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MODELLING OF CHELATING RESIN PROTONATION EQUILIBRIA

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SUMMARY

The computer model COMICS has been modified to describe the heterogeneous protonation equilibria of chelating exchange resins. It has been established experimentally that a linear relationship exists between the degree of dissociation of the resin, $\bar{a}$, and the concentration of counter-ion in the resin phase, $\bar{m}_M$. Use of this relationship has enabled equilibrium concentrations of the different protonated resin forms to be calculated as a function of solution pH, and hence the theoretical $\bar{a}$ values could be determined. These matched closely the experimental $\bar{a}$ data, hence validating the protonation constants determined by Szabadka *et al.*
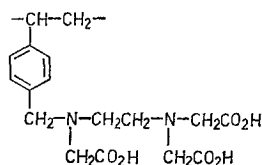
INTRODUCTION

The aim of this work was to develop computer models to describe chelating resin–proton–metal ion equilibria in an analogous manner to the modelling of ligand–proton–metal ion equilibria in homogeneous aqueous systems. Modelling of such systems must be based upon accurate values of protonation and metal ion–resin stability constants, and the preliminary investigation discussed in this paper utilizes protonation data which arise from studies of resins which have been synthesized and characterized by Szabadka *et al.*[1–3]. These resins contain polyamino polycarboxylic acid functional groups on a styrene–divinylbenzene polymer matrix (Fig. 1).

Once such resins have been characterized, it is useful to be able to model the resin equilibria in order, firstly, to verify the accuracy of the protonation and stability constants obtained and, secondly, to predict equilibrium distributions of species in various resin–proton–metal ion–counter ligand systems. This assumes that the kinetics are such that equilibrium conditions are reached. Even if this is not so, the information regarding possible equilibrium distributions is still valuable.

LIGANDEX-E   RESIN

$-CH-CH_2-$

$CH_2-N-CH_2CH_2-N-CH_2CO_2H$
  CH_2CO_2H CH_2CO_2H

DTTA   RESIN

$-CH-CH_2-$

$CH_2-N-CH_2CH_2-N-CH_2CH_2-N-CH_2CO_2H$
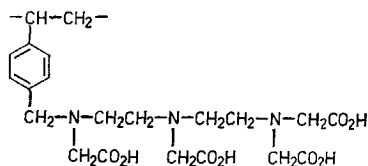 CH_2CO_2H CH_2CO_2H CH_2CO_2H

Fig. 1. Chelating resins studied

One of the several computer programmes which have been developed to model protonation, and complexing equilibria in aqueous systems —such as in natural waters and effluents— is the COMICS programme of Perrin and Sayce[4], which requires an input of values of the stability constants of all complex species being considered, and the total concentrations of all metal ions and ligands present. The equilibrium concentrations of free and complexed species may then be calculated at any specified pH.

The first objective of this present work was to use the data available to model the protonation equilibria of the chelating resins, as a preliminary step to a description of selected resin–proton–metal ion–ligand systems.

EXPERIMENTAL

The two resins were prepared according to a procedure developed by Szabadka and Inczédy. The experimental determination of the protonation constants of the resin Ligandex-E (containing ethylenediamine triacetic acid groups) has been described earlier[2] and the protonation constants of the analogue with diethylenetriamine tetraacetic acid groups (DTTA resin) have since been determined[3] (Table I).

The experimental procedure was based upon the reaction of known weights of the hydrogen-form resin with known amounts of standard potassium hydroxide solution under specified conditions of ionic strength (adjusted with potassium chloride), followed by separation of the equilibrated resin, and subsequent analysis for the amounts of chemically bound potassium ions, of potassium chloride which has migrated into the resin lattice, and of the water present in the resin phase. The pHs of the equilibrated resin–alkali solutions were measured prior to separation and analysis.

RESULTS AND DISCUSSION

Szabadka has shown that, when considering heterogeneous resin protonation

equilibria such as $\bar{R}^- + \bar{M}^+ + H^+{}_{aq} \rightleftharpoons \bar{R}\bar{H} + M^+{}_{aq}$ ($^-$ represents the resin phase), equations of the type:

$$\log K = \text{pH} + \log \frac{1 - \bar{a}}{\bar{a}} + \log \frac{a_M}{\bar{m}_M} \tag{1}$$

may be used to calculate successive protonation constants, where K is a particular protonation constant, pH is the equilibrium pH of the aqueous phase, $\bar{a}$ is the degree of dissociation of the resin, a_M is the activity of the counter-ion in the aqueous phase, and $\bar{m}_M$ is the total concentration of counter-ion in the resin phase. Such an equation has a marked resemblance to that describing a homogeneous protonation reaction:

$$\log K = \text{pH} + \log \frac{1 - a}{a} \tag{2}$$

which may be corrected for the autodissociation of water.

