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Thermodynamic Studies on Styrene Butadiene Phenolformaldehyde Cation Exchange Resin

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Equilibrium coefficients have been studied for the exchanges of Cu(II)/H(I), Co(II)/H(I) and Ni(II)/H(I) systems on strongly cation exchanger styrene butadiene phenolformaldehyde(SBPF) in aqueous and aqueous-acetone media. The ionic strength of the solution was $\simeq$0.1M, and the exchanges was studied as a function of resin compositions. All these coefficients increase with increasing organic solvent in the solution phase. Applying a statistical thermodynamic model, the thermodynamic equilibrium constants have been determined at three temperature range between 25 and 55°C. The standard free energies ΔG°, enthalpies ΔH° and entropies ΔS°, drived from the data are presented.

INTRODUCTION

The effect of temperature on ion-exchange equilibrium has been reported for uni-univalent or divalent systems, using aqueous or aqueous-organic as equilibrating media, which in many cases include the ion exchanger exhibit enhanced selectivity for certain ions[1-4]. In an earlier studies[5] the ion exchange behaviour of Ca^{2+},Sr^{2+} and Ba^{2+} against sodium ion using cation exchanger (SBPF) have been indicated that heat is absorbed. However, a very few studies on selectivities of such system have been appeared in aqueous medium[6, 7]. Measurements of the temperature dependence of the equilibrium constant for the exchange of Mg(II) and Cu(II) ions with hydrogen ion has been noticed that heat is absorbed, while in the exchange of Ba^{2+} with hydrogen ion heat is evolved[8, 9]. In this work the result of Cu(II)/H(I), Co(II)/H(I) and Ni(II)/H(I) exchanges on styrene butadiene phenolformaldehyde (SBPF) in aqueous and aqueous-acetone mixtures are investigated. The selectivity coefficients have been determined as a function of resin composition at each solvent compositions and at three different temperatures. The thermodynamic functions; enthalpy change, free energy change and entropy changes have been calculated and discussed in terms of selectivities in each solvent compositions

EXPERIMENTAL

All chemicals and organic solvent used were of E. Merck of BDH-analaR Grade.

The cation exchange resin used in this work was styrene butadiene phenolformaldehyde in hydrogen form (250-420 mesh size) having diameter *ca* 0.29cm[10]. The exchange capacity of the resin was 3.4 meq./g dry resin. The resin was ground and screened to obtain different sizes using sieves (ASTM-E 11-61). It was treatment by a double cycle (sodium-hydrogen) for exhaustion and regeneration using 1M HCl and 1M NaCl. It was then washed with deionized water till free from excess of H^+-ion, and dried at *ca* 30°C before storing in air-tight amber coloured bottles. Standard solutions, stock solutions of Co(II), Ni(II) and Cu(II) ions were prepared by dissolution of the chlorides of these metal ions in aqueous and aqueous-organic media to prepare solution for exchange studies, 0.0%, 10%; 30% and 50% (V/V) acetone in solutions.

All equilibrium studies for the exchange of M^+-M^{++} system were carried out using 1 millequivalent of the dry resin with 50 ml of different uni- and divalent electrolyte solutions. The equilibrating solutions (50 ml) vary in concentration ratios between the hydrogen and divalent ions according to the following; 90 : 10, 70 : 30, 50 : 50, 30 : 70 and 10 : 90 which in each case gives finally a total ionic strength —0.1M. in 0.0%, 10%, 30% and 50% (V/V) separately in glass stoppered flasks.

The procedure of the exchange was running in a thermostatic bath with ±0.1°C three different temperature 25°, 40° and 50°C. The reaction flasks were shaken intermittently during exchange under thermostat conditions. A sufficient good time for the attainment of equilibrium in each run was 6 hrs.

The equilibirated solution were separated by decantation and analysed for hydrogen and cation ions in the external phase. For accuracy the concentration of the above cations were determined both in the solution phase as well as in the resin, and the results of the analysis showed good agreement when the aqueous phase only analysed and the absorbed elements by differences. The elements were determined by titrated using suitable chelatometric method with EDTA-disodium salt as titrant. The indicator used were muroxide for Ni(II) and Co(II), methyl thymol blue for Cu(II) ions using a suitable buffer solutions, and where hydrogen ion was determine by sodium hydroxide solutions[11, 12]. In case of microgram quantities of the elements they were determined spectrophometerically.

