

# Excess Volume of Polymer/Solvent Mixtures and Proposed Model for Prediction of Activity of Solvents Based on Excess Volume Data

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**ABSTRACT:** Density measurements were used to evaluate the excess volume of binary mixtures of poly(ethylene glycol) in water and ethanol solvents, poly(propylene glycol) in water and ethanol solvents, and poly(vinyl alcohol) in water solvent at different temperatures for various molecular weights of polymers. The excess volumes were correlated and expressed by a polynomial in terms of the weight fraction of the polymer. The activity of the solvent was expressed in terms of three parts: excess internal energy, excess entropy, and excess volume. The excess volume was derived from the expression obtained in this work, the excess entropy was derived from Flory's lattice model, and the

excess internal energy was used as a weight average of the excess volume and entropy parts. The results indicated good agreement between the activity of the solvent calculated by the proposed model and the experimental data. The proposed model has the advantage that using only simple density measurements the activity values that are necessary in the calculation of thermodynamic properties can be evaluated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1219–1227, 2005

**Key words:** excess volume; thermodynamic model; activity; Flory–Huggins theory

## INTRODUCTION

Since 1941 when Flory and Huggins developed their well-known model for polymer mixtures, much work has been carried out in order to predict the thermodynamic properties of polymer solutions using various models. One of the newest of them is a model based on a hard-sphere limit.<sup>1</sup> The models can be classified as<sup>2</sup> noncompressible models, compressible lattice models, off-lattice models, and models based on a generalized van der Waals partition function. In the first group is Flory and Huggins theory.<sup>3,4</sup> In the compressible model the free volume concept has been utilized to consider the phase behavior of polymer mixtures. The assumptions are similar to that of Flory–Huggins and the free volume is assumed to be due to unoccupied sites in the lattice. In this respect the work of Costas and Sanctuary,<sup>5</sup> High and Danner,<sup>6</sup> Panayiotou and Vera,<sup>7</sup> and Sanchez and Lacombe<sup>8</sup> are worth mentioning. In the off-lattice model the continuity of polymer configurations is the essential assumption. Therefore, the polymer chain is considered to consist of thermal hard spheres that are connected

together.<sup>9,10</sup> In the fourth class of the models the equation of state based on the van der Waals equation of state can be mentioned. The theory of a perturbed hard chain is obtained on this grounds.<sup>11,12</sup>

In these models activity coefficients are necessary quantities when dealing with thermodynamic property calculations of mixtures. The solution nonidealities of mixtures are represented by the activity coefficients that arise from molecular interactions of components in the mixture, the volume change of pure components upon mixing, and the arrangements of molecules in the mixtures. The activity coefficient of a component  $i$  ( $\gamma_i$ ) can be derived from the well-known thermodynamic equation:

$$RT \ln \gamma_i = \left( \frac{\partial n g^E}{\partial n_i} \right)_{T,P,n_{j=1}} \quad (1)$$

where  $g^E$  is the molar excess Gibbs function and  $n$  is the total number of moles of the components ( $n = \sum_{i=1}^c n_i$ ).

The molar excess Gibbs function is defined as

$$g^E = u^E + Pv^E - Ts^E \quad (2)$$

where  $u^E$  is the molar excess internal energy,  $v^E$  is the molar excess volume, and  $s^E$  is the molar excess en-

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**TABLE I**  
**Measured Densities ( $\rho/g\text{ cm}^{-3}$ ) of Aqueous Solutions of PEG with Different Molecular Weights at Various Temperatures and Concentrations**

