Isopiestic Determination of 2-Propanol Activity in 2-Propanol + Poly(ethylene glycol) Solutions at 25 °C

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The activities of 2-propanol in poly(ethylene glycol) (PEG) (M_n: 1000, 300, 200) + 2-propanol solutions have been measured by the isopiestic method at 25 °C. Sodium iodide was used as the isopiestic standard 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 obtained experimental solvent activity data. Better agreement with the experimental data was obtained using the modified Flory−Huggins equation.

Introduction

The use and production of poly(ethylene glycol) (PEG) has increased over the last two decades. The reasons for this development can be found in the outstanding properties of PEG. Phase equilibria plays 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, which contains VLE data for some PEG + solvent systems. Here, the activity of water in aqueous PEG solutions, which have been reported by different research groups, can be found. Recently, there are other reports on the activity of water in aqueous PEG systems.[2,3] For the measurement of the activity of water in such systems, improved isopiestic,[2] differential vapor pressure,[4] vapor pressure osmometry, and membrane osmometry[3,5] methods have been used. Recently, for some binary nonaqueous polymer solutions, VLE data have been measured with a vacuum electro-microbalance cell.[6]

In regard to PEG + alcohol solutions, there are reports on VLE of PEG + ethanol, PEG + 1-propanol, and PEG + methanol systems.[1,6] However, for solutions of PEG in 2-propanol there are no activity data in the literature. In the present report, activities of 2-propanol in solutions of PEG having different molar masses (M_n: 1000, 300, 200) are measured by the improved isopiestic method.[2] The results were correlated with the Flory−Huggins equation[7] and the modified Flory−Huggins equation[8] with concentration dependent interaction parameters.

Experimental Procedure

All the chemicals were obtained from Merck. Sodium iodide (GR, min 99.5%) was dried in an electrical oven at about 110 °C for 24 h prior to use. 2-Propanol (GR, min 99.7%) was dehydrated according to the procedure in ref 9. Samples of poly(ethylene glycol) (PEG 1000, 300, 200) were used without further purification. The number average relative molar masses of PEG samples, M, were measured with an osmometer (Osmomat model 030, Gonotec, Germany). For this purpose, the osmolality of the polymer solutions is determined at different concentrations of PEG + water solutions, from which the corresponding freezing point depression can be easily calculated using the tabulated data given by the manufacturer. Then, the $\Delta T/K_sC$ versus C curve was obtained (ΔT, C, and K_s are the freezing point depression, concentration of samples (g·dm^{-3}), and cryoscopic constant, respectively). The intercept of this curve is $1/M$, from which M was obtained. Results are reported in Table 1.

Table 1. Measured Number Average Relative Molar Mass

polymer	M
PEG 1000	995
PEG 300	296
PEG 200	190

The isopiestic apparatus employed is essentially similar to the one used previously.[2] Recently, this technique has been used for the measurement of the osmotic coefficients of some lithium salts in ethanol and 2-propanol solutions.[10,11] This apparatus consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard NaI solutions, two flasks contained PEG solutions, and the central flask was used as a 2-propanol reservoir. The apparatus was held in a constant-temperature bath 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 high 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 the duplicates were less than 1%. In all cases, averages of the duplicates are reported as the total isopiestic mass fraction.

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Table 2. Experimental Isopiestic Mass Fractions w, Osmotic Coefficients Φ, and Activities of 2-Propanol for 2-Propanol (1) + PEG 1000 (2) at 25 °C

w_{NaI}	w_2[a]	Φ_{NaI}	a_1^{exp}	p^{exp}/kPa
0.0144	0.1100	0.528	0.9939	5.742
0.0183	0.1444	0.526	0.9922	5.732
0.0329	0.2324	0.531	0.9856	5.694
0.0360	0.2454	0.532	0.9842	5.686
0.0426	0.2699	0.534	0.9811	5.668
0.0521	0.3243	0.536	0.9767	5.643
0.0560	0.3649	0.536	0.9748	5.632
0.0618	0.3921	0.537	0.9721	5.616
0.0722	0.4381	0.540	0.9669	5.586
0.0781	0.4562	0.541	0.9639	5.569
0.0786	0.4652	0.542	0.9637	5.568
0.0869	0.4884	0.545	0.9593	5.542
0.0888	0.4889	0.546	0.9583	5.536

[a] Polymer mass fraction.

