

Partial Specific Volume and Thermal Expansion Coefficient of Poly(*N*-vinylimidazole)

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SYNOPSIS

The density of poly(*N*-vinylimidazole) dilute solutions in methanol, triethylene glycol, dimethyl sulfoxide, and *N,N*-dimethylformamide as well as in an aqueous neutral (with and without ionic strength) and acid solution have been measured at several temperatures. The specific volume of the polymer in bulk has been determined experimentally and theoretically, following the group additivity method, and both values were coincident. Partial specific volume and thermal expansion coefficient were found to be solvent-dependent. These results were interpreted in terms of the different types of solvation or the interaction of polymer-solvent. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The dilute solution behavior of water-soluble polymers often differs from that of the same polymers in organic solvents.¹ The partial specific volume is a particularly interesting property with regard to discerning the role of polymer-solvent interactions both in aqueous solution and in organic solvents of different characteristics. Besides, partial specific volume are required for the characterization of polymers through standard techniques.²⁻⁴ We have recently been interested in the buffering properties of poly(*N*-vinylimidazole) (PVI) hydrogels⁵ and this work presents some results on the characterization of linear PVI which could be extrapolated to the crosslinked polymer.

The partial specific volume is a property that depends on the molecular weight of the polymer when the molecular weight is low, but according to Schultz and Hoffman⁶ it becomes independent for molecular weights over 10^4 . The temperature² and the nature of the solvent also play an important role in determining the polymer specific volume.

In the case of neutral polymers such as PVI, which is soluble in water and has a hydrophilic group and

a hydrophobic skeleton, it is interesting to determine their partial specific volume in solvents of different natures to analyze the contribution of the different types of solvation. When the polymer is in an aqueous solution, it is reasonable to expect⁷ at least three types of solvation:

- (a) Hydrophilic solvation, due to the formation of the hydrogen bonds.
- (b) Hydrophobic solvation, due to the presence of the hydrocarbonated chain.
- (c) Ionic solvation, which takes place when the imidazole becomes protonated.

In organic solvents, the possible polymer-solvent interactions are the formation of hydrogen bonds and the dipolar interactions and different values of the partial specific volume must be expected in hydroxylated and nonhydroxylated solvents.^{8,9}

In this work, the partial specific volume of PVI has been measured in organic solvents such as methanol (MEOH), triethylene glycol (TEG), dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF) as well as in an aqueous neutral (with and without ionic strength) and an acid solution. Likewise, the specific volume of the polymer in bulk has been determined experimentally and theoretically, following the group additivity method.^{10,11}

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EXPERIMENTAL

Poly(*N*-vinylimidazole) was synthesized by radical polymerization from *N*-vinylimidazole (from Aldrich) in benzene (from Carlo Erba) solution at 60°C during 24 h.¹² AIBN in the concentration of $4, 7 \cdot 10^{-3} M$ was used as an initiator. The polymer was precipitated in the water-acetone system at 25°C and, later, it was viscometrically characterized. The following viscometric¹³ equation:

$$[\eta](dL/g) = 3.74 \cdot 10^{-4} M^{0.65}$$

was employed for methanol at 25°C and the viscosity-average molecular weight obtained was $1.0 \cdot 10^5$.

The solvents used were supplied by Carlo Erba (quality RPE) and were previously dried with molecular sieves (from Merck) of 4 Å. Water was distilled and purified by a MilliQ system from Millipore.

Density measurements of the polymer solutions and solvents were made with a vibrating-tube digital densimeter (ANTON PAAR DMA 58). Distilled water and air were employed for calibration. Polymer solutions were prepared by weighting. The range of concentrations covered was $w = 0-0.012$, where w represents the polymer weight fraction. In all cases, the samples were maintained in a thermostatic bath during 24 h at the measuring temperature and, later on, they were weighted to determine w . The measuring temperature was regulated within 0.01°C. The density of the polymer in bulk was determined in a glass picnometer using acetone as the nonsolvent.

