

THERMODYNAMIC STUDY OF ALKALI–HYDROGEN EXCHANGE IN AQUEOUS GLYCEROL ON *m*-CRESOL–FORMALDEHYDE RESIN

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ABSTRACT

The uni-univalent exchange of alkali cations on synthesized *m*-cresol–formaldehyde cation exchanger have been studied in pure water and aqueous glycerol solutions of total ionic strength 0.1 M with respect to the metal ions under investigation ($M^+ = Li^+, Na^+$ and K^+).

The experimental results showed that the rational thermodynamic equilibrium constants were directly proportional to both temperature and glycerol concentration. The relation between $\ln K$ and $1/T$ is represented by a straight line. An increase in glycerol concentration in the outer solution caused a marked increase in entropy and enthalpy. This could be attributed to the release of bound water in the glycerol–water system. Graphical representation of ΔS^0 as a function of ΔH^0 showed the entropy change to be directly proportional to the enthalpy change.

INTRODUCTION

Considerable effort has been made to explain quantitatively ion exchange equilibria in aqueous organic solvents. Formal thermodynamic treatment of the selectivity behaviour in these media has been developed through the works of a number of authors [1–5]. The process of ion exchange usually involves little evolution or absorption of heat as it is not a chemical reaction. The temperature dependence of ion exchange equilibria in general is related to the standard enthalpy changes (ΔH^0) which accompany the reaction and can be given by the relation

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \quad (1)$$

where K is the rational thermodynamic equilibrium constant and ΔH^0 is the standard enthalpy change for an exchange reaction



where the subscripts w and R refer to ions in the solution and resinous exchanger, respectively. Experimentally, this dependence of equilibria on temperature has been studied calorimetrically as heats of exchange, as well

as by studying the effect of temperature on selectivity coefficients. The selectivity coefficient of a resin, K_a , is given by [6–8]

$$K_a = \frac{X_{A_R} C_{B_w^+}}{X_{B_R} C_{A_w^+}} \quad (3)$$

where the X and C terms correspond to the resinates and the concentrations in the aqueous phase, respectively.

The rational thermodynamic constants can be evaluated from the selectivity coefficient values at several X_{B_R} values between 0 and 1 by graphical integration using the expression [9–12]

$$\ln K = \int_0^1 \ln K_a \, dX_{B_R} \quad (4)$$

The applicability of this equation to mixed solvents is conditional. Thus under the conditions of low ionic strength (10^{-1} M) and the same solvent composition inside and outside the resin phase, the equation can be applied to exchange systems in mixed solvents. Earlier studies carried out in aqueous solutions [6–13] showed the dependence of the selectivity coefficient on factors such as water uptake, ionic strength of the outer solution and resin structure.

Little information exists concerning heats of exchange in mixed solvents [12–14], especially in aqueous glycerol systems. In the present work, glycerol–water mixtures have been used to study alkali–hydrogen exchange on synthesized *m*-cresol–formaldehyde [13] (as cation exchange resin) at four temperatures. The selectivity coefficients have been determined as a function of resin composition at four temperatures for three glycerol–water mixtures (i.e. 10, 30 and 50% v/v). The thermodynamic quantities such as free energy ΔG^0 , enthalpy ΔH^0 , and entropy ΔS^0 for Li^+/H^+ , Na^+/H^+ and K^+/H^+ exchanges have been calculated assuming that all the reactants and products were in their standard conditions [15,16]. Thus, ΔG^0 and ΔH^0 were calculated using the relations

$$\Delta G^0 = -RT \ln K \quad (5)$$

and

$$\Delta H^0 = \frac{-RT_1 T_2}{(T_2 - T_1)} \ln \frac{K_{T_2}}{K_{T_1}} \quad (6)$$

The entropy ΔS^0 is given by the relation

$$\Delta S^0 = \frac{(\Delta H^0 - \Delta G^0)}{T} \quad (7)$$

The data obtained are discussed.

EXPERIMENTAL

Materials

The exchanger used in the present work was *m*-cresol-formaldehyde in hydrogen form (250–420 mesh size with capacity of 2.6 mequiv. g⁻¹ of dry resin) prepared as described elsewhere [13]. It was conditioned by a double cycle (H–Na) of exhaustion and regeneration using 1 M NaCl and HCl solutions and was finally converted to the hydrogen form, then washed with deionized water until free from acidity, and air dried (~ 30°C) before storing in air-tight amber coloured bottles.

The stock electrolyte solutions (0.5 M) were prepared using B.D.H. Analar nitrates of lithium, sodium and potassium. To prepared solutions for exchange studies these were suitably diluted with distilled water and glycerol (prolabo, Analar) to give 0, 10, 30 and 50% (v/v) aqueous glycerol solutions of 0.1 M strength with respect to the metal ions under investigation.

