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Ion Exchange Equilibria between Alkali Metals and Hydrogen Ions on Iron(III) Antimonate, an Inorganic Ion Exchanger

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(Received July 19, 1982)

Ion exchange equilibria of alkali metal ions (Li^+, Na^+, K^+ and Rb^+)/H^+ systems have been studied at 30, 40, 50, and 60 °C on iron(III) antimonate as a cation exchanger. The exchange isotherms have been measured for both forward and backward reactions with solutions of ionic strength 0.1 by the batch technique. The isotherms showed S-shaped curves for each exchange system except Li^+/H^+. Selectivity coefficients vary with the equivalent fraction ($\overline{X}_M$) of the alkali metal ions in the exchanger and give linear functions against $\overline{X}_M$ in the range from 0—0.40. The selectivity sequence shows $Na^+ < Li^+ < K^+ < Rb^+$. The overall thermodynamic data are evaluated.

Synthetic inorganic ion exchangers have been developed in recent years. The primary aim of most of the studies done in this field has been to achieve the separations. Besides the preparation of new materials and their applications to the separations interest has also been developed towards the study of ion exchange equilibria on these materials. Because of their thermal stability, their rigid structure and consequently negligible swelling, the ion exchange equilibrium studies at different temperatures on these materials will be simpler than on organic ion exchange resins which swell quite appreciably and are prone to thermal instability. The contributions of Larsen Vissers,[1] Ruvarac,[2] Amphlett,[3] Alberti,[4] Nancollas & Dyer[5] are noteworthy in this field. Recently Abe and Sudoh[6,7] described the ion exchange equilibrium studies on antimonic acid for the systems of transition metal ions/H^+ and from these results the appropriate thermodynamic data were derived.

The influence of temperature on the equilibrium between alkaline earth metal ions and hydrogen ion on tantalum arsenate has been described in our earlier paper.[8] Similar studies on the equilibria between alkaline earth metal ions and sodium ion on iron(III) antimonate have also been described.[9] The ion exchange characteristics of iron(III) antimonate are of considerable interest since it behaves as a cation exchanger with different selectivities for cations.[10]

Limiting our attention to series of ions belonging to the same group of the periodic table, that is having the same valency and similar electronic structure, we can study the effects of ion size and hydration upon equilibria eliminating the problem of the influence of eletronic and valency differences. Alkali metal ions can be taken as models for metal ions since they have univalent positive charge. Furthermore, they form inoic bonds and the effect of complex formation can be avoided.

Experimental

The iron(III) antimonate was prepared as described previously.

Determination of Maximum Uptake of Alkali Metal Ions on Iron(III) Antimonate. A 0.1 mol dm^{-3} solution of alkali metal chloride was passed continuously through the iron(III) antimonate column in H^+ form until the change in concentration of the alkali metal ion was negligible between the influent and effluent. The equivalent fraction of H^+ and M^+ in iron(III) antimonate was calculated on the basis of total exchange capacity.

Ion Exchange Equilibria. In the forward reactions the iron(III) antimonate (0.5 g) in H^+ form was immersed in 20 cm^3 of a mixed solution of varying ratio of alkali metal chloride/hydrochloric acid in the conical flasks with intermittent shaking at 30±1, 40±1, 50±1 and 60±1 °C. The ionic strength in the mixed solution was adjusted to 0.1 with hydrochloric acid.

In the reverse reactions the ion exchanger iron(III) antimonate in the respective alkali metal forms corresponding in weight (0.5 g in the hydrogen form) was immersed in the 20 cm^3 of the mixed solution of alkali metal chloride/hydrochloric acid at an ionic strength of 0.1.

Theoretical Aspects. The ion exchange reactions of the univalent alkali metal ions/H^+ exchange systems on iron(III) antimonate can be represented by the following expression:

$$\overline{H}^+ + M^+ \rightleftharpoons \overline{M}^+ + H^+, \tag{1}$$

where the bar refers to iron(III) antimonate phase and M^+ is the alkali metal ion.