Consequently, it should be possible to use the COMICS model to describe heterogeneous resin equilibria, provided some modifications are made. There are two obvious changes that would convert eqn. 1 for the heterogeneous systems into the form of eqn. 2 which describes homogeneous systems:

(a) Modify the $\log \bar{K}$ values:

$$\log \bar{K} = \text{pH} + \log \frac{1 - \bar{a}}{\bar{a}}$$

where

$$\log \bar{K} = \log K - \log \frac{a_M}{\bar{m}_M};$$

(b) Modify the pH value:

$$\log K = \text{p}\bar{\text{H}} + \log \frac{1 - \bar{a}}{\bar{a}}$$

where

$$\text{p}\bar{\text{H}} = \text{pH} + \log \frac{a_M}{\bar{m}_M}$$

Of the two, expression (a) is rather unsatisfactory in that it infers that the protonation constants are not actually constants, but vary with $\bar{m}_M$, which is a function of the degree of titration of the resin ($\bar{a}$), and of the concentration of counter-ions that have migrated into the resin lattice. Expression (b), on the other hand, requires modification of the pH term to reflect the fact that one is dealing with a two-phase system, with a hydrogen ion activity in the resin phase which differs from that of the solution phase —just as the activities of counter-ions in aqueous and resin phases will differ. Thus to modify the COMICS programme to describe resin protonation equilibria, one must substitute p$\bar{\text{H}}$ or ($\bar{\text{H}}^+$) for the analogous parameters pH or (H^+).

In the particular experiments carried out $\bar{m}_M$ is given by:

$$\bar{m}_M = \frac{\bar{m}_{K^+} + \bar{m}_{KCl}}{\overline{H_2O}}$$

where $\bar{m}_K$ is the molality (g^{-1} dry hydrogen-form resin) of chemically bound potassium ions, $\bar{m}_{KCl}$ is the molality of KCl which has invaded the resin lattice and $\overline{H_2O}$ is the

TABLE I

PROTONATION CONSTANTS OF LIGANDEX-E AND DTTA RESINS

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
Ligandex-E	10.3	5.9	3.3	—
DTTA	10.5	8.2	4.2	2.8

molality of water in the resin phase. Thus in fact $\bar{m}_M$ is a function of both $\bar{a}$ and the solution ionic strength, although the latter term will be kept constant for a particular "titration" run.

Analysis of variance shows that the functional relationship of $\bar{m}_M$ and $\bar{a}$ may be described by a simple linear regression, $\bar{m}_M = b \cdot \bar{a} + a$, which is valid over quite a wide range of $\bar{a}$. Departure from linearity is observed at low $\bar{a}$ values ($\bar{a} < 1$) for high ionic strengths and sometimes at high $\bar{a}$ values. Typical plots are shown for the Ligandex-E and DTTA resins in Fig. 2. Regression coefficients, intercepts, correlation coefficients, and the $\bar{a}$ range over which the linear relationships have been observed to hold are listed in Table II. The modified COMICS subroutine COGS, which used these linear relationships, is summarized in Fig. 3.

The modified COMICS programme gave values of equilibrium "concentrations" of the protonated resin forms and the $\bar{a}$ values as a function of the solution pH for a specified ionic strength. In all cases the total "concentration" of resin introduced into the system referred to one gram of dry hydrogen-form resin per 100 cm^3
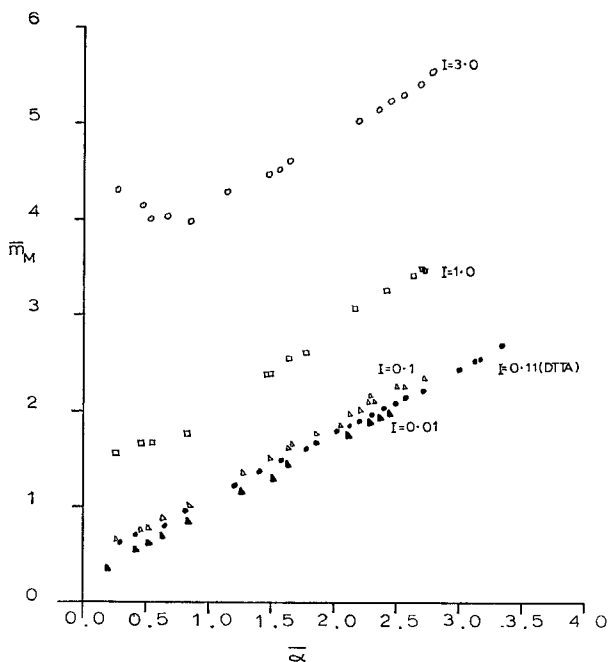

Fig. 2. Plots of $\bar{m}_M$ against $\bar{a}$ for Ligandex-E and DTTA resins.

