H^+ -Ca^{+2} exchange equilibrium on the polyacrylic cation exchangers

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H^+-Ca^{+2} exchange isotherms on the carboxylic polyacrylic cation-exchange resins (Lewatit CNP 80, Purolite C 104, Relite CNS) have been measured. Strong dependences of apparent equilibrium constants on the composition of resinates solution which for the three investigated ion exchangers within the limits of experiments error coincide were found. The theoretical model has been proposed. It describes non-ideality of sorption phase and suggests the presence of two kinds of the exchange centers differing in their acid properties in the exchange resins.

1. INTRODUCTION

Prospects of improvement of technical and economic parameters of processes of demineralization and deep water softening with ion-exchange resins are primarily concerned with introduction of carboxylic cation-exchange resins synthesized on the basis of polyacrylic acid into water preparation practice. Application of ion-exchange resins of this type has allowed implementing the process of the combined production of demineralized and largely softened water, due to full recycling of demineralization unit wastewaters achieving practically stoichiometry consumption of reagents and high operation capacity of cation-exchange resins with large softening water production.

However, the data about equilibrium at sorption from water of bicharged cations by the H-form of polyacrylic ion-exchange resins are extremely scarce [1-3], though such information is necessary for a priori calculation of technological parameters of softening process [4-7]. Available data [1-3] do not

allow to judge, how large the difference between the sorption isotherms of bicharged ions on different carboxylic cation-exchange resins is.

Therefore, the aim of this paper was to study H^+-Ca^{+2} exchange equilibrium on different polyacrylic cation-exchange resins and to substantiate the theoretical model of such a phenomenon.

2. THEORETICAL DEVELOPMENT

The exchange of singly charged hydroxonium ions for bicharged cations may be analyzed in two aspects depending on arrangement geometry of fixed exchange centers in the polymeric matrix of carboxylic ion-exchangers [2].

In the first model all fixed exchange groups of the cation exchange resin are identical and the calcium ion can be sorbed on any two neighbouring exchange centers.

$$-CH_2 - CH(COOH) - CH_2 - CH(COOH) - CH_2 - CH(COOH) -$$

In this case the exchange reaction should be written down as

$$Ca^{+2} + 2RCOOH = 2H^+ + (RCOO)_2 Ca \tag{1}$$

The second approach to consider the exchange mechanism of single- and bicharged cations on carboxylic cation exchangers assumes [2] that the fixed exchange centers are located in pairs.

$$- CH_2 - CH(COOH) - CH(COOH) - CH_2 - CH_2 - CH(COOH) - CH(COOH) - CH_2 -$$
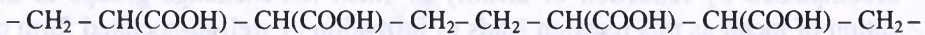
In this case two exchange centers enter the exchange reaction as a single whole with calcium ion which is reflected in the equation

$$Ca^{+2} + (RCOOH)_2 = 2H^+ + (RCOO)_2 Ca \tag{2}$$
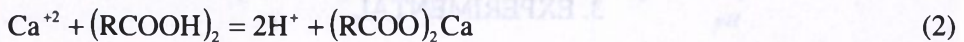
The value of apparent equilibrium constant K_{sp} for equation (1) is as follows:

$$2pH - pCa = pK_{od} + lg\{\alpha(2-\alpha)/[4(1-\alpha)^2]\} \tag{3}$$

The equilibrium constant pK_{sp} for the coupled exchange centers is determined from the equation

$$2pH - pCa = pK_{sp} + \lg\{\alpha/(1-\alpha)\} \qquad (4)$$

where pH, pCa, pK_{od} and pK_{sp} are negative logarithms for both activities of the hydroxonium and calcium ions and the equilibrium constants pK_{od} and pK_{sp}.

According to equations (3), (4) with accomplishment of H^+-Ca^{+2} exchange by any mechanism at ideality of resinates solution properties in the coordinates $2pH - pCa$ on $\lg\{\alpha(2 - \alpha)/[4(1 - \alpha)^2]\}$ or $\lg\{\alpha/(1 - \alpha)\}$ linear dependences should be observed, and the slope ratio of straight lines is equal to unity.