$T$ ( $^{\circ}\text{C}$ )	Mass fraction of PEG200 in solution									
	0.0999	0.2003	0.2996	0.3998	0.4998	0.6000	0.7002	0.8000	0.8997	1.0000
25	1.0186	1.0347	1.0508	1.0659	1.0805	1.0984	1.1069	1.1190	1.1231	1.1256
35	1.0152	1.0325	1.0466	1.0624	1.0769	1.0910	1.1039	1.1122	1.1179	1.1196
45	1.0111	1.0280	1.0411	1.0547	1.0707	1.0843	1.0964	1.1054	1.1102	1.1122
55	1.0037	1.0220	1.0356	1.0486	1.0640	1.0766	1.0888	1.0966	1.1022	1.1044
65	1.0005	1.0155	1.0288	1.0378	1.0560	1.0682	1.0800	1.0889	1.0934	1.0964
	Mass fraction of PEG300 in solution									
	0.0998	0.2002	0.3002	0.4001	0.4997	0.6000	0.7000	0.8007	0.9000	1.0000
25	1.0231	1.0363	1.0553	1.0682	1.0821	1.1019	1.1096	1.1226	1.1269	1.1304
35	1.0208	1.0332	1.0534	1.0653	1.0804	1.0960	1.1066	1.1152	1.1205	1.1224
45	1.0169	1.0275	1.0471	1.0572	1.0704	1.0870	1.0984	1.1065	1.1120	1.1156
55	1.0112	1.0202	1.0424	1.0531	1.0612	1.0776	1.0882	1.0988	1.1043	1.1080
65	1.0067	1.0150	1.0348	1.0447	1.0563	1.0701	1.0786	1.0895	1.0962	1.1000
	Mass fraction of PEG600 in solution									
	0.1117	0.2008	0.3006	0.4027	0.5015	0.6026	0.7007	0.8007	0.9004	1.0000
25	1.0144	1.0304	1.0473	1.0642	1.0809	1.0953	1.1068	1.1169	1.1212	1.1225
35	1.0094	1.0249	1.0417	1.0580	1.0743	1.0883	1.0995	1.1080	1.1137	1.1151
45	1.0058	1.0205	1.0371	1.0527	1.0683	1.0817	1.0932	1.1018	1.1057	1.1065
55	1.0022	1.0167	1.0317	1.0476	1.0621	1.0746	1.0851	1.0935	1.0984	1.0992
60	0.9975	1.0119	1.0272	1.0427	1.0581	1.0709	1.0814	1.0904	1.0949	1.0965
	Mass fraction of PEG2000 in solution									
	0.0547	0.1002	0.1515	0.2055	0.2513	0.3071	0.3512	0.4039	0.4522	0.5004
25	1.0131	1.0216	1.0306	1.0389	1.0478	1.0563	1.0651	1.0736	1.0820	1.0906
35	1.0054	1.0162	1.0251	1.0343	1.0429	1.0516	1.0599	1.0689	1.0781	1.0861
45	0.9942	1.0078	1.0187	1.0279	1.0372	1.0460	1.0546	1.0634	1.0719	1.0803
55	0.9889	1.0026	1.0134	1.0228	1.0323	1.0407	1.0493	1.0580	1.0671	1.0751
60	0.9865	1.0003	1.0107	1.0205	1.0301	1.0391	1.0468	1.0556	1.0649	1.0726

tropy. To obtain  $\gamma_i$  at temperature  $T$  and pressure  $P$  exact composition dependent functions for  $u^E$ ,  $v^E$ , and  $s^E$  are required. However, attempts to obtain the exact functionality for  $g^E$  have not been successful and the proposed activity coefficient models suffer from limitations imposed by the assumptions. In this respect the Margules and van Laar<sup>13</sup> models can be cited where, by considering that the mixing of components is random, it is assumed that  $s^E = 0$ . Another assumption in these models is imposed by the assumption of no volume change upon mixing, that is,  $v^E = 0$ . Therefore, the solution nonidealities are merely attributed to the molecular interactions between pair molecules and a functionality for  $u^E$  is derived.

In some models nonrandomness is considered as the main cause for deviation of mixtures from ideal behavior. Nonrandom two liquid mixtures is an example of these models.

Flory's pioneer work<sup>14</sup> derived  $s^E$  for polymer/solvent mixtures by utilizing the lattice theory previously proposed by Guggenheim. In the Flory model the arrangement of polymer chains and solvent in the lattice are taken into account and then an equation for

$s^E$  is obtained. The value of  $s^E$  in the Flory model is in the following form:

$$\frac{S^E}{R} = -x_1 \ln \left[ 1 - (1 - \phi_1) \left( 1 - \frac{1}{r} \right) \right] - x_2 \ln [r - \phi_2(r - 1)] \quad (3)$$

where  $x$  and  $\phi$  are the mole fraction and volume fraction of the solvent (1) and polymer (2), respectively, and  $r$  is the number of segments in the polymer chain. The volume fraction is expressed as

$$\phi_1 = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2} \quad \text{and} \quad \phi_2 = 1 - \phi_1 \quad (4)$$

and  $r$  is defined as the ratio of the molar volume of the polymer (2) to that of the solvent (1):

$$r = \frac{v_2}{v_1} \quad (5)$$

TABLE II  
Measured Densities ( $\rho/\text{g cm}^{-3}$ ) of Aqueous Solutions of PPG425 at Various Temperatures and Concentrations

$T$ ( $^{\circ}\text{C}$ )	Mass fraction of PPG425 in solution									
	0.0982	0.1995	0.3002	0.4001	0.4992	0.5914	0.6975	0.8004	0.9005	1.000
25	1.0170	1.0253	1.0312	1.0391	1.0380	1.0419	1.0426	1.0347	1.0311	1.0193
35	1.0135	1.0216	1.0277	1.0341	1.0339	1.0373	1.0373	1.0262	1.0255	1.0125
45	TP	TP	TP	TP	TP	TP	1.0279	1.0198	1.0189	1.0054
55	TP	TP	TP	TP	TP	TP	TP	1.0102	1.0109	0.9962
65	TP	TP	TP	TP	TP	TP	TP	TP	1.0020	0.9881

