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Donnan membrane equilibrium studies of mercury salts with Nafion-117 membrane

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ABSTRACT

The Donnan membrane equilibrium experiments using two compartment cell have been carried out to understand the effect of speciation on the transport behavior of mercury ion through Nafion-117 ion-exchange membrane. The mercury ions have been observed to rapidly permeate to Cl^- side from $Hg(NO_3)_2$ solution, showing the extraordinary preference of mercury ions for Cl^- ion in aqueous solution. On the other hand, from $HgCl_2$ solution, slow permeation of mercury ions through the membrane has been observed. Also the transport of mercury ion from $HgCl_2$ solution has been found to be higher than expected based on Donnan membrane equilibrium principle considering the ionic concentration of $HgCl_2$ calculated using speciation diagram. This has been attributed to the leakage of neutral $HgCl_2$ molecules through the membrane. The leakage of neutral $HgCl_2$ species through Nafion-117 membrane has been confirmed in different cationic forms of the membrane. An attempt has been made to determine the concentration of cationic mercury species in aqueous $HgCl_2$ solution using conditions of Donnan membrane equilibrium. The total cationic mercury species has been found to be higher than that predicted by speciation calculations.

Keywords: Mercury Speciation; donnan equilibrium; ion-exchange; Nafion-117; $Hg(NO_3)_2$; $HgCl_2$

1. Introduction

Techniques such as precipitation, ion-exchange, reverse osmosis and adsorption are employed for the treatment of wastewater containing mercury [1,2]. Donnan dialysis and chelation in combination with ultrafiltration are also considered to be potential techniques for removal of mercury from waste water treatment [2]. Studies on the effect of speciation of mercury on its transport behavior through ion-exchange membranes are important for designing such separation processes. Among mercury salts, $HgCl_2$ has received special attention due to its appreciable solubility in water and its high toxicity [3]. Literature indicates that it mostly exists as neutral $HgCl_2$ molecule [4]. On the other hand, mercury exists as Hg^{2+} ion in acidic $Hg(NO_3)_2$ solution due to its ionic nature and hydrolyzes at higher pH.

Ion-exchange membranes allow counter-ions 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 such as Donnan dialysis and electrodialysis [5]. Nafion-117 is an poly(perfluorosulfonic) acid ion-exchange membrane having PTFE backbone

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with pendant side chains containing -SO_3H groups. The membrane is extensively used in many Donnan and electrodialysis based applications such as in chlor-alkali industries [6]. There is limited literature on the transport behavior of mercury ions through ion-exchange membranes. Oehmen et al. studied the removal of heavy metals from drinking water supplies using an ion-exchange membrane bioreactor [7]. Ersoz has reviewed the use of liquid membranes containing calixarene carriers for selective transport of mercury [8].

In our earlier studies on isotopic and counter-ion-exchange, marked differences in the diffusion of mercury ions through Nafion-117 membrane were observed depending upon the type of anion present in the solution [9]. The self-diffusion coefficients for mercury ions in the membrane were determined which indicated that the mercury ions diffused into the membrane from $HgCl_2$ solution mainly as monovalent species while from the $Hg(NO_3)_2$ solution, the mercury ions diffused into the membrane as bivalent cation.

In this work, Donnan membrane equilibrium between two compartments separated by Nafion-117 membrane has been studied. Different mercury salt solutions ($HgCl_2$, $Hg(NO_3)_2$) and sodium salt solutions (NaCl, $NaNO_3$) were taken in the two compartments. The results have been interpreted in terms of different speciation behavior of $Hg(NO_3)_2$ and $HgCl_2$ salt solutions and the present work broadly corroborates our earlier observations from the diffusion experiments [9]. An attempt has been made to estimate the total cationic concentration in aqueous $HgCl_2$ solution. This has been done using the principle given in Ref. [10] and the results have been compared with the speciation calculations. Two compartment experiments containing $HgCl_2$ and H_2O on the two sides of the membrane have been carried out in order to study the leakage rate of $HgCl_2$ through the ion-exchange membrane. In order to study the effect of water content of the membrane on the leakage rate, the different cationic forms of the membrane have been used in the experiments.

2. Speciation of mercury

In our earlier work, the speciation calculations of mercury in Cl^- and NO_3^- salt solutions were carried out as a function of pH using the chemical equilibrium modeling software MINTEQA2 [11]. The major species in $Hg(NO_3)_2$ solution was found to be Hg^{2+} till pH 2, beyond which hydroxide precipitate was observed. In $HgCl_2$ solution in the pH range 2–7, mercury was found to practically exist as neutral $HgCl_2$ molecule. Concentration of $HgCl^+$ is also very small, about 0.1% of $HgCl_2$ concentration.

3. Experimental

Analytical grade chemicals ($HgCl_2$, HgO, NaCl and $NaNO_3$), deionized water (18 MΩ/cm, Gradient A-10 model, Milli-Q USA) and Analytical grade HNO_3 (Merck, Germany) were used in the present work. $Hg(NO_3)_2$ solution was prepared dissolving a known amount of HgO in 0.01 M HNO_3. The pH of the resulting solution was ~2 above which $Hg(OH)_2$ precipitated [4]. $HgCl_2$ solution was prepared by dissolving a known amount of $HgCl_2$ in water. The pH of the solution was measured as 3.3. The observed pH was due to hydrolysis of $HgCl_2$ to HgClOH [4]. Nafion-117 ion-exchange membrane with an equivalent weight of 1,100 g and thickness of 178 µm was used. Radiotracers ^{203}Hg and ^{22}Na were obtained from the Board of Radiation and Isotope Technology, Mumbai, India. All the experiments were carried at room temperature ($T = 27^oC$).

The Donnan membrane equilibrium experiments were carried out in a two compartment dialysis cell separated by Nafion-117 membrane. Volume of each compartment was 25 ml. A set of experiments involving exchange of mercury and Na^+ counter-ions were carried out taking 0.05 M mercury salt solution (chloride or nitrate) in one compartment and 0.1 M sodium salt solution (chloride or nitrate) in other compartment. Another set of four experiments involving transport of neutral mercury species were carried out taking 0.2 M mercuric chloride solution in one compartment and deionized water in the other compartment. The membranes equilibrated with H^+, Na^+, Cs^+ and $HgCl_2$ solutions were used in the experiments. The solution in each compartment was continuously stirred during the course of experiment to minimize the effect of film diffusion. The solution in one of the compartments was initially spiked with ^{203}Hg radiotracer giving ~1500 counts per minute per 100 µl solution. The radiotracer spiked compartment is subsequently referred as the feed compartment while the other compartment is referred as receiver compartment. The radioactivity in each compartment was measured pipetting out 100 µl of solution at regular time interval until the equilibrium was reached. The counting of the samples was done in a NaI (Tl) detector coupled to 4k Multichannel Analyzer. Each experiment was repeated two-to-three times.

In order to estimate the total ionic concentration in aqueous $HgCl_2$ solution, the membrane was loaded with Na^+ ion, spiked with ^{22}Na radiotracer and used in two compartment cell. $HgCl_2$ (0.2 M) solution was taken in one compartment while the other compartment was filled with HNO_3 solution of different concentrations (0.004 M and 0.0008 M). The distribution of ^{22}Na radiotracer in the two compartments was measured after about an hour during which no significant transport of salt/ions was expected.

4. Results and discussion

Fig. 1 shows the results of Donnan membrane equilibrium experiments. The results are also summarized in Table 1. According to Donnan membrane equilibrium principle [12], the ratio of equilibrium concentration of the counter-ions in the solutions in the two compartments is given by:

$$\left(\frac{C_{i,\text{donor}}}{C_{i,\text{acceptor}}}\right)^{1/Z_i} = \left(\frac{C_{j,\text{donor}}}{C_{j,\text{acceptor}}}\right)^{1/Z_j} \tag{1}$$

where C_i and C_j refers to the concentration of *i*th and *j*th species and Z_i and Z_j are the charges on the *i*th and the *j*th species. When $Hg(NO_3)_2$ (pH ~ 2) and $NaNO_3$ (pH = 7) solutions were taken in the feed and receiver compartments respectively, the calculated equilibrium concentration following Donnan membrane equilibrium principle for the Hg^{2+} ion was found to be 47% (see Table 1). The experimental value of 50% is close to what is expected. The calculated pH in the feed and receiver compartments at equilibrium was found to be 2.3. At this pH, as seen from the speciation diagram [9], the precipitation of mercury is not expected.

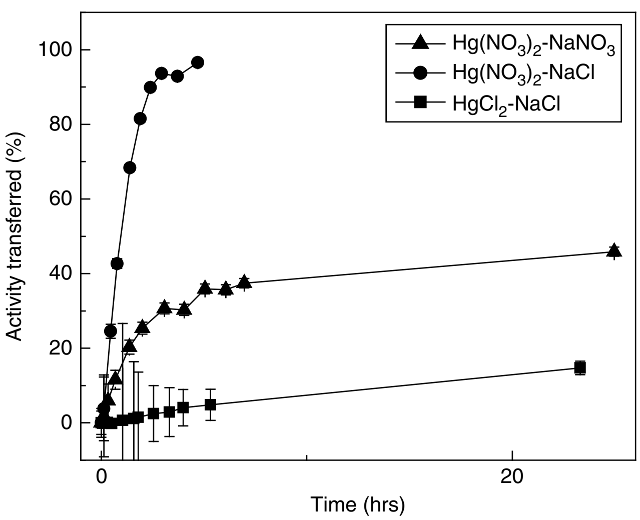

Fig. 1. The time profile of radioactivity transferred to the receiver compartment in Donnan equilibrium experiments involving the exchange $X^{n+} \leftrightarrows Na^+$, where X^{n+} is the species of mercury present in mercury salt solution.

On the contrary, when $Hg(NO_3)_2$ (pH ~ 2) and NaCl (pH = 7) solutions were taken in the feed and receiver compartments respectively, nearly 100% of Hg^{2+} ion transported rapidly through the membrane to the receiver side violating the prediction of Donnan equilibrium (see Table 1). Also the rate of transport of Hg^{2+} ion in this case was much faster than the previous experiment. As observed from the speciation diagram given in Ref. [9], mercury exists mostly as neutral species in $HgCl_2$ solution. Thus the equilibrium distribution of Hg^{2+} between $Hg(NO_3)_2$ and NaCl solutions can be understood from the fact that the Hg^{2+} ions form neutral $HgCl_2$ species in the receiver (NaCl) compartment, thereby making the free Hg^{2+} ion concentration negligible and allowing almost quantitative transport of Hg^{2+} from the $Hg(NO_3)_2$ compartment. The faster rate of transport can be understood as being due to the prevalence of high concentration gradient of mercury ion across the membrane as a result of formation of neutral $HgCl_2$ species in the receiver side. The faster rate could also be due to the leakage of the Cl^- ion in the membrane as was observed during the ion exchange kinetics study of $Hg^{2+}_{(m)} \leftrightarrows Na^+$ with NaCl as external salt solution [9]. It is to be noted that similar affinity of Cl^- ion for Hg^{2+} was observed when Hg^{2+} was extracted from aqueous HNO_3 solution into *n*-octyl (phenyl) *N*,*N*-diisobutyl carbomoyl methyl phosphine oxide (CMPO), Tributylphosphate (TBP) and dodecane mixture in presence and absence of Cl^- ion [13]. Mercury was extracted into the organic medium from acidic solution of less than or equal to ~2M HNO_3 as $HgCl_2$ species.

Table 1
Composition of the two compartments for different sets of experiments

Expt. No.	Composition in the two compartments		Donnan equilibrium concentration (%) in the receiver compartment	
	Feed	Receiver	Expected	Observed
1.	$Hg(NO_3)_2$ (pH ~ 2)	$NaNO_3$ (pH = 7)	47	50 ± 3
2.	$Hg(NO_3)_2$ (pH ~ 2)	NaCl (pH = 7)	47	97 ± 5
3.	$HgCl_2$ (pH = 3.3)	NaCl (pH = 7)	50[a]	15[c] ± 1
			0.1[b]	

[a]Assuming fully dissociated $HgCl_2$.
[b]Based on the ionic concentration of $HgCl_2$ calculated using speciation diagram [9].
[c]Not equilibrium value (see text for explanation).

When $HgCl_2$ (0.05 M) and NaCl (0.1 M) solutions were taken in the feed and the receiver compartment respectively, the rate of mercury transport was found to be very sluggish relative to the transport rate of mercury from $Hg(NO_3)_2$ solution (Fig. 1). The equilibrium did not reach even after 25 h. This slow kinetics indicate the mechanism of transport is different relative to the $Hg(NO_3)_2$ solution. This can be explained based on the negligible cationic concentration present in mercuric chloride solution, leading to negligible ratio of $HgCl^+$ and Na^+ ion concentration (of the order of 0.0005) in the two compartments. Thus, according to Donnan equilibrium principle (Eq. (1)), hardly any Na^+ ion transport is expected to the other compartment while all the cationic mercury species (~0.1% of the $HgCl_2$ concentration) should be transported to the receiver side. However, it was observed that the transport of mercury radiotracer to the receiver side is higher than this prediction, possibly indicating the slow leakage of neutral $HgCl_2$ molecules through the membrane to the receiver side.

An attempt was made to estimate the total cationic concentration in the mercuric chloride solution under the given experimental conditions [10]. This was done by studying the distribution of $^{22}Na^+$ radiotracer, initially present in the membrane, in the two compartments containing $HgCl_2$ and HNO_3 solution respectively. Following the conditions for Donnan membrane equilibrium, the sodium tracer is expected to distribute itself in the two compartments in the ratio of cationic concentration of the solutions on the two sides, as given by:

$$\frac{^{22}Na_I}{^{22}Na_{II}} = \frac{IC_I}{IC_{II}} \quad (2)$$

where $^{22}Na_I$ and $^{22}Na_{II}$ represent the count rate of the gamma ray peak of ^{22}Na in I and II compartment and IC_I and IC_{II} represent the cationic concentration in the two compartments respectively. The use of sodium tracer $^{22}Na^+$ permitted convenient and accurate measurement of the relative concentration of sodium ion in the two solutions at an absolute concentration too low to affect the concentration of other ions in the solutions [10]. In the case when the cationic concentrations on the two sides are equal, the ratio of the tracer activity is expected to be unity. When equimolar $HgCl_2$ and HNO_3 solutions were taken in the two compartments, all the $^{22}Na^+$ was observed to be distributed to the HNO_3 side, clearly indicating the presence of very low concentration of ionic species in $HgCl_2$ solution. Since the speciation calculation of $HgCl_2$ solution shows the presence of only 0.1% of the $HgCl^+$ species in $HgCl_2$ solution (~0.0002 M in a 0.2 M $HgCl_2$ solution), the experiments were carried out at a lower H^+ concentration (0.004 M and 0.0008 M) in the acidic compartment [9]. The total cationic concentration present in the compartment I was calculated using Eq. (2) and includes the concentration of the cationic mercury species as well as of the hydrogen ion present naturally in $HgCl_2$ solution (pH = 3.3) due to its hydrolysis. Thus, the cationic concentration of the mercury species present in $HgCl_2$ solution was obtained from the total cationic concentration by subtracting the known hydrogen ion concentration (pH = 3.3) present in the solution. The results have been summarized in Table 2. The $HgCl^+$ concentration obtained is higher by a factor of about 2 from what is obtained from the speciation calculations.

In order to study the leakage of $HgCl_2$ through membrane, experiments were carried out taking $HgCl_2$ solution in one compartment and deionized water in the receiver compartment. Since the receiver solution does not contain any ionic species, the possibility of counter ion exchange between the two compartments is excluded. Hence, the transfer of any mercury activity to the receiver solution is indicative of the transport of neutral mercury species which in the present case is $HgCl_2$ molecule as observed from the speciation calculations [9]. The leakage of neutral mercuric chloride species through the membrane was studied with the membrane equilibrated with H^+, Na^+, Cs^+ and $HgCl_2$ solution. This was done to see the influence of the presence of different cations in the membrane on the transport rate of mercury species. These cations were chosen as they represent different water content in the membrane. As seen from Fig. 2, the mercury activity is slowly transported to the receiver compartment in all the cases, indicating the

Table 2
Cationic concentration of $HgCl_2$ determined using the principle given in ref. [10]

Concentration of species in the two compartments (M)		Activity ratio ($^{22}Na_I/^{22}Na_{II}$)	Concentration of total cationic species in compartment I (M)	Concentration of cationic species of mercury in compartment I (M)
$HgCl_2$	HNO_3			
0.2	0.2	Practically no ^{22}Na activity went to the first compartment		
0.2	0.004	0.263	1.05E-3	5.50E-4
0.2	0.0008	1.31	1.04E-3	5.48E-4

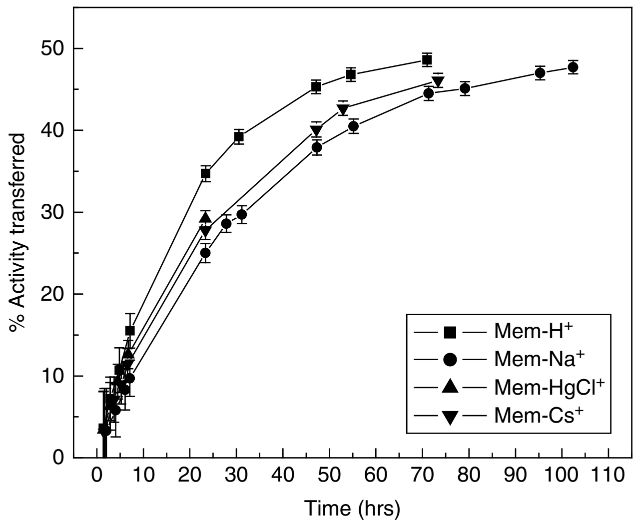

Fig. 2. The time profile of activity in the receiver compartment in Donnan equilibrium experiments. The equilibrating solution containing mercuric chloride in the feed compartment and deionized water in the receiver compartment with membrane in different ionic forms were used.

leakage of neutral $HgCl_2$ molecules. From the figure, it can be seen that the rate of transport of $HgCl_2$ molecules across the membrane is comparable in all the cases except when the membrane is loaded with H^+. The faster rate of transport of $HgCl_2$ molecules when the membrane is loaded with H^+ ion may be because of higher water content of the membrane in H^+ form which may be facilitating $HgCl_2$ transport across the membrane.

5. Conclusions

The present studies show that the speciation of mercury in different salt solutions strongly influences the transport behavior of mercury through a cation exchange membrane and the results of Donnan membrane equilibrium studies confirm the behavior expected from the diffusion experiments and speciation calculations. The $HgCl^+$ concentration in $HgCl_2$ solution is found to be higher than what is expected from speciation calculation. Slow leakage of neutral $HgCl_2$ molecules through Nafion-117 membrane is observed.

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