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Crosslinking Reactions

Solvation of Ion Pairs with Poly(Ethylene Oxide)

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SUMMARY

Solvation of ion pairs of the alcoxide type with poly(ethylene oxide) (PEO) has been studied by optical spectroscopy. Values of binding constants 200-400 l/mol indicate a sufficiently effective ion-pair cation solvation. Being cross-linked PEO preserves its ability to bind and localize ion pairs.

INTRODUCTION

The ability of PEO for solvation binding of cations is well known, but in recent years it continues to attract great attention in connection with investigations on ion transport and separation, interphase catalysis, etc. (YAMAZAKI et al. 1979; YANAGIDA et al. 1977; HIRAO et al. 1978; LEE and WRIGHT 1978). Interest in this problem is also associated with the development of the concept of a special role played by macromolecules in the solvation of propagating active centres, which explains many of the specific regularities in the anionic polymerization of heterocycles, in particular, ethylene oxide (see KAZANSKII 1981). Investigations in this field are also stimulated by the expanding flow of the information concerning the interaction of various alkali salts with macrocyclic complexing agents - crown-ethers and cryptands, as well as with macromolecules containing similar groups in side chains (see MELSON 1979; SINTA and SMID 1980).

At the same time, in most of the studies on the formation of PEO complexes with a number of reagents primary emphasis is placed upon qualitative effects of these interactions, with the quantitative aspect elaborated inadequately, which does not permit predicting with assurance their effects in different systems.

A sufficiently detailed study that produced quantitative characteristics of the binding of free alkali cations was previously performed by us (ARKHIPOVICH et al. 1982), but the examined model can only be regarded as the simplest one, very far from actual reality. Investigation of ion-pairs binding appears to be the next step in the modelling of solvation processes with the participation of macromolecules. The compounds chosen for study in the present work were picrates of potassium (PiK) and sodium (PiNa) in THF, as well as potassium salt of tetrabromophenolphthalein ethyl ester (KTBF) in chloroform (CF).

EXPERIMENTAL

PEO of molecular weight 6000 (Merck) was used without further purification after prolonged drying in vacuo at room temperature. PiK and PiNa were obtained by neutralizing picric acid of "chemically pure" grade with the corresponding hydroxide and recrystallized from dry ethanol. Absorption spectra parameters were used as criteria of the purity of picrates. These amounted to:

Salt	in water λ_{max}, nm	 ε, $l.mol^{-1}\ cm^{-1}$	in THF λ_{max}, nm	 ε, $l.mol^{-1}\ cm^{-1}$
PiNa	356 (354)	14,500 (14,500)	354 (351)	16,600 (16,600)
PiK			360 (357)	16,800 (16,800)

In brackets the data of WONG and SMID 1980; BOURGOIN et al. 1975 are given.

KTBF was used without further purification. THF was refluxed over metallic sodium, and CF - over calcium hydride, repeatedly distilled, and freshly distilled portions were used.

Spectrophotometric measurements were performed on "Specord--UV-VIS" (Carl Zeiss, Jena) instrument, and conductometry measurements - with the use of "Tesla BM-434" bridge at 1547 Cps in a cell with parallel-plate electrodes and cell constant about 0.05 cm^{-1}. All the experiments were performed at 25^{o}. Beer's law was observed in all cases both for initial reagents and complexes.

The equilibrium of picrates binding with PEO was studied by recordind absorption spectra of solutions with a constant picrate concentration (C_o) and a variable polymer concentration. PEO concentration was raised till no changes occurred in the spectra, i.e. till complete binding of picrate into a complex. The fraction of PiMt bound was calculated from relationship

$$x = [PiMt]_{bound} / C_o = (\varepsilon - \varepsilon_o) / (\varepsilon_{\infty} - \varepsilon_o) ,$$

where ε_o and ε_{∞} are absorption coefficients of the initial picrate and the complex, and ε is the apparent absorption coefficient of solution at a given PEO concentration.

