

The integration constants  $M$  and  $N$  are evaluated from the initial and boundary conditions (iv)-(vii). Laplace transforms of conditions (iv)-(vii) are

$$\left. \begin{aligned} \bar{\Psi}(x, 0) = C^0/S; \bar{\Psi}(\infty, t) = C^0/S \\ \bar{C}_R(x, 0) = 0; \bar{C}_R(\infty, t) = 0 \end{aligned} \right\} \dots(\text{iva})$$

$$\left. \frac{d\bar{\Psi}(x, S)}{dx} \right|_{x=0} = 0 \dots(\text{va})$$

$$\left. \frac{d\bar{C}_R(x, S)}{dx} \right|_{x=0} = -\frac{\theta}{nFAD S^2} \text{ (ramp current) } \dots(\text{via})$$

$$\left. \frac{d\bar{C}_R(x, S)}{dx} \right|_{x=0} = -\frac{1}{nFAD} \left\{ \frac{\theta}{S} + \frac{B\omega}{\omega^2 + S^2} \right\} \text{ (ac chronopotentiometry) } \dots(\text{viia})$$

Differentiation of Eqs. (8) and (9) with respect to  $x$  under conditions (iva)-(viia) leads to the values  $M$  and  $N$

$$M = 0$$

$$N = \frac{\theta}{nFAD^{\frac{1}{2}} S^2 (S + k_f C_0^{\frac{1}{2}})^{\frac{1}{2}}}$$

and

$$N = \frac{1}{nFAD^{\frac{1}{2}} (S + k_f C_0^{\frac{1}{2}})^{\frac{1}{2}}} \left( \frac{\theta}{S} + \frac{B\omega}{\omega^2 + S^2} \right)$$

for ramp and ac chronopotentiometry respectively. Inverse transform of Eq. (12) is available in standard tables; that for Eqs. (13) and (20) are evaluated by convolution.

The authors thank the UGC, New Delhi, for sponsorship of the research project "Thermodynamics and electrochemistry of molten salts", and the Centre of Advanced Study in Chemistry (University of Delhi) for the award of a junior research fellowship (to R.K.J.).

#### Nomenclature

- A = area of the electrode  
 B = amplitude of ac. of frequency  $\omega$   
 $C_i(x, t)$  = concentration of the species  $i$  at a distance  $x$  from the electrode surface at a time  $t$  after the start of electrolysis  
 $C_i^0$  = initial concentration of  $i$  species  
 $D_O, D_R$  = diffusion coefficient of  $O$  and  $R$  respectively  
 $erf$  = the error function defined as  
 $erf(\lambda) = 2/\pi \int_0^\lambda \exp(-Z^2) dZ$   
 $\theta$  = magnitude of impulse current  
 $t$  = time of electrolysis  
 $k_f, k_b$  = the formal rate constants for the forward and backward processes respectively

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## Ion Adsorption Properties of Molybdenum Ferrocyanide, Tungsten Ferrocyanide & Multiloaded Molybdenum Ferrocyanide-Dowex Exchangers

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Received 22 August 1975; accepted 17 February 1976

Adsorption of alkali, alkaline earth metal ions and some di-, ter and tetravalent cations on ferrocyanide molybdate (FeMo), ferrocyanide tungstate (FeW) and Dowex-1 loaded with FeMo has been studied. Adsorption decreases with increase in the hydrated radii of the alkali ions. FeMo loaded on Dowex-1 has lower adsorption capacity as compared to unsupported FeMo.

SINCE the revival of interest in the field of inorganic ion exchangers<sup>1</sup>, considerable work has appeared in the literature<sup>2</sup> on the ion exchange properties of inorganic ferrocyanide compounds. In a search for an inorganic ion exchanger for the removal of Cs and Sr, Baetsle and coworkers synthesized molybdenum ferrocyanide or ferrocyanide molybdate<sup>3</sup> (FeMo) and the more acid-resistant ferrocyanide tungstate<sup>4,5</sup> (FeW). Krtil prepared tungsten ferrocyanide and studied its ion exchange properties<sup>6</sup>. Watari and coworkers have done considerable amount of work on inorganic ion exchangers loaded on organic resins (multi-loaded metal salt ion exchangers) and have studied the behaviour of copper, iron, nickel ferrocyanides<sup>7,8</sup>. In the present investigation ion adsorption properties of FeMo and FeW and resins loaded with FeMo were studied.

