

## THERMODYNAMIC STUDIES ON STYRENE BUTADIENE PHENOLFORMALDEHYDE CATION EXCHANGE RESIN

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Ion-exchange equilibrium reactions between  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$  and  $\text{Ba}^{+2}$  and sodium - form of styrene butadiene Ph-formaldehyde cation exchange resin (SBPF) over the temperature range  $25^\circ - 45^\circ$  in aqueous and aqueous-acetone have been investigated. Thermodynamic equilibrium constant  $K_{th}$  is greater than unity over the entire temperature range, and increase with increasing of temperature. The thermodynamic functions  $\Delta F^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  have been calculated for this exchange at each solvent compositions. The variation of these functions in mixed solvent have been shown to be controlled by the entropy  $\Delta S^\circ$  changes, where  $\Delta H^\circ$  controls the selectivities in aqueous medium. Moreover,  $\Delta S^\circ$  changes increase with increasing of both the heat of exchange and solvent compositions.

Key words: Cation exchange resin, Ion exchange resin, Selective studies, Thermodynamic studies.

### INTRODUCTION

Numerous reports the ion exchange reaction of uni-univalent [1-3] or divalent [4] systems using aqueous or non-aqueous solvent as equilibrating media have been appeared, which in many cases include the ion exchanger exhibit enhanced selectivity for certain ions.

The heat of ion exchange reaction have been investigated either calorimetrically [5-6] or by studying the effect of temperature [7-8] on selectivity coefficients.

A rigorous thermodynamic treatment which explain the enhanced selectivity of ion exchanger in mixed solvents or in non-aqueous media has been reported and experimentally verified [9-11]. Though a many data are available on the distribution coefficients of multivalent metal ion exchange equilibria in mixed solvent [12-13], however, a very few studies on selectivities of such system have been reported [14-15].

In this paper the result of  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$  and  $\text{Ba}^{+2}/\text{Na}^+$  exchanges on styrene butadiene Ph-formaldehyde in acetone-water mixture are investigated. The selectivity coefficients have determined as a function of resin composition at temperature range  $25^\circ - 45^\circ$  for each acetone - water mixtures. The thermodynamic functions; enthalpy changes  $\Delta H^\circ$ , free energy changes  $\Delta F^\circ$  and entropy changes  $\Delta S^\circ$  have been calculated and discussed in terms of selectivities in each solvent compositions.

### EXPERIMENTAL

*Procedure and materials.* The exchanger used in the present studies was styrene butadiene phenolformaldehyde cation exchange resin [17] in sodium form (250-420

mesh size). It was treatment by a double cycle (hydrogen-sodium) for exhaustion and regeneration using 1MNaCl and 10% HCl solutions and finally converted to sodium form. It was then washed with deionized water till free from excess of Na-ion. It was air dried ( $\approx 30^\circ$ ) before storing in air-tight amber coloured bottles.

The stock electrolyte solutions (0.5M) were prepared by using BDH-Analar chlorides of calcium, strontium and barium ions, to prepare solutions for exchange studies these were suitably diluted with distilled water and acetone (BDH-Analar) to give 0.0%, 10%, 30% and 50% (vol/vol) acetone in solutions.

All equilibrium studies for the exchange of uni-divalent system were carried out using 1 millequivalent of the dry resin with 50ml of different uni- and divalent electrolyte solutions. The equilibrating solutions (50ml) vary in concentration ratios between the sodium and divalent ions according to the following; 90%: 10%, 70%: 30%, 50%: 50%, 30%: 70% and 10%: 90% each system gives finally a total ionic strength 0.1M, (in aqueous or aqueous-acetone) separately in glass-stoppered flasks. The exchange was carried out in a thermostatic bath with  $\pm 0.1^\circ$  three different temperatures  $298^\circ$ ,  $308^\circ$  and  $318^\circ\text{K}$ . The reaction flasks were shaken intermittently during exchange under thermostat conditions. A sufficient good time for the attainment of equilibrium in each case was 4hr.

*Analysis.* The equilibrated solutions were separated by decantation and analysed for sodium and cation ions in the external phase. For accuracy the concentrations of the above cations were determined both in the solution phase as well as the resin phase and the results of analysis showed good agreement when the aqueous phase only

analysed. In case for sodium ions using a flame photometer of the Milan type (Elvi 550), the cations were analysed using suitable chelatometric method with EDTA-disodium salt as the titrant [28-29]. In case of microgram quantities of the elements are determined spectrophotometrically using (Beckman model B spectrophotometer type) -1 cm cell is used.

