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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 are polyvinylpyrrolidone, polyethyleneoxide, polyvinylalcohol, hydroxyethylcellulose, polyethylenimine, polymethylvinylether.

The experimental data were reduced with Hino's lattice model that distinguishes between interactions due to London dispersion forces and those due to hydrogen bonding.

Introduction

Water-soluble polymers have a variety of industrial applications; e.g. they are used in petroleum extraction (Glass, 1986), in metallurgy (Louai *et al.*, 1991, a and b), in pharmacology (Davidson, 1980; Thurmond *et al.*, 1996), in the paper and coating industries (Croll *et al.*, 1986; Davidson, 1980), as well as in biotechnology (Albertsson, 1986; Tanaka *et al.*, 1987; Zhao *et al.*, 1990; Abbott *et al.*, 1992; Walter *et al.*, 1994; Uludag *et al.*, 1997).

Numerous studies have reported equilibrium properties of aqueous polymer solutions (Siow *et al.*, 1972; Molyneux, 1983; Hefford, 1984; Allen *et al.*, 1984; Azuma *et al.*, 1988; Maeda *et al.*, 1990; Louai *et al.*, 1991, c; Katime *et al.*, 1991; Tager *et al.*, 1994; Miyata *et al.*, 1995), or their aqueous solutions with proteins (Nichol *et al.*, 1967; Edmond *et al.*, 1968 and 1970; Comper *et al.*, 1978; Knoll *et al.*, 1983; Baskir, *et al.*, 1988; Forciniti *et al.*, 1991; Abbott *et al.*, 1993; Carlsson *et al.*, 1993; Scotchford, *et al.*,

1997; Lebreton *et al.*, 1998; van der Schoot, 1998; Antonov *et al.*, 1999). However, most attention has been given to dilute solutions (Mariani *et al.*, 1955; Senti *et al.*, 1955; Alexandrowicz, 1959; Polik *et al.*, 1983; Molyneux, 1983; Pradip *et al.*, 1991; Koike *et al.*, 1995; Nemoto *et al.*, 1996; Shibayama *et al.*, 1996; Gunduz, 1996; Takada *et al.*, 1998; Freyssingeas *et al.*, 1998). Only a few studies have reported results for concentrated aqueous solutions (Courval *et al.*, 1983; Petrik *et al.*, 1991; Hsu *et al.*, 1993; Sun *et al.*, 1996; Schult *et al.*, 1997; Kim *et al.*, 1998; Hwang *et al.*, 1998).

The goal 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.

Experimental

Materials

Distilled water was degassed with a standard freeze-thaw procedure described by Panayiotou and Vera (1984).

Polymer properties are shown in Table 1. Density measurements (Pritchard, 1970; Molyneux, 1983) indicated that the crystallinity of PVA is insignificant. Even at very low vapor-phase water pressures, PVP gave a liquid-like appearance.

Apparatus

Vapor-liquid-equilibrium data were obtained using a gravimetric-sorption method previously described by several authors, e.g. Bonner *et al.*, 1974; Bonner, 1975; Gupta *et al.*, 1995. Figure 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.

Experimental procedure

Polymer samples of known mass (20–35 mg) are placed into previously weighed aluminum pans. The system is then vacuum-dried for 12 to 24 hours to remove residual moisture and solvent. To obtain reproducible data, 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 pressure at experimental temperature. After a waiting period from 12 to 24 hours, 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 hours to a few days after each

solvent injection. Equilibrium is assumed when measurements in spring length do not change more than ± 0.05 mm in a 12-hour period.

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

Because the polymer is nonvolatile, the total pressure is equal to the vapor-phase water pressure above the polymer solution. Because experimental pressures are low (less than 100 kPa), the vapor is considered to be an ideal gas. Solvent activity, a_1 , is given by the ratio of the measured pressure to the water saturation pressure at system temperature; water saturation pressures are from Daubert and Danner (1989).

Cathetometer measurements have an uncertainty of 0.05 millimeter. Replicate measurements indicate that mass readings have a precision of 0.1 mg, while pressure readings have a precision of 0.04 kPa. 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 published experimental vapor-liquid-equilibrium data for polystyrene in chloroform at 50°C (Bawn and Wajid, 1956). Measured chloroform activities agree within about $\pm 5\%$ with the older data.

Results and Discussion

Table 2 shows the new data. Figure 2 shows the sorption measured for different polymer samples. At equal water activity, PEI, HEC, PVP (characterized by more

electronegative 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. Figures 3 and 5 indicate that, at constant water activity, water sorption increases with molecular weight. Figure 4 suggests that absorption may rise slightly with temperature but the observed rise is only within the experimental uncertainty.

