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The extraction of sodium and potassium picrates with poly[(benzo-15-crown-5)maleimide], poly[(benzo-15-crown-5) maleimide-alt-α-methylstyrene] and benzo-15-crown-5

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Abstracts

The distribution of complexes of sodium picrate and potassium picrate with poly[(benzo-15-crown-5)maleimide], poly[(benzo-15-crown-5)maleimide-alt-α-methylstyrene] and benzo-15-crown-5 (b15/5) between water and CH_2Cl_2 was investigated. Concentration of Na-ion with homopolymer in CH_2Cl_2 was 52%, while the concentration of complex of alternating copolymer and b15/5 with Na-ion was 22% and 20% respectively. Concentration of K-ion complex in CH_2Cl_2 with homopolymer and alternating copolymer was 90% and with b15/5 the concentration of complex was 40%. The large difference in the complexation ability of Na-ion and K-ion with homopolymer and alternating copolymer is considered to be the consequence of the formation of 1:1 complex with Na-ion and 2:1 complex with K-ion.

Introduction

The ability of crown ethers to form complexes with cations of alkali metals and alkaline earth metals is the subject of a large number of papers and monographs. Detailed description of the mechanism of complex formation has been reviewed by Hiraoka (1), and many examples which illustrate the formation of polymeric crown ether complexes with metal ions are described in a recent article by Tunca and Yagci (2). In most cases it is shown that polymeric crown ethers exhibit higher ability to ion

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binding than the analogous low molecular weight compounds.
In the present paper is described the complexation behaviour of poly[4'-N(benzo-15-crown-5)maleimide] (poly-b15/5MI) (I) and poly[4'-N(benzo-15-crown-5)maleimide-alt-α-methylstyrene] (poly-b15/5MI-alt-α-MeSt) (II) with sodium picrate and potassium picrate respectively. Although benzo-15-crown-5 (III) is not the model compound of repeat units in polymers I and II, its ability to complexation is also inclucded and compared with the complexation of polymers.

Experimental

Materials

(Benzo-15-crown-5)maleimide, homopolymer and alternating copolymer with α-methylstyrene were prepared according to the procedure described in reference (3). Benzo-15-crown-5 was a commercial product (Aldrich Europe, Belgium).

Extraction

The method described by Pedersen (4) and subsequently used by Kopolow and coworkers (5) was used: picric acid (0.01603 g; $7.0\text{x}10^{-5}$ mol) was dissolved in 10 mL of 0.1 M NaOH or 0.1 M KOH and 1 mL of this solution was diluted to 100 mL with 0.1 M NaOH or 0.1 M KOH respectively. Ten milliliters of diluted solution of metal picrate ($7.0\text{x}10^{-7}$ mol) was vigorously shaken for 10 mins in a separatory funnel with equal volume of CH_2Cl_2 which contains $7.0\text{x}10^{-6}$ mol of crown ether compounds. The organic layer was removed, filtered to remove cloudiness and the picrate concentration was determined by optical spectroscopy at λ_m 357 nm in aqueous phase and at λ_m 378 nm in CH_2Cl_2. Measurements were made on Carry 1, Model 1E UV/VIS spectrophotometer. For each cation-crown system the measurements were carried out at five different crown concentrations, using picrate-to-crown ratios in mL: 10:10; 10:7; 10:5; 10:3; and 10:1. (Figs. 1 and 2). Crown ether solutions in all measurements were diluted to 10 mL with CH_2Cl_2. The absorbance of Na-picrate solution is 1.0396, and of K-picrate 1.0237, while the absorbances of 0.1 M NaOH and 0.1 M KOH are 0.0659 and 0.0518 respectively.

Results and discussion

The most striking characteristic of crown compounds is their ability to form stable complexes with alkaline and alkaline earth cations. The binding of metal ions with crown compounds is of special interest since it enables the transfer of metal ions from aqueous solution to various organic solvents including non-polar solvents. The determination of equilibrium constants and thermodynamic factors in the transfer of metal ions to organic solvents which contain crown compounds is a very complicated procedure. In order to determine the overall extraction equilibrium of metal picrate with crown ether it is necessary to analyse the equilibria of all components in aqueous and organic phase, the solubilities and partition coefficients of various complexed and uncomplexed species, and the influence of various experimental conditions to the complexation equilibria (6). However a rather simple method for the determination of complexing ability of crown compounds with

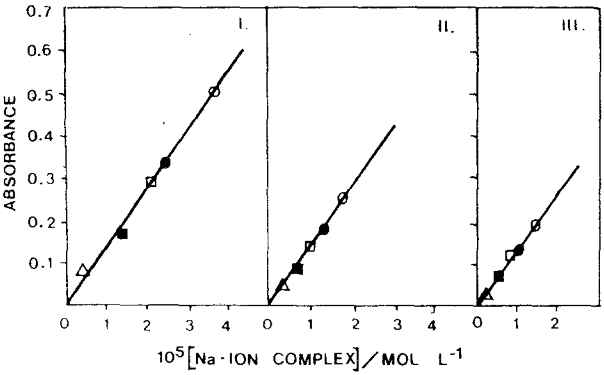

Fig.1. The plot of absorption against molar concentration of Na-picrate complex with poly-b15/5MI (I), poly(b15/5MI-alt-α-MeSt) (II) and b15/5 (III); Na-picrate to crown compound solution in mL: 10:10 (○); 10:7 (●); 10:5 (□); 10;3 (■); 10:1 (△).

metal ions was developed by Pedersen (4,7). The Pedersen's method was applied in the present work.

