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Effect of molecular weight of poly(oxyethylene) on its complexation with potassium thiocyanate in methanol

J. Horský* and Z. Walterová

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague 6, Czechoslovakia

Summary

The viscosity behaviour of poly(oxyethylene) in methanolic KSCN indicates that both an expansion and a contraction of the macromolecule due to the association of alkali cations can occur. Such behaviour is in a qualitative agreement with a model proposed by Leibler et al. This model, however, fails to predict the effect of molecular weight of poly(oxyethylene) on the association.

Introduction

The behaviour of neutral polymers in the presence of complexing ions has attracted considerable attention, not only due to the scientific appeal of this phenomenon, but also because of its importance for industrial application. Recently, Leibler et al (1) have presented a Flory-type model describing the viscosity behaviour of a polymer solution in the presence of complexing ions.

One of the most often studied systems of this type is poly(oxyethylene) (POE) in various solutions of alkali metal salts. Various methods have been used in these studies (cf 2). In spite of the frequent use of viscometry, there is no systematic study of the viscosity behaviour of POE in alkali metal salt solutions, and the interpretation of results is sometimes superficial.

In this paper some new data on the viscosity of the POE KSCN methanol system is presented and compared with a model of the viscosity behaviour of neutral polymers in the presence of complexing ions proposed by Leibler et al (1). The effect of molecular weight is of particular interest. Some literature data on the complexation of potassium ions with POE in methanol is reexamined, and some general conclusions are drawn.

Experimental

Samples. Commercial poly(oxyethylene)s of nominal molecular weight 40000 (POE–40), 6000 (POE–6) and 1500 (POE–1.5) were used.

Methanol and Potassium Thiocyanate were of analytical grade purity. The water content in methanol was below 0.1%. The salt had been dried under vacuum and kept over phosphorus pentoxide.

Viscosity Measurements were made in Ubbelohde viscometers adapted for subsequent dilution. The temperature was kept at 25°C with deviation below 0.02°C. In pure

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*To whom offprint requests should be sent methanol, the plots reduced viscosity *vs* polymer concentration were linear. The intrinsic viscosity $[\eta]$ and the Huggins constant k_H were, respectively: POE–40: 44.3 cm^3/g, 0.32; POE–6: 14.6 cm^3/g, 0.36 and POE–1.5: 5.6 cm^3/g, 0.46.

Results

The ratio of the reduced viscosity of POE–40 in methanolic solutions of KSCN, η_{red}, to that in pure methanol, $(\eta_{red})_o$, at the same polymer concentration is plotted in Fig. 1 against the polymer concentration for various KSCN concentrations. The viscosity behaviour of POE in KSCN methanolic solutions is rather complicated. If compared with the values in pure methanol, the reduced viscosity at a given polymer concentration is lower at higher concentrations of KSCN, but higher at its lower concentrations. The polyelectrolyte nature of the POE complex could be implied from the fact that the reduced viscosity increases above the values for pure methanol.

The viscosity data for POE 6 and POE–1.5 are presented in Figs 2 and 3 in the same form as in Fig. 1. At higher salt concentrations the effect of KSCN is similar to POE–40 (the reduced viscosity is lower), but there is a significant difference at lower concentrations. The reduced viscosity in the salt solution never exceeds that in pure methanol.

Discussion

Comparison with the Leibler Model. Our results on the viscosity behaviour of poly(oxyethylene) in methanolic KSCN solutions can be compared qualitatively with the model proposed by Leibler et al. The model combines the one-dimensional lattice model of ion complexation with the Flory model of the viscosity behaviour of polymers. Coulombic interactions between bound ions and their effect on the binding constant and on the expansion of the molecule are taken into account, together with the attractive

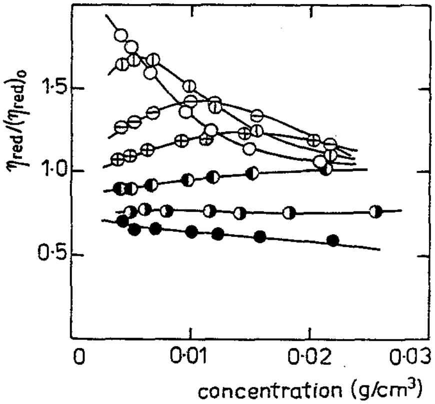

Figure 1: The effect of KSCN on the viscosity behaviour of POE-40 in methanol at 25°C. $(\eta_{red})_o$ is the reduced viscosity in pure methanol at a given concentration of POE. Concentration of KSCN: (○) .005 M, (⦶) .01 M, (⊖) .02 M, (⊕) .03 M, (◐) .05 M, (◑) .1 M, (●) .5 M.

interactions between bound ions and free binding sites. If all necessary data are known, it is possible to solve self-consistently the set of equations describing the model and to calculate the intrinsic viscosity for a given concentration of the free (unbound) salt.

