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EQUATION FOR THE EVALUATION OF THE PROTONATION CONSTANTS OF COMPLEX-FORMING RESINS

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SUMMARY

A general equation has been derived that describes the protonation equilibria of chelating exchange resins, by consideration of the equilibria existing between the components of the resin and solution phases. When applied to water-soluble ligands, the equation reduces to the well known Schwarzenbach relationship.

The application of the general equation to the study of resins containing polyamino and polyamino–polycarboxylic ligands is discussed.

It appears that the resin phase behaves like a concentrated electrolyte solution.

INTRODUCTION

Published attempts to describe the protonation equilibria of chelating resins fall into two classes: firstly, the empirical ones utilizing sometimes several arbitrary constants, and secondly, ones based upon thermodynamic principles, such as the equation derived by Chatterjee and Marinsky¹, which however describes only single protonation reactions.

We describe here a general equation for resin protonation equilibria that can be applied to overlapping protonation processes.

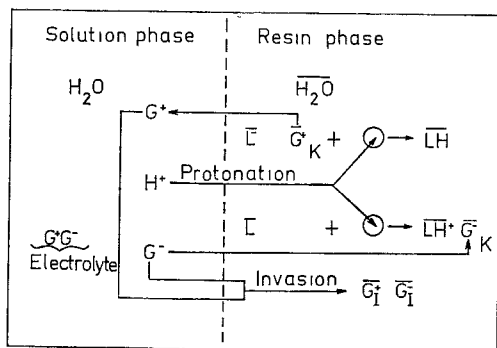
THEORETICAL

The protonation reaction of a resin containing chelating functional groups can be treated as a heterogeneous chemical equilibrium. Fig. 1 summarizes the processes existing in such a system.

In the solution phase the following components are present: the water; protons; and the electrolyte, G^+G^- , used to adjust the ionic strength. The components in the resin phase are as follows: the water; the fixed basic group, which can be either a basic anion (acetate) or a neutral base (amine); the conjugate acid formed in the protonation reaction; and the counter ions.

In Fig. 1 the components in the resin phase are indicated with a bar, as in $\overline{H_2O}$.

The presence of the counter ions has to be postulated because the protonation reaction is always accompanied by the uptake of positive charges. Consequently,



$$(G) = \frac{\overline{G}_K + \overline{G}_I}{H_2O}$$

$$C_L = (L) + (LH) = \frac{Q}{H_2O}$$

$$\left. \begin{array}{l} \overline{G}_K \\ \overline{G}_I \\ Q \end{array} \right\} \text{mmol per gram dry resin}$$

$$H_2O \text{ gram per gram dry resin}$$

Fig. 1. Protonation process of complex-forming resins.

either the base or its conjugate acid will be an ion whose charge should be compensated for by an equivalent amount of the counter ions.

When the active group is a negative base its protonation is accompanied by the release of the positive counter ions, \overline{G}_K^+ . When, however, the base is neutral, its protonation is accompanied by the uptake of the negatively charged counter ions, \overline{G}_K^- .

The electrolyte, $\overline{G}_I^+ \overline{G}_I^-$, in the resin phase has migrated from the solution by the so-called electrolyte invasion process.

Fig. 1 also shows that the concentration of the counter ions in the resin phase is the sum of the chemically bound and the invaded amount of the counter ions divided by the water content of the resin. In the same way, the analytical concentration of the base, C_L , is given by the ratio of the capacity, Q , and the water content of the resin.

If a fully protonated base is an N-basic acid that is titrated by a strong base, then making use of the chemical equilibria shown in Fig. 1 the following general relationship can be derived:

$$\sum_{j=0}^N (\overline{\alpha}^* - N + j) \beta'_j (H)^j = 0 \quad (1)$$

where $\overline{\alpha}^*$ is the molar fraction of the free, non-protonated base.

