

The Effect of Urea on Volumetric and Viscometric Properties of Aqueous Solutions of Poly(ethylene oxide)

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The density and the viscosity of aqueous PEO solutions are observed with the several concentrations of PEO at 20 °C. The effects of urea on them are also observed. The apparent and the partial specific volumes of PEO are calculated from the density data, which result that the polymer-polymer interaction is dominating in the binary aqueous PEO solutions, while the polymer-solvent interaction is dominating in the ternary aqueous urea-PEO solutions. It is explained by the urea induced breakage of the structured water originated from the hydrophobic interactions and the binding of the urea to the PEO chain. The concentration dependence of relative viscosity and the density dependence of fluidity is also discussed with the concept of the polymer-solvent and the polymer-polymer interactions of aqueous urea-PEO solutions.

Introduction

Poly(ethylene oxide) (PEO) is a well-known polymer, and its high solubility in water makes it a very interesting industrial material.^{1,2} The repeating unit of the polymer is $-\text{CH}_2-\text{CH}_2-\text{O}-$, in which hydrophilic oxygens are separated by hydrophobic ethylene units. The amphoteric character of the polymer is reflected by the fact that organic solvents as well as water are able to solvate PEO.

PEO is known to be crystalline and to have a 7_2 -helical conformation in the solid state.³ Most of the experimental results on PEO solutions lead to the conclusion that the polymer is in its disordered or coiled form in organic solvents.^{4,5} However, the situation is not so straightforward and many singular behaviours are observed when water is used as solvent.^{6,7}

In the PEO/water system, the hydrophobic character of the chain manifest itself in a number of ways. As long as the polymer chains are not too short ($N > 50$), the solution shows a lower critical solution temperature.^{8,9} Furthermore, PEO has a low partial molar volume, and a negative entropy change is recorded upon addition of PEO to water.¹⁰ These phenomena are thought to be interrelated, and are primarily due to the reduction in entropy of the water at the hydrophobic interface. This is commonly referred to as the hydrophobic hydration.¹¹ Some experimental results indicate that PEO in aqueous solutions retains some of its crystalline structure and its helical structure changes to a new, less ordered but not completely disordered one.⁴ The result of a viscometric study shows that the PEO chain adopts a more compact conformation as the temperature increases.¹² This is probably due to a weakening of polymer-solvent interactions, leading to a chain contraction by the hydrophobic interactions between the intrachain hydrophobic groups, the ethylene units.

On the other hand, urea is known to increase the solubility of aliphatic and aromatic amino acids and nucleotides.¹³ It may be due to the specific interactions of the solutes with urea or may be due to the effect of urea on the structure of water. This speculation has been made the suggestion that the addition of urea causes a breakdown and/or alteration in

the water structure.¹⁴ It is believed that the alteration of the water structure could causes disruption of hydrophobic bonds in proteins and results in denaturation.¹⁴ Such alteration also would occur in the water structure around the PEO chain, and the study on the effects of the urea on the properties of aqueous PEO solution could offer additional information about the characteristics of solute-solute and solute-solvent interactions within aqueous PEO solutions.

In order to elucidate the structural interactions (*i.e.*, solute-solute, solute-solvent, and solvent-solvent) occurring in solutions, the apparent and the partial specific volumes in dilute aqueous solutions have been applied and used extensively by many researchers.^{15,16}

In this work, we present the results of an exploratory study for the effects of the concentration of urea on aqueous PEO by the measurements of the apparent specific volume and the viscosity. The conformational behavior of PEO and the structural interactions within aqueous PEO solutions will be discussed.

Experimental

Materials. PEO was obtained from Aldrich Chemical Co. with average molecular weight of 1.0×10^5 . The urea of A.C.S. reagent grade was also received from Aldrich Co. Freshly distilled deionized water was used as solvents. 1 M and 4 M aqueous urea solutions were always prepared just prior to use. Twelve concentrations (ranging from 0 to 0.02 mass fractions) of aqueous PEO solutions were prepared by weighing at room temperature.