TP, two-phase mixture

However, Flory assumed that  $v^E = 0$ ; therefore,  $g^E$  was approximated as

$$g^E = u^E - Ts^E \quad (6)$$

and  $u^E$  was obtained from the Scatchard–Hildebrand model.<sup>13</sup>

In this work a simple model for prediction of solvent activities in polymer solutions is proposed. The excess volume can be evaluated easily by density measurements using simple laboratory equipment with the lowest cost and in a short time.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) (PEG) with number-average molecular weights of 200 (PEG200), 300 (PEG300), 600 (PEG600), and 2000 (PEG2000); poly(propylene glycol) (PPG) with number-average molecular weights of 425 (PPG425), 1025 (PPG1025), and 2025 (PPG2025); and poly(vinyl alcohol) (PVA) with a number-average molecular weight of 15000 (PVA15000) were used. The polymers and pure ethanol were provided by Merck. The binary polymer/solvent solutions were made with pure ethanol and double-distilled water as the solvents.

### Methods

All of the solutions were prepared by mass on an analytical balance (Sartorius) with  $\pm 0.1$  mg accuracy. The density measurements were carried out using a

10-cm<sup>3</sup> glass pycnometer. The volume of the pycnometer was calibrated as a function of temperature by using double-distilled water. The density measurements were carried out at 293.2, 308.2, 313.2, 318.2, 328.2, 333.2, and 338.2 K. A constant temperature water bath was used to control the temperature of the solutions to an accuracy of  $\pm 0.1$  K. Each measurement was repeated 5 times. The reproducibility of the density measurements was estimated as  $\pm 0.0002$  g cm<sup>-3</sup>. The measured densities are reported in Tables I–V.

The excess volume of a binary solution ( $v^E$ ) can be determined by density measurements using the following equation:

$$v^E = \frac{1}{\rho} - \left( \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \right) \quad (7)$$

where  $\rho$  is the density of the solution,  $w_1$  and  $w_2$  are the weight fractions of components 1 and 2, respectively; and  $\rho_1$  and  $\rho_2$  are the densities of pure components.

### Modeling

Excess volume

The density data are usually fitted to a polynomial of the following form<sup>15,16</sup>:

$$\rho/(\text{g cm}^{-3}) = A + Bw_2 + Cw_2^2 + Dw_2^3 \quad (8)$$

where  $\rho$  is the measured density of the solution;  $A$ ,  $B$ ,  $C$ , and  $D$  are coefficients of the polynomial (g cm<sup>-3</sup>);

TABLE III  
Measured Densities ( $\rho/\text{g cm}^{-3}$ ) of Aqueous Solutions of PVA15000 at Various Temperatures and Concentrations

$T$ ( $^{\circ}\text{C}$ )	Mass fraction of PVA15000 in solution									
	0.0982	0.1995	0.3002	0.4001	0.4992	0.5914	0.6975	0.8004	0.9005	1.000
25	1.0170	1.0253	1.0312	1.0391	1.0380	1.0419	1.0426	1.0347	1.0311	1.0193
35	1.0135	1.0216	1.0277	1.0341	1.0339	1.0373	1.0373	1.0262	1.0255	1.0125
45	TP	TP	TP	TP	TP	TP	1.0279	1.0198	1.0189	1.0054
55	TP	TP	TP	TP	TP	TP	TP	1.0102	1.0109	0.9962
65	TP	TP	TP	TP	TP	TP	TP	TP	1.0020	0.9881

**TABLE IV**  
**Measured Densities ( $\rho/g\text{ cm}^{-3}$ ) of Aqueous Solutions of PEG200 and Ethanol Solutions at Various Temperatures and Concentrations**

T (°C)	Mass fraction of PEG200 in solution									
	25	0.0999	0.2005	0.2995	0.4002	0.5008	0.6010	0.7001	0.8001	0.9007
35	0.8177	0.8453	0.8745	0.9050	0.9394	0.9707	1.0072	1.0453	1.0854	1.1256
45	0.8088	0.8355	0.8651	0.8962	0.9282	0.9630	0.9985	1.0364	1.0758	1.1196
55	0.7996	0.8269	0.8570	0.8878	0.9202	0.9546	0.9899	1.0293	1.0686	1.1122
65	0.7907	0.8187	0.8483	0.8799	0.9122	0.9468	0.9830	1.0206	1.0603	1.1044
65	0.7813	0.8110	0.8396	0.8718	0.9034	0.9378	0.9750	1.0124	1.0532	1.0964

T (°C)	Mass fraction of PEG300 in solution									
	25	0.0991	0.2014	0.2995	0.3995	0.4992	0.6001	0.7008	0.7998	0.8925
35	0.8215	0.8497	0.8789	0.9093	0.9425	0.9785	1.0137	1.0502	1.0897	1.1304
45	0.8118	0.8403	0.8696	0.9004	0.9339	0.9688	1.0057	1.0432	1.0820	1.1224
55	0.8041	0.8315	0.8611	0.8928	0.9262	0.9606	0.9971	1.0356	1.0747	1.1156
65	0.7938	0.8227	0.8521	0.8838	0.9180	0.9517	0.9893	1.0277	1.0661	1.1080
65	0.7838	0.8134	0.8434	0.8747	0.9102	0.9428	0.9817	1.0195	1.0577	1.1000

and  $w_2$  is the mass fraction of the polymer in the solution. The values of these coefficients were obtained by regression and are given in Table VI.

