

A POLYMER ANALOG OF DMSO: INTERACTIONS OF ALKALI METALS PICRATES WITH POLYMERS CONTAINING BOUND SULFOXIDE GROUPS

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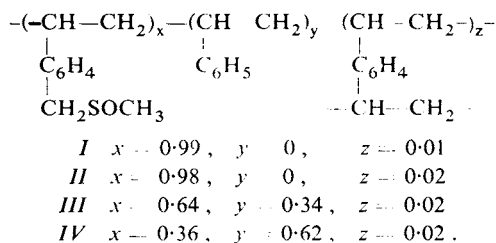
Dedicated to Dr. B. Sedláček on the occasion of his 60th birthday.

The equilibria of interactions of alkali metals ($\text{Li}^{(+)}$, $\text{Na}^{(+)}$, $\text{K}^{(+)}$) picrates with a polymer analog of dimethyl sulfoxide derived from crosslinked polystyrene were investigated in an aqueous medium in order to obtain quantitative information on the complex-binding properties of sulfoxide groups covalently bound to the polymer. By using the spectrophotometric analysis, the binding constants and stoichiometry of the complex-forming process were determined as a function of the cation size, the degree of crosslinking of polystyrene, and the degree of its functionalization with sulfoxide groups. The values of the binding constants of alkali picrates reflect the structurally different character of the polymer the more the larger the alkali metal cation. The stoichiometric ligand-cation ratio lies in the range between 6 and 9.

Dimethyl sulfoxide is a dipolar aprotic solvent in which the reactivity of anions in reactions proceeding by the nucleophilic mechanism is much higher than in protic solvents. The activating effect of this solvent is explained by its ability to dissociate ionic salts, and also to solvate only cations, thus making possible the formation of "naked" anions¹. Recently, the preparation of a polymer analog of dimethyl sulfoxide based on polystyrene has been reported^{2,3}. This polymer appeared to be an effective catalyst of some substitution reactions carried out under the conditions of three-phase catalysis³⁻⁶. Its catalytic effect is explained either by the formation of complexes of salt cations (complex-forming mechanism) or/and by microhomogenization of both immiscible phases inside the polymer matrix (micellar mechanism). A similar explanation is offered also for the catalytic effect of other solid-phase cosolvents and of crown-ethers covalently bound to the polymer⁷. Properties of polymers containing covalently bound crown-ether groups were extensively investigated by Smid and coworkers as regards their complex-forming ability with respect to the alkali metals cations^{8,9}. These authors suggested a procedure for the investigation of complex formation and by employing the spectrophotometric method determined the binding constants of these polymers with alkali metals picrates and the

stoichiometry of the respective complexes as a function of the size of the crown-ether macroring, its content in the polymer matrix, its distance from the matrix (spacer), and of the cation size, solvent, and temperature. No such investigation has yet been carried out with the other polymers of the solid-phase cosolvent type, including the polymer analog of dimethyl sulfoxide.

This study brings the first quantitative data on the interaction of alkali metals picrates with polymers containing covalently bound sulfoxide groups as a function of the contents of these groups and of the degree of crosslinking of the polymer matrix. Polymers with bound sulfoxide groups were derived from crosslinked chloromethylated polystyrene²:



Polymers with freely pendent sulfoxide groups differ in the degree of crosslinking of the polymer matrix (1% or 2% divinylbenzene as the crosslinking agent) and in the degree of functionalization of the carrier with sulfoxide groups. They were equilibrated with aqueous solutions of alkali metals picrates having the concentration in the range $33\text{--}165\ \mu\text{mol l}^{-1}$ at 30°C and 50°C . The time needed for reaching equilibrium between the picrate bound in the polymer and free picrate in solution was determined from kinetic curves describing the consumption of picrate in the

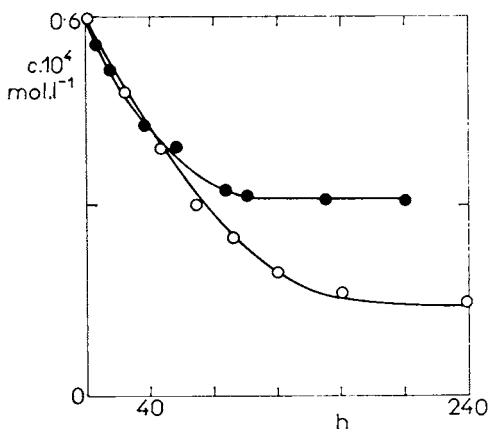
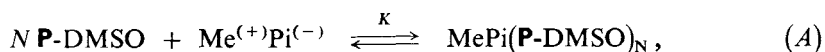