Hino's theory

The experimental data were reduced using Hino's theory (Hino *et al.*, 1993). This theory is based on an incompressible-lattice model which considers both specific and nonspecific interactions. Each contact point of a molecule is assumed to interact in a nonspecific manner with interaction energy ε_{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 2. Water activity, a_1 , is given by:

$$\ln a_1 = (1 - \phi_1) \cdot \left(1 - \frac{1}{r_2}\right) + \ln \phi_1 + \frac{z}{2} \cdot \left[q_1 \cdot \ln \frac{\phi_1}{\phi_1} + (1 - \phi_1) \cdot \left(\frac{q_2}{r_2} - q_1\right) \right] + \int_0^{\frac{1}{T}} \frac{1}{2} \cdot \frac{\bar{\omega}}{\varepsilon} \cdot \left[(1 - \phi_1)^2 \cdot (A + B \cdot (1 - 2 \cdot \phi_1) + C \cdot (1 - 2 \cdot \phi_1)^2) + \phi_1 \cdot (1 - \phi_1) \cdot (-2 \cdot B \cdot (1 - \phi_1) - 4 \cdot C \cdot (1 - 2 \cdot \phi_1) \cdot (1 - \phi_1)) \right] d\left(\frac{1}{T}\right) \quad (1)$$

where volume fraction ϕ and surface fraction φ are defined by:

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

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

In these definitions, N_i is the number of molecules of component i while r_i and q_i are size and surface parameters, inter-related by the lattice coordination number, z (set equal to 6):

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

In Equation 1, ε is the interchange energy due to nonspecific London dispersion forces while ω is defined by:

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

with

$$f_{ij} = \frac{1}{1 + g_{ij} \cdot \exp\left(\frac{\delta\varepsilon_{ij}}{k \cdot T}\right)}. \quad (6)$$

Equation 6 gives the fraction of all i - j interactions that are specific, as suggested by ten Brinke *et al.*, (1984); g_{ij} is a “degeneracy” parameter. Different values have been tested for this parameter (e.g. 500, 5,000 and 50,000), without appreciable difference in the fits obtained. Because $g_{ij} = 5,000$ has been successful for describing temperature-composition coexistence curves for several systems (Hino *et al.*, 1993), this value has been adopted here. \tilde{T} is a dimensionless temperature defined as:

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

with k the Boltzmann constant. A , B , and C were obtained from computer-generated simulation results (Lambert *et al.*, 1993) which take into account nonspecific interactions. As previously discussed by Hino *et al.* (1993), the effect of specific (hydrogen-bond) interactions has been incorporated, as a first approximation. Following Lambert, but substituting ω for ε , we obtain:

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

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

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

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

$$C = 1.20 \cdot \left[\exp\left(\frac{\omega}{k \cdot T}\right) - 1 \right]. \quad (12)$$

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 experimental temperature from the correlation proposed by Daubert and Danner (1989); PEO density was set equal to 1.1 g/ml (Jain *et al.*, 1979); PVA density was set equal to 1.2 g/ml (Daubert *et al.*, 1989) and, because density data are 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 polymer chains was neglected.

- $\delta\epsilon_{11}$, 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 hydrogen-bond energy.
- $\delta\epsilon_{12}$ and ϵ were fit to the experimental water-activity data.

To obtain physically meaningful parameters, a hydrogen bond should be between -1 and -10 kcal/mol (Prausnitz *et al.*, 1999). 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 parameters obtained from fitting the new data. Table 4 reports parameters obtained from fitting the data of Hwang *et al.* (1998) and those of Kim *et al.* (1998).

Figures 6 and 7 show a comparison of 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 polymers characterized by lower hydrophilicity (e.g. PVME and PCA) present higher values of the London interchange energy ϵ . This parameter, assumed to be temperature independent in its first derivation (Hino *et al.*, 1993), reflects polymer-solvent interactions; the lower its value, the higher the amount of water absorbed, as noted by Flory (1953). This general trend is indicated by the results presented here. When the volume fraction of water is plotted against ϵ 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 $\delta\epsilon_{ij}$ contribute to temperature-dependent parameter ω as shown in Eq. (5). At fixed T , the lower ω , the larger the amount of water absorbed.

While this lattice-model gives a reasonable correlation of the data, it is not predictive. If the model were off-lattice, it might be better because in that event, compressibility effects could be included.

Conclusions

New vapor – liquid equilibria data are reported for some concentrated binary aqueous solutions of linear polymers.

Data were reduced with Hino's theory that takes into account both London and specific solvent – solvent and solvent - solute interactions.

Hino's model was also applied to some literature data, even though they are 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 now available but only for correlation, not prediction.

