Short Communication

Anion-exchange selectivity of cyclic phosphate oligomers

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(Received February 23rd, 1993)

ABSTRACT

The distribution coefficients, K_d, of inorganic cyclic phosphate oligomers, $P_nO_{3n}^{n-}$, for the Bio-Rad AG 1-X4 resin were determined in potassium chloride and tetramethylammonium chloride solutions. Considerable differences in the K_d of the same cyclic phosphate anion at the same Cl^- concentration for the potassium chloride and tetramethylammonium chloride systems were observed. The anion-exchange selectivity of the cyclic phosphate anion was discussed.

Cyclic phosphate anions, members of the group known as inorganic condensed phosphate anions and presented as $P_nO_{3n}^{n-}$, are very interesting materials from the viewpoint of electrolyte solution chemistry because of the high negative charges on their relatively compact molecules [1–3]. We have reported the separation of these cyclic oligomers by HPLC and have discussed their retention mechanism on the HPLC column. As we have described previously [4,5], the retention times of each phosphate anion can be predicted from the Cl^- concentration dependence of the distribution coefficient. The relationship between the distribution coefficient of the phosphates and the concentration of the eluting ion, Cl^-, is governed by the thermodynamic selectivity coefficient for the anion-exchange reaction. However, the thermodynamic selectivity coefficient could not be estimated since it is almost impossible at the present time to estimate the activity coefficient terms of such highly charged cyclic phosphate anions in both aqueous and exchanger phases. Therefore, the true anion-exchange behaviour of the cyclic phosphates cannot be discussed; however, in this work a qualitative explanation for the exchange reaction has been attempted by measuring the distribution coefficient in potassium chloride and tetramethylammonium chloride solutions and determining the apparent selectivity coefficient, K_{ex}.

The distribution coefficient, K_d, of cyclic phosphate oligomers for the Bio-Rad AG 1-X4 resin was determined as a function of the chloride ion concentration. Potassium and tetramethylammonium ions were used as co-ions of the chloride ion. Considerably different distribution coefficients were obtained in potassium chloride and tetramethylammonium chloride solutions at the same chloride ion concentrations. For the $P_8O_{24}^{8-}$ ion, the K_d for the tetramethylammonium chloride system was 3600 times greater than that for the potassium chloride system. K_d values were reduced by the presence of potassium ions,

which form ion pairs with the cyclic phosphate anions. However, the slope of the log K_d vs. log $[Cl^-]$ plots for both systems agreed with the structural charge of cyclic phosphate anions according to the law of mass action. The ion pair formed in potassium chloride solutions might dissociate when the phosphate anions are adsorbed into the exchanger phase. The apparent selectivity coefficient of each cyclic phosphate on the exchange resin, where the acivity coefficient term was neglected, was determined in the tetramethylammonium chloride solution. The apparent selectivity coefficient significantly depends on the equivalent fraction of Cl^- in the exchanger phase. From the apparent selectivity coefficient obtained, the anion exchange behaviour was analysed.

EXPERIMENTAL

Chemicals

Sodium salts of cyclotri- (P_{3m}) and cyclo-tetraphosphate (P_{4m}) were prepared by the usual methods [6]. Sodium cyclohexa- (P_{6m}) and cyclooctaphosphate (P_{8m}) were synthesized by the methods of Griffith and Buxton [7] and Schülke [8], respectively. All other chemicals were of analytical reagent grade and commercially available.

Determination of the distribution coefficient

Distribution coefficients for the Bio-Rad AG 1-X4 resin were measured by the usual batch method at 25°C. The phosphate contents in the solution phase were analysed spectrophotometrically with the Mo(V)–Mo(VI) reagent [3]. Since the tetramethylammonium ion contained in the test solution interfered with the colour development of the Mo(V)–Mo(VI) reagent, it was eliminated by an ion-exchange method.

Measurement of the apparent selectivity coefficient

Bio-Rad AG 1-X4 resin of Cl^- form, the exchange capacity of which was determined accurately, was converted to each phosphate form. A known amount of the resin of the phosphate form was equilibrated with a known amount of tetramethylammonium chloride solu-

tion at 25°C, and the phosphate content in the aqueous phase was determined spectrophotometrically.

