

# Vapor–liquid equilibria for some concentrated aqueous polymer solutions

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## Abstract

Vapor–liquid-equilibrium data were obtained for binary aqueous solutions of six water-soluble linear polymers in the range 70–95°C. A classical gravimetric sorption method was used to measure the amount of solvent absorbed as a function of vapor-phase water pressure. Polymers studied were polyvinylpyrrolidone, polyethyleneoxide, polyvinylalcohol, hydroxyethylcellulose, polyethylenimine, polymethylvinylether. The experimental data were reduced with Hino's lattice model that distinguished the interactions due to London dispersion forces and those due to hydrogen bonding. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Vapor–liquid equilibrium; Polymers; Gravimetric-sorption method

## 1. Introduction

Water-soluble polymers have a variety of industrial applications; e.g. they are used in petroleum extraction [1], in metallurgy [2,3], in pharmacology [4,5], in the paper and coating industries [4,6], as well as in biotechnology [7–12].

Numerous studies have reported the equilibrium properties of aqueous polymer solutions [13–22], or their aqueous solutions with proteins [23–35]. However, most attention has been given to dilute solutions [36–46]. Only a few studies have reported the results for concentrated aqueous solutions [47–53].

The aim of the present study is to improve our understanding of concentrated aqueous polymer solutions.

This work presents some new experimental vapor–liquid data in the range 70–95°C. These data, along with some previously published results, are here interpreted using Hino's lattice theory for hydrogen-bonded systems.

## 2. Experimental

### 2.1. Materials

Distilled water was degassed with a standard freeze-thaw procedure described by Panayiotou and Vera [54]. The polymer properties are shown in Table 1. Density measurements

[55,14] indicated that the crystallinity of PVA is insignificant. Even at very low vapor-phase water pressures, PVP gave a liquid-like appearance.

### 2.2. Apparatus

Vapor–liquid-equilibrium data were obtained using a gravimetric-sorption method previously described by several authors, e.g. Bonner and Prausnitz [56]; Bonner [57]; Gupta and Prausnitz [58]. Fig. 1 shows a schematic diagram of the apparatus. The entire system is submerged in an air bath controlled to within  $\pm 0.3^\circ\text{C}$ .

Each glass chamber contains one aluminum pan suspended from a quartz spring (Ruska Instruments Corp., Houston, TX). The calibrated springs have a sensitivity of about 1 mg/mm and a maximum load of 250 mg. Within this range, the elongation of each spring is linear with respect to change in mass.

A cathetometer (Wild, Heerbrugg, Switzerland) is used to measure the extension of the springs and the mercury levels of the manometer.

### 2.3. Experimental procedure

Polymer samples of known mass (20–35 mg) are placed into previously weighted aluminum pans. The system is then vacuum-dried for 12–24 h to remove residual moisture and solvent. To obtain reproducible data, the solvent (water) is introduced by opening and then closing the valve between the solvent flask and the evacuated glass chambers, increasing the pressure up to one half of the water saturation

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Table 1

Polymer properties ( $M_w$ , weight average molecular weight;  $T_g$ , glass transition temperature;  $T_m$ , melting temperature; PVP, polyvinylpyrrolidone; PEO, polyethyleneoxide; PVA, polyvinylalcohol; PVME, polymethylvinylether; PEI, polyethylenimine; HEC, hydroxyethylcellulose)

Polymer	Supplier	Lot #	$M_w$	$T_g$ (°C)	$T_m$ (°C)
PVP	Aldrich	03514 MT	10 000	86 <sup>a</sup>	–
PVP	Polysciences, Inc.	446473	1000 000	86 <sup>a</sup>	–
PEO	Aldrich	02421 AT	100 000	–	65
PEO	Aldrich	00613 MP	4000 000	–	65
PVA	Aldrich	00918 AG	124–186 000	85	230 <sup>a</sup>
PVME	Aldrich	10819 JQ	60 000	–34	<sup>b</sup>
PEI	Aldrich	12922 PQ	750 000	–23.5	58.5
HEC	Polysciences, Inc.	96775	90–105 000	–	–

<sup>a</sup> From Molyneux [14].

<sup>b</sup> Amorphous in commercially available samples [14].

pressure at the experimental temperature. After a waiting period from 12 to 24 h, the system is evacuated one more time for several days; only then are dry polymer-sample weights measured.

The pressure is increased a little by briefly opening the valve to the solvent flask. The system is allowed to equilibrate anywhere from 6 h to a few days, after each solvent injection. Equilibrium is assumed when measurements in spring length do not change more than  $\pm 0.05$  mm in a 12-h period.

When the pressure is about 90% of the water saturation pressure at the experimental temperature, it is lowered to almost half of its value and the corresponding sorption measured. An experiment is considered successful only when the last desorption datum agrees with the previously measured absorption data.

As the polymer is nonvolatile, the total pressure is equal to the vapor-phase water pressure above the polymer solution. The vapor is considered to be an ideal gas because the experimental pressures are low (less than 100 kPa). Solvent

activity,  $a_1$ , is given by the ratio of the measured pressure to the water saturation pressure at the system temperature; water saturation pressures are from Ref. [59].

Cathetometer measurements have an uncertainty of 0.05 mm. Replicate measurements indicate that mass readings have a precision of 0.1 mg, while pressure readings have a precision of 0.04 kPa. The uncertainty in solvent weight fraction  $w_1$  is 5% for  $w_1 \geq 0.05$  and somewhat higher for  $w_1 \leq 0.05$ .

Reliability of the apparatus was established by reproducing the published experimental vapor–liquid-equilibrium data for polystyrene in chloroform at 50°C [60]. Measured chloroform activities agree within about  $\pm 5\%$  with the earlier data.

