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EFFECT OF HYDROGEN BONDING ON THE SELECTIVITY OF ANION-EXCHANGE EQUILIBRIA

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SUMMARY

Ion-exchange equilibria of oxalate, maleate and fumarate anions were studied on a strongly basic anion-exchange resin in the chloride form. Equilibrium and calorimetric measurements were made in aqueous solution at 25°C in order to obtain the thermochemical parameters of the exchange reaction. The resin shows a pronounced selectivity only for the monovalent maleate anion; the other species studied are not adsorbed preferentially by the resin. The selectivity for the monovalent maleate anion can be explained by its ability to form a strong intramolecular hydrogen bond. Owing to this bond formation the hydration ability of the ion is dramatically decreased which, in turn, markedly influences the distribution of the ion between the two phases. The free energy of the system is lowered considerably when this poorly hydrated species is transferred into the resin phase where the relative permittivity is much lower than that of the aqueous solution phase. This case is an example of the system where the selectivity is not governed by the interaction in the resin phase but rather by the interactions in the solution phase. The relatively small enthalphy and entropy changes of the exchange reactions also indicate the lack of a strong resin phase interaction.

INTRODUCTION

In previous papers thermochemical data were reported for the heat of exchange of hydroxide and orthophosphate anions on a strongly basic anion-exchange resin in the chloride form[1,2]. This paper is concerned with the exchange reaction of the mono- and bivalent anions of oxalic, maleic and fumaric acids on the same type and form of resin that was used previously.

The above systems are interesting for several reasons. Anion-exchange chromatography has been widely used for the separation of organic acids[3]. There is no general rule, however, for the prediction of the selectivity (*i.e.*, elution) order for the organic ions. The selectivity is a result of a number of interactions and an adequate assessment of the governing interaction is not always possible. Thermochemical parameters of the exchange reaction or structural data for the distributing species may be useful in the prediction or interpretation of selectivity.

EXPERIMENTAL

Selection of the useful pH range

The pH range where the distribution of the acid anions can be studied was established from the molar fraction distribution diagram of oxalic (H_2Ox), maleic (H_2M) and fumaric (H_2F) acids. From Fig. 1, it appears that at pH > 8 all three acids are present in a fully ionized form in the solution. The ion-exchange distribution of the bivalent acid anions can therefore be studied if care is taken to maintain the pH above 8 in the equilibrium solution.
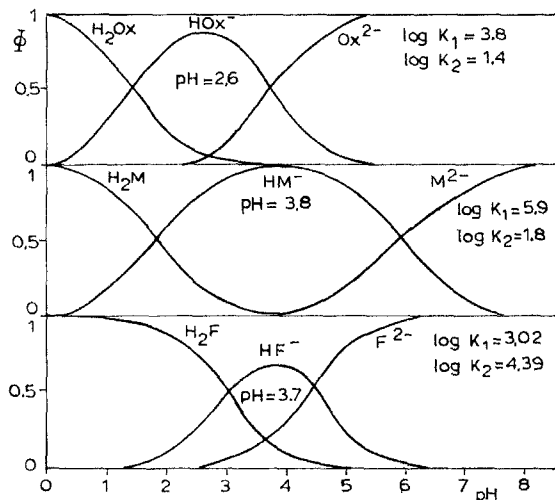

Fig. 1. Molar fraction distribution diagrams of the acids investigated. The protonation constants, K, are taken from ref. 4.

From the curves in Fig. 1 it also appears that the molar fraction of the mono-valent oxalate and maleate acid anions approaches almost 1 at pH 2.6 and 3.8, respectively. For fumarate, however, it reaches only about 0.7 at its maximum, the remainder being none and fully dissociated acid. The HF^-/Cl^- exchange reaction therefore cannot be studied without serious interference.

Ion-exchange resin and chemicals

Dowex 1-X8 was prepared and its capacity determined as described earlier[1]. Maleic acid (Schuchardt, Munich, G.F.R.), fumaric acid and oxalic acid (Reanal, Budapest, Hungary) were reagent-grade chemicals.

Solutions

For the monovalent acid anions (Y^-) the Y^-/Cl^- exchange reaction was studied as a function of the resin composition at a total normality of 0.1 ($TN = c_Y z_Y + c_{Cl} z_{Cl}$). From 0.1 mol/dm³ maleic acid and sodium chloride stock solutions mixed solutions (500 cm³) were prepared by mixing the appropriate volumes of the stock solutions. In the mixed solutions the equivalent fraction of the acids ($x_Y = c_Y z_Y/TN$) were set at 0.1, 0.2, 0.3, 0.5, 0.7, 0.8 and 0.9 (in the case of mono-/mono-

valent exchange the equivalent and molar fractions are, of course, identical). The pHs of the 500-cm³ mixed solutions were set at the appropriate value (in the H_2Ox–NaCl mixtures to 2.6 and in the H_2M–NaCl mixtures to 3.8) by addition of solid potassium hydroxide.