By using eqs. (7) and (8), the  $v^E$  values of the studied mixtures are calculated and example results are shown in Figures 1–4.

Activity model

Equation (1) can be written in terms of the mole fraction of solvent ( $x_1$ ) in the following form:

$$RT \ln \gamma_1 = g^E + (1 - x_1) \frac{\partial g^E}{\partial x_1} \tag{9}$$

By using eq. (2) in eq. (9) we have

$$RT \ln \gamma_1 = u^E + Pv^E - Ts^E + (1 - x_1) \frac{\partial}{\partial x_1} (u^E + Pv^E - Ts^E) \tag{10}$$

or

$$RT \ln \gamma_1 = \left[ u^E + (1 - x_1) \frac{\partial}{\partial x_1} (u^E) \right] + \left[ Pv^E + (1 - x_1) \frac{\partial}{\partial x_1} (Pv^E) \right] + \left[ -Ts^E + (1 - x_1) \frac{\partial}{\partial x_1} (-Ts^E) \right] \tag{11}$$

Now, from eq. (11) it is seen that the activity coefficient of the solvent ( $\gamma_1$ ) can be divided into three parts: internal energy ( $\gamma_1^U$ ), volume ( $\gamma_1^V$ ), and entropy ( $\gamma_1^S$ ):

$$\gamma_t = \gamma_1^U \gamma_1^V \gamma_1^S \tag{12}$$

**TABLE V**  
**Measured Densities ( $\rho/g\text{ cm}^{-3}$ ) of PPG and Ethanol Solutions at Various Temperatures and Concentrations**

T (°C)	Mass fraction of PPG1025 in solution									
	25	0.1002	0.4995	0.6003	0.6988	0.7999	0.9002	1.0000		
35	0.8087	0.8938	0.9170	0.9413	0.9662	0.9903	1.0176			
45	0.8007	0.8858	0.9076	0.9328	0.9574	0.9820	1.0096			
55	0.7925	0.8776	0.8995	0.9244	0.9494	0.9740	1.0022			
65	0.7839	0.8689	0.8909	0.9168	0.9408	0.9672	0.9938			
65	0.7748	0.8594	0.8808	0.9077	0.9322	0.9585	0.9863			

T (°C)	Mass fraction of PPG2025 in solution									
	25	0.0996	0.2011	0.3010	0.4005	0.5000	0.6007	0.7006	0.8002	0.8990
35	0.8147	0.8286	0.8536	0.8735	0.8959	0.9206	0.9437	0.9683	0.9912	1.0155
45	0.8040	0.8203	0.8452	0.8654	0.8894	0.9138	0.9361	0.9594	0.9852	1.0074
55	0.7965	0.8129	0.8378	0.8582	0.8812	0.9031	0.9275	0.9522	0.9755	0.9990
65	0.7875	0.8036	0.8289	0.8499	0.8719	0.8951	0.9195	0.9438	0.9677	0.9910
65	0.7786	0.7940	0.8193	0.8415	0.8615	0.8854	0.9100	0.9344	0.9595	0.9828

