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SOLUTION PROPERTIES OF POLY(ETHYLENE OXIDE) AS DETERMINED BY VISCOMETRIC MEASUREMENTS IN AQUEOUS SALT SOLUTIONS

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ABSTRACT

The properties of dilute solutions of poly(ethylene oxide) (PEO) in aqueous salt solutions are studied by measurements of intrinsic viscosity $[\eta]$ in theta and nontheta solvents. The unperturbed dimensions in various salt solutions were found larger than those in pure water. These results are attributed to a change in the polymer hydration sheath, in the *gauche-trans* equilibrium in the PEO chain in aqueous solutions, and in the water structure because of the added salt. Also, for carboxylic anions, similar behavior is expected due to the interaction of the ether oxygens of PEO with the weak acids through hydrogen bonding. The enthalpy and entropy dilution parameters χ_H and χ_S were observed to take on negative and positive values, respectively.

INTRODUCTION

It is known that aqueous salt solutions of poly(ethylene oxide) (PEO) show lower critical solution temperatures and theta temperatures in aqueous salt solutions depending on the nature and concentration of the salt. Theta tem-

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*Deceased.

peratures for various salts have been obtained from cloud point temperatures [1-4].

The thermodynamic quantities in aqueous salt solutions have been analyzed previously for a limited number of neutral salts [3, 5]. In this study the configurational and conformational behavior of PEO molecules in aqueous salt solutions is investigated by viscometry. It is known that solubility of PEO in water is due to specific hydrogen-bond formation between the ether oxygens of PEO and water [6, 7]. The change in the enhanced water structure around the polymer caused by added salt is expected to play an important role in the solution characteristics of PEO. It is of interest to study the effect of the interaction of ions with PEO in aqueous solutions from the unperturbed point of view because the interaction could affect the *gauche* conformation around the C–C bond and the *gauche-trans* equilibrium in the PEO chain.

In the present study the viscosity behavior of PEO in aqueous salt solutions was studied at 25°C and at the theta temperature, and the thermodynamic parameters χ_H and χ_S and the unperturbed dimensions of PEO were evaluated.

THEORETICAL

In the theory of Flory and Fox [8] and of Kurata et al. [9, 10], the intrinsic viscosity $[\eta]$ is related to K_0, the molecular weight M, and the hydrodynamic expansion factor α_η by

$$[\eta] = \varphi\left(\frac{<r^2>_0}{M}\right)^{3/2} M^{1/2}\alpha_\eta{}^3 = K_0 M^{1/2}\alpha_\eta{}^3, \tag{1}$$

where φ is a universal constant, which was taken as 2.5×10^{21} [11]; and $<r^2>_0{}^{1/2}$ denotes the unperturbed root-mean-square end-to-end distance.

The characteristic ratio C_n is defined [9] by

$$C_n = <r^2>_0/\sum n_i l_i^2. \tag{2}$$

In this study the C–C and C–O bond lengths are taken as 0.153 and 0.143 nm, respectively.

The steric parameter σ is calculated from

$$\sigma^2 = (1 + \cos\theta)\langle r^2\rangle_0/(1 - \cos\theta)nl^2, \tag{3}$$

where θ is the angle between the bonds and is taken as 110°.

The linear expansion factor α has been related to χ and χ_S through the Flory-Fox [8] equations

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi)M^{1/2} \tag{3}$$

and

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi_S)\left(1 - \frac{\theta}{T}\right)M^{1/2}. \tag{5}$$

The interaction parameter χ is the sum of $\chi_H + \chi_S$, where χ_H and χ_S are the enthalpy and entropy dilution parameters, respectively.

C_M is calculated from

$$C_M = 27v_2{}^2M^{3/2}/[2NV_1\,(2\pi\langle r^2\rangle_0)^{3/2}], \tag{6}$$

where v_2 is the partial specific volume of the polymer, N is Avogadro's number, and V_1 is the molar volume of the solvent.