The absolute optical density changes being small (see Fig. 1), for the accuracy to be increased the spectra were measured in the transmission mode, with the investigated solution spectrum taken against the picrate solution having the same concentration. The series of obtained spectral curves is shown in Fig. 2.

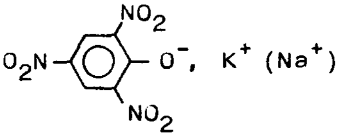
Equilibrium binding constants (K_n) were calculated from equation

$$K_n = \frac{n\ x}{(1 - x)\ [O]_o} , \qquad (1)$$

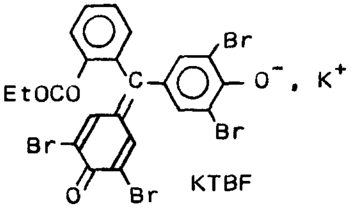
were $[O]_o$ is the initial concentration of ether oxygen and n is the stoichiometry of the complex, i.e. the number of monomeric PEO units bound with one cation. Since the stability of complexes in this case proves to be insufficient for reliable determination of n from the binding isotherms, by anology with free cations (see ARKHIPOVICH et al. 1981, 1982) we took $n = 6$.

RESULTS AND DISCUSSION

It was previously shown that free cations are effectively bound by PEO with equilibrium constants from ~ 2500 (Na^+) to ~150 (Cs^+) l/mol, with the binding proceeding by the cooperative mechanism (ARKHIPOVICH et al. 1981, 1982; KAZANSKII 1981). Cation "freedom" was achieved by using a polar solvent (nitromethane) and large counterions. When one turns to investigating similar interactions with ion pairs it is necessary to use salts with a higher dissociation stability in low polarity media. With the problems of the solubility of polymers and their complexes being taken into account, these requirements are adequately satisfied by two systems: alkali metal picrates in ether media (e.g. in THF) and KTBF soluble in CF and similar solvents. In both cases the dissociation constants are sufficiently low, and the sensitivity of the electronic structure of anions to the state of ion pairs (interionic distance variation) permits using spectrophotometry for their investigation. It is important to note that picrates and KTBF, being ion pairs of the alcoxide type, are an appropriate model of the active centre of ethylene oxide anionic polymerization.



PiMt



KTBF

PiK and PiNa are known to exist at room temperature in THF exclusively in the form of contact ion pairs (PiK dissociation constant in THF at 25° is 9.2×10^{-8} mol/l) with absorption maxima at 357 and 351 nm, respectively. On adding a solvating agent two other bands appear, assigned to peripherally solvated (357-362 nm) and solvent separated (380 nm) ion pairs (see FRENSDORF 1971; BOURGOIN et al. 1975; SMID 1976).

Figure 1 shows the qualitative changes in PiK and PiNa spectra in THF when PEO was added. In its pure form the solvent separated state is evidently reached only when PiK and PiNa are dissolved directly in liquid low-molecular PEO ($\lambda_{max} = 380$ nm). In the condition of experiment PEO addition to PiNa can be assumed to result in the formation of mainly the peripherally solvated ion pair ($\lambda_{max} = 365$ nm), while in the case of PiK ($\lambda_{max} = 375$ nm) the portion of the solvent separate state is larger. Figure 3 shows the PiNa and PiK binding isotherms obtained by processing the spectral curves (Fig. 2) at 30,000 and 26,000 cm^{-1}. It is to be noted that, despite the insufficiently clearly defined isosbestic point, as well as the presence of an unresolved peak in the initial picrate spectrum and those of solution with PEO added (shoulder at 24,000 cm^{-1}), only two states were taken into account in calculations - corresponding to the free and the bound

PiMt, with the contribution of the other possible states assumed to be small. Calculation by equation (1) result in equilibrium binding constants K_6, i.e. for a complex of $Mt(O)_6$ composition of ca. 200 and 400 l/mol for PiNa and PiK, respectively, which, as seen from the figure, describe quite well the experimental data in conjunction with the conventional isotherms of the Langmuir-Klotz type (KLOTZ et al. 1946; WONG and SMID 1980; SINTA and SMID 1980).

