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Effect of Electrolyte Concentration on Viscous Flow of Polymer Solutions

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The viscosity of potassium chloride in a mixture of poly(vinyl alcohol) and water (1.0 g·L^{-1} to 5.0 g·L^{-1}) was measured at different concentrations of the solute (1.0 × 10^{-2} to 9.0 × 10^{-2}) mol·dm^{-3}at various temperatures ranging from 303 K to 323 K at intervals of 5 K. Ionic interactions in terms of Jones−Dole coefficients *A* and *B* were interpreted as a function of salt concentration, polymer concentration, and temperature. The negative values of the *B*-coefficient led to the conclusion that potassium chloride solution in aqueous polyvinyl alcohol behaves as a structure maker.

Introduction

Poly(vinyl alcohol) is an industrially important polymer, and this is shown by the fact that its production increases every year.[1−5] It exhibits a high degree of compatibility with inorganic salt solutions,[6] natural and synthetic resins, and other chemicals.[7,8] Small amounts effectively stabilize emulsions,[9] dispersions, and suspensions.[10] It also forms chemical complexes of practical importance.[11] The intrinsic viscosity [η], a measure of the size of the isolated molecules, and Huggin's constant K_H,[12] a measure of their interactions with solvent, are both influenced by changes of solvent power[13] and temperature.[14] Besides theoretical interest, such measurements are also important for technical reasons such as polymer addition in motor oil recovery. Advances in the preparation of stereoregular polymers have stimulated the need to characterize their microtacticity and fine structure.[15]

A number of studies and experimental techniques were used to characterize the nature of polymers in different solvents, but there seems to be few systematic studies of the dilute solution properties in different solvents, restricted to one or two temperatures.[16,17] As far as the polymers are concerned, the viscosity method can be successfully employed for the determination of the nature of the compound and their behavior in different solvents. Viscosity is affected by a number of parameters such as molecular mass, shape, and size of molecules, concentration, temperature, and intermolecular attractions, that is, ion−ion and ion−solvent interactions.[6,18] Ahmed et al., Takada et al., and Wang et al.[19−21] studied the thermodynamics of supermolecular order of the polymer poly(vinyl alcohol) (PVOH) in aqueous solutions by the viscometric behavior and light scattering studies.[20,21] Khan et al., Lu et al., and Aggour et al.[5,22,23] studied the photodegradation of poly(vinyl alcohol) in air. Solution properties of polymers in the region of extreme dilution are of great importance both theoretically and experimentally. The quality of the solvent is important particularly both for processing of polymers and during the service of the articles made from them. The effect of the electrolytic nature of the solvent is much more pronounced, showing interaction of polymer with the salt molecules.[6] The effect of the electrolyte on the flow process of the solvent can be explained in terms of Jones−Dole coefficients:[18]

$$\eta/\eta_0 = 1 + AC^{1/2} + BC \qquad (1)$$

where *A* and *B* represent ion−ion and ion−solvent interactions, respectively, and *C* is the molar concentration. The theory of ion−ion interaction is based on a hypothetical model which can be pictured sharply for ions in the solution. In solution each ion is associated with a spherically symmetric ionic cloud of opposite charge sharing forces. The forces are generated under an applied linear velocity gradient and cause the ionic cloud to deform from a spherical to an ellipsoidal form. The opposing forces of electrostatic interaction and thermal agitation tend to restore the more stable equilibrium distribution, and there is a finite "time of relaxation" for this purpose. The *B*-coefficient of the Jones−Dole equation is a better measure of the interaction of the added electrolyte.[18] The present study concerns the effect of potassium chloride on the viscosity of poly(vinyl alcohol) (PVOH) as a function of electrolyte concentration, polymer concentration, and temperature.

Experimental Section

All the glassware used were of Pyrex A grade quality. Poly(vinyl alcohol) (PVOH; <98% from Merck) was used without further purification. A stock solution of poly(vinyl alcohol) was prepared by taking 1.0 g of polymer in a known volume of hot (80 ± 0.1) °C doubled distilled water having a conductivity of 0.06 μS/cm. The solution was constantly stirred in the thermostatic water bath. When a clear solution was formed, the solution was cooled to room temperature and made up to the mark of 100 mL. Different compositions ranging from (1.0 to 5.0) g·L^{-1} were prepared. The concentration of electrolyte (potassium chloride) in poly(vinyl alcohol) solvent was varied in the range (1 × 10^{-2} to 9 × 10^{-2} ± 0.001) mol·dm^{-3}.

