Experimental Results and Modeling of Solvent Activities in Binary Polymer Solutions

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ABSTRACT: A new model based on Eyring's absolute rate theory for the prediction of solvent activities in binary polymer solutions is presented. This model requires experimental viscosity and density data. The model results for various solutions of poly(ethylene glycol)s with molecular weights of 200, 300, and 6000 in water and for poly(propylene glycol) with a molecular weight of 2025 in ethanol are compared with experimental data at different temperatures and concentrations. There is good agreement between the calculated and experimental results, and the overall average mean relative deviation of the model is less than 1.2%. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1059–1063, 2005

Key words: modeling; viscosity

INTRODUCTION

The activity is one of the most important thermodynamic properties of solutions and can be used for calculating many other properties. Many studies have been conducted to predict the thermodynamic properties of polymer solutions with various models, such as noncompressible models, compressible lattice models, off-lattice models, and models based on a generalized van der Waals partition function.[1] In the first group, we can mention the Flory–Huggins theory.[2,3] In compressible models, the concept of free volume has been used to consider the phase behavior of polymer mixtures. Its assumptions are similar to those of the Flory–Huggins theory, and the free volume is assumed to be due to unoccupied sites in the lattice. In this respect, the works of Costas and Sanctuary,[4] High and Danner,[5] Panayioutou and Vera,[6] and Sanchez and Lacomb[7] are worth mentioning. In off-lattice models, the continuity of polymer configurations is the essential assumption. Therefore, a polymer chain is considered to consist of athermal hard spheres that are connected together.[8,9] In the fourth class of models, the equation of state based on the van der Waals equation can be mentioned. The theory of perturbed hard chains was obtained on this basis.[10,11]

In this work, a new thermodynamic model based on Eyring's absolute rate theory is presented for calculating the solvent activities in binary polymer solutions with density and viscosity data. The model results are in good agreement with the experimental data. These experimental data were taken from the literature or were measured by us with vapor pressure osmometry (VPO).

EXPERIMENTAL

Poly(propylene glycol) (PPG), with a number-average molecular weight of 2025, was acquired from Reidel-de Haen (Seelze, Germany). Ethanol (>99.8%) as a solvent and urea as a calibration substance for the VPO apparatus were obtained from Merck (Darmstadt, Germany). The solutions were prepared by mass with an analytical balance with ±0.1-mg accuracy. A vapor pressure osmometer from Knauer (Berlin, Germany) was used for measuring the activities of ethanol in the PPG solutions. The measuring method has been reported elsewhere.[12,13] The results obtained at 318.2 and 328.2 K for 10, 20, 30, and 40 wt % polymer concentrations are reported in Table I.

MODELING

According to Eyring's viscosity model, the viscosity of a liquid solution can be calculated as follows:[14,15]

$$\ln(\eta\nu) = \sum_i x_i \ln(\eta_i\nu_i) + \frac{g^{*E}}{RT} \quad (1)$$

where η and ν are the viscosity and molar volume of the solution, respectively; x_i is the molar fraction of component i in the mixture; η_i and ν_i are the viscosity and molar

TABLE I
Measured Activities of Ethanol in Ethanol (1)–PPG 2025 (2) Solutions at 318.2 and 328.2 K

w_2	318.2 K	328.2 K
0.1000	0.9960	0.9971
0.2000	0.9923	0.9941
0.3000	0.9851	0.9901
0.4000	0.9799	0.9844

volume of pure component i, respectively; R is the gas constant; T is the absolute temperature; and g^{*E} is the excess Gibbs energy of viscous flow required to move the fluid particles from a stable state to an activated state. An equivalence can be assumed between the excess Gibbs free energy of activation for flow (g^{*E}) and the equilibrium excess Gibbs free energy of mixing (g^E):[16]

$$\frac{g^E}{RT} = \ln(\eta\nu) - \sum_i x_i \ln(\eta_i\nu_i) \qquad (2)$$

On the right side of this equation, the first term is related to the real viscosity of the solution, and the second term is related to the ideal viscosity of the solution. In this work, we introduce dimensionless terms instead of the real and ideal viscosities as follows:

$$\frac{g^E}{RT} = \left(\frac{\eta\nu}{\eta_R\nu_R}\right) - \sum_i \frac{x_i(\eta_i\nu_i)}{\eta_R\nu_R} \qquad (3)$$

where η_R and ν_R are the viscosity and molar volume of a reference component, respectively. We chose the polymer (component 2) as a reference component:

$$\frac{g^E}{RT} = \left(\frac{\eta\nu}{\eta_2\nu_2}\right) - \sum_{i=1}^{2} \frac{x_i(\eta_i\nu_i)}{\eta_2\nu_2} \qquad (4)$$

