For a component i in a mixture

$$\ln \varphi_i = 2 \ln\left(\frac{2v}{2v-b}\right) + \frac{1}{bRT}\left(a + \frac{\partial a}{\partial x_i} - \frac{a}{b}\frac{\partial b}{\partial x_i}\right)\ln\left(\frac{v}{v+b}\right) - \left(\frac{2}{2v-b} - \frac{1}{bRT}\frac{a}{v+b}\right)\left(b - \frac{\partial b}{\partial x_i}\right) - \ln Z \quad (8)$$

In this formula a and b equal a_M and b_M of eq 4.

Glossary

a, b	parameters in equation of state (1)
k	binary interaction coefficient
p	total pressure, bar
R	gas constant (83.1448 bar·cm^3/mol·K)
T	absolute temperature, K
t	$0.001T$
v	molal volume, cm^3/mol
x	mole fraction in liquid
y	mole fraction in vapor
Z	compressibility factor pv/RT
α_1	relative volatility y_1x_2/x_1y_2
φ	fugacity coefficient
Ω_a, Ω_b	numerical factors in a and b, eq 2 and 3

Subscripts

1, 2	refer to propylene and propane, respectively
i, j	refer to any of the components
c	critical
M	mixture

Registry No. Propylene, 115-07-1; propane, 74-98-6.

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Vapor–Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 3. Poly(ethylene glycols)

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The activity of water in solutions of poly(ethylene glycols) (PEGs, molecular weights 200, 600, 1500, 6000) was measured over a wide range of weight fractions at 293.1, 313.1, and 333.1 K. The data were obtained by an isopiestic method. A comparison between the measured activities and predicted values by the UNIFAC method gives a good agreement for PEG 200 solutions only.

Introduction

Poly(ethylene glycols) are polymers that find a wide range of industrial applications due to their high solubility in water. They are commonly used in the pharmaceutical industry as excipients in drug formulation, as surface-active agents in water treatment, as fiber-forming aids in the textile industry, in the manufacture of lubricants and mold release agents, and recently as reactive moieties in the preparation of hydrophilic polyurethane networks for medical purposes (*1*, *2*). The properties of the aqueous solutions of poly(ethylene glycols) have been extensively studied by various methods (*3*–*6*).

Malcolm and Rowlinson (*7*) measured the vapor pressures of aqueous solutions of poly(ethylene glycol) of molecular weights 300, 3000, and 5000 at 303–338 K. The water activity was calculated from the data. Adamcova (*8*) employed an isopiestic method to measure the water activity in aqueous solutions of poly(ethylene glycols) (molecular weights 200–20 000) at 298 K. This study was limited to relatively dilute solutions (polymer weight fraction less than 0.5).

In this work we have enlarged the body of available data on the activity of aqueous PEG solutions by obtaining data for polymers in the molecular weight range of 200–6000 over the entire concentration range.

Experimental Section

The isopiestic apparatus employed in this study is described in detail elsewhere (*9*). The reference solute was lithium chloride, manufactured by Merck Co. Its purity analyzed by atomic absorption and titration was better than 99.8%. The poly(ethylene glycols), manufactured by BDH, were used as supplied. After the salt and the polymers were dried at 120 °C, their water content measured by Karl Fischer analysis was less than 0.3% and 0.7%, respectively.

Results and Discussion

The water activity was calculated from the expression

$$\ln a_w = -\nu_r m_r \phi_r / 55.51 \quad (1)$$

where ν_r, m_r, and ϕ_r are the number of ions, the molality, and

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Table I. Water Activity in Poly(ethylene glycol)–Water Solutions