### 3. Results and discussion

Table 2 shows the new data. Fig. 2 shows the sorption measured for different polymer samples. At equal water activity, PEI, HEC, PVP (characterized by more electro-negative and well-exposed polar sites) absorb more water than PEO and PVA, while PVME (whose structure is dominated by hydrophobic groups) presents a very low water sorption, up to a water activity equal to 0.9. Figs. 3 and 5 indicate that, at constant water activity, water sorption increases with molecular weight. Fig. 4 suggests that absorption may rise slightly with temperature but the observed rise is only within experimental uncertainty.

#### 3.1. Hino's theory

The experimental data were reduced using Hino's theory [61]. This theory is based on an incompressible-lattice model that considers both specific and nonspecific interactions. Each contact point of a molecule is assumed to interact in a nonspecific manner with interaction energy  $\varepsilon_{ij}$  or in a specific manner with interaction energy  $\varepsilon_{ij} + \delta\varepsilon_{ij}$ , where  $i = 1$  (solvent) or 2 (solute), and  $j = 1$  or

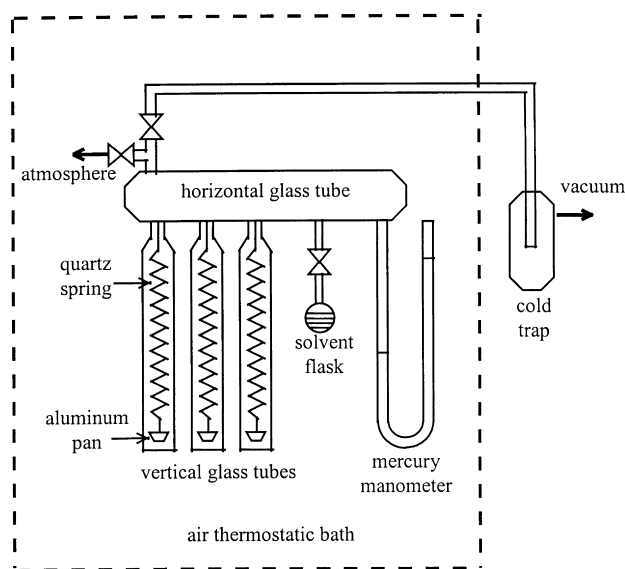


Fig. 1. Experimental apparatus.

Table 2  
Vapor–liquid equilibria for aqueous solutions of linear polymers

System	Water weight fraction, $w_1$	Water activity, $a_1$
Aqueous PVP	0.023	0.103
( $M_w$ 10 000)	0.042	0.218
$T = 73.2^\circ\text{C}$	0.061	0.333
$P_1^{\text{sat}} = 35.76$ kPa	0.092	0.472
	0.102	0.521
	0.124	0.611
	0.152	0.699
	0.189	0.787
	0.218	0.851
	0.249	0.899
Aqueous PVP	0.029	0.150
( $M_w$ 10 000)	0.044	0.243
$T = 94.5^\circ\text{C}$	0.061	0.328
$P_1^{\text{sat}} = 82.94$ kPa	0.083	0.442
	0.114	0.556
	0.145	0.652
	0.185	0.751
	0.243	0.847
Aqueous PVP	0.018	0.111
( $M_w$ 1000 000)	0.038	0.218
$T = 93.5^\circ\text{C}$	0.060	0.322
$P_1^{\text{sat}} = 79.93$ kPa	0.085	0.410
	0.116	0.508
	0.149	0.605
	0.183	0.683
	0.212	0.740
	0.221	0.756
	0.285	0.844
Aqueous PEO	0.010	0.218
( $M_w$ 100 000)	0.018	0.341
$T = 73.2^\circ\text{C}$	0.031	0.472
$P_1^{\text{sat}} = 35.76$ kPa	0.038	0.521
	0.049	0.599
	0.070	0.703
	0.096	0.778
	0.132	0.851
	0.166	0.899
Aqueous PEO	0.010	0.150
( $M_w$ 4 000 000)	0.017	0.243
$T = 94.5^\circ\text{C}$	0.025	0.328
$P_1^{\text{sat}} = 82.94$ kPa	0.035	0.442
	0.053	0.558
	0.073	0.652
	0.107	0.751
	0.178	0.847
Aqueous PVA	0.007	0.111
( $M_w$ 124–186 000)	0.016	0.218
$T = 93.5^\circ\text{C}$	0.026	0.322
$P_1^{\text{sat}} = 79.93$ kPa	0.037	0.411
	0.049	0.508
	0.064	0.605
	0.084	0.683
	0.106	0.740
	0.114	0.756
	0.212	0.848
Aqueous HEC	0.020	0.149
( $M_w$ 90–105 000)	0.033	0.243
$T = 94.5^\circ\text{C}$	0.046	0.328
$P_1^{\text{sat}} = 82.94$ kPa	0.069	0.442
	0.103	0.558
	0.137	0.652
	0.188	0.751

Table 2 (continued)

System	Water weight fraction, $w_1$	Water activity, $a_1$
Aqueous PEI	0.282	0.847
( $M_w$ 750 000)	0.019	0.106
$T = 82.5^\circ\text{C}$	0.055	0.223
$P_1^{\text{sat}} = 52.34$ kPa	0.093	0.336
	0.126	0.420
	0.174	0.537
	0.220	0.637
	0.281	0.741
	0.290	0.754
	0.345	0.838
	0.370	0.863
	0.392	0.902
	0.403	0.908
Aqueous PVME	0.001	0.109
( $M_w$ 60 000)	0.003	0.225
$T = 82.5^\circ\text{C}$	0.004	0.340
$P_1^{\text{sat}} = 52.34$ kPa	0.005	0.336
	0.007	0.420
	0.010	0.537
	0.013	0.634
	0.019	0.754
	0.024	0.838
	0.028	0.902
	0.031	0.908