TABLE II
Activity of Water in Aqueous Solutions of PEG 200 (2) at Various Temperatures and Concentrations

w_2	$a_1^{\exp 19}$	a_1^{cal}	RD
$T = 313.2$ K			
0.8991	—	0.7947	—
0.7120	0.7422	0.8248	11.129
0.6411	0.7916	0.8301	4.8636
0.5197	0.8790	0.8638	−1.7292
0.4481	0.9125	0.8930	−3.1370
0.2220	0.9706	0.9823	1.2054
$T = 333.2$ K			
0.8375	—	0.8244	—
0.7328	0.7508	0.8319	10.8018
0.5586	0.8753	0.8640	−1.2910
0.4670	0.9154	0.8966	−2.0537
0.3828	0.9350	0.9279	−0.7593
0.2329	0.9728	0.9705	−0.2364
0.1493	0.9849	0.9824	−0.2538

TABLE III
Activities of Water in Aqueous Solutions of PEG 300 (2) at Various Temperatures and Concentrations

w_2	$a_1^{\exp 12}$	a^{cal}	RD^a
$T = 308.2$ K			
0.3926	0.9410	0.9479	0.7333
0.2987	0.9643	0.9616	−0.2800
0.1998	0.9815	0.9780	−0.3566
0.1080	0.9917	0.9922	0.0504
$T = 318.2$ K			
0.3926	0.9458	0.9443	−0.1586
0.2987	0.9670	0.9586	−0.8687
0.1998	0.9821	0.9759	−0.9613
0.1080	0.9915	0.9907	−0.0807
$T = 328.2$ K			
0.3926	0.9499	0.9547	0.5053
0.2987	0.9690	0.9625	−0.6708
0.1998	0.9829	0.9778	−0.5189
0.1080	0.9919	0.9947	0.2823
$T = 338.2$ K			
0.3926	0.9533	0.9605	0.7553
0.2987	0.9707	0.9646	−0.6284
0.1998	0.9829	0.9775	−0.5494
0.1080	0.9919	0.9936	0.1714

^{a} $RD = 100 \times (a^{cal} - a^{\exp})/a_1^{\exp}$.

Equation (4) can satisfy the boundary-limiting conditions; that is, for $x_1 = 0$ (or $x_2 = 1$) and $x_2 = 0$ (or $x_1 = 0$), g^E is 0.

To use eq. (4) to calculate the excess Gibbs free energy, we need the viscosity and molar volume of the solution

TABLE IV
Activity of Water in Aqueous Solutions of PEG 6000 (2) at Various Temperatures and Concentrations

w_2	$a_1^{\exp 12}$	a_1^{cal}	RD
$T = 308.2$ K			
0.3552	—	0.9606	—
0.1974	0.9961	0.9918	−0.4317
0.0982	0.9992	0.9990	−0.0200
0.0601	0.9996	0.9994	−0.0200
0.0399	0.9998	0.9995	−0.0300
$T = 318.2$ K			
0.3552	—	0.9600	—
0.1974	0.9960	0.9912	−0.4819
0.0982	0.9986	0.9990	0.0400
0.0601	0.9993	0.9996	0.0300
0.0399	0.9998	0.9998	0.0000
$T = 328.2$ K			
0.3552	—	0.9615	—
0.1974	0.9973	0.9914	−0.5916
0.0982	0.9995	0.9988	−0.0700
0.0601	0.9998	0.9993	−0.0500
0.0399	0.9999	0.9995	−0.0400
$T = 338.2$ K			
0.3552	—	0.9616	—
0.1974	0.9977	0.9910	−0.6715
0.0982	0.9995	0.9986	−0.0900
0.0601	0.9997	0.9992	−0.0500
0.0399	0.9998	0.9994	−0.0400

TABLE V
Activity of Ethanol (1) in PPG 2025 (2) Solutions at Various Temperatures and Concentrations

w_2	a_1^{exp}	a_1^{cal}	RD
$T = 318.2$ K			
0.1000	0.9960	0.9932	−0.2811
0.2000	0.9923	0.9962	−0.3915
0.3000	0.9851	0.9783	−0.6903
0.4000	0.9799	0.9415	−4.0876
$T = 328.2$ K			
0.1000	0.9971	0.9933	−0.3811
0.2000	0.9941	0.9961	0.2012
0.3000	0.9901	0.9778	−1.2423
0.4000	0.9844	0.9392	−4.5916

and pure components 1 and 2. The density and viscosity of the solution used to verify this model were measured and fitted by second- and third-order polynomial equations, respectively.[17] By placing these equations into eq. (4), we obtained the following relation:

$$\frac{g^E}{RT} = \left[\frac{(a + bw_2 + cw_2^2)\,(a' + b'w_2 + c'w_2^2 + d'w_2^3)}{\eta_2 \nu_2} \right]$$
$$- \left(\frac{x_1 \eta_1 \nu_1}{\eta_2 \nu_2} \right) - \left(\frac{x_2 \eta_2 \nu_2}{\eta_2 \nu_2} \right) \quad (5)$$

