BEHAVIOUR OF POLYMER (POLY(VINYL CHLORIDE)) MEMBRANE SYSTEMS

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Summary

Radiotracer studies are discussed for alkaline earth metal ion-permeation through poly(vinyl chloride) matrix membranes containing sensors based on organophosphates and on the tetraphenylborates of the complex of barium with a polyethoxylate. There is selective permeation of calcium ions, from among alkaline earth cations, through the phosphate-based membranes, but the polyethoxylate membranes do not permeate ions to any significant extent.

The phosphate-based membranes maintain stable current flows over prolonged periods under conditions of applied potential and are not affected by polarity reversals. For example, current flows of 5 - 6 μA are maintained for 2 V applied potential. Current flows fall rapidly for the polyethoxylate membranes and do not recover on repeated polarity reversal of the applied potential.

The possibility of the permeation of metal ions of the first transition series through the phosphate-based membranes is discussed briefly.

Introduction

The use of poly(vinyl chloride) (PVC) as a support matrix for liquid ion-exchangers produces membranes that are by now well established as sensor membranes for cations and anions in ion-selective electrodes [1, 2]. The devices are analogous to glass membrane electrodes for sensing hydrogen ions.

This paper summarises radiotracer studies on PVC matrix membranes containing liquid ion-exchangers and the data are presented on the premise that the observed ion permeation behaviour may be of wider interest than simply to demonstrate an ion transport mechanism for ion-selective electrode response. One such area of possible interest is that of separator membranes in electrochemical energy storage.

The mechanism of selective ion-transport through the PVC membranes containing trapped liquid ion-exchangers is prompted by the parallel patterns between selectivity coefficients of the electrodes with the ion-pair extraction

constants for the related solvent extraction systems. The degree of parallelism is strikingly close for systems based on tetraalkylammonium sensors used for nitrate and perchlorate ion-selective electrodes [3]. There is also a similar pattern [4, 5] between electrode selectivity coefficients and extraction coefficients of alkaline earth cations from 4M sodium nitrate into di(2-ethylhexyl)phosphoric acid in benzene (Table 1).

TABLE 1

Extraction coefficients of alkaline earth cations from 4M sodium nitrate into di(2-ethylhexyl)phosphoric acid in benzene and $k_{Ca,B}^{pot}$ data for PVC matrix membrane ion-selective electrodes with dialkylphosphate sensors

Counter-ion B	Log of extraction coefficient*		$k_{Ca,B}^{pot}$ **		
	pH = 7.0	pH = 5.2	Ca di(2-ethyl-hexyl)phosphate sensor with decan-1-ol 25 °C	Orion 92-20-02 liquid ion-exchanger	
				25 °C	35 °C
Be^{2+}	4.3	4.3	2.6 (5×10^{-5})	12.0 (5×10^{-5})	14.0 (5×10^{-5})
Mg^{2+}	1.2	1.4	1.0	0.01 (4×10^{-1})	0.052 (4×10^{-4})
Ca^{2+}	0.9	2.2	1.0	1.0	1.0
Sr^{2+}	−0.2	0.1	0.5 (4×10^{-4})	0.05 (4×10^{-4})	0.09 (4×10^{-4})
Ba^{2+}	−0.6	−0.5	0.5 (4×10^{-4})	0.002 (4×10^{-4})	0.01 (4×10^{-4})

*Based on data from ref. 4.
**Data from ref. 5. Numbers in parentheses are the molarity of the interfering counter-ion, B.

The radiotracer studies [5 - 10] summarised here are for cation permeation through PVC matrix membranes containing sensors based, firstly on organophosphates, and secondly on complexes of a nonylphenoxypolyethoxylate with metal ions. The main emphasis of the organophosphate systems relates to selective calcium ion permeation, whilst barium ion permeation characterises those based on the polyethoxylate complexes. Most of the data presented are for conditions of free diffusion under zero potential conditions, but some experiments under applied potentials are also discussed.