The Y^{2-}/Cl^- exchange reactions were studied at total normalities of 0.1 and 0.01. For these investigations 0.05 mol/dm³ acid and 0.1 mol/dm³ sodium chloride stock solutions were prepared and mixed to obtain the same equivalent fractions as in the case of the mono-/monovalent exchange. The pHs of these solutions were set between 8 and 10. For the measurements at a total normality of 0.01 the above solutions were diluted with water and their pHs were adjusted as necessary.

Equilibrium measurements

Known amounts of the resin (*ca.* 0.5 g) were weighed into 100-cm³ glass-stoppered flasks and exactly 100 cm³ of the stock or mixed solutions were added using a pipette. The flasks were left overnight for equilibration at $25 \pm 0.1°C$ in a thermostated bath. Before separation and analysis of the equilibrium phases the pH of the solution phase was measured with a calibrated glass electrode. For the calculation of the composition of the phases in equilibrium aliquots were taken both from the original and from the equilibrium solutions. The chloride contents of the samples were titrated with 0.05 mol/dm³ mercury(II) nitrate solution[5].

RESULTS AND DISCUSSION

The results of the equilibrium measurements can be represented in terms of ion-exchange isotherms. For the reactions studied these are shown in Fig. 2.
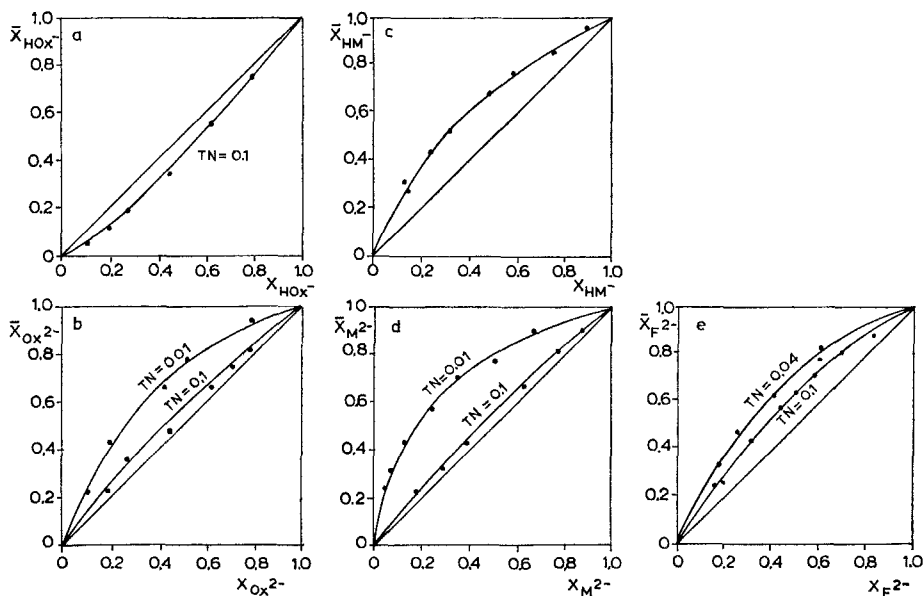

Fig. 2. Ion-exchange isotherms at 25°C for the studied equilibria: (a) HOx^-/Cl^-; (b) Ox^{2-}/Cl^-; (c) HM^-/Cl^-; (d) M^{2-}/Cl^-; (e) F^2/Cl^-.

In Fig. 2a the isotherm shows that the adsorption of the monovalent oxalate anion is not preferred by the chloride-form resin. In the heterovalent exchange the distribution of the ions is strongly influenced by electroselectivity, which makes the bonding of the bivalent oxalate anion preferred as the total normality of the solution decreases (Fig. 2b).

In contrast to the monovalent oxalate anion, the chloride-form resin shows a high affinity for the maleate anion (HM^-), as demonstrated in Fig. 2c. Isotherms for the bivalent maleate and fumarate anions (Fig. 2d and e) demonstrate again the above-mentioned effect of electroselectivity.

For an adequate assesment and comparison of the selectivities of the reactions, the thermodynamic equilibrium constants should be calculated and used.

