JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

# Vapor–Liquid Equilibria of Aqueous Polymer Solutions from Vapor-Pressure Osmometry and Isopiestic Measurements

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**ABSTRACT:** Water activity data of several binary water + polymer systems were determined experimentally using both vapor-pressure osmometry (VPO) and improved isopiestic methods. The polymers were poly(ethylene glycol) dimethyl ether 250, poly(ethylene glycol) dimethyl ether 500, poly(ethylene glycol) dimethyl ether 2000, poly(ethylene glycol) monomethyl ether 350, poly(ethylene glycol) 200, poly(ethylene glycol) 6000, and poly(propylene glycol) 400. The obtained water activities data were used to calculate the vapor pressure of solutions as a function of concentration. Water activity of all investigated solutions increased with increasing temperature and polymer molar mass. A comparison is given between the vapor–liquid equilibrium data inferred from VPO and isopiestic methods, for different aqueous polymer solutions at 298.15 K, and there is a good agreement between the results of the investigated methods. Furthermore, the segment-based local composition models, nonrandom two-liquid (NRTL), Wilson, and universal quasichemical (UNIQUAC), were used to correlate the experimental activity data.

## INTRODUCTION

Vapor–liquid equilibria (VLE) in polymer + solvent systems are necessary for a variety of applications including surface acoustic-wave vapor sensors,[1,2] recovery of organic vapors from waste-air streams using a polymeric membrane,[3,4] pervaporation,[5] and other polymeric membrane-separation processes like polymer devolatilization[6] and vapor-phase photografting[7] and for the optimum formulation of paints and coatings. For rational process and product design, experimental data correlations based on molecular thermodynamics are required.

Several experimental techniques have been employed to measure the solvent activity of mixtures. These have included freezing-point depression, boiling point elevation, dynamic and static vapor-pressure measurements, osmotic pressure measurements, hygrometrics, vapor sorption, the isopiestic method, and vapor-pressure osmometry (VPO). In this study, the isopiestic and VPO methods have been used to obtain the water activity of water + polymer systems.

The isopiestic method is based on the phenomenon that different solutions that contain nonvolatile solutes, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. At equilibrium the chemical potentials (and therefore solvent activity) of the solvent in each of the solutions in the closed system are identical. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system.[9]

The VPO is based on a precise determination of the temperature difference between a drop of solution and a drop of solvent hanging on temperature-recording thermistors. Thermistors are placed in a chamber filled with a saturated vapor of solvent. Since the vapor pressure of the solution is less than that of the pure solvent, the solvent vapor condenses on the solution droplet and causes a change in its temperatures. Temperature differences between the two thermistors are represented as the voltage difference measured by a digital voltmeter.

VLE data for some polymer solutions have been compiled by Wohlfahrt.[8] However, water activity data for some aqueous polymer solutions such as poly(ethylene glycol) (PEG),[9−17] poly(propylene glycol) (PPG),[10,16,18,19] and poly(vinyl pyrrolidone)[20,21] have been reported in the literature. However, similar information on the VLE of aqueous solutions of poly(ethylene glycol) dimethyl ethers and polyethylene glycol monomethyl ethers is scarce. In the present report, vapor pressures of water + poly(ethylene glycol dimethyl ether) 250 (PEGDME250), + PEGDME500, + PEGDME2000, + poly(ethylene glycol) monomethyl ether 350 (PEGMME350), + poly(ethylene glycol) 200 (PEG200),+PEG6000, and+poly(propylene glycol) 400 (PPG400) are measured by the improved isopiestic method[9] at 298.15 K and by the VPO method at (298.15, 303.15, and 308.15) K. The results were correlated with the segment-based local composition nonrandom two-liquid (NRTL),[22] Wilson,[23] and universal quasichemical (UNIQUAC)[24] models.

## EXPERIMENTAL PROCEDURE

Sodium chloride, PEGDME250, PEGDME500, PEGDME2000, PEG200, and PEG6000 were obtained from Merck, and PEGMME350 and PPG400 were obtained from Fluka. Sodium chloride (GR, minimum 99.5 % in mass) was dried in an electrical oven at about 110 °C for 24 h prior to use.

In this study, the isopiestic method was used to obtain the water activities of water + polymer systems. The isopiestic apparatus used in this work was similar to the one used by Ochs et al.[9] This apparatus consists of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard NaCl + water solutions, two flasks contained the polymer solutions, and the central flask was used as a solvent reservoir. The apparatus was held in a constant-temperature bath at least 120 h for

**Special Issue:** John M. Prausnitz Festschrift

**Received:** February 20, 2010
**Accepted:** June 3, 2010
**Published:** June 16, 2010

dx.doi.org/10.1021/je100178s | J. Chem. Eng. Data 2011, 56, 789–799

**Table 1. Activity of Water ($a_1$) and Vapor Pressure ($p$) for Different Water (1) + Polymer (2) Systems Obtained from the Isopiestic Method at 298.15 K**

| $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa |
|---|---|---|---|---|---|---|---|---|
| Water (1) + PEGDME250 (2) | | | Water (1) + PEGDME2000 (2) | | | Water (1) + PEGMME350 (2) | | |
| 0.0844 | 0.9932 | 3.147 | 0.1753 | 0.9932 | 3.147 | 0.0890 | 0.9932 | 3.147 |
| 0.1075 | 0.9915 | 3.142 | 0.2127 | 0.9915 | 3.142 | 0.1211 | 0.9915 | 3.142 |
| 0.1164 | 0.9906 | 3.139 | 0.2222 | 0.9906 | 3.139 | 0.1265 | 0.9906 | 3.139 |
| 0.1168 | 0.9903 | 3.138 | 0.2394 | 0.9894 | 3.135 | 0.1280 | 0.9903 | 3.138 |
| 0.1313 | 0.9894 | 3.135 | 0.2504 | 0.9880 | 3.131 | 0.1463 | 0.9894 | 3.135 |
| 0.1393 | 0.988 | 3.131 | 0.2971 | 0.9823 | 3.112 | 0.1514 | 0.9880 | 3.131 |
| 0.1924 | 0.9823 | 3.112 | 0.3370 | 0.9750 | 3.089 | 0.20579 | 0.9823 | 3.112 |
| 0.2384 | 0.9750 | 3.089 | 0.3633 | 0.9706 | 3.075 | 0.2514 | 0.9750 | 3.089 |
| 0.2678 | 0.9706 | 3.075 | 0.3773 | 0.9679 | 3.067 | 0.2811 | 0.9706 | 3.075 |
| 0.2829 | 0.9679 | 3.067 | 0.3841 | 0.9664 | 3.062 | 0.2964 | 0.9679 | 3.067 |
| 0.2876 | 0.9664 | 3.062 | 0.3987 | 0.9628 | 3.051 | 0.2983 | 0.9664 | 3.062 |
| 0.3065 | 0.9628 | 3.051 | 0.4148 | 0.9592 | 3.039 | 0.3205 | 0.9628 | 3.051 |
| 0.3483 | 0.9526 | 3.018 | 0.4350 | 0.9526 | 3.018 | 0.3618 | 0.9526 | 3.018 |
| 0.3561 | 0.9501 | 3.010 | 0.4499 | 0.9484 | 3.005 | 0.3688 | 0.9501 | 3.010 |
| 0.3621 | 0.9484 | 3.005 | 0.4741 | 0.9391 | 2.976 | 0.3756 | 0.9484 | 3.005 |
| 0.3977 | 0.9391 | 2.976 | 0.5097 | 0.9258 | 2.933 | 0.4051 | 0.9391 | 2.976 |
| 0.4325 | 0.9258 | 2.933 | 0.6173 | 0.8695 | 2.755 | 0.4442 | 0.9258 | 2.933 |
| 0.4579 | 0.9158 | 2.902 | 0.6422 | 0.8556 | 2.711 | 0.4704 | 0.9158 | 2.902 |
| 0.4936 | 0.9019 | 2.857 | | | | 0.4767 | 0.9122 | 2.890 |
| 0.5553 | 0.8741 | 2.769 | | | | 0.5023 | 0.9019 | 2.857 |
| 0.5639 | 0.8695 | 2.755 | | | | 0.5578 | 0.8741 | 2.769 |
| 0.5913 | 0.8556 | 2.711 | | | | 0.5642 | 0.8695 | 2.755 |
| | | | | | | 0.5834 | 0.8556 | 2.711 |
| Water (1) + PPG400 (2) | | | Water (1) + PEG200 (2) | | | Water (1) + PEG6000 (2) | | |
| 0.2126 | 0.988 | 3.131 | 0.0615 | 0.9932 | 3.147 | 0.2041 | 0.9932 | 3.147 |
| 0.3056 | 0.9823 | 3.113 | 0.0786 | 0.9915 | 3.142 | 0.2399 | 0.9915 | 3.142 |
| 0.5421 | 0.9685 | 3.069 | 0.0851 | 0.9906 | 3.139 | 0.2643 | 0.9895 | 3.135 |
| 0.5663 | 0.9671 | 3.064 | 0.0908 | 0.9903 | 3.138 | 0.2903 | 0.9869 | 3.127 |
| 0.6121 | 0.9637 | 3.053 | 0.0984 | 0.9894 | 3.135 | 0.3055 | 0.9846 | 3.120 |
| 0.6556 | 0.9596 | 3.040 | 0.1041 | 0.9880 | 3.131 | 0.3261 | 0.9818 | 3.111 |
| 0.7112 | 0.9533 | 3.020 | 0.2389 | 0.9679 | 3.067 | 0.3297 | 0.981 | 3.108 |
| 0.7217 | 0.9503 | 3.011 | 0.2632 | 0.9628 | 3.051 | 0.3334 | 0.9805 | 3.107 |
| 0.7328 | 0.9484 | 3.005 | 0.3064 | 0.9526 | 3.018 | 0.3549 | 0.9768 | 3.095 |
| 0.7788 | 0.9391 | 2.976 | 0.3215 | 0.9484 | 3.005 | 0.3592 | 0.9756 | 3.091 |
| 0.8089 | 0.9258 | 2.933 | 0.3565 | 0.9391 | 2.976 | 0.3952 | 0.9678 | 3.066 |
| 0.8382 | 0.9122 | 2.890 | 0.3962 | 0.9258 | 2.933 | 0.3958 | 0.9677 | 3.066 |
| 0.8401 | 0.9088 | 2.879 | 0.4346 | 0.9122 | 2.890 | 0.4125 | 0.9628 | 3.051 |
| 0.8760 | 0.8695 | 2.755 | 0.4429 | 0.9088 | 2.879 | 0.4319 | 0.9577 | 3.035 |
| 0.8837 | 0.8556 | 2.711 | 0.5255 | 0.8695 | 2.755 | 0.4458 | 0.9526 | 3.018 |
| | | | 0.5499 | 0.8556 | 2.711 | 0.4514 | 0.9505 | 3.012 |
| | | | | | | 0.4751 | 0.9413 | 2.982 |
| | | | | | | 0.5010 | 0.9303 | 2.948 |
| | | | | | | 0.5101 | 0.9258 | 2.933 |
| | | | | | | 0.5416 | 0.9122 | 2.890 |

