219

Density Dependence of the Viscosity and Excess Volume of Aqueous Solutions of Polyvinylpyrrolidone

Massoumeh Foroutan

School of Chemistry, University College of Science, University of Tehran, Tehran, Iran.

Abstract

A model for the estimation of density dependence of the viscosity of aqueous solutions of polyvinylpyrrolidone is presented. The proposed representation of the viscosity of PVP solutions expresses the viscosity as a function density and temperature. From the density data, the excess molar volumes of this system are also calculated.

Keywords: Density, Viscosity, Excess volume, Polyvinylpyrrolidone, Aqueous solution.

Introduction

In recent years, numerous studies have been carried out on density dependence of the viscosity of gases. Rainwater and Friend have developed a microscopically based theoretical model for the second transport virial coefficients of moderately dense gases.[1-3] The viscosity η is expressed in terms of the second viscosity virial coefficient, B_η according to

$$\eta = \eta_0(1 + B_\eta \rho + ...) \qquad (1)$$

where η_0 is the limiting low-density viscosity and ρ is the number density. In this model, B_η is dependant on the interatomic potential and temperature.

An expansion of viscosity as a power series in the density is consistent with Bogoliubov's theory of non equilibrium statistical mechanics[4], viz.

$$\eta = \eta_0(1 + B_\eta \rho) + \eta_2 \rho^2 + ..., \qquad (2)$$

where η_0 is the Chapman-Enskog zero-density coefficient which depict the effect of local binary collisions only and B_η and η_2, etc., are the density coefficients which account, among other things, for the effect of ternary, quaternary, and higher order collisions.

It has been suggested[5] that $\eta_2\rho^2$ needs to be replaced by $\eta'\rho^2\ln(\rho) + \eta_2\rho^2$. Thus, one has instead of Eq. (2) for the viscosity,

$$\eta = \eta_0(1 + B_\eta \rho) + \eta_2 \rho^2 + \eta_2 \rho^2 \ln(\rho) + ... \qquad (3)$$

The detailed nature of the terms beyond the quadratic term in Eq.(3) are not known but it appears that the expression contains terms which are products of powers of ρ and $\ln\rho$.[6,7] For higher gas densities, use is made of the empirical observations that the viscosity shows a regular dependence on density. The dependence of a $\eta(\rho,T)$ can always be written[8] as the sum of three contributions

$$\eta(T,\rho) = \eta_0(T) + \Delta\eta(T,\rho) + \Delta\eta_C(T,\rho) \qquad (4)$$

where $\eta_0(T)$ and $\Delta\eta(T,\rho)$ are the zero-density limit of viscosity and the excess viscosity which represents the increase in the viscosity at elevated density over the dilute gas value at same temperature, and $\Delta\eta_c(\rho,T)$ a critical enhancement accounting for the increase in viscosity in the immediate vicinity of the critical point.

The excess viscosity contribution describes how the viscosity of the fluid behaves as a function of density outside of the critical region. The current state of knowledge does not provide a satisfactory theory for the calculation of the excess viscosity over the whole phase space. However; in practice power series expansion in density for the representation of the excess viscosity has often been found to be adequate.[9-12]

The series adopted here is of the following form,

$$\Delta\eta(\rho,T) = \sum_{i=1}^{n} b_i(T)\rho^i \qquad (5)$$

where η, ρ and T are viscosity, density and absolute temperature. It is customary to represent the temperature dependence of the density coefficients, $b_i(T)$, by a functional relationship of the form

$$b_i = \sum_{j=1}^{m} d_{ij}/T^{*(j-1)} \qquad (6)$$

where T^* is the reduced temperature and defined as $T^*=KT/\varepsilon$ and K/ε is the energy scaling parameter. The coefficient d_{ij} are to be determined by fitting the experimental data for the viscosity to Eqs. (5) and (6).

Our research has the aim to determine density dependence of the viscosity of aqueous solution of

Table 1. Densities $\rho/(\text{g.cm}^{-3})$ and viscosities $\eta/(\text{mPa.s})$ of PVP (aq) as a function of the polymer mass fraction w_2 and temperature T.

