Volumetric Study of Aqueous Solutions of Poly(ethylene glycol) from 283.15 to 313.15 K and at 0.1 MPa

Raphael da C. Cruz,[1] Rosana J. Martins,[1,2] Márcio J. E. de M. Cardoso,[1] Oswaldo E. Barcia[1]

[1]*Laboratório de Físico-Química de Líquidos e Eletroquímica, Departamento de Físico-Química, Instituto de Química, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco A, Sala 411, Cidade Universitária, CEP 21949-900, Rio de Janeiro, RJ, Brazil*
[2]*Departamento de Físico-Química, Instituto de Química, Universidade Federal Fluminense, Outeiro de São João Batista s/n, CEP 24020-150, Niterói, RJ, Brazil*

ABSTRACT: Density measurements of binary aqueous solutions of poly(ethylene glycol), with a nominal average molecular weight of 6000, were used to determine the specific volumes of the solutions with solute-to-solvent mass ratios (mass of the solute/mass of the solvent) of 0.0483–0.5493 and at seven different temperatures (283.15, 285.15, 293.15, 298.15, 303.15, 308.15, and 313.15 K). The difference between the specific volume of a solution and the specific volume of a pure solvent, at a given temperature, was expanded by a virial-type equation, in terms of the solute concentration. The first-order coefficient was the partial specific volume of a solute at infinite dilution. The higher order coefficients corresponded to the contribution of pairs, triplets, and higher order solute aggregates according to the constant-pressure theory of solutions. The functional dependence of the virial coefficients on the temperature was examined in terms of solute–solute and solute–solvent interactions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2685–2689, 2004

Key words: density; solution properties; thermodynamics

INTRODUCTION

Poly(ethylene glycol) (PEG) is a linear polymer that is soluble in water and in a large number of organic solvents, and it presents lower and upper critical solution temperatures.[1–4] Because of its lubricity, good stability, and low toxicity, it is used in lubricants, electronics, cosmetics, and pharmaceuticals. Another important use of PEG, mixed with other polymers or salts, is as a biomolecular partitioning medium.[5] Because PEG is compatible with biopolymers, it can replace them, providing insight into their behavior and biological functions.[6] In addition, its ability to inhibit protein adsorption makes PEG micelles, PEG gels, and other aggregates of PEG good candidates for drug delivery.[7,8]

In contrast to normal polymer behavior, in which the solubility increases with the temperature, the solubility of PEG decreases, and a phase transition occurs above a critical temperature, which is dependent on the molecular weight.[1–4]

Some works on the volumetric properties of PEG can be found in the literature. Kirinčič and Klofutar[9] studied several PEGs, with different nominal molecular weights, at 298.15 K. Wurzburger et al.[10] studied the volumetric properties of aqueous solutions of some small-chain polyols, between 273.65 and 298.15 K, and some alcohols and diols, at 298.15 K. Tawfik and Teja[11] measured the density of aqueous solutions of monoethylene, diethylene, triethylene, tetraethylene, and pentaethylene glycol, between 398 and 423 K. Müller and Rasmussen[12] also measured the density and calculated the excess volume of aqueous solutions of monoethylene, diethylene, triethylene, and tetraethylene glycol and PEG with an average molecular weight of 400 at 298.15, 308.15, 318.15, and 328.15 K. They also measured the density of aqueous solutions of PEG 2000 and 10000 at 328.15 K. Eliassi et al.[13] measured the density of aqueous solutions of PEG 400, PEG 4000, and PEG 6000 at six different temperatures. Zafarani-Moattar and Salabat[14] studied the volumetric properties of aqueous electrolytic solutions of PEG 1000 and PEG

6000 with several salts at 298.15, 308.15, and 318.15 K. Finally, Comelli et al.[15] measured the density and other properties of binary mixtures of PEG 200 and PEG 400 in dimethoxymethane or in 1,2-dimethoxyethane at 298.15 K.

