

Activation Energy, Free Energy, Enthalpy, and Entropy Changes Associated with Viscometric Changes of Extremely to Moderately Dilute Aqueous Solutions of Polyvinylpyrrolidone at 288.15–313.15 K

Man Singh, Sanjay Kumar

Chemistry Research Laboratory, Deshbandhu College, University of Delhi, New Delhi 110019, India

Received 29 May 2003; accepted 4 February 2004

DOI 10.1002/app.20376

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Viscometric behavior of polyvinylpyrrolidone (PVP) was investigated for extremely dilute (0.002–0.010 g dL⁻¹), dilute (0.02–0.10 g dL⁻¹), and moderately dilute (0.20–1.00 g dL⁻¹) solutions at 288.15, 290.15, 293.15, 295.15, 298.15, 300.15, 303.15, 305.15, 308.15, 311.15, and 313.15 K. The experimental data were plotted according to Jones–Dole, Fuoss, and Fedors equations. Intrinsic viscosity ($[\eta]$) variation with temperature indicated the existence of different hydrodynamic states of PVP in solution at different temperatures. The PVP was found to show polyelectrolyte behavior in extremely dilute solutions, probably attributable

to the presence of partially polarizable >C=O groups in the chain. Activation energy (ΔE), differential enthalpy ($\partial\Delta H$), entropy ($\partial\Delta S$), and free energy ($\partial\Delta G$) changes of viscous flow were derived from flow velocity and taken into account for interpretation of the results to better understand the hydrodynamic and conformational behavior of PVP. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 47–55, 2004

Key words: polyvinylpyrrolidone; viscosity; activation energy; conformational analysis; polyelectrolytes

INTRODUCTION

Polymers carrying hydrophobic and partially polarizable groups, within the same chain, are of increasing interest for a wide variety of industrial applications such as flocculants, thickening agents in oil recovery, latex paints, and cosmetics because of the advantage conferred by effects of both the partially charged and hydrophobic groups.^{1–4} Viscometry is the most widely used experimental method to investigate the conformational behavior of macromolecules in solution.^{5,6} Viscosity is substantially affected by the chemical structure of the macromolecule, its size, charge density, and nature of the surrounding environment such as polarity of the solvent.^{7,8} Intrinsic viscosity is considered to be fixed for each macromolecule of definite molecular weight in the ambient temperature range. Viscosity of polyvinylpyrrolidone (PVP) in aqueous and aqueous salt solutions has been studied over a wide concentration range.^{9–14} In all these studies the concentration of PVP was >1 g dL⁻¹. To date, investigations on differential enthalpy ($\partial\Delta H$), entropy ($\partial\Delta S$), and free energy ($\partial\Delta G$) of viscous flow and conformational transition of PVP in aqueous solution have not been reported in the literature. In the present

work intrinsic viscosity values of PVP, for extremely to moderately dilute solutions, were determined. The data were analyzed, to exclude information about PVP chain conformation in saltless aqueous solutions, and confined to extremely dilute, dilute, and moderately dilute concentration ranges.

EXPERIMENTAL

Materials

PVP of 40,000 M_v (product no. PVP-40) was procured from Sigma (St. Louis, MO) and stored in a vacuum desiccator with P₂O₅ before use. Solutions were prepared in triple-distilled degassed water, deionized by passing through two Cole–Parmer bed ion exchangers (Cole–Parmer Instrument Co., Vernon Hills, IL). For a stock solution of 1 g dL⁻¹, 5 g PVP was dissolved in 500 mL water and the rest of the solutions were prepared by dilution.

Density (ρ) and dynamic viscosity (η) measurements

Densimetric and viscometric measurements of PVP solutions were carried out at each chosen temperature with a double-armed pycnometer and Ubbelohde viscometer (Cannon–Ubbelohde, State College, PA), respectively. An electronic timer (1×10^{-2} s accuracy) was used for efflux time. The pycnometer and viscom-

Correspondence to: S. Kumar (kumaraquaris@yahoo.com).

TABLE I
Limiting Densities (ρ^0) and Slope Constants (S_d) of the Equation $\rho = \rho^0 + S_d c$

Temperature (K)	0.002–0.010 g dL ⁻¹ PVP		0.020–0.100 g dL ⁻¹ PVP		0.200–1.000 g dL ⁻¹ PVP	
	ρ^0 (g cm ⁻³)	S_d (dL g ² cm ⁻³)	ρ^0 (g cm ⁻³)	S_d (dL g ² cm ⁻³)	ρ^0 (g cm ⁻³)	S_d (dL g ² cm ⁻³)
288.15	0.9998	-0.0736	0.9992	0.0018	0.9992	0.0016
290.15	0.9989	-0.0177	0.9987	0.0027	0.9989	0.0017
293.15	0.9985	-0.0272	0.9982	0.0019	0.9984	0.0015
295.15	0.9981	-0.0175	0.9979	0.0036	0.9979	0.0018
298.15	0.9974	-0.0330	0.9971	0.0015	0.9972	0.0018
300.15	0.9967	-0.0111	0.9966	0.0011	0.9966	0.0018
303.15	0.9958	-0.0191	0.9957	0.0016	0.9957	0.0020
305.15	0.9948	-0.0059	0.9948	0.0014	0.9947	0.0020
308.15	0.9947	-0.0344	0.9944	0.0023	0.9944	0.0020
311.15	0.9927	-0.0040	0.9927	0.0015	0.9926	0.0020
313.15	0.9922	-0.0232	0.9922	0.0009	0.9921	0.0018

eter, filled with solvent or solution, were thermostated for 20 min at $\pm 0.02^\circ\text{C}$ control before measurements. The uncertainty in weighing was $\pm 1 \times 10^{-5}$ g.

