Zirconium-Bis(triethylamine): A New Class of Chelate Ion and Anion Exchanger

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A new inorganic ion exchanger, zirconium-bis(triethylamine) has been synthesized. The material has been studied for its anion exchange capacity, sorption capacity, K_d values, composition, infrared spectrum and thermodynamic behavior. Analytically important separation of anions have been achieved. Ion exchange equilibria of $Cr_2O_7^{2-}$, CrO_4^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, and MnO_4^- systems have been studied at 30, 40, 45, and 60 °C. The exchange isotherms have been measured for both forward and backward reactions with solutions of ionic strength 0.10 by batch process. The isotherms showed S shaped curves. The overall thermodynamic data are also calculated.

In the continued effort to synthesize a new inorganic anion exchanger based on metal hydroxides with amino groups, some materials of this kind have been tried: Tin(IV)-bis(diethanolamine),[1] titanium-bis(diethanolamine),[2] aluminium triethanolamine,[3] and thorium triethanolamine.[4] The studies on these materials pave the way to develop some analytically important separations on the basis of their anion exchange behavior and for sorption of metal ions on the basis of their chelating action. Therefore the studies were extended to synthesize another material of this kind, zirconium-bis(triethylamine). The material has been studied for its anion exchange capacity, sorption capacity and distribution of different anions to measure selectivity. Composition and IR studies are made to characterize the exchanger. Thermodynamic study is actually the study of ion exchange equilibrium, which tells the possibility of an ion exchange process, it's spontaneity for different exchange systems can be compared by the free energy concept. Therefore, such a study was made on this exchanger, zirconium-bis(triethylamine).

Experimental

Apparatus. An electric temperature controlled SICO shaker, a Bausch and Lomb Spectronic 20 (USA) and an Elico pH-meter model Li-10 (India) were used for shaking, spectrophotometric determination and pH measurements, respectively.

Reagents. Zirconium dichloride oxide (BDH) and triethylamine (E. Merck) were used. The other chemicals were of analytical grade.

Synthesis. Zirconium-bis(triethylamine) was prepared by mixing 0.10 mol dm^{-3} zirconium dichloride oxide solution with 0.10 mol dm^{-3} solution of triethylamine in the ratio of 1:2 (Table 1). The precipitate thus obtained was kept standing for 24 h at room temperature (25±1 °C). The precipitate was then filtered and washed with deionized water. It was dried in an air oven at 40 °C and then kept in the air for 12 h. The dried material on immersion in water broke down in small pieces. The exchanger granules were converted into nitrate form by keeping in 1.0 mol dm^{-3}

Table 1. Conditions of Preparation and Properties of Zirconium-Bis(triethylamine) Exchanger

Sample	Conditions of synthesis: Molarity of reagent: Zirconium dichloride oxide	Triethylamine	Mixing volume ratio	Nature of precipitate	Propertie: Ion exchange capacity ($Cr_2O_7^{2-}$)	Sorption capacity [Cu(II)]
	mol dm^{-3}	mol dm^{-3}			meq g^{-1}	meq g^{-1}
S-1	0.10	0.10	1 : 1	Precipitate appears but dissolves on shaking.	—	—
S-2	0.10	0.10	2 : 1	Precipitate appears but dissolves on shaking.		
S-3	0.10	0.10	1 : 2	A thick precipitate.	3.20	0.42
S-4	0.10	0.10	1 : 3	Precipitate appears but dissolves.	—	—
S-5	0.10	0.10	3 : 1	Precipitate appears but dissolves.	—	—

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sodium nitrate solution overnight intermittently replacing the supernatant liquid with fresh solution of sodium nitrate. It was finally washed and dried at 40 °C. The anion exchange capacity of zirconium-bis(triethylamine) was determined by column method. The anion exchanger weighing one gram was poured in a glass column measuring 20 cm in length and 0.60 cm diameter with a glass wool support. The capacity was calculated for different anions, namely chromate, dichromate, chloride, bromide, iodide, thiosulfate, sulfate, and thiocyanate by converting the exchanger in the required form with sodium or potassium salts of the required ions. The column was washed with deionized water. The eluent used was 1.0 mol dm^{-3} sodium nitrate. The elution rate was fixed at 0.5 cm^3 min^{-1}. Anion exchange capacities for Cl^-, Br^-, I^-, SO_4^{2-}, $S_2O_3^{2-}$, SCN^-, CrO_4^{2-}, and $Cr_2O_7^{2-}$ were 0.20, 0.16, 0.10, 1.00, 0.27, 0.15, 2.50, and 3.20 meq g^{-1}, respectively.

For sorption capacity 1.0 g of the exchanger was taken in the column, 10.0 cm^3 of 0.10 mol dm^{-3} copper(II) solution was poured over the column at a rate of 0.5 cm^3 min^{-1}. The effluent was then titrated and copper ions were determined. A fresh sample of 10.0 cm^3 of 0.01 mol dm^{-3} copper(II) nitrate was added over the column and the effluent was again titrated. The readings of EDTA consumed for total effluent was subtracted from the reading of EDTA consumed for total influent (0.01 mol dm^{-3} copper nitrate). The sorption capacity was then calculated from these readings. For the determination of copper(II) ions, the solution was titrated against 0.01 mol dm^{-3} EDTA solution using buffer of pH 3.6 and 1-(2-pyridylazo)-2-naphthol (PAN).