where w_2 is the mass fraction of the polymer and a, b, c, a', b', c', and d' are adjustable parameters. The values of these parameters are given in the appendix for the considered systems. The average relative deviation (RD) of the viscosity and density correlations are reported in a previous work.[17]
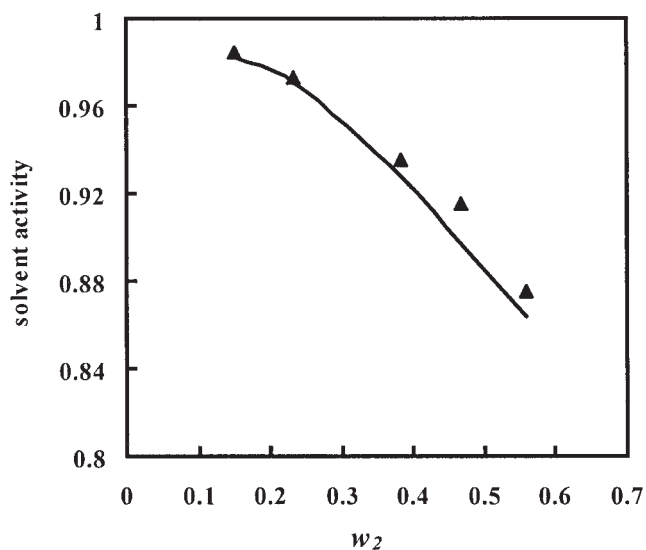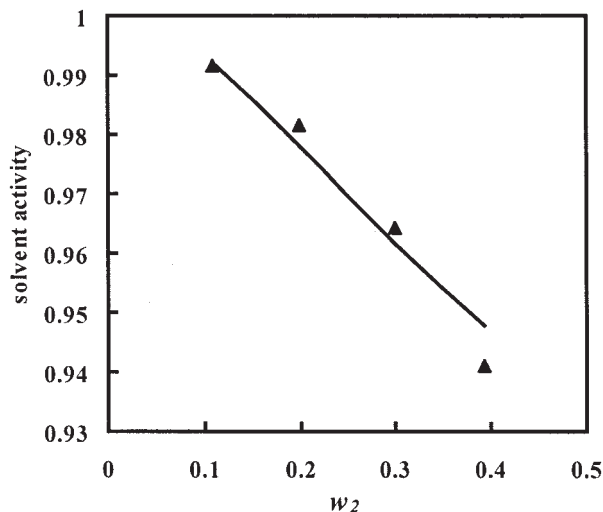

Figure 2 Activity of water in H_2O (1)–PEG 300 (2) solutions at 308.2 K: (▲) experimental data at 308.2 K[12] and (—) model results.

According to the principles of classical thermodynamics, the following relations can be written:[18]

$$RT \ln \gamma_1 = g^E + (1 - x_1) \frac{\partial g^E}{\partial x_1} \quad (6)$$

$$a_1 = x_1 \gamma_1 \quad (7)$$

where γ_1 and a_1 are the activity coefficient and activity of the solvent, respectively.

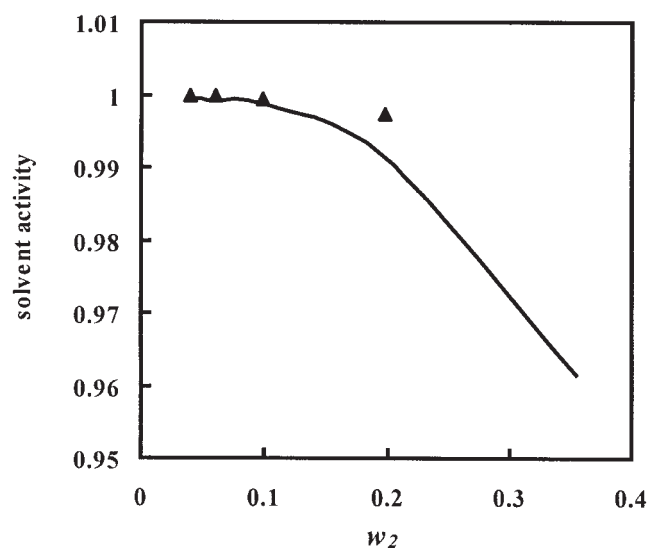Using eqs. (5)–(7), we can calculate the activity of a solvent in binary polymer mixtures.

Figure 1 Activity of water in H_2O (1)–PEG 200 (2) solutions at 333.2 K: (▲) experimental data at 333.2 K[19] and (—) model results.