For the ion-exchange reaction

$$n R_m X^m + m Y^n \rightleftharpoons m R_n Y^n + n X^m \tag{1}$$

the thermodynamic equilibrium constant can be defined by

$$K^T = K'_x \frac{[f(Y)]^m}{[f(X)]^n} \tag{2}$$

where

$$K'_x = \frac{[\bar{x}(Y)]^m [x(X)]^n}{[\bar{x}(X)]^n [x(Y)]^m} \cdot \frac{[\gamma(X)]^n}{[\gamma(Y)]^m} \cdot \frac{n^m}{m^n} \cdot TN^{n-m} \tag{3}$$

Eqn. 3 contains only experimentally accessible quantities although the ratio of the solution phase activity coefficients can only be estimated for the systems studied. With the lack of a better approximation, the Davies equation[6] was used to estimate the above activity ratio.

When K' is calculated from the equilibrium measurements then, as is usually observed, it depends on the extent of conversion of the resin, i.e., on the equivalent fraction of the counter ions [$\bar{x}(Cl)$ or $\bar{x}(Y)$]. These functions are shown on log K' versus $\bar{x}_{Cl}$ diagrams in Fig. 3.

For the evaluation of the thermodynamic equilibrium constant the method of Freeman[7] was used. This method uses the concept of excess free energies to equate the deviations from ideality, whereby a simultaneous calculation of the equilibrium constant and the acitivity coefficients is made possible. For the calculation of the thermodynamic equilibrium constant the following equation was derived by Freeman:

$$RT \ln K' = RT \ln K^T - \sum_{\nu=0}^{N} G_\nu [-(2\bar{x}_{Cl} - 1)^{\nu+1}$$
$$+ 2\nu \bar{x}_{Cl}(1 - \bar{x}_{Cl})(2\bar{x}_{Cl} - 1)^{\nu-1}] \tag{4}$$

The experimental values of ln K' are fitted parametrically to the equation above using as many terms in the summation as the precision requires ($\nu = 0, ..., N$). The application of a least-squares procedure yields the values of K^T and the G_ν fitting parameter. Freeman proved also that the G_ν parameter describes the course of ln f(Cl) and ln f(Y) as a function of x(Cl) and these functions are given by the following equations:

$$RT \ln f(Cl) = z_{Cl}(1 - \bar{x}_{Cl})^2 \sum_{\nu=0}^{N} G_\nu [2(\bar{x}_{Cl} - 1)^\nu + 2\nu \bar{x}_{Cl}(2\bar{x}_{Cl} - 1)^{\nu-1}] \tag{5}$$
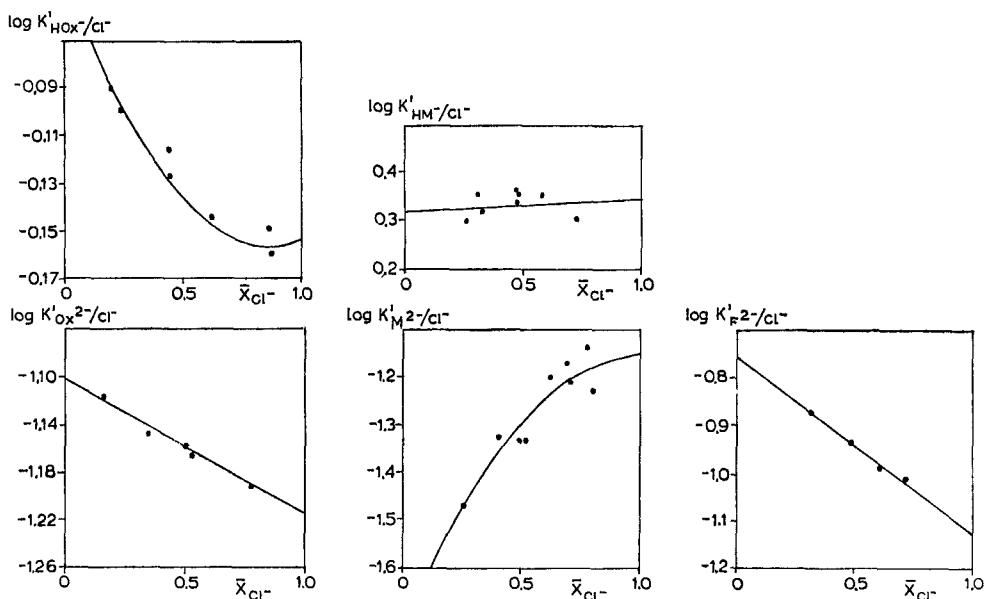
Fig. 3. Dependence of the selectivity coefficient, K', on the composition of the resin phase for the HOx^-/Cl^-, Ox^{2-}/Cl^-, HM^-/Cl^-, M^{2-}/Cl^- and F^{2-}/Cl^- systems.

$$RT \ln f(Y) = z_Y \bar{x}_{Cl} \sum_{\nu=0}^{N} G_\nu[(2\bar{x}_{Cl} - 1)^\nu - 2\nu(1 - \bar{x}_{Cl})(2\bar{x}_{Cl} - 1)^{\nu-1}] \qquad (6)$$

The calculated thermodynamic equilibrium constants are given in Table I, and as an application of eqns. 5 and 6 the calculated activity coefficient functions are shown for the HOx^-/Cl^- and Ox^{2-}/Cl^- systems in Fig. 4.