**Ferrocyanide molybdate (FeMo)** — Ferrocyanic acid was prepared by passing a known concentration of potassium ferrocyanide through Dowex-50 in the H<sup>+</sup>-form. To this solution requisite amount of sodium molybdate was added to get a Mo/Fe ratio of 2, 3 and 4, and the pH of the mixture adjusted to 3 and was allowed to stand for 6 hr. The FeMo gel was washed with 0.1M HCl, decanted and later filtered and dried at 50°. It was then treated with 1M HCl, filtered and dried.

**Ferrocyanide tungstate (FeW)** — It was prepared by adding requisite amount of sodium tungstate to ferrocyanic acid so as to get a W/Fe ratio of 3. The final pH was adjusted to 1 and the whole mixture allowed to stand for 24 hr. The gel was washed with 1M HCl, filtered and dried at 70°.

**Multiloaded exchanger: FeMo-Dowex 1** — Dowex 1 (50-100 mesh) was equilibrated with potassium ferrocyanide and was washed with water. It was then equilibrated with necessary amount of sodium molybdate (to give Mo/Fe ratio = 3) and washed with water. This cycle of loading with FeMo was repeated five times. It was later washed and dried.

**Characterization of FeMo and FeW by Mössbauer spectroscopy** — Matas and Zemick<sup>9</sup> had studied a series of ferro- and ferricyanides. In the case of ferrocyanides, chemical shift was found to decrease

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with the increase of electronegativity of the cation. They did not, however, study the ferrocyanides of the type FeMo and FeW. It was considered appropriate to characterize the above preparations by Mössbauer spectroscopy.

Mössbauer spectra were recorded at 298° and 78°K with a constant velocity spectrometer using a 2 millicurie <sup>57</sup>Co(Cr) source. FeMo and FeW were pelletized and mounted on a glass cryostat for low temperature work. The experimental data are given in Table 1. The spectra showed no quadrupole splitting indicating that in both FeMo and FeW preparations, the ferrocyanide ion (or a part thereof) did not oxidize to ferricyanide. Apart from slightly lower chemical shift values (as compared to potassium ferrocyanide), there was no other change. The structure of FeMo consists of protonated ferrocyanide and protonated molybdenyl sheets arranged in parallel and the protons associated with them are exchangeable<sup>10</sup>. Since Mo and W are structurally part of oxygenated anions and H<sup>+</sup> being the cation, one should consider only the difference in electro-

negativity between K<sup>+</sup> and H<sup>+</sup>. On this basis the decrease in chemical shift is quite understandable.

*Adsorption experiments: As a function of time* — Experiments were performed with 0.5 g of the exchanger and 25 ml of the solution of the particular cation of known concentration. The cations were suitably labelled with active isotopes [<sup>24</sup>Na, <sup>41</sup>K, <sup>137</sup>Cs, <sup>45</sup>Ca, <sup>140</sup>Ba, <sup>60</sup>Co, <sup>51</sup>Cr, <sup>147</sup>Nd, <sup>152+154</sup>Ru, <sup>144</sup>Ce were used]. After equilibrating for a known period of time, each mixture was filtered and 2 ml of the filtrate counted in a scintillation counter and was compared against the blank. <sup>45</sup>Ca was counted in a GM counter. Tables 2, 3 and 4 show the results of such experiments.

*As a function of solution pH* — Experiments were carried out with 0.5 g of the exchanger and 25 ml of the solution of a particular cation, which has been preadjusted to a known pH. The capacities for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Co<sup>2+</sup> and Nd<sup>3+</sup> ions were determined by measuring the change in the [H<sup>+</sup>]. The capacities for Mg<sup>2+</sup> and Ca<sup>2+</sup> were determined by directly measuring the concentration of the ions before and after the equilibration, using EDTA, Table 5 lists the results of such experiments.