FIG. 1
Rate of consumption of potassium picrate from the aqueous solution in the presence of polymer *I* at 30°C (○) and at 50°C (●)

solution above the polymer. An example of the kinetics of establishing equilibrium for the system potassium picrate–polymer $I-H_2O$ at 30°C and 50°C is shown in Fig. 1. It can be seen that processes leading to the equilibrium are very slow and are affected by temperature not only as regards their rate, but also with respect to the mass balance. Similar kinetic curves were obtained also for the other polymers and for lithium and sodium picrates. In all cases, at 50°C the time needed for reaching the equilibrium was shorter than 100 hours. Slowness of the process of formation of the picrate-polymeric sulfoxide complex strongly distinguishes these polymers from those containing crown-ether groups. For the latter it has been observed that with increasing polarity of the solvent used the rate of the complex-forming process increases, and the equilibrium is reached within tens of minutes at most⁹. In our case the complex-forming processes are slower by an order of magnitude, in spite of the use of water in which, under the concentration conditions employed, the alkali metals picrates are present in their dissociated form. It was also observed that with 1,4-dioxane as solvent in which the alkali metals picrates are present in the nondissociated form no perceptible decrease in the concentration of potassium picrate above the polymer takes place at 50°C after ten days.

The process of bond formation between alkali metals picrates and polymeric sulfoxides may be described summarily by the equilibrium



where $\mathbf{P}\text{-DMSO}$ is the polymer with bound sulfoxide groups (I–IV), $\text{Me}^{(+)}\text{Pi}^{(-)}$ is a free alkali metal picrate in solution, and $\text{MePi}(\mathbf{P}\text{-DMSO})_N$ is the complex of the alkali metal picrate with polymeric sulfoxide. If $[\mathbf{P}\text{-DMSO}]_0$ is the initial concentration of sulfoxide groups in the polymer in moles per one litre of the picrate solution, and N is the number of ligands in the complex with alkali picrate, then for the equilibrium concentration of sulfoxide groups without interaction with the alkali metal picrate we have

$$[\mathbf{P}\text{-DMSO}] = [\mathbf{P}\text{-DMSO}]_0 - [\text{MePi}(\mathbf{P}\text{-DMSO})]. \quad (1)$$

The concentration of picrate bound in the polymer can be determined from the difference between the starting and equilibrium concentration of free alkali metal picrate, $[\text{Me}^{(+)}\text{Pi}^{(-)}]_0 - [\text{Me}^{(+)}\text{Pi}^{(-)}]$. Both concentrations can be exactly determined in the system by employing the spectrophotometric method. The values of the binding constants can then be calculated by using the Klotz equation¹⁰, modified as in an earlier procedure^{9,11}

$$\frac{1}{R} = \frac{1}{n} + \frac{1}{nK[\text{Me}^{(+)}\text{Pi}^{(-)}]}, \quad (2)$$

where $1/R = [\text{P-DMSO}]_0/[\text{MePi(P-DMSO)}]$ and $n = 1/N$. The graphic dependences $1/R$ vs $1/[\text{Me}^{(+)}\text{Pi}^{(-)}]$ allow us to determine the stoichiometry of the complexes formed (ratio of sulfoxide groups to alkali metal picrate inside the polymer) and to calculate the binding constants (K). These dependences measured for the case of an interaction between picrates of $\text{Li}^{(+)}$, $\text{Na}^{(+)}$, $\text{K}^{(+)}$ and polymeric sulfoxides I–IV are given in Fig. 2.

It can be seen that the stoichiometry of complex-forming interactions is high and lies in the range 6–9 sulfoxide groups per one cation of alkali metal picrate.