2. Water activity,  $a_1$ , is given by:

$$\begin{aligned} \ln a_1 &= (1 - \phi_1) \left( 1 - \frac{1}{r_2} \right) + \ln \phi_1 \\ &+ \frac{z}{2} \left[ q_1 \ln \frac{\varphi_1}{\phi_1} + (1 - \phi_1) \left( \frac{q_2}{r_2} - q_1 \right) \right] \\ &+ \int_0^{1/\bar{T}} \frac{1}{2} \frac{\omega}{\varepsilon} \left[ (1 - \phi_1)^2 (A + B(1 - 2\phi_1) + C(1 - 2\phi_1)^2) \right. \\ &\left. + \phi_1(1 - \phi_1)(-2B(1 - \phi_1) - 4C(1 - 2\phi_1)(1 - \phi_1)) \right] \\ &\times d \left( \frac{1}{\bar{T}} \right), \end{aligned} \quad (1)$$

where the volume fraction  $\phi$  and the surface fraction  $\varphi$  are defined by:

$$\phi_i = \frac{N_i r_i}{N_1 r_1 + N_2 r_2}, \quad (2)$$

$$\varphi_i = \frac{N_i q_i}{N_1 q_1 + N_2 q_2}. \quad (3)$$

In these definitions,  $N_i$  is the number of molecules of component  $i$ , while  $r_i$  and  $q_i$  are the size and surface parameters, interrelated by the lattice coordination number,  $z$

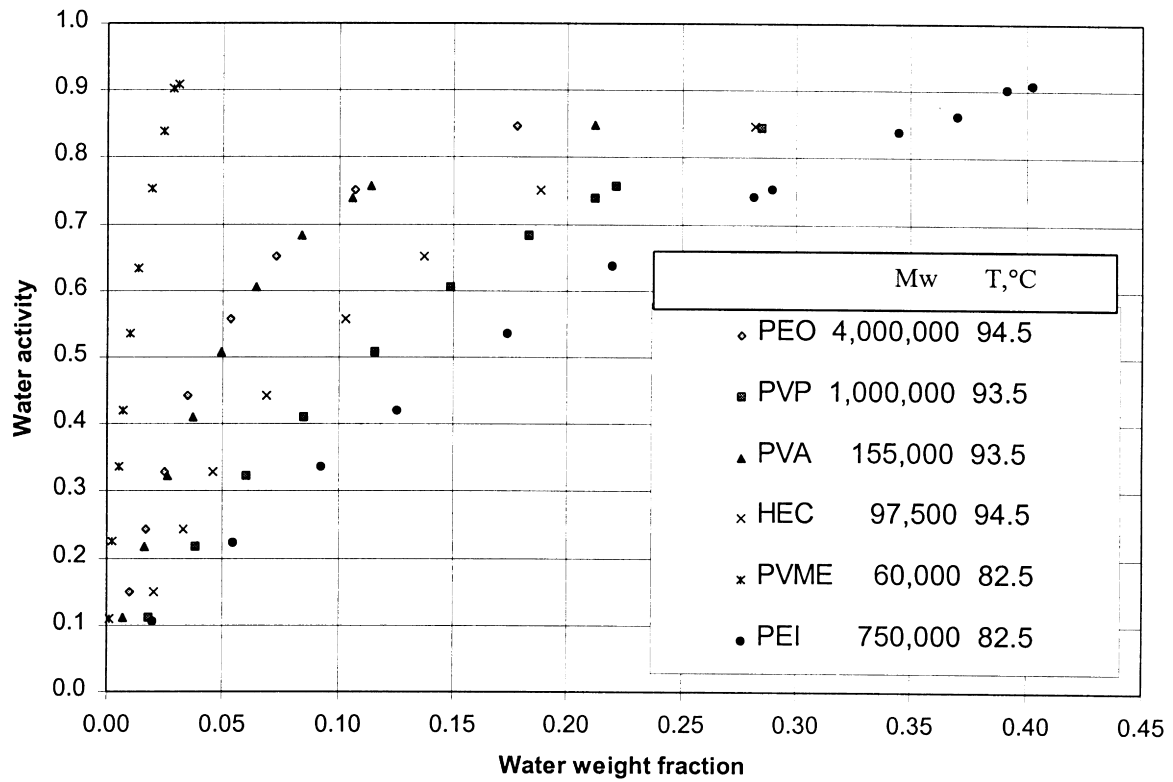


Fig. 2. Measured sorption at equal water activity: PEI, HEC, PVP (characterized by more electronegative polar sites) absorb more water than PEO and PVA, while PVME (whose structure is dominated by hydrophobic groups) presents a very low water sorption up to a water activity equal to 0.9.