However, systematic studies of the functional temperature dependence of the parameters in the virial expansion of volume for PEG in aqueous solutions have not been reported in the literature so far. Thus, the solute–solute and solute–solvent interactions have not been studied in terms of this temperature dependence.

In this work, we studied the volumetric properties of aqueous solutions of PEG with a nominal average molecular weight of 6000 (PEG 6000) at seven different temperatures (283.15, 285.15, 293.15, 298.15, 303.15, 308.15, and 313.15 K) with solute-to-solvent mass ratios (w) of 0.0483–0.5493.

The organization of the rest of this article is as follows. In the next section, details of the experimental procedure are given. The Theory section reviews the basic theory related to the interpretation of the experimental data. In the Results and Discussion section, the results are presented and discussed. Finally, in the last section, our conclusions are summarized.

EXPERIMENTAL

Materials

PEG 6000 was supplied from Isofar (Rio de Janeiro, Brazil), was used without further purification, and was stored in a vacuum desiccator over silica gel. The solutions were prepared by mass with a digital balance (JK-180, Chyo YMC, Kyoto, Japan), with a precision of ±0.01 mg, in airtight stopped bottles. Double-distilled degassed water was used in the preparation of all solutions. To avoid evaporation and solvent contamination, we used the solutions immediately after preparation. The estimated error in the mass fraction was less than 1×10^{-4}.

Density measurements

The density measurements were carried out in an Anton Paar DMA 4500 digital density meter (Graz, Austria) with an uncertainty of 5×10^{-5} g/cm^3. The cell temperature of the density meter was controlled within ±0.03 K. For all compositions, the density was measured at least twice. Triple-distilled degassed water and dry air were used as calibrating substances.

THEORY

With the so-called constant-pressure solution theory,[16–18] it is possible to express the volume of a solution by a virial-type expansion in terms of w:

$$v = v^0_{\text{solvent}} + \bar{v}^\infty_{\text{solute}} w + v_2 w^2 + v_3 w^3 + v_4 w^4 + \cdots \quad (1)$$

where v is the specific volume of a solution per unit of mass of the solvent; v^0_{solvent}, a zero-order term, is the volume of a pure solvent per unit of mass of a solvent ($v^0_{\text{solvent}} = 1/\rho_{\text{solvent}}$, where ρ_{solvent} is the density of a pure solvent at the temperature and pressure of the solution);[19] $\bar{v}^\infty_{\text{solute}}$, a first-order term, is the partial specific volume of a solute at infinite dilution; and v_2, v_3, and v_4, the second-, third-, and fourth-order terms, represent the contributions of a pair, triplet, and quartet of solute molecules, respectively, to the specific excess volume of a solution (v^E).

For a solution with one mass unit of a solvent, it is possible to write the following expression:[9,10]

$$v = \frac{1 + w}{\rho} \quad (2)$$

where ρ is the density of the solution.

v^E is defined as follows:[10]

$$v^E = v - v^0_{\text{solvent}} - \bar{v}^\infty_{\text{solute}} w = v_2 w^2 + v_3 w^3 + v_4 w^4 + \cdots \quad (3)$$

It is also possible to rewrite eq. (1) as follows:

$$v - v^0_{\text{solvent}} = \bar{v}^\infty_{\text{solute}} w + v_2 w^2 + v_3 w^3 + v_4 w^4 + \cdots \quad (4)$$

Equation (4) has been used to fit the experimental data to obtain the adjusted virial coefficients by means of a SIMPLEX algorithm.[20,21]

RESULTS AND DISCUSSION

The measured ρ data and calculated v values, at different temperatures, are presented as functions of w in Table I. The values, at 298.15 K, are in good agreement with those found in the literature.[9,14] The ρ values of the solutions decrease with the temperature for all concentrations.

For all the studied systems, the virial-type expansion of v [eq. (1)] up to second-order terms is sufficient to describe the experimental data adequately, as can be seen in Figure 1.