The composition of zirconium-bis(triethylamine) was determined by dissolving 1.0 g exchanger in 50.0 cm^3 aqua regia. Heating was avoided for preparing solution. It was then made upto the mark in a 100 cm^3 volumetric flask with deionized water. The amount of zirconium present in the sample was determined by chelometric titrations using copper PAN indicator while quantitative determination of triethylamine in another portion of the sample was done spectrophotometrically by ninhydrin.[5]

To check the chemical stability of the exchanger, zirconium-bis(triethylamine), 0.5 g of the exchanger was shaken with different solvents for 4 h. The amount of zirconium present in the supernatant liquid was determined by titrating a known volume of the solution against EDTA and the amount of triethylamine was determined spectrophotometrically in another sample by ninhydrin. The stability of the exchanger in different solvent systems reveal that the exchanger is stable in deionized water, methyl alcohol, ethyl alcohol, aqueous ammonia (10.0 mol dm^{-3}). However, the exchanger is less stable in concentrated solutions of acids.

Different samples of zirconium-bis(triethylamine) were heated in a muffle furnace for 4 h. The capacity of the exchanger at 60, 100, 150, 200, 300, and 400 °C were determined, respectively.

To characterize the exchanger infrared studies were performed. The spectrum of zirconium-bis(triethylamine) was observed by using KBr disc. The results are presented in Fig. 1.

IR spectrum of zirconium-bis-(triethylamine) exchanger shows the absorption peaks at different values of wave number as given below: (a) A broad peak ranging from 3300—3550 cm^{-1} is due to O–H stretching vibrations. (b) A strong peak at 1380 cm^{-1} is due to C–N vibrations and C–H bending vibrations. (c) A medium peak lies at 2930 cm^{-1} due to C–H stretching vibrations. (d) A strong C–C stretching vibration is observed in the frequency range of 1620—1660 cm^{-1}. (e) A medium C–N bending frequency lies in the frequency range 1070—1080 cm^{-1}, and (f) A medium peak in the frequency range of 800—840 cm^{-1} is observed due to metal oxygen bending vibrations.

pH Titrations of the exchanger were performed by shaking 0.50 g of the exchanger with solution of 0.01 mol dm^{-3} HCl and its salts of 0.01 mol dm^{-3} concentration by Topp and Pepper method.[6] The volume of the reaction mixture was kept 50.0 cm^3 in each case. The pH of the solution was noted after equilibrating the solution for 4 h. Results are plotted in Fig. 2.

K_d Values for anions were determined by batch process.

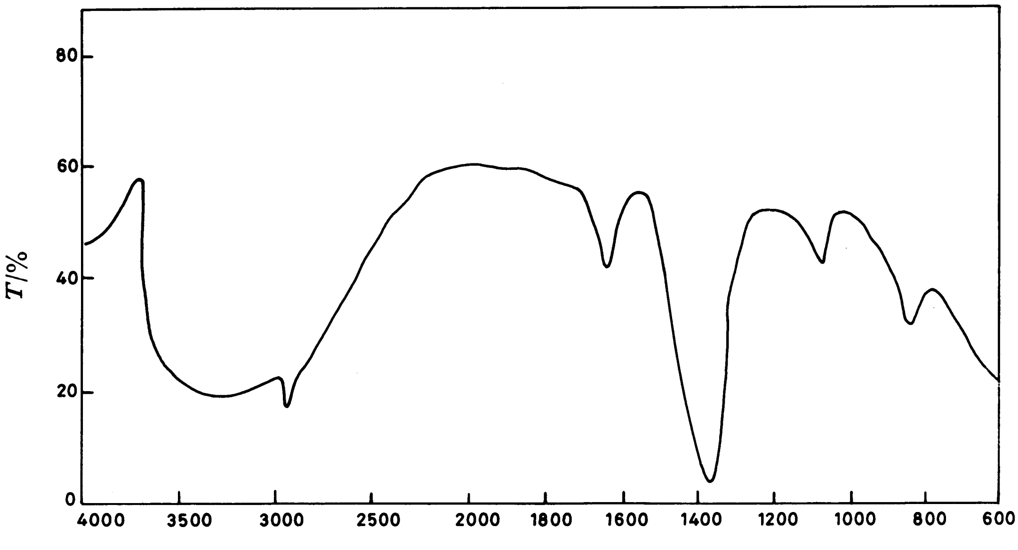

Fig. 1. IR spectrum of zirconium-bis(triethylamine) exchanger.