Calculations

Values of ρ and η were calculated from eqs. (1) and (2), as follows:

$$\rho_{\text{soln}} = \frac{w_{\text{soln}}}{w_{\text{solv}}} \times \rho_{\text{water}} + \rho_{\text{air}} \left(1 - \frac{w_{\text{soln}}}{w_{\text{solv}}} \right) \quad (1)$$

where w_{soln} and w_{solv} are the weight of the solution and the solvent, respectively; ρ_{water} is the buoyancy correction; and ρ_{air} is the air density, calculated from $\rho_{\text{air}} = 0.001293/(1 + 0.00367 \times t^\circ\text{C})$.

$$\eta = \left(At - \frac{V}{8\pi lt} \right) \rho \quad (2)$$

where A is the viscometer constant with water and $V/8\pi l$ (V is the flow volume obtained from Poiseuille's relation and l is the length of capillary) is the

kinetic energy correction. Relative viscosity (η_r) was calculated from eq. (3) and flow volume V was calculated from Poiseuille's eq. (4).

$$\eta_r = \frac{\eta_{\text{soln}}}{\eta_{\text{solv}}} \quad (3)$$

$$V = \frac{h\rho g \pi r^4 t}{8\eta l} \quad (4)$$

where h is height of the water column including capillary (17 cm), ρ is the density of water (in g cm⁻³), g is gravity (980 cm s⁻²); r is radius of the capillary (0.025 cm), t is flow time, l is length of the capillary (11 cm), and η is the dynamic viscosity of water taken from the literature.¹⁵

Flow velocity v_f , calculated from eq. (5), was used to replace the rate constant k in Arrhenius eq. (6) to calculate the activation energy of viscous flow. In the Arrhenius relation, k represents the rate constant of chemical reaction. However, here we consider only the viscous flow and interactions that take place

TABLE II
Limiting Dynamic Viscosities (η^0) and Slope Constants (S_{dv}) of the Equation $\eta = \eta^0 + S_{dv} c$

Temperature (K)	0.002–0.010 g dL ⁻¹ PVP		0.020–0.100 g dL ⁻¹ PVP		0.200–1.000 g dL ⁻¹ PVP	
	η^0 (cp)	S_{dv} (cp dL g ⁻¹)	η^0 (cp)	S_{dv} (cp dL g ⁻¹)	η^0 (cp)	S_{dv} (cp dL g ⁻¹)
288.15	1.1460	0.6041	1.1502	0.0818	1.1275	0.2741
290.15	1.0876	0.1845	1.0858	0.1875	1.0740	0.2546
293.15	1.0097	0.4090	1.0094	0.1652	1.0029	0.2260
295.15	0.9663	0.1153	0.9648	0.2127	0.9560	0.2251
298.15	0.8991	0.8740	0.9065	0.0807	0.8923	0.1987
300.15	0.8662	0.0855	0.8651	0.1581	0.8576	0.2008
303.15	0.8133	0.2166	0.8109	0.1797	0.8024	0.1824
305.15	0.7701	0.0963	0.7694	0.1131	0.7560	0.1703
308.15	0.7333	0.7310	0.7358	0.1419	0.7265	0.1602
311.15	0.6856	0.1057	0.6827	0.1443	0.6770	0.1422
313.15	0.6668	0.8021	0.6716	0.1361	0.6634	0.1407