Methods

Membranes were prepared by standard procedure [11, 12], that is, by dissolving PVC (0.17 g) in a solution of liquid ion-exchanger (0.4 g, and consisting of 0.04 g of sensor plus 0.36 g of plasticising solvent mediator) in tetrahydrofuran (6 cm^3) and removing the solvent by slow evaporation from a shallow glass ring (35 mm dia.) resting on a flat glass surface at room temperature. Monitoring involved the movement of a radiotracer at 35 °C between two solutions (10^{-3} M metal chlorides) separated by the master membrane, cemented to a wide bore PVC tube in an assembly permitting the

solutions to be continuously stirred and sampled from time to time in order to take radioactive counts [5, 9, 10]. The migration of radiotracers is conveniently represented by $d(C''/C')/dt$ for those conditions where the tracer flux between the initially inactive (tracer concentration, C'') and active (tracer concentration, C') solutions increases linearly with time [5 - 8], but permeation through the alkoxylate type membranes was insufficient for such a representation [9].

The tracer in the membrane at the end of some of the organophosphate membrane experiments was monitored by placing the membrane, sliced off from the supporting PVC tubing, on a planchette under the Geiger–Müller tube in the same position as the specimens of solution sampling [6]. In the alkoxylate membrane experiments, and for some of those based on organophosphates, both sides of the membranes were monitored for tracer, and finally the membranes were dissolved in tetrahydrofuran in order to determine the total tracer uptake [9, 10].

Most experiments on organophosphate membranes relate to calcium-form exchanger [5 - 10], but some are based on the exchanger converted to the appropriate ionic form [6 - 10]. In some cases, hydrochloric acid was added to the 10^{-3}M metal chloride solution on one side of the membrane [6].

Results and discussion

Orion 92-20-02 liquid ion-exchanger in membranes at zero applied potential Experiments with ^{45}Ca

Table 2 summarises $d(C''/C')/dt$ data for calcium ion migration through the membrane (based on dialkylphosphate plus dioctylphenyl phosphonate in PVC) into various metal chlorides. The low $d(C''/C')/dt$ values for such

TABLE 2

$d(C''/C')/dt$ data for solution/membrane systems [5]
Membranes: Calcium form Orion 92-20-02 liquid ion-exchanger in PVC. (Exchanger Batch A.)

Series	Solution A(internal) (10^{-3}M solution)	Solution B(external) (10^{-3}M solution)	$d(C''/C')/dt$ (10^{-7} s^{-1})
1	^{45}CaCl$_2$	CaCl$_2$	18
2	CaCl$_2$	^{45}CaCl$_2$	19
3	^{45}CaCl$_2$	BeCl$_2$	2.5
4	BeCl$_2$	^{45}CaCl$_2$	2.2
5	^{45}CaCl$_2$	MgCl$_2$	8.0
6	MgCl$_2$	^{45}CaCl$_2$	8.4
7	^{45}CaCl$_2$	SrCl$_2$	8.5
8	SrCl$_2$	^{45}CaCl$_2$	9.1
9	^{45}CaCl$_2$	BaCl$_2$	8.4
10	BaCl$_2$	^{45}CaCl$_2$	7.5

migration into chlorides of magnesium (Series 5 and 6), strontium (Series 7 and 8), and barium (Series 9 and 10) relative to those for migration between calcium solutions (Series 1 and 2) match the low electrode selectivity coefficients ($k_{Ca,B}^{pot}$) for these ions (Table 1). This pattern may be attributed to the relative reluctance of the B ions to even enter the membrane, as illustrated by the trend of lower extraction coefficients (Table 1). This must decrease the migration of calcium ions in the reverse direction.

The low $d(C''/C')/dt$ values for the migration of calcium into beryllium solutions at the 10^{-3}M level (Series 3 and 4) seem surprising in terms of the explanation for magnesium, strontium and barium. It is possible, however, that beryllium ions block the liquid ion-exchanger sites because of the high affinity of the exchanger for beryllium, as shown by extraction and $k_{Ca,B}^{pot}$ data (Table 1). Kinetic forces may also be at work as in the exchange of solvent water with hydrated metal ions which, in the case of beryllium, has a rate constant over six orders of magnitude less than that for calcium [13].