## RESULTS AND DISCUSSION

The ion-exchange reactions between divalent ions and the Na-form of the exchanger may be represented by the following equation;



where  $MCl_2$  is the salt of divalent cation and R is the exchange resin.

The equilibrium constant of the above exchange reaction is given by;

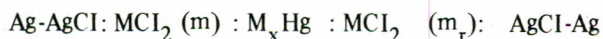
$$K_{th} = \frac{N^{1/2} MR_2 \quad m_{NaCl} \quad f_{MR_2} \quad v^4 NaCl}{N_{NaR} \quad m_{MCl_2} \quad f_{NaR}^2 \quad v^3 MCl_2} \quad (2)$$

Where (N) indicates the molar fraction of the ion in the solid phase, m's being the aqueous phase molarity, (f) being the activity coefficients of the solid phase, and (v) is the solution phase activity coefficients.

The equilibrium constant ( $K_{th}$ ) and or equilibrium quotient selectivity coefficient ( $k_a$ ) are related to the concentration of the ion C, and their activity coefficients (v) and can be expressed by the equation<sup>1</sup>;

$$K_{th} = \int_0^1 \frac{f^{1/2} MR_2 \quad v^4 NaCl}{k_a \quad f NaCl \quad v^3 MCl_2} \quad (3)$$

For simplicity we utilize the values of the mean activity coefficients (v) computed, using the following cell [18]



This electromotive force of this cell is given by;

$$E = \frac{3RT}{2F} \ln \frac{v_{\pm m}^{\pm}}{v_{\pm m_r}^{\pm}} \quad (4)$$

This equation was used by Tippet and Newton before [19], from which it is clear that ( $v_{\pm}$ ) relative to its value, ( $v_{\pm r}$ ) at a reference concentration may be computed.

Under these conditions the calculated values of  $K_{th}$  are in error, referred to the activity coefficient ratio (f)

of the ions in the resin phase were assumed to be unity. This assumption was run because a few activity coefficient values are available in mixed solvent for univalent [20] ions. However, the activity coefficient data required for the calculation of equilibrium constant for divalent ion in this studies in aqueous medium are available [20].

To overcome this error, the equilibrium constant for each exchange reaction has been calculated by integrating the equation [21-22],

$$\ln K_{th} = \int_0^1 \ln k_a \frac{v^4 NaCl}{v^3 MCl_2} dN \quad (5)$$

Where (N) is the equivalent fraction of  $MCl_2$  in resin phase.

The calculated values of the thermodynamic functions for each system  $Ca^{+2}$ ,  $Sr^{+2}$  and  $Ba^{+2} / Na^{+}$  at different temperature, and at solvent compositions are given in Table 2 using the following equation;

$$\Delta F^{\circ} = - RT \ln K_{th} \quad (6)$$

$$\ln K_2/K_1 = \frac{-\Delta H^{\circ}}{R} (1/T_2 - 1/T_1) \quad (7)$$

$$\Delta S^{\circ} = \Delta H^{\circ}/T_{35^{\circ}C} - \Delta F^{\circ}/T_{35^{\circ}C} \quad (8)$$

The heats of ion-exchange reaction are usually investigated by studying the influence of temperature on selectivity coefficients. It has been found out from the present studies at different acetone concentrations the thermodynamic equilibrium constants ( $K_{th}$ ) increase with increase in temperature.

In  $Ca^{+2}/Na^{+}$  exchange an increase in entropy and enthalpy has been observed with increase in acetone concentration in solution phase. The increase in entropy changes is due to the release of bound water by acetone molecules which enter the matrix of exchanger. This effect increases with increase of organic solvent, and hence the increase in  $\Delta S^{\circ}$  values. These results are in agreement with the results obtained in our laboratory [10,20,23] and by several other authors [9,12].

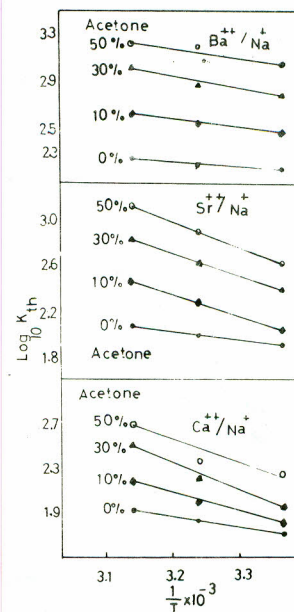
Studies were carried for  $Sr^{+2}/Na^{+}$  exchanges in aqueous acetone have yield similar trends, increase in entropy and absorbed of heat has been observed. The values of  $\Delta S^{\circ}$  in case of  $Sr^{+2}$  and  $Ca^{+2}/Na^{+}$  are less than of  $Ba^{+2}/Na^{+}$  exchanges. This may be attributed 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 [11,23], Table 1 and Fig. 1.