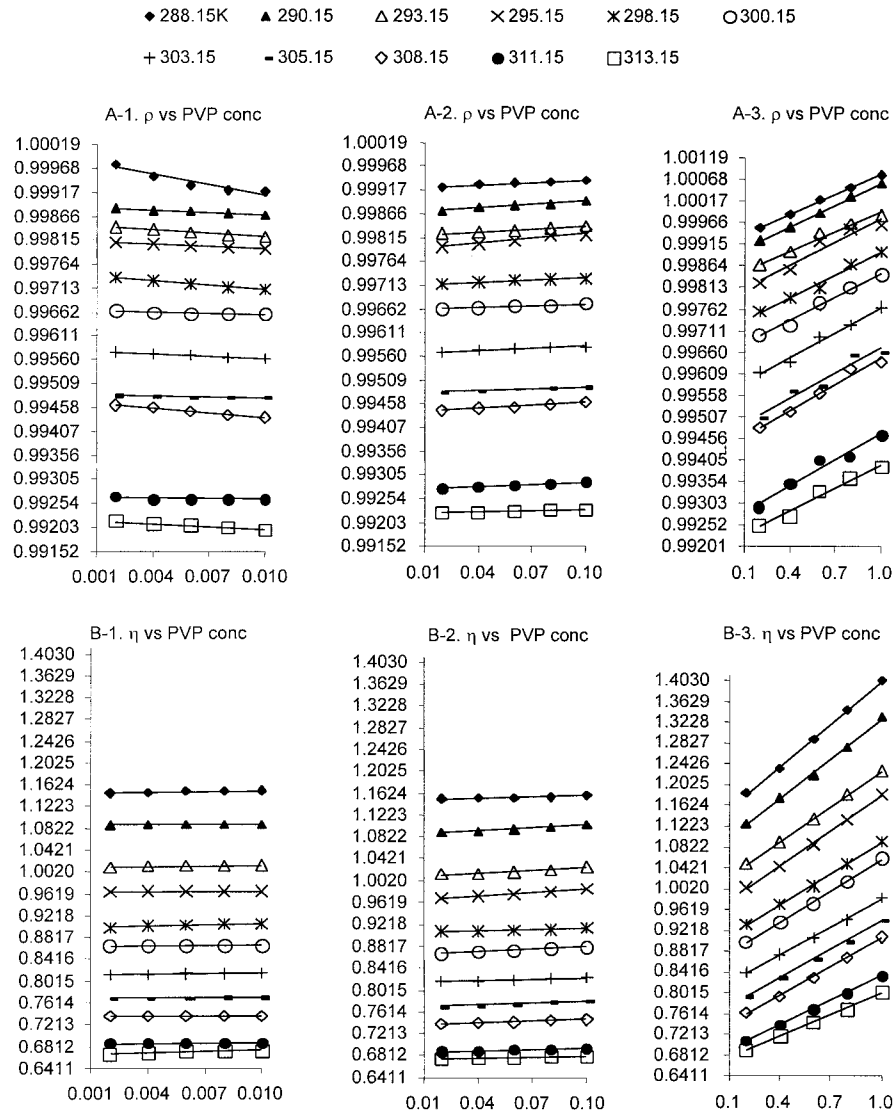


Figure 1 Variation of ρ (g cm^{-3}) and η in centipoise (cp) as a function of PVP concentration (g dL^{-1}); -1, -2, and -3 represent extremely dilute, dilute, and moderately dilute solutions, respectively.

within the solution during flow. The structural or conformational changes during flow will affect the activation energy of viscous flow. Given that, for a particular concentration, the velocity of flow remains the same and varies with temperature, v_f was chosen to replace k . The value of E_{avf} was obtained from the slope of $\log v_f$ versus $1/T$ [eq. (6)].

$$v_f = \frac{V}{\pi r^2 t} \quad (5)$$

$$\log v_f = \log A - \frac{E_{avf}}{2.303RT} \quad (6)$$

$$E_{avf} = -\text{slope} \times 2.303R \quad (7)$$

Values of ΔH , ΔS , and ΔG were determined from eqs. (8), (9), and (10), as follows:

$$\Delta H_{vf} = E_{avf} - 2RT \quad (8)$$

$$A = \frac{Rk_b T^2}{hp^0} e^2 e^{\Delta S/R}$$

$$e^{\Delta S/R} = \frac{hp^0 A}{Rk_b e^2 T^2}$$

$$e^{\Delta S/R} = 3.26843 \times 10^{-12} \frac{A}{T^2}$$

$$\Delta S = 4.576522 \log \frac{A}{T^2} - 52.5644 \quad (9)$$

where $\log A$ is the intercept of eq. (5).

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

RESULTS AND DISCUSSION

Values of ρ and η were found to be best fitted to $\rho = \rho^0 + S_d c$ and $\eta = \eta^0 + S_{dv} c$, respectively. The ρ^0 and η^0

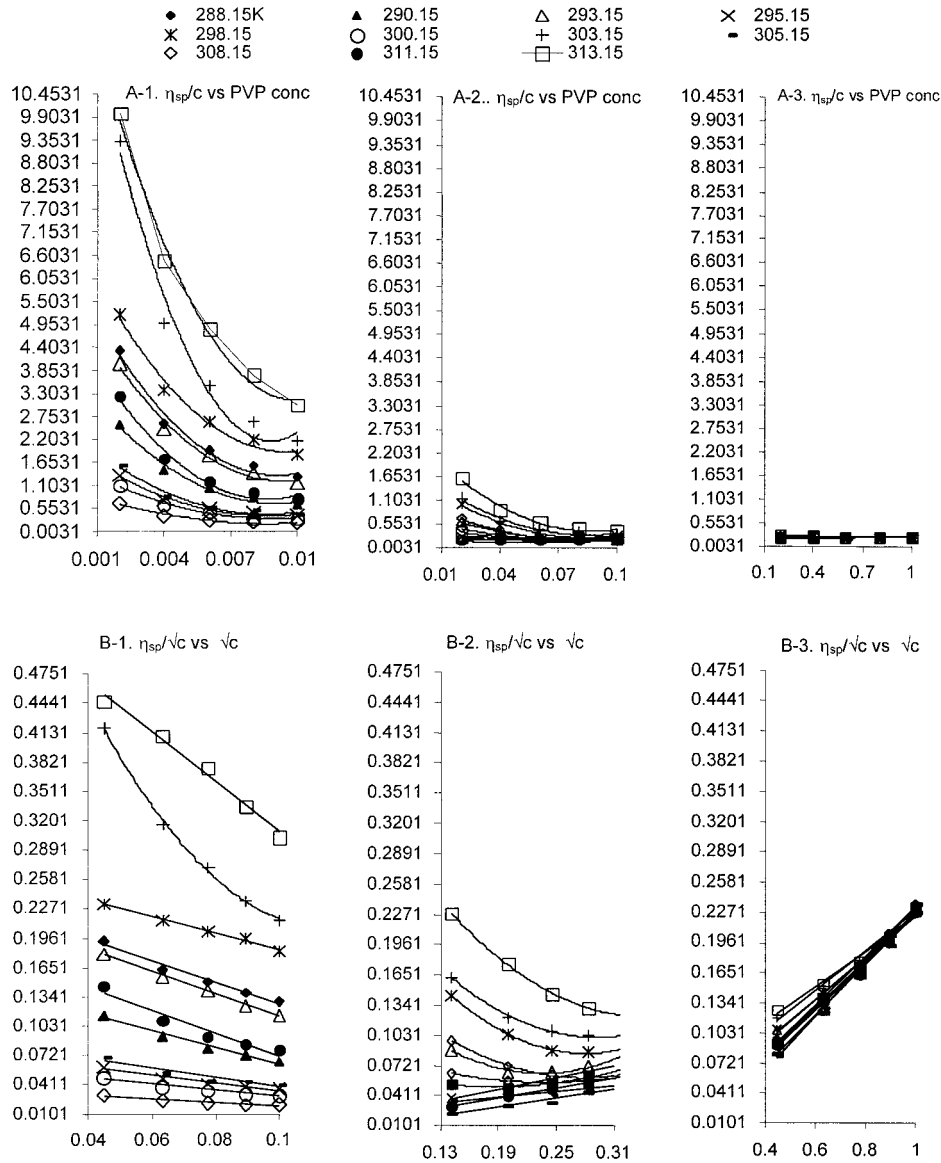


Figure 2 Plots of graphs for: A-1, A-2, and A-3, where y -axis and x -axis represent, respectively, $10^4 \eta_{sp}/c$ (in dL g^{-1}) and c (in g dL^{-1}); B-1, B-2, and B-3, where y -axis and x -axis represent, respectively, η_{sp}/\sqrt{c} (in $\text{dL}^{1/2} \text{g}^{-1/2}$) and \sqrt{c} (in $\text{g}^{1/2} \text{dL}^{-1/2}$).