The parameter α is related to α_η either by equating it to α_η [9] or by using the relation

$$\alpha_\eta{}^3 = \alpha^{2.43} \tag{7}$$

given by Kurata and Yamakawa [12].

EXPERIMENTAL

The polymer (20000 S) used in this study has a narrow molecular weight distribution and was obtained from Hoechst. Its number-average molecular weight and MW distribution were determined previously [5] as $\overline{M}_n = 20\,000$ (± 700) and $\overline{M}_w/\overline{M}_n = 1.08$, respectively.

Viscosity measurements were made by using an Ubbelohde suspended-level dilution viscometer at 25°C and at the theta temperatures previously determined [2-4]. Temperatures were controlled within ±0.02°C, and the efflux times were reproducible with ±0.1% error. Kinetic energy and density corrections were applied. Densities of all solutions were determined by using a pycnometer. The effect of the shear rate was ignored since the molecular weight of the polymer was not to high.

The concentration of PEO, c, in aqueous salt solutions was changed in the range of 0.4-1.2 g/dL. $[\eta]_\Theta$ was evaluated as an average value of the intercepts of the plots of η_{sp}/c versus c [14] by the least squares method. The error in the intrinsic viscosity was not greater than ±1%.

RESULTS AND DISCUSSION

The intrinsic viscosities $[\eta]$ and Huggins constants k', α_η, and α are given in Table 1. They are calculated through

$$\alpha_\eta^3 = [\eta]/[\eta]_\Theta, \tag{8}$$

where $[\eta]$ and $[\eta]_\Theta$ are the intrinsic viscosities at 25°C and theta temperature, respectively. After determining α_η, α can be computed by means of Eq. (7).

The interaction parameter χ was calculated by knowing the excess enthalpy of dilution and excess entropy of dilution from

$$\chi - \frac{1}{2} = \chi_H - \left(\frac{1}{2} - \chi_S\right), \tag{9}$$

where χ_S is found by Eq. (5) and χ_H is determined from

$$\Theta = \chi_H T \left(\frac{1}{2} - \chi_S\right)^{-1}. \tag{10}$$

Finally, $<r^2>_0$ is found with the help of Eq. (1).

The Huggins constant k' is expected to be 0.35 in good solvents and higher in poor solvents. As can be seen from Table 1, most of the k' values found in this study are higher than the predicted range of 0.5-0.7 [15], and this is thought to be the consequence of polymer-solvent interactions. The high k' values found for solutions of formate and acetate anions may be a result of the interaction of the anion with the hydroxyl end group of the polymer and also of the interaction of the weak acid formed by the hydrolysis of the anions with ether oxygen through hydrogen bonding. Interaction of the ether oxygen of PEO with the hydroxyl end group is a well-known behavior [16]. For the

TABLE 1. Viscosity Data for Aqueous Salt Solutions of PEO

Solvent	t, °C	k'	$[\eta]$, dL/g	α	α_η
1.50 M CH_3COONa	55[a]	0.896	0.208	–	–
1.50 M CH_3COONa	25	0.563	0.289	1.145	1.116
1.50 M $HCOONa$	52[a]	0.982	0.212	–	–
1.50 M $HCOONa$	25	0.567	0.295	1.146	1.116
0.65 M NaH_2PO_4	48[a]	0.800	0.230	–	–
0.65 M NaH_2PO_4	25	0.554	0.295	1.108	1.086
2.40 M KNO_3	53[a]	0.871	0.200	–	–
2.40 M KNO_3	25	0.548	0.260	1.114	1.091
0.30 M Na_2HPO_4	45[a]	0.776	0.248	–	–
0.30 M Na_2HPO_4	25	0.561	0.294	1.073	1.058
0.30 M K_2HPO_4	48[a]	0.591	0.244	–	–
0.30 M K_2HPO_4	25	0.476	0.302	1.092	1.074
0.30 M $NaNH_4HPO_4$	52[a]	0.833	0.228	–	–
0.30 M $NaNH_4HPO_4$	25	0.492	0.309	1.133	1.107
0.40 M $Na_2S_2O_3$	52[a]	0.876	0.222	–	–
0.40 M $Na_2S_2O_3$	25	0.592	0.303	1.137	1.111
0.50 M MgS_2O_3	52[a]	0.871	0.232	–	–
0.50 M MgS_2O_3	25	0.666	0.309	1.125	1.100
0.20 M Na_3PO_4	43[a]	0.686	0.232	–	–
0.20 M Na_3PO_4	25	0.492	0.303	1.116	1.093
Water	30	0.456	0.365	–	–
Water	25	0.394	0.377	–	–