equilibrium at (298.15 ± 0.01) K. The temperature was controlled to within ± 0.01 K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance with an uncertainty of ± $1 \cdot 10^{-7}$ kg. From the mass of each flask after equilibrium and the initial mass of salt and polymer, the mass fraction of each solution was calculated. The water activities for the standard aqueous NaCl solutions at different concentrations have been calculated from the correlation of Clarke and Glew.[25] It was assumed that the equilibrium condition was reached when the differences between the mass fractions of each duplicate were less than 1 %. In all cases, averages of the duplicate are reported as the total isopiestic mass fraction. The uncertainty in the measurement of solvent activity was estimated to be $\pm 2 \cdot 10^{-4}$.

Table 2. Activity of Water ($a_1$) and Vapor Pressure ($p$) for Different Water (1) + Polymer (2) Systems Obtained from the VPO Method at 298.15 K

| $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa |
|---|---|---|---|---|---|---|---|---|
| Water (1) + PEGDME250 (2) | | | Water (1) + PEGDME500 (2) | | | Water (1) + PEGDME2000 (2) | | |
| 0.0090 | 0.9996 | 3.1675 | 0.0101 | 0.9998 | 3.1679 | 0.0112 | 0.9998 | 3.1687 |
| 0.0143 | 0.9993 | 3.1665 | 0.0395 | 0.9985 | 3.1640 | 0.0216 | 0.9997 | 3.1677 |
| 0.0207 | 0.9987 | 3.1645 | 0.0622 | 0.9973 | 3.1602 | 0.0407 | 0.9994 | 3.1666 |
| 0.0404 | 0.9973 | 3.1602 | 0.0792 | 0.9964 | 3.1571 | 0.0613 | 0.9989 | 3.1650 |
| 0.0613 | 0.9955 | 3.1544 | 0.0998 | 0.9950 | 3.1528 | 0.0850 | 0.9978 | 3.1616 |
| 0.0806 | 0.9939 | 3.1492 | 0.1169 | 0.9936 | 3.1483 | 0.1036 | 0.9969 | 3.1587 |
| 0.0962 | 0.9928 | 3.1459 | 0.1435 | 0.9915 | 3.1417 | 0.1191 | 0.9961 | 3.1561 |
| 0.1112 | 0.9916 | 3.1420 | 0.1576 | 0.9904 | 3.1381 | 0.1341 | 0.9954 | 3.1539 |
| 0.1215 | 0.9903 | 3.1379 | 0.1873 | 0.9875 | 3.1291 | 0.1467 | 0.9948 | 3.1522 |
| 0.1397 | 0.9890 | 3.1339 | 0.2013 | 0.9861 | 3.1245 | 0.1692 | 0.9934 | 3.1476 |
| 0.1589 | 0.9871 | 3.1276 | 0.2184 | 0.9840 | 3.1178 | 0.1997 | 0.9913 | 3.1412 |
| 0.1714 | 0.9852 | 3.1216 | | | | 0.2204 | 0.9899 | 3.1368 |
| 0.1793 | 0.9836 | 3.1166 | | | | 0.2367 | 0.9887 | 3.1329 |
| | | | | | | 0.2674 | 0.9854 | 3.1222 |
| Water (1) + PEGMME350 (2) | | | Water (1) + PEG200 (2) | | | Water (1) + PEG6000 (2) | | |
| 0.0112 | 0.9996 | 3.1673 | 0.0107 | 0.9990 | 3.1655 | 0.0674 | 0.9991 | 3.1659 |
| 0.0213 | 0.9990 | 3.1655 | 0.0304 | 0.9968 | 3.1586 | 0.0897 | 0.9988 | 3.1648 |
| 0.0412 | 0.9979 | 3.1621 | 0.0615 | 0.9925 | 3.1450 | 0.1229 | 0.9982 | 3.1631 |
| 0.0600 | 0.9967 | 3.1582 | 0.0877 | 0.9896 | 3.1356 | 0.1554 | 0.9970 | 3.1593 |
| 0.0806 | 0.9947 | 3.1518 | 0.0962 | 0.9884 | 3.1319 | 0.1802 | 0.9958 | 3.1554 |
| 0.1000 | 0.9930 | 3.1464 | 0.1094 | 0.9870 | 3.1273 | 0.2089 | 0.9942 | 3.1502 |
| 0.1187 | 0.9914 | 3.1412 | 0.1218 | 0.9843 | 3.1189 | 0.2407 | 0.9922 | 3.1438 |
| 0.1285 | 0.9905 | 3.1386 | | | | 0.2946 | 0.9872 | 3.1282 |
| 0.1483 | 0.9884 | 3.1319 | | | | 0.3179 | 0.9833 | 3.1158 |
| 0.1563 | 0.9877 | 3.1296 | | | | | | |
| 0.1827 | 0.9847 | 3.1201 | | | | | | |
| Water (1) + PPG400 (2) | | | | | | | | |
| 0.0100 | 0.9993 | 3.1666 | | | | | | |
| 0.0205 | 0.9988 | 3.1649 | | | | | | |
| 0.0489 | 0.9972 | 3.1598 | | | | | | |
| 0.0815 | 0.9957 | 3.1551 | | | | | | |
| 0.1064 | 0.9945 | 3.1513 | | | | | | |
| 0.1260 | 0.9933 | 3.1476 | | | | | | |
| 0.1547 | 0.9916 | 3.1420 | | | | | | |
| 0.1935 | 0.9896 | 3.1356 | | | | | | |