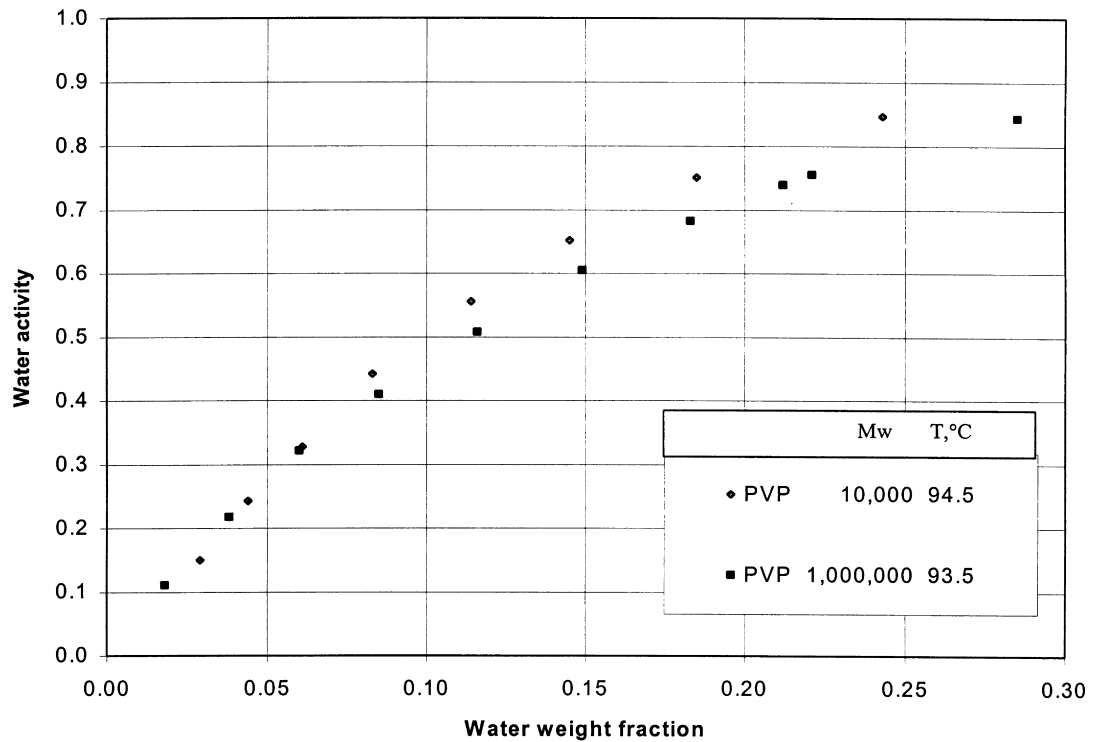


Fig. 3. Aqueous PVP characterized by different molecular weights: increasing  $M_w$ , at equal water activity, slightly increases the water sorption.

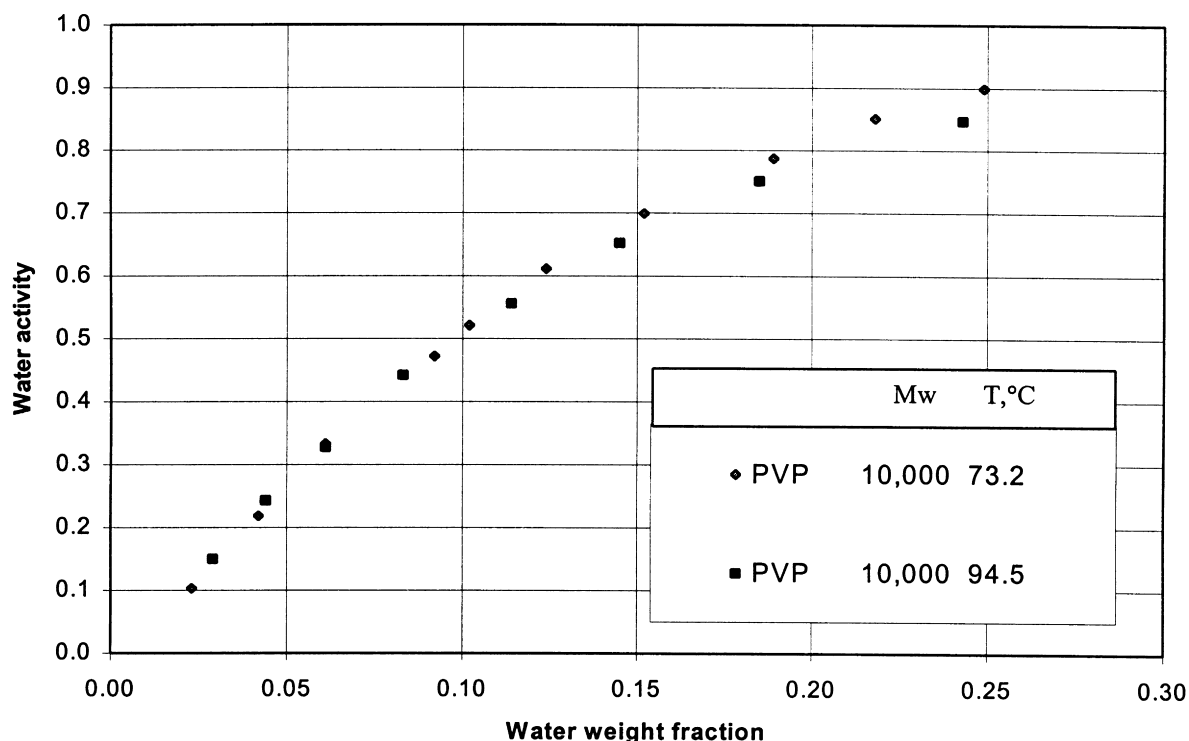


Fig. 4. Aqueous PVP,  $M_w = 10\,000$ : increasing the temperature may slightly increase the water sorption but the observed increase is within experimental uncertainty.

(set equal to 6):

$$zq_i = r_i(z - 2) + 2. \quad (4)$$

In Eq. (1),  $\varepsilon$  is the interchange energy due to nonspecific London dispersion forces, while  $\omega$  is defined by:

$$\omega = \varepsilon + f_{11}(-\delta\varepsilon_{11}) + f_{22}(-\delta\varepsilon_{22}) + f_{12}(2\delta\varepsilon_{12}) \quad (5)$$

with

$$f_{ij} = \frac{1}{1 + g_{ij}\exp(\delta\varepsilon_{ij}/kT)}. \quad (6)$$

Eq. (6) gives the fraction of all  $i - j$  interactions that are specific, as suggested by ten Brinke and Karasz [62];  $g_{ij}$  is a “degeneracy” parameter. Different values have been tested for this parameter (e.g. 500, 5000 and 50 000), without appreciable difference in the fits obtained. As  $g_{ij} = 5000$

has been successful in describing the temperature-composition coexistence curves for several systems [61], this value has been adopted here.  $\tilde{T}$  is a dimensionless temperature defined as:

$$\tilde{T} = \frac{kT}{\varepsilon}, \quad (7)$$

where  $k$  is the Boltzmann constant.  $A$ ,  $B$  and  $C$  were obtained from computer-generated simulation results [63] which consider the nonspecific interactions. As previously discussed by Hino et al. [61], the effect of specific (hydrogen-bond) interactions was incorporated, as a first approximation. Following Lambert, but substituting  $\omega$  for  $\varepsilon$ , we obtain:

$$A = \bar{a}_0(r_2) + \bar{a}_1(r_2) \left[ \exp\left(\frac{\omega}{kT}\right) - 1 \right], \quad (8)$$