Deviations of properties of resinate solutions from ideality can be quantitatively described within the framework of the exchange equilibrium theory [2, 3]. It is known that the exchange of single-charged ions for bicharged ions on the carboxylic cation-exchange resins can be described as follows.

- Polyacrylic cation-exchange resins are supposed to contain two kinds of centers: the coupled exchange centers and the spatially separated centers.
- The coupled exchange centers exhibit much greater selectivity with respect to bicharged cations than the spatially separated ones.
- The share of coupled fixed groups in the cation-exchangers is insignificant.
- The exchange balance on the coupled exchange centers is assumed to have the properties of ideality as with the complete transfer of the coupled centers into the salt form the neighbouring spatially separated centers remain in a weakly dissociated acid form and the electrostatic repulsion of neighbouring ionogenic groups does not take place.
- Each spatially separated center generally has i neighbours.
- Transfer of the neighbouring exchange centers into the salt form is accompanied by reduction of affinity of fixed ion-exchange groups to the cation of metal as this reaction leads to formation of well dissociated form of ion-exchange resins, and, hence, to repulsion of neighbouring ionogenic groups.

3. EXPERIMENT

The objects of research were porous polyacrylic ion-exchange resins (Lewatit CNP 80 [Bayer], Purolite C 104 [Purolite], Relite CNS [Resindion S.R.L]). Experiments were carried out with the use of procedure [2, 3] which allows to measure H^+-Ca^{+2} exchange isotherms with high accuracy (up to 2 %) in the range of change of resinates composition.

4. RESULTS AND DISCUSSION

In Figure 1 the potentiometric titration curves of cation exchangers are compared in the coordinates: a degree of translation of ion exchanger into the salt form $\alpha = e / E_0$ on pH, where e – the quantity of Ca^{+2} ions absorbed per unit mass of ion exchanger, mg–equiv/g; E_0 – the full exchange capacity of cation exchanger, mg-equiv/g. The full exchange capacity of cation exchanger is determined in [8] on the basis of measurement of isotherms of exchange H^+-Na^+. As it can be seen in the figure, H^+-Ca^{+2} exchange isotherms on the ion exchangers Lewatit CNP 80, Purolite C 104 and Relite CNS are practically identical. The analysis of measurement errors has shown that scattering of the points about the single curve for all ion exchangers is within the limits of measurement errors.
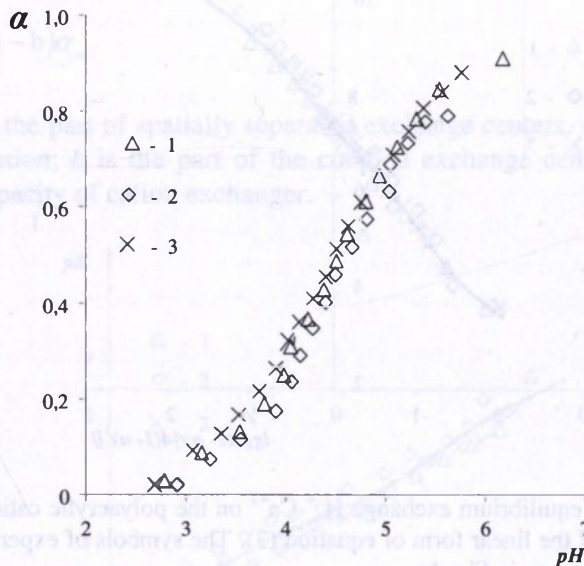

Fig. 1. Curves of potentiometric titration of the polyacrylic cation exchangers: 1 – Lewatit CNP 80, 2 – Purolite C 104, 3 – Relite CNS.

Experimental data for H^+-Ca^{+2} equilibrium exchanges on the carboxylic polyacrylic cation exchangers on the coordinates of linear forms of equations (3) are presented in Figure 2 as an example. The linear dependences are only approximate as follows from Figure 2. However, the inclinations of the straight lines do not correspond to the theoretical value for an ideal solution of resinates, in these situations generalized equation [9] should be held well.

$$2pH - pCa = pK_{od} + n_{od} \lg\{\alpha(2-\alpha)/[4(1-\alpha)^2]\}$$

$$2pH - pCa = pK_{sp} + n_{sp} \lg\{\alpha/(1-\alpha)\}$$

where $n_{od}=2\pm0.7$, $n_{sp}= 2.5\pm0.25$, and $pK_{od}=7.5\pm0.2$, $pK_{sp}=7.3\pm0.2$.