If the base is a negatively charged ion then

$$\overline{\alpha}^* = \frac{\overline{G}_K^+}{Q} + \frac{(H) - (OH)}{C_L} \quad (2)$$

If, on the other hand, the base is neutral, then

$$\bar{\alpha}^* = N - \frac{\bar{G}_k}{Q} + \frac{(H) - (OH)}{C_L} \quad (3)$$

Here the proton activity, (H), in the resin phase is given by

$$(H) = [H] \left[\frac{(G)}{a_G} \right]^\nu \quad (4)$$

$\nu = +1$ if the counter ion is \bar{G}^+ and -1 if the counter ion is \bar{G}^- , [H] and a_G are the proton activity and the counter ion activity in the solution phase, respectively, (G) is the concentration of the counter ions in the resin phase and β'_j is the overall protonation constant:

$$\beta'_j = K'_1 K'_2 \dots K'_j \quad (5)$$

where K'_1, K'_2, \dots, K'_j are the protonation constants of the 1st, 2nd, ..., j th protonation step, respectively. The K' 's are given by

$$K' = \frac{K}{K_{\bar{\nu}}} \quad (6)$$

where K is the thermodynamic (activity) protonation constant; the interactions in the resin phase are combined together in the $K_{\bar{\nu}}$ term:

$$K_{\bar{\nu}} = \frac{\gamma_{LH}}{\gamma_L (\gamma_G)^\nu} \quad (7)$$

For water-soluble bases eqn. 1 becomes identical with the well known Schwarzenbach relationship². The derivation of eqns. 1-7 will be given in ref. 5.

EXPERIMENTAL

Eqn. 1 was used to calculate the protonation constants of chelating resins containing various polyethylene-polyamino and polyethylene-polyamino-polycarboxylic acid functional groups.

Table I lists the resins that were synthesised³, and the corresponding water-soluble monomers.

In order to prepare the resin titration curve, we used potassium chloride solution to adjust the ionic strength, potassium hydroxide solution as a strongly basic reactant with the protonated form of the resins, and hydrochloric acid for protonation of the polyamino resins. Under these circumstances there will be a transfer of counter ions between the solution and resin phases: with negatively charged groups, potassium ions; and with neutral or positively charged groups, chloride ions.

After determination of the water content of the resin⁴, the counter ions, which consist of chemically bound ions and also migrated ions, are determined by the following procedures. For negatively charged groups the potassium and chloride ions were eluted from the resin with a known volume of standard nitric acid solution.

TABLE I
COMPLEX-FORMING MATERIALS SYNTHESIZED AND STUDIED

Materials	Functional groups
Chelating resins	Ethylenediamine (EDA)
	Diethylenetriamine (DTA)
	Iminodiacetic acid (IDA)
	Ethylenediaminetriacetic acid (EDT)
	Diethylenetriametetraacetic acid (DTT)
Water-soluble monomers	N-Benzylethylenediamine (BEDA)
	N-Benzylidiethylenetriamine (BDTA)
	N-Benzyliminodiacetic acid (BIDA)
	N-Benzylethylenediaminetriacetic acid (BEDTA)
	N-Benzylidiethylenetriametetraacetic acid (BDTTA)

The titration of the residual acidity in this eluate gives a figure for the chemically bound potassium ions, and the migrated potassium ions are determined from an argentimetric titration. For the other types of resin the elution was carried out with a known volume of standard potassium hydroxide solution and titration of the residual excess of base in the eluate gives the chemically bound chloride ions, while the argentimetric titration gives the total chloride, from which the amount of migrated chloride counter ion can be calculated.

RESULTS AND DISCUSSION

For the practical application of the general equation it is necessary to establish the inter-relationships between the experimentally accessible parameters: $\bar{\alpha}^*$, \bar{G}_K , \bar{G}_I , Q , H_2O , etc. These relationships are summarized in Figs. 2–4 for one of the ligands studied, EDT resin.

Fig. 2 shows the amount of the chemically bound counter ion as a function of $p(H)$ [$p(H) = \log(H)$] of the resin phase at various ionic strengths (I).