Relative viscosities were measured with an Ostwald viscometer type Techniconominal constant 0.1 cycles per second (Cs/S) capillary ASTMD 445. The viscometer was placed inside a glass tube connected with a thermostatic water bath (type VWP Scientific, model 1120, SER 9143791) having a constant circulation of water throughout the

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Table 1. Viscosities of Potassium Chloride in Polyvinyl Alcohol (1.0 to 5.0 g·L^{-1}) at Various Temperatures (303 K to 323 K)

	η/m·Pa·s				
[PVOH]/g·L^{-1}	303 K	308 K	313 K	318 K	323 K
		$C_{KCl} = 1 \times 10^{-2}$ mol·dm^{-3}			
1.0	8.214 ± 0.004	7.610 ± 0.002	6.762 ± 0.002	5.926 ± 0.001	5.848 ± 0.001
2.0	9.301 ± 0.002	8.372 ± 0.004	7.450 ± 0.002	7.056 ± 0.002	6.249 ± 0.001
3.0	9.777 ± 0.003	8.909 ± 0.001	8.096 ± 0.004	7.454 ± 0.001	9.576 ± 0.004
4.0	10.409 ± 0.001	9.526 ± 0.004	8.736 ± 0.004	7.612 ± 0.002	7.175 ± 0.004
5.0	11.087 ± 0.003	10.064 ± 0.004	9.259 ± 0.001	8.199 ± 0.004	7.030 ± 0.002
		$C_{KCl} = 3 \times 10^{-2}$ mol·dm^{-3}			
1.0	8.490 ± 0.001	7.607 ± 0.001	6.868 ± 0.002	5.861 ± 0.002	5.753 ± 0.001
2.0	9.248 ± 0.001	8.155 ± 0.001	7.417 ± 0.004	7.067 ± 0.001	6.367 ± 0.001
3.0	10.292 ± 0.002	9.236 ± 0.004	8.128 ± 0.001	7.437 ± 0.002	6.602 ± 0.002
4.0	10.810 ± 0.001	9.510 ± 0.003	8.728 ± 0.001	7.506 ± 0.001	7.121 ± 0.001
5.0	11.196 ± 0.004	10.091 ± 0.001	9.393 ± 0.002	8.500 ± 0.001	7.048 ± 0.001
		$C_{KCl} = 5 \times 10^{-2}$ mol·dm^{-3}			
1.0	8.413 ± 0.001	7.694 ± 0.001	6.905 ± 0.004	5.832 ± 0.001	5.705 ± 0.002
2.0	9.294 ± 0.003	8.247 ± 0.002	7.319 ± 0.002	6.894 ± 0.003	6.368 ± 0.001
3.0	9.916 ± 0.002	8.932 ± 0.004	8.057 ± 0.003	7.358 ± 0.001	6.551 ± 0.003
4.0	10.629 ± 0.001	9.745 ± 0.001	8.652 ± 0.001	7.490 ± 0.001	7.111 ± 0.002
5.0	11.444 ± 0.004	10.175 ± 0.002	9.278 ± 0.003	8.329 ± 0.002	6.961 ± 0.002
		$C_{KCl} = 7 \times 10^{-2}$ mol·dm^{-3}			
1.0	8.405 ± 0.003	7.687 ± 0.001	7.061 ± 0.001	5.829 ± 0.001	5.652 ± 0.002
2.0	9.308 ± 0.001	8.142 ± 0.002	7.183 ± 0.003	6.837 ± 0.001	6.309 ± 0.001
3.0	10.06 ± 0.001	8.919 ± 0.002	8.094 ± 0.001	7.308 ± 0.002	6.680 ± 0.001
4.0	10.952 ± 0.002	9.603 ± 0.002	8.833 ± 0.001	7.568 ± 0.002	7.061 ± 0.001
5.0	11.649 ± 0.001	10.248 ± 0.002	9.281 ± 0.003	8.812 ± 0.001	6.842 ± 0.002
		$C_{KCl} = 9 \times 10^{-2}$ mol·dm^{-3}			
1.0	7.963 ± 0.002	7.773 ± 0.003	6.531 ± 0.003	5.815 ± 0.001	5.646 ± 0.001
2.0	9.289 ± 0.001	8.165 ± 0.004	7.015 ± 0.001	6.947 ± 0.003	6.266 ± 0.003
3.0	10.072 ± 0.002	8.943 ± 0.002	7.913 ± 0.004	7.268 ± 0.002	6.552 ± 0.002
4.0	10.941 ± 0.001	9.619 ± 0.002	8.963 ± 0.003	7.748 ± 0.002	7.019 ± 0.001
5.0	11.850 ± 0.001	10.464 ± 0.004	7.249 ± 0.001	8.602 ± 0.001	6.927 ± 0.002