RESULTS AND DISCUSSION

The partial specific volume of the polymer was calculated through density (ρ) measurements on poly-

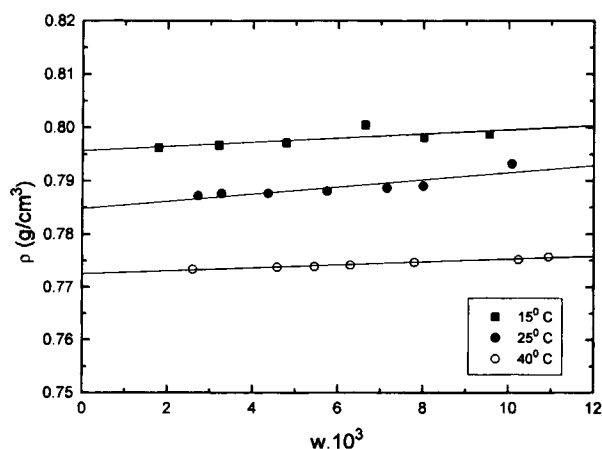


Figure 1 Density of PVI dilute solutions in MEOH as a function of the polymer weight fraction at different temperatures.

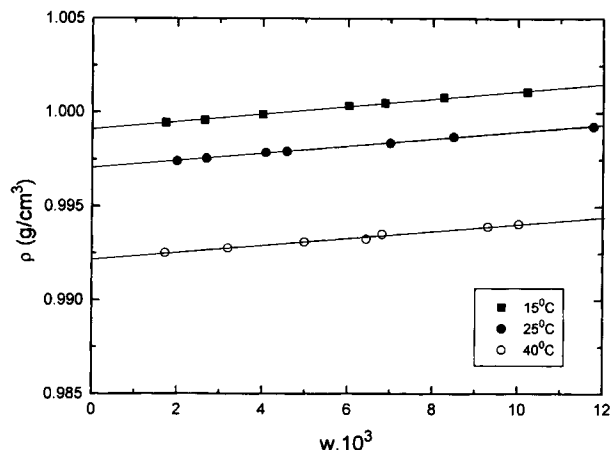


Figure 2 Density of PVI aqueous dilute solutions as a function of the polymer weight fraction at different temperatures.

mer solutions as a function of the concentration of solute w , using the expression²

$$v_2^0 = \rho_1^{-1} (1 - \rho_1^{-1} (\delta\rho/\delta w)^0)$$

Subindex 1 refers to the pure solvent; subindex 2, to the polymer; and superindex 0, to the limit value when $w \rightarrow 0$.

Figures 1-3 show the dependence of the density of PVI solutions on polymer concentration in three different solvents and at three different temperatures. The variation of the density with w in the range of low concentrations covered in our measurements is practically lineal and, therefore, $(\delta\rho/\delta w)^0$ represents just the slope of the straight lines plotted in Figures 1-3. The linear dependence is also indicative of the absence of conformational changes or aggregations which take place in similar polymers¹⁴ in aqueous solutions.

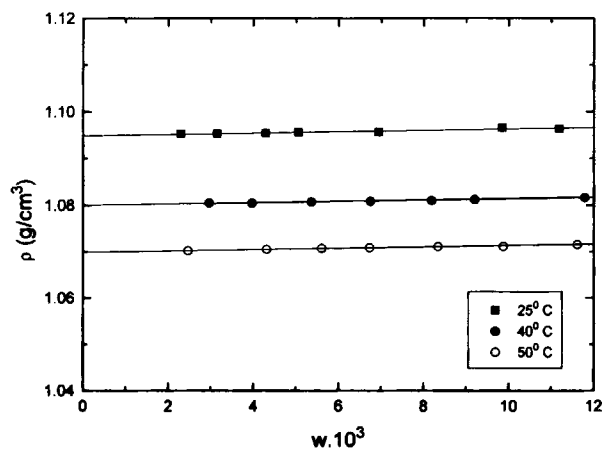


Figure 3 Density of PVI dilute solutions in DMSO as a function of the polymer weight fraction at different temperatures.