VPO was performed with the help of an Osmomat K-7000 (Knauer Inc.). The measuring chamber of osmometer contains a reservoir of solvent, paper wicks to provide a saturated solvent atmosphere, and two thermistors that are placed in an airtight cell which measure resistance changes caused by changes in temperature. First, a droplet of pure solvent is attached to each thermistor with the help of a microsyringe, and after 5 min of equilibration, the reading is adjusted to zero. Then the pure solvent on one thermistor is replaced by the polymer solution, and condensation of solvent from the vapor phase into the polymer solution at the thermistor takes place. Because of the heat of condensation, the thermistor containing polymer solution will be warmed, and vapor pressure rises. These processes continue until the vapor pressure of the polymer solution equals the vapor pressure of the pure solvent. The change in temperature changes the resistance of the thermistors. A bridge circuit measures the resistance difference of both thermistors. As long as changes in temperature are small, the resistance is proportional to $\Delta T$. Generally, a time of (4 to 8) min suffices to reach this steady state. First, the instrument was calibrated using aqueous NaCl solutions as a reference with known osmotic coefficients in the proper concentration range, yielding a function that correlates the panel readings to the corresponding concentrations of the reference solutions and therefore their osmotic coefficients. Then in the same conditions, the panel readings were measured for the studied polymer solutions. For each solution, at least five determinations (zero point adjustment and new solution) were performed, and the mean value is reported. Generally, the deviations from the mean value were less than 1 %. The cell temperature, which is electronically controlled, has a standard uncertainty of $\pm 1 \cdot 10^{-3}$ K. For a certain polymer solution which has a same instrument reading as a sodium chloride solution with

**Table 3. Activity of Water ($a_1$) and Vapor Pressure ($p$) for Different Water (1) + Polymer (2) Systems Obtained from the VPO Method at 303.15 K**

| $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa |
|---|---|---|---|---|---|---|---|---|
| Water (1) + PEGDME250 (2) | | | Water (1) + PEGDME500 (2) | | | Water (1) + PEGDME2000 (2) | | |
| 0.0017 | 0.9999 | 4.2446 | 0.0057 | 0.9998 | 4.2441 | 0.0052 | 0.9998 | 4.2443 |
| 0.0032 | 0.9998 | 4.2442 | 0.0113 | 0.9996 | 4.2433 | 0.0100 | 0.9998 | 4.2443 |
| 0.0066 | 0.9996 | 4.2434 | 0.0161 | 0.9995 | 4.2428 | 0.0131 | 0.9998 | 4.2442 |
| 0.0081 | 0.9996 | 4.2434 | 0.018 | 0.9994 | 4.2424 | 0.0202 | 0.9997 | 4.2439 |
| 0.0107 | 0.9994 | 4.2424 | 0.022 | 0.9993 | 4.2419 | 0.0253 | 0.9996 | 4.2434 |
| 0.0249 | 0.9986 | 4.2391 | 0.0402 | 0.9985 | 4.2387 | 0.0494 | 0.9993 | 4.2420 |
| 0.0344 | 0.9979 | 4.2360 | 0.0629 | 0.9977 | 4.2355 | 0.0788 | 0.9986 | 4.2392 |
| 0.0402 | 0.9974 | 4.2339 | 0.0824 | 0.9968 | 4.2314 | 0.0782 | 0.9985 | 4.2386 |
| 0.0611 | 0.9960 | 4.2281 | 0.1021 | 0.9957 | 4.2270 | 0.1181 | 0.9972 | 4.2331 |
| 0.0753 | 0.9948 | 4.2231 | 0.125 | 0.9944 | 4.2214 | 0.1593 | 0.9956 | 4.2264 |
| 0.0801 | 0.9946 | 4.222 | 0.1395 | 0.9934 | 4.2169 | 0.1777 | 0.9943 | 4.2207 |
| 0.0891 | 0.9939 | 4.2189 | 0.1571 | 0.9920 | 4.2110 | 0.2004 | 0.9924 | 4.2130 |
| 0.1008 | 0.9930 | 4.2152 | 0.1789 | 0.9904 | 4.2043 | 0.2209 | 0.9910 | 4.2068 |
| 0.1166 | 0.9915 | 4.2089 | 0.1913 | 0.9895 | 4.2004 | 0.2464 | 0.9888 | 4.1976 |
| 0.1372 | 0.9895 | 4.2003 | 0.2046 | 0.9881 | 4.1944 | 0.2538 | 0.9883 | 4.1953 |
| 0.1601 | 0.9875 | 4.1918 | 0.2213 | 0.9866 | 4.1883 | 0.2936 | 0.9844 | 4.1788 |
| 0.1724 | 0.9862 | 4.1862 | 0.2224 | 0.9864 | 4.1874 | | | |
| 0.1878 | 0.9850 | 4.1812 | | | | | | |
| 0.2015 | 0.9839 | 4.1766 | | | | | | |
| Water (1) + PEGMME350 (2) | | | Water (1) + PEG200 (2) | | | Water (1) + PEG6000 (2) | | |
| 0.0027 | 0.9999 | 4.2446 | 0.0036 | 0.9998 | 4.2441 | 0.0654 | 0.9995 | 4.2430 |
| 0.0039 | 0.9998 | 4.2441 | 0.0055 | 0.9996 | 4.2434 | 0.0860 | 0.9993 | 4.2422 |
| 0.0063 | 0.9997 | 4.2436 | 0.0082 | 0.9994 | 4.2424 | 0.1024 | 0.9990 | 4.2408 |
| 0.0082 | 0.9995 | 4.2429 | 0.0103 | 0.9992 | 4.2416 | 0.1225 | 0.9987 | 4.2394 |
| 0.0121 | 0.9993 | 4.2421 | 0.0313 | 0.9972 | 4.2334 | 0.1470 | 0.9980 | 4.2366 |
| 0.0154 | 0.9991 | 4.2414 | 0.0494 | 0.9959 | 4.2275 | 0.1529 | 0.9979 | 4.2360 |
| 0.0206 | 0.9989 | 4.2405 | 0.0648 | 0.9949 | 4.2233 | 0.1693 | 0.9974 | 4.2339 |
| 0.0415 | 0.9977 | 4.2355 | 0.0786 | 0.9934 | 4.2171 | 0.1961 | 0.9961 | 4.2285 |
| 0.0589 | 0.9966 | 4.2307 | 0.0992 | 0.9912 | 4.2077 | 0.2102 | 0.9955 | 4.2261 |
| 0.0796 | 0.9955 | 4.2261 | 0.1065 | 0.9905 | 4.2046 | 0.2162 | 0.9950 | 4.2239 |
| 0.0935 | 0.9945 | 4.2218 | 0.1178 | 0.9892 | 4.1992 | 0.2368 | 0.9940 | 4.2194 |
| 0.1053 | 0.9937 | 4.2185 | 0.1330 | 0.9863 | 4.1870 | 0.2484 | 0.9932 | 4.2163 |
| 0.1223 | 0.9924 | 4.213 | 0.1401 | 0.9854 | 4.1829 | 0.2619 | 0.9924 | 4.2126 |
| 0.1373 | 0.9909 | 4.2065 | 0.1502 | 0.9839 | 4.1764 | 0.2787 | 0.9908 | 4.2061 |
| 0.1583 | 0.9888 | 4.1976 | | | | 0.2862 | 0.9900 | 4.2027 |
| 0.1663 | 0.9881 | 4.1943 | | | | 0.2987 | 0.9887 | 4.1972 |
| 0.1816 | 0.9863 | 4.1867 | | | | 0.3194 | 0.9869 | 4.1892 |
| 0.1952 | 0.9847 | 4.1799 | | | | 0.3352 | 0.9851 | 4.1815 |
| Water (1) + PPG400 (2) | | | | | | | | |
| 0.0100 | 0.9998 | 4.2442 | | | | | | |
| 0.0214 | 0.9991 | 4.2414 | | | | | | |
| 0.0400 | 0.9983 | 4.2377 | | | | | | |
| 0.0565 | 0.9975 | 4.2343 | | | | | | |
| 0.0720 | 0.9971 | 4.2328 | | | | | | |
| 0.0928 | 0.9958 | 4.2274 | | | | | | |
| 0.0954 | 0.9957 | 4.227 | | | | | | |
| 0.1243 | 0.9943 | 4.2208 | | | | | | |
| 0.1626 | 0.9926 | 4.2135 | | | | | | |
| 0.1867 | 0.9916 | 4.2092 | | | | | | |
| 0.2070 | 0.9906 | 4.2051 | | | | | | |
| 0.2255 | 0.9894 | 4.2001 | | | | | | |