course of the experiment. The temperature of the water bath was kept constant with the help of a temperature control device type Haake Delab instrument (Elektro Laboratoriet, Copenhagen) within ±0.1 °C. Continuous circulation of water in the glass tube maintained the solution temperature constant. A known volume of solvent and solution, respectively, was placed in the viscometer for at least 15 min to attain the required temperature. The time flow between the two marks of the viscometer was recorded with the help of stopwatch and was always at least 0.25 s. Densities of solvent and solutions were measured with the help of a relative density bottle having a capacity of 10 mL at different temperatures. Temperature was kept constant by keeping the solutions in a thermostatic water bath for at least 15 min. The reproducibility of the results was checked by repeating the measurement three times. The uncertainty in the experimental data for density and viscosity data was found to be ±0.001 g·mL^{-1} and ±0.002 mPa·s, respectively.

Result and Discussion

The viscosities of potassium chloride solutions in poly(vinyl alcohol)s were measured at different temperatures and different concentrations. From these data the relative, specific, and reduced viscosities were calculated. The viscosities are tabulated in Table 1. The results show that viscosities increase with the concentration of potassium chloride and also with percent compositions of poly(vinyl alcohol) and decrease with an increase in temperature.

The Mark–Houwink equation was used for estimation of the average molecular weight (M_ν) of the poly(vinyl alcohol) (PVOH)[24] in water at 30 °C:

$$[\eta]_{\text{int}} = kM_\nu^{\alpha} \tag{2}$$

where $[\eta]_{\text{int}}$ is intrinsic viscosity, M_ν is average molecular weight, and k and α are empirical constants characteristic of a polymer pair. The values of k and α for the poly(vinyl alcohol) at 30 °C are 33.88×10^{-5} and 0.716, respectively. Thus, the relation becomes

$$[\eta]_{\text{int}} = (33.88 \times 10^{-5})M_\nu^{0.716} \tag{3}$$

$[\eta]_{\text{int}}$ can be obtained by Huggin's equation:

$$\lim_{c\to 0} \eta_{\text{sp}}/C = [\eta]_{\text{int}} \tag{4}$$

where η_{sp} is the specific viscosity given by

$$\eta_{\text{rel}} - 1 = \eta_{\text{sp}}\,(\text{dimensionless}) \tag{5}$$

as η_{rel} is the relative viscosity obtained by

$$\eta_{\text{rel}} = \eta/\eta_0\,(\text{dimensionless}) \tag{6}$$

where η and η_0 are the viscosities of solution and solvent, respectively.

The plots of η_{sp}/C against C at fixed temperature are straight lines, with the intercept showing the value of $[\eta]_{\text{int}}$, and the average molecular weight thus found was approximately 34588 Da. A representative plot of η_{sp}/C versus C is shown in Figure 1.

The values of ion–ion and ion–solvent interactions in terms of Jones–Dole coefficients A and B were determined for potassium chloride solutions at different temperatures and concentrations of polymer and are tabulated in Table 2. The values of the A- and B-coefficients were determined from the intercept and slope of the linear plots of $\eta_{\text{sp}}/\sqrt{C}$ against square root of the potassium chloride concentration. A representative plot of $\eta_{\text{sp}}/\sqrt{C}$ versus square root of

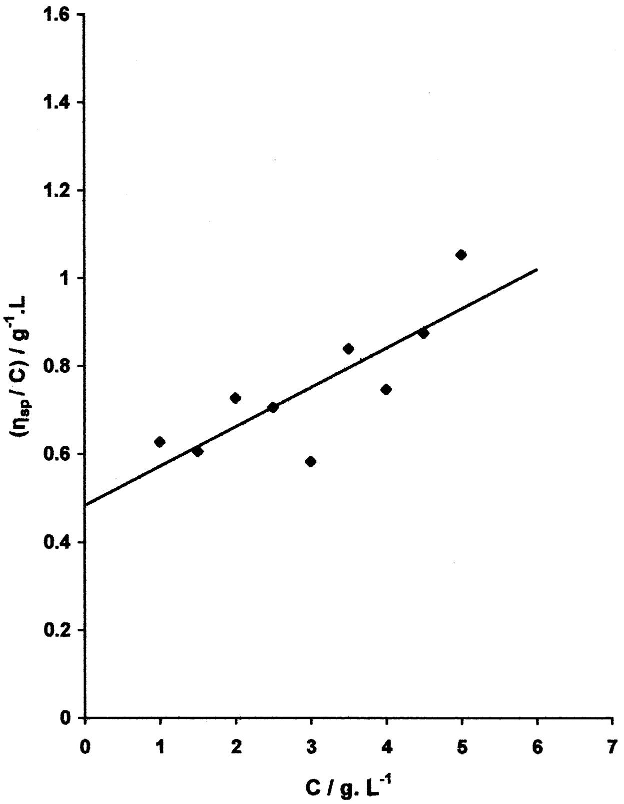

Figure 1. Plot of η_{sp}/C versus concentration for PVOH at 318 K.

