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CALORIMETRY STUDY OF THE EXCHANGE EQUILIBRIUM BETWEEN LIGANDS OR METAL–LIGANDS AND AN ANION-EXCHANGE RESIN

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ABSTRACT

The exchange equilibrium between the arylsulphonate ion, free or bound to a metal, and the chloride ion of an anion-exchange resin has been studied by means of a spectrophotometric and calorimetric method. The correction terms due to the dilution of the anions and to the swelling effect of the resin have been evaluated. On the basis of these calorimetric data, a thermodynamic parameter may be obtained that is related to the selectivity coefficient of the anion-exchange resin.

INTRODUCTION

Exchange reactions used for the selective uptake of anions by an anion-exchange resin have been studied for many years [1–3], but several important aspects (i.e. the dependence of selectivity coefficients on ion-charge, size, polarizability and on exchanger cross linking) remain substantially unsolved problems [4]. The calorimetric measurements reported in this preliminary work were performed to determine whether information on the enthalpy changes connected with the various phenomena involved in the exchange process would lead to a better understanding of the causes of the affinity sequence of the anion-exchange.

EXPERIMENTAL

All the calorimetric measurements were performed at 312.9 K with a Calvet-type microcalorimeter (the C-80 calorimeter distributed by Setaram,

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France), equipped with twin cells (10 ml). A new device was designed for breaking the diaphragm and for stirring. The choice of insulating material for these agitators was such that the thermal flow, which can strongly interfere with the quality of the baseline, is decreased.

In a typical exchange experiment, weighted quantities of the resin are dispersed in known volumes of water in the down part of the cell. The ligand or metal ligand solution is put in the upper part of one cell, while water is put in the other. A full isotherm must obviously be constructed to calculate the exact amount of the anion exchanged by the resin.

The resin used in this work was analytical grade Bio-Rad AG MP 1 macroporous anion-exchange resin, 100–200 mesh, in chloride form.

The surface area of the dried resin was 23 m^2 g^{-1}. The resin will hereafter be referred to as AER.

The ligands studied [1,2-dihydroxy-3,5-benzenedisulphonic acid (Fluka), (Tiron: TI), and 8-hydroxyquinoline-5-sulphonic acid (Aldrich), (SOX)], were of analytical reagent grade.

Metal stock solutions 1000 mg l^{-1} (Merck) for atomic absorption were diluted as required.

Absorbance measurements were made with a UV-visible double-beam spectrophotometer (Hitachi 150-20) and the metal concentrations were evaluated using inductively coupled plasma emission spectrometry (Plasma 300, Allied Analytical System).

All experiments were performed at pH 6.5.

All calorimetric determinations were repeated at least five times to check reproducibility.

RESULTS AND DISCUSSION

Heat of swelling

Some experiments were performed on the swelling caused by the transition of the exchanger from a partially hydrated state (relative moisture pressure 0.6) to a fully hydrated one (i.e. wet-swollen). Under these conditions the heat of swelling for Bio-Rad AG MP 1 was endothermic and equal to 0.657 ± 0.04 J g^{-1}.

This value is ascribed to the completion of the primary hydration of the ionogenic groups resulting from the assimilation of hydrated counterions and exchange groups. As the swelling experiment produced an endothermic heat, it must be assumed that the system configuration entropy increases. This is in disagreement with forecasts based on the statistical theory of swelling for polymers [5]. However, the Flory Rehner theory seems unable to explain the behaviour of highly cross-linked ion-exchangers [6].

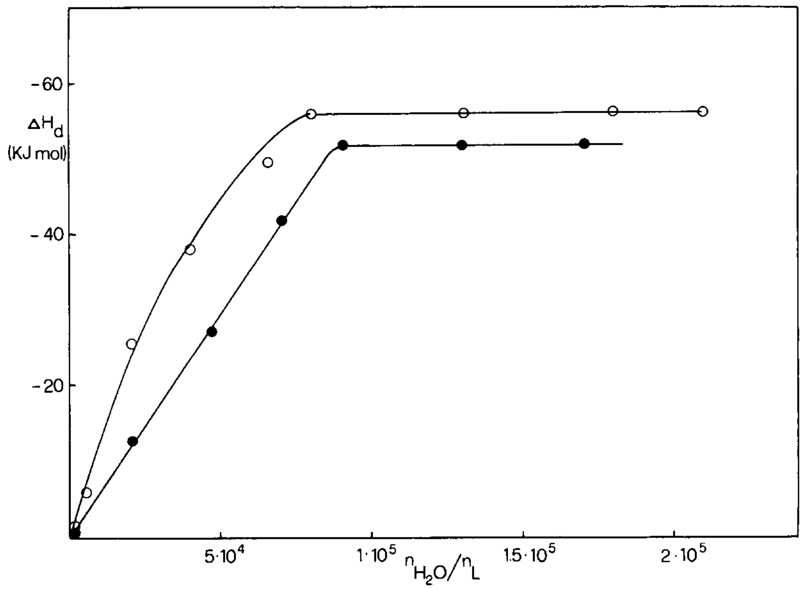

Fig. 1. Integral heats of dilution, ΔH_d, of ligands in water at 319.9 K as a function of the dilution ratio: ●, TI; ○, Cu(TI)$_2$.