RESULTS AND DISCUSSION

In exchanges of uni-divalent ions the exchange reaction has been expressed by the equation;

$$\tfrac{1}{2}(M^{++})_o + (B^+)_i \rightarrow \tfrac{1}{2}(M^{++})_i + (B^+)_o \qquad (1)$$

where (M^{++}) and (B^+) are the cations involved in the exchanger and the subscript (i) and (o) represent by the resin phase and the aqueous phase solution respectively. The thermodynamic equilibrium constant K and the selectivity coefficient k are related to the concentration of the ion C, and their activity coefficient (ν) by the equation[5, 6].

$$K = \frac{C^{1/2}_{(M^{++})_i} C_{(B^+)_o} f^{1/2}_{(M^{++})_i} \nu^{2}_{(B^+)_o}}{C^{1/2}_{(M^{++})_o} C_{(B^+)_i} \nu^{3/2}_{(M^{++})_o} f_{(B^+)_i}}$$

$$= \int_0^1 k \frac{f^{1/2}_{(M^{++})_i} \nu^{2}_{(B^+)_o}}{\nu^{3/2}_{(M^{++})_o} f_{(B^+)_i}} \qquad (2)$$

For simplicity we utilize the values of the mean activity coefficient(ν) calculated, using the following cell[13].

$Ag\text{-}AgCl{:}MCl_2(m){:}M_xHg{:}MCl_2\ (m_r)\ AgCl\text{-}Ag$

The electromotive force of the cell is given by;

$$E = \frac{3RT}{2F} \ln \frac{\nu_{\pm m}}{\nu_{\pm m_r}} \qquad (3)$$

Equation (3) was used by Tippette and Newton[14] from which it is clear that ($\nu_{\pm m}$) relative to its value, ($\nu_{\pm m_r}$) at a reference concentration may be computed.

Under these conditions the calculated values of the thermodynamic equilibrium constant, K, are in error referred to the mean molal activity coefficients MCl_2 and HCl in the resin phase were assumed to be unity. This assumption was made because a few activity coefficient values are available in mixed solvent for univalent ion[15]. While, the activity coefficient data required for the calculation of equilibrium constant data for divalent ion in this work in aqueous medium are available[15]. The value of K may be corrected for any exchange in mixed aqueous solutions are known.

However, to overcome this error, the equilibrium constant for each exchange reaction has been calculated by integration the equation[16–17].

$$\ln K = \int_0^1 \ln k \frac{\nu^2(B^+)_o}{\nu^{3/2}(M^{++})_o}\, dX \qquad (4)$$

Where (X) is the equivalent fraction of the preferred ion in the resin phase. In the calculation of these equilibrium constants it has been necessary to ignore the activity coefficient ratios of univalent to divalent as data for these activity coefficients are not available at all of the temperature.

The free energies $\Delta G°$, heats $\Delta H°$ and entropies $\Delta S°$ of exchange systems can be obtained using the following expression;

$$-\Delta G° = \frac{1}{Z_{M^{++}} Z_{M^{+}}} RT \ln K^{M^{++}}_{M^{+}} \qquad (5)$$

$$\Delta H° = \frac{R \ln K_2/K_1}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \qquad (6)$$

$$\Delta S° = \Delta H°/T_{40°C} - \Delta G°/T_{40°C} \qquad (7)$$

The calculated values of the thermodynamic functions for the exchanges in 0, 10, 30 and 50% (V/V) acetone are given in Table–2.

The heat of ion-exchange reaction are usually investigated by studying the effect of temperature on selectivity coefficients. It has been observed that from this work at different proportion of acetone the thermodynamic equilibrium constant K, increase with increase in temperature. From the plots of K against 1/T, Fig.–1, shows a regular change in K with temperature, which indicates that, such measurements dependance on temperature. The values of enthalpy ΔH° for all the exchanges with hydrogen ions on the resin show that heat was absorbed, and increases with increasing of temperature and acetone concentration. It is noticed that, the ΔH° is greater in mixed solvents than in pure aqueous medium, thus it could not account for the reversal of selectivity observed in all exchanges in the presence of organic solvent i.e. acetone. Thus it is the increase of acetone in the system which is responsible for this reversal of selectivity. In aqueous system, on the other hand, it is enthalpy change which is the controlling factor[18].

Free energies of exchange: For all the exchange systems the free energies changes are negative signs, which indicates probably such reaction are in accordance with the spontaneous nature of the reactions with increasing proportion of organic solvent in the outer phase, however, the negativity of the free energy changes increased. Therefore it can be concluded that the exchange increases for solution containing large proportion of acetone.

Entropies of exchange: The entropies of exchange, shown in Table–2 as $T\Delta S$, illusterate the interest of this factor in determining the free energies of exchange. $T\Delta S$ has been evaluated only for these exchanges that do not involve slow process. The positive ΔS° values found in this work therefore may be taken as supporting evidence for 'site binding' of M^{++} ions by styrene butadiene phenolformaldehyde exchanger. The question whether or not the sulphonic group replaces water and enters first coordination sphere of the ion cannot be decided from the evidence available. The signs and positive of $T\Delta S$ are similar to those reported for other systems[5, 9]. For the divalent metal ions and hydrogen ion the replacement of divalent by the hydrogen ions is associated with positive entropy change. The increases in entropy with increasing acetone concentration is attributed to the rejection of bound water in acetone-water mixture, so that the resin takes up acetone. Thus with respect to acetone, therefore is a great similarity between the composition of the resin and the external phase[17]. This phenomena increases with increasing acetone concentration in the exchanging medium, and consequently the entropy change values increase. The addition of acetone results in a small but positive contribution to the entropy changes.