TABLE I

THERMOCHEMICAL DATA FOR THE EXCHANGE REACTIONS STUDIED

Y^{n-}	K^T	ΔG° (kJ equiv.$^{-1}$)	ΔH (kJ equiv.$^{-1}$)	ΔS (J $^\circ K^{-1}$ equiv.$^{-1}$)
HOx^-	0.753	+0.70	+3.58	+ 1
Ox^{2-}	0.107	+2.77	+6.35	+13
HM^-	2.150	−1.85	−5.51	−12
M^{2-}	0.045	+3.84	+7.80	+13
F^{2-}	0.119	+2.64	+8.11	+18

From the calculated equilibrium constants the free energy of the exchange, ΔG°, was obtained by using the relationship

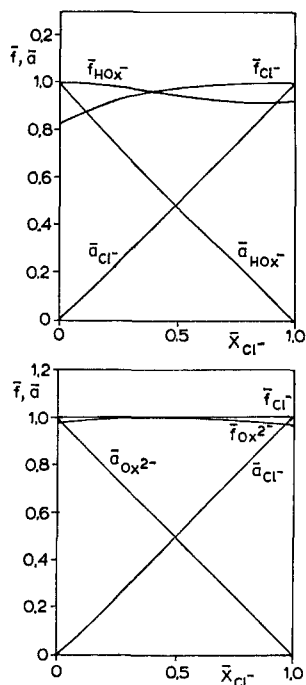$$\Delta G^\circ = -\frac{1}{z_{Cl} z_Y} \cdot RT \ln K^T \qquad (7)$$

Fig. 4. Calculated activity and activity coefficient functions for the HOx^-/Cl^- and Ox^{2-}/Cl^- systems.

These data are also given in Table I. The enthalpy and entropy values of the exchange reactions were taken from ref. 8.

From a comparison of the thermodynamic data in Table I it appears that with the exception of the HM^-/Cl^- system the free energy changes are positive. These positive free energy values originate solely from the unfavourable (positive) enthalpy change because the entropy values are otherwise favourable (positive).

Thermochemical data can often be used to draw conclusion regarding a certain type of interaction. When, for example, complexes are formed in aqueous solution the electrostatic type of bonding is usually accompanied by a large gain of entropy, while the enthalpy change generally counteracts the reaction. With covalent bonding, however, the reaction is accompanied by a considerable decrease in enthalpy.

In the field of ion exchange these principles may work, e.g., in the case of a weak acid cation exchange, but the application of these guidelines to anion exchange would either be very formal or may lead to unrealistic comparisons.

For the reactions studied the thermochemical parameters do not show to any specific mode of the above-mentioned interactions. The source of the interaction that governs selectivity should therefore be sought not within the resin phase but rather in the solution phase.

Of the anions investigated the chloride-form resin shows preference only for the monovalent maleate anion (MH^-). The interaction that may lead to this excep-

tional selectivity is the ability of this ion to form an intramolecular hydrogen bond:
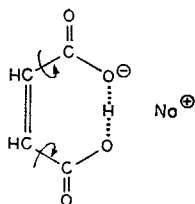
This interaction decreases dramatically the polarizing ability of the single negative charge, being spread over a very large species. A well known consequence of this interaction is the low solubility of NaHM in water. The poorly hydrated HM^- ion is therefore transferred into the resin phase. The free energy of the system is thereby considerably lowered because the relative permittivity of the solid phase is lower than that of the aqueous phase.

When the acid is fully ionized the ionic repulsion between the carboxylate groups cause a large rotation around the C–C single bond (shown by arrows in the formula), which prevents the formation of a strong intramolecular hydrogen bond[9]. This distortion leads to a higher degree of hydration of the M^{2-} ion, which is manifested in the lower value of the selectivity coefficient. The latter structural information became evident from single crystal diffraction studies of Na_2M. These studies also revealed that there are no similar distorsions in the case of H_2M and KHM, which makes the O ... H ... O bond fairly stable.

Similar explanations do not apply of course, either to fumaric acid, where the C=C double bond fixes the carboxylate groups in a *trans*-position, or to oxalic acid, where the C–C single bond allows free rotation of the groups.

The examples presented show again that anion exchange is a fairly complex phenomenon and selectivity is unlikely to be explained by a simple resin phase-dominated electrostatic interaction, as is often possible with cation exchangers.

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