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CHEMICAL EQUILIBRIA IN ION-EXCHANGE CHROMATOGRAPHY

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SUMMARY

Equations for the calculation of distribution coefficients of cations, anions and basic molecules depending on the pH and composition of the eluent are given. Some general rules concerning anion-exchange equilibrium constants are also discussed.

INTRODUCTION

The rapid development and wide range of applications of ion-exchange chromatographic methods can be explained in terms of two main advantages. The first is the wide selectivity range. The distribution coefficient of the species to be separated can be influenced by chemical reactions, usually on a very large scale. The second advantage follows from the first, namely that the distribution coefficients and the related retention volumes can be calculated in most instances, and the optimum conditions of the separations can be predicted.

CALCULATION OF DISTRIBUTION COEFFICIENTS AND OPTIMUM CONDITIONS

The ion-exchange process taking place between an ion exchanger loaded with monovalent ions A and a solution containing B ions of valence z is described by the following equation (the charges being omitted for simplicity):

$$z\text{RA} + \text{B} \rightleftharpoons \text{R}_z\text{B} + z\text{A} \tag{1}$$

It was shown earlier[1] that the logarithm of the distribution coefficient of the B ions can be calculated to a good approximation using the following equation:

$$\log D_\text{B} = \log K^x + z \log Q - z \log [\text{A}] \tag{2}$$

where D_B is the distribution coefficient of the B ions, Q denotes the capacity of the resin and [A] is the concentration of the monovalent eluent ions.

In the derivation of eqn. 2, it was considered that the concentration of the eluted B ions is much lower than that of the eluent ions, and the value of the mass action ratio of the ion-exchange reaction, K^x, can be assumed to be constant.

If there are side-reactions of the B ions, forming neutral or oppositely charged

species in the solution, eqn. 2 can be extended by using the side-reaction functions, introduced and widely used by Ringbom[2] in complex chemistry, to give

$$\log D_B = \log K^x - \log \alpha_{B(X)} + z \log Q - z \log [A] \tag{3}$$

where X denotes the species (ligands, protons, etc.) that reacts with the B ions to form complexes, protonated species, etc. If the concentration of the reacting species X and the equilibrium constants, β, of the side-reactions are known, the α values can easily be calculated:

$$\alpha_{B(X)} = 1 + [X] \beta_1 + [X]^2 \beta_2 + \cdots \tag{4}$$

In those cases where the adsorption behaviour of the components to be separated is very similar, *i.e.*, the K^x values are very similar, in the presence of complex-forming ions (metal ions or ligands) the selectivity can be increased due to the side-reaction function.

The equations can be used for planning both cation-exchange and anion-exchange chromatography in general[1,3,4]. In the case of organic bases, the ligand-exchange reactions, introduced by Helfferich[5], can also be used successfully. As shown earlier[6], the distribution coefficients and their dependence on the metal ion concentrations can also be in ligand exchange in the approximation

$$\log D_B \approx Q \, d_B \cdot \frac{\bar{\beta}_1}{\alpha_{B(M)}} \tag{5}$$

where d_B denotes the distribution constant of the ligand, $\bar{\beta}_1$ is the stability complex of the 1:1 complex and M is the complex-forming metal ion.

If the distribution coefficients of the species and their dependence on the pH or the concentration of the reagent X are known, the most suitable conditions for chromatographic separations, the elution volumes and the number of theoretical plates required for quantitative separations[7] can be calculated.

ION-EXCHANGE EQUILIBRIUM CONSTANTS

If we wish to calculate the distribution coefficient of a substance using eqn. 2 or 3, one of the most important problems is to establish the proper value of the ion-exchange equilibrium constant, the logarithm of which is the first term on the right-hand side of eqns. 2 and 3.

Although several studies have been made in recent years on the elucidation of the general rules of the absorption behaviour of cations and anions, there has so far been a lack of data and rules that can be used in calculations. In the field of cation exchange on strongly acidic resins, the situation is better as extensive collections of distribution coefficients of metal ions in mineral acid solutions were given by Strelow and coworkers[8,9] and also by other workers. In most instances, the selectivity order of the metal cations is in agreement with the classical theories of Gregor[10] and Glueck-auf[11]. The field of anion exchange has been more neglected.

On account of these problems, and also on account of some separation prob-
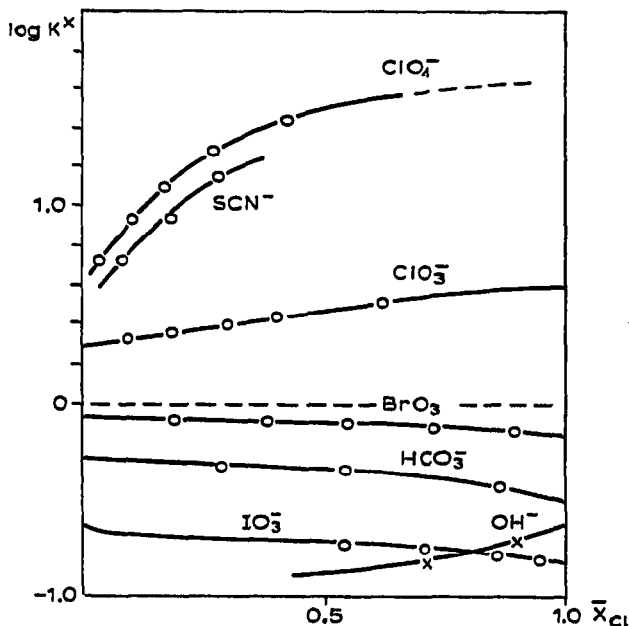
Fig. 1. Logarithm of K^x values of some monovalent ions relative to chloride as a function of the mole fraction of the chloride ($\bar{X}_{Cl}$) in the resin (Dowex 1-X8) at 28°.