In case of Cu(II)/H(I) exchange an increase in entropy and enthalpy

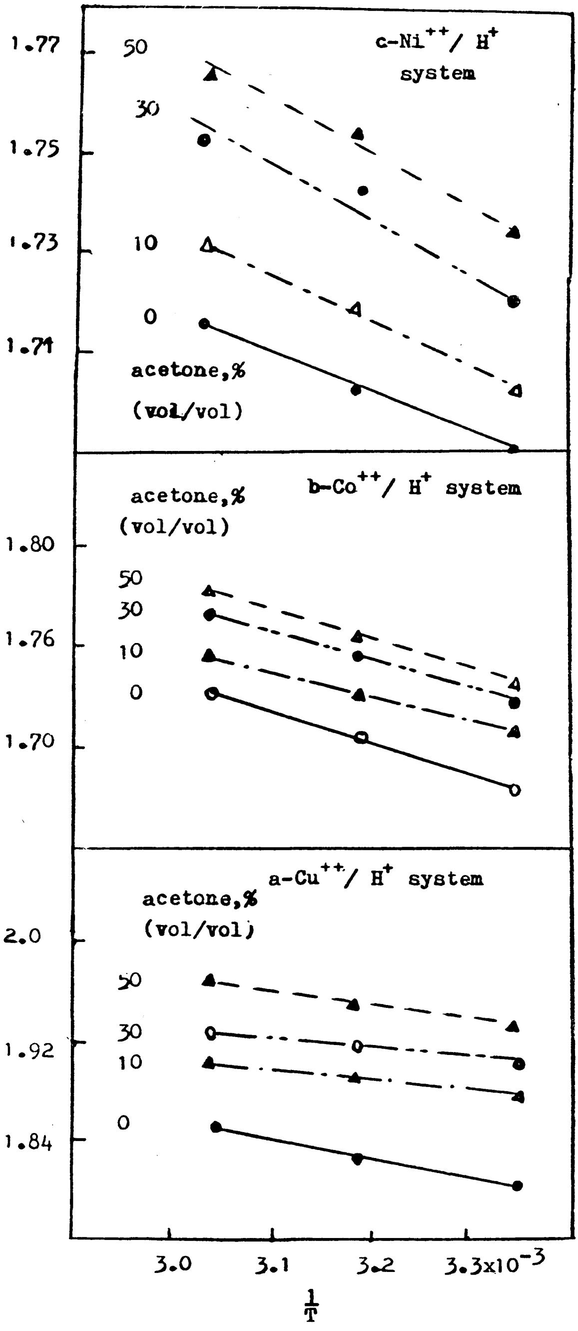

Fig. 1. Plots of ln K. vs. $\frac{I}{T}$.

TABLE 1

THERMODYNAMIC EQUILIBRIUM CONSTANTS AT DIFFERENT ACETONE COMPOSITIONS AND AT DIFFERENT TEMPERATURES

Temp. °C	Thermodynamic equilibrium constant; K			
a-Cu(II)/H(I) exchange	Acetone, % (vol/vol)			
	0	10	30	50
25	6.11	6.50	6.67	6.91
40	6.19	6.65	6.82	7.03
55	6.33	6.74	6.93	7.18
b-Co(II)/H(I) exchange				
25	5.55	5.61	5.69	5.72
40	5.62	5.70	5.81	5.85
55	5.71	5.79	5.89	5.94
c-Ni(II)/H(I) exchange				
25	5.42	5.48	5.59	5.66
40	5.48	5.58	5.72	5.78
55	5.56	5.65	5.77	5.85

TABLE 2

THERMODYNAMIC QUANTITIES FOR Cu(II), Co(II) AND Ni(II)/H(I) SYSTEMS AT VARIOUS ACETONE CONCENTRATIONS ON STYRENE BUTADIENE PHENOLFORMALDEHYDE CATION EXCHANGER

