

ION-EXCHANGE EQUILIBRIA OF Ca(II), Mg(II), Co(II), Ni(II), Cu(II), AND Co(II), Ni(II) /Cu(II) EXCHANGE ON LEWATITE S-100 CATION-EXCHANGE

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(Received July 9, 1980)

The exchange systems $\text{Ca}^{2+} - \text{H}^+$, $\text{Mg}^{2+} - \text{H}^+$, $-\text{Co}^{2+} - \text{H}^+$, $\text{Ni}^{2+} - \text{H}^+$, $\text{Cu}^{2+} - \text{H}^+ - \text{H}^+ - \text{Cu}^{2+}$ and $\text{Ni}^{2+} - \text{Cu}^{2+}$ were studied using Lewatite 5-100 at 25° and ionic strengths of 0.025, 0.05, 0.1, 0.3 and 0.5M. Activity corrections were made by method of graphical integration for the ions in the aqueous solution phase to obtain the true exchange-equilibrium constant. The resulting selectivity coefficients increase with ionic strength of the medium and follow the sequence $\text{Ca}(11) > \text{Mg}(11) > \text{Co}(11) > \text{Ni}(11) > \text{Cu}(11)$.

This order is found to correlate well with the order of hydrated ionic radii. The above sequence for Co^{2+} and Ni^{2+} is reversed at ionic strengths of 0.25 and 0.05 M. The characteristic maximum water uptake of the resin in such ionic forms decrease with the increase in the values of selectivity coefficient.

INTRODUCTION

Jacob [1] determined the selectivity coefficients in the exchange of calcium, strontium, cobalt, nickel, zinc and cadmium ions with hydrogen ion on different cross-linked polystyrene sulphonated cation - exchange resin at 25° in dilute solutions of HClO_4 . The divalent ion is always preferred by the resin phase. Experiments were carried out to determine the selectivity coefficient at ionic strengths of 0.025, 0.05 and 0.1 M. on cross-linked *m*-cresol-formaldehyde ion-exchanger. Activity coefficient correction for some divalent ions, the maximum water uptake of the resins have been taken into consideration [2].

The effect of ionic strength on the ion-exchange equilibria; $\text{Ag}^+ - \text{H}^+$ and $\text{Na}^+ - \text{H}^+$ has been studied on Amberlite IR - 120 at ionic strengths of 0.1, 0.3, 0.6 and 1.0M [3]. Gaines and Thomas [4] treatment of ion-exchange equilibria was followed in calculating the equilibrium constant. The variation of the selectivity coefficient (K) with ionic strength is comparatively small even when electrolyte uptake is not taken into consideration confirming that the effect of ionic strengths on ion-exchange equilibria is almost entirely due to transfer of water between the resins and the outside solution, and electrolyte uptake plays a secondary role. Equilibrium studies at 25° between Dowex - 50 and aqueous $\text{Ag}^+ - \text{Na}^+$ at five ionic strengths ranging from 0.01, to 1.0 M are investigated [5]. The separation factors, the activity coefficients of the resin components and the equilibrium constants were also reported.

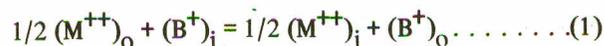
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EXPERIMENTAL

For the study of exchange reactions two forms of the resin were used; hydrogen, and copper forms. The hydrogen form was prepared by passing 6 N HCl through a column of the resin until the effluent gave no further test for sodium ion. Pure copper form of the resin was prepared by placing the hydrogen resin in a column and copper nitrate was passed through until the concentration of copper in the effluent showed no more than a negligible decrease from that of the effluent. The equilibrated solutions were separated by decantation and analysed for the H^+ ions and cations in the external aqueous phase. In case of coloured solutions of Co^{2+} , Cu^{2+} and Ni^{2+} , the hydrogen ion concentration was determined by titration against standard alkali using bromophenol blue indicator, The accuracy of the titration, of metal and hydrogen ions was generally of the order of 0.2 - 0.3 %. Studies of the water uptake of the various forms of the resin in definite electrolyte concentrations were made following the cited procedure [3].