The most stable product of FeMo is the one with Mo/Fe ratio between 2 and 3. FeMo dissolves slowly at pH 3 and completely above pH 7. The capacity of FeMo increases with increase in the Mo/Fe ratio from 2 to 4 and also when pH is increased from 2 to 6 (Table 5). Capacity values are lower when calculated on the basis of H<sup>+</sup> ion release as compared to direct measurements (Tables 2 and 5). This could be due to the practical difficulty in measuring accurately the small change in (H<sup>+</sup>). But these values, no doubt, throw light on the general trend in the adsorption of alkali metal ions. Taking

TABLE 1 — MOSSBAUER SPECTRA OF FERROCYANIDE MÖLYBDATE (FeMo) AND FERROCYANIDE TUNGSTATE (FeW)

Compound	Temp. °K	Absorption %	Line width (mm/sec)	Chemical shift (mm/sec)
Potassium ferrocyanide	298	40	0.34	0.10
FeMo	298	6	0.66	0.04
	78	7	0.72	0.05
FeW	298	4	0.70	0.05
	78	5	0.68	0.06

TABLE 2 — ADSORPTION OF CATIONS ON FeMo AS A FUNCTION OF TIME

[Cation conc. = 1M]

Cation	Mo/Fe	pH of the soln	Capacity (meq/g) after equilibration for (hr)							
			1	2	3	4	5	6	7	8
Na <sup>+</sup>	3	5.7	0.69	0.74	0.84	0.89	0.99	1.04	1.06	—
Na <sup>+</sup>	4	5.7	0.43	0.89	0.94	0.97	1.14	1.21	1.26	1.29
K <sup>+</sup>	4	5.7	1.44	2.04	2.3	3.04	3.14	3.59	5.34	5.34
Cs <sup>+</sup>	3	5.7	0.98	1.1	1.09	1.2	1.27	1.3	—	—
Nd <sup>3+</sup>	3	3.0	1.22	1.3	1.33	1.53	1.57	1.61	1.64	—

TABLE 3 — ADSORPTION OF CATIONS ON FeW AS A FUNCTION OF TIME

[W/Fe = 3; solutions prepared in 2M HNO<sub>3</sub>]

Ions	Normality	Adsorption (%) after the contact period (hr)					
		1	2	3	4	5	6
Na <sup>+</sup>	10 <sup>-3</sup> N	1.4	1.8	2.0	3.8	3.9	4.0
Cs <sup>+</sup>	10 <sup>-3</sup> N	16.6	17.4	18.6	—	—	—
Ca <sup>2+</sup>	2 × 10 <sup>-3</sup> N	3.3	4.8	7.0	8.4	8.7	—
Ba <sup>2+</sup>	2 × 10 <sup>-3</sup> N	12.4	16.2	16.4	19.6	26.0	—
Co <sup>2+</sup>	2 × 10 <sup>-3</sup> N	26.4	34.0	42.2	56.0	58.0	—
Cr <sup>3+</sup>	3 × 10 <sup>-3</sup> N	3.2	4.2	4.4	4.5	6.1	—
Nd <sup>3+</sup>	3 × 10 <sup>-3</sup> N	5.0	5.4	5.4	—	—	—
Eu <sup>3+</sup>	3 × 10 <sup>-3</sup> N	2.5	3.3	5.0	5.6	5.7	5.9
Ce <sup>4+</sup>	4 × 10 <sup>-3</sup> N	9.6	11.0	11.1	11.5	—	—

into consideration the effect of concentration, time for attaining equilibrium, etc., the following affinity series can be formulated for the alkali and alkaline earth metal ions:  $Cs > K > Na > Li$  and  $Ca > Mg$ , on FeMo and  $Cs > Na, Ba > Ca, Nd > Cr > Eu$  on FeW. Hydration of alkali ions plays a role in the ion exchange processes: the higher the hydrated ionic volume, the smaller the number that may be incorporated. Trivalent rare earth ions, alkaline earth ions and the lower alkali metal ions are adsorbed to a lesser extent than  $Cs^+$ . The higher adsorption of  $Cs^+$  has been attributed to the chemical reaction between structural hydrogen ions in the

ferrocyanide-molybdenyl sheets which form the backbone of the exchanger and the almost unhydrated  $Cs^+$  ions. The lower adsorption exhibited by trivalent ions and  $Ce^{4+}$  at higher acid concentration as compared to  $Cs^+$  (Table 3) can readily be understood when one recalls<sup>1</sup> that in increasingly acid solutions the distribution coefficient curves on log paper have a slope of  $-1$  for uni-univalent exchange and  $-3$  for tri-univalent exchange. The high adsorption exhibited by  $Co^{2+}$  on both FeMo and FeW (Tables 4 and 5) is due to the chemical interaction between the transition metal ion and the layer of protonated ferrocyanide groups. Comparing the adsorption values for different ions on FeMo and FeMo-Dowex 1 (Tables 2 and 4), it is found that the multiloaded exchanger is less effective as compared to pure FeMo. The high adsorption exhibited by FeMo-Dowex 1 for  $Nd^{3+}$  may be due to some specific interaction with the matrix or with the organic anion exchanger. FeW exhibits good adsorption at higher acidities ( $2M HNO_3$ ) while FeMo is useful in the near neutral pH range.