[a] Theta temperature.

salts investigated previously, k' was found to be highest for 2.4 M KCl and 2.4 M NaCl solutions, which was attributed to the binding of chloride anion to the ether oxygen of PEO [5]. The above values of k' decrease almost by half for 2.4 M KNO_3 solution, which has a similar salting-out effect on PEO in aqueous salt solutions. This supports the idea that the k' value is a consequence of polymer-solvent interaction, rather than a measure of the solvent power. Theoretical values given for k' as a measure of solvent power also vary. While Sakai [15] proposes $0.5 < k' < 0.7$ for Θ solvents, Yamakawa [17] suggests the value of 0.5. The other suggested values of 0.894 [18] and 0.754 [19] are not very far from the k_Θ' values found in this study. However, the values found in aqueous salt solutions are rather high compared to those in organic solvents.

In contrast to this increase of k' in aqoeous salt solutions, values of $[\eta]$ decrease relative to those in water. This shows that, with an increasing degree of hydrophobic interaction of ethylene segments, the intramolecular association of the coil increases and the coil contracts.

Polymer Dimensions

According to the concept of the theta state, the unperturbed dimensions should be independent of the nature of solvent. However, as seen from Table 2, the K_0 and $\langle r^2 \rangle_0{}^{1/2}$ values are scattered over quite a wide range, and they vary even in similar solvents. In aqueous salt solutions, hindrances due to the effect of salts on the hydration sheath of PEO change the rotation angle around the C–O bond, so that the chain is more rigid. Na_2HPO_4 and K_2HPO_4 give the highest K_0 values, about 1.75×10^{-3} dL/g which are within the range of the limit value of 1.8×10^{-3} dL/g proposed for aqueous solutions [20]. The K_0 values previously obtained for aqueous salt solutions scatter over a wide range, $(1.1\text{-}1.87) \times 10^{-3}$ dL/g [3, 5, 20, 21].

Conformational characteristics of PEO chains have been thoroughly investigated [22-30]. A PEO chain strongly prefers the *gauche* state about the constituent C–C bond and a *trans* conformation is preferred around the C–O bonds [6, 22-30]. Thus, the PEO chain could be expected to interact favorably with water. It is suggested [28] that an increase in the *gauche* form was observed in hydrogen-bond-forming solvents and the *gauche* arrangement may be stabilized by hydrogen bonding with water molecules.

Since the addition of salt changes the hydrogen-bond structure of water and the hydration sheath of PEO in aqueous solutions, the interaction of solvent and different conformers of the PEO chain should be changed, and consequently internal rotations around the main chain would vary. The $\langle r_2 \rangle_0{}^{1/2}$

TABLE 2. Unperturbed Dimension and Enthalpy and Entropy of Dilution Quantities (t = 25°C) in Aqueous Salt Solutions of PEO