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Figure captions:

Fig. 1: Experimental apparatus

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 water sorption

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

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

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, $M_w=1,000,000$, $T=93.5^\circ\text{C}$; PEO: A, $M_w=100,000$, $T=73.2^\circ\text{C}$; B, $M_w=4,000,000$, $T=94.5^\circ\text{C}$)

Fig. 7: Data reduction by Hino's lattice model: dots represent recently published experimental data (a, Hwang *et al.*, 1998; b, Kim *et al.*, 1998), while lines represent correlated data

Table 1: Polymer Properties:

Polymer	Supplier	lot #	Mw	T _g (°C)	T _m (°C)
PVP	Aldrich	03514 MT	10,000	86*	-
PVP	Polysciences, Inc.	446473	1,000,000	86*	-
PEO	Aldrich	02421 AT	100,000	-	65
PEO	Aldrich	00613 MP	4,000,000	-	65
PVA	Aldrich	00918 AG	124-186,000	85	230*
PVME	Aldrich	10819 JQ	60,000	-34	**
PEI	Aldrich	12922 PQ	750,000	-23.5	58.5
HEC	Polysciences, Inc.	96775	90-105,000	-	-

Mw = 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.

* from Molyneux (1983)

** amorphous in commercially available samples (Molyneux, 1983)

Table 2: Vapor-Liquid Equilibria for Aqueous Solutions of Linear Polymers.

System	Water Weight Fraction w_1	Water Activity a_1
Aqueous PVP (Mw 10,000) T=73.2°C $P_1^{\text{sat}}=35.76$ kPa	0.023	0.103
	0.042	0.218
	0.061	0.333
	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 (Mw 10,000) T=94.5°C $P_1^{\text{sat}}=82.94$ kPa	0.029	0.150
	0.044	0.243
	0.061	0.328
	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
(Mw 1,000,000)	0.038	0.218
T=93.5°C	0.060	0.322
$P_1^{\text{sat}}=79.93 \text{ kPa}$	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
(Mw 100,000)	0.018	0.341
T=73.2 °C	0.031	0.472
$P_1^{\text{sat}}=35.76 \text{ kPa}$	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
(Mw 4,000,000)	0.017	0.243
T=94.5 °C	0.025	0.328
$P_1^{\text{sat}}=82.94 \text{ kPa}$	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
(Mw 124-186,000)	0.016	0.218
T=93.5 °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
(Mw 90-105,000)	0.033	0.243
T=94.5 °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
	0.282	0.847
 Aqueous PEI	 0.019	 0.106
(Mw 750,000)	0.055	0.223
T=82.5 °C	0.093	0.336
$P_1^{\text{sat}}=52.34$ kPa	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
(Mw 60,000)	0.003	0.225
T=82.5 °C	0.004	0.340
$P_1^{\text{sat}}=52.34 \text{ kPa}$	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

Table3: Parameters in Hino's Lattice Theory for New Data.

Polyme r	Mw 10 ⁻³	T (°C)	r ₂	ε (kcal/mol)	δ _ε ₁₂ (kcal/mol)	ω (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	1,000	93.5	54,162	0.190	-5.372	-0.066
PEO	100	73.2	4,954	0.376	-4.983	1.240
PEO	4,000	94.5	196,751	0.310	-4.854	1.330
PVA	155	93.5	6,770	0.253	-4.892	1.210
HEC	97.5	94.5	5,275	0.161	-5.163	0.509
PEI	750	82.5	40,746	0.105	-5.330	-0.112
PVME	60	82.5	3,259	2.155	-5.798	-0.040

Table 4: Parameters in Hino's Lattice Theory for Recently-published Data (^aHwang *et al.*, 1998; ^bKim *et al.*, 1998).

PCA = polycarbonate; PAA = polyacrylic acid.

Polymer	r ₂	ε (kcal/mol)	δ _ε ₁₂ (kcal/mol)	ω (kcal/mol)
PVA ^a	4,045	0.221	-5.226	-0.805
PAA ^a	68,951	0.151	-5.213	-0.805
PCA ^a	1,324	1.748	-5.483	-0.682
PVA ^b	4,045	0.211	-5.224	-0.805