are limiting constants, and S_d and S_{dv} are slope constants. The values are given in Tables I and II. Figure 1 presents the variation of ρ and η with PVP concentration. The negative S_d values, for extremely dilute solutions, reflect the weaker PVP–PVP interactions. In the extremely dilute concentration range, PVP coils are fully expanded and form larger hydrospheres, thereby lacking short-range PVP–PVP interactions. Figure 2 shows the variation of reduced viscosity with concentration of PVP. In extremely dilute solutions PVP has typical polyelectrolyte behavior; that is, the η_{sp}/c values increased with dilution of the solution because of the expansion of PVP chains. This is attributed to the progressively enhanced intramolecular repulsive interactions between the partially polarized groups ($>\text{C}=\text{O}$) along the chain. The trend of ρ also

supports this behavior. The η_{sp}/c values become temperature independent in moderately dilute solutions; that is, η_{sp}/c values converge to approximately the same value at all chosen temperatures. This indicates stronger PVP–PVP interactions, than that of PVP–water, resulting in entanglement of macromolecular chains with each other. The Fuoss¹⁶ and Fedors^{17–19} equations [eqs. (11) and (12), respectively] were applied to analyze the relative viscosity data (Fig. 3).

$$\frac{\eta_r - 1}{c} = \frac{A}{1 + Bc^{1/2}} \quad (11)$$

$$1/[2(\eta_r^{1/2} - 1)] = 1/[\eta]c - 1/[\eta]c_M \quad (12)$$

The intrinsic viscosity $[\eta]$ values, evaluated from Jones–Dole, Fuoss, and Fedors equations, are given in

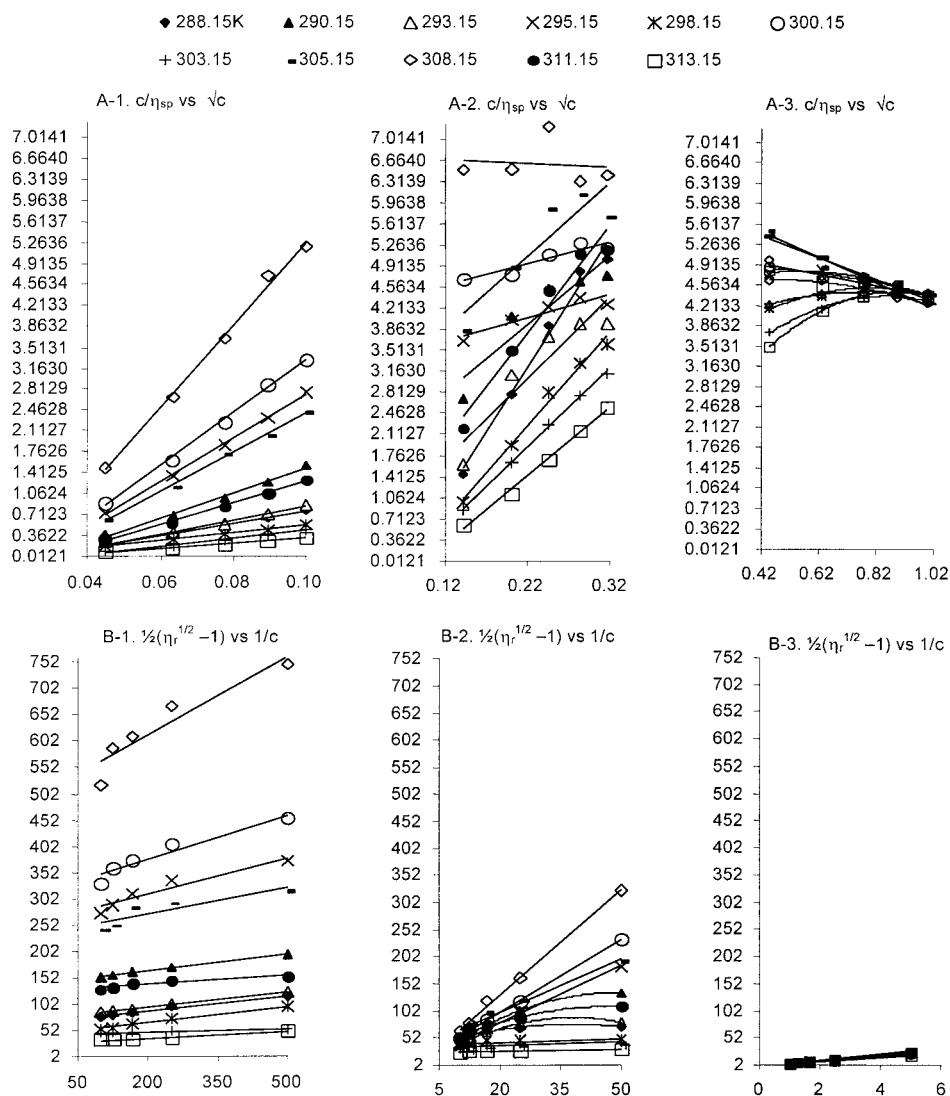


Figure 3 A and B denote plots of Fuoss and Fedors equations, respectively; -1, -2, and -3 are used for extremely dilute, dilute, and moderately dilute solutions, respectively.