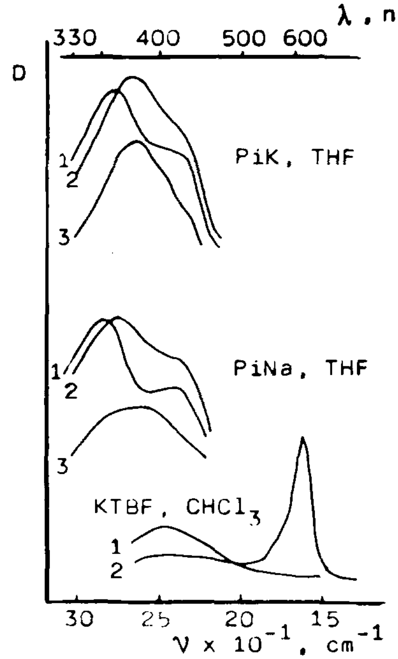


Fig. 1. Changes in the absorption spectra of ion pairs, under complexing with PEO: 1 - without additions; 2 - with PEO addition, $[O]_o = 0.5$ mol/l; 3 - in low-molecular PEO as solvent.

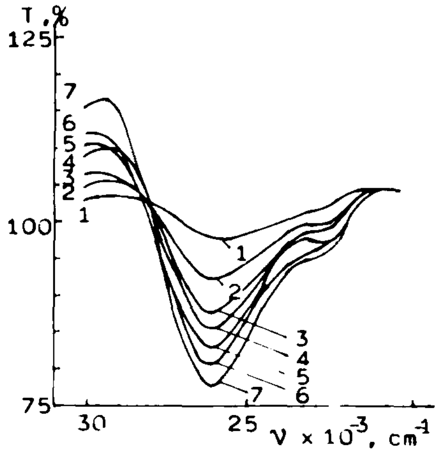
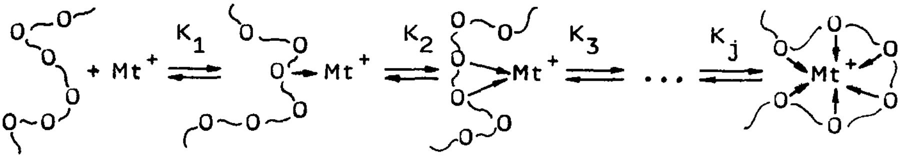


Fig. 2. Typical spectral curves obtained when the spectra of investigated solutions contained PEO were recorded against initial solution of the same salt concentration: PiNa, $C_o = 3.8 \times 10^{-5}$ mol/l; $[O]_o = 3.8 \times 10^{-3}$ (1), 9.5×10^{-3} (2), 0.019 (3), 0,038 (4), 0.076 (5), 0.114 (6) and 0.190 (7) mol/l.

Comparison of the values of equilibrium binding constants for cations in picrates and in the free state shows that, as would be expected, the anion decreases markedly the solvation of cation by the polymer. This seems to be taking place owing to steric hindrances and mutual electrostatic repulsion. In the case of Na^+ that forms a more stable ion pair the anion effect is more pronounced, which leads to inversion of constants.

This also agrees with the recent data of DIMOV et al. 1982, where the equilibrium constants of picrate binding with PEO decreased in the series of $K^+ > Na^+ > Li^+$. It is necessary to note that the absolute values of constants in the mentioned work differ drastically from those we have obtained, these discrepancies clearly exceeding the experimental error. It is also unlikely that the differences in the procedure of calculating the constants - from PEO concentration necesary for the binding of half the initial picrate concentration (as it was done by DIMOV et al. 1982) or using the whole isotherm - can explain such large-scale discrepancies. It, therefore, seems impossible at present to comment on these differences.