Table 3  
Parameters in Hino’s lattice theory for new data

Polymer	$M_w \cdot 10^{-3}$	$T$ (°C)	$r_2$	$\varepsilon$ (kcal/mol)	$\delta\varepsilon_{12}$ (kcal/mol)	$\omega$ (kcal/mol)
PVP	10	73.2	545	0.219	-5.342	-0.165
PVP	10	94.5	541	0.217	-5.382	-0.061
PVP	1000	93.5	54 162	0.190	-5.372	-0.066
PEO	100	73.2	4954	0.376	-4.983	1.240
PEO	4000	94.5	196 751	0.310	-4.854	1.330
PVA	155	93.5	6770	0.253	-4.892	1.210
HEC	97.5	94.5	5275	0.161	-5.163	0.509
PEI	750	82.5	40 746	0.105	-5.330	-0.112
PVME	60	82.5	3259	2.155	-5.798	-0.040

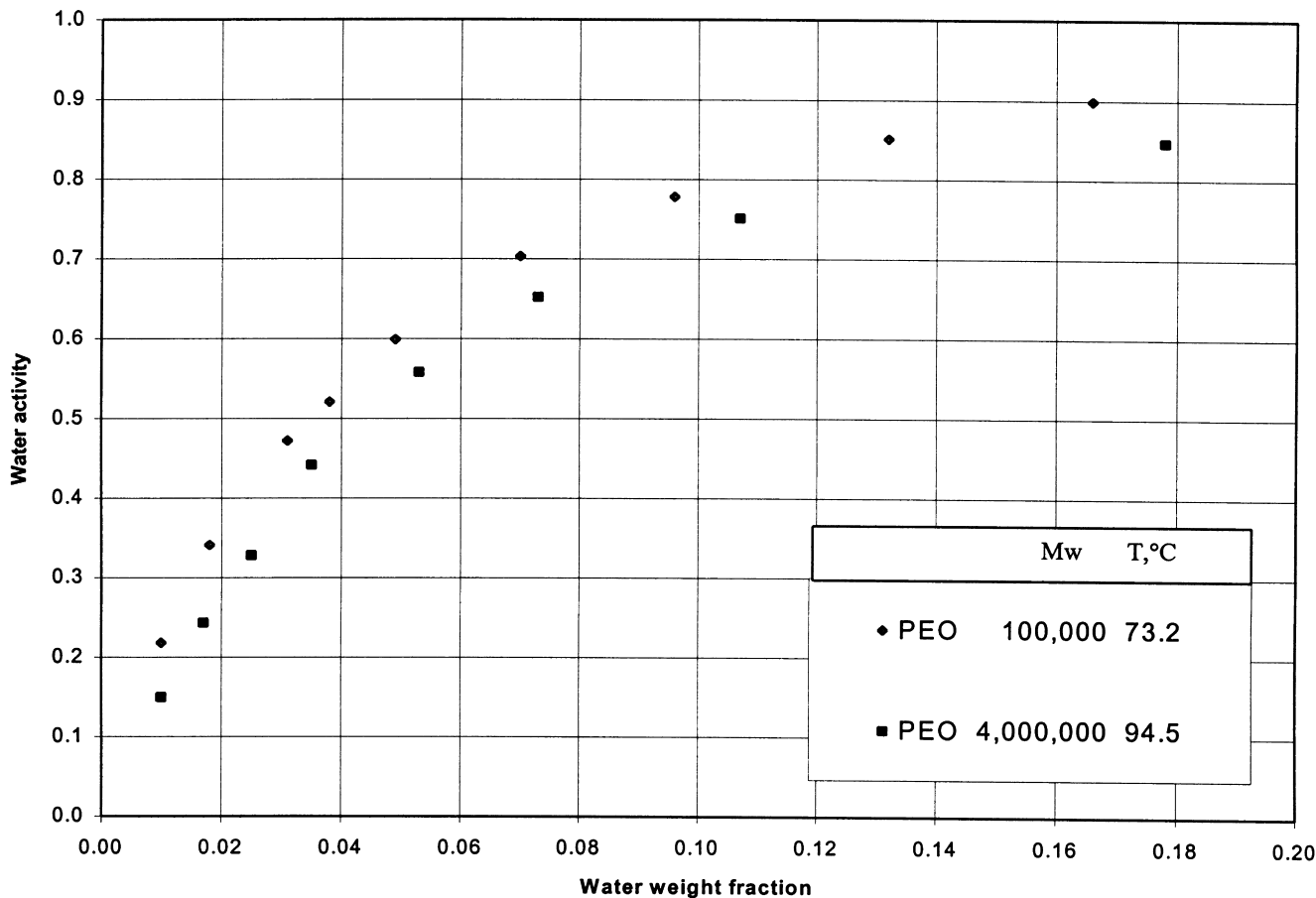


Fig. 5. Aqueous PEO: combined effect of molecular weight and temperature on sorption. Increasing both the parameters sensibly increases the water sorption at equal water activity.

$$\bar{a}_0(r_2) = 6 - \frac{0.9864(r_2 - 1)}{1 + 0.8272(r_2 - 1)}, \quad (9)$$

$$\bar{a}_1(r_2) = -1.2374 - \frac{0.09616(r_2 - 1)}{1 + 0.14585(r_2 - 1)}, \quad (10)$$

$$B(r_2) = \frac{0.8186(r_2 - 1)}{1 + 0.76494(r_2 - 1)}, \quad (11)$$

$$C = 1.20 \left[ \exp\left(\frac{\omega}{kT}\right) - 1 \right], \quad (12)$$

In this work,  $r_1$  was set equal to 1 and  $r_2$  was set equal to the ratio of molar volumes of polymer chain and water. The density of water was obtained at the experimental temperature from the correlation proposed by Daubert and Danner [59]. The PEO density was set equal to 1.1 g/ml [64], the PVA density set equal to 1.2 g/ml [59] and, as the density data were lacking, all other polymer densities were set equal to 1.0 g/ml.