TABLE II

DEPENDENCE OF $\bar{m}_M$ UPON $\bar{a}$ FOR LIGANDEX-E AND DTTA RESINS

	Ionic strength (I)				
	0.01	0.1	1.0	3.0	0.11*
Regression coefficient (b)	0.74	0.74	0.82	0.76	0.66
Intercept (a)	0.20	0.36	1.19	3.32	0.41
Correlation coefficient	0.999	0.999	0.996	0.998	0.9996
$\bar{a}$ range	0.3–2.4	0.2–2.7	0.2–2.7	0.8–2.7	0.2–3.3

* Refers to DTTA resin.

```
Calculate dummy variables TERM(K) and TERN(K), using a_H+ in
the initial expression

    TERM(K) = B(K)*UX**MN(K)    (S.0008 of COGS)
                      n
i.e. TERM(K) = β_K·a_H+, referring to species K with stability

constant β_K and containing  n  protons.
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↓

```
Calculate total concentrations of metal ions and improved values
for concentrations of free metal ions, VY(I). (This part is
redundant if only protonation equilibria are considered.
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Calculate total concentrations of ligands, and improved values
for free ligand concentrations, TY(I).
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Check for convergence by comparison of calculated and actual
total concentrations of metal ions and ligands. If satisfactory,
output concentrations of all species and  ā  for the resin.
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If not converged satisfactorily, use  ā  value to calculate pH
and hence, for resin species only, calculate new TERM(K) values.
Then repeat iteration using the new values of free metal ion and
free ligand concentrations.   Return to repeat cycle just after
S.0008
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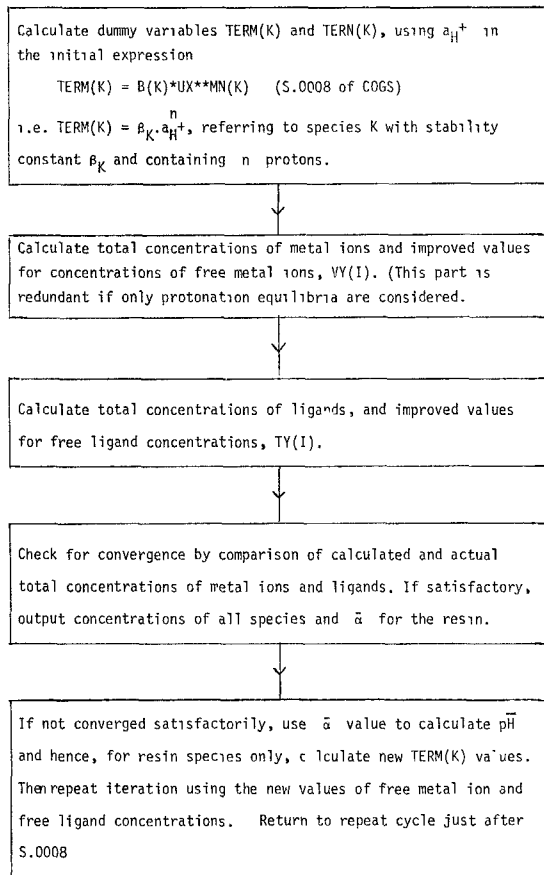
Fig. 3. Modified COGS subroutine.

of solution. Thus for Ligandex-E, with a capacity of 2.50 mmol K^+ per gram of resin, 1 g of resin per 100 cm^3 of solution gave a "molarity" of $0.25 \cdot 10^{-1}$ M.

A comparison of the theoretical pH–$\bar{a}$ curves with the experimental ones showed a good fit for ionic strengths up to 1.0 I, but the correlation was not so good at higher ionic strengths, where the $\bar{m}_M$–$\bar{a}$ relationship showed some deviation from linearity. This is also to be seen in the analysis of variance tests in Table III, where

TABLE III

CORRELATION OF $\bar{a}_{calc.}$ and $\bar{a}_{expt.}$ FOR LIGANDEX-E AND DTTA RESINS

I	σ^2 (due to regression)	σ^2 (about regression)	% fit	N
0.01	10.716	1.11 — 03	99.8	18
0.1	10.601	8.5 — 04	99.9	18
1.0	9.671	2.34 — 03	99.7	13
3.0	9.641	0.01	98.7	15
0.11*	23.816	8.75 — 03	99.7	24

* Refers to DTTA resin.

$\bar{a}_{calc.}$ and $\bar{a}_{expt.}$ are compared. The results do show, however, that the protonation constants determined by Szabadka et al. may be used to describe the protonation equilibria of the Ligandex-E and DTTA resins over a wide range of ionic strengths, from $I = 0.01$ to 3.0. Similar modifications to the COMICS programme may be necessary in order to model satisfactorily resin–proton–metal ion–counter ligand equilibria, and further work is now in progress to study the influence of ionic strength and pH upon the distribution of metal ions between chelating resins and aqueous phases.

ACKNOWLEDGEMENTS

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