The authors are grateful to Dr V. Ramshesh and Dr B. Venkataramani for helpful discussions.

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TABLE 4 — ADSORPTION OF CATIONS ON FeMo-DOWEX 1 AS A FUNCTION OF TIME

[Conc. of cation  $10^{-3}M$ ; acidity of solns  $0.01M$  (in HCl)]

Cations	Adsorption (%) after the contact period (hr)		
	1.5	3	4.5
$Cs^{3+}$	0.64	1.0	2.4
$Ca^{2+}$	1.2	2.1	4.2
$Ba^{2+}$	1.3	2.2	3.9
$Co^{2+}$	1.0	1.5	1.6
$Nd^{3+}$	54.1	91.9	97.1

TABLE 5 — ADSORPTION OF IONS ON FeMo AS A FUNCTION OF pH

(Time of contact 3 hr)

Cation	Conc.	Mo/Fe	pH of the soln		Capacity meq/g	Remarks
			Initial	Final		
$Li^+$	$1M$	3	2.0	1.9	0.13	Capacity calculated on the basis of $H^+$ release
			3.0	2.4	0.15	
			4.0	2.45	0.17	
			6.0	2.45	0.18	
$Na^+$	$1M$	3	2.0	1.9	0.13	do
			6.04	2.35	0.22	
$K^+$	$1M$	3	2.0	1.9	0.13	do
			4.0	1.95	0.56	
		4	2.0	1.7	0.5	do
			4.0	1.8	0.8	
$Mg^{2+}$	$0.1M$	3	2.0	*	0.36	Capacity calculated by measuring the cation concentration
			3.0	*	0.36	
$Ca^{2+}$	$0.1M$	2	2.0	*	0.47	do
			3.0	*	0.48	
		3	2.0	*	0.44	
			3.0	*	0.54	
		4	2.0	*	0.41	
			3.0	*	0.46	
$Co^{2+}$	$1M$	3	2.0	1.3	2.0	Capacity calculated on the basis of $H^+$ release
		4	2.0	0.95	5.11	
$Nd^{3+}$	$1M$	3	3.0	2.5	0.16	do
		4	3.0	2.15	0.30	

\*Not determined, as the capacities were calculated by direct measurements of the cation concentrations.

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### Apparent Molal Volume of Tetraalkylammonium Iodides in Dioxane-Water Mixtures of Varying Dielectric Constants

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Received 27 August 1975; accepted 29 January 1976

Dependence of the slope ( $S_v$ ) of the plots of apparent molal volume ( $\phi_v$ ) versus  $\sqrt{C}$  for some tetraalkylammonium salts on the dielectric constant has been examined in water-dioxane mixtures of different dielectric constants. The results indicate that the nature of slope (positive or negative) mainly depends on the dielectric constant of the medium. A high dielectric constant and the large size of  $R_4N^+$  ions favour a negative slope.

IN an earlier study<sup>1</sup> we observed that the slope ( $S_v$ ) of the Mason's empirical equation  $\phi_v = \phi_0 + S_v\sqrt{C}$  ... (1) in the case of some tetraalkylammonium iodides in water-methanol mixtures depends on the dielectric constant of the solvent medium. The study has now been extended to dioxane-water mixtures in order to see if a similar dependence of  $S_v$  on the dielectric constant of the solvent medium is valid.

Conductivity water and doubly distilled AR dioxane were used for preparing solvent mixtures. Due to rapid decrease in solubility of the  $R_4N$  iodides with the increase in dioxane content of the mixture, only mixtures containing 2, 6 and 10% dioxane (by weight) could be used in the present study. Tetraalkylammonium iodides (M/s Distillation Products Industries, USA) were purified in the usual manner<sup>2</sup>. Rest of the experimental procedure was the same as described elsewhere<sup>5,12,13</sup>. The density data thus obtained were used to calculate the apparent molal volume ( $\phi_v$ ).