The concentration of free salt is not known for our experiments but can be calculated from the overall salt concentration, c_s, and the polymer concentration, c_p, on the basis of mass balance. It was therefore possible to apply the Leibler procedure to the polymer and salt concentrations in agreement with our experiments. The results obtained with a suitable set of parameters of the Leibler model are plotted in Fig. 4 as $[\eta]/[\eta]_o$ *vs* c_p for various c_s values. The symbol $[\eta]$ refers to the intrinsic viscosity. For a finite polymer concentration this means that all interactions between macromolecules have been neglected. In other words, the polymer concentration was used in the calculation of the free salt concentration only.

On the contrary, the reduced viscosity values, η_{red} (influenced by interactions between macromolecules), are plotted in Figs 1 through 3. Thus, these figures are not exactly comparable to Fig. 4. However, by using relative quantities with respect to pure methanol (subscript o), the difference is reduced.

The Leibler model predicts important features of the viscosity behaviour of POE in methanolic solutions of KSCN, namely, an decrease in viscosity at higher salt concentrations and an increase above the value for pure solvent at lower salt concentrations. However, it does not predict additional features of the viscosity behaviour of POE in methanol, particularly the effect of molecular weight of the polymer.

Leibler et al have suggested a modification which should be valid for very good solvents, where small-loop formation predominates. However, the modified equation predicts the effect of molecular weight for a contraction rather than for an expansion. The decrease in intrinsic viscosity should be proportional to molecular weight but our experiments show that, e.g., in 0.1 M KSCN the decrease in reduced viscosity is greater for POE–1.5 and POE–6 than for POE–40.

Below, we discuss in brief possible reasons why the Leibler model fails to predict

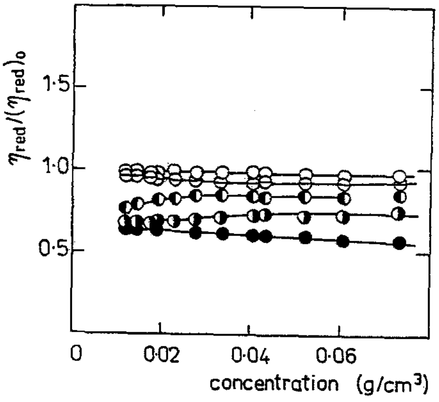

Figure 2: The effect of KSCN on the viscosity behaviour of POE–6 in methanol at 25°C. $(\eta_{red})_o$ is reduced viscosity in pure methanol at a given concentration of POE. Concentration of KSCN: (○) .005 M, (⊖) .02 M, (◐) .05 M, (◑) .1 M, (●) .5M.

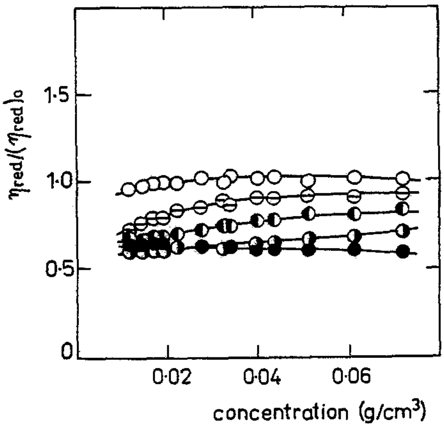

Figure 3: The effect of KSCN on the viscosity behaviour of POE–1.5 in methanol at 25°C. $(\eta_{red})_o$ is the reduced viscosity in pure methanol at a particular concentration of POE. Concentration of KSCN: (○) .005 M, (⊖) .02 M, (◐) .05 M, (◑) .1 M, (●) .5 M.

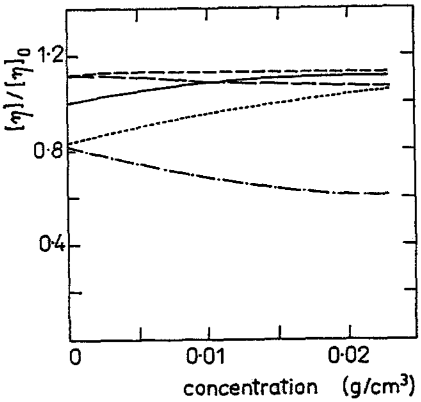

Figure 4: The effect of salt on the viscosity behaviour a of neutral polymer in methanol at 25°C. $[\eta]/[\eta]_o$ is the ratio of intrinsic viscosities in methanol according to the model of Leibler et al (1). Concentration of salt (▬ ▬) .005 M, (- - -) .02 M, (———) .05 M, (···) .1 M, (- · -) .5 M. (Parameters used — in the Leibler notation — K_o =10 mol/L, a=0.5 nm, ν=.17 nm³, ukN_A=1.4 L/mol).

fully the viscosity behaviour of POE in methanolic KSCN.

