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# Measurement of Activity of Water in Aqueous Poly(ethylene glycol) Solutions (Effect of Excess Volume on the Flory–Huggins χ-Parameter)

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Activities of water are reported for aqueous solutions of poly(ethylene glycol) (PEG) with number average molecular weights of 300, 400, 4000, and 6000 are measured at 35, 45, 55, and 65 °C and at various concentrations from 0 to 40 wt % of PEG using vapor-pressure osmometry. A cubic equation in terms of PEG concentrations is sufficient for correlation of activities. Using measured activities, the Flory–Huggins interaction parameters have been calculated. The effect of temperature, molecular weight of PEG and its concentration, and volume change upon mixing on interaction parameter have been considered. Ignoring the volume change of mixing can lead to an average error of 2.5% with a maximum error of 5.3%.

## Introduction

Mixtures of poly(ethylene glycol) (PEG) + Dextrane (DX) + water form a two-phase liquid–liquid system. The upper liquid phase is rich in PEG, and the lower phase is rich in DX. Proteins, nucleic acids, enzymes, and other biomolecules have different solubilities in these phases and can be separated from each other (Albertsson, 1986; Zaslavsky, 1995). In thermodynamic modeling for such separation methods, activities are the essential variables. There are different methods to measure the activities of components in these systems, such as differential vapor pressure (Haynes et al., 1989), improved isopiestic methods (Ochs et al., 1990), vapor pressure osmometry, and membrane osmometry (Gaube et al., 1993).

In the present report, activities of water in different solutions of PEG having different molecular weights are measured by vapor pressure osmometry at various temperatures and compositions. The results are given by the Flory–Huggins (FH) equation (Flory, 1953)

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \varphi_1) + \chi_{12}(1 - \varphi_1)^2 \quad (1)$$

where $a_1$ and $\varphi_1$ are activity and 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. $\chi_{12}$ is the interaction parameter of the system.

According to Flory and Huggins (Flory, 1953), $\chi_{12}$ 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 $\chi_{12}$ dependent on concentration and molecular weight of the polymer, in addition to temperature, to fit the activity data of components of the solution (Kamide et al., 1985; Qian et al., 1991).

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The polymer solution systems of interest in this work are aqueous solutions of PEG in which both PEG and water are polar and there is a change of volume upon mixing. Therefore the effects of temperature, concentration, molecular weight of polymer, and volume change of mixing must be considered by a person who wants to calculate interaction parameter.

## Experimental Procedure

Samples of poly(ethylene glycol)s (PEG 300, PEG 400, PEG 4000, and PEG 6000) and urea, the calibration substance, were obtained from Merck. Double-distilled water was used in making up the aqueous polymer solutions. Solutions were prepared by mass, using an analytical balance with ±0.1 mg accuracy (Shimadzu, model AEU210). A vapor pressure osmometer (VPO) manufactured by Knauer (Germany) was used for measuring the activities of water in the aqueous PEG solutions. This apparatus consists of a chamber filled with a saturated vapor of solvent. Two thermistors are provided. A droplet of solvent is placed on one of the thermistors, and a droplet of polymer solution is placed on the other. Since the vapor pressure of solvent and polymer solution differ from each other, the solvent vapor condenses onto the polymer solution droplet and causes a change in its temperature. Temperature differences between the two thermistors are represented as voltage difference measured by a digital voltmeter. The voltage difference has the following relation with the activity of solvent (Brown, 1967)

$$\ln a_1 = -\frac{\Delta V M_1}{1000 I} \quad (2)$$

where $a_1$ is the activity of solvent, $\Delta V$ is the voltage difference, $M_1$ is the molecular weight of solvent, and $I$ is the calibration constant. The calibration constant has various values at different temperatures that must be

**Table 1. Measured Number Average Molecular Weights**

|          | PEG 300 | PEG 400 | PEG 4000 | PEG 6000 |
|----------|---------|---------|----------|----------|
| $M_n$    | 296     | 430     | 4237     | 5989     |