RESULTS AND DISCUSSION

Suppose a solution containing the cyclic phosphate anion, P^{n-}, is agitated with the anion-exchange resin of Cl^- form (RCl), and the equilibrium is presented as:

$$n\text{RCl} + P^{n-} \rightleftharpoons R_nP + n\text{Cl}^- \qquad (1)$$

The thermodynamic selectivity coefficient, K_{ex}, can be written as

$$K_{ex} = \frac{(a_{P^{n-}})_r a_{Cl^-}^n}{(a_{Cl^-})_r^n a_{P^{n-}}} \qquad (2)$$

where subscript r refers to the resin phase.

This equation can be rewritten as:

$$K_{ex} = \frac{[P^{n-}]_r [Cl^-]^n (f_{P^{n-}})_r f_{Cl^-}^n}{[Cl^-]_r^n [P^{n-}] (f_{Cl^-})_r^n f_{P^{n-}}} = K_{ex} \frac{(f_{P^{n-}})_r f_{Cl^-}^n}{(f_{Cl^-})_r^n f_{P^{n-}}} \qquad (3)$$

where

$$K_{ex} = \frac{[P^{n-}]_r [Cl^-]^n}{[Cl^-]_r^n [P^{n-}]} \qquad (4)$$

and the terms f designate the activity coefficient terms of each species. The distribution coefficient of the cyclic phosphate anion, K_d, is defined as:

$$K_d = \frac{[P^{n-}]_r}{[P^{n-}]} \qquad (5)$$

The dependence of log K_d of the four cyclic phosphate anions on log $[Cl^-]$ for the potassium chloride system is shown in Fig. 1. The log K_d vs. log $[Cl^-]$ plots show good linear relations and the slopes of the straight lines agreed with their anionic charge. From eqn. 4, the following relation can be derived:

$$\log K_d = -n \log [Cl^-] - n \log [Cl^-]_r + \log K_{ex} \qquad (6)$$

In this equation, $[Cl^-]_r$ can be assumed to be constant since the amount of the cyclic phos-

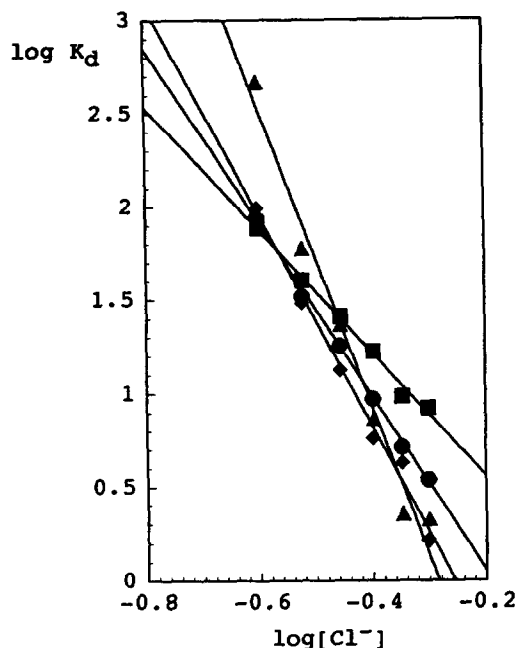Fig. 1. Plots of log K_d vs. log [Cl$^-$] for the potassium chloride system. ■ = P_{3m}; ● = P_{4m}; ◆ = P_{6m}; ▲ = P_{8m}.

Fig. 2. Plots of log K_d vs. log [Cl$^-$] for the tetramethylammonium chloride system. ■ = P_{3m}; ● = P_{4m}; ▲ = P_{6m}; ◆ = P_{8m}.

