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Determination of Solvent Activity in Poly(vinylpyrolidone) + Methanol, + Ethanol, + 2-Propanol, + and 1-Butanol Solutions at 25 °C

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The activities of methanol, ethanol, 2-propanol, and 1-butanol in poly(vinylpyrolidone) (PVP) (weight-average relative molar mass, $M_w = 10\,000$) solutions have been measured by the isopiestic method at 25 °C. Sodium iodide and calcium chloride were used as the isopiestic standards for the calculation of activities. A polynomial equation, the original Flory−Huggins equation, 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.

Introduction

Phase equilibria play an important role in the processing and application of polymers. In this respect, a quantitative description of the vapor−liquid equilibria (VLE) behavior in solvent + polymer systems is often necessary in order to design a polymer manufacturing process or to predict process performance.

VLE data for some polymer solutions have been compiled in ref 1. Here, in regard to PVP solutions, however, no data have been given. Although there is some VLE data for aqueous solutions of PVP in the literature, for its nonaqueous solutions there are no activity data in the literature. This work is a continuation of our study[2,3] on the thermodynamics of polymer + solvent systems. In the present report, activities of methanol, ethanol, 2-propanol, and 1-butanol in solutions of PVP ($M_w = 10\,000$) are measured by the improved isopiestic method at 25 °C. The results were correlated with a polynomial and the Flory−Huggins (FH)[4] and modified FH equations.[5]

Experimental Procedure

All chemicals were obtained from Merck, except PVP10000, 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 electric 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.[6] 1-Butanol (GR, minimum 99.5% by mass) and PVP10000 were used without further purification. The density and refractive index of the alcohols were measured in the previous work[3] and compared with literature values. The number-average relative molar mass of PVP was obtained, $M_n = 13\,750$, by gel permeation chromatography (GPC).

The isopiestic apparatus employed is essentially similar to the one used previously.[7] Recently, this technique has been used for the measurement of the activity of the four mentioned alcohols in alcohol + poly(propylene glycol)[3] systems and 2-propanol in 2-propanol + poly(ethylene glycol)[2] systems with different molar masses of the polymer. This apparatus consisted of a five-legged manifold attached to round-bottom flasks. Two flasks contained the standard NaI or $CaCl_2$ solutions, two flasks contained PVP 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 (25.0 ± 0.005) °C. 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, 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.

Results and Discussions

Experimental Results. At isopiestic equilibrium, the activity of the solvent in the reference and PVP 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) + PVP (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.[8−10] Similarly, because reliable activity data are available for solutions of $CaCl_2$ in 1-butanol,[11] this salt was chosen as an isopiestic reference for 1-butanol solutions. To calculate the solvent activity for methanol, ethanol, and 2-propanol solutions, we used the following relations:

$$\ln a_1 = -\nu m_{\mathrm{NaI}} \Phi_{\mathrm{NaI}} M_{\mathrm{S}} \tag{1a}$$

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

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Table 1. Experimental Isopiestic Mass Fractions w, Osmotic Coefficients Φ, and Activities of Methanol for Methanol (1) + PVP 10 000 (2) at 25 °C

w_{NaI}	w_2[a]	Φ_{NaI}	a_1^{exptl}	p^{exptl}/kPa
0.0122	0.1225	0.840	0.9956	16.882
0.0200	0.1579	0.833	0.9928	16.834
0.0328	0.2092	0.837	0.9879	16.750
0.0403	0.2297	0.843	0.9850	16.700
0.0407	0.2425	0.844	0.9848	16.696
0.0409	0.2902	0.859	0.9793	16.602
0.0606	0.3108	0.869	0.9763	16.550
0.0900	0.3823	0.918	0.9619	16.302
0.1066	0.4163	0.951	0.9526	16.143
0.1578	0.4867	1.070	0.9178	15.545
0.2125	0.5697	1.223	0.8685	14.699
0.2330	0.6007	1.286	0.8462	14.317
0.2712	0.6401	1.411	0.7989	13.508
0.3209	0.6968	1.569	0.7337	12.393
0.3514	0.7351	1.703	0.6736	11.368
0.3893	0.7753	1.848	0.6044	10.190

[a] Polymer mass fraction.