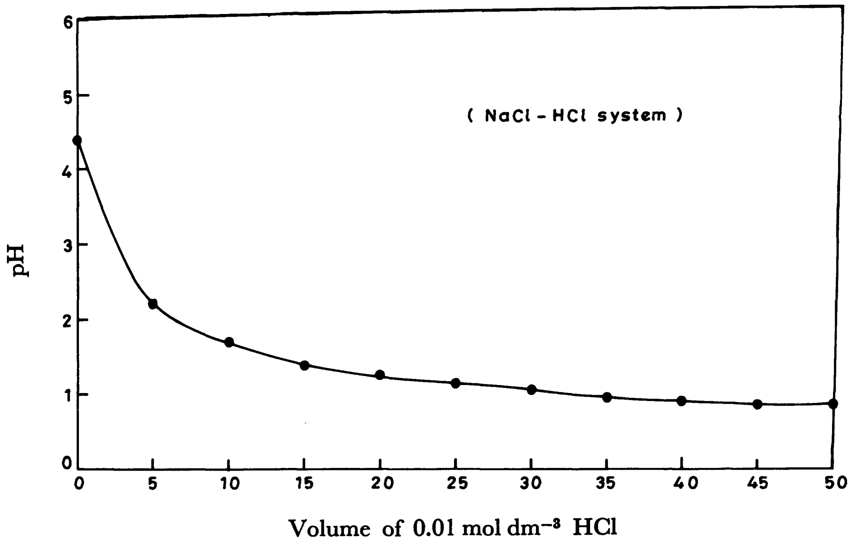

Fig. 2. Potentiometric titration curve for zirconium-bis(triethylamine) exchanger.

Table 2. K_d Values for Different Anions in Different Solvents

Sample No.	Anion	K_d value in				
		Water	NaOH 10^{-4} mol dm^{-3}	NaOH 10^{-3} mol dm^{-3}	NaOH 10^{-2} mol dm^{-3}	NaOH 10^{-1} mol dm^{-3}
1	Chloride	267±5	256±4	171±3	48±2	42±3
2	Bromide	200±3	175±2	153±4	20±2	8±2
3	Iodide	115±4	79±3	72±2	43±3	34±3
4	Dichromate	T.A.	T.A.	T.A.	4±1	0
5	Chromate	T.A.	T.A.	271±3	60±1	0
6	Thiosulfate	T.A.	T.A.	T.A.	11±4	2±1
7	Thiocyanate	132±2	116±3	108±2	10±1	0
8	Iodate	800±2	620±4	414±5	56±6	0
9	Peroxodisulfate	566±5	263±6	100±2	54±1	5±1
10	Bromate	1114±8	466±6	372±5	31±5	11±2
11	Sulfate	T.A.	T.A.	T.A.	0	0
12	Sulfite	T.A.	T.A.	T.A.	34	23
13	Hexacyanoferrate(III)	T.A.	T.A.	300±4	0	0
14	Hexacyanoferrate(II)	T.A.	T.A.	150±3	4±1	0
15	Arsenite	T.A.	T.A.	T.A.	1750±6	58±2
16	Phosphate	T.A.	2750±5	230±2	125±2	20±2
17	Vanadate	570±3	340±2	120±3	25±2	25±2

T.A. = Total adsorption.

1.0 cm^3 of anionic solution was taken in a 50.0 cm^3 volumetric flask. The remaining volume was filled up with NaOH solution in which its distribution studies were to be studied. This solution was then shaken for 4 h with the exchanger weighing 0.50 g in a shaker. The anions which remained in the solution after equilibration were then determined. Total amount of anions were also determined without equilibration. Results of the K_d values in deionized water and different concentrations of sodium hydroxide solutions are summarized in Table 2.

The anions having large differences in K_d values were tried for the separations. The column was prepared using 2.0 g of the exchanger (150—200 mesh size) in nitrate form in a glass column having a height of 30 cm and diameter 0.60 cm. A mixture of anionic solutions was poured on to the column. The solution was allowed to flow down very slowly through the column. These anions were adsorbed at the top of the exchanger bed forming initial zone. Column was washed with deionized water. The anions were then eluted by appropriate eluting reagent. The amount of anions were then determined by standard methods.

To study the thermodynamic behavior of the exchanger, the material (50—100 mesh) was converted to other anionic form by placing the material in a column and passing 1.0 mol dm^{-3} potassium or sodium salts of the respective anions until the concentration of anions in the eluent and eluate was identical. The sample was washed with deionized water until it was free from anions. After drying the exchanger it was stored in the stoppered bottle.

The equilibrium experiments were performed by taking 20 cm^3 solution containing sodium or potassium nitrate solution and appropriate anion solution. The ionic strength of the total content was kept 0.10 mol dm^{-3} in the stoppered conical flasks. To this 0.20 g of the exchanger in nitrate form was added and flasks were shaken thoroughly in a temperature controlled shaker for 4 h at desired temperatures. Equilibrium was attained within this period and aliquots from supernatant solutions were analyzed for anions.

Experiments were also performed by equilibrating the exchanger in the particular anionic form with sodium nitrate solution at 30 °C.

Results and Discussion

The results of Table 1 show that for complete precipitation to occur, zirconium dichloride oxide to triethylamine ratio must be kept 1:2.

Anion Exchange Capacity. Anion exchange capacity of the exchanger is quite high. The capacity for dichromate, chromate, and sulfate is 3.20, 2.50, and 1.00 meq g^{-1}, respectively. A very high value of ion exchange capacity towards chromate ion (3.2 meq g^{-1}) is in accordance with the results of zirconia. The order for capacity for halides is $Cl^- > Br^- > I^-$. The capacity of the exchanger decreases as the ionic size of the halide increases and for some other ionic species the capacity decreases in the order $Cr_2O_7^{2-} > SO_4^{2-} > S_2O_3^{2-}$. Thus the exchanger behaves a chelating as well as an anion exchanger. On the basis of the above discussions it is concluded that zirconium-bis(triethylamine) shows anion exchange capacity due to the presence of $-N^+-$ group and chelating properties due to the presence of $-\underset{|}{\ddot{N}}-$ group.

