

values of Q^* , and E have been calculated from the data reported in our previous paper¹.

Eq. (1) relates the water flux J_w when pressure, difference ΔP and temperature difference ΔT are simultaneously operating on the system.

$$J_w = -L_{11} \frac{v}{T} [\Delta P - \Delta P_0 \{1 - \exp(-\Delta P / \Delta P_0)\}] + L_{12} \left(\frac{-\Delta T}{T^2} \right) \quad \dots(1)$$

$$J_q = L_{21} \left(\frac{-v\Delta P}{T} \right) + L_{22} \left(\frac{-\Delta T}{T^2} \right) \quad \dots(2)$$

Assuming the validity of Eq. (2) which relates² the heat flux, J_q , in the presence of both ΔP and ΔT , and Onsager's reciprocal relation, the equation showing connection between heat of transport and thermo-osmotic pressure can be written as (Eq. 3):

$$\left(\frac{[\Delta P - \Delta P_0 \{1 - \exp(-\Delta P / \Delta P_0)\}]}{\Delta T} \right)_{J_w=0} = - \frac{Q^*}{vT} \quad \dots(3)$$

In the region where $\Delta P \gg \Delta P_0$ Eq. (3) reduces to linear form

$$\left(\frac{\Delta P - \Delta P_0}{\Delta T} \right)_{J_w=0} = - \frac{Q^*}{vT} \quad \dots(4)$$

In Eqs. (1) to (4), ΔP_0 is the extrapolated intercept on the ΔP -axis, v is the specific volume of water and L_{ik} are the phenomenological coefficients. For the sake of simplicity the present discussion is confined to the linear region where Eq. (4) holds good. The values of Q^* have been calculated from Eq. (4).

It is evident from Eq. (4) that $(\Delta P - \Delta P_0 / \Delta T)_{J_w=0}$ should decrease with increase in temperature. This is found to be true. Although L_{12} has been shown¹ to be more or less invariant with T , both L_{11} and specific volume increase with increase in temperature. The values of Q^* are recorded in Table 1. The values of heat of transport, defined² as $Q^* = L_{21}/L_{11}$, show a decreasing trend with increase in temperature.

The activation energy for water flow through bentonite has been calculated by a procedure similar to that used earlier³. The value of E estimated from the temperature-dependence data of water flow comes out to be 10.13 kcal/mole which is very high in comparison to the values of Q^* given in Table 1. A similar trend has been noticed earlier^{3,4} and the explanation provided earlier holds good for the present system also.

The very low values of heat of transport in the present system suggest that molecules involved in diffusion

jumps do not have to gather appreciable energy by forming bonds again at new equilibrium sites. But instead the flow appears to be governed by such fraction of water molecules as are quite free from bonds of any kind and are mobile. This is achieved through thermal motion when some of the hydrogen bonds in hydrogen-bonded water molecules break down. It also appears that the mechanism of heat of transport is not related to activation energy in the present case. These interpretations are in agreement with the previous views^{3,4} that activation energy in such a system reflects changes in hydrogen bond rather than any specific mechanism of flow.

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Sorption of Radioiodine on Bismuth Hydroxide

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The sorption characteristics of bismuth hydroxide for the removal of radioiodine from aqueous solutions have been evaluated under different conditions of pH, time and amounts of sorbent used. Effect of competing anions such as chloride, nitrate, sulphate and phosphate on the sorption equilibrium has also been studied. The distribution coefficient (K_d), has been found to be of the order of 4×10^4 suggesting the utility of the sorbent in the decontamination of radioactive waste waters generated in the nuclear power plants.

RADIOIODINE (¹³¹I) is produced as a result of fission process in nuclear reactors. In the event of fuel failures, iodine finds its way into the coolant and consequently appears in the radioactive liquid effluents. Its removal is important from the radiation safety point of view.

Sorption of ¹³¹I on a number of sorbents has been described in a series of papers¹⁻⁸. Removal of radioiodine by coprecipitation with lead sulfate was tried by Cohen⁹. Bismuth hydroxide has a tendency to adsorb strongly the acid anions. Based on this, its sorption characteristics for the removal of radioiodine from aq. solutions were studied in detail and the results are reported in this note.

The sorbent was prepared by the dropwise addition of 1M NaOH to 0.1M bismuth nitrate with constant stirring at $28 \pm 3^\circ$. After the precipitation was complete at pH 5.6, the mixture was kept overnight for settling. It was filtered through Whatman No. 42 filter paper, washed with distilled water,

TABLE 1 — DEPENDENCE OF $(\Delta P - \Delta P_0 / \Delta T)_{J_w=0}$ AND Q^* ON TEMPERATURE

Temperature (°K)	$(\Delta P - \Delta P_0 / \Delta T)_{J_w=0}$ $\times 10^{-5}$ (dyne cm ⁻² deg ⁻¹)	Q^* (cal/mole)
308	0.0893	0.0658
313	0.0627	0.0469
318	0.0480	0.0369
323	0.0387	0.0299

dried at 100° and powdered. X-ray diffraction pattern of the powdered sample indicated that the product was amorphous. The chemical analysis showed it contain 78.5% bismuth corresponding to a composition of BiO(OH).