w_2	T =298.15 K		T =308.15 K		T =318.15 K		T =328.15 K	
	ρ	η	ρ	η	ρ	η	ρ	η
0.0530	1.007011	1.3498	1.006599	1.2001	1.002569	0.9813	0.997068	0.7711
0.0621	1.009865	1.4981	1.009573	1.3011	1.005487	1.1119	1.000744	0.8748
0.0945	1.015689	1.6989	1.023001	2.0015	1.014552	1.3102	1.009541	1.1245
0.1595	1.030706	3.6862	1.027007	2.8544	1.022612	1.8102	1.017592	1.7807
0.2005	1.039827	5.6529	1.035925	4.1287	1.031333	3.0892	1.026191	2.5353
0.2636	1.054257	10.5298	1.041257	5.5831	1.040124	4.4567	1.033245	3.5124
0.2981	1.062412	15.9273	1.050015	7.7427	1.045159	5.8795	1.039754	4.5242
0.3168	1.066833	19.8458	1.057964	11.4453	1.052923	8.4904	1.039754	4.5242
0.3389	1.075001	27.4865	1.062272	13.8645	1.057132	10.4501	1.047342	6.2011
0.3712	1.079968	34.5897	1.070012	19.4562	1.062001	12.4001	1.052112	7.5412
0.3802	1.083546	39.8976	1.076167	24.9656	1.066021	15.1201	1.056451	9.2057
0.3944	1.085835	44.8655	1.080767	30.7981	1.070716	17.8233	1.064813	13.0603
0.4195	1.091457	57.2503	1.084021	36.4578	1.075211	21.3067	1.069212	15.8261
0.4367	1.093001	62.3145	1.087094	42.3916	1.079012	25.4687	1.073001	18.9029
0.4409	1.096101	69.8974	1.091011	49.2456	1.081388	29.4858	1.075261	20.7472
0.4522	1.098001	77.9987	1.093457	55.1246	1.086521	35.9871	1.079121	25.1451
0.4649	1.104001	96.8017	1.096001	61.7012	1.089911	42.0841	1.083091	30.0779

polyvinylpyrrolidone (PVP). This polymer has many uses in biotechnology. In this work, also we have calculated the excess volume of aqueous solutions of PVP.

Experimental

Materials

Polyvinylpyrrolidone with an average molecular weight of 10000 (K 15) was obtained from Aldrich and was used without further purification.

Apparatus and procedures

The solutions are prepared by weighing an appropriate amount of polymer using an analytical balance with an accuracy of $\pm$ 1.10^{-4} g. Densities of solutions were measured with a precision of $\pm1.10^{-6}$ g.cm^{-3} using a vibrating-tube densimeter (Anton Paar DSA 5000, Austria) which measures oscillating periods, calculates density and controls temperature with a precision of 0.001 C. The densimeter was calibrated with dry air and with double distilled and degasified water.

Viscosity measurements were carried out with an Ostwald-type viscometer, suspended in a thermostat at required temperature ($\pm$ 0.001 °C). The solutions were kept about 20 minutes prior the measurements for temperature equilibrium. The efflux time was determined with an accuracy of $\pm$ 0.1 s.

Results and discussion

The density, viscosity and excess molar volumes of various PVP aqueous solutions determined at T= (298.15, 308.15, 318.15 and 328.15) K are given in Tables 1 and 2.

Viscosity

For determining the density dependence of the viscosity we use the excess viscosity in Eq.(4). The excess viscosity contribution describes how the viscosity of the fluid behaves as a function of density outside of the critical region. The treatment of the viscosity in the zero-density limit and the critical enhancement will not be considered because no information is available.

Table 2. Experimental excess molar volumes V^E (cm^3.mol^{-1}) of PVP (aq) as a function of the polymer mole fraction x_2 and temperature T.

x_2	T=298.15 (K)	T=308.15 (K)	T=318.15 (K)	T=328.15 (K)
0.0000003	-0.00947	-0.02558	-0.02467	-0.00866
0.0000011	-0.02632	-0.04205	-0.04097	-0.02473
0.0000031	-0.06876	-0.08360	-0.08191	-0.06531
0.0000041	-0.09076	-0.10517	-0.10310	-0.08629
0.0000051	-0.10955	-0.12354	-0.12130	-0.10432
0.0000063	-0.13705	-0.15046	-0.14777	-0.13047
0.0000073	-0.15983	-0.17277	-0.16978	-0.15221
0.0000086	-0.18895	-0.20129	-0.19775	-0.20293
0.0000111	-0.24168	-0.25291	-0.24863	-0.23015
0.0000135	-0.29394	-0.30404	-0.29891	-0.27992
0.0000161	-0.35077	-0.35961	-0.35362	-0.33399
0.0000213	-0.46537	-0.47160	-0.46371	-0.44275
0.0000311	-0.68835	-0.68919	-0.67733	-0.65365
0.0000374	-0.83436	-0.83141	-0.81648	-0.78999
0.0000438	-0.98448	-0.97754	-0.95971	-0.93182
0.0000484	-1.09768	-1.08770	-1.06768	-1.03800
0.0000549	-1.25346	-1.23952	-1.21628	-1.18436