Sorption Capacity. The sorption capacity of copper(II) was found to be 0.42 meq g^{-1} of zirconium-bis(triethylamine). When zirconium-bis(triethylamine) in H$^+$ form was kept in contact with a solution of sodium nitrate, no release of H$^+$ was observed. When exchanger was kept in Cu(II) solution it turned blue in appearance. Copper(II) ions were so strongly attached to zirconium-bis(triethylamine) exchanger that even strong chelating group EDTA did not completely detach copper(II) from the exchanger. Hence sorption capacity was calculated by column method. Due to this great affection of exchanger for metal ions like copper(II), K_d values were not calculated for the metal ions.

Composition. The results of composition studies show that zirconium and triethylamine are present in the molar ratio of 1:2 in the exchanger. Results show that the exchanger is quite stable in aqueous and basic media. The use of acidic solutions of greater concentrations must be avoided.

Effect of Heating. The results of effect of temperature on the capacity of the exchanger, show that the capacity decreases with the increase in temperature. At higher temperatures the water molecules and amine molecules are lost from the exchanger thereby decreasing the capacity. As a result the capacity at higher temperatures is much low. Loss in weight per gram of the exchanger at different temperatures shows that at 100 °C the weight loss is because of loss in water molecules and amine molecules upto 300 °C. Above 300 °C there is no appreciable weight loss since all the amine is lost. These results are in accordance with the results of capacity at different temperatures.

Structural Studies. It is quite clear that the exchanger, zirconium-bis(triethylamine), contains amino group and the metal oxygen bond. It confirms that in the formation of this type of exchanger the amine is incorporated with the metal oxide forming the matrix.

Potentiometric Titrations. pH titrations of the exchanger, zirconium-bis(triethylamine) were performed by shaking 0.50 g of the exchanger with solution of 0.10 mol dm^{-3} HCl and its salts of 0.01 mol dm^{-3} concentration by Topp and Pepper method. The volume of reaction mixture was kept 50 cm^3 in each case. The pH of the solution was noted after equilibration of the solution for 4 h. Results plotted in Fig. 2 show that the exchanger behaves as monofunctional anion exchanger.

Table 3. Quantitative Separations of Anions on Zirconium-Bis(triethylamine)

Sample No.	Mixture	Eluent	Eluate	Amount loaded	Amount found	Percent recovery
			ml	mg	mg	
1	Br^-	0.0001 mol dm^{-3} NaOH	90	2.640	2.480	93.93
	CrO_4^{2-}	0.1 mol dm^{-3} NaOH	120	11.078	10.846	97.90
2	I^-	0.001 mol dm^{-3} NaOH	90	2.667	2.603	97.60
	CrO_4^{2-}	0.1 mol dm^{-3} NaOH	100	11.078	10.904	98.42
3	Cl^-	0.001 mol dm^{-3} NaOH	120	2.023	1.917	94.76
	AsO_2^-	0.1 mol dm^{-3} NaOH	90	3.050	2.890	94.75
4	SCN^-	0.0001 mol dm^{-3} NaOH	120	3.509	3.422	97.52
	$Cr_2O_7^{2-}$	0.1 mol dm^{-3} NaOH	120	13.068	12.852	98.34

Distribution Studies. The distribution behavior of anions given in Table 2 indicates that the K_d values were high when deionized water was used as a medium. Distribution values were less when sodium hydroxide solution was used for studies. Distribution values decreased as the concentration of sodium hydroxide solution was increased. Being a weak anion exchanger, zirconium-bis(triethylamine) has a high affinity for hydroxide ions, hence anions other than hydroxide ion showed less uptake in the presence of hydroxide ions.

Separations. Separations of $Cr_2O_7^{2-}$ from Br^-, I^-; AsO_2^- from Cl^-; CrO_4^{2-} from I^-, Br^-; and $Cr_2O_7^{2-}$ from SCN^- were successfully achieved. The quantitative separations of anions on zirconium-bis-(triethylamine) exchanger given in Table 3, also show a high selectivity towards CrO_4^{2-} and $Cr_2O_7^{2-}$ as predicted by capacity.

The exchange isotherms for various anions at different temperatures are plotted in Figs. 3—7. From these results equivalent fractions of anions, selectivity coefficients and thermodynamic equilibrium constants can be evaluated.

The plot of $\ln K_c$ versus equivalent fraction of anion in exchanger phase are presented in Figs. 8—12.