Density Measurements. The density of solutions was determined with an oscillating tube densimeter (Anton Paar, DMA 60) operated in a phase-locked loop mode using two measuring cells (DMA 602). The precision of the measurements was found to be better than 2×10^{-6} g/cm³. The temperature was maintained at 20 °C within 0.01 °C by using a closed loop temperature controller (Model 9510, Polyscience Co.). The densities (d) of solutions are related to the period (τ) of the oscillating tube through the equation

$$d - d_0 = A(\tau^2 - \tau_0^2), \quad (1)$$

where d_0 and τ_0 are the density and the period of the solvent (water), respectively. The calibration constant, A , was obtained by measuring τ for water ($d=0.998207 \text{ g/cm}^3$)¹⁷ and for air ($d=0.001205 \text{ g/cm}^3$).¹⁷ The densities of the ternary systems (PEO in aqueous urea solutions) were determined at a fixed urea concentrations (1 M and 4 M) as a function of the PEO concentrations. The apparent specific volumes (ϕ_{sp}) of PEO in water and aqueous urea solutions were calculated by using the following equation^{16,18}

$$\phi_{sp} = \frac{1}{d} - \frac{(1-w_2)(d-d_0)}{w_2 d d_0}, \quad (2)$$

where w_2 is the mass fraction of PEO in solution. d and d_0 are the densities of solution and water, respectively.

Viscosity Measurements. The viscosity measurements were performed at $20 \pm 0.01 \text{ }^\circ\text{C}$ using an automatic viscosity measuring system (Model AVS 440, Schott Gerate GmbH) with an Ubbelohde capillary viscometer (Model 52601, capillary i.d.=0.46 mm, Schott Gerate GmbH). No kinetic energy corrections were necessary. The viscosities of aqueous PEO solutions were calculated by using the following equation¹⁹

$$\frac{\eta}{\eta_0} = \frac{d t}{d_0 t_0}, \quad (3)$$

where η and η_0 are the viscosities of solution and water ($\eta_0=1.002 \text{ cp}$ at $20 \text{ }^\circ\text{C}$),¹⁷ respectively. t and t_0 are the flow times (through the capillary) of solution and water, respectively.

Results and Discussion

The densities of aqueous PEO solutions and the apparent specific volumes of PEO for twelve different mass fractions of PEO in water and two different aqueous urea solutions are collected in Table 1. The plots of densities vs. mass fractions of PEO is presented in Figure 1. The densities of solutions increase slightly and linearly as the mass fractions of PEO increase.

The apparent specific volumes of PEO vs. mass fractions

of PEO in water and aqueous urea solutions are plotted in Figure 2. The partial specific volumes of solutes at infinite dilution in water are thermodynamic properties which have been utilized successfully by many authors to obtain information about solute-solvent interactions.^{15,16,20} The partial specific volumes of PEO at infinite dilution are obtained from the intercepts of the corresponding apparent specific volume in the more dilute regions (linear region) among the investigated concentrations of PEO. (The linear relationship of the thermodynamic properties of solutes vs. the solute concentrations is not usually obeyed as the concentration of solute increase large.) The higher value of

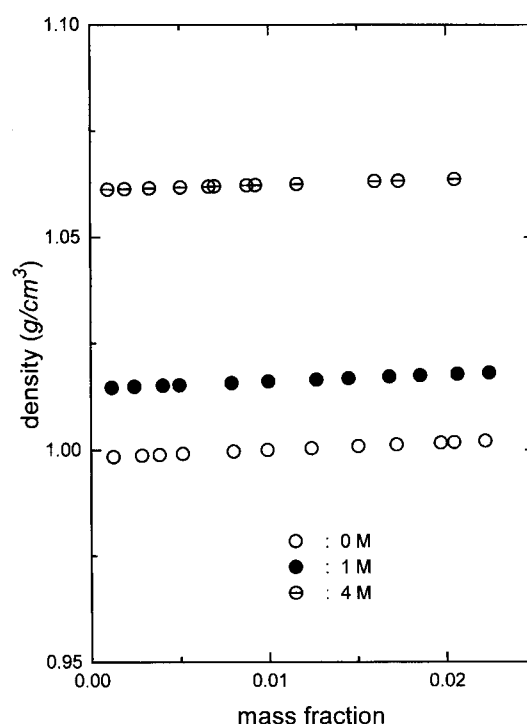


Figure 1. Densities of aqueous PEO solutions as a function of PEO concentration in 0, 1, and 4 M aqueous urea solutions.