Following this method which has been used for the calculation of the viscosity of carbon dioxide in the customary way as a function of density and temperature[13], a power series expansion in density for the representation of viscosity of aqueous solutions of PVP was considered

$$\eta(\rho,T) = \sum_{i=1}^{n} b_i(T)\rho^i \qquad (7)$$

where $b_i(T)$ has been defined as

$$b_i = \sum_{j=1}^{4} d_{ij} / T^{(j-1)} \qquad (8)$$

In examining the ability of the mentioned method to calculate the viscosity of an aqueous solution of polymer, PVP serves as our primary test, because of the abundance of available viscosity data over a wide range of temperature and concentration.

As shown in figure 1, there is good agreement between calculated and experimental viscosity of aqueous solutions of PVP at different temperatures.

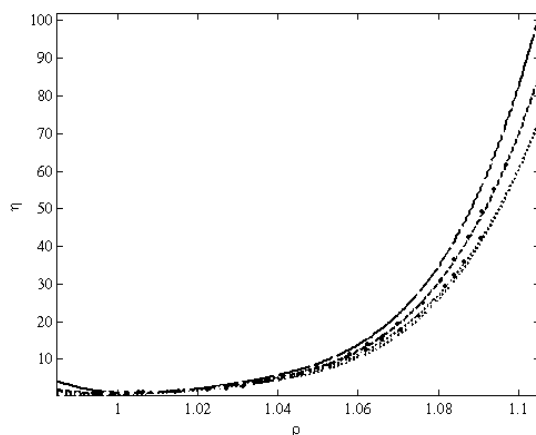The resulting coefficients of Eq. (8) at each temperature are given in Table 3.

Figure 1. Calculated and experimental viscosity of aqueous solutions of PVP at different isotherms. The calculated values are based on Eq. (8). (—) 298.15 K, (---) 308.15 K, (…) 318.15 K and (····) 328.15 K. [ρ in g.cm^{-3}and η in mPa.s].

Table 3. Coefficients of the representation of the viscosity of the PVP aqueous solutions, Eq. (9). [T in K; ρ in g.cm^{-3}and η in mPa.s].

d_{11}	0.123020×10^{10}	d_{12}	-0.110805×10^{13}
d_{21}	-0.489076×10^{10}	d_{22}	0.439807×10^{13}
d_{31}	0.732171×10^{10}	d_{32}	0.657483×10^{13}
d_{41}	0.119518×10^{10}	d_{42}	-0.106911×10^{13}
d_{13}	0.331510×10^{15}	d_{14}	-0.329037×10^{17}
d_{23}	-1.313459×10^{15}	d_{24}	1.300967×10^{17}
d_{33}	1.960402×10^{15}	d_{34}	1.938184×10^{17}
d_{43}	0.317373×10^{15}	d_{44}	-0.312178×10^{17}

Excess molar volumes

The values of excess molar volumes (V^E) can be calculated from the experimental data according to the following equation:

$$V^E = \frac{\sum_{i=1}^{2} x_i M_i}{\rho} - \sum_{i=1}^{2} x_i V_i \qquad (9)$$

where ρ is the mixture density and x_i, M_i and V_i are the mole fraction, the molecular weight and molar volume of the ith component of the mixture, respectively. The equation $V_1 = M_1/\rho_1$ describes the molar volume of pure water, while that of PVP is described by $V_2 = \Phi_2^\infty$ where Φ_2^∞ is the apparent specific volume at infinite dilution of PVP, which must be determined on the basis of data on apparent specific volume.

The apparent specific volume of the polymer, Φ_2 is computed from the density of the solution by using the following equation

$$\Phi_2 = \frac{1}{w_2}(\frac{1}{\rho} - \frac{1-w_2}{\rho_1}) \qquad (10)$$

where w_2 is the polymer mass fraction. The Φ_2 values can be fitted to the following equation[14]

$$\Phi_2 = \Phi_2^\infty + b_v m_{w_2} + b_{vv} m_{w_2}^2 \qquad (11)$$

where b_v and b_{vv} are the empirical parameters which depend on solute, solvent and temperature, and m_{w2} is the weight molality of polymer.