TABLE 1 — VALUES OF THE SLOPE ( $S_v$ ) FOR SOME  $R_4NI$  SALTS IN WATER-DIOXANE MIXTURES

Weight % of dioxane in mixture	Dielectric constant at 40°C	$S_v$ at 40°C for			
		$Me_4NI$	$Et_4NI$	$Pr_4NI$	$Bu_4NI$
0	73.1	5.1	-0.2	-1.0	-6.3
2	71.5	5.8	0.8	-0.4	-5.8
6	68.1	7.2	1.8	0.6	-4.5
10	64.4	8.4	3.0	1.7	-3.2

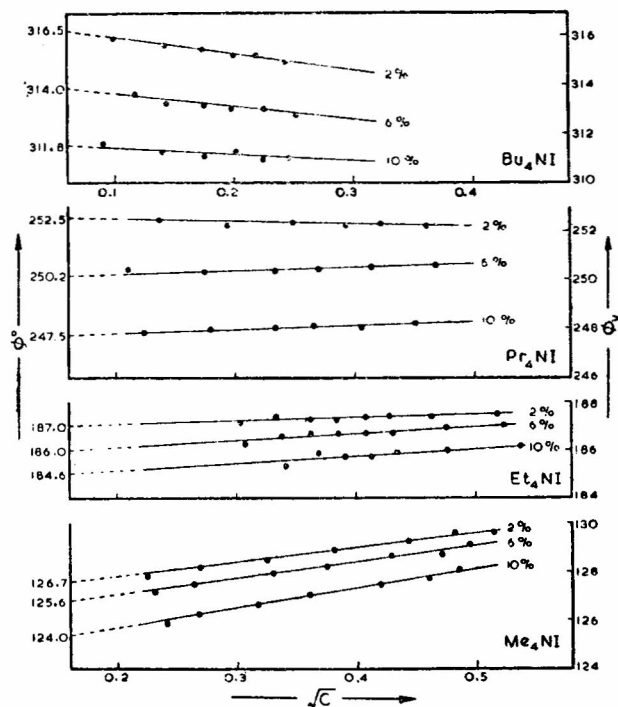


Fig 1 — Plots of  $\phi_v$  versus  $\sqrt{C}$  for different salts at 40°

Using the  $\phi_v$  values, as obtained above, the plots of  $\phi_v$  versus  $\sqrt{C}$  for different salts at 40° were drawn (Fig. 1). These plots were almost linear indicating applicability of the Mason's empirical relation (1) within the concentration range studied presently. It may also be noted from Fig. 1 that the slope  $S_v$  is positive for  $Me_4NI$  and  $Et_4NI$  salts in all the three mixtures. However, for  $Pr_4NI$ , it is slightly negative in a mixture containing 2% dioxane ( $\epsilon = 71.5$ ) but becomes positive in a mixture containing 6% ( $\epsilon = 68.1$ ) and 10% ( $\epsilon = 64.7$ ) dioxane. The slope remains negative in all the three solvent systems for  $Bu_4NI$  and the interpolation procedure suggests that  $S_v$  in this case would become positive when the dielectric constant is reduced further. Since a lower dielectric constant enhances electrostatic interionic attraction, it appears reasonable to infer that the positive slope is due to this effect. For the negative slope, as found in the case of higher homologues ( $R_4NX$ ) and some common salts in solvents of high dielectric constants, various explanations have been suggested<sup>6-11</sup> and need not be discussed here. It may be emphasized, however, that the factors responsible for the negative slope are non-electrostatic ion-solvent interactions and depend on the shape and size of the solvent molecules and ions.

The dependence of the nature of slope on the dielectric constant of the medium may be examined a little more closely. The  $S_v$  values are given in Table 1 along with the corresponding values in water for different salts for the sake of comparison.

It may be noted from Table 1 that  $S_v$  increases with the decrease in dielectric constant of the medium. It remains positive for  $Me_4NI$  in all the solvent systems. However, for  $Et_4NI$ ,  $S_v$  changes from negative to a positive value at about  $\epsilon \approx 74$ ,