293.1 K		313.1 K		333.1 K	
w_p[a]	a_w[b]	w_p	a_w	w_p	a_w
		Molecular Weight 200[c]			
0.1493	0.9849	0.1473	0.9843	0.1493	0.9849
0.2215	0.9707	0.2220	0.9706	0.2329	0.9728
0.5135	0.8654	0.4481	0.9125	0.3828	0.9350
0.5735	0.8231	0.5197	0.8790	0.4670	0.9154
0.6912	0.7294	0.5332	0.8721	0.5438	0.8819
0.8445	0.5170	0.5815	0.8415	0.5586	0.8753
0.8932	0.4106	0.6411	0.7916	0.7328	0.7508
0.9695	0.1976	0.7120	0.7422	0.7805	0.6663
		0.8011	0.6102	0.8375	0.5937
		0.8419	0.5540	0.8564	0.5650
		0.8670	0.4915	0.9020	0.4493
		0.8725	0.4806	0.9370	0.3215
		0.8991	0.4404	0.9693	0.2430
		0.9180	0.3735		
		0.9576	0.2454		
		0.9663	0.2096		
		Molecular Weight 600[c]			
0.4800	0.9182	0.2310	0.9868	0.2670	0.9858
0.5021	0.9056	0.3266	0.9738	0.3662	0.9729
0.5998	0.8462	0.4734	0.9367	0.4172	0.9633
0.7065	0.7591	0.5392	0.9100	0.5672	0.9186
0.7815	0.6851	0.5395	0.9089	0.6737	0.8644
0.8082	0.6547	0.6340	0.8570	0.7644	0.7953
0.8905	0.5280	0.6905	0.8130	0.8261	0.7266
0.9011	0.4996	0.7028	0.8071	0.9136	0.5584
0.9492	0.3569	0.7245	0.7908	0.9648	0.3446
0.9650	0.2718	0.7470	0.7661	0.9761	0.2616
0.9846	0.1512	0.8083	0.6938	0.9849	0.1909
		0.8368	0.6658		
		0.8473	0.6518		
		0.8929	0.5713		
		0.9000	0.5548		
		0.9131	0.5235		
		0.9548	0.3708		
		0.9632	0.3150		
		0.9823	0.1932		
		Molecular Weight 1500[c]			
0.3454	0.9714	0.5035	0.9392	0.5746	0.9333
0.4631	0.9358	0.5995	0.8958	0.6481	0.9037
0.5437	0.8964	0.6095	0.8903	0.7071	0.8709
0.5825	0.8732	0.6259	0.8823	0.7734	0.8284
0.6378	0.8346	0.7223	0.8178	0.8506	0.7522
		0.8175	0.7379	0.9163	0.6288
		0.8930	0.6395	0.9779	0.3248
		0.9075	0.6060		
		Molecular Weight 6000[c]			
		0.3292	0.9862	0.3248	0.9905
		0.4408	0.9624	0.5068	0.9595
		0.5341	0.9344	0.5344	0.9524
		0.6280	0.8892	0.5800	0.9376
		0.7047	0.8464	0.6832	0.8985
				0.7852	0.8411
				0.8095	0.8207
				0.8761	0.7498
				0.8932	0.7244
				0.9375	0.6170
				0.9677	0.4826
				0.9761	0.4162
				0.9910	0.3576

[a] Polymer weight fraction. [b] Water activity. [c] The average molecular weights given by the manufacturer are as follows: PEG 200, 190–210; PEG 400, 380–420; PEG 1500, 1430–1570; PEG 6000, 6000–7500.

the osmotic coefficient of the reference electrolyte (LiCl in this study). The osmotic coefficient was calculated from the Gibbard and Scatchard (*10*) correlation.

The data for the four poly(ethylene glycols) are listed in Table I. The effect of the temperature on PEG 200 solutions is illustrated in Figure 1.

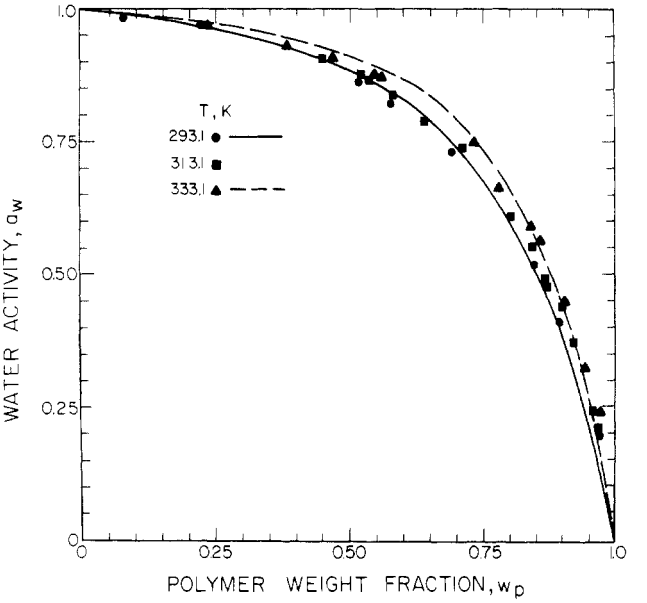

Figure 1. Effect of temperature on the activity of water in poly(ethylene glycol) 200 aqeuous solution. Points—experimental data; curves—UNIFAC predictions.

In the limited number of cases where direct comparison is possible the agreement between our data and the data obtained by Malcolm and Rowlinson (*7*) is very good. Our data show similar agreement with the experiments of Adamcova (*8*) but due to the limited range of concentrations in the latter the significance of such an agreement is minor.

The UNIFAC method for predicting the solvent activity in polymer solutions was tested successfully in various systems (*11*). The interaction parameters for the glycol–water systems were estimated in a previous study (*12*). While the agreement of the model with data is good for PEG 200 as demonstrated by the curves in Figure 1, large discrepancies are found for PEG 600, 1500, and 6000 at weight fractions lower than 0.9. Furthermore, the correction due to the free volume as proposed by Olshi and Prausnitz (*11*) cannot be used in aqueous systems since the value of the reduced volume of water ($\tilde{v}_1 \cong 1$) makes the free volume term excessively large. It should be pointed out that the UNIFAC method gives good predictions for the system PEG–benzene (*11*).

A possible explanation for this behavior is the hydrogen-bond complex between water and polymer molecules. The association of three water molecules with each unit of the polymer (*5*) as well as one water molecule with each unit (*6*) has been reported. These effects cannot be handled by the UNIFAC method.

Registry No. Poly(ethylene glycol) (SRU), 25322-68-3; water, 7732-18-5.

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