E, F	parameters for eq 4
A_i	least-squares coefficients of eq 7 and 8
r_i	powers of eq 7 and 8
$\gamma_\pm$	mean molal activity coefficient of solute
a_1	water activity
M_1	molecular mass of water
a, B'	parameters of Bahe's equation (eq 10)
$\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, α_1, α_2, C^Φ	parameters of Pitzer's equation
A^Φ	Pitzer's Φ equation Debye-Hückel constant for 1-1 electrolytes
σ	standard deviation of fitting equations

Registry No. $MnCl_2$, 7773-01-5; $MnSO_4$, 7785-87-7; RbCl, 7791-11-9.

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Vapor-Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 2. Tetraethylene Glycol and Estimation of UNIFAC Parameters

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The activity of water in tetraethylene glycol solutions has been measured at 298.1 K. Vapor-liquid equilibrium data in aqueous solutions of tri- and tetraethylene glycols are used to estimate the interaction parameters for the UNIFAC group contribution model. The activity of water in poly(ethylene glycol) 300 and poly(propylene glycol) 400 is calculated by the UNIFAC method. Good agreement with experimental data is obtained for the former and moderate agreement for the latter.

Introduction

The UNIFAC method for predicting activity coefficients in mixtures of nonelectrolyte solutions has been widely used in recent years (*1*). It is based on the group contribution concept which assumes that the liquid mixture consists of functional groups such as CH_2, CH_2O rather than molecules of various components. The activity coefficients are divided into a combinatorial part and a residual part.

$$\ln \gamma_i = \ln \gamma_i^{c} + \ln \gamma_i^{R} \tag{1}$$

The combinatorial part is a function of the mole fractions and the reduced van der Waals parameters. The residual part depends on adjustable parameters called group interaction parameters. The equations of γ_i^c and γ_i^R and a list of parameters are given elsewhere (*1*, *2*).

The water activity in triethylene glycol solution was recently measured by an isopiestic method (*3*). These data together

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Table I. Isopiestic Data and Calculated Activity Coefficients in Tetraethylene Glycol Solutions at 298.1 K

x_w[a]	m_{LiCl}[b]	ϕ[c] LiCl	ϕ[c] TeEG	a_w[d]	γ_w[e] exptl	γ_w[e] calcd[f]
0.2566	17.07	3.037	0.4982	0.1546	0.6026	0.6199
0.3102	15.38	2.990	0.5756	0.1909	0.6150	0.6319
0.5114	11.11	2.619	0.8471	0.3510	0.6862	0.6918
0.5183	11.09	2.617	0.8618	0.3519	0.6916	0.6944
0.5412	10.53	2.540	0.8778	0.3818	0.7054	0.7033
0.5869	9.789	2.431	0.9406	0.4246	0.7234	0.7227
0.6311	9.039	2.312	0.9948	0.4712	0.7467	0.7438
0.6353	8.959	2.300	0.9989	0.4763	0.7498	0.7459
0.6803	8.192	2.171	1.053	0.5272	0.7749	0.7703
0.6984	7.861	2.114	1.070	0.5498	0.7873	0.7810
0.7343	7.208	2.000	1.108	0.5952	0.8106	0.8039
0.7511	6.954	1.955	1.112	0.6130	0.8162	0.8153
0.7585	6.738	1.917	1.129	0.6282	0.8282	0.8205
0.8163	5.643	1.723	1.202	0.7047	0.8633	0.8646
0.8302	5.329	1.668	1.210	0.7262	0.8746	0.8761
0.8455	5.029	1.616	1.238	0.7463	0.8827	0.8891
0.8500	4.949	1.602	1.268	0.7516	0.8843	0.8930
0.8577	4.664	1.554	1.215	0.7704	0.8982	0.8997
0.8708	4.299	1.492	1.204	0.7938	0.9115	0.9113
0.8907	3.757	1.404	1.195	0.8271	0.9286	0.9290
0.9293	2.534	1.216	1.127	0.8950	0.9631	0.9626

[a] Mole fraction of water. [b] Molality of LiCl. [c] Osmotic coefficient. [d] Water activity. [e] Water activity coefficient. [f] Van Laar.

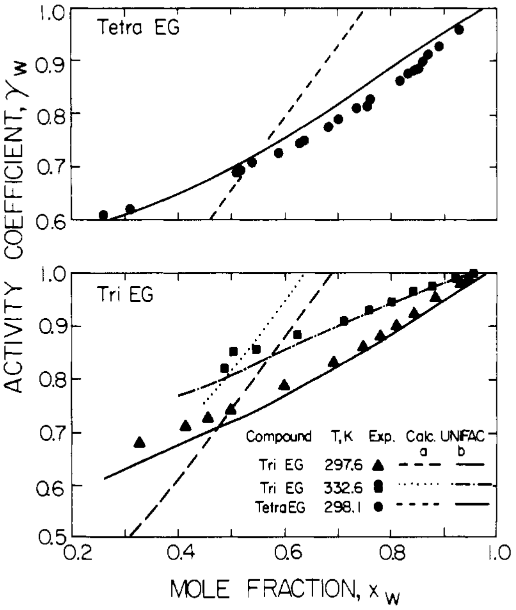

Figure 1. Activity of water in tri- and tetraethylene glycol solutions: (a) old interaction parameters; (b) new interaction parameters.