**Table 2. Experimental Results of Activity of Water in Aqueous Solutions of PEG 300, PEG 400, PEG 4000, and PEG 6000 at Various Temperatures and Concentrations**

| | $t/°C$ | | | |
|-------|--------|--------|--------|--------|
| $w_1$ | 35 | 45 | 55 | 65 |
| | PEG 300 | | | |
| 0.6074 | 0.9410 | 0.9458 | 0.9499 | 0.9533 |
| 0.7013 | 0.9643 | 0.9670 | 0.9690 | 0.9707 |
| 0.8002 | 0.9815 | 0.9821 | 0.9829 | 0.9837 |
| 0.8920 | 0.9917 | 0.9915 | 0.9919 | 0.9924 |
| | PEG 400 | | | |
| 0.6850 | 0.9691 | 0.9707 | 0.9720 | 0.9710 |
| 0.7549 | 0.9802 | 0.9820 | 0.9828 | 0.9828 |
| 0.8208 | 0.9878 | 0.9888 | 0.9890 | 0.9889 |
| 0.9377 | 0.9968 | 0.9972 | 0.9970 | 0.9971 |
| 0.9502 | 0.9974 | 0.9978 | 0.9976 | 0.9977 |
| 0.9695 | 0.9983 | 0.9987 | 0.9986 | 0.9987 |
| 0.9790 | 0.9991 | 0.9991 | 0.9990 | 0.9993 |
| 0.9880 | 0.9996 | 0.9996 | 0.9995 | 0.9997 |
| | PEG 4000 | | | |
| 0.6051 | 0.9726 | 0.9766 | 0.9829 | 0.9846 |
| 0.7060 | 0.9878 | 0.9897 | 0.9920 | 0.9935 |
| 0.8006 | 0.9953 | 0.9960 | 0.9968 | 0.9975 |
| 0.9510 | 0.9996 | 0.9997 | 0.9995 | 0.9997 |
| | PEG 6000 | | | |
| 0.6448 | | 0.9832 | 0.9872 | |
| 0.7069 | | 0.9900 | 0.9925 | 0.9939 |
| 0.8026 | 0.9961 | 0.9960 | 0.9973 | 0.9977 |
| 0.9018 | 0.9992 | 0.9986 | 0.9995 | 0.9995 |
| 0.9207 | 0.9994 | 0.9989 | 0.9997 | 0.9996 |
| 0.9399 | 0.9996 | 0.9993 | 0.9998 | 0.9997 |
| 0.9601 | 0.9998 | 0.9998 | 0.9999 | 0.9998 |
| 0.9797 | ~1 | ~1 | ~1 | ~1 |

**Table 3. Coefficients of Eq 3 for Various PEG Solutions and at Various Temperatures**

| $t/°C$ | $a$ | $b$ | $c$ | $d$ | ARD%[a] |
|--------|-----|-----|-----|-----|---------|
| | | PEG 300 | | | |
| 35 | 0.3678 | −1.1814 | 1.3223 | 0.4912 | 0.01 |
| 45 | 0.4471 | −1.3269 | 1.3874 | 0.4925 | 0.01 |
| 55 | 0.3613 | −1.0878 | 1.1621 | 0.5644 | 0.00 |
| 65 | 0.2692 | −0.8426 | 0.9423 | 0.6321 | 0.00 |
| | | PEG 400 | | | |
| 35 | 0.3503 | −1.1032 | 1.2019 | 0.5508 | 0.01 |
| 45 | 0.4591 | −1.3845 | 1.4371 | 0.4884 | 0.01 |
| 55 | 0.5311 | −1.5421 | 1.5434 | 0.4678 | 0.01 |
| 65 | 0.6469 | −1.8548 | 1.8243 | 0.3839 | 0.02 |
| | | PEG 4000 | | | |
| 35 | 0.4149 | −1.2333 | 1.2311 | 0.5873 | 0.00 |
| 45 | 0.3683 | −1.0879 | 1.0796 | 0.6401 | 0.01 |
| 55 | 0.2490 | −0.7373 | 0.7359 | 0.7524 | 0.01 |
| 65 | 0.3055 | −0.8712 | 0.8352 | 0.7305 | 0.01 |
| | | PEG 6000 | | | |
| 35 | 0.3992 | −1.1921 | 1.1920 | 0.6009 | 0.00 |
| 45 | −0.4397 | 1.1361 | −0.9518 | 1.2554 | 0.01 |
| 55 | 0.2723 | −0.8177 | 0.8216 | 0.7239 | 0.01 |
| 65 | 0.4086 | −1.1696 | 1.1202 | 0.6408 | 0.00 |