Table 2. Experimental Isopiestic Mass Fractions w, Osmotic Coefficients Φ, and Activities of Ethanol for Ethanol (1) + PVP 10 000 (2) at 25 °C

w_{NaI}	w_2	Φ_{NaI}	a_1^{exptl}	p^{exptl}/kPa
0.0200	0.1389	0.743	0.9908	7.798
0.0245	0.1525	0.737	0.9887	7.781
0.0247	0.1732	0.737	0.9887	7.781
0.0314	0.1902	0.731	0.9856	7.757
0.0404	0.2313	0.727	0.9814	7.724
0.0451	0.2556	0.726	0.9792	7.707
0.0514	0.2670	0.727	0.9761	7.682
0.0493	0.2686	0.727	0.9771	7.690
0.0595	0.2849	0.729	0.9735	7.662
0.0634	0.3028	0.732	0.9700	7.634
0.0715	0.3235	0.739	0.9657	7.600
0.0722	0.3267	0.739	0.9652	7.596
0.0808	0.3495	0.748	0.9604	7.559
0.0899	0.3737	0.760	0.9549	7.515
0.0980	0.3835	0.773	0.9497	7.474
0.1045	0.3956	0.784	0.9454	7.440
0.1311	0.4515	0.840	0.9251	7.281
0.1611	0.4963	0.922	0.8970	7.059
0.1671	0.5031	0.940	0.8906	7.009
0.1684	0.5070	0.945	0.8891	6.997
0.1872	0.5395	1.007	0.8669	6.823
0.2037	0.5689	1.062	0.8463	6.660
0.2129	0.5870	1.095	0.8336	6.560
0.2371	0.6295	1.183	0.7978	6.279

where υ is the sum of the stoichiometric numbers of anions and cations in the reference solutions and m_{NaI} and w_{NaI} are, respectively, the substance concentration and mass fraction of NaI, which is in isopiestic equilibrium with the polymer solutions. M_S and M_{NaI} are, respectively, the relative molar masses 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,[12] including the $\beta^{(2)}$ term as described in the previous papers.[13−15] For solutions of NaI in each of these solvents, it was shown that,[13−15] 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 + PVP solutions, the activities for the isopiestic reference $CaCl_2$ in 1-butanol solutions were calculated using the polynomial equation presented in our previous work[3] with a standard deviation of about 0.001. Hence, the solvent activity data reported in Table 4 for 1-butanol + PVP solutions are also given to three decimal places.

Table 3. Experimental Isopiestic Mass Fractions w, Osmotic Coefficients Φ, and Activities of 2-Propanol for 2-Propanol (1) + PVP 10 000 (2) at 25 °C

w_{NaI}	w_2	Φ_{NaI}	a_1^{exptl}	p^{exptl}/kPa
0.0216	0.1461	0.527	0.9907	5.723
0.0321	0.1715	0.531	0.9860	5.696
0.0350	0.1804	0.532	0.9847	5.688
0.0363	0.2004	0.532	0.9841	5.685
0.0483	0.2277	0.535	0.9784	5.652
0.0579	0.2573	0.537	0.9739	5.625
0.0575	0.2591	0.537	0.9741	5.627
0.0637	0.2746	0.538	0.9711	5.609
0.0684	0.2888	0.539	0.9688	5.596
0.0772	0.3019	0.541	0.9644	5.570
0.0801	0.3178	0.542	0.9629	5.561
0.0947	0.3413	0.550	0.9550	5.515
0.1009	0.3585	0.554	0.9514	5.494
0.1010	0.3618	0.555	0.9510	5.492
0.1400	0.4449	0.605	0.9241	5.336
0.1508	0.4663	0.628	0.9146	5.280
0.1762	0.5083	0.699	0.8871	5.120
0.1960	0.5515	0.773	0.8598	4.962
0.2345	0.6058	0.979	0.7864	4.535