Experiments with an extended range of tracers

Many of the above explanations have been tested with a wider range of tracers and by taking forms other than calcium in the liquid ion-exchanger of the membrane [6]. The relevant data, but referred to different batches of Orion 92-20-02 liquid ion-exchanger, are summarised in Table 3 along with an estimate, based on membrane surface counts, of the proportion of radiotracer remaining in the membrane at the end of the experiment.

The very short half-lives of magnesium isotopes have prevented their use in these studies. ^{89}Sr and ^{133}Ba (Series 13 - 16), however, show, by the near zero values for $d(C''/C')/dt$, that there is little or no tendency for strontium or barium ions to pass through the PVC matrix membranes in strontium, barium and calcium forms into solutions containing strontium or barium chloride. This inhibition of migration, because of the low affinity of strontium and barium for sites in the liquid ion-exchanger, is confirmed by the relatively low proportion of radiotracer associated with the membrane at the end of the various experiments (Table 3). The greater relative permeation of calcium ions between calcium chloride and strontium or barium chloride through calcium-form membranes (Series 1, 2, 7 - 10, 11 and 23) is to be expected in view of the higher affinity of calcium ions for the exchanger.

The low affinity of strontium and barium ions for the sites of the PVC-trapped liquid ion-exchanger is confirmed by Series 23 - 25. Here, calcium ions permeate through barium (Series 24) and strontium (Series 25) membranes at about the same rate as through calcium membranes (Series 23). These experiments also rule out slow kinetics as a factor leading to low permeation by barium and by strontium ions.

The strong affinity of beryllium ions for the ion-exchange sites on the membrane is indicated by Series 13 and 17 where a high proportion of the tracer collects in the membrane, with little or none appearing in the other solution. The trend is regular for the few experiments conducted but, because of the very low count-rates in these experiments, the possibility of

TABLE 3

$d(C''/C')/dt$ data and membrane radiotracer content for solution/membrane systems [6]
Membranes: Various forms of Orion 92-20-02 liquid ion-exchanger in PVC.

Series	Form of exchanger in membrane	Active solution* $(10^{-3}M)$	Inactive solution $(10^{-3}M)$	$d(C''/C')/dt$ $(10^{-7} s^{-1})$	Proportion of radiotracer in membrane at end of experiment (%)
Batch B of Orion 92-20-02 liquid ion-exchanger					
11	Ca	$CaCl_2$	$CaCl_2$		1.7
12	Be	$BeCl_2$	$BeCl_2$	0	39 Two
					72 experiments
13	Sr	$SrCl_2$	$SrCl_2$	0.23	0.5
14	Ba	$BaCl_2$	$BaCl_2$	0	0.4
15	Ca	$SrCl_2$	$SrCl_2$	0	0.3
16	Ca	$BaCl_2$	$BaCl_2$	0	0.7
17	Ca	$BeCl_2$	$BeCl_2$	0	93 Two
					94 experiments
18	Ca	$CaCl_2$ in 0.01M HCl	$CaCl_2$	0	0.3
19	Ca	$CaCl_2$	$CaCl_2$ in 0.01M HCl	5.5	0.7
20	Ba	$BaCl_2$ in 0.01M HCl	$BaCl_2$	0	very low (<0.1)
21	Ba	$BaCl_2$	$BaCl_2$ in 0.01M HCl	0	0.6
22	Ca	$BaCl_2$ in 0.01M HCl	$BaCl_2$	0	very low (<0.1)
Batch of Orion 92-20-02 liquid ion-exchanger					
23	Ca	$CaCl_2$	22	3.5	
24	Ba	$CaCl_2$	$CaCl_2$	20	2.3
25	Sr	$CaCl_2$	$CaCl_2$	22	2.9

*Labelled with ^{7}Be, ^{45}Ca, ^{89}Sr, or ^{133}Ba.

some beryllium ions passing through the membrane into the other solution should not be entirely discounted.