The results of enthalpy change $\Delta H°$, free energy

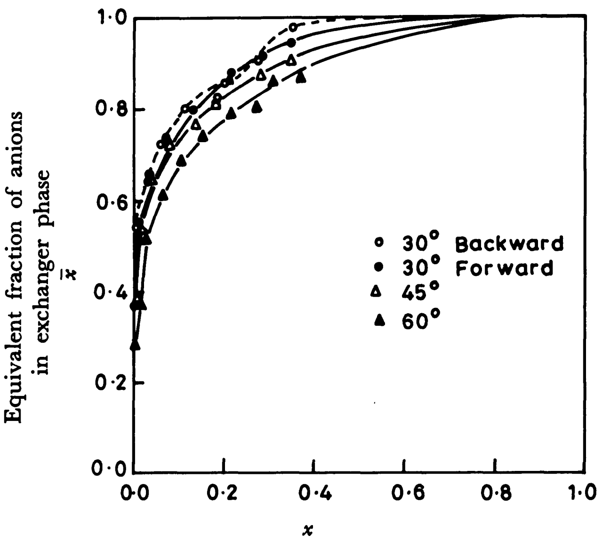

Fig. 3. Ion exchange isotherm of dichromate ions on zirconium-bis(triethylamine).

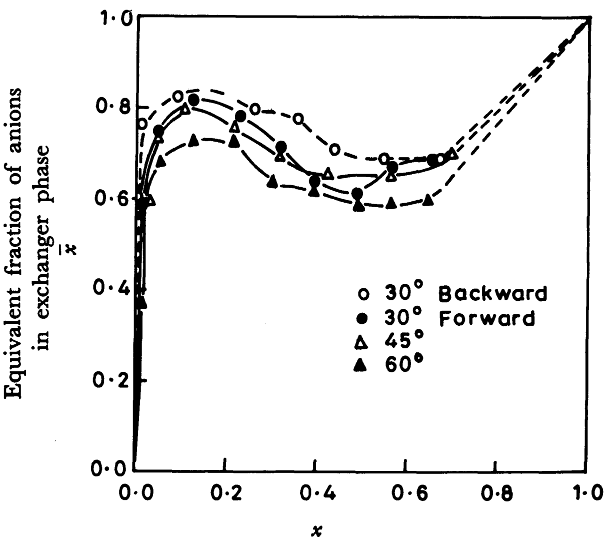

Fig. 5. Ion exchange isotherm of thiosulfate ions on zirconium-bis(triethylamine).

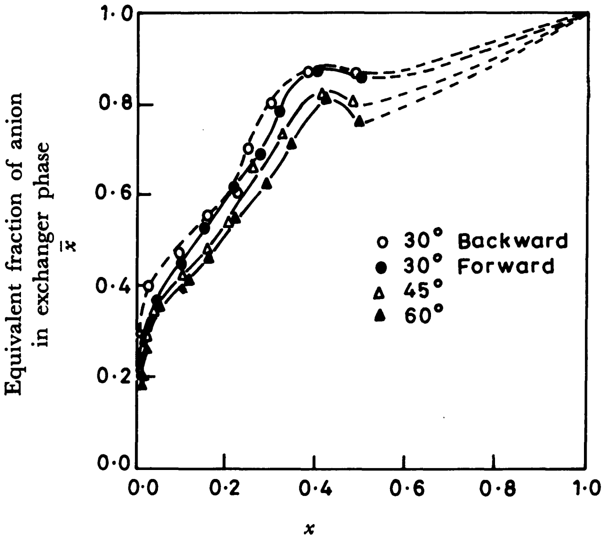

Fig. 4. Ion exchange isotherm of chromate ions on zirconium-bis(triethylamine).

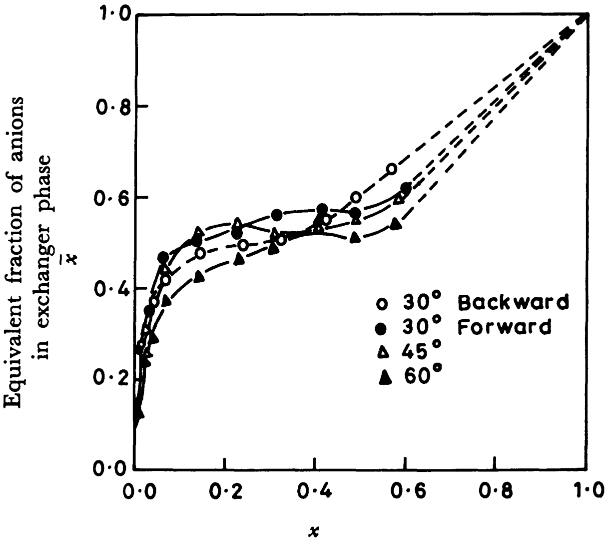

Fig. 6. Ion exchange isotherm of sulfate ions on zirconium-bis(triethylamine).

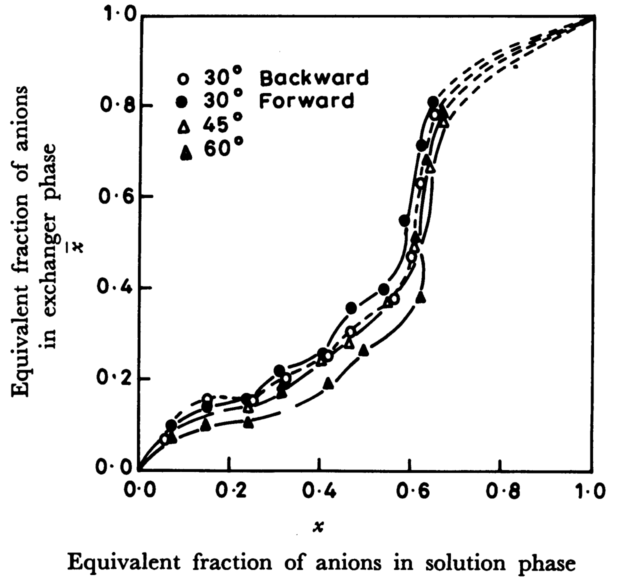

Fig. 7. Ion exchange isotherm of permanganate ions on zirconium–bis(triethylamine).