In Figure 1 are plotted the molar concentrations of the complexes of sodium picrate with crown ether compounds in CH_2Cl_2 against the absorbance in 0.1 M NaOH. The concentration of complexes was determined from the values of decrease of absorbance of aqueous solution caused by the transfer of Na-ion to CH_2Cl_2 solution.

The data in Fig.1 show that homopolymer (I) has higher ability to capture Na-picrate than alternating copolymer (II). There is no significant difference in the complexation ability between alternating copolymer (II) and b15/5 (III).

The plot of absorption against the molar complex concentration of K-ion with poly-b15/5MI (I), poly-(b15/5MI-alt-α-MeSt) (II) and b15/5 (III) is shown in Fig.2. The data in Fig.2 indicate that molar concentration of K-ion with poly-b15/5MI and alternating copolymer poly(b15/5MI-alt-α-Mest) are practically the same, while the concentration of complex with b15/5 is two times lower.

In all cases the concentration of complexes with K-picrate is higher than the concentration of Na-picrate complexes. A marked

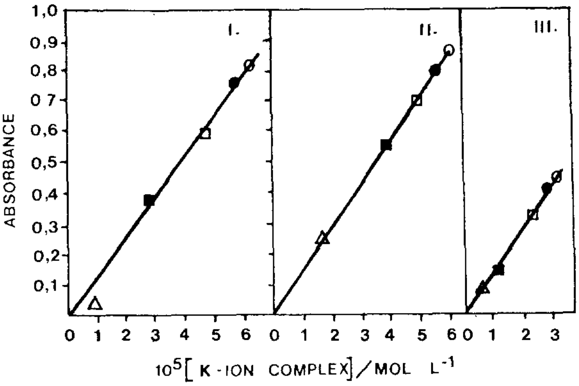

Fig.2. The plot of absorbance against molar concentration of K-picrate complexes with poly-b15/5MI (I), poly(b15/5MI-alt-α-MeSt) (II) and b15/5 (III); K-picrate-to-crown compound solution in mL: 10:10 (○); 10:7(●); 10:5 (□); 10:3 (■); 10:1 (△).

difference is observed in the ability to complexation between alternating copolymer with Na-picrate and K-picrate. While the ability to complexation of alternating copolymer and homopolymer with K-picrate is high and practically the same, alternating copolymer has low tendency to complexation with Na-picrate. The concentration of Na-ion complex with poly(b15/5MI-alt-α-MeSt) does not exceed the concentration of Na-ion complex with b15/5.

The per cent of metal picrate complex transferred from the aqueous solution to CH_2Cl_2 plotted against the ratio of crown compound over metal picrate in aqueous solution is presented in Figs. 3 and 4.

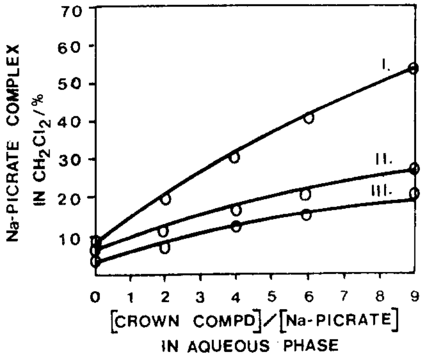

Figure 3. The plot of Na--picrate complex in CH_2Cl_2 (%) against the molar ratio of crown compounds over Na--picrate in aqueous solution; poly-b15/5MI(I);poly(b15/5MI--alt-α-MeSt)(II); b15/5(III).

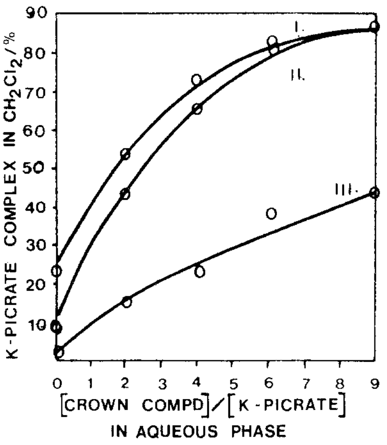

Figure 4. The plot of K--picrate complex in CH_2Cl_2 (%) against the molar ratio of crown compounds over K--picrate in aqueous solution; poly(b15/5MI(I);poly(b15/5MI-alt-α-Mest)(II); b15/5(III).

The results shown in Figs. 3 and 4 are based on the same experimental data as those presented in Figs. 1 and 2 so that the general conclusions are the same.

It is again evident from the data in Fig.3 that Na-picrate has higher ability to complexation with homopolymer (I) which has densly packed side chains than with alternating copolymer (II) and low molecular weight benzo-15-crown-5 (III). Fig.4 indicates that in the presence of homopolymer (I) and alternating copolymer (II) respectively, 90% of K-picrate is transferred from aqueous solution to CH_2Cl_2 while in the presence of b15/5 (III) 40% of complex with K-picrate was detected in CH_2Cl_2. Relatively low concentration of Na-picrate complex with benzo-15-crown-5 containing compounds in comparison with high concentration of complex with K-picrate can be explained by the fact that Na-ion forms 1:1 complex while K-ion forms sandwitched type 2:1 complex with 15-crown-5 compounds (8). Sandwitched type complex between K-ion and b15/5 containig polymers can be formed through intermolecular and intramolecular interaction what can explain the equal ability to complexation of homopolymer and alternating copolymer.

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