- $\delta\varepsilon_{22}$  was set equal to 0 because hydrogen bonding between the polymer chains was neglected.
- $\delta\varepsilon_{11}$ , for water–water specific interactions, considered independent of the particular system analyzed, was set

equal to  $-5.9$  kcal/mol. This value, used by Hino, is a reasonable estimate of the hydrogen-bond energy.

- $\delta\varepsilon_{12}$  and  $\varepsilon$  were fit to the experimental water-activity data.

To obtain physically meaningful parameters, a hydrogen bond should be between  $-1$  and  $-10$  kcal/mol [65]. When numerical integration was necessary in Eq. (1), Simpson's rule was used at 101 equally spaced points along the axis of the reciprocal of the dimensionless temperature.

Table 3 reports the parameters obtained from fitting the new data. Table 4 reports the parameters obtained from fitting the data of Hwang and Kim [53] and those of Kim

Table 4  
Parameters in Hino's lattice theory for recently published data (PCA, polycarbonate; PAA, polyacrylic acid)

Polymer	$r_2$	$\varepsilon$ (kcal/mol)	$\delta\varepsilon_{12}$ (kcal/mol)	$\omega$ (kcal/mol)
PVA <sup>a</sup>	4045	0.221	-5.226	-0.805
PAA <sup>a</sup>	68 951	0.151	-5.213	-0.805
PCA <sup>a</sup>	1324	1.748	-5.483	-0.682
PVA <sup>b</sup>	4045	0.211	-5.224	-0.805

<sup>a</sup> From Hwang et al. [53].

<sup>b</sup> From Kim et al. [52].

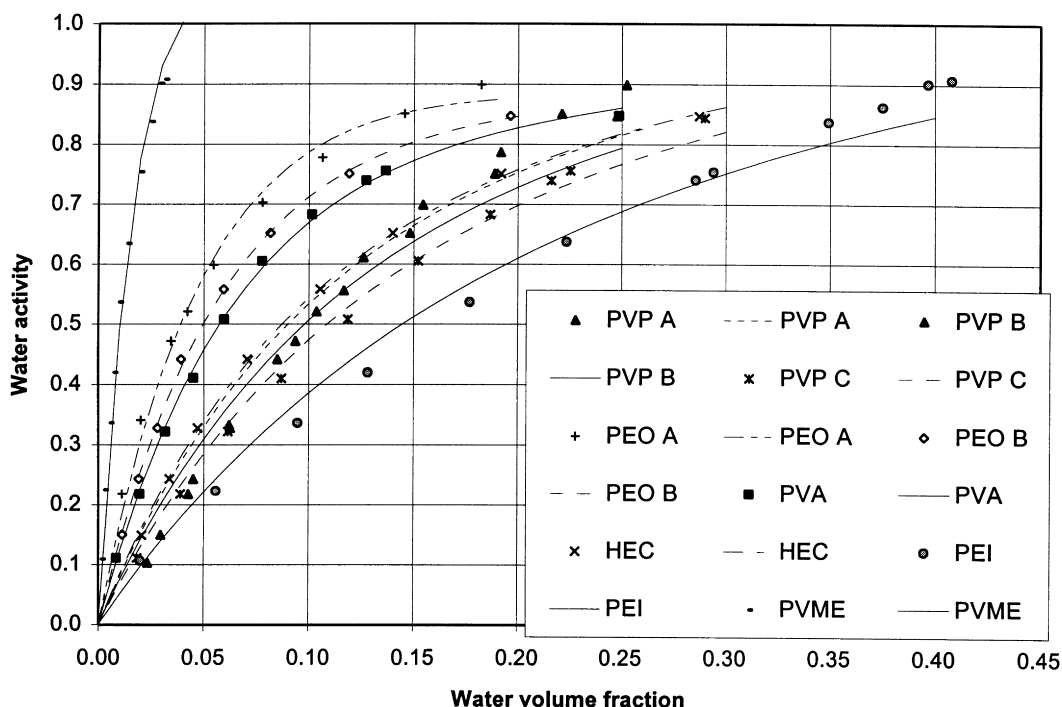


Fig. 6. Data reduction with Hino's lattice model: dots represent experimental data obtained in this work, while lines represent correlated data (PVP: (a)  $M_w = 10\,000$ ,  $T = 73.2^\circ\text{C}$ ; (b)  $M_w = 10\,000$ ,  $T = 94.5^\circ\text{C}$ ; (c)  $M_w = 1000\,000$ ,  $T = 93.5^\circ\text{C}$ . PEO: (a)  $M_w = 100\,000$ ,  $T = 73.2^\circ\text{C}$ ; (b)  $M_w = 4000\,000$ ,  $T = 94.5^\circ\text{C}$ ).

[52]. Figs. 6 and 7 show a comparison of the fitted and experimental results for all systems considered here. The fit is reasonably good at low activities but only fair at higher activities.