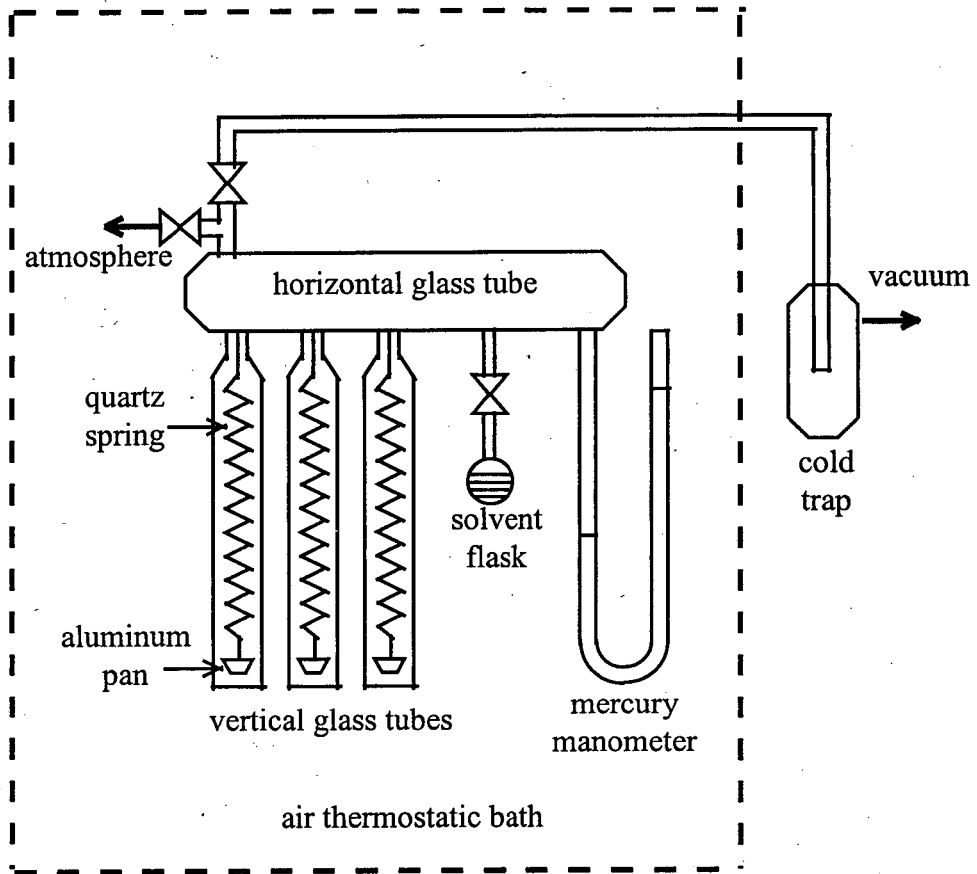


Fig. 1: Experimental apparatus

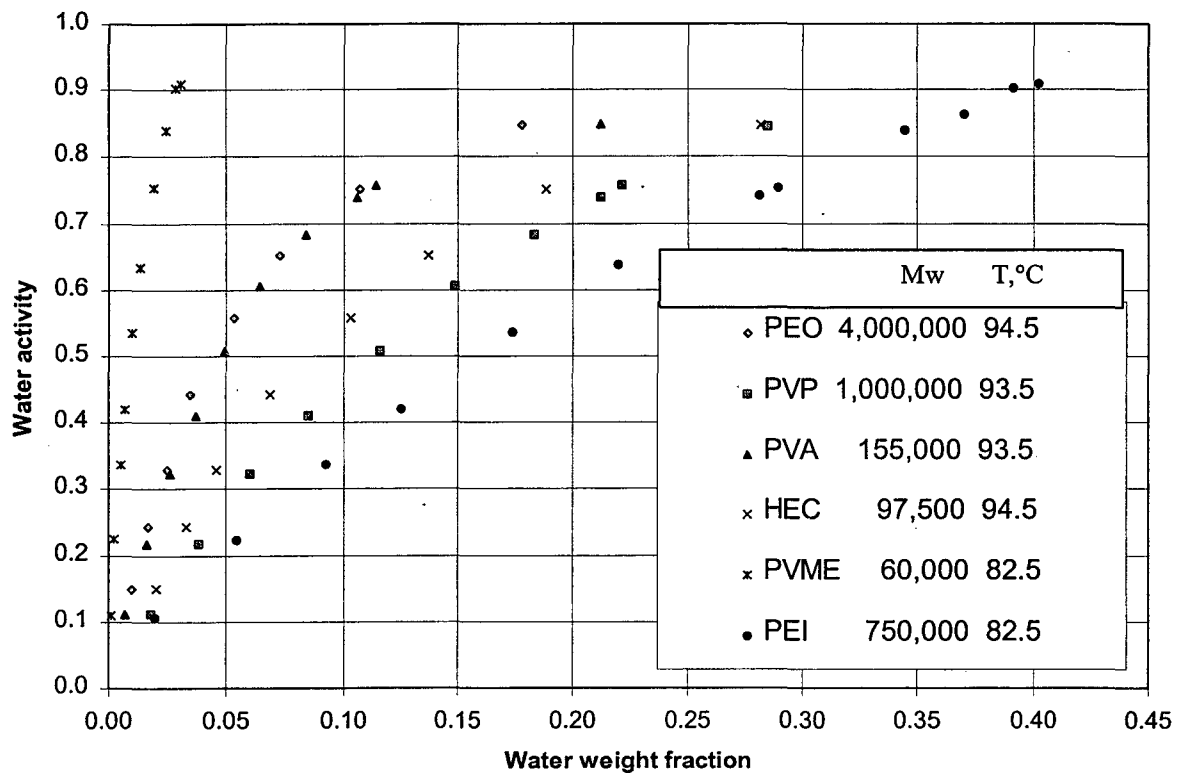


Fig. 2: Measured sorption at equal water activity: PEI, HEC, PVP (characterized by more electronegative polar sites) absorb more water than PEO and PVA, while PVME (whose structure is dominated by hydrophobic groups) presents a very low water sorption up to a water activity equal to 0.9