TABLE VI  
Coefficients of Eq. (8) for Various Systems

$T$ (°C)	$A$ (g/cm <sup>3</sup> )	$B$ (g/cm <sup>3</sup> )	$C$ (g/cm <sup>3</sup> )	$D$ (g/cm <sup>3</sup> )	$E^a$
PEG200 + H <sub>2</sub> O					
25	0.9985	0.1723	0.0284	-0.0726	0.1306
35	0.9957	0.1736	0.0131	-0.0612	0.1059
45	0.9922	0.1652	0.0190	-0.0633	0.1232
55	0.9865	0.1648	0.0113	-0.0574	0.0825
65	0.9828	0.1491	0.0242	-0.0589	0.1440
PEG300 + H <sub>2</sub> O					
25	0.9999	0.1870	-0.0088	-0.0467	0.1898
35	0.9969	0.1956	-0.0302	-0.0388	0.1662
45	0.9937	0.1832	-0.0329	-0.0275	0.2057
55	0.9889	0.1857	-0.0638	-0.0009	0.2229
65	0.9835	0.1861	-0.0765	0.0082	0.1964
PEG600 + H <sub>2</sub> O					
25	0.9976	0.1481	0.0918	-0.1148	0.0360
35	0.9938	0.1410	0.0941	0.1143	0.0320
45	0.9902	0.1366	0.0971	-0.1176	0.0262
55	0.9862	0.1409	0.0646	-0.0920	0.0297
65	0.9810	0.1426	0.0676	-0.0946	0.0271
PEG2000 + H <sub>2</sub> O					
25	0.9984	0.2534	-0.3159	0.3587	0.0752
35	0.9937	0.2317	-0.1955	0.2032	0.0375
45	0.9878	0.1904	0.0395	0.1081	0.1107
55	0.9835	0.1770	0.0761	-0.1271	0.1242
65	0.9807	0.1830	0.0773	-0.1570	0.1205
PEG425 + H <sub>2</sub> O					
25	0.9998	0.1525	-0.1488	0.0177	0.1806
35	0.9970	0.1528	-0.1616	0.0260	0.1990
PVA15000 + H <sub>2</sub> O					
25	0.9998	0.4663	-2.7708	8.0913	0.1539
35	0.9948	0.3090	-1.0209	2.9644	0.0510
45	0.9906	0.2573	-0.6137	1.9880	0.0444
55	0.9858	0.2047	0.1081	-0.3144	0.0250
PEG200 + C <sub>2</sub> H <sub>5</sub> OH					
25	0.7911	0.2574	0.0631	0.0148	0.0508
35	0.7814	0.2623	0.0495	0.0261	0.0394
45	0.7725	0.2636	0.0503	0.0257	0.0401
55	0.7631	0.2694	0.0432	0.0285	0.0344
65	0.7541	0.2727	0.0379	0.0316	0.0499
PEG300 + C <sub>2</sub> H <sub>5</sub> OH					
35	0.7919	0.2751	0.0493	0.0154	0.1038
45	0.7826	0.2712	0.0605	0.0097	0.0896
55	0.7741	0.2743	0.0544	0.0146	0.0999
65	0.7649	0.2605	0.1114	-0.0283	0.1985
65	0.7547	0.2769	0.0621	0.0074	0.0787
PPG1025 + C <sub>2</sub> H <sub>5</sub> OH					
25	0.7917	0.1767	0.0587	-0.0103	0.0832
35	0.7821	0.1901	0.0310	0.0056	0.0758
45	0.7730	0.1973	0.0174	0.0137	0.0571
55	0.7642	0.1961	0.0217	0.0123	0.0610
65	0.7556	0.1925	0.0215	0.0169	0.0775

TABLE VI Continued

$T$ (°C)	$A$ (g/cm <sup>3</sup> )	$B$ (g/cm <sup>3</sup> )	$C$ (g/cm <sup>3</sup> )	$D$ (g/cm <sup>3</sup> )	$E^a$
PPG2025 + C <sub>2</sub> H <sub>5</sub> OH					
25	0.7925	0.1809	0.0679	-0.0253	0.1344
35	0.7826	0.1879	0.0638	-0.0265	0.1271
45	0.7736	0.1987	0.0383	-0.0110	0.1136
55	0.7643	0.1997	0.0405	-0.0134	0.1183
65	0.7554	0.1983	0.0379	-0.0081	0.1489

<sup>a</sup>  $E = \frac{100}{n} \sum_{i=1}^n \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right|$ ,  $n$ , number of experimental data;  $\rho_i^{\text{exp}}$  and  $\rho_i^{\text{cal}}$ , experimental and calculated densities using eq. (8), respectively.

where

$$RT \ln \gamma_1^U = u^E + (1 - x_1) \frac{\partial u^E}{\partial x_1} \quad (13)$$

$$RT \ln \gamma_1^V = Pv^E + (1 - x_1) \frac{\partial(Pv^E)}{\partial x_1} \quad (14)$$

$$RT \ln \gamma_1^S = -Ts^E + (1 - x_1) \frac{\partial(-Ts^E)}{\partial x_1} \quad (15)$$

The activity of the solvent ( $a_1$ ) is expressed as

$$a_1 = x_1 \gamma_1 \quad (16)$$

Then,

$$x_1^3 \gamma_1 = x_1 \gamma_1^U x_1 \gamma_1^V x_1 \gamma_1^S \quad (17)$$

or

$$a_1 = \frac{1}{x_1^2} (a_1^U a_1^V a_1^S) \quad (18)$$

where  $a_1^U$ ,  $a_1^V$ , and  $a_1^S$  are the internal energy, volume, and entropy parts of the activity, respectively. By using eq. (14) the excess volume part of the activity of solvent is expressed as

$$\ln a_1^V = \frac{P}{RT} \left( v^E + (1 - x_1) \frac{\partial v^E}{\partial x_1} \right) + \ln x_1 \quad (19)$$

and the excess enthalpy part of the activity of solvent can be derived from eq. (3) as

$$\ln a_1^S = \ln \phi_1 + \left( 1 - \frac{1}{r} \right) (1 - \phi_1) \quad (20)$$

It is obvious that the internal energy part of the activity is affected by the molecular interactions that depend on the molecular arrangements defined by entropy and molecular separations defined by vol-