Table 4. Experimental Isopiestic Mass Fractions w and Activities of Butanol for Butanol (1) + PVP 10 000 (2) at 25 °C

w_{CaCl_2}	w_2	a_1^{exptl}	p^{exptl}/kPa
0.0165	0.1358	0.981	0.81
0.0217	0.1632	0.975	0.80
0.0232	0.1706	0.974	0.80
0.0470	0.2691	0.943	0.78
0.0610	0.3018	0.923	0.76
0.0650	0.3206	0.916	0.76
0.0686	0.3309	0.911	0.75
0.0709	0.3394	0.907	0.75
0.0738	0.3440	0.902	0.74
0.0813	0.3629	0.889	0.73
0.0807	0.3659	0.890	0.73
0.0905	0.4046	0.871	0.72
0.0981	0.4371	0.856	0.71
0.1389	0.5256	0.754	0.62
0.1509	0.5407	0.717	0.59
0.1818	0.5884	0.605	0.50

Table 5. Parameters of Equation 3 along with the Corresponding Absolute Relative Percentage Deviations

system	c_0	c_1	c_2	c_3	ard%[a] (a_1)
PVP + methanol	−0.0029	−0.3344	0.7436	−1.5033	0.22
PVP + ethanol	−0.0083	−0.4420	0.9600	−1.7200	0.23
PVP + 2-propanol	0.0031	−0.7837	2.2992	−3.2106	0.17
PVP + 1-butanol	0.0065	−1.5060	3.9389	−5.5342	0.65

[a] ard% = $100\sum_{i=1}^{n}\frac{|(a_1^{cal} - a_1^{exp})/a_1^{exp}|}{n}$, where n is the number of experimental data points.

From the calculated solvent activity data, we determined the vapor pressures of the investigated solutions, p, 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.[3] 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.

Table 6. Parameters of Flory−Huggins and Modified Flory−Huggins Equations along with theCorresponding Absolute Relative Percentage Deviations

	concentration range	Flory−Huggins		modified Flory−Huggins		
system	W_2	χ_{12}	ard% (a_1)[a]	a	f	ard% (a_1)
PVP + methanol	0.1225−0.7735	−0.4491	0.60	−0.2389	0.9117	0.33
PVP + ethanol	0.1389−0.6295	−0.5339	0.23	−0.5321	0.0104	0.23
PVP + 2-propanol	0.1461−0.6058	−0.6463	0.52	−1.2910	−4.4494	0.44
PVP + 1-butanol	0.1358−0.5884	−2.0741	1.26	−2.4161	−0.5788	1.19

[a] ard% $= 100\sum_{i=1}^{n}\frac{|(a_1^{\text{cal}} - a_1^{\text{exp}})/a_1^{\text{exp}}|}{n}$, where n is the number of experimental data points.

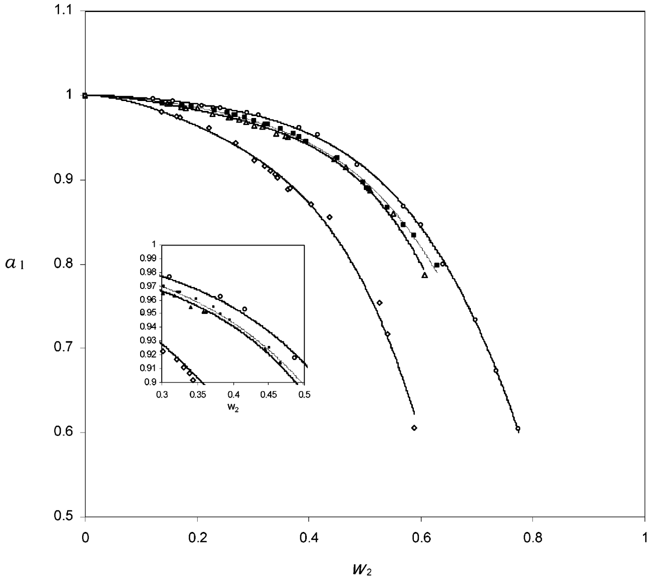

Figure 1. Solvent activity data for alcohol (1) + PVP 10 000 (2) at 25 ° C: methanol; ethanol; 2-propanol; 1-butanol. Lines were generated from fitting the experimental activity data to eq 3.