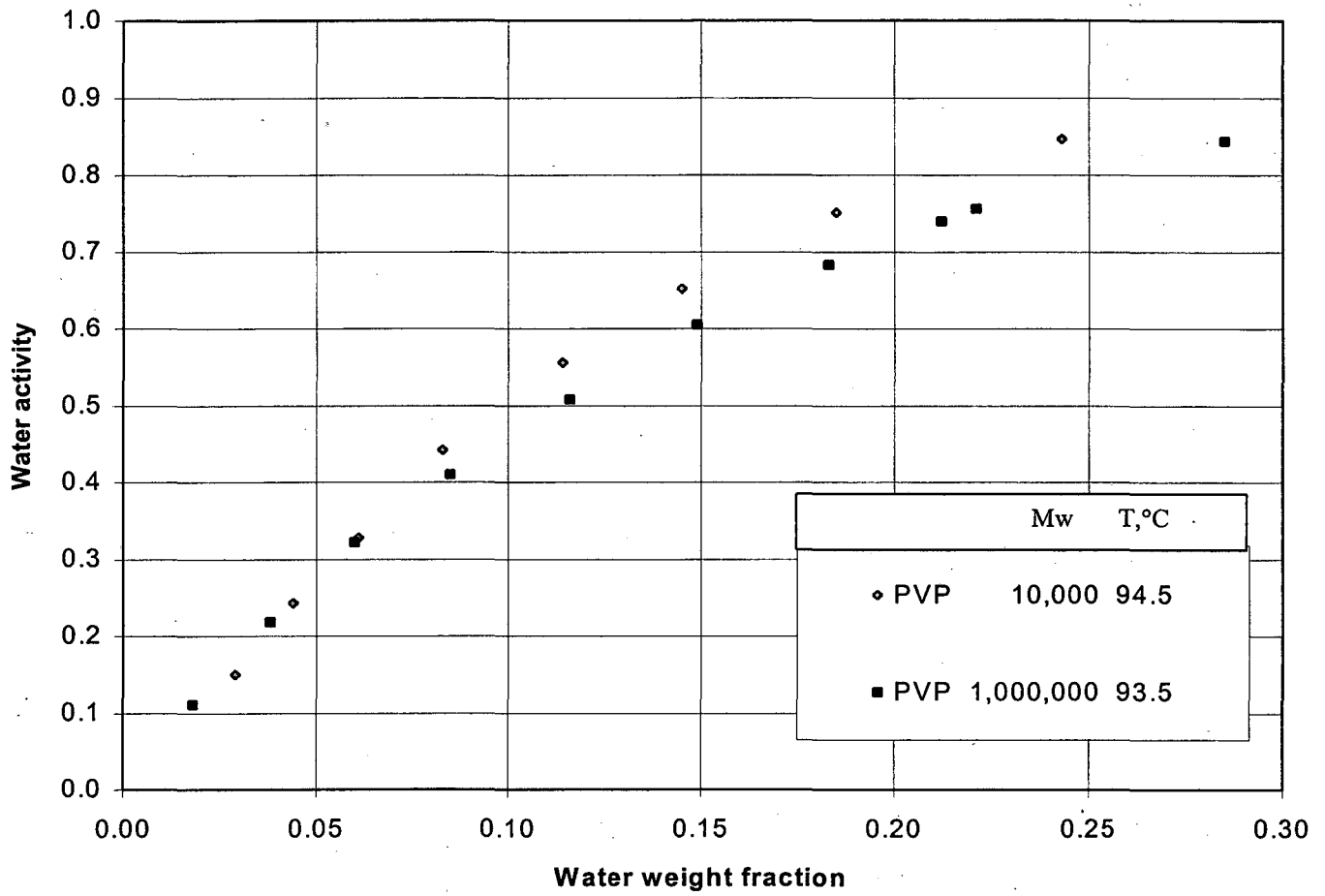


Fig. 3: Aqueous PVP characterized by different molecular weights: increasing M_w , at equal water activity, slightly increases water sorption