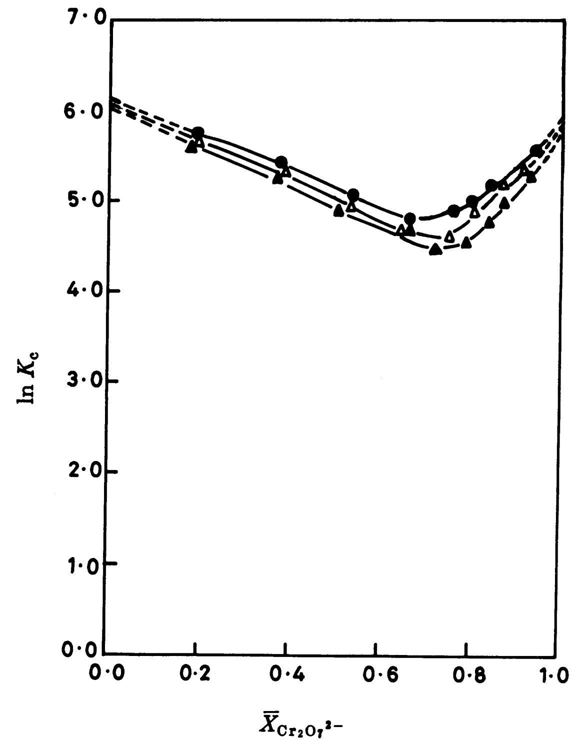

Fig. 8. Selectivity coefficients vs. equivalent fractions of $Cr_2O_7^{2-}$ in exchanger, phase.

change $\Delta G°$, and entropy change $\Delta S°$ were calculated and are reported in Table 4.

The ion exchange equilibria with certain ion exchangers, especially inorganic ion exchangers can be studied by the application of mass-action law modified in terms of activities. For the exchanger in nitrate form and solution having univalent counter ion A^- at equilibrium the exchange may be represented as:

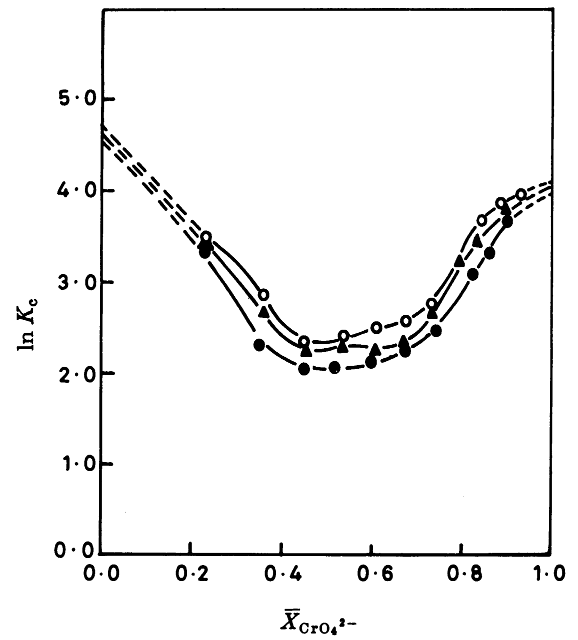

Fig. 9. Selectivity coefficients vs. equivalent fractions of CrO_4^{2-} in exchanger phase.

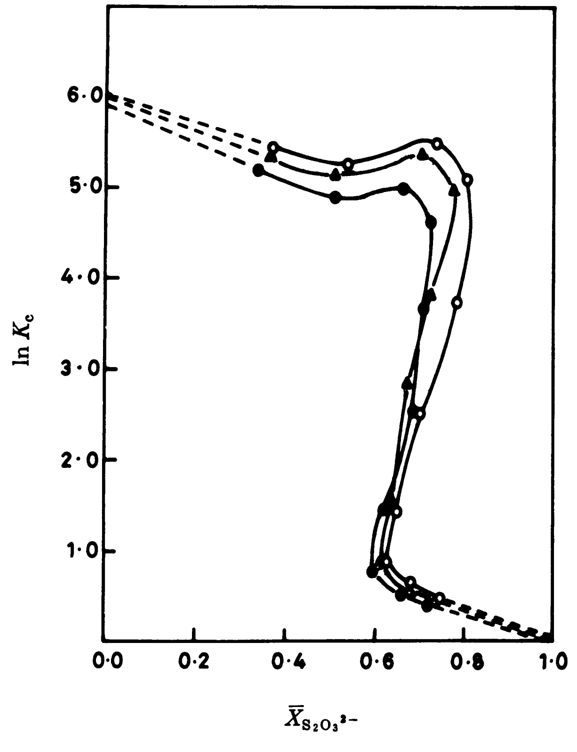

Fig. 10. Selectivity coefficients vs. equivalent fractions of $S_2O_3^{2-}$ in exchanger phase.