Table II reports the adjusted values of $\bar{v}^\infty_{\text{solute}}$ and v_2, at different temperatures. They agree with those obtained by Kirinčič and Klofutar[9] at 298.15 K.

At infinite dilution, it can be considered that only the solute–solvent interactions are significant. From adjusted $\bar{v}^\infty_{\text{solute}}$ values, we can infer the solute behavior to be structure-making or structure-breaking of the solvent structure.[10] It is possible to interpret $\bar{v}^\infty_{\text{solute}}$ in terms of two contributions.[10,22] The first contribution is due to the intrinsic volume of the nonhydrated solute molecule, and the second one considers the

TABLE I
w, ρ, and v of Aqueous Solutions of PEG 6000 at 283.15, 288.15, 293.15, 298.15, 303.15, 308.15, and 313.15 K

w	ρ (g cm^{-3})	v (cm^3 g^{-1})	w	ρ (g cm^{-3})	v (cm^3 g^{-1})
283.15 K					
0.0483	1.00794	1.040087	303.15 K		
0.1009	1.01633	1.083218	0.0483	1.00319	1.045011
0.1494	1.02352	1.122963	0.1009	1.01084	1.089101
0.1976	1.03010	1.162645	0.1494	1.01736	1.129763
0.2500	1.03700	1.205420	0.1976	1.02330	1.170371
0.3018	1.04312	1.247993	0.2500	1.02952	1.214178
0.3412	1.04766	1.280165	0.3018	1.03500	1.257784
0.3981	1.05381	1.326674	0.3412	1.03905	1.290773
0.4525	1.05921	1.371288	0.3981	1.04455	1.338435
0.5031	1.06387	1.412865	0.4525	1.04936	1.384160
0.5493	1.06799	1.450710	0.5031	1.05353	1.426731
288.15 K			0.5493	1.05718	1.465544
0.0483	1.00714	1.040913	308.15 K		
0.1009	1.01532	1.084295	0.0483	1.00144	1.046838
0.1494	1.02231	1.124292	0.1009	1.00894	1.091152
0.1976	1.02872	1.164204	0.1494	1.01533	1.132022
0.2500	1.03542	1.207259	0.1976	1.02115	1.172835
0.3018	1.04135	1.250114	0.2500	1.02723	1.216885
0.3412	1.04576	1.282491	0.3018	1.03257	1.260744
0.3981	1.05173	1.329297	0.3412	1.03653	1.293911
0.4525	1.05696	1.374207	0.3981	1.04189	1.341852
0.5031	1.06150	1.416019	0.4525	1.04657	1.387850
0.5493	1.06548	1.454127	0.5031	1.05064	1.430656
293.15 K			0.5493	1.05419	1.469700
0.0483	1.00606	1.042030	313.15 K		
0.1009	1.01405	1.085653	0.0483	0.99949	1.048880
0.1494	1.02087	1.125878	0.1009	1.00679	1.093482
0.1976	1.02710	1.166041	0.1494	1.01312	1.134491
0.2500	1.03363	1.209350	0.1976	1.01882	1.175517
0.3018	1.03940	1.252460	0.2500	1.02477	1.219806
0.3412	1.04368	1.285047	0.3018	1.02999	1.269302
0.3981	1.04948	1.332147	0.3412	1.03387	1.297240
0.4525	1.05455	1.377348	0.3981	1.03911	1.345442
0.5031	1.05897	1.419402	0.4525	1.04368	1.391693
0.5493	1.06281	1.457780	0.5031	1.04764	1.434753
298.15 K			0.5493	1.05108	1.474049
0.0483	1.00474	1.043399			
0.1009	1.01252	1.087294			
0.1494	1.01921	1.127712			
0.1976	1.02530	1.168088			
0.2500	1.03166	1.211659			
0.3018	1.03727	1.255031			
0.3412	1.04144	1.287811			
0.3981	1.04708	1.335201			
0.4525	1.05201	1.380673			
0.5031	1.05631	1.422977			
0.5493	1.06006	1.461562			

increase in the volume of the bare solute molecule due to the hydration process. This difference is explained by a reordering of the water structure from the bulk to cospheres of hydration, which takes into account the capability of the solute to make or destroy the ordering of water. Figure 2 shows the $\bar{v}_{\text{solute}}^{\infty}$ values versus the temperature. The values of $\bar{v}_{\text{solute}}^{\infty}$ increase with temperature. Thus, it is possible to conclude that the hydration cospheres grow with temperature. This behavior agrees with the observations reported for small-chain alcohols and glycol derivatives.[23]

In Figure 3, v_2 is presented against the temperature. It has been proposed that v_2 varies linearly with the volume change (which increases with increasing temperature) of the hydrated molecules with the solute concentration.[24–27] This is a result of the overlapping of the hydration cospheres of a pair or is due to the redistribution between a solute pair when this overlap does not take place. In contrast to the $\bar{v}_{\text{solute}}^{\infty}$ values, the v_2 results can provide information about solute–solute and solute–solvent interactions.
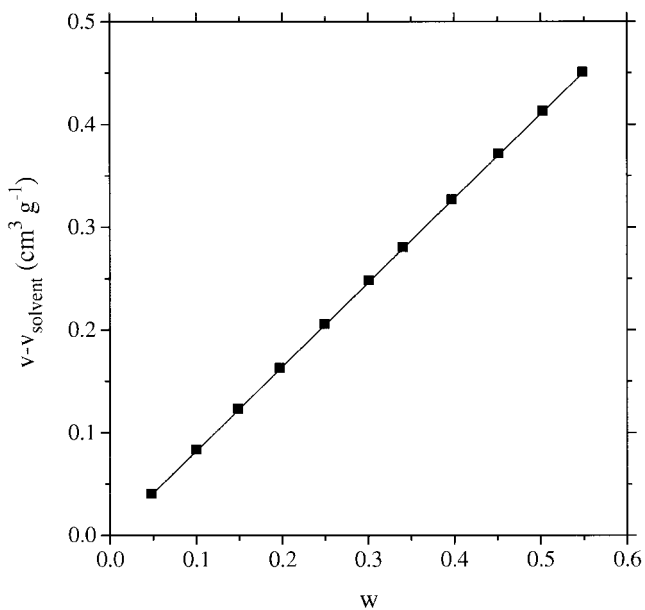
Figure 1 Concentration dependence of $v - v_{\text{solvent}}$: (■) experimental data and (—) calculated values.

To discuss our volumetric results for PEG 6000 in water, we applied the solvation model,[9,10,28] which correlates the v_2 parameter with the volume change of the hydration solute cospheres. The results of v_2 are not dependent on the nature of the sociative phenomena.[10] Therefore, the v_2 values (or, in stricter terms, the sign of v_2) indicate the nature of the solute–solvent interaction, that is, if the solute is structure-making or structure-breaking. If all the results obtained for the investigated solutions are negative until a determined temperature value, becoming positive over this value, it is correct to infer that PEG 6000 presents a structure-making effect on the water structure up to temperatures near 303.7 K. Above this temperature, PEG 6000 has a structure-breaking effect on the water structure.