Table 1. The densities of aqueous PEO solutions and the apparent specific volumes of PEO for twelve different mass fractions of PEO in water and aqueous urea solutions (0, 1, and 4 M)

0 M			1 M			4 M		
w_2^a	d^b	ϕ_{sp}^c	w_2	d	ϕ_{sp}	w_2	d	ϕ_{sp}
0	0.99821		0	1.01441		0	1.06111	
0.00126	0.99844	0.81721	0.00117	1.01460	0.84568	0.00098	1.06124	0.52621
0.00286	0.99873	0.81754	0.00244	1.01483	0.82884	0.00193	1.06136	0.82918
0.00384	0.99891	0.81761	0.00403	1.01510	0.82893	0.00331	1.06154	0.82600
0.00514	0.99915	0.81797	0.00496	1.01520	0.82923	0.00504	1.06176	0.82720
0.00800	0.99967	0.81847	0.00789	1.01570	0.82704	0.00664	1.06196	0.82814
0.00991	1.00002	0.81877	0.00997	1.01610	0.82801	0.00695	1.06202	0.82658
0.01240	1.00045	0.82109	0.01268	1.01652	0.82653	0.00877	1.06223	0.82895
0.01504	1.00091	0.82226	0.01449	1.01682	0.82628	0.00927	1.06228	0.83048
0.01720	1.00130	0.82212	0.01680	1.01720	0.82628	0.01160	1.06255	0.83251
0.01970	1.00171	0.82420	0.01854	1.01749	0.82631	0.01599	1.06325	0.82393
0.02044	1.00184	0.82430	0.02063	1.01784	0.82608	0.01733	1.06329	0.83096
0.02219	1.00214	0.82469	0.02242	1.01812	0.82687	0.02049	1.06369	0.83078

^{a,b,} and ^c mean the mass fractions of PEO in solvent, density of aqueous PEO solutions (g cm^{-3}), and apparent specific volume of PEO in solvent ($\text{cm}^3 \text{ g}^{-1}$), respectively.

the partial specific volume of the solute indicates the larger occupied volume space per unit mass due to the solute-solvent interactions. The intercepts are 0.817, 0.829, and 0.833 cm^3/g for water, 1 M, and 4 M aqueous urea solutions, respectively, which show that the stronger PEO-solvent (water, 1 M, and 4 M aqueous urea solutions) interactions appear as the urea is added. As the urea is added to the aqueous PEO solutions, the structured water around the hydrophobic sites of PEO is destroyed and the interactions between the polymer and aqueous urea solution is favored,^{7,21-24} which promote the chain extension and increase the occupied volume of the PEO chain due to the attraction of urea to the polymer chain. This phenomena may be explained by the binding of urea²⁵ to the PEO chain through the breakage of the structured water that hinders the solvent binding to PEO.

It has been ascertained that the concentration dependence of the apparent specific volume is to be ascribed to the solute-solute interactions.¹⁸ The dependences of the apparent specific volume on the mass fraction of PEO are examined for aqueous urea solutions with different urea concentrations, and the results are shown in Figure 2. When the mass fraction is less than 0.01, the dependence shows good linearity, and the slopes are calculated to be 0.183, -0.297 , and -0.575 for 0 M (water), 1 M, and 4 M aqueous urea solutions, respectively. The slope characterizes pair interactions between molecules of the dissolved compounds in solution.^{16,18} In aqueous solutions it is directly related to the so-called "hydrophobic interactions" between solutes.^{16,18} The positive slope for PEO in water mean that the intermolecular hydrophobic interaction between polymers is increased while the intramolecular hydrophobic interaction inducing the chain contraction is decreased. The result is the