Finite Polymer Concentration. No intermolecular interactions between polymer complexes and no complex formation with more than one polymer molecule are considered in the Leibler model. The resulting equations can be applied only to the solution at infinite dilution. Extrapolation of experimental data to zero polymer concentration could be misleading, because the free salt concentration varies with that of the polymer.

According to the Huggins equation (1)

$$\eta_{red} = [\eta] + k_H[\eta]^2 c_p \tag{1}$$

the ratio of reduced viscosities approaches the ratio of the corresponding intrinsic viscosities for low polymer concentrations and equals the square of that ratio for a high polymer concentration (if the k_H value is not affected by complexation).

Quality of Methanol as POE Solvent. Though methanol is a good solvent of POE, the exponent in the Mark-Houwink equation is only 0.68, i.e., lower than the limiting value 0.8 corresponding to the viscosity model used by Leibler et al. A mild effect of molecular weight of the polymer in a solution of complexing ions could be inferred from equations describing the intrinsic viscosity of systems with a less pronounced excluded volume effect.

Counterion Condensation. Leibler et al disregarded the counterion condensation which — according to the Manning theory — occurs when the average distance along the chain between neighbouring charges is lower than the Bjerrum length Q. This assumption seems to be justified for water (Q=0.7 nm), but counterion condensation could not *a priori* be neglected for methanol (Q=1.7 nm). The existence of counterion condensation has indeed been established for alkali salt — POE complexes in nitromethane (Q=1.5 nm) (3).

If counterion condensation is operative (i.e. after the fraction of bound sites has exceeded a certain critical value), further increase in the number of bound ions could only bring about contraction of the molecule, not its expansion. This is in agreement with the existence of maxima on the curves in Fig. 1 for low salt concentrations.

Effect of Molecular Weight of the Polymer on Electrostatic Interaction in the Complex. Leibler et al considered an infinite lattice. If the molecular weight of the polymer and the fraction of bound sites are low enough, only very small number of ions is bound per molecule. If this number is unity or less, no intramolecular electrostatic interactions between bound ions can occur, and the polymer molecule is not expanded by the polyelectrolyte effect. From ultrafiltration experiments, Quina et al (2) found that the ratio of the concentration of bound ions to the polymer concentration is 0.015 for POE at 0.01 g/mL in 0.005 M KSCN. Such ratio corresponds approximately to one bound ion per two POE–1.5 molecules and to two bound ions per one POE–6 molecule.

Multiple Site Binding of Alkali Ions to POE. It is generally recognized that alkali metal ions coordinate with several monomeric POE units. The usual procedure for obtaining the concentration of the binding sites, C, is to divide the concentration of POE monomeric units, c, by the number n of monomeric units coordinated with an ion. For example, Ono et al (cf 3) used this method in their treatment of conductometric data. It was shown, however, that such approach is not correct, because an equidistant binding on the lattice is supposed (4). In fact, the number of binding sites on a naked lattice of N monomeric units is larger, being (4)

$$C = c(N - n + 1)/N \tag{2}$$

If we define the binding constant, K, for the association of ions and the corresponding binding sites, and the constant K_1 for binding the first ion per molecule, we obtain from Eq. 2

$$K_1 = KN - (n - 1)K \tag{3}$$

Equation 3 is in agreement with equation 4

$$K_1 = 241N - 1280 \tag{4}$$

found by Okada in a chromatographic study of the association of low-molecular weight POE with K^+ ions in methanol (4). According to Eq. 3, however, the number of monomeric units coordinated to one cation is estimated to be 6.3 rather than 5.3 as supposed by Okada.

The multiple site binding is in agreement with experimental results for low molecular weight polymers but contradicts the data for higher molecular weights. Quina et al (2) reported the values of the ratio of the concentration of bound ions to the polymer concentration up to 0.37 for POE in methanolic KSCN solutions, but with $n = 6.3$ it would be less than 0.16. Short chains are relatively stiff, hence the coordination shell is formed by neighbouring monomer units and a relatively significant portion of the chain is blocked by complexation with the alkali ion. For higher molecular weights of POE, the necessary cavity could be formed by oxygen atoms from different parts of the chain.

Conclusions

The association of neutral polymers with ions is a complex process and this complexity is reflected in the viscosity behaviour of such systems. Leibler et al (1) concentrated in their model on the most significant factor, i.e., electrostatic interactions between bound ions. We have shown that other factors may be important, such as counterion condensation, molecular weight of the polymer, quality of the solvent used, and multiple site character of binding. Any of these factors may become predominant under certain conditions. The strong dependence of the apparent binding constant on experimental conditions is characteristics of the polymer-salt complexation. Therefore, standard techniques for the determination of complexation constants routinely used for low molecular weight substances must be reconsidered before any attempt is made to apply them to polymeric systems.

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