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THERMODYNAMICS OF ION EXCHANGE PROCESSES INVOLVING ALKALI IONS ON H^+-FORM *m*-CRESOL FORMALDEHYDE IN AQUEOUS ACETONE

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ABSTRACT

The equilibrium constants for exchanging Li^+, K^+ Na^+ and Rb^+ ions with the H^+-form of *m*-cresol formaldehyde resin at constant ionic strength (0.1 M) in aqueous acetone solutions have been evaluated at temperatures of 25, 35 and 45°C. The thermodynamic equilibrium constant increases with increasing temperature and acetone content of the exchanging medium. The free energies, enthalpies of the reaction, and the corresponding entropy values have been calculated for all the exchange systems and solvent compositions. The variation of thermodynamic functions with acetone percentage showed that the entropy changes rather than enthalpy changes define the selectivities of the resin to alkali ions in the presence of organic solvents.

INTRODUCTION

The selectivity coefficient (S_H^M) of the reaction

$$RH + M^+ \rightleftharpoons RM + H^+ \qquad (1)$$

is defined by [1–4]

$$S_H^M = \frac{\bar{X}_M}{C_{M^+}} \frac{C_{H^+}}{\bar{X}_H} \qquad (2)$$

where $\bar{X}_M$ and $\bar{X}_H$ are the equivalent ionic fractions of the metal and hydrogen in the resin phase, and C_{M^+} and C_{H^+} are the concentrations of the metal and hydrogen ions in the solution phase, respectively.

The rational thermodynamic equilibrium constant can be calculated by graphical integration of the logarithmic values of the selectivity coefficients, log S, against the equivalent ionic fractions in the exchanger phase, $\bar{X}_M$, as reported in the following expression [5,6]

$$\ln K_H^M = \int_0^1 \ln S_H^M d\bar{X}_M \qquad (3)$$

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Assuming that all the reactants and products are in their standard states [7,8] the thermodynamic functions have been calculated.

The free energy changes ΔG^0 for the ion exchange were calculated from the thermodynamic equilibrium constant using the general expression

$$\Delta G^0 = -\frac{RT}{Z_H Z_M} \ln K_H^M \tag{4}$$

The ΔH^0 values were calculated from a plot of $\log_{10} K_H^M$ vs. $1/T$.

The entropy changes, ΔS^0, corresponding to the ion exchange process were calculated using the following relation

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{5}$$

Ion exchange equilibria between hydrogen and lithium on various cross-linked Dowex 50 resins have been made over the temperature range 0–90°C at constant ionic strength (0.1 M). Calorimetric measurements have been conducted on these resins at 25°C. The heat of exchange is greatly influenced by resin composition [9]. Several studies on the temperature dependence of the ion exchange reaction on synthetic organic resins in mixed solvents have been reported [10,11]. Gupta et al. [12] studied the equilibria of Li^+–H^+ on Amberlite IR 120 in methanol–water mixtures. The selectivity coefficients have been determined at three temperatures for each system. Bhatnagar and Sharma [13] determined the equilibrium exchange of alkali metal and hydrogen ions on Dowex 50 w X-8 at three temperatures for aqueous solutions and three acetone–water mixtures.

Recently, the thermodynamics of exchange of alkali ions in glycerol–water mixtures on H^+-form synthetic *m*-cresol formaldehyde resin was studied by Mourad et al. [14].

The present report concerns the influence of temperature on the equilibria: Li^+–H^+, Na^+–H^+, K^+–H^+ and Rb^+–H^+ with respect to synthetic *m*-cresol formaldehyde cation exchanger in aqueous solution and aqueous organic solvent at constant ionic strength within the temperature range 25–45°C.

EXPERIMENTAL

Reagents

Lithium, sodium and rubidium chlorides (BDH) were used. All chemicals and organic solvents were of Analar grade.

m-Cresol formaldehyde resin, synthesized as reported in an earlier investigation [15], was sieved to 250–420 mesh and washed free of fine particles. It was then subjected to sodium–hydrogen cycles and air dried (room temperature 25°C) to constant weight. The exchange capacity of the resin was 2.5 meq g^{-1} dry H^+-form as determined by weight titration with standardized NaOH. The solvents used were 0, 10, 30 and 50% (v/v) acetone in water.