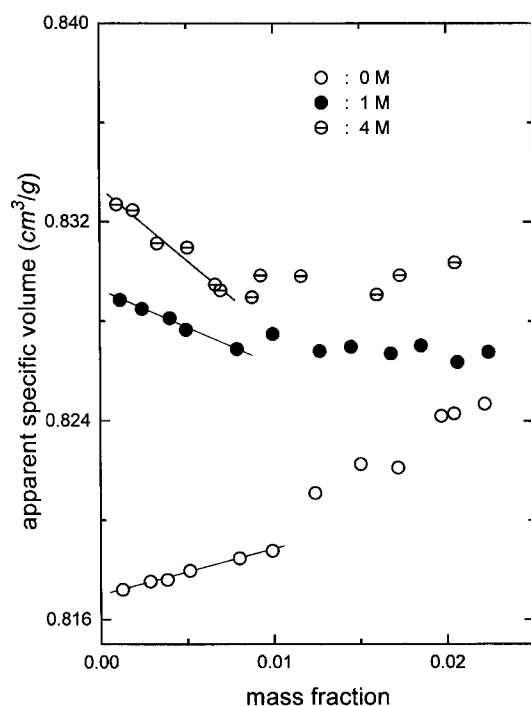


Figure 2. Apparent specific volume of aqueous PEO solutions as a function of PEO concentration in 0, 1, and 4 M aqueous urea solutions.

increase in the occupied volume space per unit mass with the increase in PEO concentration. As the urea is added to make the aqueous urea solution, solvent can bind to the polymer chain *via* the favorable polymer-solvent interactions²⁵ and the extent of interactions between the polymers can be decreased with the increase in the amounts of PEO, which promotes the PEO chain to be coiled in a small volume space. This phenomenon is resulted by the negative concentration dependence of the apparent specific volume (decreasing the occupied volume space per unit mass of PEO) and more pronounced with the increase in urea concentration.

The viscosity is a measure of the hydrodynamic volume of the macromolecules dissolved in solvents.^{26,27} Table 2 reports the viscosities of aqueous PEO solutions for some mass fractions of PEO in 0, 1, 4 M aqueous urea solutions, with the aid of above obtainable density data. The viscosity is also increased with the increase in concentration of PEO. To see the tendency of them, the relative viscosities of aqueous PEO solutions to that of solvent (water, and 1 and 4 M aqueous urea solutions) are plotted against the mass fractions of PEO in Figure 3. The increase in relative viscosity is pronounced for 4 M aqueous urea solutions, which can be explained by the increase in polymer-solvent interactions.

The liquid solutions can flow freely and quickly as the dissolved solutes are diminished, *i.e.*, the density of the solution affects the fluidity of the solution. The property that characterizes a fluid's resistance to flow is its viscosity.²⁷ The reciprocal viscosity ($1/\eta$) is fluidity.²⁸ So the study of the density dependence of the fluidity in terms of the concept of the solute-solvent and solute-solute interactions as the variation of the added amounts of urea is meaningful. They are plotted in Figure 4 and the results are interesting. The density is increased with the gradual addition of PEO to the solvent and makes the solution dense, which can be observed in Figure 1. The density dependence of the fluidity of aqueous PEO solutions are different from that of ternary aqueous urea-PEO solutions. The former and the latter have

Table 2. The viscosities of aqueous PEO solutions for some mass fractions of PEO in 0, 1, and 4 M aqueous urea solutions