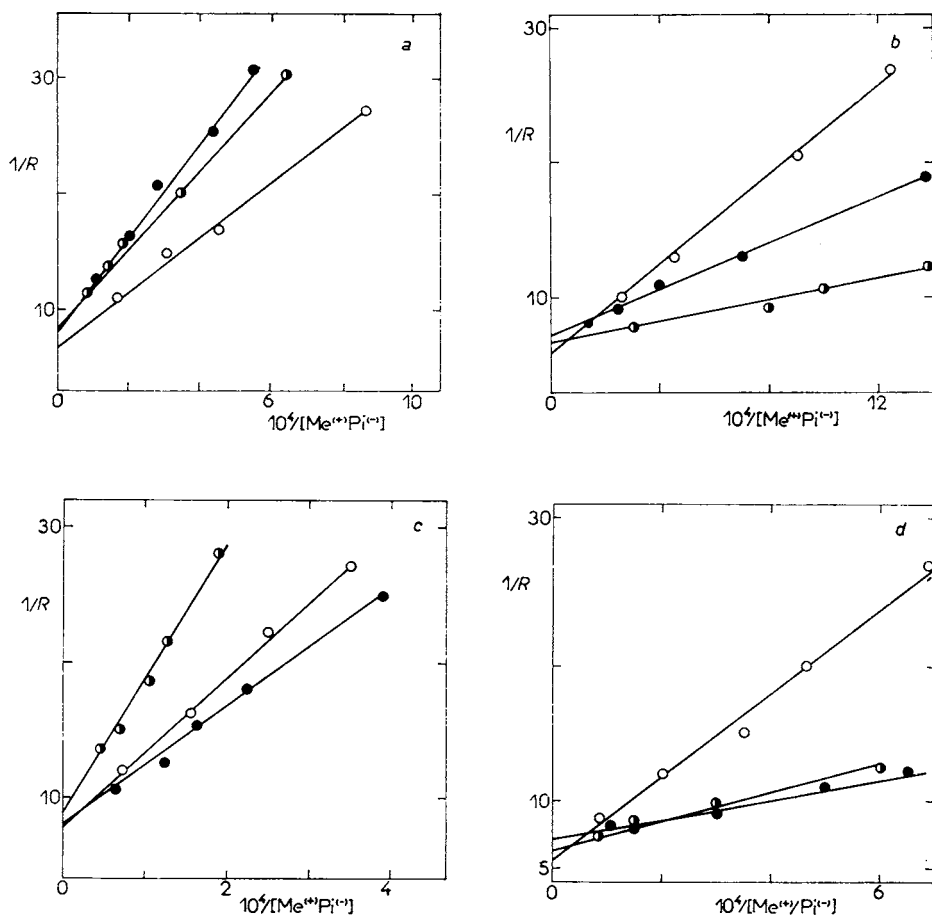


FIG. 2

Interactions of polymers I–IV with alkali metals picrates in water at 50°C. Picrates: ○ lithium, ● sodium, ◐ potassium. Polymers: a) I, b) II, c) III, d) IV

These values are well comparable with those which have been found for the interaction between alkali metals cations and polymers containing bound crown-ether macrorings⁹. Bearing in mind the highly dipolar character of the >S—O bond in dialkyl sulfoxides, one may assume that rearrangement of such a high number of sulfoxide groups in the process of complex formation with the alkali metal cation which gives a geometrically more regular structure than that existing in the starting polymer is energetically disadvantageous and brings about reorganization of the whole polymer matrix. These are factors which may explain the slower character of the complex-forming process compared with polymers containing covalently bound crown-ether groups, where the energetically advantageous grouping of ligands is given in advance⁹. Values summarized in Table I show both the dependence of the stoichiometry of interactions and of the size of cations (best seen when lithium and potassium picrates are compared with each other), and the effect of the degree of crosslinking of the polymer matrix (*cf.* polymers *I* and *II*) and of the degree of functionalization of the carrier (*cf.* polymers *II–IV*) on the stoichiometry of complexes. It is evident that the polymer allowing to reach the highest degree of coordination is polymeric sulfoxide *III*. A factor unfavourable to the high coordination is both a higher degree of crosslinking of the polymeric sulfoxide and a too high or too low content of sulfoxide groups in the polymer matrix.

The binding constants K calculated from the slope of the straight-line dependence $1/R$ vs $1/\text{Me}^{(+)}\text{Pi}^{(-)}$ (Fig. 2) are given in Table I. In most cases the K values are lower by an order of magnitude than those which were found in the case of crosslinked polymers containing bound crown-ether groups ($1.6\text{--}410\text{ mmol}^{-1}$). This agrees

TABLE I

Binding constants (K , 10^{-4} mol^{-1}) and stoichiometry of interactions of alkali metals picrates with polymeric sulfoxides *I–IV* in water at 50°C . N gives the number of sulfoxide groups per one cation in the complex polymer – alkali metal picrate