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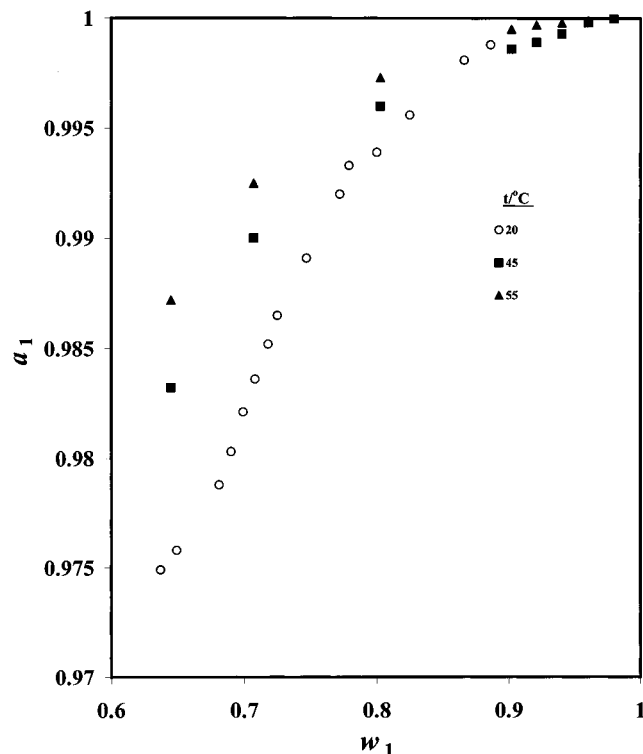


**Figure 1.** Activity of water in aqueous solution of PEG 6000. The empty circles are measured by Grossman et al. (1995), and the others are the present measurements.

determined. The calibration material should be soluble in the solvent. Urea and NaCl are suggested by the manufacturer as appropriate calibration materials for aqueous solutions. When a droplet of solvent and a droplet of solution are placed on each of thermistors, $\Delta V$ increases and reaches a maximum at the quasi steady state. The required time for reaching this condition depends on the type of solution and its temperature. However, usually 3−5 min is adequate. In this manner, one is able to measure the activities of solvents in aqueous polymer solutions with the molecular weight of polymer less than 10 000 and its concentration less than 40%. Each measurement is repeated five to eight times, and then the average voltage difference is used in eq 2. The accuracy of the $\Delta V$ measurements is estimated to be better than ±1%.

### Results and Calculations

Initially, number average molecular weights of PEG samples were measured by VPO. Results are reported in Table 1. Then, the solvent activities were measured by VPO for aqueous solutions of PEG300, PEG400, PEG4000, and PEG6000. Experimental results are reported in Table 2. The experimental activity data are well fitted to a third-order polynomial

$$a_1 = aw_1^3 + bw_1^2 + cw_1 + d \qquad (3)$$

with respect to water mass fraction, $w_1$. The coefficients of eq 3 along with its absolute percentage deviation are reported in Table 3. The low ARD% values reported in Table 3 indicate the high accuracy of eq 3 for activity correlation.

Figures 1 and 2 shows activities measured in this work and also activities reported before (Grossman et al., 1995; Lin et al., 1996) for PEG 6000 and PEG 4000. The consistency between the results are very good.