lems, we carried out investigations on the ion-exchange equilibria of some anions[12]. In Fig. 1, the logarithm of the K^x values of some monovalent ions referred to the chloride ion, found experimentally, are plotted against the mole fraction of the chloride ion inside the resin phase ($\bar{X}_{Cl}$). It can be seen that the selectivity of all ions that have a lower hydration tendency than that of the chloride ion increases with decreasing amount of the ion in question. The hydroxide ion shows the opposite behaviour, corresponding to the fact that its hydration tendency is greater than that of the reference ion.

For the calculation of chromatographic separations, log K^x values relating to high $\bar{X}_{Cl}$ values are to be used.

The other important question in chromatographic separations is the order of adsorption strengths of the anionic species of the same polybasic acids and the dependence of the adsorption strength on valence. For metal cations, there is a general rule that on the sulphonic type of strongly acidic resins multivalent ions are bound more strongly than monovalent ions. According to our investigations, there is an opposite rule among anions, because on strongly basic anion-exchange resins the anion that has a lower valence has a greater K^x value if the counter ion is the same, e.g., chloride ion.

For example, the K^x value for the sulphate–chloride exchange is 0.1, while for the hydrosulphate–chloride exchange it is about 4 (ref. 13).

Nakamura et al.[14] investigated the adsorption of different polyphosphate anions on anion-exchange resins at various pH values and at various chloride concentrations. Using their data, and eqns. 2 and 3, we calculated the log K^x values (Table I).

TABLE I

CALCULATED ION-EXCHANGE EQUILIBRIUM CONSTANTS OF POLYPHOSPHATE
IONS OF VARIOUS VALENCES RELATIVE TO CHLORIDE ION

Resin: Dowex 1-X4.

Anion	Log K^x	Anion	Log K^x
$H_2P_3O_{10}^{3-}$	−1.1	$HP_4O_{13}^{5-}$	−2.7
$HP_3O_{10}^{4-}$	−1.7	$P_4O_{13}^{6-}$	−3.6
$P_3O_{10}^{5-}$	−2.25		
		$HP_5O_{16}^{6-}$	−3.1
		$P_5O_{16}^{7-}$	−5.0

It can be seen that the log K^x values decrease in the order of polymerization number, and for a given acid in the order of increasing valence.

This behaviour of the ions of polybasic acids is in agreement with the results obtained by thermoanalytical measurements. We found by thermal analysis that if we use slow heating, with increasing temperature the water content of the air-dried (conditioned) anion-exchange resin sample is removed in two distinct steps. The first step (rate maximum at 120°) corresponds to the removal of water of swelling, while the second step (rate maximum at 170°) corresponds to the water of hydration bound strongly to the ions. Thermal analysis curves are given in Fig. 2. By carrying out the measurements with resin samples loaded with different phosphate ions, the proportions of the two types of water were obtained from the TG curves.

From the data, the number of water molecules per equivalent of resin was calculated (Table II). It can be seen that the amount of the more strongly bound water molecules increases with valence (similar results were obtained with sulphate- and hydrosulphate-form resins). Hence the difference between the hydration ability of the
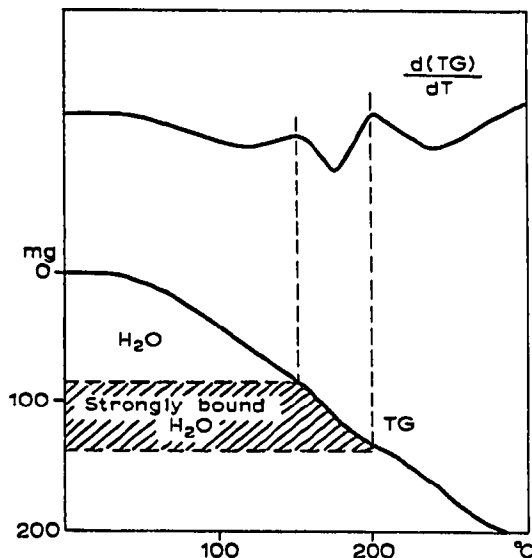

Fig. 2. Derivatogram of 500 mg of air-dried PO₄-form Dowex 1-X8 resin sample. Heating rate: 3.0°/min.

TABLE II

STRONGLY AND LOOSELY BOUND WATER CONTENTS OF AIR-DRIED H_2PO_4-, HPO_4- AND PO_4-FORM RESIN SAMPLES

Resin form	Strongly bound water (moles per equiv. resin)	Loosely bound water (moles per equiv. resin)
H_2PO_4	0.3	3.8
HPO_4	1.8	3.1
PO_4	2.1	3.0

ion in question and that of the chloride ion is an important factor in the selectivity. The volume of the hydrated ion is less important. Multivalent ions have a larger hydration tendency, and therefore their adsorption strength is lower.

EXPERIMENTAL

The determination of ion-exchange equilibrium constants of the monovalent and multivalent anions were determined by means of the dynamic method of Harvey et al.[15]. The description of the measurements and the results have been published elsewhere[12]. The thermal analytical investigations were carried out with a derivato-graph (Paulik–Paulik–Erdey system, MOM, Hungary).

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