Table 3. Experimental Isopiestic Mass Fractions, Osmotic Coefficients, and Activities of 2-Propanol for 2-Propanol (1) + PEG 300 (2) at 25 °C

w_{NaI}	w_2	Φ_{NaI}	a_1^{exp}	p^{exp}/kPa
0.0314	0.0658	0.531	0.9863	5.698
0.0578	0.1231	0.537	0.9740	5.627
0.0602	0.1310	0.537	0.9728	5.620
0.0764	0.1709	0.541	0.9648	5.574
0.0903	0.2019	0.547	0.9574	5.531
0.0928	0.2094	0.548	0.9560	5.523
0.0959	0.2200	0.550	0.9543	5.513
0.1044	0.2327	0.557	0.9493	5.484
0.1062	0.2438	0.559	0.9482	5.478
0.1114	0.2525	0.564	0.9449	5.459
0.1196	0.2736	0.573	0.9395	5.428
0.1363	0.3233	0.598	0.9271	5.356
0.1410	0.3458	0.607	0.9232	5.334
0.1475	0.3715	0.620	0.9176	5.301
0.1490	0.3761	0.624	0.9162	5.293
0.1555	0.3916	0.639	0.9100	5.257
0.1557	0.3908	0.639	0.9098	5.256
0.1587	0.4016	0.647	0.9068	5.239
0.1616	0.4117	0.655	0.9038	5.222
0.1686	0.4529	0.675	0.8962	5.178

Table 4. Experimental Isopiestic Mass Fractions, Osmotic Coefficients, and Activities of 2-Propanol for 2-Propanol (1) + PEG 200 (2) at 25 °C

w_{NaI}	w_2	Φ_{NaI}	a_1^{exp}	p^{exp}/kPa
0.0530	0.0796	0.536	0.9762	5.640
0.0614	0.0947	0.537	0.9722	5.617
0.0772	0.1131	0.541	0.9644	5.572
0.0774	0.1215	0.541	0.9643	5.571
0.0902	0.1418	0.547	0.9575	5.532
0.0909	0.1489	0.547	0.9571	5.529
0.1136	0.1877	0.566	0.9435	5.451
0.1269	0.2166	0.583	0.9343	5.398
0.1292	0.2216	0.587	0.9326	5.388
0.1461	0.2641	0.617	0.9188	5.308
0.1463	0.2635	0.618	0.9186	5.307
0.1500	0.2788	0.626	0.9153	5.288
0.1554	0.2859	0.639	0.9101	5.258
0.1562	0.2872	0.641	0.9093	5.253
0.1647	0.3203	0.663	0.9005	5.202
0.1703	0.3365	0.680	0.8942	5.166
0.1726	0.3403	0.687	0.8915	5.151
0.1795	0.3578	0.710	0.8830	5.101

Table 5. Flory−Huggins Interaction Parameters of 2-Propanol (1) + PEG 300 (2) Solutions at Various Weight Fractions of Polymer (w_2)

w_2	χ_{12}	w_2	χ_{12}
0.0658	0.4420	0.2736	0.5401
0.1231	0.4841	0.3233	0.5562
0.1310	0.5480	0.3458	0.5927
0.1709	0.5950	0.3715	0.6137
0.2019	0.5626	0.3761	0.6124
0.2094	0.5758	0.3916	0.5927
0.2200	0.6031	0.3908	0.5876
0.2327	0.5279	0.4016	0.5914
0.2438	0.5791	0.4117	0.5935
0.2525	0.5426	0.4529	0.6473

Results and Discussion

Experimental Results. At isopiestic equilibrium, the activity of the solvent in the reference and PEG solutions must be the same. Therefore, the isopiestic equilibrium mass fractions with reference standard solutions of NaI in 2-propanol as reported in Tables 2−4 enabled the calculation of the solvent activity, a_1, in the solutions of 2-propanol (1) + PEG (2) from that of reference solutions using the relations

$$\ln a_1 = -\nu m_{NaI} \Phi_{NaI} M_S, \quad m_{NaI} = \frac{w_{NaI}}{M_{NaI}(1 - w_{NaI})} \qquad \text{(1a,b)}$$

where υ is the sum of the stoichiometric numbers of the anion and the cation in the reference solutions, 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}. 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 paper.[11] It was shown that,[11] using $\alpha_1 = 2$ kg$^{1/2}$·mol$^{-1/2}$, $\alpha_2 = 10$ kg$^{1/2}$·mol$^{-1/2}$, $b = 3.2$ kg$^{1/2}$·mol$^{-1/2}$, $\beta^{(0)} = -0.111\,239$ kg·mol^{-1}, $\beta^{(1)} = 1.385\,824$ kg·mol^{-1}, $\beta^{(2)} = -22.179\,244$ kg·mol^{-1}, and $C^{\phi} = 0.183\,492$ kg^2·mol^{-2}, the osmotic coefficients Φ_{NaI} are reproducible with a standard deviation of 0.005.