The conclusion about non-ideality of resinates solution is confirmed in Figure 3 where dependence of equilibrium constant calculated by equation (3) is shown. The K values change by two orders of magnitude with α increase. Similar data are obtained for equation (4).
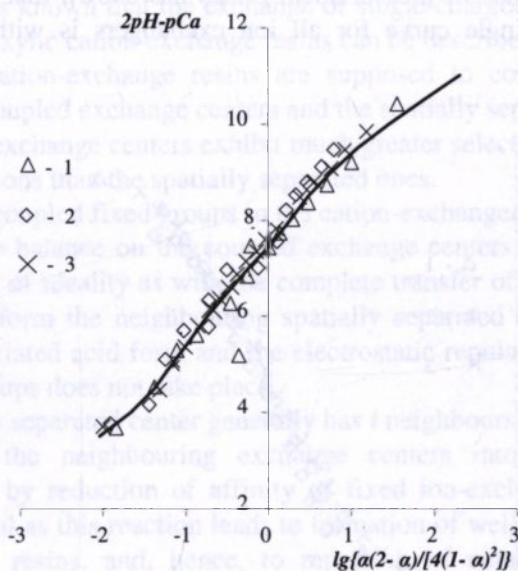

Fig. 2. Isotherms of equilibrium exchange H$^+$-Ca^{+2} on the polyacrylic cation-exchangers on the coordinates of the linear form of equation (3). The symbols of experimental points and curves are the same as in Fig. 1.

Therefore change of local equilibrium constant of spatially separated centers $(K(j))$ with the change of resinates composition in the neighbouring environment occurs in steps. It is not important which neighbouring fixed ions are in the salt form, but their quantity is essential. The number of the neighbouring exchange centers which are present in the salt form is characterized by the parameter j.

H$^+$-Ca^{+2} exchange on the Lewatit CNP 80 polyacrylic cation exchanger is well described by the partial model equation [2]. It assumes the presence of only three neighbouring exchange centers affecting the exchange constant of any

considered center. Moreover, simplification of such a model, is correct as the local constants $K(j=1)$ and $K(j=2)$ are equal. In this case equilibrium on the spatially separated center is described by the equation:

$$\alpha^2 \left[2\beta(j=1)-\beta(j=0)-\beta(j=2)\right] + \alpha\{2[\beta(j=0)-\beta(j=1)]-1\} + [1-\beta(j=0)] = 0 \quad (5)$$

where $\beta(j) = \left[1 + 4 \cdot K(j) \cdot 10^{2pH-pMe}\right]^{-1/2}$, $K(j)$ is the local equilibrium thermodynamic constant of equation (1), and the fraction of the fixed coupled centers α_{sp} is found from equation (4)

$$\alpha_{sp} = K_{sp} \cdot 10^{2pH-pCa} / \left(1 + K_{sp} \cdot 10^{2pH-pCa}\right) \quad (6)$$

As a whole the ion-exchange equation is defined by equation:

$$\alpha = b\alpha_{sp} + (1-b)\alpha_{od} \quad (7)$$

where α_{od} is the part of spatially separated exchange centers, connected with the bicharged cation; b is the part of the coupled exchange centers in the general exchange capacity of cation exchanger.
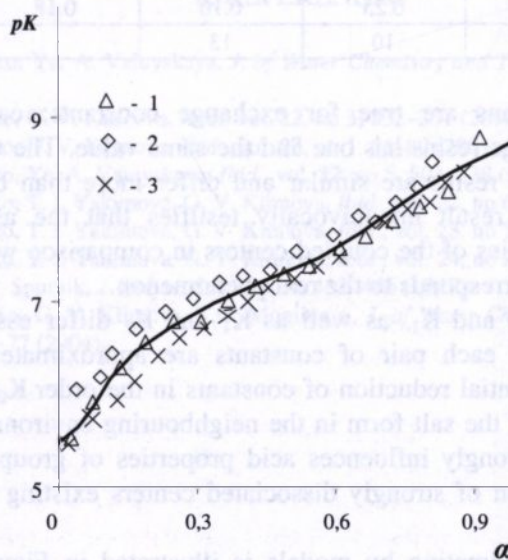

Fig. 3. Dependences of apparent equilibrium constants on the degree of translation of the polyacrylic cation exchangers to the salt form. The symbols of the experimental points and curves are the same as in Figure 1.