CONCLUSIONS

In this work, the volumetric properties of aqueous solutions of PEG 6000 were systematically studied as a function of temperature. $\bar{v}^{\infty}_{\text{solute}}$ was determined, and the hydration process of solute molecules was found
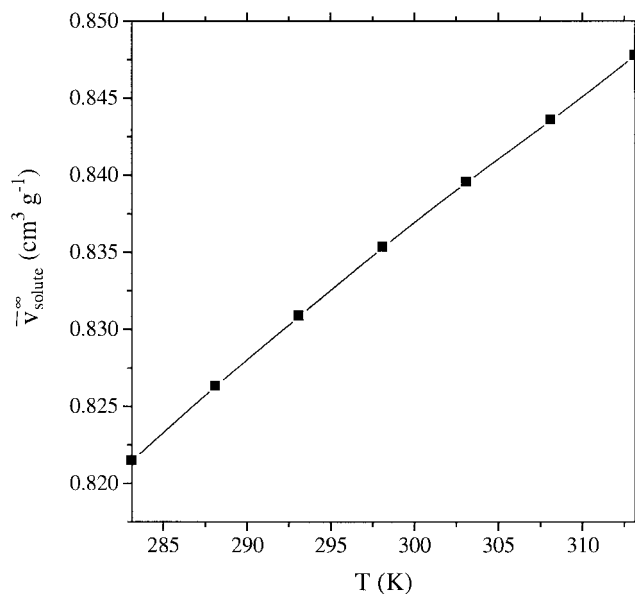

Figure 2 Temperature dependence of $\bar{v}^{\infty}_{\text{solute}}$: (■) experimental data and (—) calculated values.

to be deeply affected by the temperature. The solute hydration cosphere increased with the temperature. The v_2 values were also determined. It was found that PEG 6000 had a structure-making effect and a structure-breaking effect on the water structure, these effects depending on the solution temperature.

NOMENCLATURE

v specific volume of a solution ($\text{cm}^3\ \text{g}^{-1}$)

v^0_{solvent} volume of a pure solvent per unit of mass of a solvent ($\text{cm}^3\ \text{g}^{-1}$)

TABLE II
Temperature Dependence of $\bar{v}^{\infty}_{\text{solute}}$ and v_2

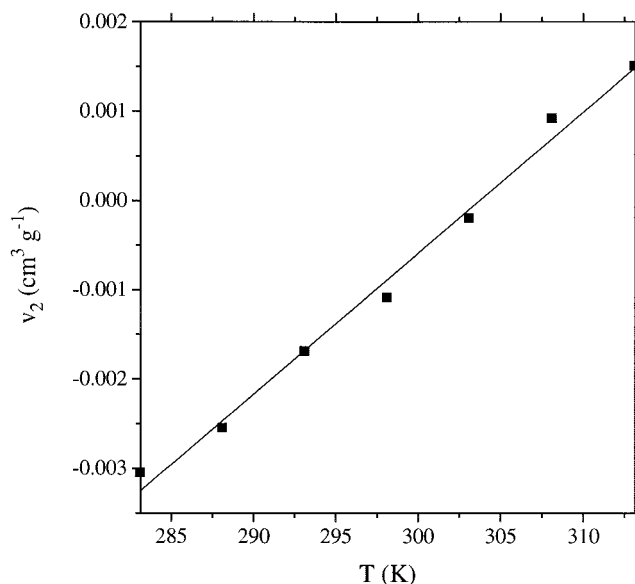| Temperature (K)	$\bar{v}^{\infty}_{\text{solute}}$ ($\text{cm}^3\ \text{g}^{-1}$)	$v_2 \times 10^3$ ($\text{cm}^3\ \text{g}^{-1}$)
283.15	0.82146	−3.0518
288.15	0.82631	−2.5531
293.15	0.83085	−1.6918
298.15	0.83533	−1.0933
303.15	0.83954	−0.20090
308.15	0.84355	0.91138
313.15	0.84774	1.4993

Figure 3 Temperature dependence of v_2: (■) experimental data and (—) calculated values.