**Table 3. Continued**

| $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa |
|---|---|---|---|---|---|---|---|---|
| 0.2402 | 0.9883 | 4.1951 | | | | | | |
| 0.2522 | 0.9878 | 4.1931 | | | | | | |
| 0.2831 | 0.9862 | 4.1865 | | | | | | |
| 0.3001 | 0.9855 | 4.1833 | | | | | | |

**Table 4. Activity of Water ($a_1$) and Vapor Pressure ($p$) for Different Water (1) + Polymer (2) Systems Obtained from the VPO Method at 308.15 K**

| $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa |
|---|---|---|---|---|---|---|---|---|
| Water (1) + PEGDME250 (2) | | | Water (1) + PEGDME500 (2) | | | Water (1) + PEGDME2000 (2) | | |
| 0.0008 | 0.9999 | 5.6256 | 0.0036 | 0.9999 | 5.6260 | 0.0101 | 0.9999 | 5.6257 |
| 0.0049 | 0.9997 | 5.6249 | 0.0088 | 0.9997 | 5.6248 | 0.0159 | 0.9998 | 5.6253 |
| 0.0081 | 0.9996 | 5.6241 | 0.0104 | 0.9997 | 5.6246 | 0.0192 | 0.9998 | 5.6252 |
| 0.0100 | 0.9995 | 5.6234 | 0.0287 | 0.9990 | 5.6208 | 0.0414 | 0.9994 | 5.6231 |
| 0.0140 | 0.9993 | 5.6221 | 0.0405 | 0.9985 | 5.6179 | 0.0600 | 0.9991 | 5.6211 |
| 0.0255 | 0.9986 | 5.6183 | 0.0697 | 0.9974 | 5.6114 | 0.0844 | 0.9986 | 5.6186 |
| 0.0307 | 0.9982 | 5.6164 | 0.0907 | 0.9965 | 5.6067 | 0.0998 | 0.9984 | 5.6171 |
| 0.0323 | 0.9982 | 5.6160 | 0.1026 | 0.9960 | 5.6040 | 0.1212 | 0.9978 | 5.6141 |
| 0.0499 | 0.9972 | 5.6105 | 0.1154 | 0.9954 | 5.6007 | 0.1377 | 0.9972 | 5.6105 |
| 0.0503 | 0.9971 | 5.6102 | 0.1300 | 0.9948 | 5.5970 | 0.1591 | 0.9963 | 5.6053 |
| 0.0665 | 0.9960 | 5.6038 | 0.1419 | 0.9939 | 5.5922 | 0.1817 | 0.9952 | 5.5993 |
| 0.0714 | 0.9956 | 5.6017 | 0.1581 | 0.9928 | 5.5860 | 0.2007 | 0.9940 | 5.5925 |
| 0.0797 | 0.9951 | 5.5989 | 0.1713 | 0.9918 | 5.5798 | 0.2179 | 0.9932 | 5.5878 |
| 0.0962 | 0.9939 | 5.5919 | 0.1819 | 0.9911 | 5.5760 | 0.2369 | 0.9916 | 5.5789 |
| 0.1026 | 0.9935 | 5.5894 | 0.2009 | 0.9895 | 5.5673 | 0.2595 | 0.9891 | 5.5650 |
| 0.1208 | 0.9923 | 5.5828 | 0.2199 | 0.9878 | 5.5577 | 0.2742 | 0.9876 | 5.5567 |
| 0.1325 | 0.9912 | 5.5767 | 0.2378 | 0.9862 | 5.5487 | | | |
| 0.1360 | 0.9907 | 5.5740 | 0.2484 | 0.9852 | 5.5428 | | | |
| 0.1467 | 0.9897 | 5.5680 | | | | | | |
| 0.1515 | 0.9889 | 5.5635 | | | | | | |
| 0.1636 | 0.9874 | 5.5552 | | | | | | |
| 0.1732 | 0.9859 | 5.5466 | | | | | | |
| Water (1) + PEGMME350 (2) | | | Water (1) + PEG200 (2) | | | Water (1) + PEG6000 (2) | | |
| 0.0064 | 0.9996 | 5.6242 | 0.0053 | 0.9998 | 5.6254 | 0.0635 | 0.9996 | 5.6241 |
| 0.0095 | 0.9995 | 5.6237 | 0.0082 | 0.9995 | 5.6237 | 0.0880 | 0.9993 | 5.6226 |
| 0.0127 | 0.9994 | 5.6231 | 0.0108 | 0.9993 | 5.6224 | 0.1030 | 0.9991 | 5.6211 |
| 0.0147 | 0.9993 | 5.6221 | 0.0129 | 0.9991 | 5.6213 | 0.1152 | 0.9989 | 5.6199 |
| 0.0202 | 0.9990 | 5.6208 | 0.0154 | 0.9989 | 5.6199 | 0.1263 | 0.9986 | 5.6186 |
| 0.0337 | 0.9985 | 5.6176 | 0.0245 | 0.9979 | 5.6144 | 0.1418 | 0.9983 | 5.6167 |
| 0.0509 | 0.9973 | 5.6109 | 0.0402 | 0.9963 | 5.6053 | 0.1546 | 0.9979 | 5.6147 |
| 0.0614 | 0.9967 | 5.6076 | 0.0550 | 0.9948 | 5.5969 | 0.1635 | 0.9977 | 5.6131 |
| 0.0725 | 0.9959 | 5.6030 | 0.0678 | 0.9937 | 5.5908 | 0.1657 | 0.9976 | 5.6128 |
| 0.0815 | 0.9954 | 5.6003 | 0.0798 | 0.9927 | 5.5853 | 0.1741 | 0.9973 | 5.6109 |
| 0.1003 | 0.9938 | 5.5915 | 0.0963 | 0.9907 | 5.5739 | 0.1844 | 0.9968 | 5.6083 |
| 0.1191 | 0.9926 | 5.5846 | 0.1110 | 0.9889 | 5.5635 | 0.1933 | 0.9964 | 5.6060 |
| 0.1365 | 0.9914 | 5.5778 | 0.1241 | 0.9863 | 5.5488 | 0.1985 | 0.9961 | 5.6043 |
| 0.1479 | 0.9905 | 5.5730 | | | | 0.2067 | 0.9956 | 5.6016 |
| 0.1570 | 0.9894 | 5.5667 | | | | 0.2185 | 0.9949 | 5.5978 |
| 0.1694 | 0.9881 | 5.5590 | | | | 0.2218 | 0.9948 | 5.5970 |
| 0.1811 | 0.9864 | 5.5494 | | | | 0.2436 | 0.9935 | 5.5894 |
| | | | | | | 0.2546 | 0.9926 | 5.5846 |
| | | | | | | 0.2720 | 0.9912 | 5.5767 |
| | | | | | | 0.2837 | 0.9900 | 5.5698 |
| | | | | | | 0.3042 | 0.9881 | 5.5590 |

