

# Particle Diffusion Controlled Kinetics of $\text{Li}^+/\text{H}^+$ , $\text{Na}^+/\text{H}^+$ & $\text{K}^+/\text{H}^+$ Exchanges on Dowex 50W $\times$ 8 in Acetone-Water Mixtures

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The kinetic behaviour of  $\text{Li}^+/\text{H}^+$ ,  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchanges on Dowex 50W $\times$ 8 resin has been investigated in aqueous and 20.9 and 44.2% (w/w) acetone-water mixtures. Interionic diffusion coefficients ( $\bar{D}$ ) in the resin phase have been computed for the various exchanges and media.  $\text{K}^+/\text{H}^+$  exchanges are the fastest and  $\text{Li}^+/\text{H}^+$  the slowest in the water-acetone mixtures as observed earlier in aqueous medium. However, on adding acetone to the extent of 44.2%,  $\bar{D}$  values decrease by 33% for  $\text{Li}^+/\text{H}^+$  and by 20% for  $\text{Na}^+/\text{H}^+$ ,  $\text{K}^+/\text{H}^+$  exchanges. A comparison of  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchanges in acetone-water with our earlier data on these exchanges in methanol-water mixtures shows that the rates are in general higher in acetone-water. The analysis of these results suggests that the viscosities of these mixtures may play an important role in these systems. Other possible factors influencing the rates have also been identified.

**K**INETIC behaviour of  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchange systems on Dowex 50W $\times$ 8 resin under particle diffusion conditions in aqueous methanol solutions has been reported recently<sup>1</sup>. In the present paper we are reporting kinetic data on  $\text{Li}^+/\text{H}^+$ ,  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchanges on Dowex 50W $\times$ 8 in aqueous, 20.9 and 44.2% (w/w) acetone-water mixtures.

## Materials and Methods

Experiments were conducted at  $25 \pm 1^\circ$  under infinite bath conditions<sup>1-3</sup>. Intraparticle diffusion conditions were ensured by using electrolyte solutions (chlorides of lithium, sodium and potassium) of 0.11M concentration. The experimental and analytical procedures were the same as described

earlier<sup>1</sup>. The bead radii measured by Kressman and Kitchener's method<sup>4</sup> are given in Table 1. The kinetic data for these exchanges could not, however, be obtained for solvent mixtures containing greater amounts of acetone ( $\sim 70\%$ ) mainly due to the cracking of beads. Besides, evaporational losses due to stirring the cage<sup>1</sup> in those solutions were also significant.

Experiments were also conducted to ascertain the composition of the solvent inside the  $\text{H}^+$  resin in equilibrium with 20.9 and 44.2% acetone-water. Procedure was the same as employed in the case of study using MeOH-water mixtures<sup>5</sup>. Analysis of acetone was performed by the salicylaldehyde method<sup>6</sup>. Average composition obtained from two sets gave 19.9% and 39.6% acetone in the pore solvent of  $\text{H}^+$ -form of resin.

TABLE 1 — BEAD RADII ( $r$ ), DIFFUSION COEFFICIENTS ( $\bar{D}$ ) AND HALF EXCHANGE TIME ( $t_{1/2}$ ) IN AQ. ACETONE AND AQ. METHANOL SYSTEMS

Wt % organic solvent ( $\pm 0.1\%$ )	Acetone-water systems				Methanol-water systems			
	$r$ ( $\mu$ )	$t_{1/2}$ (sec)	$\bar{D} \times 10^6$ ( $\text{cm}^2/\text{sec}$ )	Viscosity (millipoise)	$r$ ( $\mu$ )	$t_{1/2}$ (sec)	$\bar{D} \times 10^6$ ( $\text{cm}^2/\text{sec}$ )	Viscosity (millipoise)
<b>Li<sup>+</sup>/H<sup>+</sup> EXCHANGE SYSTEM</b>								
0.0	359	25.0	2.14	8.95	—	—	—	8.95
20.9	356	32.0	1.67	10.70	—	—	—	14.10
44.2	355	37.0	1.46	10.00	—	—	—	15.75
<b>Na<sup>+</sup>/H<sup>+</sup> EXCHANGE SYSTEM</b>								
0.0	359	16.5	3.34	8.95	517	25	3.44	8.95
20.9	356	18.5	3.08	10.70	516	34	3.00	14.10
44.2	355	21.0	2.68	10.00	513.5	38	2.43	15.75
<b>K<sup>+</sup>/H<sup>+</sup> EXCHANGE SYSTEM</b>								
0.0	368	7.0	6.22	8.95	517	17	6.14	8.95
20.9	367	10.0	5.46	10.70	516	22	4.81	14.10
44.2	365	12.0	4.91	10.00	513.5	27	3.14	15.75

**Results and Discussion**

$F(t)$  [fractional attainment of the equilibrium exchange] vs  $t$  (sec) plots for aqueous (20.9 and 44.2%) acetone media for  $\text{Li}^+/\text{H}^+$ ,  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchanges have been shown in Fig. 1. Half exchange time ( $t_{1/2}$ ) values for the various systems, listed in Table 1, clearly indicate the rate sequence as  $\text{K}^+/\text{H}^+ > \text{Na}^+/\text{H}^+ > \text{Li}^+/\text{H}^+$  in any solvent medium. Further, increased acetone content reduces rates for a particular exchange and this effect is most pronounced in the  $\text{Li}^+/\text{H}^+$  systems.