Polymer ^a	Li(+)		Na(+)		K(+)	
	K	N	K	N	K	N
<i>I</i>	2.4	7	1.6	8	1.8 ^b	8 ^b
<i>II</i>	2.5	6	8.8	7	13.4 ^c	7 ^c
<i>III</i>	1.9	8	1.8	8	1.1	9
<i>IV</i>	2.2	6	7.4	6	7.4	7

^a In the case of nonfunctionalized poly[styrene(98)-*co*-divinylbenzene(2)] no interaction with solutions of alkali metals picrates was recorded. ^b At 30°C $K = 15.0 \cdot 10^{-4}\text{ mol}^{-1}$, $N = 7$. ^c At 30°C $K = 19.5 \cdot 10^{-4}\text{ mol}^{-1}$, $N = 6$.

well with the results of measurements of the equilibrium constants of competition of crown-ethers and of dimethyl sulfoxide with the polymer complex of lithium picrate¹². The results show that dimethyl sulfoxide is a ligand weaker by several orders of magnitude than compounds with the 18-crown-6 structure. Differences in the K values of polymers *I–IV* increase with increasing size of the cation; in the case of the interaction of lithium picrate the K values do not reflect the differences in the structure of polymeric sulfoxides *I–IV*. With increasing rigidity of the polymer matrix (higher content of the crosslinking component) the values of the binding constants increase the more the larger the alkali metal cation (*cf.* polymers *I* and *II*). A decrease in the degree of functionalization of the polymer carrier due to sulfoxide groups has no monotonic effect on the values of the binding constants. The same has been observed in the case of the stoichiometry of complexes. The weakest binding power with respect to alkali metals picrates has been found with polymers *I* and *III*. On the other hand, however, polymer *III* is the most active catalyst in nucleophilic substitution reactions carried out under the conditions of three-phase catalysts^{5,6}. The K values can be regarded as the measure of bound strength of the polymer–salt cation $\text{Me}^{(+)}$. $\text{Y}^{(-)}$ interaction. Assuming that complex-forming processes similar to those observed in the case of alkali metals picrates (which do not vary qualitatively with a change of the $\text{Y}^{(-)}$ anion and temperature) play an important role in the mechanism of three-phase catalysis, the process of dissociation of such polymer complexes can therefore be regarded as yet another factor affecting the reaction kinetics under the conditions of three-phase catalysis.

The formation of complexes between the polymer analog of DMSO and alkali metals picrates is obviously a very complicated process in which a number of effects are acting and counteracting. The kinetics and balance of the equilibrium process are determined by observing changes in the concentration of the picrate anion. The complex-forming process itself, however, is a process of interaction between sulfoxide groups inside the hydrophobic polymer matrix and alkali metals cations. This process may generally precede that of binding of the picrate anion to the polymer. The measured N and K values should therefore be evaluated by assuming that they quantitatively describe the overall process of formation of the complex $\text{MePi}(\text{P-DMSO})_N$.

EXPERIMENTAL

Chemicals. The polymers were synthesized as described before². Lithium, sodium and potassium picrates were prepared by reacting equimolar amounts of the corresponding hydroxides (analytical purity grade, Lachema) and picric acid (analytical purity grade, POCH, Poland) in a solution in ethanol, recrystallized from ethanol and dried at 50°C and 13 Pa for 24 h. Aqueous solutions of picrates were prepared using water redistilled from KMnO_4 .

Spectrophotometric measurements. The concentrations of picrates in solutions were determined spectrophotometrically (Hewlett–Packard 8451 A) according to the Lambert–Beer equation

at λ 354 nm. The extinction coefficients of aqueous solutions of the individual picrates (ϵ) were determined from measurements at concentrations in the range 33–180 $\mu\text{mol l}^{-1}$; the ϵ values (in $10^{-4} \text{ l mol}^{-1} \text{ cm}^{-1}$) for the lithium, sodium and potassium salt were respectively 1.15, 1.21, and 1.43.

Equilibrium determination. To 1.68–3.05 mg of polymeric sulfoxide (the weight amount corresponded to $8.0 \cdot 10^{-3}$ mmol of sulfoxide groups), 15 ml H_2O was added, and the mixture was maintained at $50 \pm 0.1^\circ\text{C}$ (Term-O-Watch L6 1000 SS). After 15 min, 0.10 ml of a 0.005M solution of alkali metal picrate in water was added. During the process of establishing equilibrium, samples 1.5 ml in volume were taken, and the concentration of picrate in solution was determined. After reaching the equilibrium, 0.10 ml of a 0.005M solution of the respective picrate was added each time, and the employed procedure was the same as in the case of the first addition.

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