Table 4. Continued

| $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa | $w_2$ | $a_1$ | $p$/kPa |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 0.3150 | 0.9867 | 5.5514 |
| | | | | | | 0.3205 | 0.9861 | 5.5479 |
| Water (1) + PPG400 (2) | | | | | | | | |
| 0.0101 | 0.9996 | 5.6243 | | | | | | |
| 0.0200 | 0.9992 | 5.6218 | | | | | | |
| 0.0400 | 0.9983 | 5.6169 | | | | | | |
| 0.0517 | 0.9979 | 5.6144 | | | | | | |
| 0.0634 | 0.9974 | 5.6118 | | | | | | |
| 0.0745 | 0.9971 | 5.6099 | | | | | | |
| 0.0886 | 0.9965 | 5.6064 | | | | | | |
| 0.1030 | 0.9959 | 5.6033 | | | | | | |
| 0.1186 | 0.9951 | 5.5989 | | | | | | |
| 0.1594 | 0.9932 | 5.5881 | | | | | | |
| 0.1787 | 0.9923 | 5.5828 | | | | | | |
| 0.1852 | 0.9920 | 5.5810 | | | | | | |
| 0.2002 | 0.9913 | 5.5775 | | | | | | |
| 0.2251 | 0.9904 | 5.5724 | | | | | | |
| 0.2327 | 0.9902 | 5.5709 | | | | | | |
| 0.2504 | 0.9894 | 5.5665 | | | | | | |
| 0.2864 | 0.9881 | 5.5594 | | | | | | |
| 0.2995 | 0.9876 | 5.5564 | | | | | | |
| 0.3181 | 0.9867 | 5.5514 | | | | | | |

molality $m_{\mathrm{NaCl}}$ and osmotic coefficient $\Phi_{\mathrm{NaCl}}$, the water activity $a_1$ was obtained according to:

$$a_1 = \exp(-0.001\nu_{\mathrm{NaCl}} m_{\mathrm{NaCl}} \Phi_{\mathrm{NaCl}} M_1) \qquad (1)$$

where $\nu_{\mathrm{NaCl}}$ is the stoichiometric number of reference electrolyte and $M_1$ is the molar mass of the solvent. $\Phi_{\mathrm{NaCl}}$ is the osmotic coefficient for aqueous solutions of NaCl with molality $m_{\mathrm{NaCl}}$ calculated from the correlation of Clarke and Glew.[25] The uncertainty in the measurement of water activity was found to be better than $\pm 2 \cdot 10^{-4}$.

## RESULTS AND DISCUSSION

**Experimental Results.** Table 1 shows the experimental water activity data of the investigated polymer solutions at 298.15 K obtained from the isopiestic method. Tables 2, 3, and 4 give the data for the same systems obtained with the help of the osmometer (VPO technique) at (298.15, 303.15, and 308.15) K, respectively. From the solvent activity data, the vapor-pressure data of solutions, $p$, were determined with the help of the following equation:

$$\ln(a_1) = \ln\left(\frac{p}{p^\circ}\right) + \frac{(B - V_1^\circ)(p - p^\circ)}{RT} \qquad (2)$$

where $B$, $V_1^\circ$, and $p^\circ$ are the second virial coefficient, molar volume, and vapor pressure of pure water, respectively. $R$ is the gas constant, and $T$ is the absolute temperature. The second virial coefficients of water vapor were calculated using the equation provided by Rard and Platford.[26] Molar volumes of liquid water were calculated using the density of water at different temperatures.[27] The vapor pressures of pure water were calculated using the equation of state of Saul and Wagner.[28] The calculated vapor-pressure data of investigated polymer solutions are also given in Tables 1 to 4.

The isopiestic method is the most accurate, simple experimental technique available for measuring the solvent activity of solutions in high concentrations of solute. However, the VPO technique gives good results for the solvent activity in the low solute concentration range. A comparison between the water activity data inferred from VPO and isopiestic methods at 298.15 K is shown in Figure 1 for aqueous solutions of PEG200, PEGDME2000, and PEGMME350. As can be seen, there is a good agreement between the results obtained from the investigated methods. The measured solvent activity data for the investigated water + polymer solutions obtained from the isopiestic and VPO methods at 298.15 K are shown in Figure 2.

In Figure 3, comparisons of the experimental water activity data measured in this work with those taken from the literature have been made for some aqueous polymer solutions at 298.15 K. As can be seen, there is a good agreement between the results obtained in this work and those taken from the literature.

In fact, the solvent absorption of a polymer increases with a decrease in the molar mass of the polymer. In other words, the effect of the solute on solvent activity decreases as solute molar mass rises. As can be seen from Figures 1 and 2, for high polymer concentrations ($0.33 < w_2 < 0.7$), in the same polymer mass fraction the magnitudes of both vapor pressure and water activity have the order of PPG400 > PEG6000 > PEGDME2000 > PEGDME500>PEGMME350 > PEGDME250>PEG200. However, as can be seen from Figure 4, for low polymer concentrations ($w_2 < 0.12$), the water activities of the investigated polymer solutions follow the order PEG6000 > PEGDME2000 > PEGDME500>PPG400>PEGMME350> PEGDME250>PEG200. The investigated polymers have structures $HOCH_2[CH_2OCH_2]_n$-$CH_2OH$ (PEG), $CH_3OCH_2[CH_2OCH_2]_nCH_2OH$ (PEGMME), $CH_3OCH_2[CH_2OCH_2]_nCH_2OCH_3$ (PEGDME), and HO-

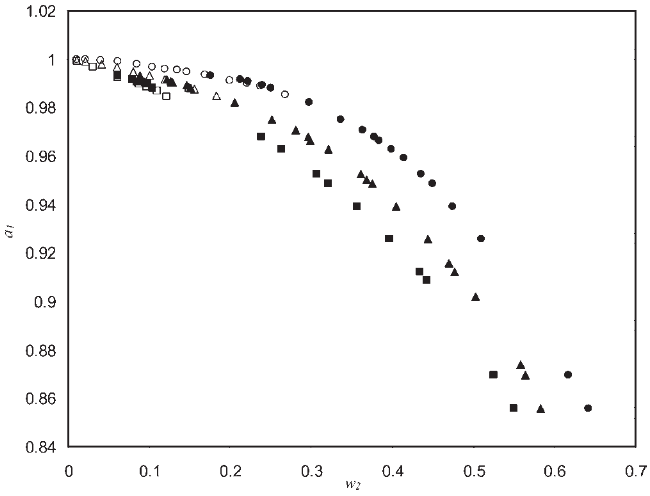

**Figure 1.** Comparison between the water activity data obtained from VPO and isopiestic methods at 298.15 K: □, PEG200 (VPO); ■, PEG200 (isopiestic); △, PEGMME350 (VPO); ▲, PEGMME350 (isopiestic); ○, PEGDME2000 (VPO); ●, PEGDME2000 (isopiestic).

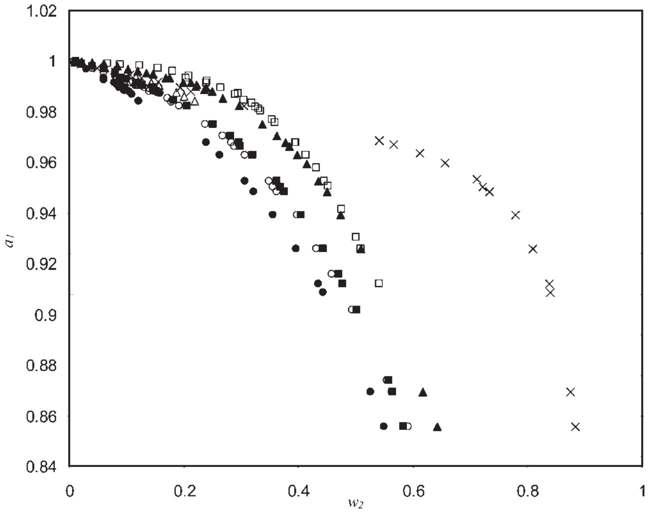

**Figure 2.** Water activity data for water (1) + polymer (2) systems obtained from the VPO and isopiestic methods at 298.15 K: ●, PEG200; ○, PEGDME250; ■, PEGMME350; △, PEGDME500; ▲, PEGDME2000; □, PEG6000; ×, PPG400.