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

$$\ln a_1 = \ln(p/p^*) + (B - V_s^*)(p - p^*)/RT \qquad (2)$$

where B, V_s^*, and p^* are the second virial coefficient, molar volume, and vapor pressure of pure 2-propanol, respectively. The values of $B = -3.424 \times 10^{-3}$ m^3·mol^{-1} and $p^* = 5.7774$ kPa (taken from ref 13) were used at 25 °C. The experimental vapor pressure data are also given in Tables 2−4.

Correlation of Data. There are several models describing VLE of polymer solutions. The model of Flory−Huggins[7] is an important lattice model which has the form

$$\ln a_1 = \ln \phi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \phi_1) + \chi_{12}(1 - \phi_1)^2 \qquad (3)$$

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. According to Flory−Huggins,[7] χ_{12} should be independent of concentration and molecular weight of polymer. However, in applying the FH equation to almost all polymer solutions, especially polar systems, it is necessary to consider χ_{12} dependent on concentration and molar mass of the polymer, in addition to temperature, to fit the activity data of components of the solution.[14,15] Indeed, using eq 3, for each system

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

	Flory−Huggins		modified Flory−Huggins		
system	χ_{12}	ARD%(a_1)[a]	d	f	ARD%(a_1)
2-propanol + PEG 1000	0.6294	0.13	0.0018	0.4457	0.07
2-propanol + PEG 300	0.6019	0.13	0.0016	0.6413	0.10
2-propanol + PEG 200	0.7029	0.16	0.0034	−1.8268	0.09

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

considered in this work we also obtain different χ_{12} values at different mass fractions and molar masses of polymer. In Table 5, the Flory−Huggins interaction parameters calculated from the experimental 2-propanol activity data are given, as an example, for the 2-propanol + PEG 300 system. As can be seen from Table 5, the values for χ_{12} vary from 0.4420 to 0.6473 for this system. However, for the concentration dependency of χ_{12}, a number of relations have been proposed in the literature. For the concentration and temperature dependency of χ_{12}, Bae et al.[8] have suggested the following relation

$$\chi_{12}(T,\phi) = D(T)\,F(\phi_2) \tag{4}$$

with

$$D(T) = d_0 + \frac{d_1}{T} + d_2 \ln T \tag{5}$$

and

$$F(\phi_2) = \frac{1}{1 - f\phi_2} \tag{6}$$

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

$$\chi_{12} = \frac{d}{1 - f(1 - \phi_1)} \tag{7}$$

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

Thus, at a constant temperature (here, 25 °C), the modified FH equation proposed by Bae et al.[8] takes the following form

$$\ln a_1 = \ln \phi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \phi_1) + \frac{d(1 - \phi_1)^2}{1 - f(1 - \phi_1)} \tag{8}$$

For the correlation of our experimental activity data, both the original FH equation and the one in which χ_{12} is expressed as eq 7 were considered. For polymer solutions with different molar masses, r_2 values were calculated using the relation $r_2 = (M/\rho_p)/(M_s/\rho_s)$, where ρ_p and ρ_s are the densities of the polymer and 2-propanol, respectively. The values for the densities of PEG 300 and PEG 200 were obtained experimentally as (1.122 28 and 1.121 18) g·cm^{-3}, respectively, using a vibrating tube densimeter (Kyoto Electronic DA-210, Japan). The method of measurement has been described previously.[16] The density value for PEG 1000 was calculated as 1.195 g·cm^{-3} using the group contribution method proposed by Zana.[17] Calculations with the FH equation show that the interaction parameter χ_{12} is concentration and molar mass dependent. In Table 6, the interaction parameter, χ_{12}, of the FH equation and the constants of eq 8 are given along with the absolute relative percentage deviation (ARD%) values of the FH and the modified FH equations. Table 6 indicates that better agreement between the experimental and the calculated activities for the aforementioned systems is obtained with the modified FH equation.

Conclusions

The accurate activity of 2-propanol in 2-propanol + poly(ethylene glycol) solutions has been measured by the isopiestic technique at 25 °C. The results have been correlated to the Flory−Huggins and the modified Flory−Huggins equations. It was found that the Flory interaction parameter is strongly concentration and molar mass dependent, so that the correlation of solvent activity data to the modified Flory−Huggins equation with concentration dependent parameters has resulted in lower absolute relative percentage deviations. Using the modified Flory−Huggins equation reduces the absolute relative percentage deviation of the fit from 0.13 to 0.07 for 2-propanol + PEG 1000, from 0.13 to 0.10 for 2-propanol + PEG 300, and from 0.16 to 0.09 for 2-propanol + PEG 200 systems.

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