TABLE III
Intrinsic Viscosity (in dL g⁻¹) Obtained from Jones–Dole (JD), Fuoss, and Fedors Equations

Temperature (K)	0.002–0.010 g dL ⁻¹ PVP			0.02–0.10 g dL ⁻¹ PVP			0.20–1.00 g dL ⁻¹ PVP		
	$[\eta]_{JD}$	$[\eta]_{Fuoss}$	$[\eta]_{Fedors}$	$[\eta]_{JD}$	$[\eta]_{Fuoss}$	$[\eta]_{Fedors}$	$[\eta]_{JD}$	$[\eta]_{Fuoss}$	$[\eta]_{Fedors}$
288.15	6.07	-4.56	10.58	1.03	-0.67	2.35	0.21	0.20	0.21
290.15	3.70	-1.74	9.58	0.49	0.69	0.48	0.20	0.20	0.20
293.15	5.63	-3.53	10.64	0.90	11.38	1.11	0.25	0.30	0.24
295.15	1.95	-1.10	4.36	0.31	0.31	0.29	0.21	0.19	0.21
298.15	7.04	-9.98	9.67	1.53	-0.87	4.07	0.26	0.38	0.25
300.15	1.60	-0.91	3.54	0.23	0.24	0.22	0.20	0.19	0.20
303.15	13.74	-5.07	58.48	1.69	-1.04	3.79	0.30	0.66	0.28
305.15	2.32	-1.21	5.89	0.34	0.41	0.31	0.18	0.16	0.17
308.15	0.97	-0.62	2.00	0.29	0.24	0.15	0.19	0.16	0.17
311.15	4.83	-1.94	18.25	0.39	-8.21	0.75	0.25	0.19	0.19
313.15	13.67	-10.25	22.78	2.36	-0.98	8.18	0.41	0.34	0.31

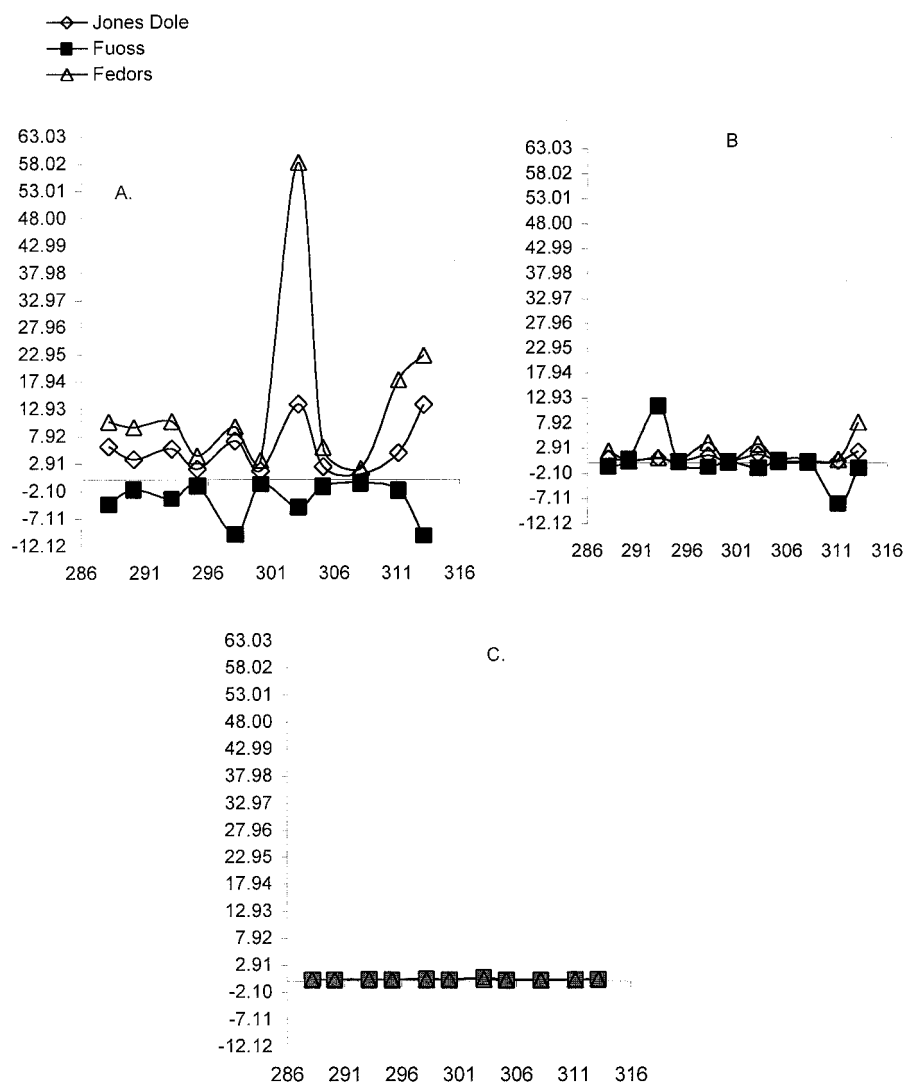


Figure 4 Variation of intrinsic viscosity with temperature for (A) extremely dilute, (B) dilute, and (C) moderately dilute solutions.