0 M		1 M		4 M	
w_2^a	η^b	w_2	η	w_2	η
0	1.0020	0	1.0394	0	1.2110
0.00225	1.2345	0.00117	1.1655	0.00098	1.3524
0.00316	1.3265	0.00244	1.3174	0.00193	1.4932
0.00398	1.4340	0.00403	1.5085	0.00331	1.7296
0.00516	1.5703	0.00496	1.6360	0.00504	2.0303
0.00774	1.9359	0.00789	2.0830	0.00664	2.3461
0.01054	2.3420	0.00997	2.4093	0.00695	2.4083
0.01316	2.7832	0.01268	2.9194	0.00877	2.8129
0.01510	3.1442	0.01449	3.2959	0.00927	2.9390
		0.01680	3.8148	0.01160	3.4987
		0.01854	4.2077	0.01599	4.7081
		0.02063	4.7381	0.01733	5.1425
				0.02049	6.2739

^a and ^b are the mass fractions of PEO in solvent and the viscosity (cp) of aqueous PEO solutions, respectively.

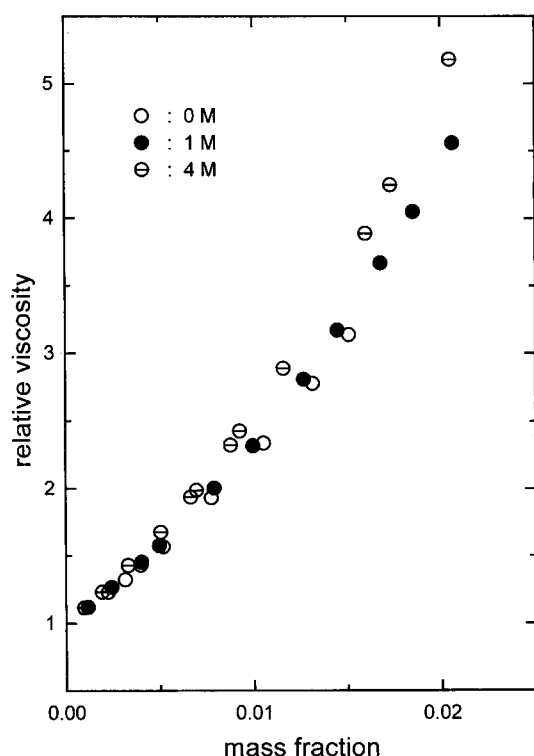


Figure 3. Relative viscosities of aqueous PEO solutions as a function of PEO concentration in 0, 1, and 4 M aqueous urea solutions.

a slight positive and negative density dependence, respectively. The negative dependence of the latter can be explained in a general way that the fluid can not be flow readily (lower value of fluidity) with the increase in density, which are observed in 1 M and 4 M aqueous urea solutions. But the positive dependence is observed in the case of aqueous PEO solutions with no urea, *i.e.*, the solution can flow easily in spite of the increase in the solution density. This phenomenon can be explained by the fact that the PEO chain itself may have the larger occupied volume space by the larger inter-molecular hydrophobic interactions (*i.e.*, solute-solute interactions) with the increase in the PEO concentrations, which is consistent in the above explained density results. The aqueous PEO solutions may have the conformation of the loose PEO chains with the compacted water as the increase in the amounts of PEO. The addition of urea breaks the structured water that promotes the intramolecular hydrophobic interactions,^{21,24} favors the polymer-solvent interactions and decrease the occupied volume space per unit mass of PEO, and makes the solution's fluidity difficult.

Conclusions

The density and the viscosity measurements of aqueous PEO solutions in 0, 1, and 4 M aqueous urea solutions with the variation of the amounts of PEO are performed at 20 °C. The results are that one PEO chain in water may be compacted and has smaller occupied volume by the intramolecular hydrophobic interactions. As the amounts of PEO is increased, the larger solute-solute interactions, *i.e.*,