$$\overline{NO_3^-} + A^-_{(aq)} \rightleftharpoons \overline{A^-} + NO_3^-{}_{(aq)} \qquad (1)$$

and for bivalent counter ion

$$\overline{2NO_3^-} + A^{2-}_{(aq)} \rightleftharpoons \overline{A^{2-}} + 2NO_3^-{}_{(aq)} \qquad (2)$$

The thermodynamic equilibrium constant for the above reactions may be written for uni-univalent

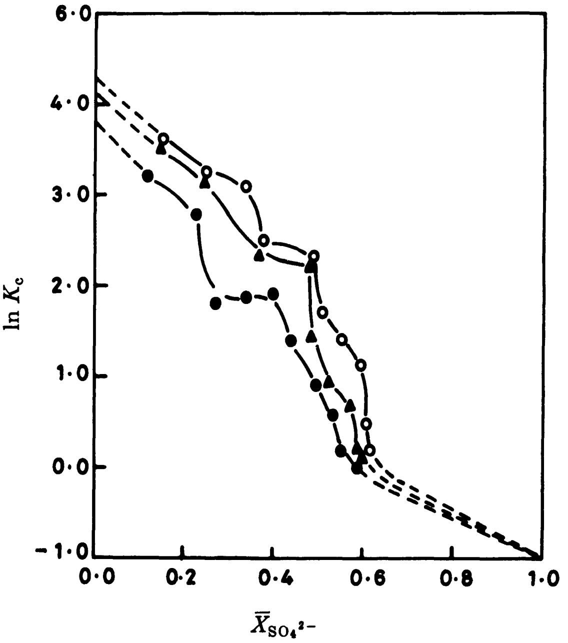

Fig. 11. Selectivity coefficients vs. equivalent fractions of SO_4^{2-} in exchanger phase.

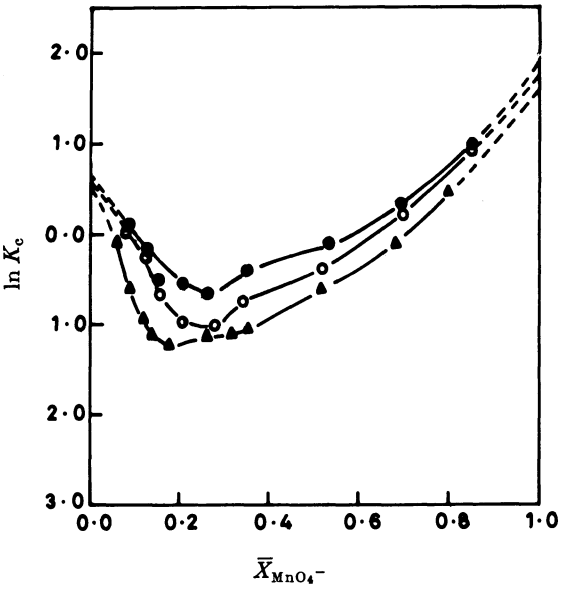

Fig. 12. Selectivity coefficients vs. equivalent fractions of MnO_4^- in exchanger phase.

exchange as:

$$K_a = \frac{\overline{a_{A^-}}a_{NO_3^-}}{\overline{a_{NO_3^-}}a_{A^-}} = \frac{[\overline{A^-}][NO_3^-]}{[\overline{NO_3^-}][A^-]} \times \frac{\gamma_{A^-}f_{NO_3^-}}{\gamma_{NO_3^-}f_{A^-}} \tag{3}$$

and uni-bivalent exchange as:

$$K_a = \frac{(\overline{a_{A^{2-}}})(a_{NO_3^-})^2}{(\overline{a_{NO_3^-}})^2(a_{A^{2-}})} = \frac{[\overline{A^{2-}}][NO_3^-]^2}{[\overline{NO_3^-}]^2[A^{2-}]} \times \frac{\gamma_{A^{2-}}f^2_{NO_3^-}}{\gamma^2_{NO_3^-}f_{A^{2-}}} \tag{4}$$

where γ represents activity coefficients in the exchanger phase and f the activity coefficient in the aqueous phase.

An examination of the ion exchange isotherms, Figs. 3—7, show that the isotherms are above the diagonal except for MnO_4^- indicating that bivalent anions are strongly preferred in comparison to nitrate by the zirconium-bis(triethylamine) exchanger. The

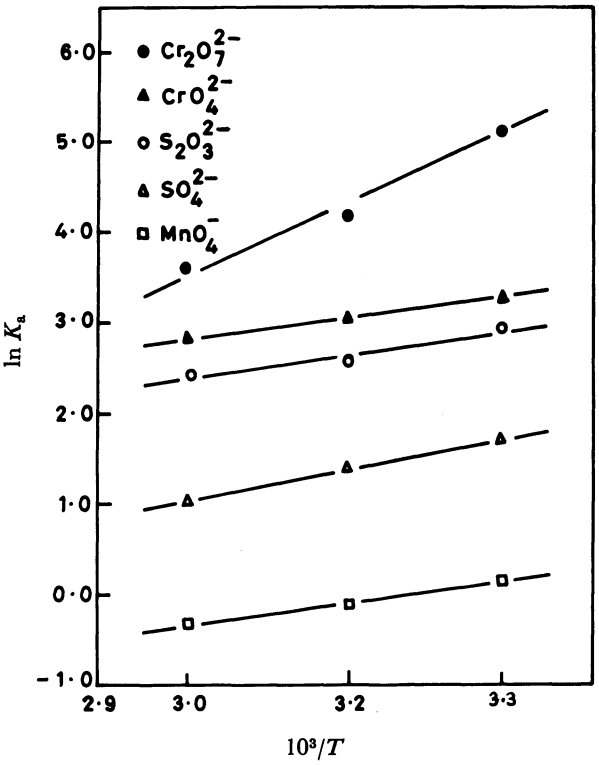

Fig. 13. Temperature dependece of the thermodynamic equilibrium constant.