Table III. Values of $[\eta]_{\text{Fuoss}}$ are observed to be negative for extremely dilute solutions. The $[\eta]_{\text{Fedors}}$ values are found to be greater than $[\eta]_{\text{JD}}$ values at all chosen temperatures. For moderately dilute solutions, intrinsic viscosity values evaluated from each equation seem to be close. The variation of $[\eta]$ with temperature, for extremely to moderately dilute solutions, shows wavelike behavior that diminishes for moderately dilute solutions (Fig. 4). These trends reflect the conformational changes that occur as a result of the rotational freedom around —C—C— single bonds within the PVP molecule in extremely dilute and moderately dilute solutions. This indicates that PVP molecules remain in different conformational states with different size of water–PVP spheres. Transitions of the first conformational states have an energy barrier that is crossed by the energy of subsequent conformational change at one temperature. Upon a further temperature increase, molecules occupy another conforma-

tional state because of rotational freedom of the pyrrolidone ring. The nitrogen atom of PVP donates a lone pair of electrons toward >C=O , resulting in a high electron density on >C=O . Dipoles of water associate with >C=O through hydrogen bonding, forming $\text{H}^{\delta+}\text{—O}^{\delta-}\text{—H}^{\delta+}\text{—O}^{\delta-}\text{—C}^{\delta+}$ linkages. Probably primary and secondary associations hold water dipoles with several >C=O . Secondary association is dominant on dilution, affecting a secondary complex formation. Water molecules will also interact with the N- quasi-cation of PVP. Solvation of both >C=O and N is more in extremely dilute solutions. Water of aqueous PVP solutions can be divided into (1) hydration water, (2) water in spaces of PVP chains, and (3) bulk water. The presence of interstices may induce extensive disorder of water, which decreases the long-range intermolecular coupling of O—H oscillators and, consequently, results in a decrease of $[\eta]$ coefficient amplitude.²⁰ The properties of water in

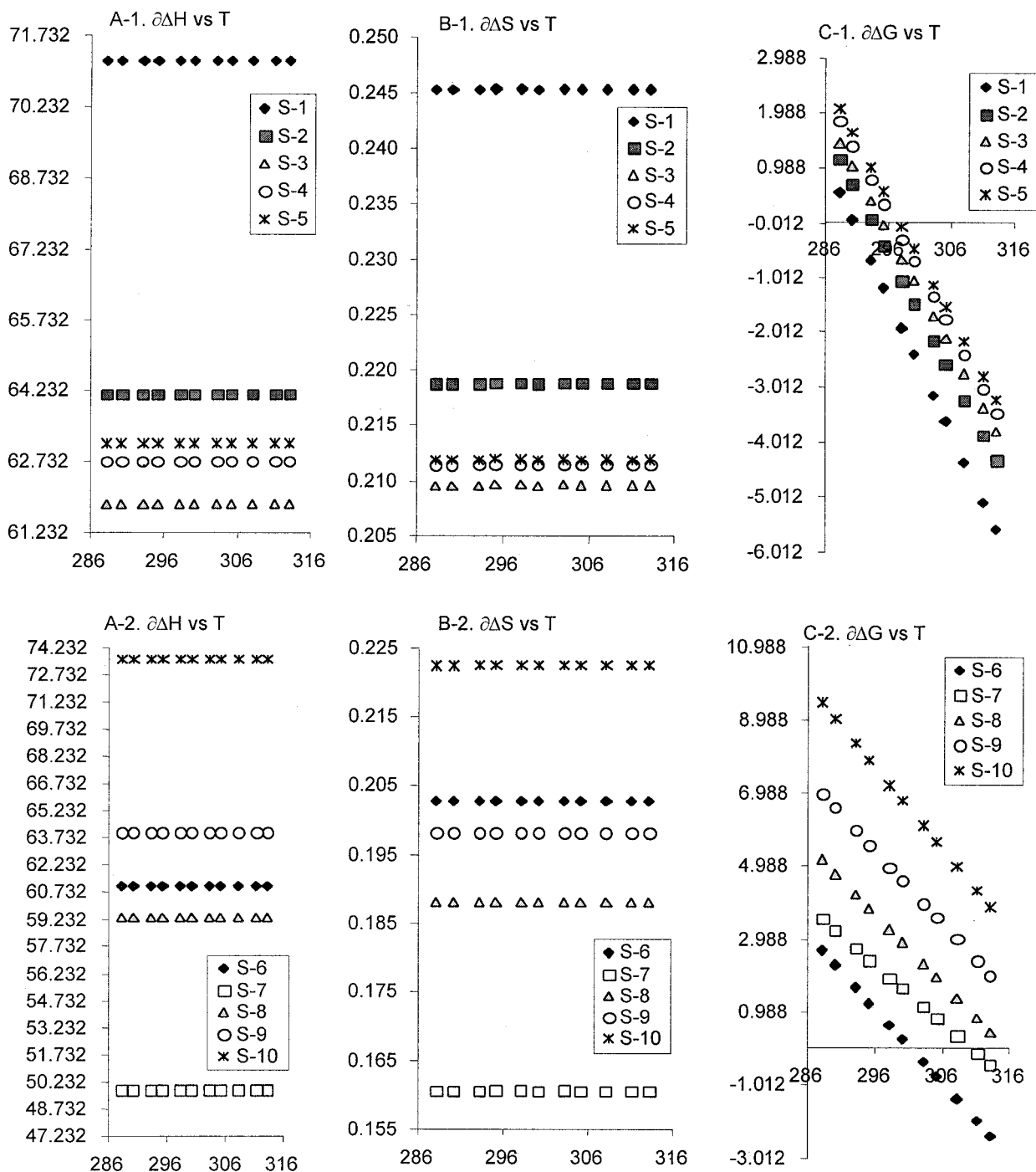


Figure 5 Differential enthalpy, free energy, and entropy change as a function of temperature. S-1 = 0.002, S-2 = 0.004, S-3 = 0.006, S-4 = 0.008, S-5 = 0.010, S-6 = 0.02, S-7 = 0.04, S-8 = 0.06, S-9 = 0.08, S-10 = 0.10 (% PVP); -1 and -2 denote extremely dilute and dilute solutions, respectively.