The corrected selectivity coefficient of the above reaction can be defined as:

$$K_c = \frac{\overline{X}_M \cdot X_H}{\overline{X}_H \cdot X_M} \frac{\gamma_H}{\gamma_M}, \tag{2}$$

where K_c is the corrected selectivity coefficient, $\overline{X}_M$ and $\overline{X}_H$ are the equivalent fractions of the metal and H^+ in the exchanger phase, respectively. X_H and X_M are the equivalent fractions of exchanging H^+ and M^+ in the solution phase, respectively. γ_H and γ_M the activity coefficients of hydrogen and the metal in solution respectively. For dilute concentrations the contribution of the activity coefficient ratio (γ_H/γ_M) may be taken as unity.

The thermodynamic equilibrium constant K_a can be calculated using the simplified form of the expression given by Gains and Thomas (11):

$$\ln K_a = \int_0^1 \ln K_c d\overline{X}_M. \tag{3}$$

The change in the free energy of the ion exchange reaction, $\Delta G°$ was calculated from the thermodynamic equilibrium constant K_a using the expression:

$$\Delta G° = -RT \ln K_a. \tag{4}$$

The standard enthalpy change, $\Delta H°$ has been calculated from the plot of $\log K_a$ against $1/T$.

The standard entropy change, $\Delta S°$ is then calculated by the relation:

$$\Delta G° = \Delta H° - T\Delta S°. \tag{5}$$

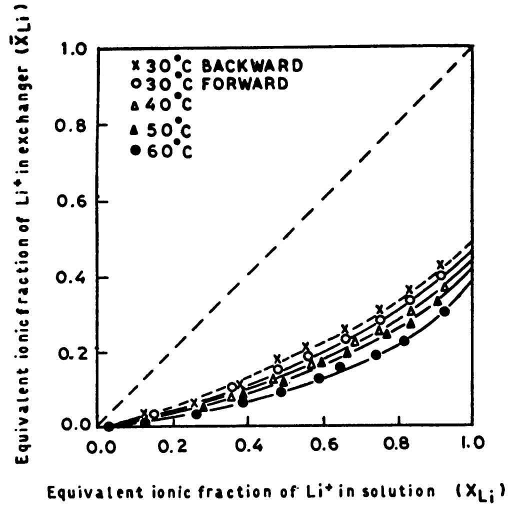

Fig. 1. Ion exchange isotherm of Li^+-H^+ exchange iron(III) antimonate.

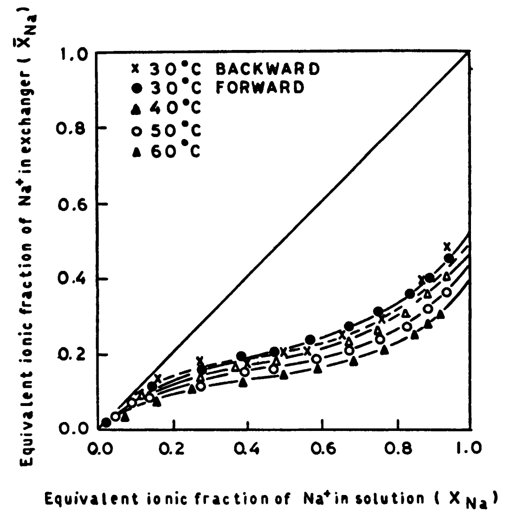

Fig. 2. Ion exchange isotherm of Na^+-H^+ exchange on iron(III) antimonate.

