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Studies on the Rates of Exchange of Hg(II), Cd(II), La(III) and Ce(III) ions in Sodium Nitrite-Aqueous Acetone Media Using an Anion-Exchanger Dowex-1 × 8(NO_3^-)

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Rate of exchange has been studied on Hg(II), Cd(II), La(III) and Ce(III) ions in sodium nitrite-aqueous acetone media using an anion exchanger Dowex-1 × 8(NO_3^-). Acetone was used to provide solvent media of 10%, 30% and 50% and temperature was used in rate studies, carried out at 30°, 40°, 50°C. Always 1 g. of Dowex-1 × 8 in nitrate form was used for distribution studies to get rate data. After suitable time intervals aliquots (1 mL) were withdrawn and metal ion concentration was found out.

INTRODUCTION

Rates of ion exchange reaction have been considered from the earliest base exchange studies of Way[1] when columns of soil were used. Wiegner[2] studied the rates of exchange in silicious exchangers and pointed out the dependence of such rates on the location of ionogenic groups inside the exchangers. He found out the rates to be faster in kaolinite than in chabozite. Samuelson[3] find out that equilibrium in a swollen polystyrene sulphonic acid type resin is attained in one minute. But when a sulphonated phenol formaldehyde resin is used, it takes about 90 min to attain equilibrium. Highly cross-linked resins were shown to be slower in exchange than those of low cross linking.[4]

Several workers[5, 6] have shown the fastness of rates of exchange in sulphonic acid type exchangers. The carboxylic type resins[7, 8] have been found to be very slow in this respect. Kunin and Barry[7] have shown that equilibrium in carboxylic type of resin is attained in about a week's time. But comparatively metal-metal exchange in aqueous solution is 5000 times as rapid as the hydrogen metal exchange in amberlite IRC-50 (a weakly acidic resin). Adamson *et al.* [9] have also reported low solid-diffusion rates for H^+ metal exchange. A decrease in rate of ionic uptake with increasing charge and volume of the ion has also been shown.[10]

In dry acetone, Vermeulen and Huffman[11] have shown the rates to be 1/2800 times slower than those in water. Similarly rates in benzene wet resin were 1/1000 times slower than in water wet resin. However, the rates in mixed solvents were shown to be in between the rates in pure non-aqueous solvents and those in water.

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The reason that may be attributed to slow rates in non-aqueous solvents is a slight swelling of the exchanger in such solvents.

Shukla and Bhatnagar[12] have studied the rates of Cu^{2+} exchange in anhydrous ethanol using vacuum dried H-form of the resin. The rates were found to be slower in such resin than in water-wet resin. The rates increased by increasing the water content of the non-aqueous system.[13]

EXPERIMENTAL

Metal Ion Solutions: All metal ion solutions were prepared from their AR nitrates to give 0.2 N stock solution.

Metal Ion Titrant: Disodium EDTA solution (0.025 N) was used as titre, for complexometric titration of Cd(II), La(III) and Ce(III). Hg(II) was estimated with ammonium thiocyanate.

Indicators: The metal indicators used in complexometric titration were bromopyrogallol red (for La and Ce), pyrocatechol violet (for Cd) and for Hg(II) estimation with ammonium thiocyanate-ferric nitrate solution was used as an indicator.

All rate studies, together with the effect of temperature, on exchange rates were performed with batch technique. Erlenmayer corning glass flasks with airtight stoppers (capacity 250 mL) were used to prepare each batch for rate study. A thermostatic bath (± 0.1°C) of usual type was used for maintaining the flasks at desired temperature from to time to time to provide complete equilibrium.

Procedure

The metal ion-sodium nitrite-aqueous acetone systems were prepared by mixing different stock solutions to provide 0.1 N concentration for metal ion and 1.5 N concentration of sodium nitrite in each batch of 50 mL. Acetone and distilled water were added to provide the required acetone concentrations in such solutions. Exactly 1 g of resin was added to each flask and stirring was continued by using a magnetic stirrer. After suitable time intervals the stirring was stopped momentarily and aliquot (1 mL) were withdrawn from these flasks and metal ion concentration in them was found out titrimetrically. Such rate studies were carried for a period exceeding *ca.* 5 h. The final equilibrium reading, *i. e.*, for infinite time, was taken after 24 h.

RESULTS AND DISCUSSION

The results of rate studies shown as fractional equilibrium attained $D(t)/D(\infty)$ in Table-1 show that Hg(II) complex exchange takes much more time to attain final equilibrium than ions like La(III) or Ce(III). But it is less than that required by Cd(II) complex. The time required for attaining final equilibrium (t_{eq}) for Hg(II) is *ca.* 65 min at 30°C at 10% acetone concentration. But similar time (t_{eq}) for Cd(II) at 30°C and in solutions containing 10% acetone is 2 h. Both ions give comparatively stabler complexes with nitrate ion, but the difference in t_{eq} must be due to the rates of formation of complexes.