Returning to the obtained values of binding constants K_6 one can note that they are sufficiently high and indicate an effective ion pair cation interaction with the macromolecule. This permits, as in the case of free cations (KAZANSKII 1981) to assume a cooperative mechanism of binding (STEINHARD and REYNOLDS 1969; ENGEL and WINKLMAIR 1972) in accordance with the following scheme:



(2)

The most difficult in such a scheme is the first stage where most of the entropy of the system is lost. All the subsequent stages, proceeding intramolecularly by cyclization with the metal ion coordination shell being saturated with oxygen atoms, go with less entropy loss. The apparent equilibrium constant can be written as

$$K_n = K_1\, K_j^{n-1} = \sigma K_j^n ,$$

where $\sigma = K_1/K_j$ is cooperativity factor, K_j is equilibrium constant for the second and any subsequent contact. If the σ value is sufficiently small the mechanism "all-or-nothing" could take place in this system, i.e. free and completely solvated ion pairs would only exist in equilibrium. According to estimation (see ENGEL and WINKLMAIR 1972) the σ value can be as low as 10^{-9} l/mol, than $K_j \simeq 70$ and the probability of the cyclization in the second and subsequent stages in scheme (2) could reach 0.95 - 0.98. This value reflects the high ability of PEO to effective multiple solvation of cation.

Effectiveness of the solvating agent with respect to the ion-pair cation can also be estimated from the tendency of its solvated state to dissociation. Under certain conditions, viz. at relatively high concentrations and a large excess of the polymer ligand, the complex scheme of the dissociation (see, e.g., SMID 1976; FRENSDORF 1971) can be reduced to the following equilibrium:

$$(MtO_n)^+, Pi^- \overset{K_D}{\rightleftharpoons} (MtO_n)^+ + Pi^- .$$

The PiK conductivity dependence on concentration in these conditions is well described by a simple dilution law with a dissociation constant of about 10^{-4} mol/l, against 2.4×10^{-5} - 4.1×10^{-5} mol/l obtained by Smid and co-workers for PiK complexes with different polycrowns (BOURGOIN et al. 1975).

KTBF is a new reagent in studying the ion-pair solvation. This compound is of special interest not only because of the widely spaced peaks of the initial (394 nm) and the solvate or free-ion states (615 nm) (Fig. 1), but also owing to the possibility of using it in very low polarity media. Investigations have shown PEO to bind readily KTBF in CF, with the isotherms, as in the case of picrates, being close to Langmuir's (Fig. 3). Calculation by equation (1) results in equilibrium binding constant $K_6 \sim 400$ l/mol.

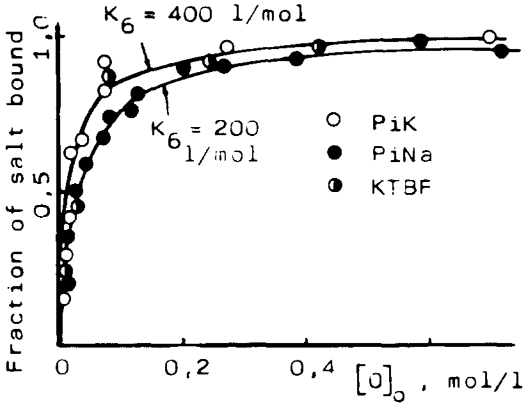


Fig. 3. Isotherms of ion-pair binding with PEO.

In going from THF to CF, which has no affinity to cations and is less polar, one would expect a great increase in binding effectiveness. This, however, is not observed if KTBF is compared with PiK. Qualitative experiments show that KTBF is bound by PEO macromolecules in THF, but only very slightly, since the reagent itself is in this case in solvated state. Thus, a decrease in polarity and solvating ability here is almost completely compensated by the anion becoming more complex. It should be noted that in the conditions of a low polarity medium there is marked interaction between KTBF and polysiloxanes that are much weaker donors than PEO, but these effects lend themselves with great difficulty to quantitative evaluation.