Table I Partial Specific Volume of PVI in Different Solvents at 25°C and Characteristics of These Solvents at the Same Temperature: Dielectric Constant (ϵ), Density (ρ), and Dipole Moment (μ)

Solvent	v_2^0 (cm ³ /g)	ρ (g/cm ³)	ϵ	μ (D)
Water (H ₂ SO ₄ 10 ⁻⁴ M)	0.811	0.99877	—	—
Water (NaCl 0.77M)	0.844	1.02742	—	—
Water	0.812	0.99704	78.4	1.82
DMSO	0.812	1.09497	46.4	4.06
DMF	0.792	0.94346	36.7	3.24
MEOH	0.763	0.78626	32.7	2.87
TEG	0.745	1.11805	23.7	5.58
Bulk theoretical	0.86	—	—	—
Bulk experimental	0.87	—	—	—

Table I summarizes the v_2^0 determined in different solvents, as well as the v_2 of the polymer in bulk experimentally determined and that theoretically estimated through the group additivity method.¹⁰ The agreement between the calculated and experimental v_2 values is excellent, as previously observed for other systems.^{3,10} The v_2^0 values in solution are smaller than v_2 in bulk and are solvent-dependent. The decrease correlates qualitatively with the dielectric constant of the solvent and seems to be independent of solvent polarity and density (Table I).

The largest decrease of v_2^0 corresponds to MEOH and TEG, these solvents having the strongest interaction with PVI since they are able to form hydrogen bonds, while the organic solvents that have just dipolar interactions (DMSO and DMF) diminish the specific volume of the polymer less. Within those two groups of solvents, v_2^0 changes similar to the solvent dielectric constant (Table I).

Water has two types of predominant interactions with nonprotonated PVI: the formation of hydrogen bonds, which would tend to diminish the value of v_2^0 as in the case of MEOH and TEG, and the hydrophobic interactions, which take out the solvent and increase the value of the partial volume, approaching the value obtained in the bulk.

The value that results for v_2^0 in water is intermediate between the one obtained in hydroxylic solvents and the one obtained in bulk. This is a quite general result for polymers soluble in water.^{4,15-18} Taking into account the large dielectric constant of water, it should be expected that v_2^0 of PVI in aqueous solution would be large, close to the v_2 value in the bulk, even without considering the influence of hydrophobic interactions. That is not the case: there is about a 7% difference between those two values, so that we can conclude that the formation

of hydrogen bonds with water has a particularly strong influence on v_2^0 and that hydrophobic interactions do not play an important role in the solvation of the PVI in pure water. In similar polymers, e.g., poly(*N*-vinylpyrrolidone), the v_2^0 in water is much larger (12%) than in methanol (0.820 [Refs. 17 and 18] and 0.730 [Ref. 19] cm³ g⁻¹, respectively), thus evidencing a larger contribution of the hydrophobic interactions than in PVI aqueous solution.

In pure water and with acids (H₂SO₄, HCl), the imidazole protonates partially and, as a result, a new type of solvation appears: the ionic solvation. In pure water, it is practically worthless, as in these conditions, less than one of 1000 of the heterocycles are protonated. Nevertheless, in measurements carried out with H₂SO₄ 10⁻⁴ M, keeping constant the concentration of the acid while changing that of the polymer, between 1 and 10% of the heterocycles are protonated. This partial protonation is reflected in a

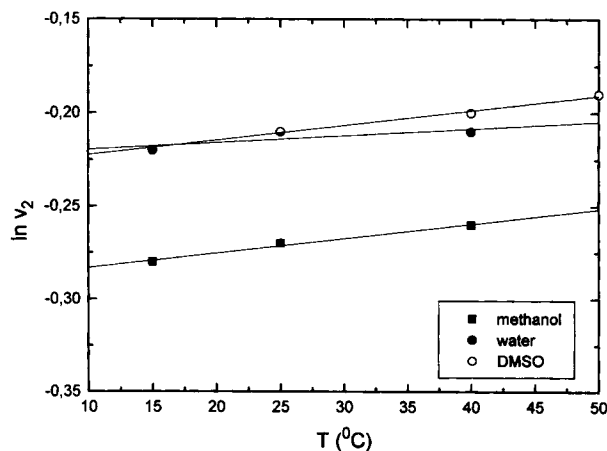


Figure 4 Partial specific volume of PVI as a function of temperature in several solvents.

Table II Thermal Expansion Coefficient of PVI in Several Solvents

Solvent	$\alpha/10^{-4}$ K
Water	3.7
Methanol	7.9
DMSO	7.9

negligible change of the specific volume, which tends to increase (Table I). The creation of charges in a polymer chain used to produce a decrease in volume by electrostriction (see Ref. 4 and references therein), but it seems that ionic effects can be discarded in PVI aqueous solution.