Method

All equilibrium studies were carried out using 0.5 g of the air-dried resin with 50 ml of different electrolyte solutions (either aqueous or mixed with glycerol) separately in glass-stoppered flasks. All exchange studies were carried out in a thermostatic bath (controlled within $\pm 0.1^\circ\text{C}$) at four different temperatures, namely 30, 50, 65 and 80°C. The reaction flasks were shaken intermittently during equilibrium under thermostatic conditions. A sufficiently good time interval (~ 10 h) was allowed for the attainment of equilibrium in each case. The solution phase was analyzed for the equilibrium exchange using an Elvi 550 (Milano) type flame photometer to estimate the concentration (in p.p.m.) of the alkali metals under study.

RESULTS

The heats of ion-exchange reactions are usually investigated by studying the effect of temperature on selectivity coefficients. It was found from the present studies (Table 1) that in general at different glycerol concentrations the thermodynamic equilibrium constants increase with increase in temperature. Plots of $\ln K$ vs. $1/T^0$ (Fig. 1) show a regular change in K value (which is a measure of the selectivity of the ion) with temperature.

The effect of composition of the outer solution on the thermodynamic functions ΔS^0 , ΔH^0 and ΔG^0 for Li^+/H^+ , Na^+/H^+ and K^+/H^+ exchanges was also investigated, and it was found that an increase in % glycerol induced a marked increase in the values of the thermodynamic functions (Table 2). Plots of ΔS^0 vs. ΔH^0 are linear (Fig. 2), in all cases showing changes in entropy with changes in enthalpy.

TABLE 1

Thermodynamic equilibrium constants at different temperatures and solvent compositions

Temp. (°C)	ln K			
	Glycerol % (v/v)			
	0	10	30	50
<i>(A) Li⁺/H⁺ exchange</i>				
30	0.151	0.249	0.311	0.350
50	0.440	0.562	0.632	0.750
65	0.651	0.881	0.922	1.050
80	0.831	1.001	1.111	1.330
<i>(B) Na⁺/H⁺ exchange</i>				
30	0.461	0.543	0.662	0.821
50	0.651	0.740	0.880	1.110
65	0.822	0.900	1.051	1.348
80	0.931	1.051	1.181	1.531
<i>(C) K⁺/H⁺ exchange</i>				
30	0.911	0.981	1.100	1.311
50	1.031	1.151	1.272	1.511
65	1.111	1.250	1.451	1.672
80	1.200	1.351	1.520	1.811

TABLE 2

Thermodynamic functions at different solvent compositions

Glycerol (%v/v)	ΔG^0 (cal mole ⁻¹) at 50°C	ΔH^0 (cal mole ⁻¹)	ΔS^0 (cal mole ⁻¹ deg ⁻¹) at 50°C
<i>(A) Li⁺/H⁺ exchange</i>			
0	-282.392	2874.809	9.774
10	-360.692	3179.200	10.959
30	-405.618	3382.128	11.727
50	-481.351	4143.106	14.317
<i>(B) Na⁺/H⁺ exchange</i>			
0	-417.812	1987.000	7.445
10	-474.933	2147.651	8.119
30	-564.785	2194.156	8.542
50	-712.399	3001.639	11.499
<i>(C) K⁺/H⁺ exchange</i>			
0	-661.697	1221.794	5.831
10	-738.713	1564.234	7.130
30	-316.371	1775.617	8.025
50	-969.761	2113.830	9.547

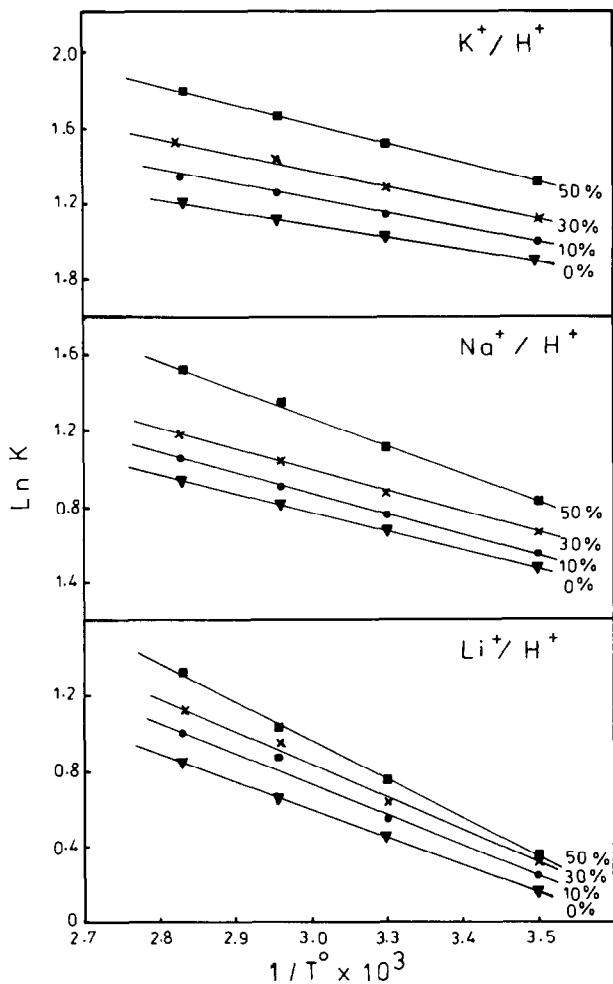


Fig. 1. Plots of $\ln K$ vs. $1/T^0$.