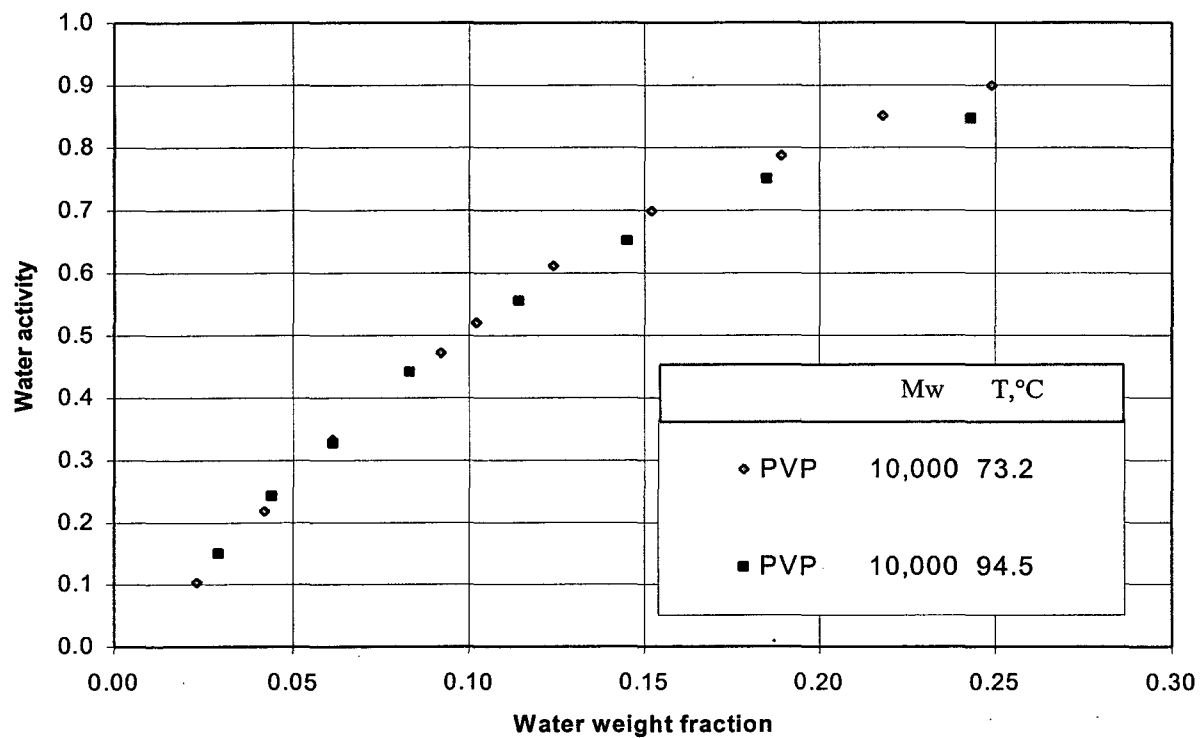


Fig. 4: Aqueous PVP, Mw=10,000: increasing the temperature may slightly increase water sorption but the observed increase is within the experimental uncertainty