The twinning assembly adopted in our experiments cancels the thermal effect of swelling caused by the water added to the exchanger. There is, of course, a swelling effect, i.e. a change in the resin volume due to the variation in the ionic composition of the solution, but such an effect was studied here thermodynamically. In other words, we studied the energetics of the interaction of the ions with the exchanger, that is correlated with variations in the hydration sphere.

Heat of dilution

Figures 1 and 2 show the heats of dilution for the ligand or metal–ligand solutions from the initial concentration down to infinite dilution. For all solutions the dilution heat resulted exothermic.

Heat of exchange

The exchange reaction between the resin chloride form and the ligand (TI or SOX = L–SO$_2$OH) or metal–ligand (M–L–SO$_2$OH) may be written schematically as

$$\begin{aligned}&(\mathrm{AER})\cdot \mathrm{Cl}_n + n'\mathrm{L{-}SO_2O^-}\ (\text{or } n'\mathrm{M{-}L{-}SO_2O^-})\\ &\rightleftharpoons (\mathrm{AER})\cdot \mathrm{Cl}_{(n-n')}\cdot(\mathrm{L{-}SO_2O^-})_{n'} + n'\mathrm{Cl^-}\\ &\text{or } (\mathrm{AER})\cdot \mathrm{Cl}_{(n-n')}\cdot(\mathrm{M{-}L{-}SO_2O^-})_{n'} + n'\mathrm{Cl^-} \qquad (1)\end{aligned}$$

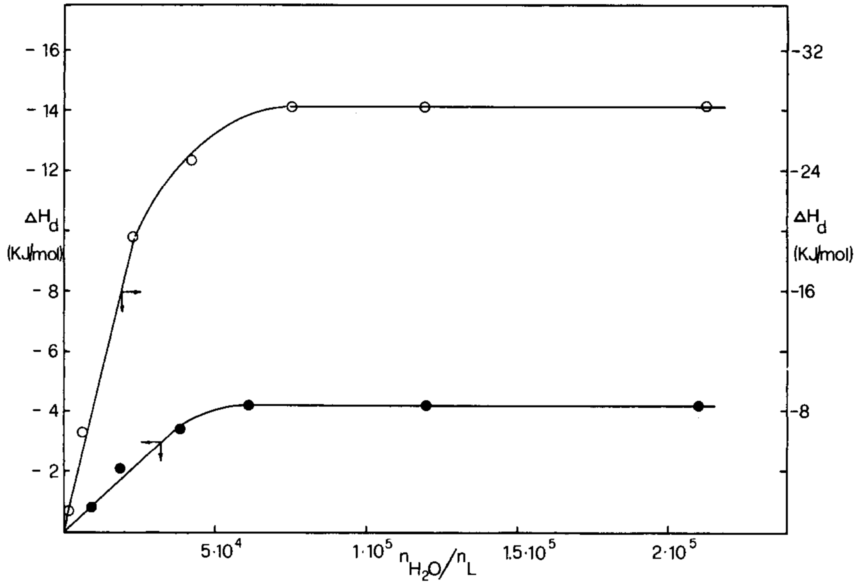

Fig. 2. Integral heats of dilution, ΔH_d, of ligands in water at 319.9 K as a function of the dilution ratio: ●, SOX; ○, $Cu(SOX)_2$.

where $n'Cl^-$ and $n'SO_2O^-$, are the number of moles of chloride and sulphonato ions, respectively, or metal complex exchanged. In this simplified model, the water contribution has not been considered.

The experimental heat detected with the twinning apparatus, which cancels the swelling thermal effect, is the result of the algebraic sum of the following contributions

$$Q_{exp} = \Delta H_{exch} + \Delta H_{dil} + \Delta H_{ads} + \Delta H'_{water} \qquad (2)$$

where ΔH_{exch} is the enthalpy variation resulting from the entering of the sulphonic group and the exit of the chloride ion from the anionic-exchange resin. This term is generally applicable, not only to the breaking and formation of anion-resin bonds, but also to the antagonistic or cooperative interactions of the two water atmospheres: i.e. the atmosphere surrounding the quaternary ammonium of the resin and the one surrounding the entering anion [7]. For this purpose we should have, in our case, a prevalent cooperative effect. It is well known that arylsulphonated ions are structural builders of the same type as quaternary ammonium ions and they should carry some of the water cages with them into the resin net volume [8].