In the presence of ionic strength, a small increase in the specific volume is observable (4%). This result is opposite what is observed for other similar polymers: e.g., for poly(*N*-vinylpyrrolidone), v_2^0 decreases 6% in a 0.2M NaCl aqueous solution with respect to pure water,^{18,20} and for polyacrylamide, v_2^0 decreases 11% in 0.2M NaCl aqueous solution with respect to pure water.^{21,22} It seems that the high ionic strength produces a salting-out effect on PVI, increasing polymer-polymer interactions with respect to polymer-solvent ones, i.e., increasing hydrophobic interactions and, consequently, v_2^0 .

The partial specific volume of a polymer generally shows a gradual increase upon increasing temperature.³ The partial specific volume of the PVI was measured at three different temperatures in MEOH, water, and DMSO (see Fig. 4) and the thermal expansion coefficient was calculated using the equation

$$\alpha = \frac{d \ln v_2^0}{dT}$$

Table II compares thermal expansion coefficients in the three solvents. They are relatively large values but do not depend much on the nature of the solvent. Since hydrophobic interactions²³ have the opposite temperature dependence to that of dipole-dipole interactions or the formation of hydrogen bonds and since there is not a small difference of α between water and the other two solvents, it can be concluded from this and previous results (i) that the most important contribution to solvation of PVI in aqueous solution is the formation of hydrogen bonds, (ii) that hydrophobic interactions play a minor role except in aqueous solutions of high ionic strength, and (iii) that protonation of the heterocycle seems to

have a negligible influence on the specific volume of PVI.

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REFERENCES

1. P. Molyneux, *Water Soluble Synthetic Polymers*, CRC Press, Boca Raton, FL, 1983.
2. M. R. Gómez-Antón, A. Horta, and I. Hernández-Fuentes, *Polym. Commun.*, **27**, 5 (1986).
3. M. R. Gómez-Antón and A. Horta, *J. Appl. Polym. Sci.*, **35**, 273 (1988).
4. I. Hernández-Fuentes, A. Horta, L. Gargallo, C. Abradelo, M. Yazdani-Pedram, and D. Radic, *J. Phys. Chem.*, **92**, 2974 (1988).
5. M. J. Molina, M. R. Gómez-Antón, E. Morales, and I. F. Piérola, U.S. Pat. (Nov. 9, 1994).
6. C. V. Schulz and M. Hoffman, *Makromol. Chem.*, **23**, 220 (1957).
7. M. Satoh, E. Yoda, and J. Komiyama, *Macromolecules*, **24**, 1123 (1991).
8. S. Terasawa, H. Itzuki, and S. Arakawa, *J. Phys. Chem.*, **79**, 2345 (1975).
9. E. J. King, *J. Phys. Chem.*, **73**, 1220 (1969).
10. D. W. van Krevelen, *Properties of Polymers*, 2nd ed., Elsevier, Amsterdam, 1976.
11. R. Zana, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 121 (1980).
12. J. S. Tan and A. Sochor, *Macromolecules*, **14**, 1700 (1981).
13. M. Tricot, G. Mertens, P. Collette, and V. Desreux, *Bull. Soc. R. Sci. Liege*, **10**, 502 (1974).
14. N. J. Crowther and D. Eagland, *J. Chem. Soc. Faraday Trans. 1*, **82**, 2791 (1986).
15. J. Horsky, V. Petrus, and M. Bohdanecky, *Makromol. Chem.*, **187**, 2621 (1986).
16. J. Carlfors and R. Rymden, *Eur. Polym. J.*, **18**, 933 (1982).
17. J. Brandrup and E. M. Immergut, *Polymer Handbook*, Wiley-Interscience, New York, 1975.
18. G. R. Andersson, *Ark. Kemi*, **20**, 513 (1963).
19. H. G. Elias, *Makromol. Chem.*, **50**, 1 (1961).
20. J. Goldfarb and S. Rodriguez, *Makromol. Chem.*, **116**, 96 (1968).
21. W. Scholtan, *Makromol. Chem.*, **14**, 169 (1954).
22. P. Munk, T. M. Aminabhavi, P. Williams, D. Hoffmann, and M. Chmelir, *Macromolecules*, **13**, 871 (1980).
23. Ch. Tandford, *The Hydrophobic Effect*, 2nd ed., Wiley-Interscience, New York, 1980.

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