DISCUSSION

The present studies were carried out at an ionic concentration ≤ 0.1 M and glycerol concentration up to 50% (v/v), since it was found that solvent uptake is practically the same in the outer and inner solutions when the mole fraction of the organic solvent in the mixture is 0.5 or less [17]. Thus the conditions for satisfactory applicability of eqn. (3) for calculating thermodynamic constants were maintained in the work.

For uni-univalent ion-exchange in aqueous systems, evolution of heat and decrease in entropy have been observed with the uptake of the preferred ion by the exchanger [9,10]. In Li^+ / H^+ exchange an increase in entropy and enthalpy was observed with increase in glycerol concentration. The increase

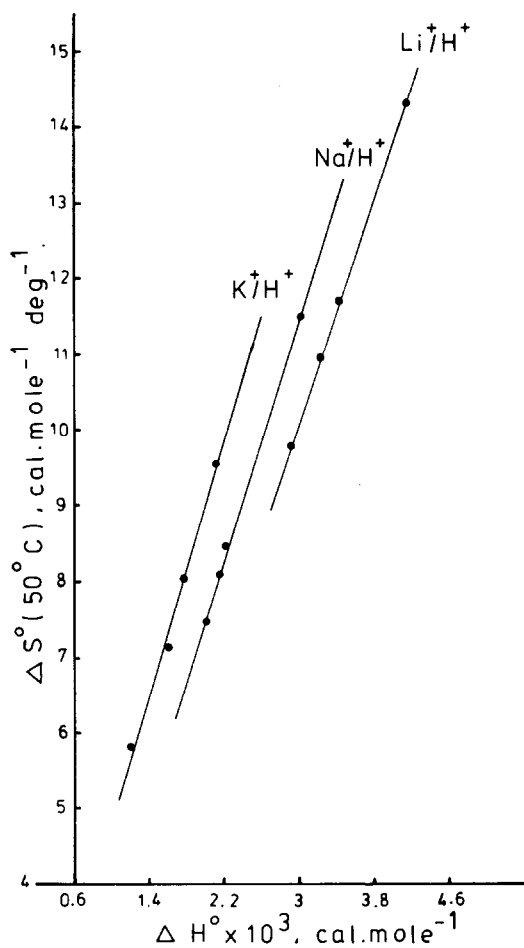


Fig. 2. Plots of ΔS^0 vs. ΔH^0 .

in ΔS^0 may be due to the release of bound water in glycerol–water systems, so that the resin imbibes glycerol, also making the composition of the resin and outer solution the same with respect to the organic solvent [17]. This effect increases with increasing glycerol concentration and hence the increase in ΔS^0 . Thus the obtained results for Li $^+$ /H $^+$ exchange in aqueous glycerol are in agreement with those obtained for exchange in both aqueous methanol [11] and aqueous acetone [12].

Studies for Na $^+$ /H $^+$ exchanges in aqueous glycerol showed that the reaction is also accompanied by an increase in entropy and evolution of heat. Although all the values for ΔS^0 are positive, their magnitudes are not in the order of their decreasing hydrated ionic sizes (which are supposed to be a measure of exchange selectivities). This may be attributed to differences in the nature of the reaction in the ions under investigation. The values of

ΔS^0 for Na^+/H^+ and K^+/H^+ exchange are less than that for Li^+/H^+ exchange, and they are in increasing order for the two alkali metal ions as expected on the basis of their decreasing hydrated ionic size.

The values of ΔG^0 for all exchanges involving uni-univalent ions have been shown to be negative and in decreasing order with increasing glycerol concentration. Thus the free energy of the exchange reaction decreases with increase in organic solvent concentration, i.e. the exchange reaction becomes slower in solutions containing increasing percentages of less polar solvents such as glycerol.

The selectivities of these ions, as measured by K , show changes by changing both of solvent composition with respect to organic component and temperature. The selectivity of the studied ions increases in the order $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ at any glycerol concentration and any temperature. Usually, less polar organic solvents enhance complex formation or other side interactions such as ion-pair formation [18,19] but temperature rise checks them [20]. Hence the overall effect, which is an increase in selectivity, is more due to the presence of organic solvent rather than the effect of temperature.

Thus the experimental results for Li^+/H^+ exchange in aqueous glycerol show that its exchange is not influenced by interactions other than exchange, i.e. it can be assumed that the formation of ion-pairs, like those formed during Li^+/H^+ exchange in aqueous acetone [12], is not possible. Although for exchanges in aqueous solutions the enthalpy changes have been supposed to be the controlling factor for selectivities, it cannot be so for mixed and partially aqueous solvents.

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