Figure 3 Activity of water in H_2O (1)–PEG 6000 (2) solutions at 328.2 K: (▲) experimental data at 328.2 K[12] and (—) model results.
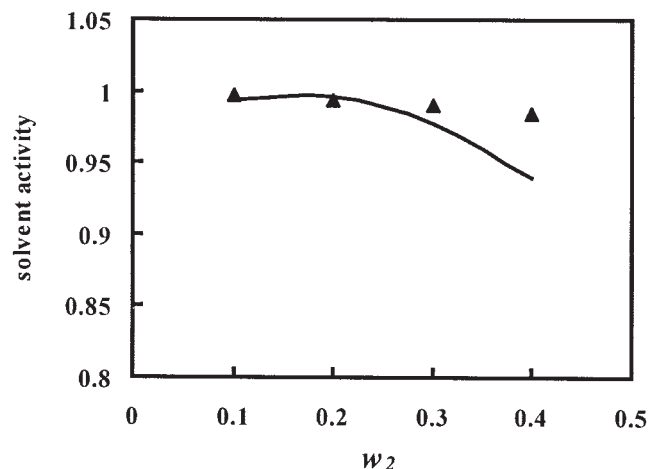
Figure 4 Activity of ethanol in C_2H_5OH (1)–PPG 2025 (2) solutions at 328.2 K: (▲) experimental data at 328.2 K (measured in this work) and (—) model results.

RESULTS AND DISCUSSION

The solvent activities have been determined with the proposed model and compared with experimental data for aqueous solutions of poly(ethylene glycol) (PEG; 200, 300, and 6000) and PPG 2025 solutions in ethanol at various temperatures and concentrations. The model performance has been evaluated through a comparison of the calculated (a_1^{cal}) and experimental (a_1^{exp}) activity values in terms of the RD percentage. The a_1^{cal}, a_1^{exp}, and RD values are reported in Tables II–V for the studied systems. The overall average mean RD of the model is 1.17%. Also, some calculated results are shown in Figures 1–4. The results show that the proposed model is reliable for the prediction of solvent activities of binary polymer solutions with viscosity and density data.

APPENDIX

TABLE A. I
Parameters of Eq. (5) for Various Aqueous Solutions

T (K)	a	b	c
PEG 200			
313.2	0.9729	0.2438	−0.1073
333.2	0.9804	0.1796	−0.0640
PEG 300			
308.2	0.9951	0.1280	0.0735
318.2	0.9898	0.1434	−0.0079
328.2	0.9885	0.1206	0.0188
338.2	0.9677	0.2263	−0.1542
PEG 6000			
293.2	1.0058	0.1835	−0.0571
308.2	0.9871	0.2296	−0.1210
318.2	0.9824	0.2149	−0.0961
328.2	0.9788	0.1906	−0.0378
338.2	0.9706	0.2065	−0.0600

TABLE A. II
Parameters of Eq. (5) for Various Aqueous Solutions

T (K)	a'	b'	c'	d'
PEG 200				
313.15	1.083	1.743	−3.707	27.437
333.15	0.402	3.055	−5.429	15.663
PEG 300				
308.15	0.916	0.310	15.934	3.416
318.15	0.754	0.732	10.484	5.581
328.15	0.713	0.696	14.018	−5.433
338.15	0.551	−0.132	10.456	−5.536
PEG 6000				
293.15	1.893	−8.662	324.686	54.667
308.15	0.393	28.338	−126.491	979.429
318.15	0.556	17.978	−74.115	765.081
328.15	0.338	16.327	−47.777	491.894
338.15	0.305	11.983	−26.597	354.128

TABLE A. III
Parameters of Eq. (5) for Various Solutions of PPG 2025 in Ethanol and PEG 300 in Ethanol

T (K)	a	b	c
PPG 2025			
308.15	0.7889	0.2817	−0.2573
318.15	0.7921	0.1665	−0.0103
328.15	0.7562	0.3830	−0.4134
338.15	0.7295	0.4799	−0.5408
PEG 300			
308.15	0.7827	0.2690	0.0692
318.15	0.7743	0.2709	0.0678
328.15	0.7645	0.2666	0.0863
338.15	0.7548	0.2754	0.0684

TABLE A. IV
Parameters of Eq. (5) for Various Solutions of PPG 2025 in Ethanol and PEG 300 in Ethanol

T (K)	a'	b'	c'	d'
PPG 2025				
308.15	0.987	3.708	11.533	7.869
318.15	0.285	14.076	−49.801	103.984
328.15	0.192	12.811	−47.094	96.509
338.15	0.484	3.995	0.112	11.453
PEG 300				
308.15	−0.028	16.198	−39.466	59.338
318.15	−0.024	13.998	−30.365	40.828
328.15	0.013	11.659	−29.409	45.483
338.15	0.001	5.812	0.813	0.003

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