Table 2. Values of Ionic Interactions of Potassium Chloride in Terms of Jones−Dole Coefficients *A* and *B* at Various Temperatures in 2.0 and 5.0 g·L^{-1} Polyvinyl Alcohol

	A and *B* coefficients of Jones−Dole equation	
T/K	[PVOH] = 2.0 g·L^{-1}	[PVOH] = 5.0 g·L^{-1}
	A/mol$^{-1/2}$·dm$^{3/2}$	
303	−0.187 ± 0.003	−0.026 ± 0.004
308	0.348 ± 0.002	−0.212 ± 0.003
313	0.467 ± 0.003	−0.265 ± 0.002
318	0.631 ± 0.001	0.367 ± 0.003
323	0.900 ± 0.001	−0.056 ± 0.004
	B/mol^{-1}·dm^{3}	
303	0.046 ± 0.002	1.000 ± 0.002
308	−1.279 ± 0.001	0.909 ± 0.001
313	−1.875 ± 0.002	0.697 ± 0.003
318	−2.032 ± 0.002	0.677 ± 0.003
323	−2.330 ± 0.001	0.829 ± 0.001

concentration of KCl for 5.0 (g·L^{-1}) PVOH and 303 K is shown in Figure 2. The negative values of the *A*-coefficient at higher concentration of poly(vinyl alcohol) show that the polymer association to water is stronger as compared to solvent interaction with ions, while at lower concentration of poly(vinyl alcohol) there were observed some ion−solvent interactions between salt and aqueous poly(vinyl alcohol). The value of the *A*-coefficient increases as the temperature increases. However, the interpenetration effect (cation−cation) and (cation−anion), which also brings ions together, may be responsible for the increase. The *B*-coefficient can be discussed in terms of factors affecting the viscosity at a particular concentration of salt and temperature:[3]

$$\eta^{E} + \eta^{A} + \eta^{D} = \eta^{o}BC \tag{7}$$

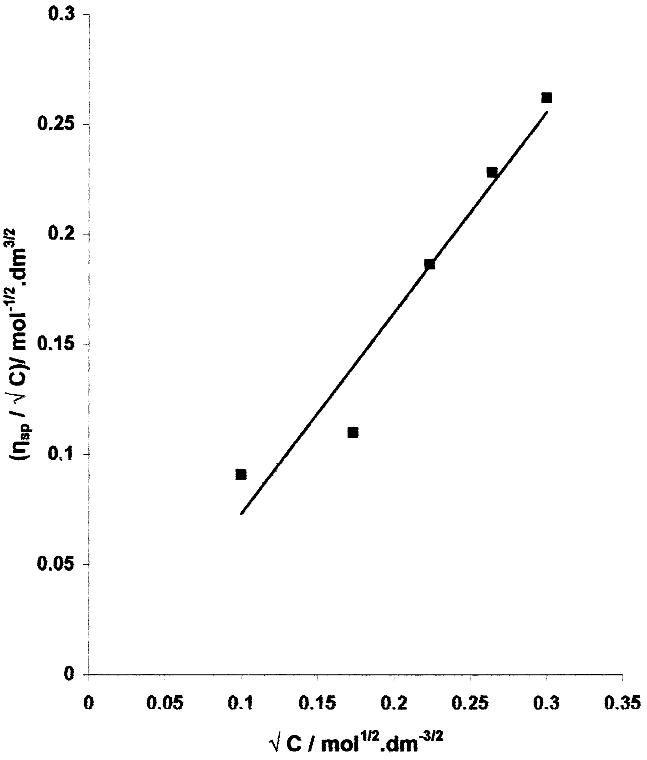

Figure 2. Plot of $\eta_{sp}/\sqrt{C}$ versus square root of concentration for KCl in 5.0 g·L^{-1} PVOH at 303 K.

where η^{E} is the positive increase in viscosity due to the shape and size of an ion, η^{A} is the increase due to alignment or orientation of the polar molecules by the ionic field, η^{D} is the decrease in viscosity arising due to the distortion of solvent structure by the ions, and η^{o} is the viscosity for the solvent. Potassium ion, having a high charge density, strongly orients solvent molecules, making a sheath of firmly attached layers. The positive and larger value of the *B*-coefficient may be attributed to the strong association between water and poly(vinyl alcohol) through multiple hydrogen bonding. Thus, the solvated ions would lead to larger values of η^{E} and η^{A}.

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