RESULTS AND DISCUSSIONS

The exchange reaction between univalent and divalent ions may be represented as;



where the symbols o, i indicate the outside solution and the resin phase, respectively.

The expression for the selectivity coefficient is [6,7]

$$K^{2+} = \frac{(m \text{ HCl})^2 N M^{2+}}{M^+ (m M \text{ Cl}_2) (N \text{ H}^+)} \quad (2)$$

Where m 's are the malorites of the electrolyte solution in the aqueous - phase, N 's denote the equivalent : for actions of both ions in the resin phase after equilibrium was attained. The thermodynamic equilibrium constant, K , and the selectivity coefficient, K , are related to the concentrations of the ions, C , and their activity coefficients, ν . The equilibrium constant may then be calculated from the equation;

$$2.303 \log k = \int_a^1 2.303 \log K aN \quad (3)$$

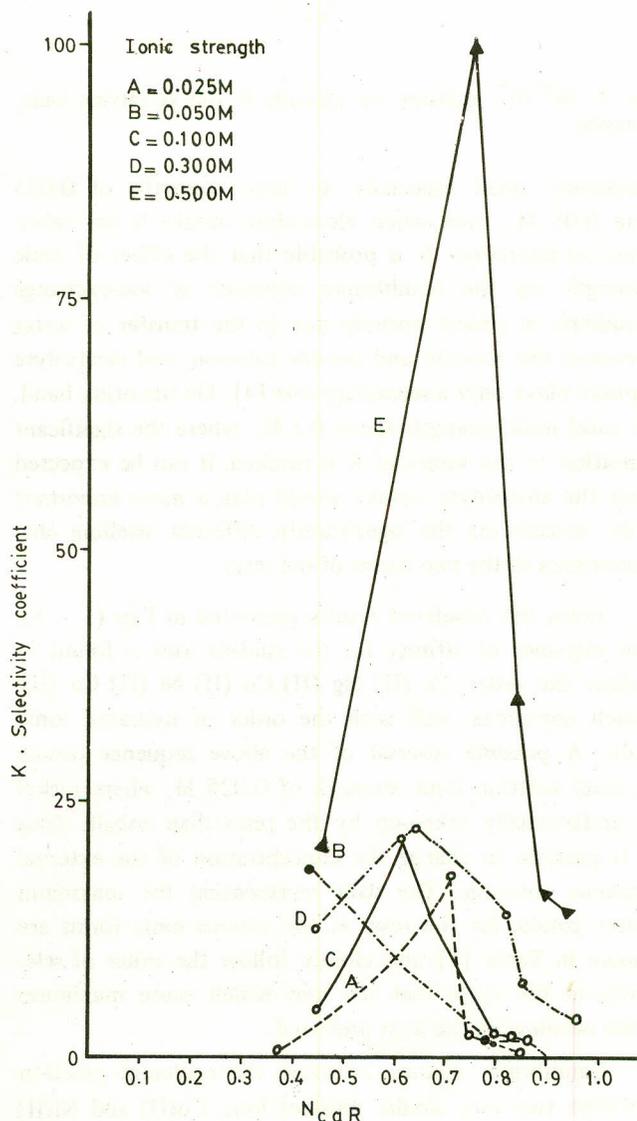


Fig. 1. $\text{Ca}^{++}/\text{H}^+$ exchange on Lewatite S-100 at varying ionic strengths.

where K is the selectivity coefficient corrected for the solution activity coefficient [6, 7].