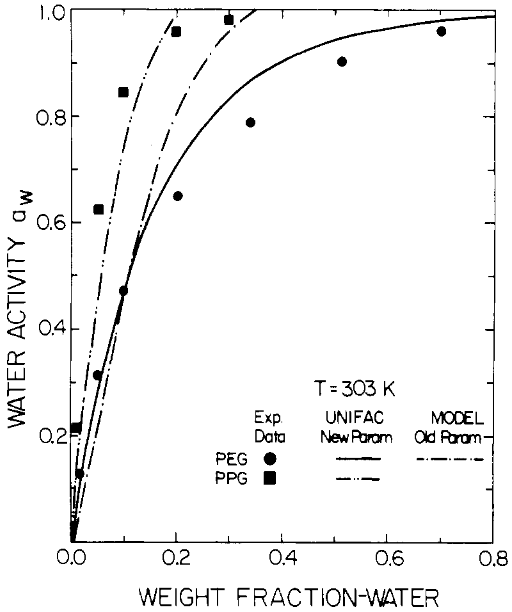

Figure 2. Activity of water in poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) solutions at 303 K. Experimental data from ref *5*.

Table II. UNIFAC Parameters

1. van der Waals Reduced Parameters

$R_{CH_2OH} = 1.204$ $Q_{CH_2OH} = 1.124$

2. Interaction Parameters, Q_{mn}, K

m	n: CH_2	H_2O	CH_2O	CH_2OH
CH_2	0	1318	251.5	3000
H_2O	300	0	540.5	748.6
CH_2O	83.36	-314.7	0	729.7
CH_2OH	88.15	-466.8	187.5	0

with experimental measurements in tetraethylene solution are used to estimate the interaction parameters.

Experimental Results and Discussion

The experimental procedure and the apparatus employed in the isopiestic measurements are described elsewhere (*3*). Data obtained at 298.1 K are listed in Table I. The activity coefficients γ_w in tetraethylene glycol solution are plotted as a function of x_w in Figure 1. They are fitted to a Van Laar equation:

$$\ln \gamma_w = \frac{A_{12}}{\left(1 + \frac{A_{12}}{A_{21}} \frac{x_w}{1 - x_w}\right)^2} \quad (2)$$

The values of A_{12} and A_{21} are -0.5511 and -2.587, respectively. The calculated values of γ_w are listed in Table I.

Estimation of Interaction Parameters

The UNIFAC method was employed to predict the activity coefficients of water in tri- and tetraethylene glycol solutions. The van der Waals and interaction parameters of the groups

Table III. Water Activity in Poly(ethylene glycol) and Poly(propylene glycol) Solutions (*5*)

wt fraction	a_w exptl	a_w UNIFAC	dev, %	a_w^{new}(UNIFAC)	dev, %
			PEG, 30 °C		
0.012	0.124	0.077	−37.9	0.120	−3.2
0.050	0.309	0.222	−28.2	0.285	−7.8
0.101	0.468	0.464	−0.9	0.481	2.8
0.200	0.648	0.803	23.9	0.716	10.5
0.341	0.789	0.994	26.0	0.870	10.3
0.512	0.900	1.000	11.1	0.947	5.2
0.702	0.956	1.000	4.6	0.979	2.4
			18.9 (av)		6.0 (av)
			PEG, 65 °C		
0.012	0.134	0.095	−29.1	0.088	−3.0
0.049	0.342	0.256	−25.1	0.316	−7.6
0.100	0.520	0.508	−2.3	0.526	1.2
0.199	0.707	0.837	18.4	0.766	8.3
0.338	0.833	1.000	20.0	0.907	8.9
0.511	0.926	1.000	8.0	0.967	4.4
0.701	0.970	1.000	3.1	0.986	1.6
			15.1 (av)		5.1 (av)
			PPG, 30 °C		
0.010	0.208	0.056	−73.1	0.113	−45.7
0.050	0.625	0.339	−45.8	0.463	−25.9
0.099	0.845	0.666	−21.2	0.738	−12.7
0.200	0.955	1.000	4.7	0.994	4.1
0.300	0.978	1.000	2.2	1.000	2.2
0.410	0.985	1.000	1.5	1.000	1.5
			24.8 (av)		15.3 (av)

CH_2O, CH_2, OH, and H_2O were obtained from revised tables published recently (*2*). The results, plotted in Figure 1, deviate significantly from the experimental data. Then a new group, CH_2OH, is introduced.

The interaction parameters were evaluated by a minimization method previously used for silicone compounds (*4*). Their values are listed in Table II. The values of γ_w calculated with the new set of parameters are also depicted in Figure 1. In order to test the applicability of these new parameters to a wider class of materials the activity of water in solutions of low molecular weight polyglycols has been computed. The data of Malcolm and Rowlinson (*5*) on poly(ethylene glycol) (molecular weight 300) at 30 and 65 °C and poly(propylene glycol) (molecular weight 400) at 30 °C were used. The results are depicted in Figure 2 and summarized in Table III. An improved agreement between computed values and experimental data is obtained with the new UNIFAC parameters for all three solutions and over the entire concentration range. The average deviation is reduced by a factor of 3 in the case of PEG. A smaller improvement is obtained for the PPG solution.

The reduced improvement in the case of the PPG solution indicates the smaller role played by the hydroxyl end groups in solutions of this polymer probably due to the shielding effect of the bulky methyl group in its vicinity.

Registry No. TeEG, 112-60-7; H_2O, 7732-18-5.

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Solubility, Density, and Viscosity for Sodium Sulfate–Methanol–Water Systems at 40 °C

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The solubility of sodium sulfate in water–methanol mixtures has been determined at 40 °C. Data for densities and viscosities of sodium sulfate–water–methanol systems are presented, covering the whole range from dilute to saturated solutions.

Introduction

Physical data referring to binary salt–water systems are available for nearly all substances of interest. For ternary systems like salt–water–alcohol systems there is a great lack of information. Addition of low alcohols to aqueous salt solu-

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