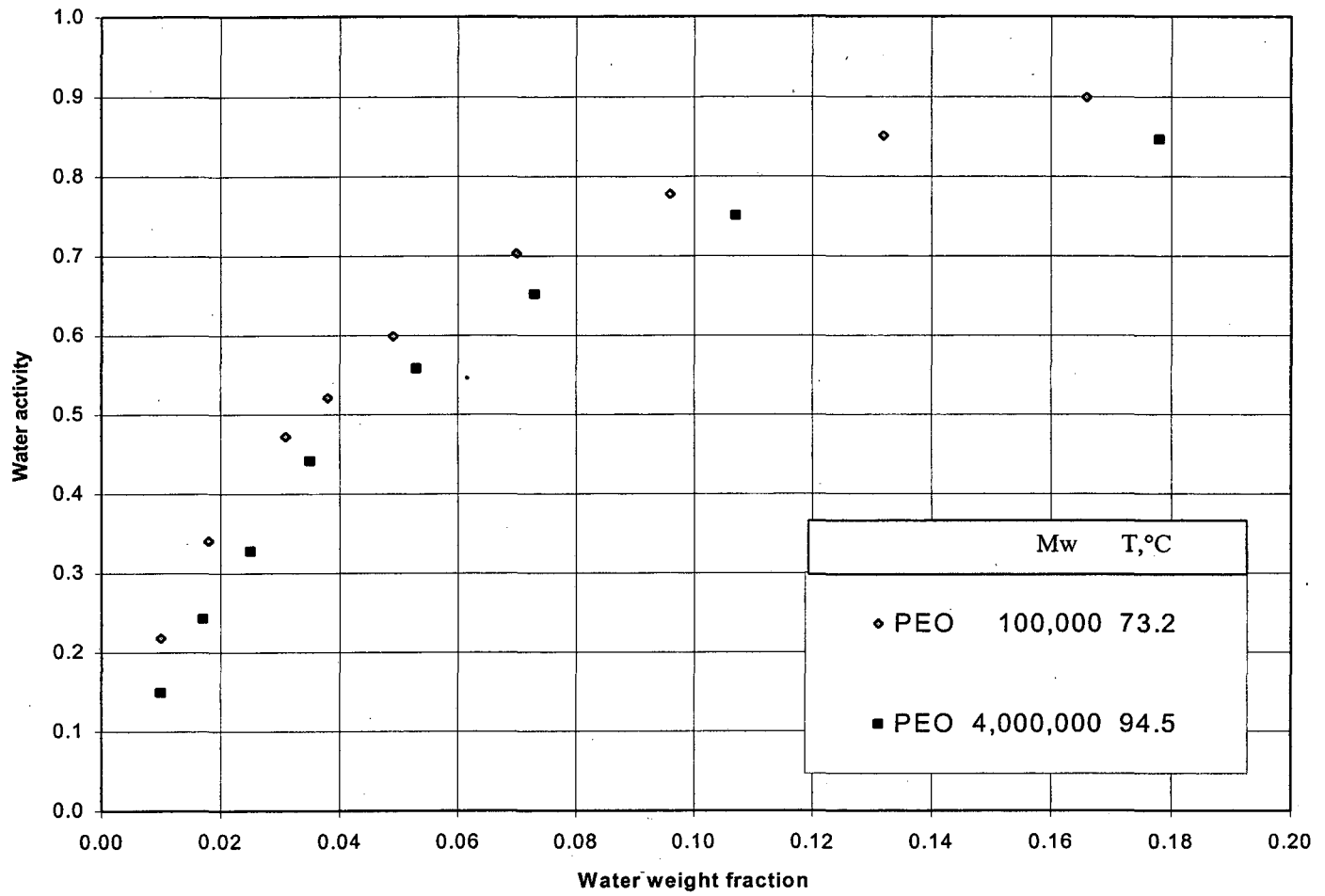


Fig. 5: Aqueous PEO: combined effect of molecular weight and temperature on sorption. increasing both parameters sensibly increases water sorption at equal water activity