For computing the values of diffusion coefficient ( $\bar{D}$ ) in the resin phase<sup>2,3</sup> for these systems,  $Bt$  vs  $t$  plots were constructed using Reichenberg's table<sup>7</sup>. Slight deviations were observed from a linear behaviour but the best linear fits drawn gave averaged behaviour needed for the purpose. Slopes of the linear plots ( $B$ ) for the various systems yielded  $\bar{D}$  values from the following relation<sup>3,7</sup>:

$$B = \frac{\bar{D}\pi^2}{r^2}$$

$r$  being the bead radius in a particular medium.  $\bar{D}$  values thus obtained are given in Table 1. The average experimental accuracy in these  $\bar{D}$  values is expected to be of the order of  $\pm 3-4\%$ .

Present  $\bar{D}$  values (Table 1) clearly show that  $\text{K}^+/\text{H}^+$  exchanges in acetone-water systems are the fastest, and  $\text{Li}^+/\text{H}^+$  the slowest among the three systems,  $\text{Na}^+/\text{H}^+$  being intermediate but closer to  $\text{Li}^+/\text{H}^+$  system. An addition of 44.2% acetone decreases  $\bar{D}$  values of  $\text{Li}^+/\text{H}^+$  exchange in aqueous medium by 33% while  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchanges are affected only to the extent of 20%. However, it is clear that these exchanges remain still quite fast even after the addition of 44.2% acetone.

$\bar{D}$  values calculated from our earlier data on  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchanges in 0.0, 20.8% and 44.1% (w/w) methanol-water media are included in Table 1 for a comparison. The  $\bar{D}$  values for  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchanges in water (present study) agree well with those given earlier<sup>1</sup> wherein a bead radius of 517  $\mu$  was employed showing that  $\bar{D}$  values