From Tables 3 and 4, it appears that the polymers characterized by lower hydrophilicity (e.g. PVME and PCA)

present higher values of the London interchange energy  $\varepsilon$ . This parameter, assumed to be temperature independent in its first derivation [61], reflects the polymer–solvent interactions; the lower its value, the higher the amount of water absorbed, as noted by Flory [66]. This general trend is indicated by the results presented here. When the volume

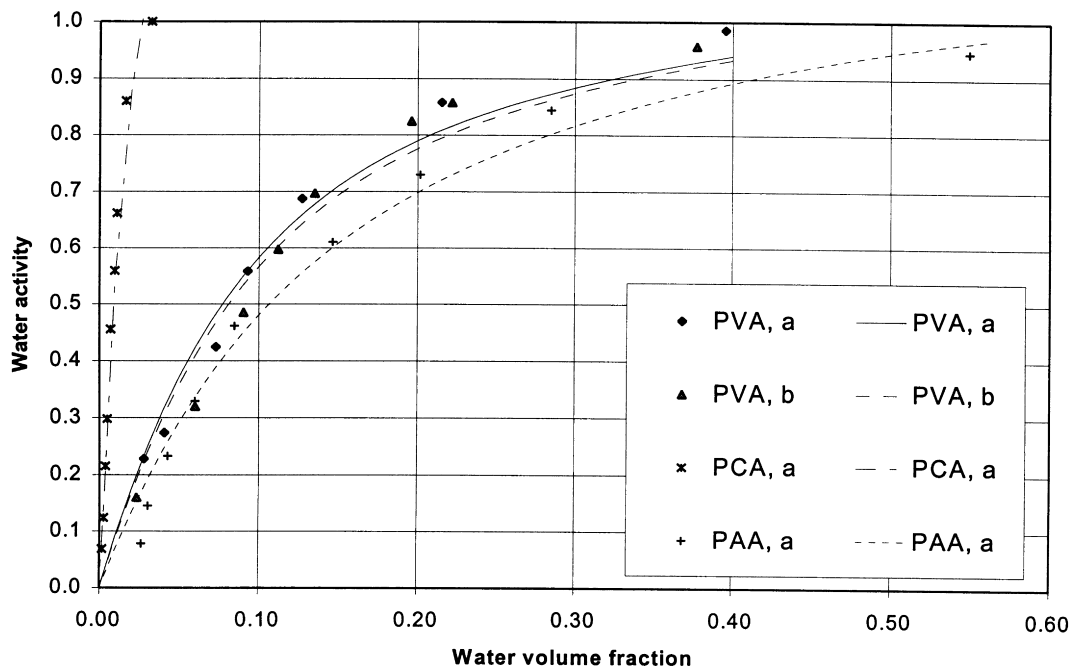


Fig. 7. Data reduction by Hino's lattice model: dots represent recently published experimental data (a) [53]; (b) [52], while lines represent the correlated data.

fraction of water is plotted against  $\varepsilon$  at constant water activity, we observe a line with negative slope; however, there is considerable scatter, especially for PVME and PCA where water sorption is low. Parameters  $\delta\varepsilon_{ij}$  contribute to temperature-dependent parameter  $\omega$  as shown in Eq. (5). At fixed  $T$ , the lower the value of  $\omega$ , the larger the amount of water absorbed.

Although this lattice-model gives a reasonable correlation of the data, it cannot be predicted. If the model were off-lattice, it might be better because the compressibility effects could be included in this case.

#### 4. Conclusions

- New vapor–liquid equilibria data were reported for some concentrated binary aqueous solutions of linear polymers.
- Data were reduced with Hino's theory that takes into account both the London and the specific solvent–solvent and solvent–solute interactions.
- Hino's model was also applied to some literature data, even though they were at 30°C, well below the glass transition temperatures for the polymers studied here.
- Reasonably good fits were obtained at low water activities, but at higher water activities, the fits were only fair.
- Hino's theory is perhaps one of the best known only for correlation, and not for prediction.

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#### References

[1] Glass JE. Water-soluble polymers. Advances in chemistry, 213. Washington, DC: American Chemical Society, 1986.

[2] Louai A, Pollet G, Francois J, Moreaux F. *J Appl Polym Sci* 1991;43:2151–2160.

[3] Louai A, Pollet G, Francois J, Moreaux F. *J Appl Polym Sci* 1991;43:2161–2168.

[4] Davidson RL. Handbook of water-soluble gums and resins. New York: McGraw Hill, 1980.

[5] Thurmond KBII, Kowalewski T, Wooley KL. *J Am Chem Soc* 1996;118:7239–7240.

[6] Croll SG, Kleinlein RL. Influence of cellulose ethers on coatings performance. Water soluble polymers. Washington, DC: American Chemical Society, 1986.

[7] Albertsson PA. Partition of cell particles and macromolecules, 3. New York: Wiley-Interscience, 1986.

[8] Tanaka H, Harada S, Kurosawa H, Yajima M. *Biotechnol Bioengng* 1987;30(1):22–30.

[9] Zhao J, Ford CF, Glatz CE, Rougvie MA, Gendel SM. *J Biotechnol* 1990;14:273–284.

[10] Abbott NL, Blankschtein D, Hatton TA. *Macromolecules* 1992;25:5192–5200.

[11] Walter H, Widen KE. *J Chromatogr A* 1994;668:185–190.

[12] Uludag Y, Ozelge HO, Yilmaz L. *J Membr Sci* 1997;129:93–99.

[13] Siow KS, Delmas G, Patterson D. *Macromolecules* 1972;5(1):29.

[14] Molyneux P. Water-soluble synthetic polymers: properties and behavior, 1. Boca Raton, FL: CRC Press, 1983.

[15] Hefford RJ. *Polymer* 1984;25:979.

[16] Allen G, Chai Z, Chong CL, Higgins JS, Tripathi J. *Polymer* 1984;25:239.