$CH(CH_3)[CH_2OCH(CH_3)]_nCH_2OH$ (PPG). As can be seen, the polymers PEG, PEGMME, and PEGDME have similar repeating units, and therefore for a certain polymer mass fraction and polymer molar mass, the water activity of aqueous solutions of PEG, PEGMME, and PEGDME has similar values. The PPG contains a greater proportion of hydrocarbon in its molecule, and also the side chain methyl groups in PPG hinder hydrogen bonding between the water molecules and the ether oxygen atoms. Gunninghame and Malcolm[29] showed that the heat of mixing with water per mole of glycol is more negative for PEG than for PPG.

As can be seen from Figure 2, the plots for PEG, PEGMME, and PEGDME show markedly larger negative slopes of the water activity or vapor pressure against polymer mass fraction above mass fractions of about 0.2 to 0.35 (depend on polymer molar mass), which implies that the interaction between the water and these polymers at high mass fractions of polymer must be of a very stable nature. In fact, larger negative slopes of the $a_1$ against $w_2$ at high mass fractions of these polymers is attributed to extensive hydrogen bonding of water molecules to the polymer. On the other hand, smaller negative slopes at low mass fraction of polymer suggests that the hydrophobic hydration of the polymer is an important factor in its dilute solution behavior, which has a maximum effect at around this mass fraction. The polymer concentration range in which the hydrophobic hydration of the polymer is a dominant factor increases by increasing polymer molar mass. PPG because of a greater proportion of hydrocarbons in its molecule has a greater polymer concentration range in

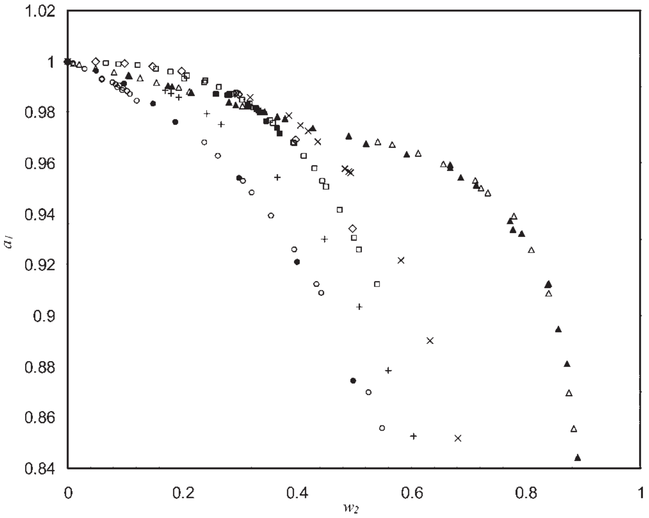

**Figure 3.** Comparisons of the experimental water activity data measured in this work with those taken from the literature for some aqueous polymer solutions at 298.15 K: ○, PEG200 (this work); □, PEG6000 (this work); △, PPG400 (this work); ▲, PPG400 (ref 19); +, PEG400 (ref 17); ×, PVP1000 (ref 21); ■, PEG6000 (ref 30); ◇, PEG6000 (ref 14); ●, PEG200 (ref 14).

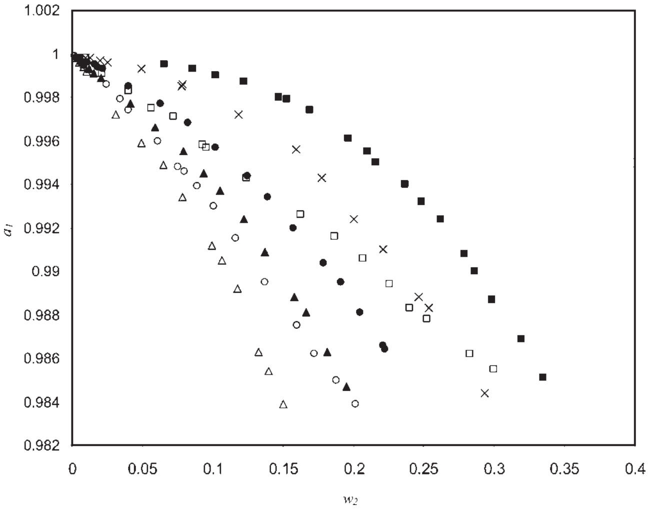

**Figure 4.** Water activity data for water (1) + polymer (2) systems obtained from the VPO method at 303.15 K: △, PEG200; ○, PEGDME250; ▲, PEGMME350; ●, PEGDME500; ×, PEGDME2000; ■, PEG6000; □, PPG400.

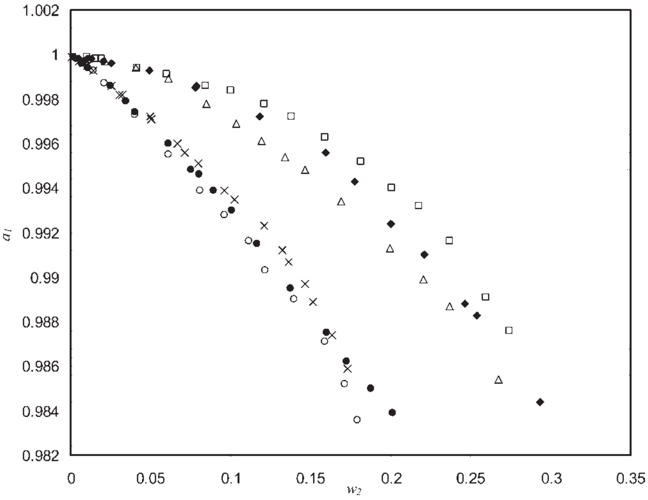

**Figure 5.** Water activity data for water (1) + polymer (2) systems obtained from the VPO method: ○, PEGDME250 (at 298.15 K); ●, PEGDME250 (at 303.15 K); ×, PEGDME250 (at 308.15 K); △, PEGDME2000 (at 298.15 K); ◆, PEGDME2000 (at 303.15 K); □, PEGDME2000 (at 308.15 K).

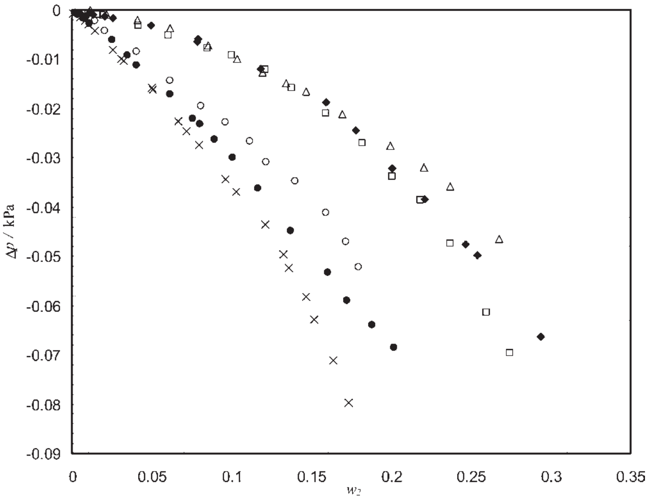

**Figure 6.** Vapor-pressure depression data for water (1) + polymer (2) systems obtained from the VPO method: ○, PEGDME250 (at 298.15 K); ●, PEGDME250 (at 303.15 K); ×, PEGDME250 (at 308.15 K); △, PEGDME2000 (at 298.15 K); ◆, PEGDME2000 (at 303.15 K); □, PEGDME2000 (at 308.15 K).

which the hydrophobic hydration of the polymer is an important factor relative to other investigated polymers. As can be seen from Figure 2, for aqueous solutions of PPG with $w_2 < 0.8$, the hydrophobic hydration of the polymer is an important factor. However, for aqueous solutions of PPG with $w_2 > 0.8$, the hydrophilic hydration of the polymer is an important factor.

As shown in Figure 5, water activity of the investigated water (1) + polymer (2) systems increases with increasing temperature. Therefore, from eq 2, we conclude that, by increasing temperature, the increase of vapor pressure of polymer (2) + $H_2O$ (1) solution is larger than those of pure water. This is because the polymers become more hydrophobic with increasing temperature. Figure 6 shows that for a given polymer mass fraction the magnitude of vapor-pressure depression increases by increasing temperature and decreasing polymer molar mass. For a given polymer mass fraction and temperature, the vapor-pressure-lowering effect is greatest for the lowest molecular molar mass, PEG200, and decreases with rising molar mass.