The equilibrium constant for the exchange reaction between two divalent ions may be calculated from equation (3). The experimental data for Ca^{++} , Mg^{++} , Co^{++} , Ni^{++} and $\text{Cu}^{++}/\text{H}^+$ exchanges are presented graphically in Figs (1 - 5) as plots of K (selectivity coefficients) as a function of the equilibrium fraction of the cation in the solid phase. Several features seem noteworthy: (a) There is relatively greater dependence of the selectivity coefficient on the equivalent loaded fraction of the preferred ions; Ca(II) , Mg(II) , Co(II) , Ni(II) and Cu(II) when exchange with the hydrogen ion specially at total ionic strengths of 0.1, 0.3 and 0.5 M. On the other hand, at ionic strengths of 0.025 M, little dependence on the ionic composition is observed for all the exchange systems. (b) The selectivity coefficients are greatly different from unity at lower and higher values of metal/acid ratios. (c) In all cases the values of the selectivity coefficient show sharp maxima at external solution ionic strength of 0.3

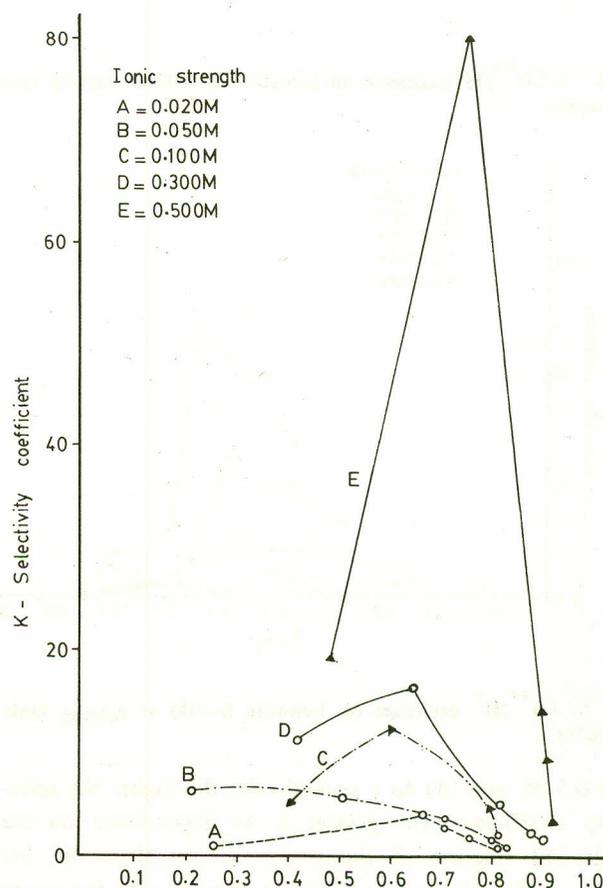


Fig. 2. $\text{Mg}^{++}/\text{H}^+$ exchange on Lewatite S-100 at varying ionic strengths.

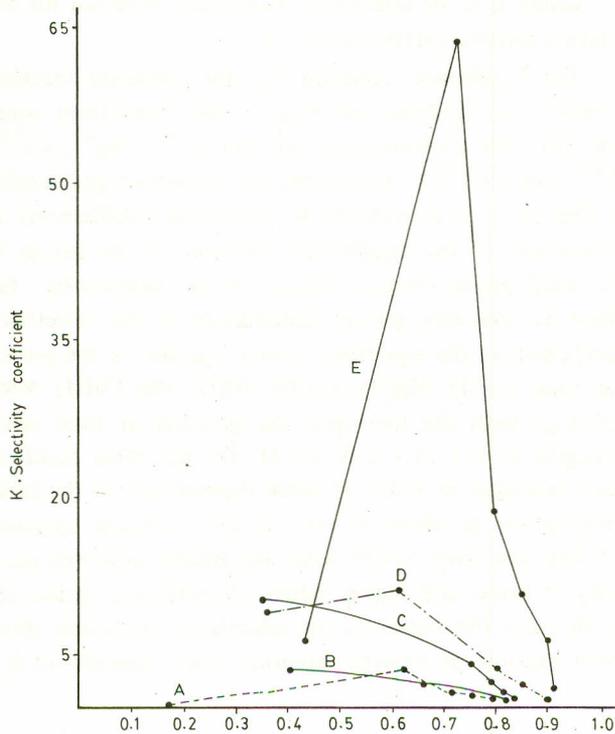


Fig. 3. $\text{Co}^{++}/\text{H}^{+}$ exchange on Lewatite S-100 at varying ionic strengths.