Equilibration methods

In the equilibration methods, 0.2-g samples of the hydrogen exchanger were shaken at the desired temperature for 12 h with 20 ml of a solution containing alkali metal chloride (0.1 M) and hydrochloric acid (0.1 M) solutions (in the absence and presence of acetone) at a total ionic strength of 0.1 M with respect to the alkali ion. The equilibrating solutions were analysed for alkali ions using a flame photometer of the Milan type (Elvi 550). Experiments were carried out at 25, 35 and 45 ± 1°C.

RESULTS AND DISCUSSION

Selectivity studies at different temperatures investigate the heats of ion exchange. It is evident from Table 1 that the thermodynamic equilibrium constants increase with increasing temperature of the equilibrating medium [12–14]. The $\Delta H°$ values are calculated from a plot of $\log_{10} K$ against $1/T$.

TABLE 1

Thermodynamic equilibrium constant ($\log_{10} K_{\mathrm{H}}^{\mathrm{M}}$) values at different temperatures and solvent compositions

Temp. (°C)	Acetone (%, v/v)			
	0	10	30	50
(A) Li^+-H^+ exchange				
25	0.122	0.195	0.298	0.389
35	0.282	0.470	0.668	0.916
45	0.389	0.959	1.171	1.411
(B) Na^+-H^+ exchange				
25	0.470	1.012	1.322	1.447
35	0.622	1.212	1.547	1.723
45	0.648	1.411	1.766	1.974
(C) K^+-H^+ exchange				
25	0.742	1.322	1.631	1.721
35	0.918	1.459	1.792	1.887
45	0.997	1.579	1.932	2.032
(D) Rb^+-H^+ exchange				
25	1.016	1.480	1.728	1.895
35	1.203	1.725	1.962	2.187
45	1.284	1.946	2.187	2.399

Straight lines (Fig. 1) were obtained, indicating a regular change with temperature. The ΔH^0 values for the exchange of alkali ions with hydrogen ions on the resin show that heat was absorbed. The entropy changes, ΔS^0, corresponding to the ion exchange process were calculated using eqn. (5). The calculated ΔS^0 values are given in Table 2.

Increasing acetone concentration in the equilibrating solution leads to an increase in both entropy and enthalpy changes (Table 2). In pure aqueous solution for mono-monovalent exchange, Boyd [5] found that both ΔH^0 and ΔS^0 decreased with increasing the resin loadings. In this investigation, since Li^+ was found to exhibit the least affinity for the exchanger, the exchange reaction is endothermic as has been observed by both the increase in ΔH^0 and ΔS^0.

The increase in entropy is attributed to the rejection of bound water in acetone–water mixtures, so that the resin takes up acetone. Thus, with respect to acetone, there is a great similarity between the composition of the