The stock solution of radioiodine tracer was prepared in distilled water from carrier-free ¹³¹I in the form of sodium iodide procured from the Isotope Division of Bhabha Atomic Research Centre, Trombay.

Procedure — The sorbent (100 mg) and the tracer stock solution (50 ml) were taken in polyethylene containers and subjected to shaking at 28 ± 3°. The two phases were separated by centrifuging and the aq. phase counted for gamma activity in a well-type NaI(Tl) detector connected to a single channel analyser.

Sorption as a function of pH was studied using NaOH and HNO₃. The composition of the sorbent was determined by estimating bismuth by titrating it against standard EDTA. The pH titration was performed by the method of Topp and Pepper¹⁰.

The results are expressed in terms of distribution coefficient, K_d (ml/g) represented by the relation (1), $K_d = (1-p)V/m\phi$... (1) where ϕ is fraction of the residual activity in aq. phase, V is volume of the solution in ml and m is the weight of the sorbent in grammes. From a plot of K_d versus time it was observed that about 25 hr equilibrium period gave maximum sorption and, therefore, the same period has been used for all other studies.

The pH did not have significant effect on the extent of sorption in the pH range of 2 to 10 as revealed by the plot of K_d versus pH. It was observed that the sorption decreased both under highly acidic and alkaline conditions. Under these conditions partial dissolution of the sorbent was noticed (46, 10 and about 5% of the sorbent dissolved at pH 1.0, 2.5 and 10.0 respectively). This aspect was however taken into account for evaluating K_d values. Sharp decrease in the sorption above pH 10 is probably due to the formation of Bi(OH)₃ (ref. 12).

Dependence of sorption on the amounts of sorbent used at pH 2.5 and 10 (most favourable for maximum sorption) is shown in Fig. 1. It was observed that at pH 10 there is a sharp increase in the sorption with the decrease in V/m ratio from 2500 to 500 and beyond this it does not have any significant effect. The optimum V/m ratio was found to be 500. However, at pH 2.5 the sorption is nearly independent of V/m ratio.

The effects of competing anions such as nitrate, chloride, sulphate and phosphate on the sorption equilibrium at pH 2.5 and 10 (Fig. 2) indicated that the valency of the competing anions plays an important role. Similar to exchange processes, in this case also, sorption decreased with increase in valency and concentration of the competing anions. In order of preference, this effect can be represented as trivalent > divalent > monovalent.

Results of the desorption studies are shown in Table 1. A period of ~8 hr was found to be necessary for achieving the maximum desorption. It

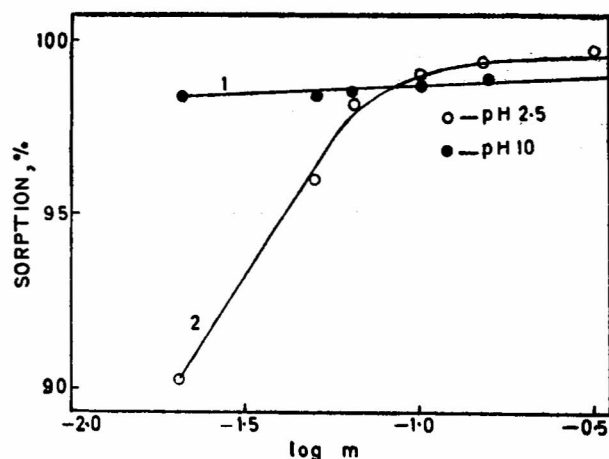


Fig. 1 — Plots showing sorption as a function of the quantity of sorbent [(1) at pH 2.5; (2) at pH 10.0]