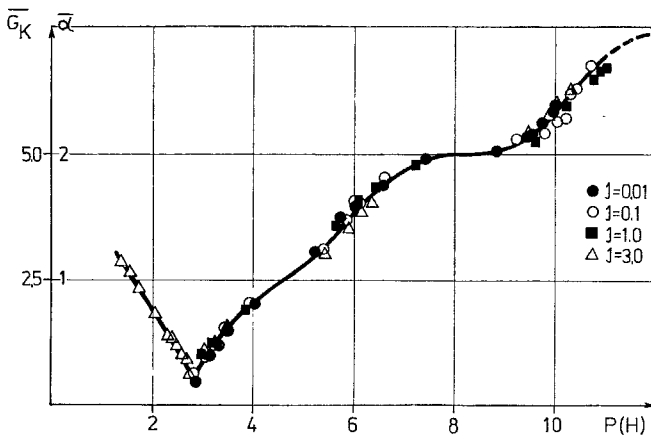


Fig. 2. Plots of \bar{G}_K against $p(H)$ for EDT resin.

Corresponding to the first three consecutive steps of the protonation, the resin releases its positive counter ion in three well defined stages. In the next two steps the group becomes positively charged, and binds negatively charged counter ions in two stages. As the curve shows, the protonation steps are equal and each gives Q , the functional group capacity of the resin.

If $\overline{G_K}$ is divided by the capacity, then $\overline{\alpha}$ is obtained:

$$\overline{\alpha} = \frac{\overline{G_K}}{Q}$$

Fig. 3 shows the water uptake of the resin, $\overline{H_2O}$, as a function of the chemically bound potassium ions at four different ionic strengths. It appears that water uptake of the resin phase in the first step of neutralization is strongly dependent on the ionic strength. For a given value of chemically bound potassium ions, the lower the ionic strength the greater is the amount of the absorbed water.

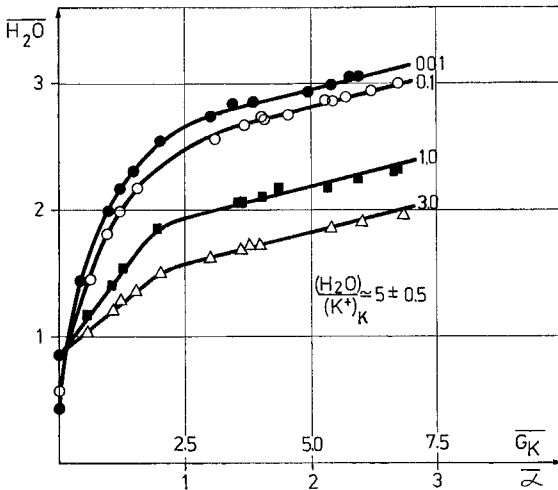


Fig. 3. Plots of $\overline{H_2O}$ against $\overline{G_K}$ and $\overline{\alpha}$ for EDT resin.

In the second and third steps of neutralization for a given ionic strength, the water uptake increases proportionally with the amount of the chemically bound potassium ions, so that the water uptake as a function of neutralization is represented by a series of parallel straight lines. From the slope of these linear plots, it can be seen that 5.0 ± 0.5 water molecules are transferred into the resin phase by each potassium ion:

$$\frac{\overline{H_2O}}{\overline{K^+}_K} = 5.0 \pm 0.5$$

The shape of these plots shows that the uptake of the chemically bound counter ions is always accompanied by the uptake of water from the solution phase. However, this water uptake is dictated by the actual structure of the resin lattice and one there-

fore finds that the uptake of water and therefore of chemically bound counter was limited at high $\bar{\alpha}$ values.

Fig. 4 shows the titration curves at three different ionic strengths for EDT resin. If the solution pH is plotted as a function of the degree of resin phase dissociation, then different curves are obtained at different ionic strengths. If, however, the resin phase $p(H)$ is used then, independently of the ionic strength, all the points fall on the same curve.