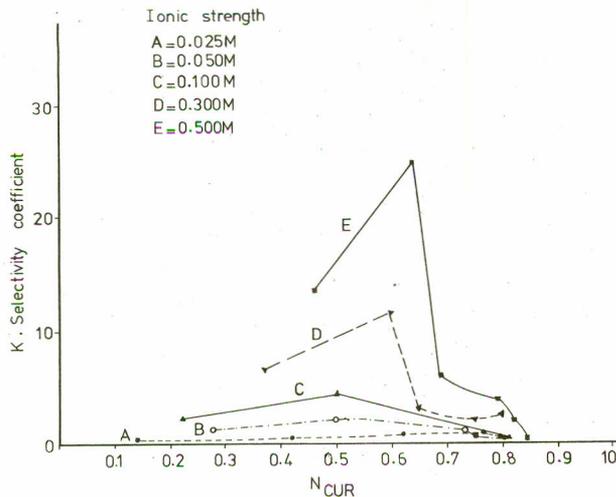


Fig. 5. $\text{Cu}^{++}/\text{H}^{+}$ exchange on Lewatite S-100 at varying ionic strengths.

and 0.5 M, and (d) As a general rule, the higher the selectivity coefficient, the greater is its dependence on the equivalent fraction of the preferred ion. Moreover, the values of the selectivity coefficient increase with increasing the ionic strength of the external aqueous solutions.

At low ionic strength, the variations in (K) are com-

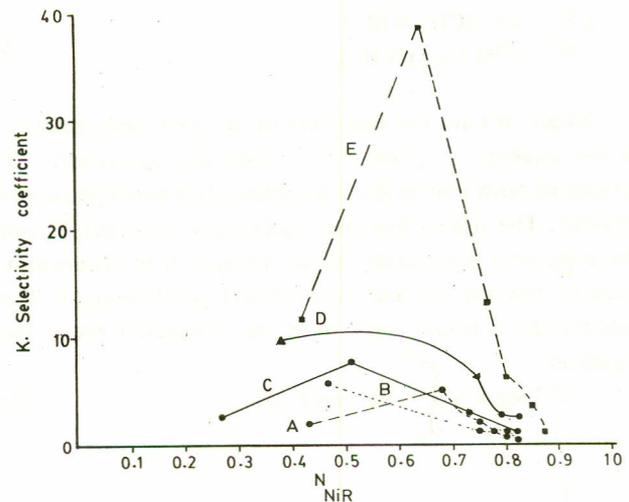


Fig. 4. $\text{Ni}^{++}/\text{H}^{+}$ exchange on Lewatite S-100 at varying ionic strengths.

paratively small especially at ionic strengths of 0.025 and 0.05 M., even when electrolyte uptake is not taken into consideration. It is probable that the effect of ionic strength on the equilibrium constant of ion-exchange equilibria is almost entirely due to the transfer of water between the resin and outside solution, and electrolyte uptake plays only a secondary role [4]. On the other hand, at total ionic strength above 0.1 M., where the significant variation in the values of K is reached, it can be expected that the electrolyte uptake would play a more important role, considering the significantly different swelling characteristics of the two forms of the resin.

From the tabulated results presented in Figs (1 - 5), the sequence of affinity for the studied ions is found to follow the order; Ca (II) Mg (II) Co (II) Ni (II) Cu (II), which correlates well with the order of hydrated ionic radii. A possible reversal of the above sequence occurs at total solution ionic strength of 0.025 M, where nickel is preferentially taken-up by the resin than cobalt. Thus it is possible to change the concentration of the external aqueous solution. The data representing the maximum water uptake for the resin in the various ionic forms are shown in Table [1] and closely follow the order of selectivity in the sense that the ions which cause maximum resin swelling are the least preferred.

