality of fitting with the modified FH model is very similar to that of the local composition models used. As an example, to show the performance of the NRF model the difference between the calculated and the experimental activity data are plotted against polymer concentration in Figure 2.

Conclusions

The accurate activity of the solvent in poly(ethylene glycol) methacrylate + methanol, ethanol, 2-propanol, and 1-butanol solutions has been measured by the isopiestic method at 298.15 K. The activities of alcohols tend to increase in the order 1-butanol > 2-propanol > ethanol > methanol. The results have been correlated to the Flory−Huggins equation, the modified Flory−Huggins equation, the NRF model, and two versions of the NRTL models. The Flory−Huggins interaction parameters obtained for these systems imply that the interaction between PEGMA and alcohols increases in the order 1-butanol > 2-propanol > ethanol > methanol. Good agreement with the experimental results was found with all of these models.

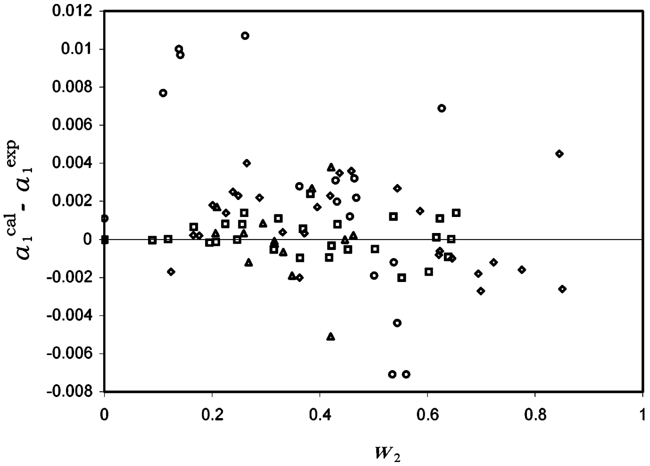

Figure 2. Difference between the experimental and calculated activity data with the NRF model for the investigated alcohol (1) + PEGMA 360 (2) system at 298.15 K: ◊, methanol; Δ, ethanol; ○, 2-propanol; □, 1-butanol.

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