Correlation of Data. There are several models describing the VLE of polymer solutions. Some authors use empirical equations. For instance, Eliassi et al.[16] have found that a polynomial equation is sufficient for the correlation of water activities in the poly(ethylene) glycol + water system. There are also theoretical models such as Flory−Huggins[4,5] and NRTL[17] for the correlation of solvent activity data for polymer solutions. In this work, for the correlation of solvent activity for the investigated systems a polynomial equation, the FH equation,[4] and the modified FH equation[5] with concentration-dependent interaction parameters were considered.

The solvent activity data are well fitted to the polynomial equation

$$a_1 - 1 = c_0 w_2 + c_1 {w_2}^2 + c_2 {w_2}^3 + c_3 {w_2}^4 \tag{3}$$

with respect to polymer mass fraction, w_2. The coefficients of eq 3 along with their absolute relative percentage deviations (ard%) are reported in Table 5.

In Figure 1, the measured solvent activity data for alcohol (1) + PVP10000 (2) systems are shown together with the generated lines using eq 3 with the corresponding parameters reported in Table 5. As one can see from Figure 1, eq 3 fits the data well. Also, the activities of alcohols tend to increase in the order 1-butanol > 2-propanol > ethanol > methanol. A similar trend was observed with the system poly(propylene glycol) + alcohol.[3]

The solvent activity data were also fitted to the model of Flory−Huggins,[4] which has the form

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \varphi_1) + \chi_{12}(1 - \varphi_1)^2 \tag{4}$$

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. Using the group contribution data reported by Zana,[18] we estimated the required molar volume for the polymer to be 7.849×10^{-3} m^3 mol^{-1}. The obtained interaction parameters, χ_{12}, for the studied systems are presented in Table 6 along with the corresponding absolute relative percentage deviations (ard%) of the fit. On the basis of obtained ard% values, we conclude that the FH equation[4] is also a suitable model for representing our solvent activity data. Although the quality of the fit to eq 3 with four adjustable parameters is better than the fit to eq 4, a single Flory−Huggins interaction parameter, χ_{12}, obtained from the FH equation (eq 4) for each PVP + alcohol system, is important from a theoretical as well as a practical viewpoint. Table 6 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, which has the strongest hydrogen bonding. This prevents PVP 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 be decreased, leading to stronger interaction between the solvent and PVP. This is represented by lower values of the FH parameter. This trend was also observed for solutions of poly(propylene glycol) + these alcohols.[3]

The experimental activity data were also fitted to the modified FH equation given by Bae et al.[5] in which the concentration dependence of χ_{12} was considered. As shown previously,[2] at constant temperature (here, 25 °C), the Bae et al.[5] equation can be written as

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \varphi_1) + \frac{d(1 - \varphi_1)^2}{1 - f(1 - \varphi_1)} \tag{5}$$

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

Conclusions

Accurate activities of solvent in poly(vinylpyrolidone) + methanol, ethanol, 2-propanol, and 1-butanol solutions have been measured by the isopiestic method at 25 °C. The activities of alcohols tend to increase in the order 1-butanol > 2-propanol > ethanol > methanol. The results have been correlated to the polynomial and the Flory−Huggins and the modified Flory−Huggins equations. Flory−Huggins interaction parameters obtained for these systems imply that interaction between PVP and alcohols increases in the order 1-butanol > 2-propanol > ethanol > methanol.

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