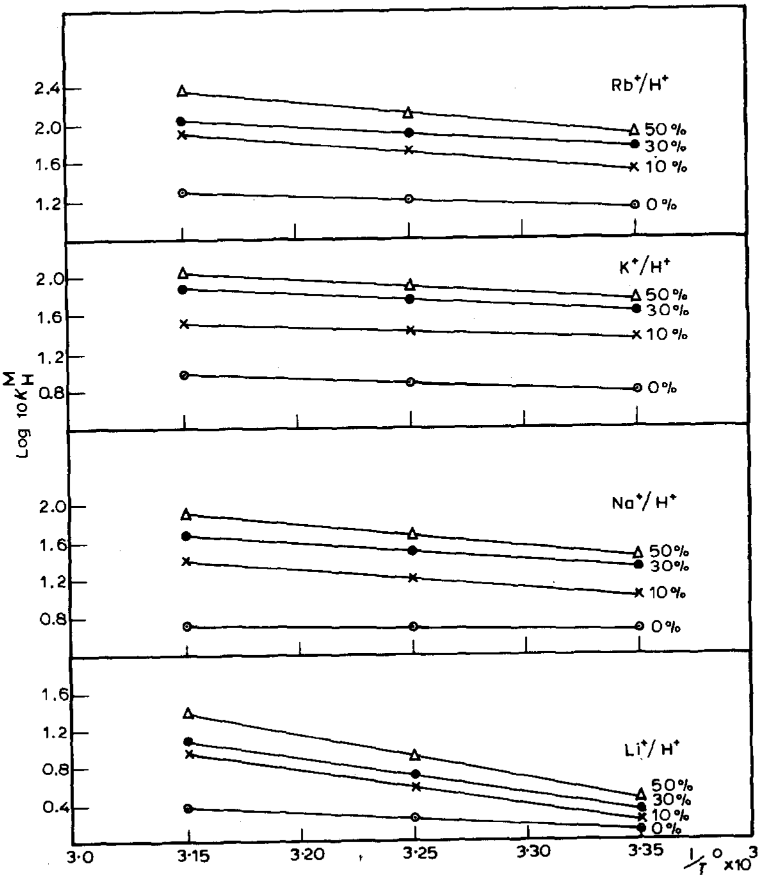

Fig. 1. Plot of $\log_{10} K$ against $1/T$.

TABLE 2

Thermodynamic properties for the exchange of alkali metal ions with hydrogen ion on *m*-cresol formaldehyde at different solvent compositions

Acetone (%)	ΔG^0 (cal mol^{-1}) (35°)	ΔH^0 (cal mol^{-1})	ΔS^0 (cal mol^{-1} deg^{-1})
(A) Li^+-H^+ exchange			
0	−172.58	3009.69	17.43
10	−287.64	8255.08	27.73
30	−408.81	8562.16	29.12
50	−560.59	8715.70	30.12
(B) Na^+-H^+ exchange			
0	−380.66	2260.76	8.58
10	−741.74	3603.70	14.11
30	−946.76	4000.13	16.06
50	−1054.77	4759.77	18.88
(C) K^+-H^+ exchange			
0	−561.81	1492.55	6.67
10	−892.90	2321.17	10.43
30	−1096.69	2718.77	12.39
50	−1154.84	2853.99	13.01
(D) Rb^+-H^+ exchange			
0	−736.23	890.99	5.28
10	−1055.69	2208.53	10.59
30	−1200.74	2222.75	11.11
50	−1338.43	2388.63	12.07

resin and the external phase [11,13]. This phenomenon increases with increasing proportion of acetone in the exchanging solution and, consequently, the entropy change values increase. The addition of acetone results in a small but positive contribution to the entropy changes.

Our results of Li^+–H^+ exchange on *m*-cresol formaldehyde resin in aqueous acetone agree with those reported earlier [12,13] for aqueous methanol and aqueous acetone.

Similar results to those already reported for Li^+–H^+ have been obtained for Na^+–H^+ exchange. Thus, an increase in ΔS^0 and absorption of heat have been found (Table 2). It is to be noted that the magnitudes of ΔS^0 are small and not of the order of their decreasing hydrated ionic sizes [13]. This result may be due to the marked difference in the nature of the ions under investigation.

Li^+–H^+ exchange gave higher values of ΔS^0, indicating that other interactions may take place in aqueous acetone mixtures. Ion pairs in non-aqueous medium were found to be exhibited by Li^+ ions [13]. Therefore, Li^+–H^+ exchange is affected by interactions other than exchange. The entropy changes for Na^+–H^+, K^+–H^+ and Rb^+–H^+ systems are small compared to the corresponding values in Li^+–H^+ exchange. These are in increasing sequence for Na^+, K^+ and Rb^+ ions as expected on the assumption of their decreasing hydrated ionic sizes. Therefore, the side interactions in these three exchange systems are smaller than those in Li^+–H^+ exchange [13].

The disturbances in the hydration spheres of alkali metal ions, resulting from the addition of acetone to the equilibrating mixture, seem to be responsible for the large positive values of entropy changes [13]. The system of exchange was randomly controlled.