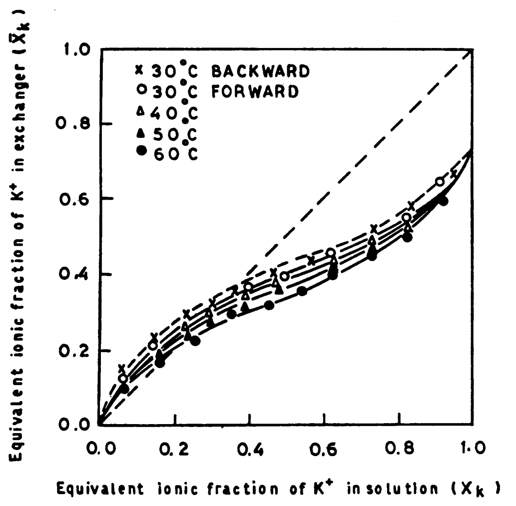

Fig. 3. Ion exchange isotherm of K^+-H^+ exchange on iron(III) antimonate.

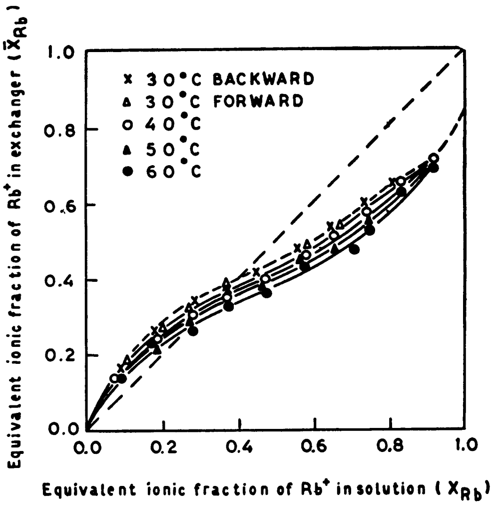

Fig. 4. Ion exchange isotherm of Rb^+-H^+ exchange on iron(III) antimonate.

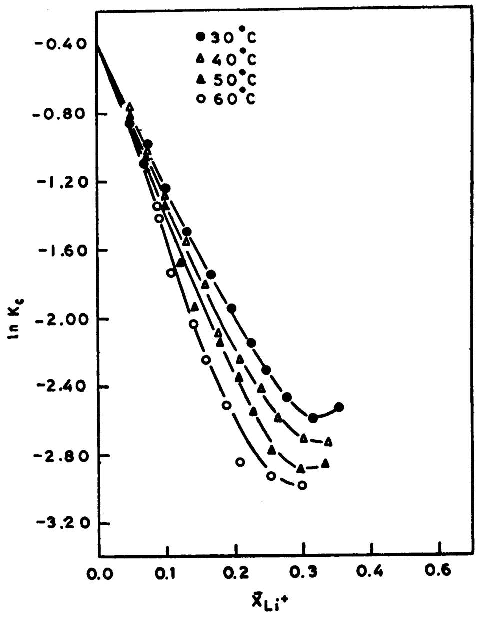

Fig. 5. Logarithms of selectively coefficient *vs.* ionic fractions of Li^+ in exchanger phase.

Results and Discussion

The equilibrium was attained for the forward and backward ion exchange reactions within 6 h shaking. The ion exchange isotherms for the systems Li^+/H^+, Na^+/H^+, K^+/H^+, and Rb^+/H^+ in a temperature range of 30—60 °C are shown in Figs. 1 to 4. Ion exchange isotherms have been used to represent graphically experimental data pertinent to ion competition (at different concentration ratios).

For Li^+/H^+ and Na^+/H^+, the isotherms showed that the exchange does not go to completion although entering cation is initially preferred and the degree of exchange gives a value lower than unity. For K^+/H^+ and Rb^+/H^+ the entering cations show a selectivity reversal with increasing equivalent fraction in the exchanger. The isotherms for the reverse exchange are performed only at 30±1 °C and can be plotted