$\bar{v}^{\infty}_{\text{solute}}$ partial specific volume of a solute at infinite dilution ($cm^3 g^{-1}$)

v^E specific excess volume of a solution ($cm^3 g^{-1}$)

v_2 second virial coefficient of power-law expansion in eq. (4) ($cm^3 g^{-1}$)

v_3 third virial coefficient of power-law expansion in eq. (4) ($cm^3 g^{-1}$)

v_4 fourth virial coefficient of power-law expansion in eq. (4) ($cm^3 g^{-1}$)

w solute-to-solvent (mass of the solute/mass of the solvent) mass ratio

Greek letter

ρ density of a solution ($cm^3 g^{-1}$)

ρ_{solvent} density of a pure solvent ($cm^3 g^{-1}$)

Subscripts

2, 3, 4...   referent to the second, third, fourth, ... virial coefficient in eq. (4)

solute   referent to a solute

solvent   referent to a solvent

H_2O referent to water

Superscripts

0   referent to pure component

∞   referent to infinite dilution

E referent to excess volume

References

1. Malcolm, G. N.; Rowlinson, J. S. Trans Faraday Soc 1957, 53, 921.
2. Bailey, F. E.; Callard, R. W. J Appl Polym Sci 1959, 1, 56.
3. Saeki, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. Polymer 1976, 17, 685.
4. Bae, Y. C.; Lambert, S. M.; Soane, D. S.; Prausnitz, J. M. Macromolecules 1991, 24, 4403.
5. Tripp, B. C.; Kaler, E. W.; Sandler, S. I.; Kopatsis, A. Colloids Surf B 1996, 6, 151.
6. Discher, B. M.; Won, Y.-Y.; Ege, D. S.; Lee, J. C.-M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. Science 1999, 284, 1143.
7. Allen, C.; Maysinger, D.; Eisenberg, A. Colloids Surf B 1999, 16, 3.
8. Riley, T.; Govender, T.; Stolnik, S.; Xiong, C. D.; Garnett, M. C.; Illum, L.; Davis, S. S. Colloids Surf B 1999, 16, 147.
9. Kirinčič, S.; Klofutar, C. Fluid Phase Equilib 1998, 149, 233.
10. Wurzburger, S.; Sartorio, R.; Guarino, G.; Nisi, M. J Chem Soc Faraday Trans 1 1988, 84, 2279.
11. Tawfik, W. Y.; Teja, A. S. Chem Eng Sci 1989, 44, 921.
12. Müller, E. A.; Rasmussen, P. J Chem Eng Data 1991, 36, 214.
13. Eliassi, A.; Modarres, H.; Mansoori, G. A. J Chem Eng Data 1998, 43, 719.
14. Zafarani-Moattar, M. T.; Salabat, A. J Chem Eng Data 1995, 40, 559.
15. Comelli, F.; Ottani, S.; Francesconi, R.; Castellari, C. J Chem Eng Data 2002, 47, 1226.
16. Hill, T. L. J Am Chem Soc 1957, 79, 4885.
17. Hill, T. L. J Chem Phys 1959, 30, 93.
18. Hill, T. L. An Introduction to Statistical Thermodynamics; Dover: New York, 1986.
19. Lide, D. R. Handbook of Chemistry and Physics, 76th ed.; CRC: Boca Raton, FL, 1995.
20. Nelder, J. A.; Mead, R. Comput J 1965, 7, 308.
21. Himmelblau, D. M. Applied Nonlinear Programming; McGraw-Hill: New York, 1972.
22. Shahidi, F.; Farrell, P. G.; Edward, J. T. J Solution Chem 1976, 5, 807.
23. Savage, J. J.; Wood, R. H. J Solution Chem 1976, 5, 733.
24. Franks, F.; Pedley, M.; Reid, D. S. J Chem Soc Faraday Trans 1 1976, 72, 359.
25. Leslie, T. E.; Lilley, T. H. Biopolymers 1985, 24, 695.
26. Jolicoeur, C.; Lacroix, G. Can J Chem 1976, 54, 624.
27. Perron, G.; Desnoyers, J. E. J Chem Thermodyn 1981, 13, 1105.
28. Friedman, H. L.; Krishnan, C. V. J Solution Chem 1973, 2, 119.