Recently the above equation has been used for the fitting of Φ_2 values for aqueous PVP solutions at different temperature and the values of infinite dilution apparent specific volume of the polymer at T=298.15, 308.15, 318.15 and 328.15 K were reported as 0.7986, 0.8044, 0.8102 and 0.8160 cm^{3}g^{-1} respectively.[15] We will apply these values in our calculations. Once the apparently specific volumes at finite dilution of PVP are known, as well as the molar volume of water and the density of the binary mixture, values V^E are determined by means of Eq. (9). Values of V^E are listed in the Table 2. Figure 2 shows experimental excess molar volumes of aqueous solutions of PVP at different temperatures. By observing the values for the excess volumes at a given temperature, it can be observed that V^E increases at the concentration of PVP increase.

As shown in this figure, the excess molar volumes for the binary systems in different temperatures are negative. This would indicate that molecular interactions between molecules of water and polymer are stronger than interactions between molecules in their pure states and attractive forces dominate the behavior of the solutions.[16]
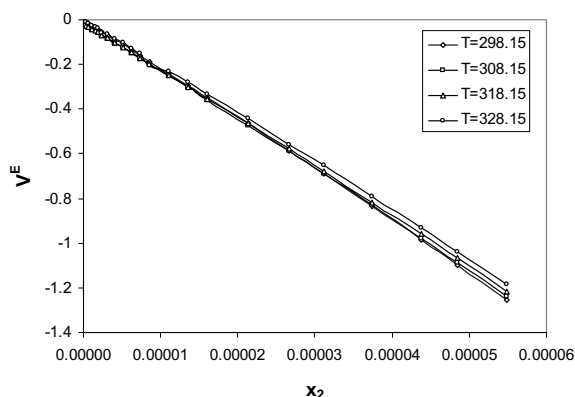
Figure 2. Experimental excess molar volumes of aqueous solutions of PVP at (◊) 298.15 K, ( ) 308.15 K, (Δ) 318.15 K and (O) 328.15 K.

Acknowledgment

References

1. J. C. Rainwater, J. Chem. Phys. **1984**, *81*, 495–510.
2. D. G. Friend, J. C. Rainwater, Chem. Phys. Lett. **1984**, *107*, 590–594.
3. J. C. Rainwater, D. G. Friend, Phys. Rev. A **1987**, *36*(2), 4062–4066.
4. N. N. Bogoliubov, J. Phys. (USSR) **1946**, *10*, 256–265.
5. H. J. M. Hanley, R. D. McCarty, J. V. Sengers, J. Chem. Phys. **1969**, *50*, 857–870**.**
6. J. R. Doefman, E. G. D. Cohen, Phys. Lett. **1965**, *16*, 124.
7. J. M. J. Van Leeuwen, A. Weijland, Phys. Lett. **1965**, *19*, 562–564.
8. J. Millat, J. H. Dymond, C. A. Nieto de Castro (Eds.), Transport properties of Fluids, Ch. 3., Cambridge University Press, New York, **1996**, pp. 25.
9. V. Vesovic, W. A. Wakeham, G. A. Olchowy, J. V. Sengers, J. T. R. Watson, and J. Millat, J. Phys. Chem. Ref. Data **1990**, *19*(3), 763–808.
10. H. J. M. Hanley, K. E. Gubbins, S. Murad, J. Phys. Chem. Ref. Data **1997**, *6* 1167–1180.
11. B. A. Younglove and J. F. Ely, J. Phys. Chem. Ref. Data **1987**, *16*, 577–798.
12. D. G. Friend, H. Ingham, and J. F. Ely, J. Phys. Chem. Ref. Data **1991**, *20*(2), 275–347.
13. A. Fenghour, W. A. Wakeham and V. Vesovic, J. Phys. Chem. Ref. Data **1998**, *27* , 31–44.
14. S. Kirincic, C. Klofutar, Fluid Phase Equilibr. **1998**, *149*, 233–247.
15. R. Sadeghi, M. T. Zafarani-Moattar, J.Chem. Thermodynamics **2004**, *36*, 665–670.
16. J. M. Prausnitz, R. N. Lichtenthaler, E. Azevedo, Molecular Thermodynamics of Fluid Phase Equilibria, 2nd Eds., Prentice Hall, Englewood Cliffs, NJ, USA, **1986**, Ch. 10.

Povzetek

V članku predstavljamo model za določanje viskoznosti vodnih raztopin polivinilpirolidona kot funkcijo gostote in temperature raztopine. Iz gostot raztopine smo izračunali tudi presežne molske prostornine.