The term ΔH_{dil} refers to the enthalpy change corresponding to the variation in the ion composition of the water solution. The exchange reaction implies the exit of the arylsulphonate ions and the entering of the chloride ions into the bulk water solution, but the latter phenomenon is energetically negligible for the concentration range of this study [9].

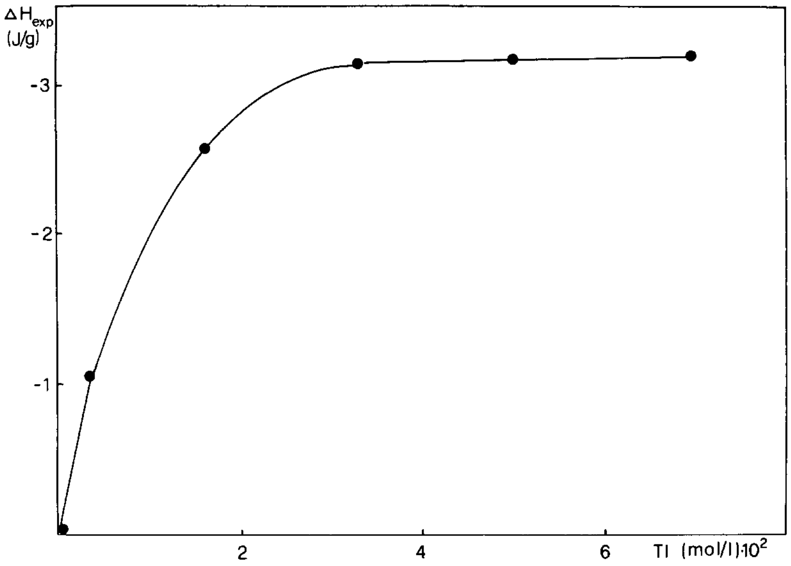

Fig. 3. The experimental heat of exchange, ΔH_{exp}, as a function of the ligand, TI, concentration.

The ΔH_{ads} term concerns the energy change connected with the adsorption of ligand or metal–ligand molecules onto the resin.

The $\Delta H_{\mathrm{water}}$ parameter, which is very difficult to estimate, is concerned with the partial displacement of adsorbed water molecules by the ligand or metal–ligand molecules fixed onto the resin.

Figure 3 shows a typical exchange-reaction calorimetric isotherm and the experimental heats of exchange of the chloride ion (of the resin) with the aryl ions, according to the schematic equation (1). These results are also listed in Table 1. All the heats in Table 1 are exothermic and the metal-complex ions give higher values.

Even if uncertainty remains with respect to ΔH_{ads} and $\Delta H_{\mathrm{water}}$, which should make a small contribution, we believe that the sign and the order of magnitude of our experimental heats of exchange are physically meaningful:

TABLE 1

Experimental heat of exchange for chlorine with the arylsulphonate ions or metal complexes in an anion-exchange resin

X	Concentration of X (mol l^{-1})		ΔH_{exch} (J per gram of resin)
	Initial	Final	
TI^{2-}	1.00×10^{-1}	6.99×10^{-2}	-3.23 ± 0.02
$Cu(TI)_2^{4-}$	5.00×10^{-2}	1.00×10^{-6}	-3.45 ± 0.02
SOX^-	2.00×10^{-2}	1.00×10^{-6}	-6.17 ± 0.02
$Cu(SOX)_2^{2-}$	1.00×10^{-2}	1.00×10^{-6}	-23.91 ± 0.03

these data are in agreement with the thermodynamic parameters obtained by Choppin et al. [10] for the ArCl $\rightleftharpoons$ ArBr and for the ArCl $\rightleftharpoons$ ArI exchanges.

A different sign was obtained for the exchange heat determined by Gregor et al. [11]. According to these authors, the effect of temperature on the selectivity coefficient of various anions against chloride for quaternary base ammonium anion-exchange resin implies an endothermic heat. However, the same authors observe that the effect of temperature is small and that the selectivity coefficient for this system must be considered as fairly independent of temperature.

The values given in Table 1 are preliminary results and are not sufficient to interpret the different heats of exchange for systems because these involve so many parameters. Further study of the heat of adsorption of the complex is needed, as well as further calorimetric measurements with different anions and variously cross-linked resins. With such data it should be possible to characterize better the exchange sites and to distinguish between random ion-pair and clustered ion-pair systems [12].

The microcalorimetric technique seems to be a useful tool for obtaining reliable thermodynamic parameters with which to interpret the selectivity coefficient of anion-exchange resins.

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