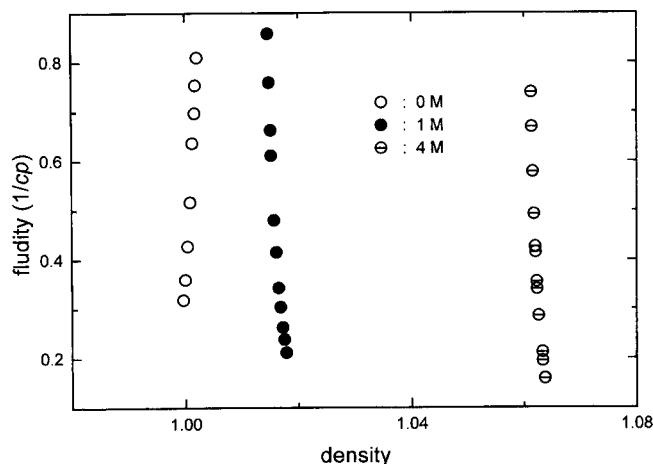


Figure 4. Dependence of fluidity on density of aqueous PEO solutions as a function of PEO concentration in 0, 1, and 4 M aqueous urea solutions.

intermolecular hydrophobic interactions between polymers may be appeared and the occupied volume space of PEO is increased, which is resulted from the positive slopes of the concentration dependence of the apparent specific volume. This phenomena is also supported by the positive density dependence of the fluidity, *i.e.*, the solution can flow easily through the solvent medium with the loosely occupied PEO chain. On the other hand, one PEO chain in aqueous urea solutions may be extended and has larger occupied volume space by the breakage of the structured water that hinders the water binding to PEO. As the concentrations of PEO are increased, the stronger polymer-solvent interactions are favored and the occupied volume space per unit mass of PEO is decreased with the urea binding to the PEO chain, which is the origin of the lower fluidity. This phenomena may be strengthened by the more amounts of urea.

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Aminolysis of Aryl Thiol-2-furoates and Thiol-2-thiophenates in Acetonitrile

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Aminolysis of aryl thiol-2-furoates and thiol-2-thiophenates with benzylamines are investigated in acetonitrile at 50.0 °C. Relatively large selectivity parameters, $\rho_X(\beta_X)$, $\rho_Z(\beta_Z)$ and ρ_{XZ} (> 0) together with the valid reactivity-selectivity principle are consistent with a stepwise acyl transfer mechanism with rate-limiting expulsion of the leaving group, thiophenolate anion, from the tetrahedral intermediate, T^\pm . The first-order kinetics with respect to the benzylamine concentration and the relatively large secondary kinetic isotope effect involving deuterated benzylamine nucleophiles suggest a four-center type transition state in which concurrent leaving group departure and proton transfer are involved.

Introduction

For the past ten years we have been developing the cross-interaction constants, ρ_{ij} , in eqs. 1 where i and j represent substituents in the nucleophile(X), the substrate(Y) or the leaving group(Z), as a mechanistic tool for organic reactions

$$\log(k_{ij}/k_{HH}) = \rho_i \sigma_j + \rho_j \sigma_i + \rho_{ij} \sigma_i \sigma_j \quad (1a)$$

$$\rho_{ij} = \frac{\partial \rho_j}{\partial \sigma_i} = \frac{\partial \rho_i}{\partial \sigma_j} \quad (1b)$$

in solution.¹ The following mechanistic criteria are proposed theoretically² and found experimentally³ to apply to the stepwise mechanism with rate-limiting breakdown of the leaving group in the aminolysis of esters and carbonates: (i) The signs of ρ_{XY} (> 0) and ρ_{YZ} (< 0) are opposite to those for the normal S_N2 processes or for acyl transfer with rate-limiting formation of the tetrahedral intermediate, T^\pm ($\rho_{XY} < 0$ and $\rho_{YZ} > 0$). The sign of ρ_{XZ} is always positive unlike for

the concerted S_N2 reactions for which ρ_{XZ} can be either positive or negative. (ii) The magnitude of ρ_{XY} , ρ_{YZ} and ρ_{XZ} are greater than those for the S_N2 processes. (iii) The positive ρ_{XZ} invariably leads to a valid reactivity-selectivity principle (RSP).⁴

In contrast to the aminolyses of oxyesters, **a**, their thioanalogs, **b-d**, were found to exhibit mechanistic varieties in the aminolysis reactions. For example, for the aminolysis of