Acetone; (V/V)	$-\Delta G^\circ$ Joule/mole 40°C	ΔH° Joule/mole	ΔS° Joule/mole 40°/deg	$T\Delta S^\circ$ Joule/mole
		a-Cu^{++}/H^{+} exchange		
0	2371.89	958.27	10.639	3330.007
10	2465.16	982.23	11.014	3444.738
30	2498.00	1035.93	11.290	3570.640
50	2537.46	1038.36	11.424	3575.712
		b-Co(II)/H(I) exchange		
0	2246.200	769.934	9.636	3016.069
10	2264.59	855.55	9.968	3119.984
30	2289.46	935.853	10.303	3126.244
50	2098.389	1022.395	10.609	3320.617
		c-Ni(II)/H(I) exchange		
0	2213.377	690.863	9.278	2904.014
10	2236.907	827.619	9.790	3064.270
30	2264.149	858.565	9.992	3127.446
50	2282.726	894.459	10.150	3177.169

has been observed with increase in acetone concentration in the solution phase, Table–1. The increase in entropy is due to the release of bound water in acetone-water system., so that the resin imbibes acetone, also making the composition of the resinate and water solution the same with respect to the organic solvent[17]. This influence increases with increase of organic solvent. The obtained results are in agreement with the results obtained by several authors[18-20].

Studies were carried for Co(II)/H(I) exchanges in aqueous acetone have yield similar trends, increase in entropy and enthalpy have been noticed. Upon adding increasing proportions of acetone to the exchanging medium, also the free energy change decreases, becoming more negative. Thus, in mixed solvent, the uptake of the preferred ion is accompanied by an adsorption of heat and increase in entropy[10, 17-19]. The heats of mixing of acetone and water will also be involved, besides the heats of dilution of both hydrogen and divalent ions. The values of ΔS° in case of

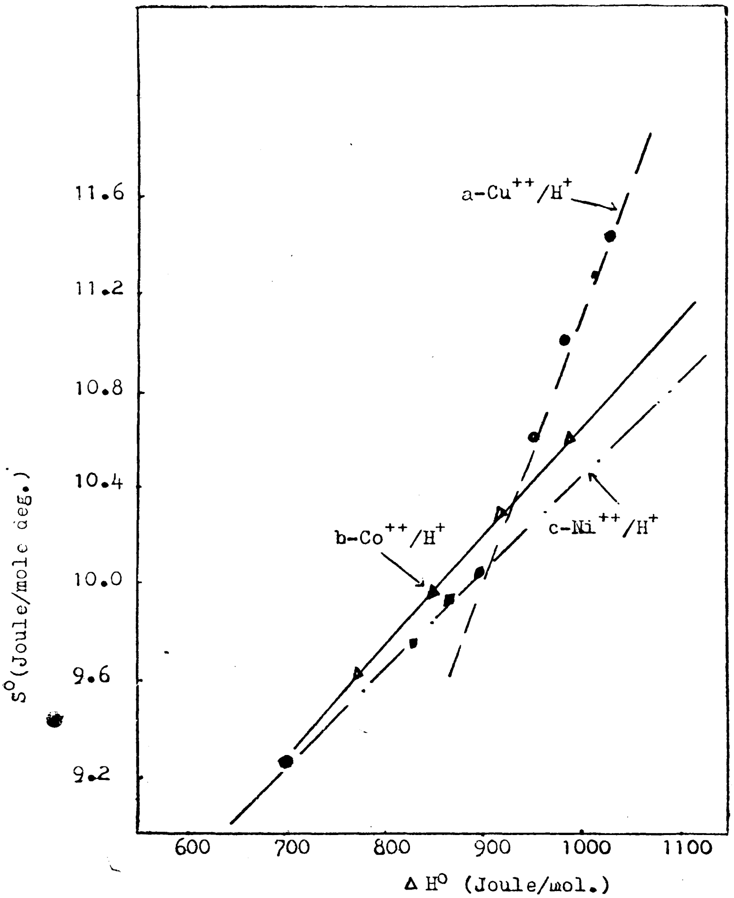

Fig. 2. Plots of ΔS° vs ΔH°.

Co(II) and Ni(II)/H(I) are less than that of Cu(II)/H(I) exchangers. This may be attributed to differences in the nature of the reaction in ions under study, and or increase in order for the two alkali metal ions as expected on the basis of their increasing hydrated ionic sizes[6, 21]. (Table–1)

The values of $\Delta G°$ for all exchange system have been shown to be negative and in decreasing order with increasing acetone concentration, indicating that the exchange reaction in this study are higher in solutions containing increasing proportions of less dielectric constant[5].

In general, in the present studies the increase of selectivity coefficient values are governed by two reasonce ion-pair interactions[22–24] of some type and, disturbances in the hydration spheres of mixed ions. These reasonce are facilitated by the presence of the organic solvent. Hence ion exchange process in organic solvents like acetone is controlled by entropy variations rather than enthalpy changes in the terms.

Fig. 2. illustrates a linear relationship was obtained in plots of $\Delta S°$ against $\Delta H°$ in all the exchange systems, this indication showed a variation change in $\Delta S°$ corresponding with changes in $\Delta H°$.

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