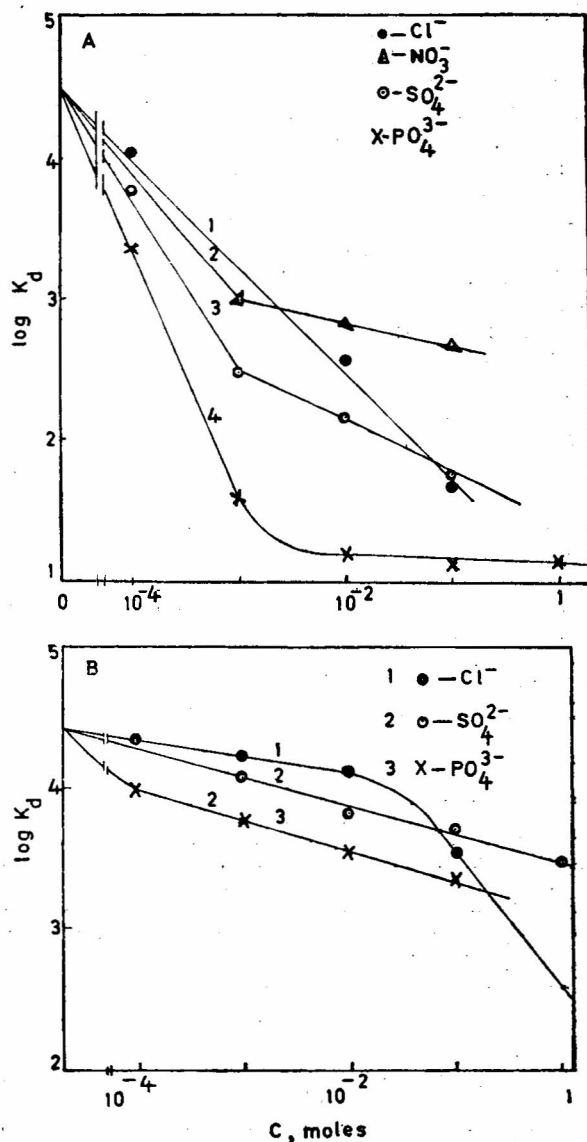


Fig. 2 — Effect of varying concentration of anions on the sorption equilibria [(A) at pH 10.0; (B) at pH 2.5]

TABLE 1 — DESORPTION OF RADIOIODINE FROM BISMUTH HYDROXIDE IN WATER AND 0.1M NaOH

Fraction of solution	Desorption (%)	Total* desorption (%)
DISTILLED WATER		
1	7.16	17.45
2	5.40	
3	4.89	
0.1M NaOH		
1	96.94	100.17
2	3.02	
3	0.21	

*Total desorption of the fractions 1-3.

Viscosities & Apparent Molar Volumes of CaCl₂ & SrCl₂ in Water at Different Temperatures

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The viscosities and apparent molal volumes of CaCl₂ and SrCl₂ have been measured in aqueous solutions at 30°, 35°, 40° and 45°. The data give a good fit to Jones-Dole and Masson's equations. The energy and entropy of activation of the viscous flow have been calculated. The ionic radii have been computed both from the viscosity and apparent molal volume data and follow the order: $r_{Ba^{2+}} > r_{Sr^{2+}} > r_{Ca^{2+}}$.

THE change in viscosity with concentration of the aqueous solutions of electrolytes is satisfactorily represented by the Jones-Dole equations¹:

$$\eta_r = 1 + A\sqrt{C} + BC \quad \dots(1)$$

where the constant A is long range interparticle (interionic) interaction coefficient and B is the solute-solvent interaction constant and C is the concentration of solute in moles/litre. In order to study the effect of temperature on solute-solvent interaction coefficient (B) the viscosities of CaCl₂ and SrCl₂ have been measured in aqueous solutions at 30°, 35°, 40° and 45°. The apparent molal volumes have been calculated from the density data.

Viscosities and densities were measured as described by Prasad and coworkers^{2,3}. The densities were measured using a pycnometer and applying the buoyancy correction. The values have an accuracy of 4 in 10⁶.

The usual procedure to test the validity of the Jones-Dole equation has been applied and the equation represents the experimental results satisfactorily. The values of A and B were calculated from the intercept and slope respectively of the plot of $\eta - 1/\sqrt{C}$ against \sqrt{C} . The relative viscosities were next calculated using these calculated values of A and B and the values are in good agreement with the observed values for the range of concentration 0.1-0.001M. Only two sets of values for each of the electrolytes have been recorded in Table 1.

The ionic B -coefficient were calculated using the procedure of Kaminsky⁴. It was found that of the ions Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ the ionic B -value is the largest for Be²⁺ and smallest for Ba²⁺ at all temperatures. Hence it is concluded that the ionic B value goes on increasing with the decrease in ionic radii. In a plot of B values against the temperature, dB/dT becomes distinctively negative and goes on decreasing as the ionic radius increases.

The plot of the ionic B -values against the crystal ionic radii at different temperatures is linear and B -ion becomes zero for radii 2.16 at 25°; 2.37 at 30°; 2.42 at 35°; 2.80 at 40°; and 3.20 at 45°.

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was possible to desorb completely ¹³¹I using 0.1M NaOH solution. The first fraction alone resulted in desorption to the extent of 96.9%. Distilled water did not prove effective for this purpose.

Excellent sorption of ¹³¹I in acid pH is probably due to the presence of a replaceable OH⁻ group attached to (BiO)⁺ radical. The latter has a good tendency to combine with halides and form insoluble oxy-compounds. The sorption mechanism may be explained on the basis that OH⁻ group is replaced by I⁻ which is retained as BiOI. Experimental observation on the effect of competing ions on sorption as discussed above also supports this view and suggests that the sorption is mainly due to exchange process. Further support for the formation of BiOI is provided by desorption studies using NaOH and water. Failure of water to desorb ¹³¹I shows the existence of stronger bonds between the sorbent and iodide. Formation of oxy-iodide was supported by pH titrations in which the sorbent showed an apparent capacity of 1.78 meq/g for the iodide ions.

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