Solvent	$<r^2>_0^{1/2}$, nm	C_n	σ	$10^3 K_0$, dL/g	χ_H	χ_S
1.50 M CH_3COONa	11.8	4.8	1.55	1.47	-0.143	0.630
1.50 M $HCOONa$	11.9	4.9	1.55	1.50	–	–
0.65 M NaH_2PO_4	12.3	5.2	1.60	1.63	-0.135	0.626
2.40 M KNO_3	11.7	4.7	1.52	1.41	-0.135	0.598
0.30 M Na_2HPO_4	12.6	5.5	1.64	1.75	-0.102	0.596
0.30 M K_2HPO_4	12.5	5.4	1.69	1.73	-0.117	0.609
0.30 M $NaNH_4HPO_4$	10.2	5.2	1.59	1.57	-0.152	0.639
0.40 M $Na_2S_2O_3$	12.1	5.1	1.58	1.57	-0.154	0.642
0.50 M MgS_2O_3	12.3	5.2	1.60	1.64	-0.142	0.630
0.20 M Na_3PO_4	12.3	5.2	1.60	1.64	-0.186	0.776

values, 11.7-12.6 nm in aqueous salt solutions in the temperature range of 43-55°C, are higher than that of 10.7 nm [31] in water at 45°C for the same sample, especially for the salts of polyvalent anions.

The C_n values obtained at around the Θ temperature in aqueous salt solutions scatter in the rather wide range 4.8-5.5, but the average value of 5.1 (± 0.4) is in good agreement with the theoretical value of 5.2 [29]. All C_n values obtained in this work are larger than that obtained experimentally for water at 45°C [31]. It is known that C_n decreases as the *gauche* fraction increases around the C–C bond. It is thus seen that the *gauche* conformation around the C–C bond probably becomes less stable in aqueous salt solutions, so that the C_n value increases.

Previous small-angle neutron scattering results have shown high C_n values, such as 9.7 [32] and 6.9 [33]. These values are higher than the ones presented in this work and those generally estimated for aqueous [3, 5] and nonaqueous solutions [20].

Although there is a slight variation of the α_η values in aqueous salt solutions, they are smaller than 1.60 [31] for an aqueous solution of PEO at 25°C. Since α_η depends on the factor $(1/2 - \chi_S)$ $[1 - (\theta/T)]$, which measures the intensity of the thermodynamic interaction, the larger the value of α_η, the better the solvent for a given molecular weight.

It is seen that σ values mostly vary according to whether the salt is 1:1, 1:2, 1:3, or 2:2. The σ value is about 1.55 in aqueous salt solutions of type 1:1 and 1.60 in aqueous salt solutions of types 1:2 and 1:3. Beech et al. [20] have given a value of 1.55 and Marchal et al. [34] have reported a value of 1.33 for PEO chains.

The Dilution Parameters χ_H and χ_S

The excess enthalpy and the excess entropy of dilution are negative for PEO in aqueous solutions [35], showing an ordered structure of water around the PEO. The value of χ_S is a measure of the degree of ordering of the polymer-solvent system. As can be seen from the values of χ_S in Table 2, the largest χ_S occurs in 0.20 *M* Na_3PO_4 solution. A decrease in conformational freedom of the polymer due to the addition of salt contributes negatively to the entropy, but there is also a positive contribution due to a decrease in the order of the water structure. The negative χ_H values are indicative of the negative excess enthalpies of dilution, and positive χ_S values are indicative of the negative excess entropy of dilution for PEO in aqueous salt solution, which are more negative than those in water. More negative χ_H values compared to that in water show that the main contribution to phase separation of the PEO in aqueous salt solutions is entropic.

Variation of χ_H and χ_S relative to the salts show no exact correlation with the relative variations of the Θ temperatures.

The values of the interaction parameter χ are around 0.48-0.49 for PEO in the salt solutions studies, in agreement with the previously published values [3, 5].

In this work it was found that changes in the average PEO chain structure and water structure due to the addition of salts to aqueous solutions of PEO may be responsible for different properties of dilute solutions. This effect is more significant for polyvalent anion salts.

The interaction of the cations with ether oxygens of PEO does not seem quite possible. As proposed by Eagland [36], interaction of the cations with the ethylene segments of PEO is more likely.

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