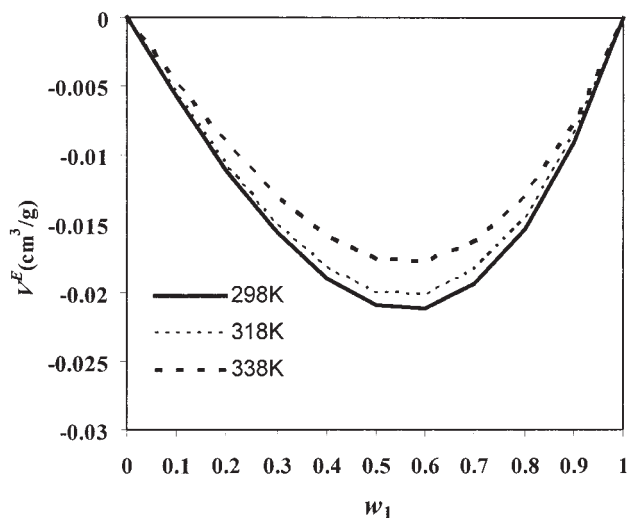


Figure 1 An excess volume of PEG200 (1) + H<sub>2</sub>O (2) solutions at three different temperatures.

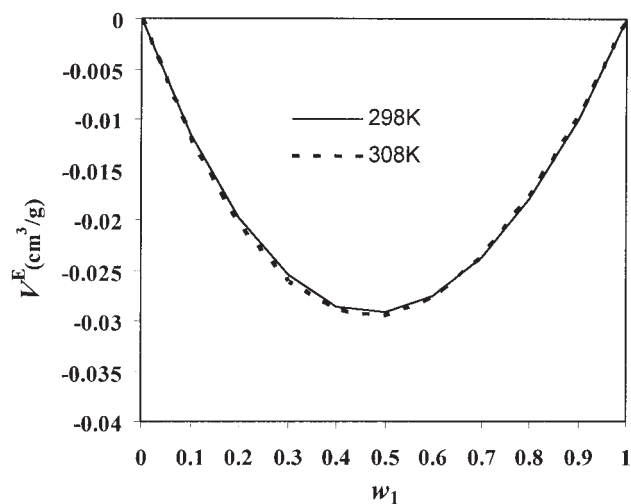
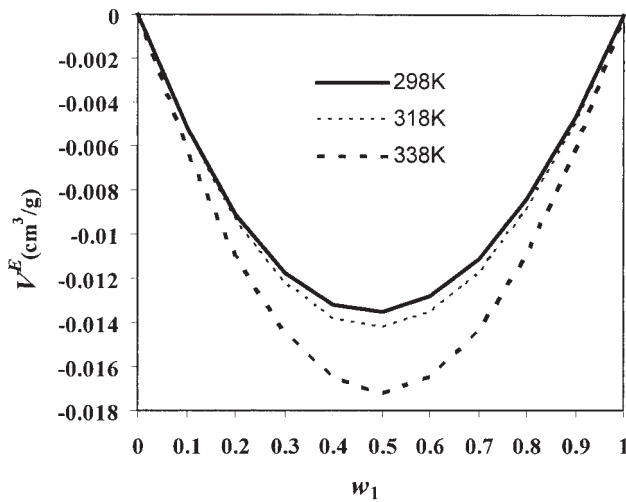
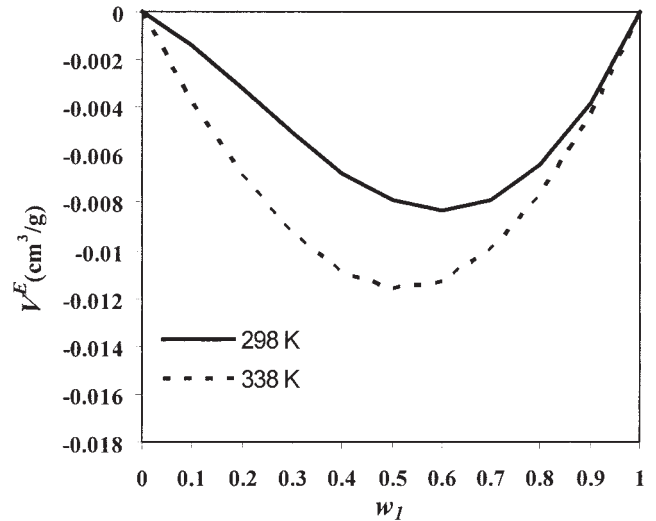


Figure 2 An excess volume of PPG425 (1) + H<sub>2</sub>O (2) solutions at two different temperatures.



**Figure 3** An excess volume of PEG300 (1) + C<sub>2</sub>H<sub>5</sub>OH (2) solutions at three different temperatures.



