MATHEMATICAL MODELLING OF ION EXCHANGE
EQUILIBRIA ON POLYMER ION EXCHANGERS

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ABSTRACT

A mathematical model for description of dependences of the ion exchange equilibria parameters on the composition of ion exchangers is suggested. It is assumed that ion exchange sites in the polymer network are different due to the difference in their micro-environment characterized by the number of the nearest neighbours and the local ionic composition. A "property-composition" equation was derived and proved to be adequate to describe the experimental data for some complicated ion exchange systems.

INTRODUCTION

In 1951 Reichenberg, Pepper and McCauley published results of their study of ion exchange equilibria of univalent ions on sulphonated copolymers of styrene and divinylbenzene (1). It was clearly shown that even for these simple systems the apparent equilibrium constant varied strongly with extent of ion exchange. (Apparent equilibrium constant is a value calculated as equilibrium constant with concentrations of the exchangeable ions in the ion exchange phase in place of their activities, \( K = \frac{\bar{X}_2 a_1}{(\bar{X}_1 a_2)} \)). Significant decrease in selectivity toward preferably sorbed ion with increasing loading of the resin was explained by irregularity of the resin exchange sites. Interpretation of this effect since then has become one of the key points of the theory of ion exchange. This work was
followed by many publications in which dependence of apparent equilibrium constants or the other parameters of equilibria on the extent of ion exchange were observed and interpreted in a similar manner. Later, the increase of the apparent equilibrium constant was reported and explained by "co-operative" effect (e.g. (2)). The combination of the irregularity of exchange sites with "co-operative" interaction can result in extremes and other complicated dependences described in the literature. Nevertheless, physical reasons for non-uniformity of the exchange sites as well as the "co-operative" effect was not clear and quantitative interpretation was not offered.

THE NEW MODEL

The model presented here suggests a quantitative interpretation of parameters of ion exchange equilibria as a function of ionic composition of ion exchanger (3,4). In this paper the case of uni-univalent exchange will be considered.

The main statements of the model are as follows. Exchange sites in an ion exchanger have different local environments characterized by number of neighbouring ions (i) and the local ionic composition. Two parameters are chosen to describe the local environment: number of ions type 2 denoted as j, and that of ions 1 denoted as i-j. Then all possible states of exchangeable ions (I) are expressed as I(i-j,j):

\[
\begin{array}{c|c|c}
\text{i, number of nearest neighbours} & \text{Possible states of ion I} \\
0 & I(0,0) \\
1 & I(1,0), I(0,1) \\
2 & I(2,0), I(1,1), I(0,2) \\
3 & I(3,0), I(2,1), I(1,2), I(0,3) \\
\ldots & \ldots \\
i & I(i-j,j), j=0-i \\
\end{array}
\]

A real ion exchange equilibrium may be regarded as a superposition of ideal "elementary" equilibria related to each of the states: