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Anion Dependence of Transport of Mercury Ion through Nafion-117 Membrane

Chhavi Agarwal, Sanhita Chaudhury, Amol Mhatre, and A. Goswami*

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India

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Studies on isotopic and ion-exchange kinetics of mercury ions in Nafion-117 membrane have been carried out with ^{203}Hg radiotracer in the presence of Cl^- and NO_3^- in solution. The results of isotopic-exchange kinetics indicate that mercury ions diffuse into the membrane as monovalent cation from HgCl_2 solution while as divalent ion from $\text{Hg}(\text{NO}_3)_2$ solution. The studies on the kinetics of ion exchange of Hg^{2+} with Na^+ follow the prediction of the Nernst–Planck equation when NaNO_3 is used as an external salt solution. The Nernst–Planck equation fails to predict the kinetics when NaCl is used as an external salt solution, indicating that the complexation of Cl^- with Hg^{2+} in the membrane influences the kinetics. Permeation studies using ^{203}Hg and ^{36}Cl radiotracer between two HgCl_2 solutions show that the permeability coefficients of mercury and chloride ions are the same, indicating the cotransport of mercury and chloride ions through the membrane. Ion-exchange equilibrium studies using a mixture of HgCl_2 and HNO_3 solution were carried out to ascertain the species transporting through the membrane. The equilibrium sorption of mercury in the membrane shows the uptake of an ionic species, presumably HgCl^+ , not a neutral salt. The speciation diagrams, calculated as a function of pH, show wide divergence of species present in HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ solution and explain the difference in membrane transport behavior for HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ solution. The results show that any ion-exchange-membrane-based separation of Hg^{2+} needs careful consideration regarding the anions present in the solution, as it influences the speciation of mercury and hence its transport behavior through the membrane.

Introduction

Ion-exchange membranes allow counterions to pass through while co-ions are excluded from the membrane. Thus, they can act as a separator between two electrolyte solutions. This property of ion-exchange membranes is utilized in the ion-exchange-based separation processes as in Donnan dialysis and electrodialysis.¹ Nafion-117 is a poly(perfluorosulfonic) acid ion-exchange membrane having a polytetrafluoroethylene (PTFE) backbone with pendant side chains containing $-\text{SO}_3\text{H}$ groups and is extensively used in many Donnan and electrodialysis-based applications such as in chlor-alkali industries.² Diffusion behavior of monovalent and multivalent ions in the Nafion-117 membranes has been widely studied.^{2,3} It has been generally observed that the self-diffusion coefficients of the ions of same valence decrease with increasing ionic size. Also, the self-diffusion coefficients of monovalent ions are distinctly higher than the divalent ions except for Cs^+ , which has a low self-diffusion coefficient. This behavior has been explained on the basis of hydration characteristics of the ions and their electrostatic interactions with the fixed charged groups in the membrane. The distinctly different behaviors of the mono- and divalent ions can be used to identify the valence state of the diffusing ions in the membrane, which in turn can be used to identify the dominant ionic species existing in solution.^{4–8} There is limited literature for the transport of mercury ions through ion-exchange membrane. Oehmen et al. have studied the removal of heavy metals from drinking water supplies through the ion-exchange membrane bioreactor by Donnan dialysis.⁹ Ersoz has reviewed the use of liquid membranes containing calixarene carriers for selective transport of mercury.¹⁰ Though not used in industrial scale, Donnan dialysis and chelation in

combination with ultrafiltration are considered to be potential techniques for membrane based wastewater treatment for removal of mercury.¹¹ Studies on speciation of mercury on the transport behavior of ions through ion-exchange membranes are important for designing such separation processes.

Hg^{2+} has a strong polarizing power and behaves as a soft acid, and prefers binding with soft donors such as Cl^- , Br^- , I^- , and S^{2-} , forming compounds having considerable covalent character.¹² If soluble, these compounds remain largely undissociated, and exhibit rich speciation depending upon the pH of the solution and anion concentration.^{13–16} HgCl_2 has received special attention due to its appreciable solubility in water and its high toxicity.¹⁷ The literature indicates that it mostly exists as neutral HgCl_2 molecules.¹⁴ On the other hand, mercury exists as Hg^{2+} in acidic $\text{Hg}(\text{NO}_3)_2$ solution due to its ionic nature, and hydrolyzes at higher pH. In view of the fact that the mercury can exist in different forms in aqueous solution of Cl^- and NO_3^- salts, in the present work, an attempt has been made to understand the transport behavior of mercury ion through Nafion-117 membrane from its chloride and nitrate salt solution. Isotopic and counterion exchange studies have been carried out using ^{203}Hg radiotracer to investigate the anion dependence of diffusivity of the mercury ion in the membrane. The transport behavior of Cl^- between two HgCl_2 solutions separated by Nafion membrane has been studied using ^{36}Cl tracer to investigate the nature of mercury species being transported. Equilibrium uptake of mercury from HgCl_2 solutions of varying mercury and acid concentration has been studied. On the basis of these measurements, an attempt has been made to identify the species transported from $\text{Hg}(\text{NO}_3)_2$ and HgCl_2 solution. The results of transport behavior have been discussed on the basis of the calculated speciation behavior of mercury in HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ solution.

* To whom correspondence should be addressed. E-mail: agoswami@barc.gov.in. Fax: +91-22-25515151.

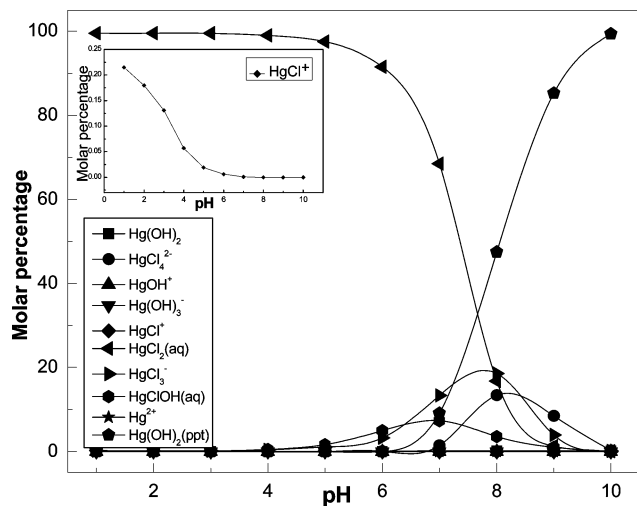


Figure 1. Mercury speciation in aqueous chloride medium with an initial concentration of 0.2 M HgCl₂. The inset shows the variation of HgCl⁺ concentration as a function of pH.

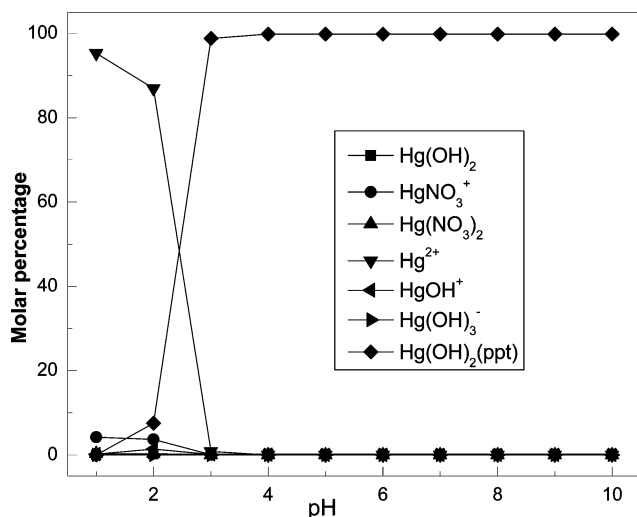


Figure 2. Mercury speciation in aqueous nitrate medium with an initial concentration of 0.2 M Hg(NO₃)₂.

Mercury Speciation

In order to have a priori knowledge about the mercury species present in Cl⁻ and NO₃⁻ solutions, the speciation calculations as a function of pH have been done using the chemical equilibrium modeling software MINTQA2.¹⁸ The values of stability constants of mercury species were taken from the library of the program. The results are shown in Figures 1 and 2 for HgCl₂ (0.2 M) and Hg(NO₃)₂ (0.2 M) solutions. It is seen from Figure 1 that mercury practically exists as neutral HgCl₂ species in the pH range 2–7, and free Hg²⁺ does not exist in the solution. The concentration of HgCl⁺ is also very small, about 0.1% of the HgCl₂ concentration. Figure 2 shows that Hg²⁺ is the major species present in Hg(NO₃)₂ solution until pH 2, beyond which hydroxide precipitation occurs.

Experimental Section

Analytical grade chemicals (HgCl₂, NaCl, and NaNO₃), deionized water (18 MΩ/cm, Gradient A-10 model, Milli-Q USA), and analytical grade HCl and HNO₃ (Merck, Germany) were used in the present study. Hg(NO₃)₂ solution was prepared by dissolving a known amount of HgO in concentrated HNO₃, and diluting the resulting solution to a pH of ~2 above which

precipitation of Hg(OH)₂ occurs, as seen from the speciation diagram (Figure 2). HgCl₂ solution was prepared by dissolving HgCl₂ in water. The pH of the solution was measured to be 3.3. The HgCl₂ solution in the concentration range of about 0.1–0.2 M has a pH of 3–4 due to hydrolysis of HgCl₂ to HgClOH.¹⁶ Nafion-117 ion-exchange membrane with an equivalent weight of 1100 g (ion-exchange capacity 0.91 mequiv/g) and thickness of 178 μm was used. As described in our earlier paper,³ the samples of Nafion-117 were treated to remove organic impurities, conditioned with 0.5 mol/L HCl and 0.5 mol/L NaOH, equilibrated with 0.2 mol/L of relevant salt solution for 18–24 h at room temperature (27 °C) for converting the membrane into the appropriate ionic form.

Radiotracers ²⁰³Hg, ²²Na, and ³⁶Cl, used in the present work, were obtained from the Board of Radiation and Isotope Technology, Mumbai, India. The measurements of isotopic-exchange and ion-exchange rates were carried out using 1.5 cm × 1.5 cm pieces of Nafion-117 membrane in the appropriate ionic form. The sorption/desorption of radiotracer counterions in the membrane samples in contact with the equilibrating solutions were monitored as a function of time to obtain the exchange rates. The experimental details are given in our previous publication and are described briefly below.³

For the isotopic-exchange experiments involving diffusion of radiotracer ions from equilibrating solution into the membrane (absorption), the membrane sample pre-equilibrated with HgCl₂ (0.2 M) or Hg(NO₃)₂ (0.2 M) solution was placed in 25 mL of salt solution containing ²⁰³Hg radiotracer ions at room temperature (27 °C). The equilibrium absorption of the radiotracer ion into the membrane is governed by the ratio of the amount of mercury ion in the membrane to that in the external solution. If the concentration of the external salt solution is kept high, only a small fraction of radiotracer ions will thus enter into the membrane from the external solution, thereby reducing the sensitivity of radioactivity measurement and requiring a larger quantity of radiotracer to be used. Thus, the concentration of HgCl₂ (pH 3.3) or Hg(NO₃)₂ (pH ~2) in equilibrating solution was kept at 0.02 M to maximize the absorption of radiotracer ions into the membrane. For the ion-exchange kinetics studies between mercury and sodium ion, the membrane was pre-equilibrated with HgCl₂ (0.2 M), Hg(NO₃)₂ (0.2 M), NaCl (0.2 M), or NaNO₃ (0.2 M) solution and placed in 25 mL of 0.2 M external salt solution with the corresponding radiotracer ions. In this case, the external salt solution concentration is kept as 0.2 M to ensure the complete exchange of ions in the membrane with the ions in the external salt solution.

The solution containing membrane sample was stirred vigorously using a magnetic stirrer (~52 rad/s) to ensure that the membrane diffusion was taking place. To monitor diffusion of radiotracer ions into the membrane as a function of time, the membrane sample was taken out at regular time intervals, washed with deionized water to remove the traces of equilibrating solution clinging to its surface, and sorbed into the membrane. The membrane sample was subsequently taken in a plastic tube and counted for γ-ray using a well type NaI (TI) detector connected to a 4k multichannel analyzer. The counting was done keeping the geometry of the sample–detector system fixed, to ensure a constant counting efficiency. The 279 keV peak of ²⁰³Hg and 511 keV peak of ²²Na were monitored. The error in recording the contact time of the membrane with equilibrating solution was expected to be of the order of ±1 s. The membrane sample was replaced again in the equilibrating solution after counting. The actual residence time of the

membrane in the equilibrating solution was used as the time of cation absorption.

For desorption experiments involving isotopic and ion-exchange studies, the membrane samples were loaded with radioactive tracers by equilibrating the membrane sample with relevant radiotracer salt solution (0.2 M). Subsequently, the membrane samples were taken out, rinsed with water, and placed in 25 mL of 0.2 M equilibrating salt solution (without radioactive tracer ions) of HgCl_2 (pH 3.3), $\text{Hg}(\text{NO}_3)_2$ (pH 2), NaCl (pH 7), or NaNO_3 (pH 7) at room temperature. The 0.2 M salt solution was used to maximize desorption of radiotracer ions from the membrane. The other experimental steps were the same as those used in the absorption experiments.

The transport studies of mercury and Cl^- ion were carried out in a two-compartment dialysis cell separated by Nafion-117 membrane. The volume of each compartment was 25 mL. The solution in each compartment was continuously stirred during the course of the experiment to minimize the film diffusion. The solution in the feed compartments was initially spiked with ^{203}Hg or ^{36}Cl radiotracer. The radioactivity in the feed as well as receiver compartment was subsequently measured by pipetting out 100 μL of solution at regular time intervals until the equilibrium was reached. The counting of ^{203}Hg samples was done in the $\text{NaI}(\text{Tl})$ detector coupled to a 4k multichannel analyzer. In the case of transport study of Cl^- , the β -radioactivity of ^{36}Cl radiotracer was measured by mixing the sample in a vial with 5 mL of scintillation cocktail-w (2,5-diphenyl oxazole (PPO) = 0.7%, 1,4-di-2-(5-phenyloxazolyl) benzene (POPOP) = 0.03%, naphthalene = 10%, and tri-*n*-octyl phosphine oxide (TOPO) = 1% in 1,4-dioxane solvent), and counting the samples with a liquid scintillation analyzer.

Ion-exchange equilibrium was determined by measuring the uptake of mercury in the membrane from a set of equilibrating solutions containing a mixture of 0.01 M HgCl_2 (pH 3.2) and 0.02 M HNO_3 (pH 1.8) in different proportions (1:0, 1:0.1, 1:0.2, 1:0.3, 1:1.0, 1:3.0), with the total number of moles of HgCl_2 and HNO_3 kept constant. The pH of the solutions varied from 1.8 to 3.2. For each experiment, a 1.5 cm \times 1.5 cm piece of Nafion-117 membrane sample in H^+ form was immersed in well-stirred (≈ 52 rad/s) equilibrating solution at 27 $^\circ\text{C}$, to eliminate the film-controlled diffusion at the membrane–solution interface. The membrane was removed and washed thoroughly with deionized water to remove any adherent solution. Mercury going into the membrane as neutral salt, if any, was also removed at this stage. ^{203}Hg radiotracer was used to study the uptake of mercury from the equilibrating solutions. Ion-exchange equilibrium was also studied at a fixed pH (3.2) by varying the concentration of HgCl_2 from 0.01 to 0.1 M.

Results and Discussion

Isotopic-Exchange Kinetics. Figure 3 shows the plot of kinetics of isotopic exchange of mercury for the equilibrium $*\text{X}^{n+}_{(\text{m})} \rightleftharpoons \text{X}^{n+}_{(\text{s})}$, where X refers to the mercury species present in the equilibrating solution containing HgCl_2 or $\text{Hg}(\text{NO}_3)_2$, n is the corresponding charge on the species, “m” and “s” refer to the membrane and solution phase, respectively, and the asterisk indicates the radiotracer tagged ion. The data for both absorption and desorption experiments are shown in the figure. It is seen that the attainment of equilibrium is much faster when the equilibrating solution contains HgCl_2 compared to $\text{Hg}(\text{NO}_3)_2$. Thus, the results show that the species diffusing into the membrane are different for the two cases. The solid lines in the figure are the least-squares fit to the plot using the analytical solution of Fick’s second law, given by the equation¹⁹

$$n(t_k) = n^* \left[1 - \left(\frac{8}{\pi^2} \right) \left\{ \exp(-D\pi^2 t_k / L^2) + \frac{1}{9} \exp(-9D\pi^2 t_k / L^2) + \dots \right\} \right] \quad (1)$$

where for the absorption experiment n^* is the total amount of the radiotracer ions in the membrane at equilibrium ($t = \infty$), $n(t_k)$ is the amount of radiotracer at any time t_k in the membrane, D is the self-diffusion coefficient, and L is the thickness of the membrane. For the desorption experiment, n^* represents the total loss of radiotracer at $t = \infty$ and $n(t_k)$ is the loss of radiotracer from the membrane at any time t_k . From the fit, the values of D are obtained as 1.2×10^{-6} and 1.2×10^{-7} cm^2/s for diffusion of mercury ions into the membrane from HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ solutions, respectively. The diffusion coefficient of mercury ion in Nafion-117 membrane is reported for the first time. The literature values of self-diffusion coefficients for typical monovalent (Na^+) and divalent (Ba^{2+}) ions are 1.0×10^{-6} and 1.5×10^{-7} cm^2/s , respectively.³ It is seen that the value of the self-diffusion coefficient of mercury ion in the membrane is comparable to a monovalent cation when uptake occurs from HgCl_2 solution, while that from a $\text{Hg}(\text{NO}_3)_2$ solution is typical of a divalent cation. This strongly suggests that the mercury ion apparently diffuses into the membrane from HgCl_2 solution mainly as a monovalent species, but from the $\text{Hg}(\text{NO}_3)_2$ solution, it diffuses as a divalent cation. However, in such a situation, for a given membrane weight, the amount of mercury uptake would be twice from HgCl_2 solution than that from $\text{Hg}(\text{NO}_3)_2$ solution, as the same number of ion-exchange sites are available in both cases. In order to confirm this, energy dispersive X-ray fluorescence (EDXRF) measurements of the membrane pieces loaded from HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ solution, respectively, were carried out. The relative height of the Hg peak (Figure 4) shows the amount of mercury loaded from HgCl_2 solution is less than the amount loaded from $\text{Hg}(\text{NO}_3)_2$ solution. This result essentially shows that mercury ions could not replace all of the

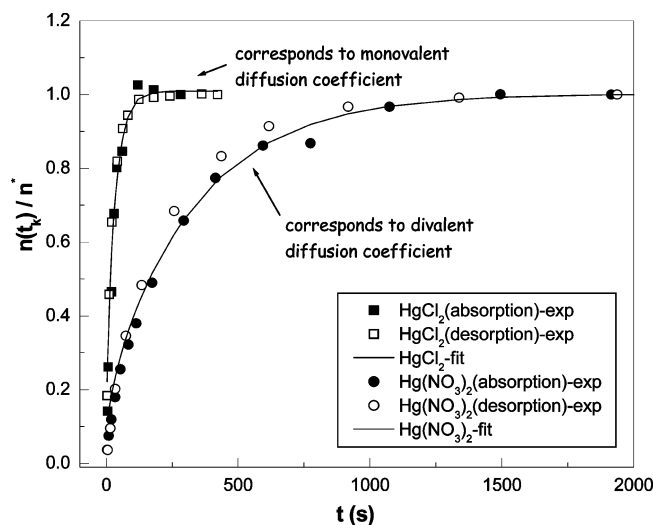


Figure 3. Plot of kinetics of the isotopic exchange $*\text{X}^{n+}_{(\text{m})} \rightleftharpoons \text{X}^{n+}_{(\text{s})}$, where X refers to the mercury species present in the equilibrating solution containing HgCl_2 or $\text{Hg}(\text{NO}_3)_2$, n is the corresponding charge on the species, “m” and “s” refer to the membrane and solution phase, respectively, and the asterisk indicates the radiotracer tagged ion. In the figure, for the absorption experiment, n^* is the total amount of the radiotracer ions in the membrane at equilibrium ($t = \infty$) and $n(t_k)$ is the amount of radiotracer at any time t_k in the membrane. For the desorption experiment, n^* represents the total loss of radiotracer at $t = \infty$ and $n(t_k)$ is the loss of radiotracer from the membrane at any time t_k .

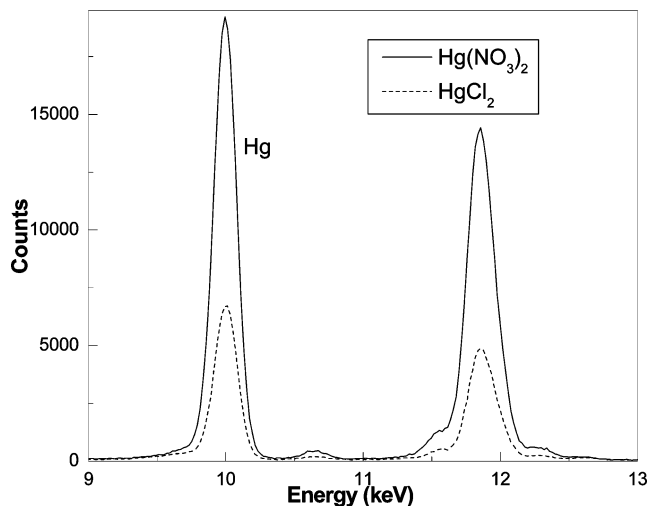


Figure 4. The energy dispersive XRF spectra of Nafion-117 membranes loaded with HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ solution, respectively.

H^+ ions from the acidic form of the Nafion-117 membrane in the case of HgCl_2 solution. This markedly different behavior of mercury ion toward the Nafion-117 membrane depending upon the anion present in the solution can be understood on the basis of the speciation diagrams. Figure 1 indicates that mercury exists as neutral HgCl_2 in the pH range studied, with very little concentration of HgCl^+ and practically no free Hg^{2+} . The absence of Hg^{2+} in the solution suggests that mercury can enter only as monovalent species (HgCl^+), giving a high self-diffusion coefficient. The poor mercury uptake in the membrane, as the EDXRF data indicates, is due to the low HgCl^+ concentration in the external solution failing to compete favorably with H^+ for the ion-exchange sites. On the other hand, Figure 2 indicates that, in nitrate solution, mercury exists as Hg^{2+} at pH ~ 2 and hence the isotopic-exchange kinetics follows the behavior expected for a divalent ion. Also, the higher charge on mercury leads to a favorable competition with H^+ for the ion-exchange sites in the membrane even at a lower pH, explaining the higher loading in the membrane.

Ion-Exchange Kinetics. In order to further explore the diffusion of mercury species into the membrane from its nitrate and chloride solution, a series of ion-exchange kinetics studies were carried out using the Na^+ and Hg^{2+} forms of membrane, and using different salt solutions. The results of the measurements with nitrate salt solution are summarized in Figure 5. As seen from the figure, when the ion-exchange kinetics for $\text{Na}^+_{(\text{m})} \rightleftharpoons \text{Na}^+_{(\text{s})}$ was followed using an external $\text{Hg}(\text{NO}_3)_2$ solution (pH ~ 2 , 0.2 M), the replacement of Na^+ by Hg^{2+} proceeded slightly slower than the rate of $\text{Na}^+_{(\text{m})} \rightleftharpoons \text{Na}^+_{(\text{s})}$ isotopic exchange, calculated using eq 1 with the literature value of the self-diffusion coefficient of Na^+ in the membrane.³ This is expected from the Nernst–Planck (NP) theory of ion-exchange kinetics, whereby a slower moving ion (Hg^{2+}) entering the membrane would retard the motion of a faster moving ion (Na^+) going out of the membrane due to electrical coupling of fluxes.^{20–22} The calculated plot obtained from NP theory for the forward exchange $\text{Na}^+_{(\text{m})} \rightleftharpoons \text{Hg}^{2+}_{(\text{s})}$ using the self-diffusion coefficients of Na^+ and Hg^{2+} is also shown in the figure as a solid line. The calculation has been performed by numerically solving the nonlinear diffusion equation describing the time and space dependence of the ion concentration in the membrane:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left[D_{AB} \frac{\partial c_i}{\partial x} \right] \quad (2)$$

where the interdiffusion coefficient D_{AB} is given by

$$D_{AB} = \frac{D_A D_B (Z_A^2 C_A + Z_B^2 C_B)}{(D_A Z_A^2 C_A + D_B Z_B^2 C_B)} \quad (3)$$

where C_i is the concentration of the i th species in the membrane and D_i and Z_i are the self-diffusion coefficient and charge on the i th species, respectively. Details of the numerical solution of eq 2 for a plane sheet of membrane using the finite difference method are given in ref 22. Similarly, the figure shows that the rate of the reverse exchange process $\text{Hg}^{2+}_{(\text{m})} \rightleftharpoons \text{Na}^+_{(\text{s})}$ (pH 7, 0.2 M NaNO_3) is faster than the rate of isotopic exchange $\text{Hg}^{2+}_{(\text{m})} \rightleftharpoons \text{Hg}^{2+}_{(\text{s})}$. This also follows the prediction of NP theory. The use of neutral equilibrating solution did not influence the kinetics of the ion exchange $\text{Hg}^{2+}_{(\text{m})} \rightleftharpoons \text{Na}^+_{(\text{s})}$, indicating that the kinetics of the ion exchange is governed by the membrane diffusion process. Thus, the results of the ion-exchange kinetics measurements are consistent with Hg^{2+} being the dominant species in $\text{Hg}(\text{NO}_3)_2$ solution.

However, the result was very different when the Cl^- was present in the external solution. Thus, the reverse exchange rate $\text{Hg}^{2+}_{(\text{m})} \rightleftharpoons \text{Na}^+_{(\text{s})}$ with NaCl (pH 7, 0.2 M) in the equilibrating solution was much faster than the case when NaNO_3 was used in the equilibrating solution and the rate was close to what was observed for isotopic exchange with HgCl_2 in external salt solution (Figure 6). The result does not follow the prediction of NP theory. Thus, it appears that the diffusion behavior of Hg^{2+} present in the membrane is modified significantly when Cl^- is present in the external salt solution. It appears that the Cl^- enters the membrane due to its strong affinity for Hg^{2+} , forming either HgCl_2 or HgCl^+ which is instantly excluded from the membrane. A similar phenomenon has been observed with ion-exchangers containing complexing cations which can act as highly selective sorbents for molecules or anions that can act as ligands, leading to the formation of complexes in the

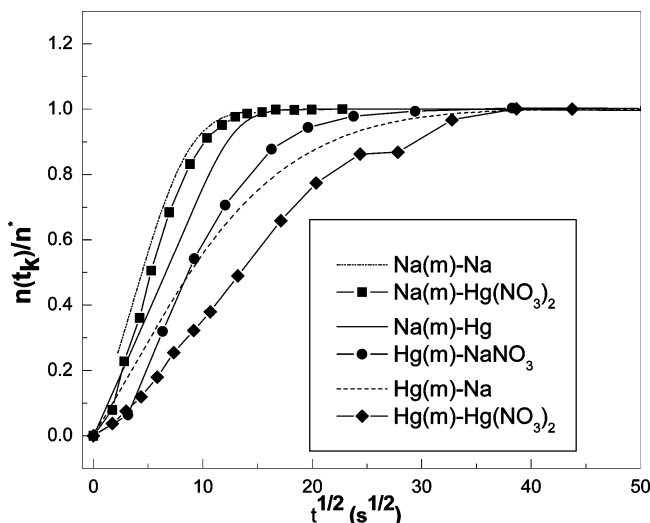


Figure 5. Plot of kinetics of the exchange $\text{Na}^+_{(\text{m})} \rightleftharpoons \text{Hg}^{2+}_{(\text{s})}$, $\text{Hg}^{2+}_{(\text{m})} \rightleftharpoons \text{Na}^+_{(\text{s})}$, and $\text{Hg}^{2+}_{(\text{m})} \rightleftharpoons \text{Hg}^{2+}_{(\text{s})}$, for the equilibrating solution containing mercury nitrate and sodium salts. Lines (bold, dot, and dash) represent the theoretically generated curves, and lines with symbols represent the experimentally obtained curves.

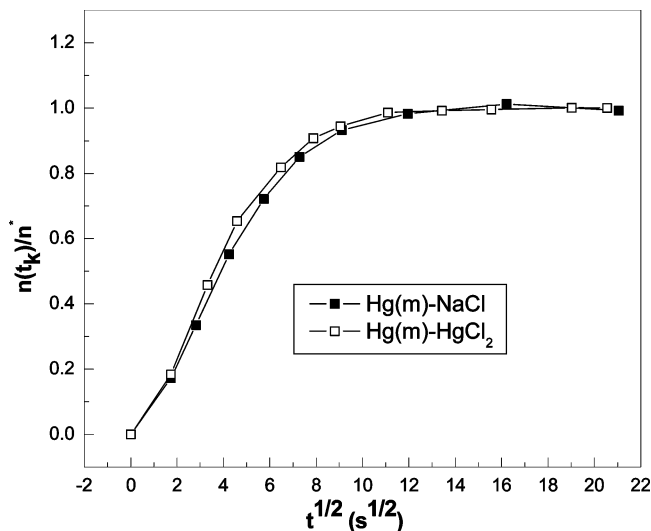


Figure 6. Plot of kinetics of the exchange $*X^{n+}_{(m)} \rightleftharpoons Na^{+}_{(s)}$ and $X^{n+}_{(m)} \rightleftharpoons *X^{n+}_{(s)}$, for the equilibrating solution containing sodium chloride and mercuric chloride, respectively, where X^{n+} represents the mercury species existing in mercuric chloride.

resin.²³ The effect of the strong affinity of Cl^{-} for Hg^{2+} was also observed when Hg^{2+} was extracted from aqueous HNO_3 solution into the CMPO, PBP, and dodecane mixture in the presence and absence of Cl^{-} .²⁴ Mercury was extracted into the organic medium from acidic solution of $\leq \sim 2$ M HNO_3 as $HgCl_2$ species.

Conversely, when the forward exchange $Na^{+}_{(m)} \rightleftharpoons *X^{n+}_{(s)}$ was studied with $HgCl_2$ salt solution (pH 3.3 and 0.2 M), where X refers to mercury species present in $HgCl_2$ salt solution and n is the charge on the species, no appreciable exchange was observed over a long period of time, showing poor selectivity of mercury ion over Na^{+} for the membrane from $HgCl_2$ solution. Again, the result can be explained by the fact that the concentration of $HgCl^{+}$ is very low (~ 0.1 mol percent of $HgCl_2$ concentration) and thus $HgCl^{+}$ cannot replace Na^{+} from the ion-exchange sites appreciably. Thus, the results of isotopic- and ion-exchange kinetics studies reflect the quite different speciation of mercury in the presence of NO_3^{-} and Cl^{-} in the solution, as shown in the speciation diagrams.

In order to further confirm the species that is transported from the $HgCl_2$ solution, transport rates of Cl^{-} as well as mercury ion across the membrane were measured using $HgCl_2$ solutions in both of the compartments. The experiments were done using ^{36}Cl and ^{203}Hg radiotracers. For comparison, the Cl^{-} transport rate across the membrane was also measured using NaCl solution in both of the compartments. Figure 7 shows the variation of the ratio of Cl^{-} as well as mercury ion radioactivity in the receiver compartment (C_r) to its radioactivity in the feed compartment (C_f) as a function of time. It is evident from this figure that the ratio C_r/C_f varies linearly as a function of time (t_k) up to about 30% transfer of the radiotracers from the feed compartment to the receiver compartment. It is interesting to observe that the slopes of the C_r/C_f versus t_k curves for both of the ions are practically the same when $HgCl_2$ solutions were used, while the slope is significantly lower for Cl^{-} when NaCl solutions were used. Under this steady state condition, the permeability coefficient of the tracer can be obtained from the slope of the curve using the equation^{23,25}

$$P(\text{exp}) = \left[\frac{VL}{A} \left(\frac{d(C_r/C_f)}{dt} \right) \right] \quad (4)$$

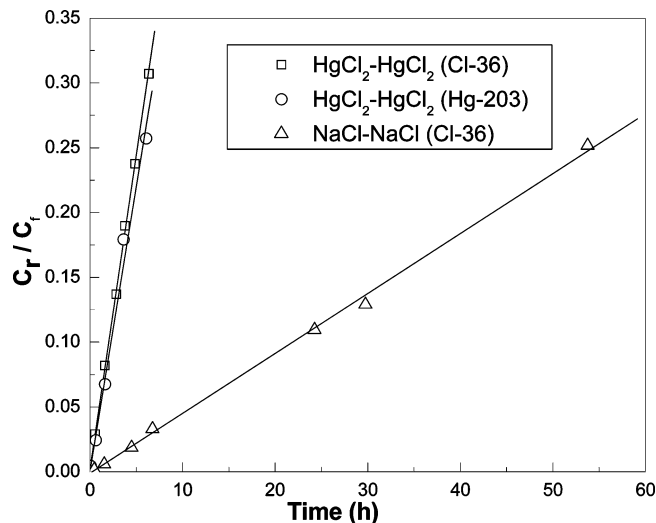


Figure 7. Variation of the ratio of mercury and chloride ion radioactivity in the receiver compartment (C_r) to its radioactivity in the feed compartment (C_f) as a function of time.

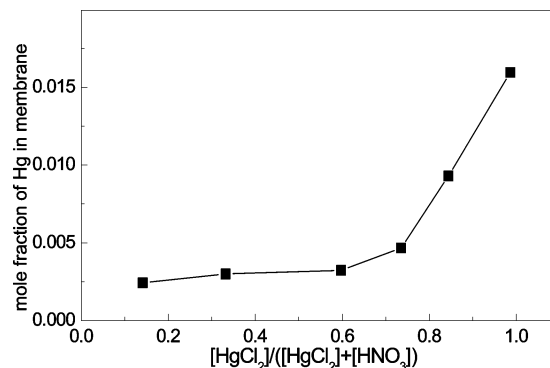


Figure 8. Equilibrium uptake of mercury from a set of equilibrating solutions containing 0.01 M $HgCl_2$ and 0.02 M HNO_3 in different proportions with the total number of moles of $HgCl_2$ and HNO_3 kept constant. The x-axis refers to the ratio of moles of $HgCl_2$ to the total number of moles of $HgCl_2$ and HNO_3 . The y-axis refers to the moles of Hg divided by the ion-exchange capacity of the membrane. The pH of the solutions varied from 1.8 to 3.2.

where A is the membrane area, V is the volume of each cell compartment, and L is the thickness of the membrane. The permeability coefficients (6.4×10^{-7} cm²/s) obtained for mercury and chloride ions were practically the same when $HgCl_2$ solutions were used, while it was about an order of magnitude lower for Cl^{-} (6.7×10^{-8} cm²/s) when NaCl solutions were used. Since the membrane is not ordinarily permeable to Cl^{-} , it can be concluded that Cl^{-} is cotransported with the mercury ion presumably as 1:1 species. However, the possibility of transport of mercury as neutral $HgCl_2$ species cannot be ruled out. The slow transport rate of Cl^{-} from NaCl compared to $HgCl_2$ solution shows the perm selective behavior of the membrane in contact with NaCl solution.

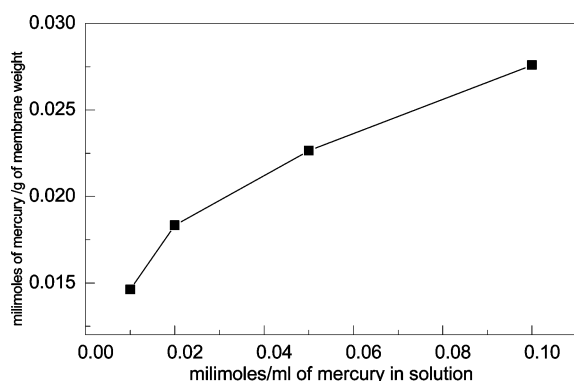
Results of measurement of equilibrium uptake of mercury from acidic $HgCl_2$ solutions of varying composition are shown in Figure 8. The positively curved nature of the curve is typical of an ion-exchange isotherm, indicating the uptake of an ionic species which is not preferred over H^{+} in the membrane. Table 1 shows the calculated concentration of different species at two different pHs of the equilibrating solution, corresponding to highest and lowest acidity. It is seen that $HgCl^{+}$ is the only ionic species that can compete with the H^{+} for the ion-exchange sites, and its uptake is expected to be highest at the lowest H^{+}

TABLE 1: Calculated Concentrations of Different Species at Two Different pH Values of the Equilibrating Solution, Corresponding to Highest and Lowest Acidity

species in solution	molar concentration	
	0.0025 M HgCl ₂ , pH 1.8	0.01 M HgCl ₂ , pH 3.2
H ⁺	1.75×10^{-2}	6.45×10^{-4}
Hg(OH) ₂	1.23×10^{-10}	3.71×10^{-8}
Cl ⁻	2.49×10^{-5}	6.70×10^{-5}
HgCl ₄ ²⁻	7.44×10^{-11}	1.85×10^{-9}
HgClOH(aq)	1.23×10^{-6}	4.26×10^{-5}
Hg ²⁺	7.18×10^{-8}	2.52×10^{-8}
OH ⁻	7.00×10^{-13}	1.63×10^{-11}
HgOH ⁺	1.36×10^{-9}	1.50×10^{-8}
Hg(OH) ₃ ⁻	1.09×10^{-23}	7.61×10^{-20}
HgCl ⁺	2.41×10^{-5}	3.09×10^{-5}
HgCl ₂ (aq)	2.47×10^{-3}	9.92×10^{-3}
HgCl ₃ ⁻	6.17×10^{-7}	6.65×10^{-6}

concentration, as observed in Figure 8. This is further confirmed from Figure 9, showing the uptake of mercury from the HgCl₂ solutions of different concentrations prepared without addition of any acid. Significant increase in mercury uptake indicates increasing favorable competition of HgCl⁺ over H⁺ for the ion-exchange sites. However, even at the highest concentration, about 2.75% of the ion-exchange sites of the membrane could be replaced by HgCl⁺.

Thus, it can be concluded from these observations that HgCl⁺ is presumably the species that is transported from the HgCl₂ solution in spite of its low concentration as the speciation diagram shows. The results show the anomalous behavior of mercury ion in the presence of Cl⁻ in the membrane transport process and the reason being the high stability constant of the species HgCl₂. The present studies also show that any ion-

**Figure 9.** Variation of equilibrium uptake of mercury with increase in HgCl₂ solution concentration at a fixed pH of 3.2.

exchange-membrane-based separation process involving mercury ion has to take into account the presence of chloride ion in the feed solution which may prevent its transport through the membrane to the receiver side. On the other hand, Hg²⁺ can be transported almost quantitatively from a chloride free medium to a receiver solution containing chloride ions.

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