**Figure 4** An excess volume of PPG2025 (1) + C<sub>2</sub>H<sub>5</sub>OH (2) solutions at two different temperatures.

ume. Therefore, the internal energy part of the activity ( $a_1^U$ ) must be a function of the excess entropy and excess volume. This can be seen from eq. (18), which by arrangement can be written as

$$\frac{a_1^U}{x_1^2} = \frac{a_1}{a_1^V a_1^S} \quad (21)$$

The right-hand side of the above equation can be expressed by the following equation:

$$\frac{a_1}{a_1^V a_1^S} = (a_1^S)^{f_1^S} (a_1^V)^{f_1^V} \quad (22)$$

where  $f_1^V$  and  $f_1^S$  are weighting factors. In a logarithmic form eq. (21) can be written as

$$\ln \frac{a_1^U}{x_1^2} = f_1^S \ln a_1^S + f_1^V \ln a_1^V \quad (23)$$

Equation (18) can be obtained as

$$\ln a_1 = (1 + f_1^S) \ln a_1^S + (1 + f_1^V) \ln a_1^V \quad (24)$$

Then, by substituting for  $a_1^V$  and  $a_1^S$  from eqs. (19) and (20), respectively, in eq. (24) we have

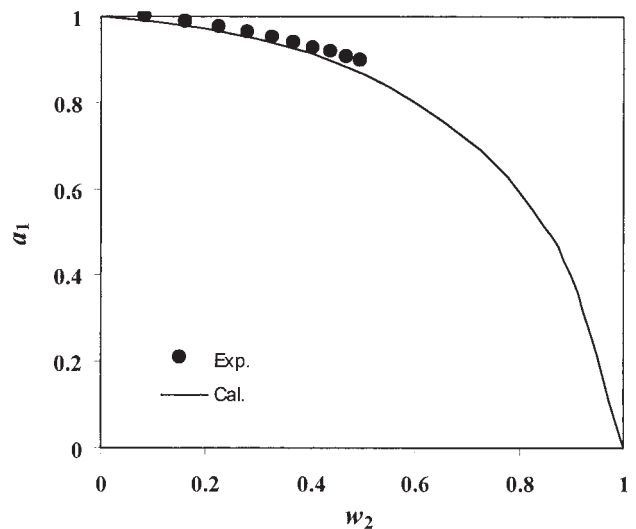
$$\ln a_1 = f^C \left[ \ln \phi_1 + \left(1 - \frac{1}{r}\right)(1 - \phi_1) \right] + f^R \left[ \frac{P}{RT} \left( v^E + (I - x_1) \frac{\partial v^E}{\partial x_1} \right) + \ln x_1 \right] \quad (25)$$

where  $f^C = (1 + f_1^S)$  and  $f^R = 1 + f_1^V$ .

Equation (25) can be written in terms of the volume fraction using eq. (4). The final form of the new activity model will be

$$\ln a_1 = f^C \left[ \ln \phi_1 + \left(1 - \frac{1}{r}\right)(1 - \phi_1) \right] + f^R \left\{ \left[ \frac{P}{RT} \left( v^E + \phi_2 \left( \phi_1 + \frac{1}{r} \phi_2 \right) \frac{\partial v^E}{\partial \phi_1} \right) \right] + \ln \left( \frac{r \phi_1}{r \phi_1 + \phi_2} \right) \right\} \quad (26)$$

For applying the above model, we need the density of polymer and solvent, their compositions in the solution, and the values of  $f^C$  and  $f^R$  as weighting factors. In this work we used the following values for  $f^C$  and  $f^R$ :



**Figure 5** The activity of water in H<sub>2</sub>O (1) + PEG200 (2) solutions at 25°C. (●) Experimental data at 25°C.<sup>17</sup>

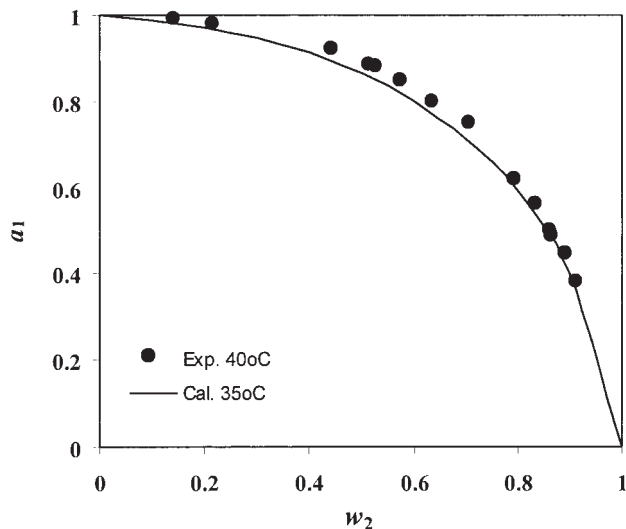


Figure 6 The activity of water in H<sub>2</sub>O (1) + PEG200 (2) solutions at 35°C. (●) Experimental data at 40°C.<sup>18</sup>

$$f^E = f^R = 0.5 \quad (27)$$

With this assumption we gave the same weight to the effects of entropy and volume part of the activity in the calculation of the activity of component 1 of a mixture.