Plotting ΔS^0 against ΔH^0 values showed a straight-line relationship (Fig. 2). This indicates that entropy changes at the same rate as the variation of enthalpy, as has been found in aqueous systems [16].

For all the exchange systems the free energy change values are negative

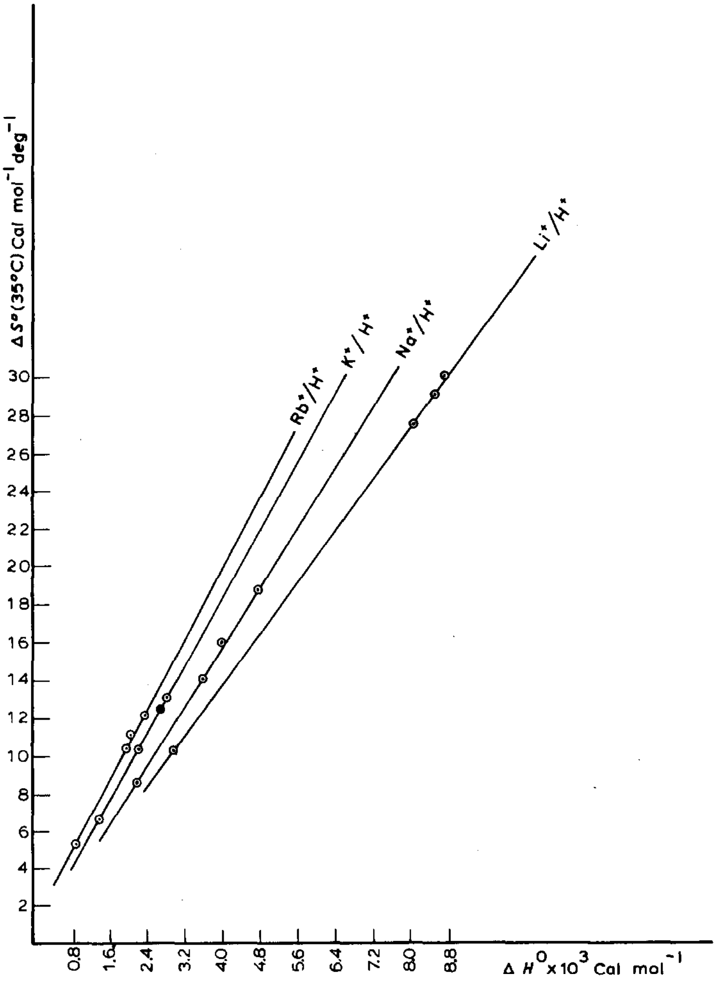

Fig. 2. Plot of ΔS^0 against ΔH^0.

[13,14] in accordance with the spontaneous nature of the reactions. When increasing proportions of acetone are present, however, the negativity decreased. It can be said that the rate of exchange decreases for solutions containing large proportions of acetone.

The selectivities of these alkali metal ions to the resin changed with changing acetone percentage and with temperature. It can be seen that the selectivity for alkali ions increases in the order: $Rb^+ > K^+ > Na^+ > Li^+$.

Solvents of low polarity aid in complex formation and ion pairing [17,18], thus, the total effect, which is an increase in selectivity, is clearly due to the presence of the organic solvent, rather than a rise in temperature.

In pure aqueous solutions the selectivity values are controlled by the values of ΔH^0, a fact which is not true for the equilibria of mixed solvents. The importance of entropy changes in selectivity reversals in mixed solvent systems has been reported by Gupta et al. [12].

The data reported for Li^+–H^+ exchange in aqueous acetone indicate that its exchange is influenced by interactions other than exchange, contrary to previous findings in the aqueous glycerol system [14]. Two main factors greatly affect the entropy changes, first, the ion pairing and second, the disturbances in the hydration sheath of metal ions. These factors appeared to be significant on the addition of acetone to the equilibrating mixture. Thus, ion exchange in aqueous acetone was controlled by ΔS^0 rather than ΔH^0 changes in the systems studied [13].

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