TABLE 1. THERMODYNAMIC PARAMETERS ON IRON(III) ANTIMONATE AT AN IONIC STRENGTH OF 0.1 AND VARIOUS TEMPERATURES

Alkali metal ion	K_a 30 °C	40 °C	50 °C	60 °C	ΔG°/kJ equiv^{-1} 30 °C	40 °C	50 °C	60 °C	ΔH°/kJ equiv^{-1} 30—60 °C	ΔS°/J equiv^{-1} deg^{-1}
Li+	0.08	0.06	0.05	0.04	6.50	7.20	8.10	8.78	17.06	77.60±0.17
Na+	0.05	0.04	0.03	0.02	7.69	8.74	9.61	10.66	22.17	98.40±0.35
K+	0.37	0.30	0.27	0.22	2.56	3.15	3.55	4.18	13.85	54.14±0.18
Rb+	0.60	0.51	0.45	0.40	1.31	1.74	2.17	2.56	11.09	40.98±0.23

TABLE 2. HYPOTHETICAL THERMODYNAMIC DATA ON "ZERO LOADING" OF THE ION EXCHANGE REACTION AT 30 °C

	Li+	Na+	K+	Rb+
$\ln K_{c\,\bar{X}_M\to 0}$	−0.35	−1.50	−2.00	−1.25
$\dfrac{\Delta G^\circ_{\bar{X}_M\to 0}}{\text{kJ equiv}^{-1}}$	0.88	3.79	5.06	3.16
$\Delta H^\circ_{\bar{X}_M\to 0}$	0.00	0.00	0.00	0.00
$\dfrac{\Delta S^\circ_{\bar{X}_M\to 0}}{\text{J equiv}^{-1}}$	−2.9	−12.5	−16.7	−10.4

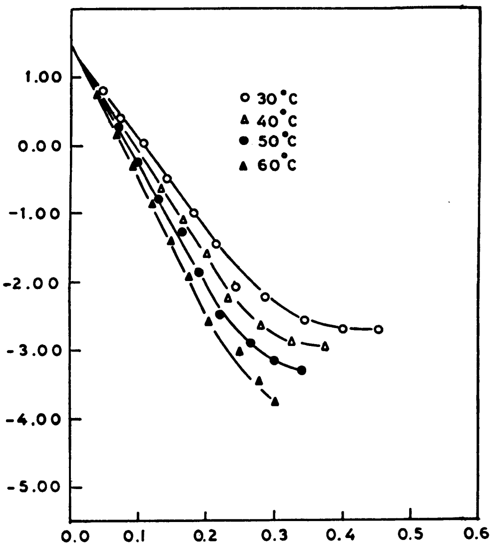

Fig. 6. Logarithms of selectivity coefficient *vs.* ionic fractions Na+ in exchanger phase.

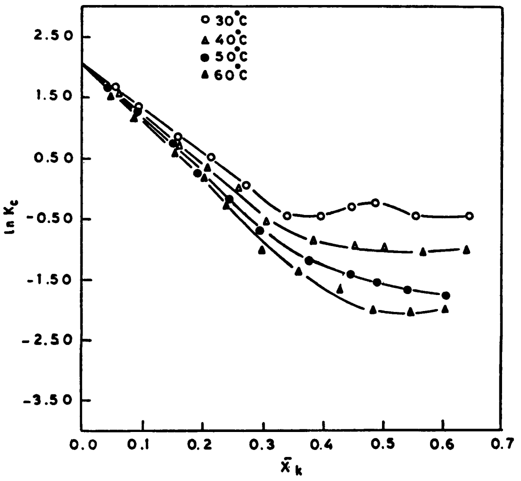

Fig. 7. Logarithms of selectivity coefficients *vs.* ionic fractions of K+ ions in the exchanger phase.