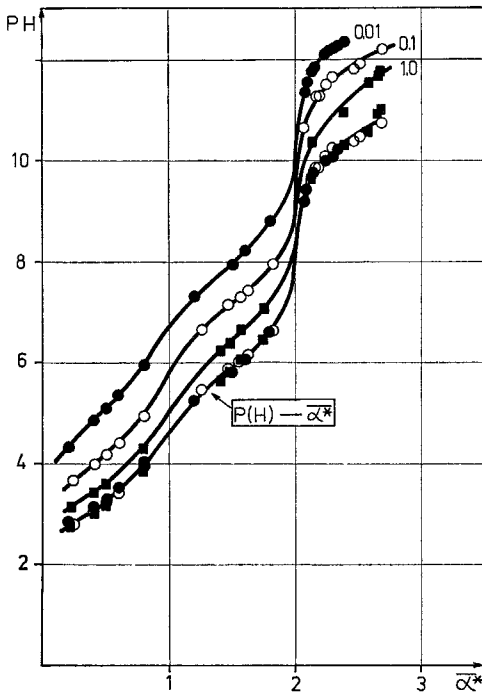


Fig. 4. Titration curves for EDT resin.

The data of the latter curve were used to calculate the protonation constants using the general equation. The results obtained are listed in Table II for all of the resins synthesized. For details of the calculation, see ref. 6.

TABLE II
CALCULATED VALUES OF PROTONATION CONSTANTS

Basic group	I	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$
EDA	1.0	9.76 ± 0.03	7.06 ± 0.04			
DTA	1.0	10.38 ± 0.07	8.59 ± 0.05	4.29 ± 0.09		
IDA	1.0	9.12 ± 0.05	3.10 ± 0.07	1.44 ± 0.03		
EDT	0.01-3.0	10.45 ± 0.07	5.90 ± 0.04	3.26 ± 0.04		
	3.0				2.35 ± 0.02	0.82 ± 0.01
DTT	0.01-1.0	10.38 ± 0.05	8.36 ± 0.05	4.30 ± 0.05	2.83 ± 0.03	

As mentioned earlier, the general equation, when it is applied to a water-soluble base, reduces to the Schwarzenbach equation and can be used for the calculation of the protonation constant of the water-soluble analogues of the polycarboxylic resins. Experiments have also been carried out to obtain these constants at various ionic strengths. These data, together with that for the immobilized ligands, are plotted in Fig. 5. Here, the open circles represent the protonation constants calculated for the given ionic strengths, and the closed circle gives the protonation constant calculated from all the points.

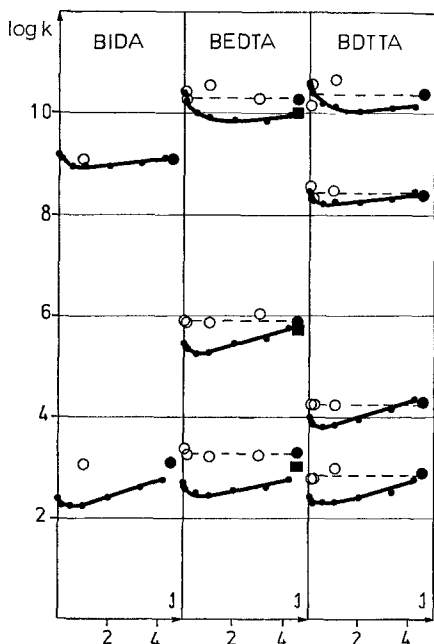


Fig. 5. Plots of $\log K$ against I for the resin phase active groups and for their water-soluble analogues.

The protonation constants calculated from all the data for a particular resin are located in the very high range of the ionic strength scale to emphasize our opinion that the resin phase is a very concentrated electrolyte solution.

During the experiments with water-soluble monomers the concentration of the bases was $5 \cdot 10^{-3}$ mol/dm³. The concentration in the resin phase, however, is about 1 mol/dm³. Therefore, a titration was carried out with the soluble monomer base (BEDTA) with its analytical concentration at 0.25 mol/dm³ and the ionic strength set at 4.2. The protonation constants calculated from this titration curve are shown by closed squares in Fig. 5.

These $\log K$ values approach best the figures that were obtained for the immobilized ligands, demonstrating again the validity of the concentrated electrolyte concept of the resin phase.

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