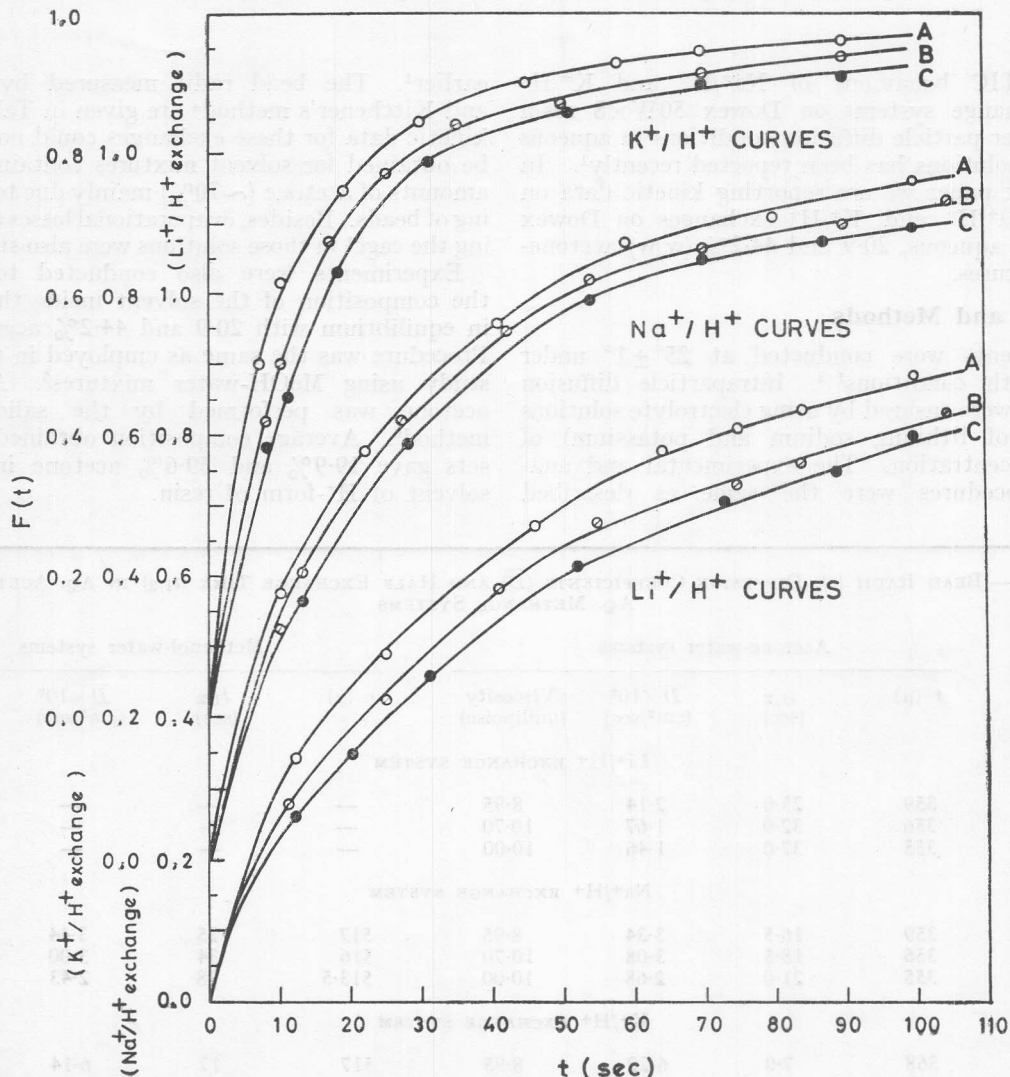


Fig. 1 —  $F(t)$  (fractional attainment of the equilibrium exchange) vs  $t$  plots for  $\text{Li}^+/\text{H}^+$ ,  $\text{Na}^+/\text{H}^+$  and  $\text{K}^+/\text{H}^+$  exchanges in aqueous acetone media [A, 0% acetone; B, 20.9% acetone; C, 44.2% acetone]

remain independent of  $r$ . This confirms that the conditions of solution concentration, etc., in the present study refer to intraparticle diffusion as desired.  $\bar{D}$  values for Na<sup>+</sup>/H<sup>+</sup> exchange for the 20.9% acetone-water and methanol-water media again agree well but the value in 44.2% aq. acetone is somewhat higher as compared to corresponding methanol-water system. On the other hand,  $\bar{D}$  values for K<sup>+</sup>/H<sup>+</sup> exchange are significantly higher in acetone-water media and the difference increases with the increase in acetone content.

The various possible factors contributing to these observations are (i) the swelling and solvent fractionation behaviour of the H<sup>+</sup> as well as metal forms of Dowex 50W×8 in the various mixed media, (ii) the solvated size of ions in these media, (iii) selectivities of the resin for various ions in various media, and (iv) the viscosities of the solvent mixtures and electrolyte solutions in these solvent mixtures. Swelling and solvent fractionation data on H<sup>+</sup>-form of resin in the present acetone-water media and the methanol-water mixtures are very similar. Presumably, other ionic forms of this resin also may not reflect any differences in their swelling and solvent fractionation characteristics.

The solvated sizes of these ions are governed by the over all solvation of the ions in the specific solvent medium. In mixed solvents, cations are, usually, preferentially solvated by water—the extent to which the organic solvent is excluded from the solvation shell depends upon the ability of the organic solvent to solvate the cation. In this context, a recent study by Zipp<sup>8</sup> shows that these alkali metal cations are solvated almost equally by both methanol and acetone. This similarity in the solvating tendency of these organic solvents for alkali metal cations implies that the cations in aqueous methanol or aqueous acetone solvents would have a solvation shell consisting of water molecules and, more or less, the same number of organic solvent molecules, depending upon the composition of the mixed solvent. Therefore, one could expect that the sizes of solvated cations in aqueous acetone or aqueous methanol solutions, containing the same amounts of the organic component, would be similar. This has been supported by Amis and Hinton<sup>9</sup> in a recent analysis of the conductivity data of potassium chloride in methanol-water and acetone-water systems. They have shown that the solvated radii of the ions in these mixed solvents, up to about 45% by weight organic solvent, remain nearly constant.

In the mixed solvent systems, ionic selectivities of the resins have also been considered as a factor influencing the rates<sup>10</sup>. These selectivities for the exchanges involved here are not very different for methanol-water and acetone-water mixtures employed in the present study<sup>11</sup>.

The viscosities of the electrolyte solutions in these solvent media are generally not available in the literature. However, the viscosities of mixed solvents themselves, may give an indication of the general variations of the viscosities of these solutions. Hence, the viscosities of the various solvent media have been taken from the literature<sup>12,13</sup> and included in Table 1. It can be seen that the viscosities of the water-acetone as well as water-methanol mixtures are significantly higher than that of water and seem to be responsible for the lowering of rates in these media as compared to aqueous medium. Further, the viscosities of methanol-water mixtures are higher than those of acetone-water mixtures. Thus, observed differences in  $\bar{D}$  values for Na<sup>+</sup>/H<sup>+</sup> and K<sup>+</sup>/H<sup>+</sup> exchanges in acetone-water and methanol-water mixtures could arise due to the viscosity differences. The variations of  $\bar{D}$  for the same exchange (Na<sup>+</sup>/H<sup>+</sup> or K<sup>+</sup>/H<sup>+</sup>) in acetone-water mixtures, as a function of per cent organic solvent, does not correlate with the viscosity variations. This again emphasizes that all the factors mentioned above should be taken into consideration. A complete understanding of the kinetics of ion exchange in mixed solvents would require information on all these points. In the absence of any experimental data on these lines, it is not possible to do so at the present.

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