The separation of the contributions of free and bound states to the spectra, conductivity, etc. makes, from the methodic point of viev, analysis of the interaction between polymers and ion pairs as well as cations (see ARKHIPOVICH et al. 1981) in solution more difficult. One could avoid these difficulties, at least partially, by using a polymer in the cross-linked form and solving the problem in question with the help of absorption methods. Such examples are avaible in literature (TAKAGISHI et al. 1980).

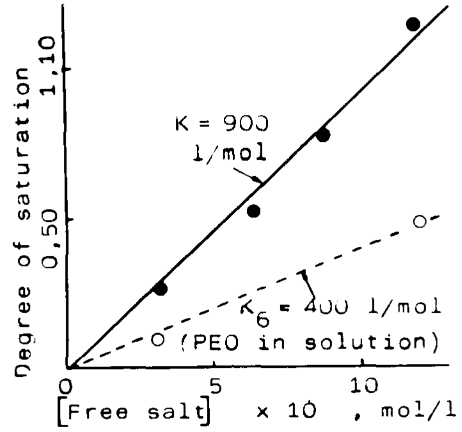


Fig. 4. Isotherms of PiK binding with cross-linked PEO gel.

We have performed preliminary experiments in which gel of PEO cross-linked by irradiation was used. After being cross-linked in aqueous medium the gel was freeze-dried and kept until equilibrium swelling in THF. Small pieces of swollen gel were placed in PiK solution in THF, with the free picrate concentration over the gel being periodically determined by spectroscopy. After the equilibrium concentration had been reached the gel was transferred into a new solution with a higher initial PiK concentration, and so on until the saturation was complete. Results of this experiment show that the gel can absorb up to 0.10 - 0.15 mol PiK per PEO unit, i.e., the capacity reached is close to that observed at binding in solution. Binding ability is also high here: calculation yields the binding constant of ca. 900 l/mol. Some uncertainty is brought into calculation by an increase in gel volume in the course of experiment, most probably caused by a partial destruction of cross-links during storage in THF.

The presently available experimental data, as well as the absence of reliable data on cross-linking density in the gels used, are insufficient to discuss the causes of the differences in the effectiveness of salts binding with PEO macromolecules in the cross-linked and the free states (Fig. 4), It is possible that complexes of another stoichiometry are formed in the gel, it contains more readily bound "traps", or this is influenced by a smaller, in comparison with solution, entropy loss by macromolecules at complexing.

It is necessary to note that the bound form is almost completely localized in the gel, and the spectra of solution over it are identical with those of initial PiK.

A spectacular, through purely qualitative, experiment was performed with KTBF: introducing gel pieces into a bright-yellow KTBF solution in CF brought about an almost instantaneous decoloration of solution, and, as the swelling increased, the gel became intensively blue in colour.

Polymer gels appear to be promising as media for investigating the kinetic stages of certain processes. This "cross-linked" solvating media can be used not only for the modelling and localization of processes in which solvation play a decisive role but also for carrying out a number of nucleophilic reactions, in particular, in the conditions of interphase catalysis (STARKS and LIOTS 1978) where low-molecular crown-ethers or cryptands, or those immobilized on polymeric carriers, predominate at present.

CONCLUSIONS

The data on the complexing of picrates with PEO lead to the conclusion that the anion competes with the polymer ligands in the cation solvate shell. As the result the binding constants of ion pairs are substantially lower then those of free cations. The picrate anion seems to be a more powerful ligand than PEO because of a higher degree of the negative charge localization. An increase in the size or in the degree of charge localization on the anion must weaken even more the cation binding. Nevertheless, solvation of ion pairs by macromolecules proceeds sufficiently effective to be responsible for the solvating effects in anionic polymerization. The ability of PEO to separate counterions in the ion pair is practically the same as that of polycrown ethers. The values of constants 200-400 l/mol, within framework of the mechanism of cooperative binding, correspond to high values of the probability of chain capture round the cation in the form of a cyclic solvate shell. Being cross-linked PEO preserves a high ability to bind and localize ion pairs, which is of interest from the point of view of preparative reactions in this media.

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