TABLE-1

TIME OF ATTAINING COMPLETE EQUILIBRIUM FOR Hg^{2+}, Cd^{2+}, La^{3+} and Ce^{3+}/NO_3^- AT DIFFERENT TEMPERATURE

Ions	Temp. (°C)	Solvent percentage %					
		10		30		50	
		t_{eq}	$t_{1/2}$	t_{eq}	$t_{1/2}$	t_{eq}	$t_{1/2}$
Hg(II)	30	65	04	75	04	120	04
	40	75	02	105	02	125	02
	50	135	02	135	02	135	02
Cd(II)	30	120	12	135	15	155	20
	40	110	15	115	15	135	15
	50	90	04	120	15	135	08
La(III)	30	35	04	25	04	20	04
	40	90	06	55	06	45	06
	50	90	08	90	06	90	06
Ce(III)	30	30	06	20	05	15	03
	40	75	04	35	04	25	04
	50	75	04	55	04	45	04

Now with increasing temperature from 30° to 40° or 50°C, the time for complete equilibrium attainment for exchange increased for Hg(II) but decreased for Cd(II). The decrease of t_{eq} for Cd(II) is indicative of the fact that the formation of complex is favoured in this case. But for Hg(II) it appears that stability of the complex Hg(II) species is hindered by it. Thus temperature increase can do both the things. It can influence the complex equilibrium in solution and can also influence the complex stability.

There is yet another value for ($t_{1/2}$) evaluated from these studies. This time for attainment of half equilibrium is indicative of the fact that the initial complex formed in solution phase is quickly exchanged on an exchanger. Hence, as far as rates of pure exchange are concerned, their comparative assessment can be done only by comparing $t_{1/2}$ values. The $t_{1/2}$ for Hg(II) complex at 30°C in 10% aqueous acetone is only *ca.* 4 minutes, while it is *ca.* 12 minutes for Cd(II) complex. Thus the rates of exchange for Hg(II) complex are faster than those for Cd(II) complex.

These studies when carried out in the solutions having higher acetone percentages (*i.e.*, 30 to 50% v/v) show that time for complete equilibrium exchange is more in solutions of higher acetone content. The rates of ion exchange in mixed organic solvents are generally slower than in aqueous media. Thus more the organic solvent in aqueous mixed media, more will be the time required to attain exchange equilibrium.

It is clear that $t_{1/2}$ does not change appreciably for Hg(II) exchange. The weaker complexes are stabilized in solvents of low dielectric constant.[14, 15] But when a complex is already a very stable species, it only increase its stability to a further degree. Since Hg(II) and Cd(II) complexes are sufficiently stable, there was no improvement in their $t_{1/2}$ values by increasing acetone concentration in the outside solution phase.

In the case of La(III) and Ce(III) exchange when studied for their rates in terms of $D(t)/D(\infty)$ data, it was observed that their exchange equilibrium times were much less than observed for Hg(II) and Cd(II). Because of these ions form complexes of a weaker nature amd hence form more quickly. (Therefore labile in character). The labile complexes have been shown to be formed by ions such as Co(II), Mn(II), Zn(II) or Cu(II), which give outer orbital complexes of the unstable type linking these general observations one can say that La(III) and Ce(III) get exchanged on an anion exchanger in nitrate complexing media on account of probably weaker outer orbital complex formations. The rate of their formation in solution phase are thus comparatively faster and therefore their exchange equilibrium is attained quickly as compared to Hg(II) complex exchange. Increase in temperature, increases t_{eq} in both these cases showing that increse in temperature doesn't favour complex formation. Similarly increasing acetone percentage in mixed aqueous solutions doesn't favour complex formation here. It appears to be more due to decreasing solubilities of the electrolytes used in these cases.

The data variation for t_{eq} and $t_{1/2}$ can be explained on account of the two competitive equilibria at work in such systems. The ion exchange equilibrium in such cases is more dependent on the complex equilibria rather than anything else. In such cases where complexing agent is present in the solution phase, it is the natural ligand interaction and its consequences which are important rate deciding factors rather than diffusional exchange process.

Hence, the present rate studies have been useful in classifying the effect of complexing agents on the overall rates of exchange of metal ions on an anion exchanger. The final equilibrium time data procured from these studies has another important use and that is in separation studies. In planning separations it is essential to obtain the complexed species to their highest extent in solution. Therefore, they are sorbed on an anion exchanger. Hence unless we have a comprehensive knowledge of t_{eq} or $t_{1/2}$ it is difficult to ascertain the complete formation of complexed species. With t_{eq} and $t_{1/2}$ data with us we can provide full time for the attainment of such equilibrums condition before starting the exchange steps.

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