Table 1. Thermodynamic equilibrium constants at different temperatures and acetone percentages

Temp. °C	$\log_{10} K_{eq}$			
	Acetone % (vol-vol)			
<b>Ca<sup>2+</sup>/Na<sup>+</sup> exchange</b>				
	0	10	30	30
25	1.70	1.80	1.95	2.05
35	1.82	1.99	2.20	2.38
45	1.92	2.20	2.50	2.70
<b>Sr<sup>2+</sup>/Na<sup>+</sup> exchange</b>				
25	1.88	2.10	2.37	2.60
35	1.98	2.29	2.60	2.89
45	2.07	2.45	2.82	3.10
<b>Ba<sup>2+</sup>/Na<sup>+</sup> exchange</b>				
25	2.11	2.43	2.75	3.02
35	2.15	2.53	2.86	3.18
45	2.21	2.61	2.98	3.32

Table 2. Thermodynamic functions for alkali earth/sodium exchange at various acetone concentrations.

Acetone; vol/vol	$-\Delta G^{\circ}$	$\Delta H^{\circ}$	$\Delta S^{\circ}$
	cal/mole 35°C	cal/mol	cal/mol. deg 35°C
<b>Ca<sup>2+</sup>/Na<sup>+</sup> exchange</b>			
0	1282.55	10635.74	38.695
10	1217.87	11509.74	41.321
30	1346.39	12073.15	43.569
50	1456.55	12402.959	44.984
<b>Sr<sup>2+</sup>/Na<sup>+</sup> exchange</b>			
0	1211.75	10368.78	37.599
10	1401.47	10986.57	40.221
30	1591.18	11205.11	41.546
50	1768.66	11228.03	42.197
<b>Ba<sup>2+</sup>/Na<sup>+</sup> exchange</b>			
0	1315.791	9863.36	36.295
10	1542.229	10114.62	37.846
30	1750.308	10204.67	38.814
50	1964.140	10352.53	39.930


 Fig. 1. Plots of  $\log K_{10}$  vs  $\frac{1}{T}$ .

For all the investigated alkali metal ions in aqueous and aqueous-organic solvent systems an increase in both entropy and enthalpy were observed with increase in acetone concentration. The increase in entropy changes can be explained to the disturbances caused by the addition of acetone to the aqueous medium, in otherwise systematised hydration spheres of these metal ions. Thus, a randomness exists in the system. Such phenomena suggested that ionpair formation should be involved [10, 24-26]. The  $\Delta S^{\circ}$  values are in increasing order with increasing the values of  $a^{\circ}$  (the mean distance of closed approach, 4.73, 4.61 and 4.45 for Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> respectively) [20].

The values of  $\Delta F^{\circ}$  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 slower in solutions containing increasing percentages of less dielectric constant i.e. acetone [11].

Although this protic solvent favours ion-pair formation [20, 24-26], the rise in temperature usually discouraged its formation [27], the increase in selectivity values observed in this study, is largely due to the presence of acetone rather than the effect of temperature [10, 22 - 25].

Fig. 2 indicates a linear relationship was obtained in plots of  $\Delta S^{\circ}$  vs.  $\Delta H^{\circ}$  in all cases, this linearity showed a regular change in entropy with changes in enthalpy, similar trends have been shown by several authors [18, 22, 25].

In general, in the present studies the increase of selectivity coefficient values are governed by two reasons

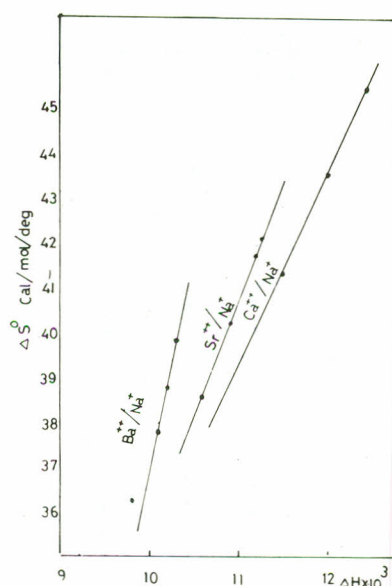


Fig. 2. Plots of  $\Delta H^\circ$  vs  $\Delta S^\circ$

ion-pair interactions of some type and, disturbances in the hydration spheres of mixed ions. These reasons 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.

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