[17] Azuma H, Hanada K, Yoshikawa Y, Baba Y, Kagemoto A. *Thermochimica Acta* 1988;123:271–283.

[18] Maeda M, Yamamoto Y, Baba Y, Kagemoto A. *Thermochimica Acta* 1990;163:155–160.

[19] Louai A, Sarazin D, Pollet G, Françoise J, Moreaux F. *Polymer* 1991;32(4):703.

[20] Katime I, Anasagasti M, Rivas I, Valenciano R. *Polymer Bull* 1991;26:587–594.

[21] Tager AA, Safronov AP, Berezyuk EA, Galaev IYu. *Colloid Polym Sci* 1994;272:1234–1239.

[22] Miyata N, Yokoyama M, Sakata I. *J Appl Polym Sci* 1995;55:201–208.

[23] Nichol LW, Ogston AG, Preston BN. *Biochemical J* 1967;102:407.

[24] Edmond E, Ogston AG. *Biochemical J* 1968;109:569.

[25] Edmond E, Ogston AG. *Biochemical J* 1970;117:85–89.

[26] Comper WD, Laurent TC. *Biochemical J* 1978;175:703–708.

[27] Knoll D, Hermans J. *J Biol Chem* 1983;258(9):5710–5715.

[28] Baskir JN, Hatton TA, Suter UW. *Biotechnol Bioengng* 1989;34:541–558.

[29] Forciniti D, Hall CK. *Biotechnol Bioengng* 1991;38:986–994.

[30] Abbott NL, Blankschtein D, Hatton TA. *Macromolecules* 1993;26:825–828.

[31] Carlsson M, Linse P, Tjerneld F. *Macromolecules* 1993;26:1546–1554.

[32] Scotchford CA, Sim B, Downes S. *Polymer* 1997;38(15):3869.

[33] Lebreton B, Huddleston J, Lyddiatt A. *J Chromatogr B* 1998;711:69–79.

[34] van der Schoot P. *Macromolecules* 1998;31:4635–4638.

[35] Antonov YA, Lefebvre J, Doublier JL. *J Appl Polym Sci* 1999;71:471–482.

[36] Mariani E, Ciferri A, Maraghini M. *J Polym Sci* 1955;18(88):303.

[37] Senti FR, Hellman NN, Ludwig NH, Babcock GE, Tobin R, Glass CA, Lamberts BL. *J Polym Sci* 1955;17:527–546.

[38] Alexandrowicz Z. *J Polym Sci* 1959;40:107–112.

[39] Polik WF, Burchard W. *Macromolecules* 1983;16:978–982.

[40] Pradip MC, Somasundaran P, Kulkarni RA, Gundiah S. *Langmuir* 1991;7:2108–2111.

[41] Koike A, Nemoto N, Inoue T, Osaki K. *Macromolecules* 1995;28:2339–2344.

[42] Nemoto N, Koike A, Osaki K. *Macromolecules* 1996;29:1445–1451.

[43] Shibayama M, Uesaka M, Inamoto S, Mihara H, Nomura S. *Macromolecules* 1996;29:885–891.

[44] Gunduz U. *J Chromatogr B: Biomed Appl* 1996;680:263–266.

[45] Takada A, Nishimura M, Koike A, Nemoto N. *Macromolecules* 1998;31:436–443.

[46] Freysson E, Thuresson K, Nylander T, Joabson F, Lindman B. *Langmuir* 1998;14:5877–5889.

[47] Courval GJ, Gray DG. *Polymer* 1983;24:323.



- [48] Petrik S, Bohdanecky M, Hadobas F, Simek L. *J Appl Polym Sci* 1991;42:1759–1765.
- [49] Hsu WP, Li RJ, Myerson AS, Kwei TK. *Polymer* 1993;34(3):597.
- [50] Sun Y, Lee H. *Polymer* 1996;37(7):3915.
- [51] Schult KA, Paul DR. *J Polym Sci B: Polym Phys* 1997;35:655–674.
- [52] Kim J, Chul Joung K, Hwang S, Huh W, Soo Lee C, Yoo K. *Korean J Chem Engng* 1998;15(2):199–210.
- [53] Hwang S, Kim J, Yoo Ki-Pung. *J Chem Engng Data* 1998;43:614–616.
- [54] Panayiotou CG, Vera JH. *Polym J* 1984;16:89.
- [55] Pritchard JC. *Poly(vinylalcohol) basic properties and uses*. London: Gordon and Breach, 1970.
- [56] Bonner DC, Prausnitz JM. *J Polym Sci, Polym Phys Ed* 1974;12:51–73.
- [57] Bonner DC. *J Macromol Sci Revs Macromol Chem C* 1975;13(2):263–319.
- [58] Gupta RB, Prausnitz JM. *J Chem Engng Data* 1995;40:784–791.
- [59] Daubert TE, Danner RP. *Physical and thermodynamics properties of pure chemicals: data compilation*. New York: Hemisphere Publishing, 1989.
- [60] Bawn CEH, Wajid MA. *Trans Faraday Soc* 1956;52:1658.
- [61] Hino T, Lambert SM, Soane DS, Prausnitz JM. *AIChE J* 1993;39(5):837.
- [62] ten Brinke G, Karasz FE. *Macromolecules* 1984;17:815.
- [63] Lambert SM, Soane DS, Prausnitz JM. *Fluid Phase Equilibria* 1993;83:59–68.
- [64] Jain RK, Simha R. *J Polym Sci: Polym Phys Ed* 1979;17(11):1929–1946.
- [65] Prausnitz JM, Lichtenthaler RM, de Azevedo EG. *Molecular thermodynamics of fluid-phase equilibria*, 3. Englewood Cliffs, NJ: Prentice Hall, 1999.
- [66] Flory PJ. Chapter XIII. *Principles of polymer chemistry*. Ithaca, NY: Cornell University Press, 1953.