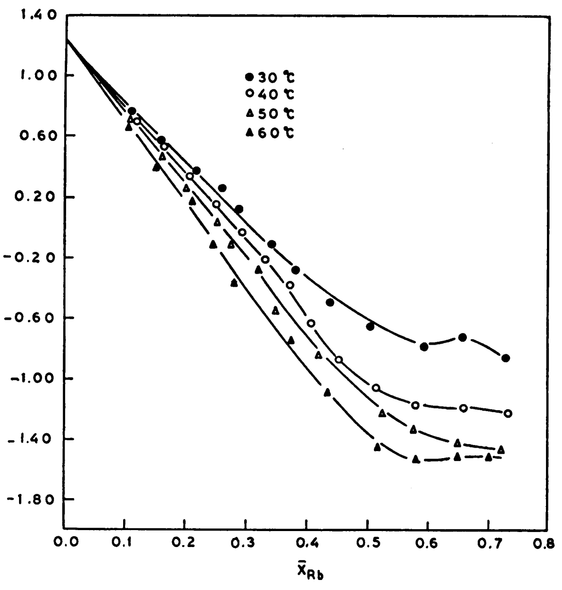

Fig. 8. Logarithms of selectivity coefficients *vs.* ionic fractions of Rb in exchanger ohase.

on the curves of the isotherms for the forwared exchange (Fig. 1 to 4). Thus the ion exchange reactions are reversible throughout the entire range of the compositions studied.

The selectivity of the exchanger can be measured in terms of K_c, which is the quantitative measure of the prefernce of the exchanger for one ion over another in solution with it. The ln K_c *vs.* $\bar{X}_M$ which is referred to as Kielland plot gave fairly straight line for all systems at lower values of $\bar{X}_M$ (Figs. 5 to 8). The linear Kielland plot was also observed for the alkali metal ions/H+ systems on crystalline antimonic acid.

The thermodynamic equilibrium constant K_a was evaluated from Eg. 3 by assuming that the relation between ln K_c *vs.* $\bar{X}_M$ remains unity over entire range 0 to 1 of $\bar{X}_M$. The ΔH° and ΔS° showed a corresponding change in their values with the change in temperature since the plots of log K_a *vs.* $1/T$ showed fairly good linearity over the entire range of temperatures studied. The thermodynamic selectivity series was found to be:

$$\mathrm{Na^+ < Li^+ < K^+ < Rb^+}.$$

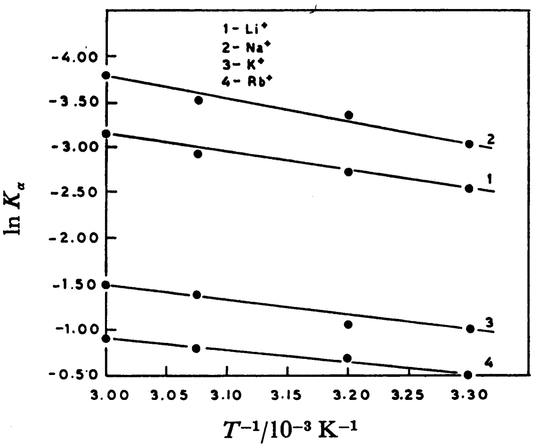

Fig. 9. Temperature dependence of thermodynamic equilibrium constant.

Interpretation of the Selectivity in the Infinitesimal Concentration of the Alkali Metals. The hypothetical thermodynamic data in infinitesimal concentration were calculated for interpretation of the selectivity of the alkali metal in the trace amounts on iron(III) antimonate and for comparison with those data obtained with other exchangers. The values of $(\ln K_c)\bar{X}_M \to 0$ were obtained by extrapolating to "zero loading" (7) of the alkali metals on Fig. 5—8. From these values the hypothetical thermodynamic data were calculated by the similar treatment as for the overall equilibrium constants. The accuracy of these values may be higher than those of the latter. The calculated $(\Delta H°)\bar{X}_M \to 0$ values indicate that there is no enthalpy change in the reaction when metal ion concentration in the solid phase approaches to zero over the entire range of temperatures. While the $(\Delta S°)\bar{X}_M \to 0$ increases with increasing ionic radii of alkali metals except for Rb^+.

The Authors are thankful to Prof. W.Rahman, Head, Department of Chemistry, Aligarh Muslim University, Aligarh. One of the authors (B.S.) is thankful to C.S.I.R., New Delhi for financial assistance.

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