Table 4. Thermodynamic Parameters on Zirconium-Bis(triethylamine) at Anionic Strength of 0.1 and Various Parameters

Anion	K_a			$\Delta G°$			$\Delta H°$/kJ equiv^{-1}	$\Delta S°$/J equiv^{-1} deg^{-1}
	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30—60 °C	30—60 °C
$Cr_2O_7^{2-}$	170.28	64.08	39.25	−12.94	−10.99	−10.16	−4.80	20.80
CrO_4^{2-}	26.31	21.04	17.68	−8.21	−8.06	−7.94	−1.33	21.23
$S_2O_3^{2-}$	19.21	13.88	11.19	−7.43	−6.95	−6.67	−1.50	17.40
SO_4^{2-}	5.59	4.16	2.73	−4.33	−3.75	−2.77	−1.92	5.41
MnO_4^-	1.18	0.89	0.74	−0.40	0.32	0.83	−1.39	−5.09

affinity for the anions decreases as the temperature increases. Figures 3—7 show that all the studied isotherms were reversible whereas the selectivity sequence was

$$Cr_2O_7{}^{2-} > CrO_4{}^{2-} > S_2O_3{}^{2-} > SO_4{}^{2-} > MnO_4{}^-$$

If K_c is the selectivity coefficient, then for univalent exchange

$$K_c = \frac{\overline{X}_{A^-} X_{NO_3^-}}{\overline{X}_{NO_3^-} X_{A^-}} \times \frac{f_{NO_3^-}}{f_{A^-}} \tag{5}$$

and for uni–bivalent exchange

$$K_c = \frac{\overline{X}_{A^{2-}} X^2_{NO_3^-}}{\overline{X^2_{NO_3^-}} X_{A^{2-}}} \times \frac{f^2_{NO_3^-}}{f_{A^{2-}}} \tag{6}$$

where $\overline{X_{NO_3^-}}$ and $\overline{X}_{A^-}$ are equivalent fractions of competing anions in exchanger phase, $X_{NO_3^-}$ and X_{A^-} the equivalent fractions of the nitrate and competing anion in solution phase respectively. $f_{NO_3^-}$ and f_{A^-}, the activity coefficients of nitrate and the competing anion, respectively in solution. The activity coefficients of the anions in solution phase were calculated using Debye–Hückel equation:

$$-\log f_i = \frac{Az_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} \tag{7}$$

where A and B are constants, a_i the ion size parameter, μ the ionic strength and z_i the charge of the ion i. The values of A and B at appropriate temperatures are taken from the table given earlier.

The results of the selectivity coefficients indicate that as the temperature increases the value of the selectivity coefficient decreases. The results plotted (Figs. 8—12) reveal that the selectivity coefficient K_c does not remain constant at all with the varying concentrations of anions in solution and therefore K_a should be calculated.

K_a, The thermodynamic equilibrium constant can be obtained according to Gaines and Thomas, from the equation:

$$\ln K_a = (Z_{X^-} - Z_{NO_3^-}) + \int_0^i \ln K_c \mathrm{d}\, \overline{X}_{A^-} \tag{8}$$

The values of thermodynamic equilibrium constant are calculated by integration under the curves of Figs. 8—12 applying Eq. 8. Variation of $\ln K_c$ with loading, X, is given in Figs. 8—12. The values of the changes in thermodynamic quantities are calculated from the respective thermodynamic equilibrium constants as follows:

$$\Delta G^\circ = -RT \ln K_a \tag{9}$$

$$\Delta H^\circ = -R\frac{\mathrm{d}(\ln K_a)}{\mathrm{d}(1/T)} \tag{10}$$

and $$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \tag{11}$$

ΔH° is obtained from Fig. 13 (expressing the variation of $\ln K_a$ with $1/T$). The results indicate that during the exchange of anions over zirconium-bis-(triethylamine) in nitrate form, the free energy change is negative in all cases except for MnO_4^- at higher temperatures. It reveals that for bivalent anions the exchange process is spontaneous and is in accordance with, mainly, on charge relations. However, for univalent anion exchange with MnO_4^- the charge being same it may depend on other factors.

The results (Table 4) giving enthalpy change in all the exchange reactions indicate that process is exothermic, i.e. the binding energy of one competing anion is lower than the two anions of nitrate. Thus nitrate ion is less tightly bound to the zirconium–bis-(triethylamine) matrix than any of the other anions studied except MnO_4^-.

The results of enthalpy changes given in Table 4 indicate that during the forward reaction the competing anionic species are more orderly arranged than that of nitrate form of zirconium–bis(triethylamine).

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