**Correlation of Data.** In this work, for the correlation of solvent activity for the investigated systems the segment-based local composition NRTL,[22] Wilson,[23] and UNIQUAC[24] models were considered. In all of these models, the activity coefficient of the solvent (1) is considered as the sum of the combinatorial, ln $\gamma_1^{\text{Comb}}$, and the residual contribution, ln $\gamma_1^{\text{Res}}$:

$$\ln \gamma_1 = \ln \gamma_1^{\text{Comb}} + \ln \gamma_1^{\text{Res}} \tag{3}$$

In this work, for all of the models the Flory−Huggins expression was used for the combinatorial contribution, and the NRTL, Wilson, and UNIQUAC models were used for the residual contribution.

**Flory−Huggins Combinatorial Term.** The Flory−Huggins equation for the combinatorial contribution of the activity coefficient of the solvent can be written as:

$$\ln \gamma_1^{\text{Comb}} = \ln \frac{\phi_1}{x_1} + \left(1 - \frac{r_1}{r_2}\right)\phi_2 \tag{4}$$

This equation accounts for the contribution for the excess entropy associated with random mixing. In this equation

$$\phi_i = \frac{r_i x_i}{r_1 x_1 + r_2 x_2} \tag{5}$$

In these relations, $x_i$ is the mole fraction of the component $i$, and $r_i$ is the number of the segments in the component $i$.

**NRTL Residual Term.**

$$\frac{1}{r_1}\ln \gamma_1^{\text{NRTL}} = \phi_2^2\left(\frac{\tau_{21}(\exp(-\alpha\tau_{21}))^2}{(\phi_1 + \phi_2 \exp(-\alpha\tau_{21}))^2} + \frac{\tau_{12}\exp(-\alpha\tau_{12})}{(\phi_2 + \phi_1 \exp(-\alpha\tau_{12}))^2}\right) \tag{6}$$

$$\tau_{ij} = \frac{a_{ij}}{RT} \tag{7}$$

where α is the nonrandomness factor and the NRTL parameters $a_{ij}$ are fitted to the experimental data.

**Wilson Residual Term.**

$$-\frac{1}{Cr_1}\ln \gamma_1^{\text{Wilson}} = \ln\left(\phi_1 + \phi_2 \exp\left(-\frac{E_{21}}{CRT}\right)\right) + \phi_1\left(\frac{1 - \left(\phi_1 + \phi_2 \exp\left(-\frac{E_{21}}{CRT}\right)\right)}{\phi_1 + \phi_2 \exp\left(-\frac{E_{21}}{CRT}\right)}\right) + \phi_2\left(\frac{\exp\left(-\frac{E_{12}}{CRT}\right) - \left(\phi_2 + \phi_1 \exp\left(-\frac{E_{12}}{CRT}\right)\right)}{\phi_2 + \phi_1 \exp\left(-\frac{E_{12}}{CRT}\right)}\right) \tag{8}$$

where $C$ is a parameter which represents the effective coordination number in the system and the Wilson parameters, $E_{ij}$, are fitted to the experimental data.

Table 5. Parameters of the NRTL, Wilson, and UNIQUAC Equations along with the Corresponding Relative Percentage Deviations (dev %) for $T = 298.15$ K

| | NRTL | | | Wilson | | | UNIQUAC | | |
|---|---|---|---|---|---|---|---|---|---|
| system | $a_{12} \cdot 10^{-3}$ | $a_{21} \cdot 10^{-3}$ | 100 ARD | $E_{12} \cdot 10^{-3}$ | $E_{21} \cdot 10^{-3}$ | 100 ARD | $a_{12} \cdot 10^{-3}$ | $a_{21} \cdot 10^{-3}$ | dev % |
| water (1) + PEGDME250 (2) | −0.119 | 1.205 | 0.10 | −1.876 | 3.127 | 0.10 | 0.104 | 0.067 | 0.09 |
| water (1) + PEGDME500 (2) | −0.119 | 1.205 | 0.01 | −1.876 | 3.127 | 0.01 | 0.104 | 0.067 | 0.02 |
| water (1) + PEGDME2000 (2) | −0.119 | 1.205 | 0.06 | −1.876 | 3.127 | 0.05 | 0.104 | 0.067 | 0.05 |
| water (1) + PEGMME350 (2) | −0.130 | 1.060 | 0.02 | −1.952 | 3.061 | 0.02 | 0.085 | 0.065 | 0.02 |
| water (1) + PEG200 (2) | −0.099 | 1.218 | 0.16 | −1.781 | 3.050 | 0.16 | 0.105 | 0.073 | 0.17 |
| water (1) + PEG6000 (2) | −0.099 | 1.218 | 0.02 | −1.781 | 3.050 | 0.02 | 0.105 | 0.073 | 0.02 |
| water (1) + PPG400 (2) | −3.996 | 9.016 | 0.01 | −6.519 | 9.974 | 0.03 | 0.050 | 2.042 | 0.03 |

Table 6. Parameters of the NRTL, Wilson, and UNIQUAC Equations along with the Corresponding Relative Percentage Deviations (dev %) for $T = 303.15$ K

| | NRTL | | | Wilson | | | UNIQUAC | | |
|---|---|---|---|---|---|---|---|---|---|
| system | $a_{12} \cdot 10^{-3}$ | $a_{21} \cdot 10^{-3}$ | 100 ARD | $E_{12} \cdot 10^{-3}$ | $E_{21} \cdot 10^{-3}$ | 100 ARD | $a_{12} \cdot 10^{-3}$ | $a_{21} \cdot 10^{-3}$ | dev % |
| water (1) + PEGDME250 (2) | −0.029 | 1.299 | 0.08 | −1.789 | 3.231 | 0.06 | 0.115 | 0.087 | 0.08 |
| water (1) + PEGDME500 (2) | −0.029 | 1.299 | 0.01 | −1.789 | 3.231 | 0.01 | 0.115 | 0.087 | 0.01 |
| water (1) + PEGDME2000 (2) | −0.029 | 1.299 | 0.06 | −1.789 | 3.231 | 0.07 | 0.115 | 0.087 | 0.05 |
| water (1) + PEGMME350 (2) | −0.070 | 1.218 | 0.01 | −1.812 | 3.128 | 0.01 | 0.100 | 0.088 | 0.01 |
| water (1) + PEG200 (2) | −0.051 | 1.306 | 0.05 | −1.721 | 3.128 | 0.05 | 0.115 | 0.087 | 0.05 |
| water (1) + PEG6000 (2) | −0.051 | 1.306 | 0.01 | −1.721 | 3.128 | 0.01 | 0.115 | 0.087 | 0.01 |
| water (1) + PPG400 (2) | −2.483 | 5.336 | 0.02 | −6.445 | 10.081 | 0.01 | 0.067 | 1.147 | 0.02 |

Table 7. Parameters of the NRTL, Wilson, and UNIQUAC Equations along with the Corresponding Relative Percentage Deviations (dev %) for $T = 308.15$ K

| | NRTL | | | Wilson | | | UNIQUAC | | |
|---|---|---|---|---|---|---|---|---|---|
| system | $a_{12} \cdot 10^{-3}$ | $a_{21} \cdot 10^{-3}$ | 100 ARD | $E_{12} \cdot 10^{-3}$ | $E_{21} \cdot 10^{-3}$ | 100 ARD | $a_{12} \cdot 10^{-3}$ | $a_{21} \cdot 10^{-3}$ | dev % |
| water (1) + PEGDME250 (2) | 0.000 | 1.370 | 0.09 | −1.738 | 3.278 | 0.09 | 0.123 | 0.096 | 0.08 |
| water (1) + PEGDME500 (2) | 0.000 | 1.370 | 0.01 | −1.738 | 3.278 | 0.01 | 0.123 | 0.096 | 0.01 |
| water (1) + PEGDME2000 (2) | 0.000 | 1.370 | 0.06 | −1.738 | 3.278 | 0.06 | 0.123 | 0.096 | 0.05 |
| water (1) + PEGMME350 (2) | −0.021 | 1.246 | 0.02 | −1.782 | 3.181 | 0.02 | 0.105 | 0.099 | 0.02 |
| water (1) + PEG200 (2) | −0.030 | 1.295 | 0.03 | −1.718 | 3.134 | 0.03 | 0.116 | 0.087 | 0.03 |
| water (1) + PEG6000 (2) | −0.030 | 1.295 | 0.01 | −1.718 | 3.134 | 0.01 | 0.116 | 0.087 | 0.02 |
| water (1) + PPG400 (2) | −2.645 | 5.781 | 0.02 | −6.979 | 11.073 | 0.02 | 0.077 | 0.869 | 0.01 |