The system of PEG + water has a volume change upon mixing. Using the density data (Eliassi et al., 1998), the excess volume

$$v^E = \frac{1}{\rho} - \left(\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}\right) \qquad (4)$$

of PEG400 + water is calculated at various temperatures

**Table 4. Flory−Huggins Interaction Parameters of PEG Aqueous Solutions at Various Temperatures and Mass Fractions of Polymer ($w_2$)**
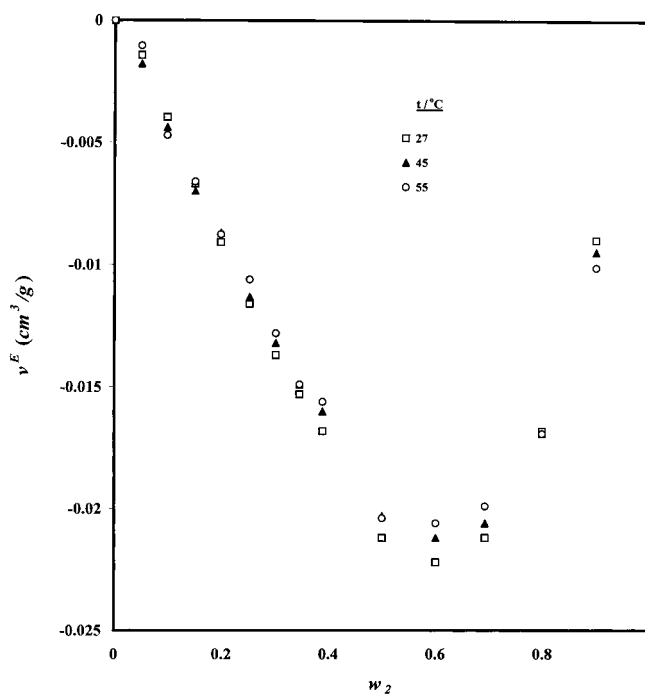
PEG 400

| $t$/°C | | $w_2$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 0.0120 | 0.0210 | 0.0305 | 0.0498 | 0.0623 | 0.1792 | 0.2451 | 0.3156 |
| 45 | $\tilde{\chi}_{12}$ | 1.8102 | 0.6400 | 0.6204 | 0.5442 | 0.5273 | 0.4376 | 0.4427 | 0.4321 |
| | ARD%[a] | (5.28) | (0.31) | (1.56) | (0.68) | (0.38) | (2.42) | (2.91) | (3.59) |
| 55 | $\tilde{\chi}_{12}$ | 0.8801 | 0.3467 | 0.4765 | 0.4363 | 0.4583 | 0.4465 | 0.4608 | 0.4500 |
| | ARD% | (3.17) | (2.83) | (0.17) | (1.06) | (0.75) | (2.20) | (2.47) | (3.15) |

PEG 4000

| $t$/°C | | $w_2$ | | | |
|---|---|---|---|---|---|
| | | 0.0490 | 0.1994 | 0.2940 | 0.3949 |
| 45 | $\tilde{\chi}_{12}$ | 0.4697 | 0.4653 | 0.4769 | 0.4923 |
| | ARD% | (1.10) | (2.62) | (3.21) | (3.77) |
| 55 | $\tilde{\chi}_{12}$ | 0.3592 | 0.4925 | 0.5124 | 0.5470 |
| | ARD% | (3.72) | (0.95) | (2.33) | (2.19) |

PEG 6000

| $t$/°C | | $w_2$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 0.0203 | 0.0399 | 0.0601 | 0.0793 | 0.0982 | 0.1973 | 0.2931 | 0.3552 |
| 45 | $\tilde{\chi}_{12}$ | 0.3791 | 0.4443 | 0.3238 | 0.3386 | 0.3751 | 0.4496 | 0.4721 | 0.4865 |
| | ARD% | (2.48) | (1.33) | (5.55) | (5.47) | (4.45) | (3.46) | (3.55) | (3.20) |
| 55 | $\tilde{\chi}_{12}$ | 0.3855 | 0.4475 | 0.4475 | 0.4901 | 0.5037 | 0.4962 | 0.4952 | 0.5095 |
| | ARD% | (0.95) | (0.68) | (0.42) | (0.43) | (0.75) | (2.09) | (2.83) | (2.84) |