Equilibrium studies involving the exchange reaction between two very similar divalent ions, Co(II) and Ni(II) on Lewatite S - 100 in the cupric form were made at ionic strengths of 0.025, 0.05 and 0.1 M. The experimental data for these two exchange systems are presented

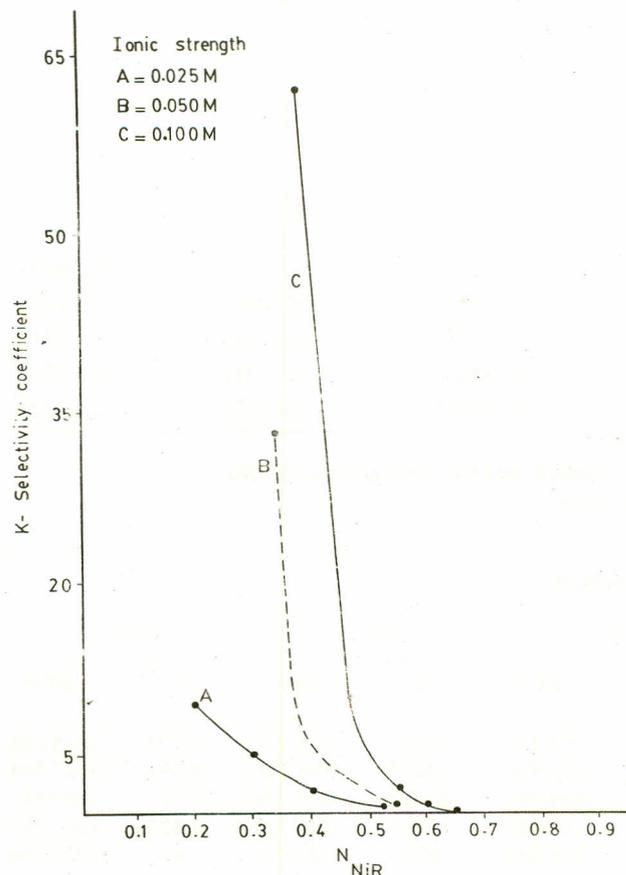


Fig. 6. Co^{++}/Cu^{++} exchange on Lewatite S-100 (Cu-form) at varying ionic strengths.

in Figs (6, 7). As previously mentioned for hydrogen resin, the affinity of the copper resin to either cobalt or nickel ions increased with the ionic strength of the aqueous solution. It is clear that the resin exhibits the lowest affinity to copper in comparison to other divalent two cations.

However, it is interesting to study the effect of converting the resin to the copper form on the sequence of affinity of the resin. It has been observed that, the order of affinity of the copper resin follows the following order:

$Ni > Co > Cu$ at three ionic strengths 0.025, 0.05 and 0.1 M.

On the other hand, the sequence of resin affinity in the hydrogen form at the same ionic strengths is $Co > Ni > Cu$. The reversal of affinity of the resin in the Cu and H, forms respectively is mainly due to the change of the medium conditions, i.e. the effect of acidity changes in the selectivity order by changing the concentration is also reported [8 - 10].