The results of data interpretation using equations (5) – (7) are in Table 1. The fraction of the coupled exchange centers for all ion exchangers is insignificant and coincides within the limits of definition error, which can be seen in Table 1. As the H^+-Ca^{+2} exchange isotherms for Lewatit CNP 80, Purolite C 104, Relite CNS coincide within the limits of errors (Figures 1 and 2), this model should be true for all ion exchangers under examination.

Tab. 1. Results of the analysis of H^+-Ca^{+2} exchange isotherms on the carboxylic polyacrylic cation exchangers according to the model (5) - (7) equations.

Parameter	Ion-exchanger			Lewatit CNP 80, Purolite C 104, Relite CNS	
	Lewatit CNP 80	Purolite C 104	Relite CNS	Average	S
B	0.09	0.07	0.14	0.10	0.04
pK_{sp}	4.00	4.40	4.15	4.18	0.20
pK_0	6.65	6.86	6.73	6.75	0.10
pK_1	7.43	7.53	7.49	7.48	0.05
pK_3	8.74	9.03	8.79	8.85	0.16
$S(b)/b$	0.41	0.78	0.10	0.43	0.34
$S(K_{sp})/K_{sp}$	0.60	1.25	0.29	0.71	0.49
$S(K_0)/K_0$	0.13	0.18	0.21	0.17	0.04
$S(K_1)/K_1$	0.09	0.12	0.08	0.10	0.02
$S(K_3)/K_3$	0.18	0.25	0.10	0.18	0.08
f	10	10	13		

Similar conclusions are true for exchange constants: each constant for different ion-exchange resins has one and the same value. The values K_{sp} and K_0 for all ion-exchange resins are similar and differ more than by two orders of magnitude. Such a result unequivocally testifies that the assumption about stronger acid properties of the coupled centers in comparison with the separated centers is fair and corresponds to the real phenomenon.

The constants K_0 and K_1, as well as K_1 and K_2 differ essentially and the differences between each pair of constants are approximately one order of magnitude. The essential reduction of constants in the order $K_0>K_1>K_2$ testifies that accumulation of the salt form in the neighbouring environment of spatially separated centers strongly influences acid properties of groups. Therefore the electrostatic repulsion of strongly dissociated centers existing in the salt form increases.

Quality of approximating by models is illustrated in Figure 2, where the curves represent the calculation results applying equation (7) and the coefficients shown in Table 1.

5. CONCLUSIONS

- It has been established that the H$^+$-Ca^{+2} exchange isotherm on the three ion exchangers examined coincides within the limits of error.
- The solution of resinates at H$^+$-Ca^{+2} exchange is not ideal as evidenced by the fact that the thermodynamic constant of equilibrium changes by two orders of magnitude while transferring from the H-form to the salt form.
- Non-ideality of resinates solution may be quantitatively taken into account within the framework of the theory of exchange equilibrium assuming the presence of two exchange centers and the influence of only three neighbouring centers on acid properties of spatially separated centers.
- The calculations based on this model have shown that the fraction of coupled exchange centers in the polyacrylic ion exchanger is insignificant and does not exceed 14% in the total exchange capacity of the cation-exchanger.
- The constants for all ion exchangers of the exchange equilibrium theory coincide within the limit of error. This allows to calculate the H$^+$-Ca^{+2} exchange isotherms for different ion exchangers using the common values of exchange constants found in this work.

6. REFERENCES

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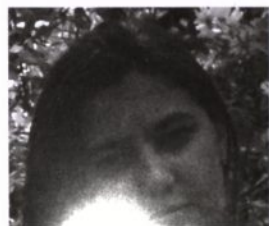
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