compartmentalized spaces are different from those of free water and the degree of difference is dependent on the size of space.²¹⁻²⁴

The ΔH , ΔS , and ΔG values of viscous flow of water were subtracted from the corresponding values of PVP solutions to obtain $\partial\Delta H$, $\partial\Delta S$, and $\partial\Delta G$. Variations of $\partial\Delta H$, $\partial\Delta S$, and $\partial\Delta G$ with temperature are shown in Figures 5 and 6 and their intensive values $\partial\Delta H^0$, $\partial\Delta S^0$,

and $\partial\Delta G^0$ are listed in Table IV. The values of $(\partial\Delta H/\partial T)_{P,c}$ and $(\partial\Delta S/\partial T)_{P,c}$ are 9×10^{-6} and 2×10^{-6} cal mol⁻¹, respectively, and do not vary with concentration, whereas $(\partial\Delta G/\partial T)_{P,c}$ is negative and does vary with concentration. The positive $\partial\Delta S^0$ reflects the structure-breaking effect of PVP on water, resulting in a large increase in the number of translational and rotational degrees of freedom in the system (there are

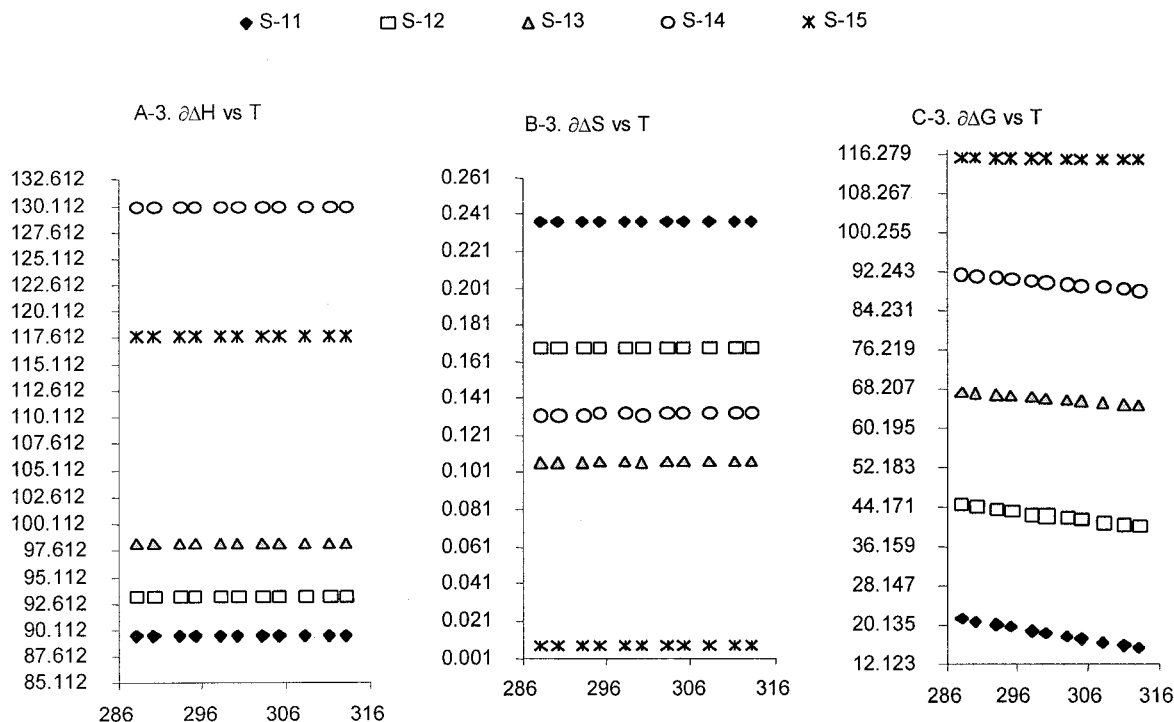


Figure 6 Differential enthalpy ($[\pi\delta\mu\phi]\Delta H$), entropy ($[\pi\delta\mu\phi]\Delta S$), and free energy ($[\pi\delta\mu\phi]\Delta G$) change as a function of temperature. S-11 = 0.20, S-12 = 0.40, S-13 = 0.60, S-14 = 0.80, S-15 = 1.00 (% PVP); -3 denotes moderately dilute solution.

now more molecules in the system). The breaking of hydrogen bonding of water takes up energy, and thus $\partial\Delta H^0$ is also positive. Lower $\partial\Delta S^0$ values are attributed to the association of PVP molecules with itself as well as with water. In association, interaction energy is evolved that compensates for the enthalpy change of disruption of nonbonding interactions; thus a decrease in magnitude of $\partial\Delta H^0$ is also observed. The positive $\partial\Delta G^0$ reflects the fact that structure-breaking interactions are dominant over structure making. This is

attributed to the presence of a major proportion of the hydrophobic part of the PVP molecule. This trend of $\partial\Delta S^0$ shows that PVP macromolecular chains become progressively overlapped, and thus there is a decrease in randomness. The trend of η_{sp}/c versus c of PVP, for moderately dilute solutions (Fig. 2, A-3, B-3), also agrees with this. Moreover the different $\partial\Delta H^0$ and $\partial\Delta S^0$ and constant $(\partial\Delta H/\partial T)_{P,c}$ and $(\partial\Delta S/\partial T)_{P,c}$ values for different concentrations reveal that the former are much more dependent on PVP–water interactions,