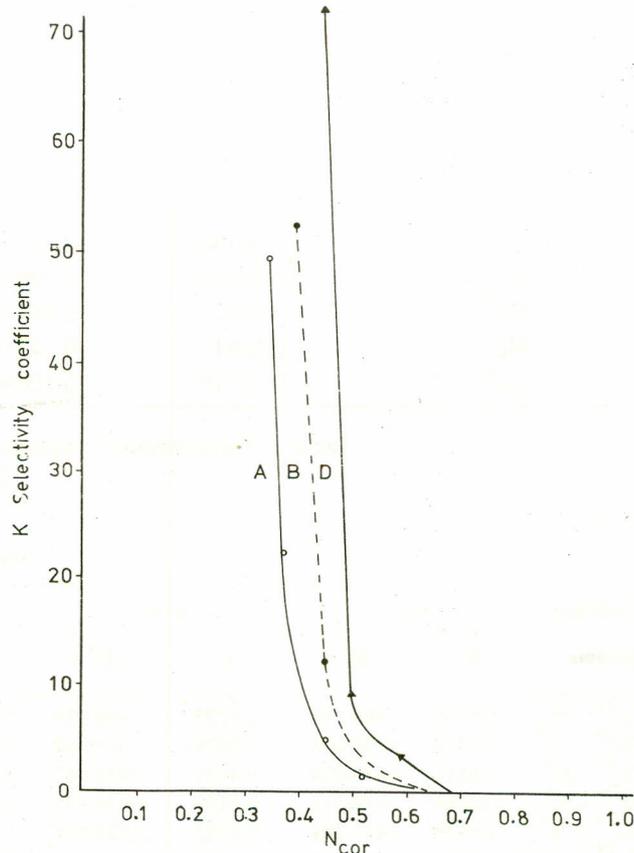


Fig. 7. Ni^{++}/Cu^{++} exchange on Lewatite S-100 (Cu-form) at varying ionic strengths.

The free energy of activation ΔF^\ddagger of the two reacting systems in different ionic strengths have been calculated using the equilibrium constant values applying equations [11].

$$\Delta F^\ddagger = -2.303 RT \log K$$

and the variations of ΔF^\ddagger with the total ionic strength of the medium is given in Table [2].

It is evident from Table [2] that as the negativity of ΔF^\ddagger increases the tendency of the exchange reaction to proceed from the hydrogen form of the resin to the bivalent form increases.

The higher the ionic strength of the medium, the more negative is the corresponding free energy of activation, showing the large tendency of the reaction to proceed simultaneously in the forward direction.

Table 1. Maximum water uptake (in g water/l gresin) for Lewatite S-100 in various ionic forms at different ionic strength.

Forms of resin	Ionic strength	Ionic strength				
		0.025	0.05	0.1	0.3	0.5
H ⁺		0.4404	0.30790	0.29050	0.26510	0.25570
Cu ²⁺		0.30140	0.302200	0.27113	0.23118	0.20891
Ni ²⁺		0.29970	0.29020	0.25581	0.20815	0.19117
Co ²⁺		0.27211	0.25410	0.23270	0.18181	0.17710
Mg ²⁺		0.26815	0.24250	0.22810	0.17780	0.15521
Ca ²⁺		0.22118	0.20080	0.19070	0.16671	0.14724

Table 2. Thermodynamic equilibrium constant and free energy of activation. F cal. mole

Exchange systems	Ionic strength, M									
	0.025		0.05		0.1		0.3		0.5	
	K	ΔF^\ddagger	K	ΔF^\ddagger	K	ΔF^\ddagger	K	ΔF^\ddagger	K	ΔF^\ddagger
Ca ²⁺ - H ⁺	1.9108	-383.190	2.2293	-490.919	5.0955	-964.111	7.643	-1204.117	22.294	-2018.228
Mg ²⁺ - H ⁺	0.6779	+229.095	1.8079	-350.462	2.7119	-590.467	6.3277	-1092.296	18.531	-1727.764
Co ²⁺ - H ⁺	0.4512	+470.464	0.4875	+425.463	3.250	-698.196	4.109	-837.290	14.95	-1600.94
Ni ²⁺ - H ⁺	0.9588	+24.545	0.4109	+526.375	1.5751	-268.642	3.900	-805.926	8.4236	-1261.391
Cu ²⁺ - H ⁺	0.4939	+417.281	0.5763	+325.916	1.8333	-358.644	2.666	-580.921	5.681	-1028.204
Co ²⁺ - Cu ²⁺	1.0718	-29.239	0.8038	+130.911	0.5359	+369.553	-----	-----	-----	-----
Ni ²⁺ - Cu ²⁺	1.344	-174.549	0.960	+24.545	1.152	-83.183	-----	-----	-----	-----

Comparing the equilibrium constant values for various exchange systems, at the same ionic strength, showed that the order of the equilibrium constant is parallel to the selectivity sequence mentioned previously.

The only possible exception is found in the nickel-copper exchange where the equilibrium constant of such a reaction decreases with increase in the ionic strength.

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