[a] ARD% $= 100 \times (\sum_{i=1}^{n}|(\chi_{12} - \tilde{\chi}_{12})/\tilde{\chi}_{12}|)/n$.
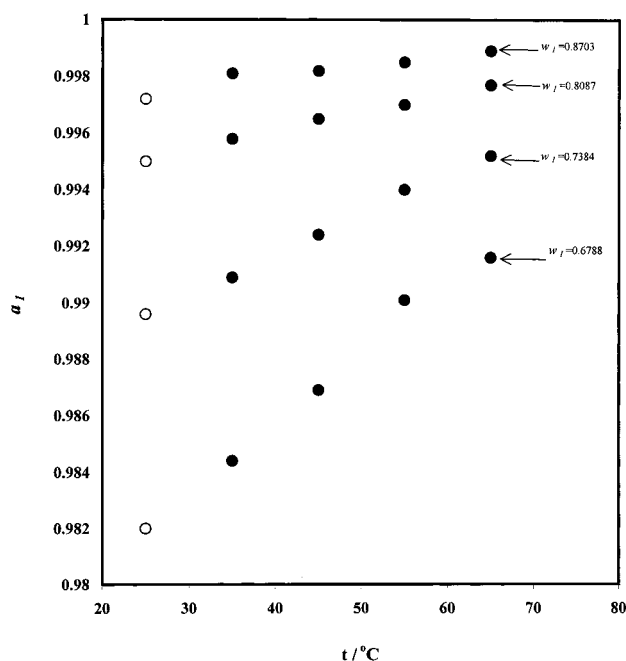


**Figure 2.** Activity of water in aqueous solutions of PEG 4000. The solid circles are from the present measurements. The empty circles are measured by Lin et al. (1996).



**Figure 3.** Excess volumes of the aqueous solutions of PEG 400.

and concentrations. In eq 4, $v^E$ is excess volume and $\rho$, $\rho_1$, $\rho_2$ are densities of PEG solution, pure water, and pure PEG, respectively. Also, $w_1$ and $w_2$ are weight fractions of water and PEG in solution, respectively. Results of excess volume calculations are reported in Figure 3. According to this figure, at about 60 wt % of PEG concentration the system has the most negative excess volume at all temperatures.

Considering the above results it is clear that the volume change upon mixing is appreciable. Therefore, volume fractions of PEG are calculated in two ways, once using the partial volumes of water and PEG (Eliassi et al., 1998) and second using pure volumes instead of partial volumes. Also, the interaction parameter of the FH equation is

calculated in two ways, namely, using the measured activities and volume fractions and ideal volume fractions, which are shown by $\tilde{\chi}_{12}$ and $\chi_{12}$, respectively. In both cases, $r_2$ is calculated by dividing molar volume of polymer to molar volume of solvent (Eliassi et al., 1998). The values of these quantities accompanying the absolute percentage deviation (ARD%) are reported for PEG400, PEG4000, and PEG6000 in Table 4.

## Conclusion

According to the measurements reported here water activity increases with increasing temperature, and the slope of the water activity versus water mass fraction

decreases with increase in PEG molecular weight. Also, variation of water activity with temperature in concentrated solutions is shown to be less than those of dilute solutions. It is also demonstrated that ignoring the volume change of mixing of PEG aqueous solutions can lead to an average error of 2.5% and a maximum error of 5.3% in calculating the Flory–Huggins interaction parameters. For the systems studied in this report it is also shown that the Flory–Huggins interaction parameters are dependent on the concentration and molecular weight of polymers considered.

## Acknowledgment

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