TABLE IV
Limiting Differential Enthalpy, Entropy, and Free Energy Constants

C (g dL ⁻¹)	$\partial\Delta H$		$\partial\Delta S$		$\partial\Delta G$	
	$\partial\Delta H^0$	$\partial\Delta H/\partial T$	$\partial\Delta S^0$	$\partial\Delta S/\partial T$	$\partial\Delta G^0$	$\partial\Delta G/\partial T$
0.002	71.207	9×10^{-6}	0.2448	2×10^{-6}	71.345	-0.2458
0.004	64.16	9×10^{-6}	0.2183	2×10^{-6}	64.298	-0.2192
0.006	61.826	9×10^{-6}	0.2091	2×10^{-6}	61.964	-0.2101
0.008	62.741	9×10^{-6}	0.211	2×10^{-6}	62.879	-0.2119
0.010	63.107	9×10^{-6}	0.2114	2×10^{-6}	63.245	-0.2123
0.020	61.093	9×10^{-6}	0.2023	2×10^{-6}	61.231	-0.2032
0.040	49.835	9×10^{-6}	0.1602	2×10^{-6}	49.973	-0.1611
0.060	59.354	9×10^{-6}	0.1876	2×10^{-6}	59.492	-0.1885
0.080	64.068	9×10^{-6}	0.1977	2×10^{-6}	64.206	-0.1986
0.100	73.542	9×10^{-6}	0.2219	2×10^{-6}	73.68	-0.2229
0.200	89.559	9×10^{-6}	0.2361	2×10^{-6}	89.697	-0.2371
0.400	93.312	9×10^{-6}	0.1684	2×10^{-6}	93.45	-0.1693
0.600	98.255	9×10^{-6}	0.1062	2×10^{-6}	98.393	-0.1071
0.800	130.02	9×10^{-6}	0.1322	2×10^{-6}	130.15	-0.1332
1.000	117.8	9×10^{-6}	0.0073	2×10^{-6}	117.93	-0.0082

rather than on the PVP–PVP interactions that affect the net change in the latter values, although, with addition of PVP, both PVP–water and PVP–PVP interactions are enhanced. The contribution of PVP–PVP interactions to net change in $(\partial\Delta H/\partial T)_{P,c}$ and $(\partial\Delta S/\partial T)_{P,c}$ values may probably be compensated by conformational energy changes.

CONCLUSIONS

Viscometric behavior of extremely to moderately dilute aqueous solutions of PVP was determined. PVP shows typical polyelectrolyte behavior in extremely dilute solutions. The intrinsic viscosities, obtained from Jones–Dole, Fuoss, and Fedors equations, were found to be approximately the same only for moderately dilute solutions but, for extremely dilute solutions they vary from temperature to temperature. It is concluded that these equations give good results for solutions having concentrations $> 0.10 \text{ g dL}^{-1}$. For extremely dilute solutions they would need some modifications. Thermodynamic functions of viscous flow were obtained from flow velocity. The $(\partial\Delta H/\partial T)_{P,c}$ and $(\partial\Delta S/\partial T)_{P,c}$ values were found to be constant, whereas $(\partial\Delta G/\partial T)_{P,c}$ was negative and varied from concentration to concentration, showing an ease of spontaneity of flow with temperature. The decrease in $\partial\Delta S^0$ with concentration proves the overlapping of PVP chains, which might be attributable to stronger PVP–PVP interactions in moderately dilute solutions.

References

1. McCormick, C. L.; Middleton, J. C.; Cummins, D. F. *Macromolecules* 1992, 25, 1201.
2. Renoux, D.; Selb, J.; Candau, F. *Prog Colloid Polym Sci* 1994, 97, 213.
3. Hwang, F. S.; Hogen-Esch, T. E. *Macromolecules* 1995, 28, 3328.
4. Volpert, E.; Selb, J.; Candau, F. *Macromolecules* 1996, 29, 1452.
5. Wang, G.-J.; Engberts, J. B. F. N. *Eur Polym Mater* 1995, 31, 409.
6. Dragan, S.; Ghimici, L. *Polymer* 2001, 42, 2887.
7. Ohtani, N.; Inoue, Y.; Kanero, Y.; Okumara, S. *J Polym Sci Polym Chem Ed* 1995, 33, 2449.
8. Ise, N. *Proc Jpn Acad* 1998, 74, 192.
9. Lozano, M.; Blanco, M. D.; Lozano, R.; Muniz, E.; Teijon, J. M. *Eur Polym Mater* 1997, 33, 391.
10. Kamenka, N.; Zana, R. *J Colloid Interface Sci* 1997, 188, 130.
11. Guner, A.; Ataman, M. *Polym Int* 1997, 44, 30.
12. Bury, R.; Desmazieres, B.; Treiner, C. *Colloids Surf A Physicochem Eng Aspects* 1997, 127, 113.
13. Sen, M.; Kantoglu, O.; Guven, O. *Polymer* 1999, 40, 913.
14. Wu, H.-D.; Wu, I.-D.; Chang, F.-C. *Polymer* 2001, 42, 555.
15. Levitt, B. P., Ed. *Findlay's Practical Physical Chemistry*; Longman: New York, 1973.
16. Fuoss, R. M.; Strauss, U. P. *J Polym Sci* 1948, 3, 246.
17. Fedors, R. F. *Polymer* 1979, 20, 225.
18. Rao, M. V. S. *Polymer* 1993, 34, 592.
19. Ghimici, L.; Popescu, F. *Eur Polym Mater* 1998, 34, 13.
20. Maeda, Y.; Kitano, H. *Spectrochim Acta Part A* 1995, 51, 2433.
21. Ikada, Y. Preprint: Seminar on Polymers and Water; Society of Polymer Science: Tokyo, Japan, 1980.
22. Murase, N.; Gonda, K.; Watanabe, T. *J Phys Chem* 1986, 90, 5420.
23. Katayama, S.; Fujiwara, S. *J Am Chem Soc* 1979, 101, 4485.
24. Kubota, K.; Fujishige, S.; Ando, I. *J Phys Chem* 1990, 94, 5154.