## RESULTS AND DISCUSSION

The results obtained for the density measurements and calculated excess volumes show that all of the considered systems are nonideal and their excess volumes are negative. For aqueous solutions of PEG the

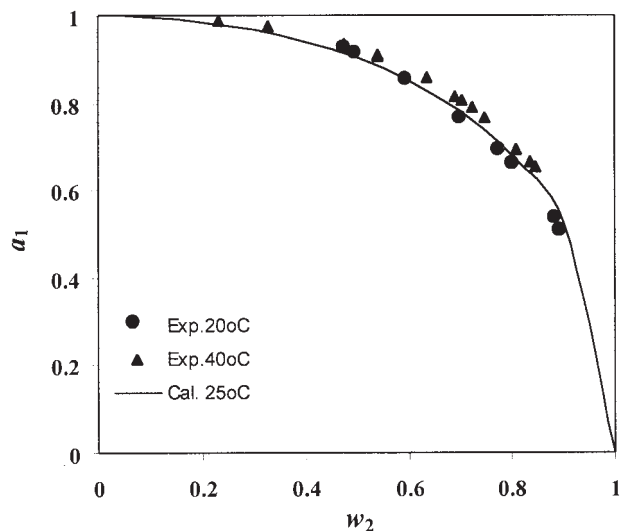


Figure 7 The activity of water in H<sub>2</sub>O (1) + PEG600 (2) solutions at 20, 25, and 40°C. (●) Experimental data at 20°C,<sup>19</sup> (▲) experimental data at 40°C,<sup>17</sup> and (—) calculated by eq. (26) at 25°C.

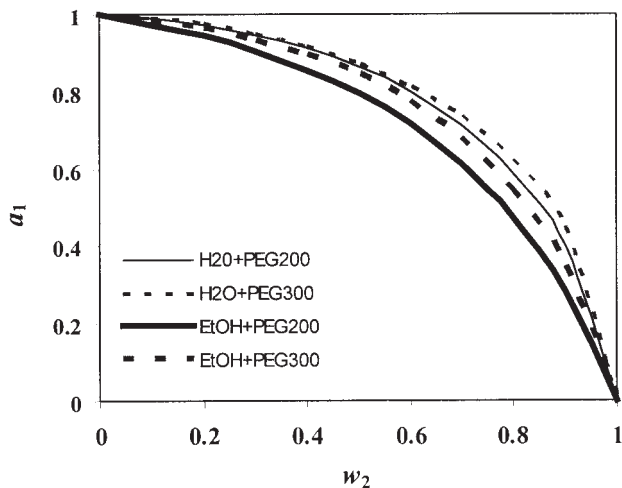


Figure 8 Comparisons of the calculated activities of water and ethanol in various solutions of PEG200 and PEG300 in water and ethanol at 25°C.

nonideality of the systems decreases with increasing temperature, but for aqueous solutions of PPG variation of the temperature does not have any considerable effect on the nonideality. The results show that the maximum absolute excess volume value of PEG–H<sub>2</sub>O systems occurred at about 0.6 mass fraction of the polymer but this value for PEG–ethanol and PPG–H<sub>2</sub>O systems are observed at 0.5. For all of the considered systems, the nonideality of the aqueous solutions is more pronounced than for polymer–ethanol mixtures. The densities of aqueous solutions of PEGs and PPGs increase with the polymer molecular weight. Another remarkable point is that the slope of the density curves versus the polymer concentration

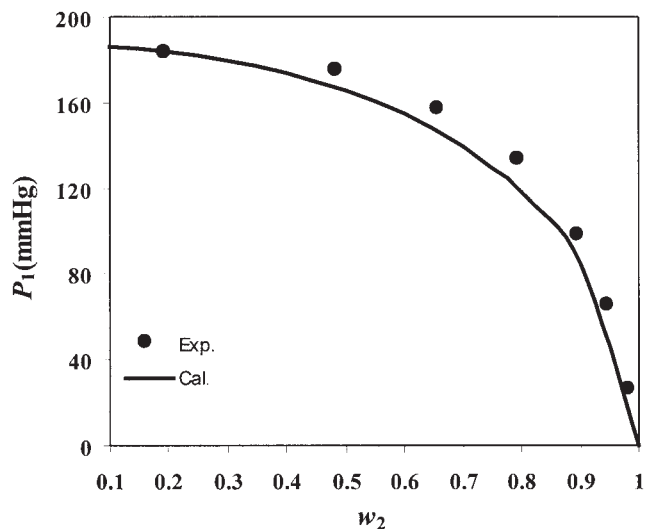


Figure 9 The vapor pressure of water in H<sub>2</sub>O (1) + PEG300 (2) solutions at 65°C. (●) Experimental data.<sup>20</sup>



for aqueous solutions of PEG or PPG are negative but when the solvent is ethanol, these slopes are positive.

Using the proposed model, the solvent activity for some polymer/solvent solutions is calculated. Calculated results are shown in Figures 5–8.<sup>17–19</sup> Figure 9 shows the ability of this model to calculate the vapor pressure of a solvent in the PEG300/water solution.<sup>20</sup>

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