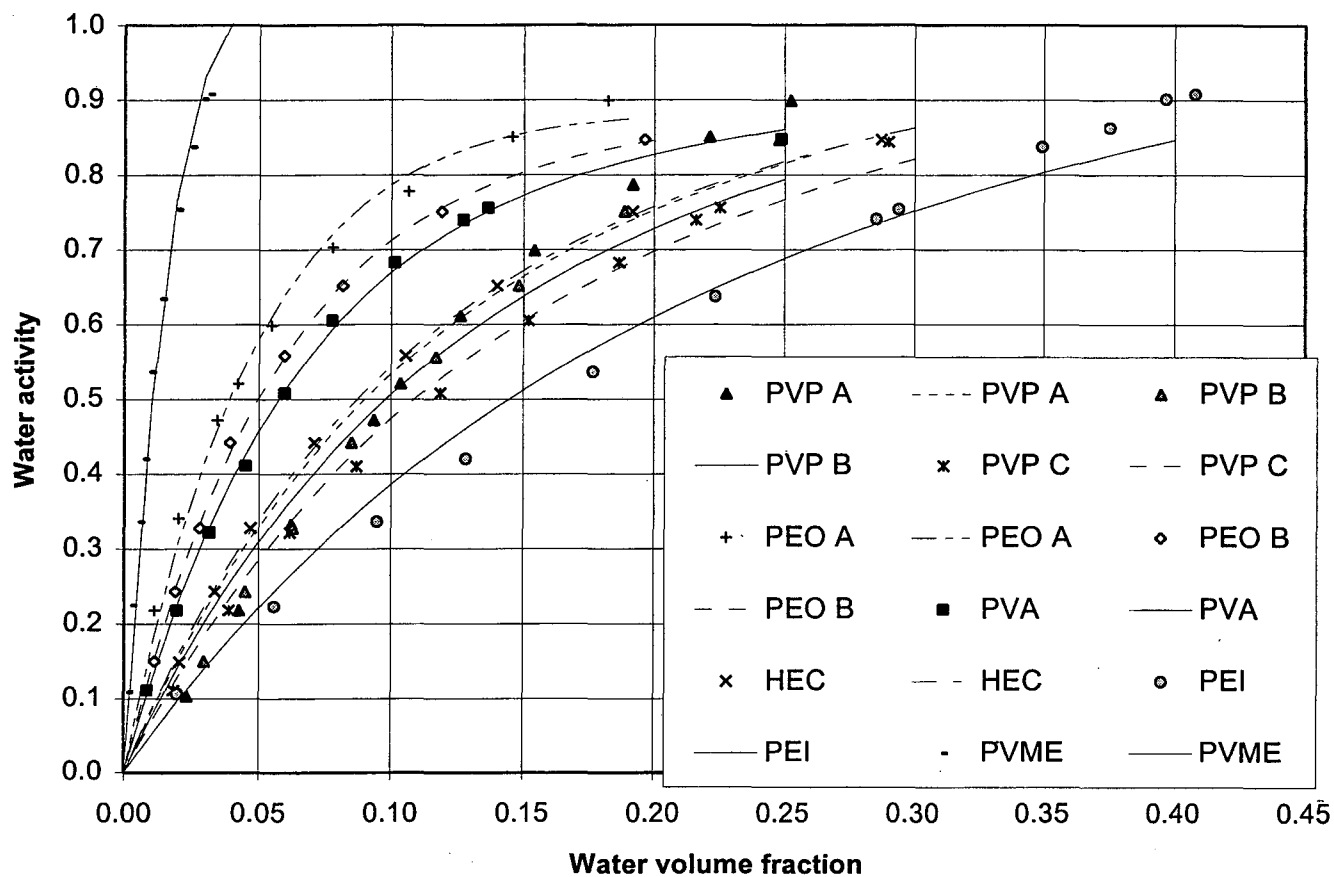


Fig. 6: Data reduction with Hino's lattice model: dots represent experimental data obtained in this work while lines represent correlated data (PVP: A, $M_w=10,000$, $T=73.2^\circ\text{C}$; B, $M_w=10,000$, $T=94.5^\circ\text{C}$; C, $M_w=1,000,000$, $T=93.5^\circ\text{C}$; PEO: A, $M_w=100,000$, $T=73.2^\circ\text{C}$; B, $M_w=4,000,000$, $T=94.5^\circ\text{C}$)

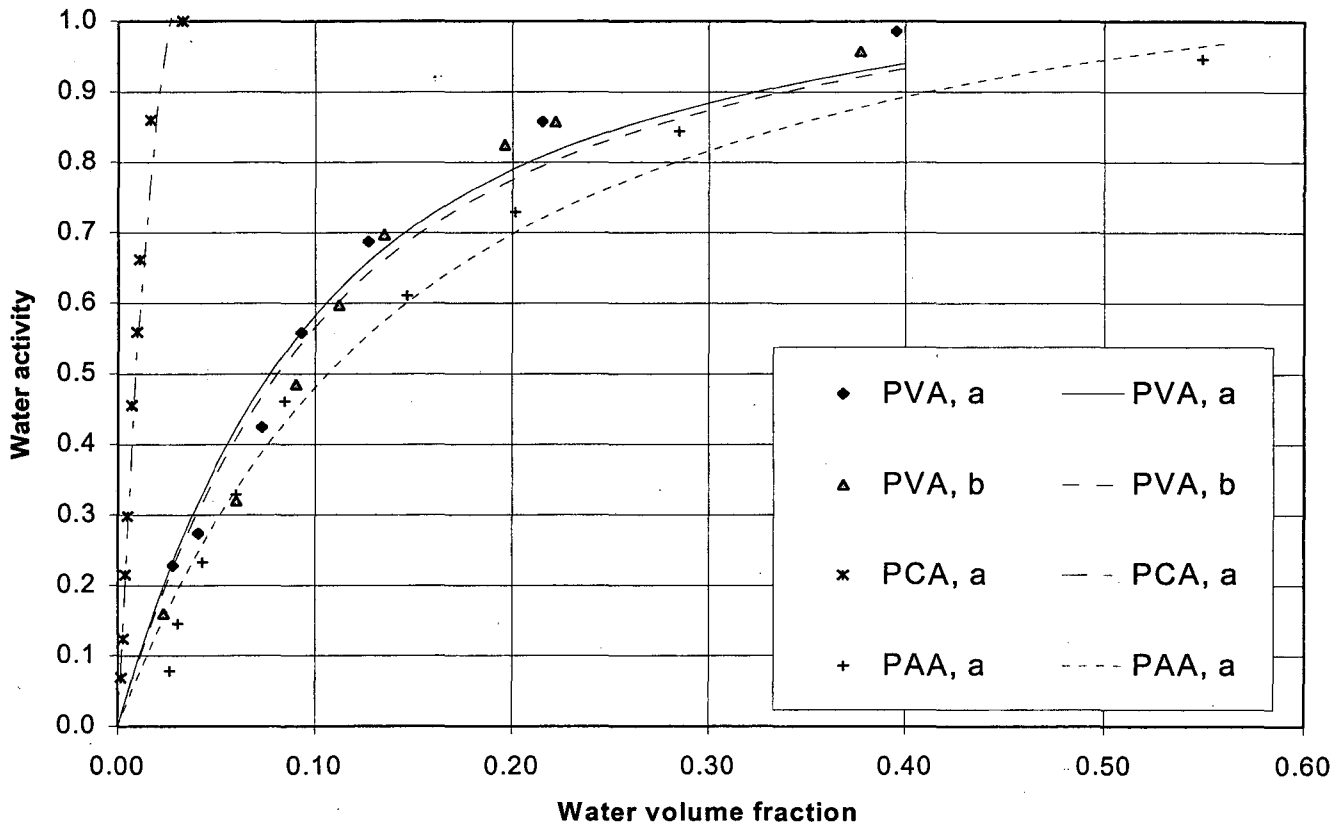


Fig. 7: Data reduction by Hino's lattice model: dots represent recently published experimental data (a, Hwang *et al.*, 1998; b, Kim *et al.*, 1998), while lines represent correlated data

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