## UNIQUAC Residual Term

$$\ln \gamma_1^{\text{UNIQUAC}} = -q_1 \ln(X_1 + X_2\tau_{21}) + q_1 X_2 \left( \frac{\tau_{21}}{X_1 + X_2\tau_{21}} - \frac{\tau_{12}}{X_2 + X_1\tau_{12}} \right) \qquad (9)$$

$$X_i = \frac{q_i x_i}{q_1 x_1 + q_2 x_2} \qquad (10)$$

$$q_i = r_i \left( 1 - 2\alpha \left( 1 - \frac{1}{r_i} \right) \right) \qquad (11)$$

$$\tau_{ij} = \exp\left( -\frac{a_{ij}}{T} \right) \qquad (12)$$

A value of $r = 1$ was used for solvents, and for a polymer the value of $r$ is the ratio of the molar volume of polymer to that of the solvent at 298.15 K. The molar volumes of polymers have been calculated from the specific volumes and the number average molar masses of polymers. The specific volume of PEGDME, PEGMME, PEG, and PPG at 298.15 K are 0.9663 (measured in this work), 0.9230 (measured in this work), 0.8387,[30] and 0.9962.[31] The values of nonrandomness factor and effective coordination number $C$ were set to 0.1[32] and 10,[33] respectively. The segment-based local composition NRTL, Wilson, and UNIQUAC models were used for the correlation of the experimental solvent activity data obtained from the VPO technique, and the obtained parameters for the studied systems are presented in Tables 5, 6, and 7 along with the corresponding relative percentage deviations (dev %) of the fit. On the basis of the deviations given in Tables 5 to 7, we conclude that the segment-based local composition NRTL, Wilson, and UNIQUAC models have similar behavior in the correlation of obtained experimental solvent activity data and all investigated models represent the experimental water activity data of polymer solutions, with good

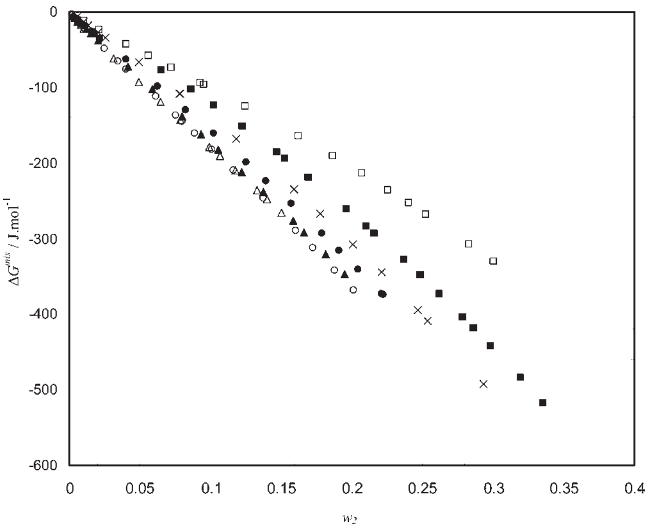

**Figure 7.** Plot of the molar Gibbs free energy change due to mixing, $\Delta G^{\text{mix}}$, against the mass fraction of polymer, $w_2$, for water (1) + polymer (2) systems obtained from the Wilson model at 303.15 K: △, PEG200; ○, PEGDME250; ▲, PEGMME350; ●, PEGDME500; ×, PEGDME2000; ■, PEG6000; □, PPG400.

accuracy. As can be seen from Tables 5 to 7, the obtained parameters are independent of polymer molar mass and increase very slightly by increasing temperature. Also, the values of the obtained parameters for polymers PEGDME, PEGMME, and PEG which have similar segments are very close to each other. However, PPG has a different segment with the other investigated polymers, and therefore, as can be seen from these tables, the values of the obtained parameters for PPG are different from those obtained for the other polymers.

The Wilson equation for the molar Gibbs free energy change due to mixing, $\Delta G^{\text{mix}}$, of binary polymer solutions has the following form:[23]

$$\frac{\Delta G^{\text{mix}}}{RT} = x_1 \ln \phi_1 + x_2 \ln \phi_2 - C\left[x_1 r_1 \ln\left(\phi_1 + \phi_2 \exp\left(\frac{-E_{21}}{CRT}\right)\right) + x_2 r_2 \ln\left(\phi_1 \exp\left(\frac{-E_{12}}{CRT}\right) + \phi_2\right)\right] \qquad (13)$$

Using the eq 13 and obtained parameters given in Tables 5 to 7, the molar Gibbs free energy change due to mixing for the investigated polymer solutions was calculated. The calculated $\Delta G^{\text{mix}}$ have negative values and become more negative by decreasing polymer molar mass and temperature which indicate that the formation of polymer solutions from the pure polymer and pure water becomes more spontaneous by decreasing polymer molar mass and temperature. Figure 7 shows that the values of $\Delta G^{\text{mix}}$ for aqueous solutions of PPG400 are less negative than those for the other polymers. As mentioned above, PPG has a greater proportion of hydrocarbon in its molecule, and therefore PPG is more hydrophobic than the other polymers investigated in this work. The investigated polymers become more hydrophobic with increasing temperature; therefore at higher temperatures, hydrogen-bond interactions between water and polymers are weakened, and hence less negative values of the molar Gibbs free energy change due to mixing are obtained at higher temperatures.

## ■ CONCLUSIONS

VLE behavior of aqueous solutions of PEGDME250, PEGDME500, PEGDME2000, PEGMME350, PEG200, PEG6000, and PPG400 has been studied experimentally using VPO and isopiestic methods. A comparison between the water activity data inferred from VPO and isopiestic methods shows that there is a good agreement between the results obtained from these methods. For high polymer concentrations, the magnitudes of both vapor pressure and water activity have the order of PPG400 > PEG6000 > PEGDME2000 > PEGDME500 > PEGMME350 > PEGDME250 > PEG200. However, for low polymer concentrations, the water activities and vapor pressures of the investigated polymer solutions follow the order PEG6000 > PEGDME2000 > PEGDME500 > PPG400 > PEGMME350 > PEGDME250 >PEG200. In fact, these results are consistent with the valid thermodynamic facts that, in a highly dilute solution of a nonvolatile solute, the activity of the volatile solvent at a given mass concentration of solute is inversely proportional to the molar mass of the solute, and this fact forms a basis for the molar mass determination by VPO. The segment-based local composition NRTL, Wilson, and UNIQUAC models have been used to correlate the experimental water activity data. All models have similar behavior in the correlation of obtained experimental solvent activity data. The values of the obtained model parameters for PEGDME, PEGMME, and PEG which have similar segments are very close to each other. However, the values of the obtained parameters for PPG are different from those obtained for the other polymers. The molar Gibbs free energy change due to mixing for the investigated polymer solutions has negative values and becomes more negative by decreasing polymer molar mass and temperature, and also, the values of $\Delta G^{\text{mix}}$ for aqueous solutions of PPG400 are less negative than those for the other polymers.

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### Funding Sources

Financial support from Elites National Foundation of Iran (Bonyade Melli Nokhbegan) and University of Kurdistan is gratefully acknowledged.

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## ■ NOTE ADDED AFTER ASAP PUBLICATION

In the original version of this article, which was published ASAP on June 16, 2010, the value of the nonrandomness factor ($\alpha$) was incorrect. The revised version with the corrected value of $\alpha$ was reposted on March 9, 2011.