phate anions adsorbed was very small. The linear relation between log K_d vs. log [Cl$^-$] shows that log K_{ex} is kept constant in the present experimental conditions. The agreement between the slopes of log K_d vs. log [Cl$^-$] plots and the anionic charge of cyclic phosphate anions suggests that the cyclic phosphate anions entered into the exchanger phase, leaving K$^+$ ions which formed ion pairs with the phosphate anions. When tetramethylammonium chloride was used as an eluting reagent instead of potassiun chloride, log K_d vs. log [Cl$^-$] plots, as shown in Fig. 2, resulted. In analogy with the case of the potassium chloride system, the plots show good linear relations and their slopes agree with their anionic charges (Table I). For each phosphate anion, the same slope values were obtained for both potassium chloride and tetramethylammonium chloride systems, however large differences in the distribution coefficients of the same cyclic phosphate at the same Cl$^-$ concentration for the potassium chloride and tetramethylammonium chloride systems were observed. For example, for $P_8O_{24}^{8-}$ at [Cl$^-$] = 0.5 M, K_d was 2.14 in potassium chloride solution but 7610 in
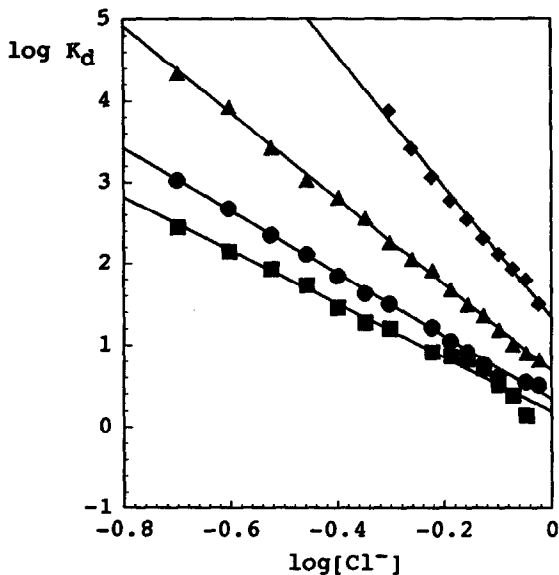
tetramethylammonium chloride solution. This indicates that the distribution coefficient of cyclic phosphate anions is significantly affected by the presence of the cations which interact with the anions. The difference became larger for the higher membered anions. Appreciable differences in the K_d between the potassium chloride, lithium chloride and sodium chloride systems were not observed. Smaller K_d values in the potassium chloride solution are attributed to the ion-pair formation occurring between K$^+$ and $P_nO_{3n}^{n-}$. The energy necessary for the dissociation of the ion pairs caused the drop in the K_d values.

The apparent selectivity coefficient, K_{ex}, where activity coefficient terms were not considered, was determined for four cyclic phosphate anions in the tetramethylammonium chloride solution. K_{ex} varied considerably with the equivalent fraction of Cl$^-$ in the resin phase, as shown in Fig. 3. However it can be tentatively concluded that K_{ex} decreases in the order $P_8O_{24}^{8-} > P_3O_9^{3-} > P_4O_{12}^{4-} > P_6O_{18}^{6-}$. As for the major factors that influence the selectivity coefficient, Coulombic forces between cyclic phosphate anions and fixed cations in the exchanger, as well as the solvation of the cyclic phosphate anions,

TABLE I

SLOPES OF LOG K_d VS. LOG $[Cl^-]$ PLOTS

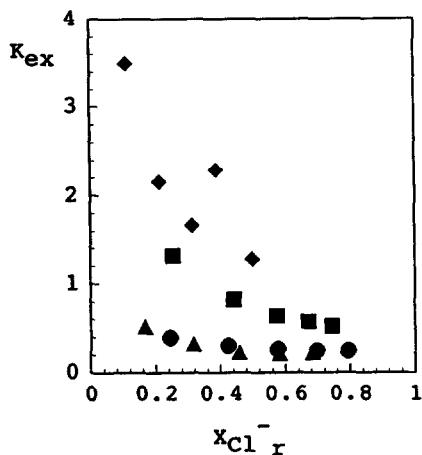|	Slope			
	$P_3O_9^{3-}$	$P_4O_{12}^{4-}$	$P_6O_{18}^{6-}$	$P_8O_{24}^{8-}$
Potassium chloride	−3.3	−4.6	−5.7	−8.0
Tetramethylammonium chloride	−3.3	−4.1	−5.4	−8.0

Fig. 3. Apparent selectivity coefficient, K_{ex}, for exchange between chloride and cyclic phosphate anions as a function of the equivalent fraction of chloride ions in the exchanger phase, $X_{Cl_r^-}$. ■ = P_{3m}; ● = P_{4m}; ▲ = P_{6m}; ◆ = P_{8m}.

might be considered. In this case, large Coulombic forces act as an increasing factor for K_{ex}, while the energies necessary for the desolvation act to decrease K_{ex}. From $P_8O_{24}^{8-}$ to $P_3O_9^{3-}$, Coulombic forces decrease, as do desolvation energies, and $P_6O_{18}^{6-}$ has the minimum value for K_{ex}.

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