Effect of acid on permeation

An interesting feature is the effect of acid, demonstrated by Series 18, 19 and 22 (Table 3) with calcium membranes. Based on data in Table 2, these should give finite values for $d(C''/C')/dt$, but this is observed only in Series 19, and the membranes in Series 18 and 22 picked up only relatively small amounts of radioactive calcium. This pattern is consistent with reports on the transport of ions against their concentration gradients [14, 15] whereby cations will permeate through a membrane into acid solutions containing higher levels of the same cations. The preferential permeation of the proton in one direction is balanced by permeation of the cation in the reverse direction in order to maintain the charge balance. It might be assumed that such is the case in Series 18 and 22; the assumption seems to be confirmed by the

lower permeation rate in Series 19 compared with that of Series 11 where the acid was on the other side of the membrane from that of the tracer.

Series 20 and 21 have just barium ions in both the solutions and in the membrane, and following the low affinity of barium ions for membrane sites, little permeation by barium ions can be expected.

Effect of solvent mediator on membranes containing calcium bis di(4-1,1,3, 3-tetramethylbutylphenyl)phosphate under zero applied potential

Compared with all the batches of Orion 92-20-02 liquid ion-exchanger examined to date (Tables 2 - 4) $d(C''/C')/dt$ is high for membranes containing dioctylphenyl phosphonate or trialkylphosphate (except tributylphosphate) solvent mediator in conjunction with di(4-1,1,3,3-tetramethylbutylphenyl)-phosphate sensor (Table 4). The sensor, particularly in conjunction with dioctylphenyl phosphonate or tripentylphosphate solvent mediator, gives superior calcium ion-selective electrodes [16, 17] and the greater ion transport can be significant in other applications of these membranes. It is otherwise difficult to draw conclusions from the data. It is noted, however, that the sensor with tributylphosphate solvent mediator gives electrodes of shorter range and lifetime, although selectivity with respect to various cations is similar to other members [16].

TABLE 4

$d(C''/C')/dt$ data for solution/membrane systems with membranes containing calcium bis-di(4-1,1,3-3-tetramethylbutylphenyl)phosphate and various solvent mediators in PVC [7] 10^{-3} M calcium chloride on each side of membrane, one side active with ^{45}Ca.

Series	Solvent mediator	$d(C''/C')/dt$	Proportion of radiotracer in membrane at end of experiment (%)	Detection limit of corresponding ion-selective electrode (M Ca^{2+})	Ion-selective electrode lifetime
26	Batch D of Orion 92-20-02 liquid ion-exchanger (for reference)	18	4.0	7.5×10^{-6}	3 months
27	Dioctylphenyl-phosphonate	32	9.6	3.0×10^{-6}	3 months
28	Tributylphosphate	2.6	5.2	1.2×10^{-5}	1 week
29	Tripentylphosphate	59	12	6.0×10^{-6}	3 months
30	Trioctylphosphate	37	6.0	1.1×10^{-5}	4 weeks
31	Tri(1,1,3,3,-tetra-methylbutyl)phosphate	25	6.5	6.0×10^{-6}	3 months

It is the solvent mediator that promotes the electrode selectivity features of the organophosphate sensors and with decanol in place of dioctyl-phenyl phosphonate there is little difference in electrode selectivity between calcium and magnesium ions [18]. The equal sensing of calcium and of

magnesium ions by the divalent ion electrode based on Orion 92-20-32 divalent exchanger (dialkylphosphate plus decanol solvent mediator) is reflected in the value of 32×10^{-7} s^{-1} for d(C''/C')/dt for permeation of ^{45}Ca from calcium chloride through the membrane of the exchanger in PVC into counter solutions of calcium chloride and magnesium chloride, respectively [8].

Metal polyethoxylate adducts in membranes

Tetraphenylborates (TPBs) of barium complexes with certain polyethoxylates, for example, Antarox CO880 (a nonylphenoxypoly(ethaneoxy)-ethanol with 30 ethaneoxy units), are useful sensors for barium ion-selective electrode membranes when used with 2-nitrophenylphenyl ether in PVC [19]. The adduct has the stoichiometry Ba$_{2.5}$.Antarox CO-880.TPB$_5$.

Experiments under zero applied potential

Relative to calcium ion permeation in the alkyl- and alkyl-phenylphosphate membranes discussed above, there is very little permeation of barium ions from initially radioactive barium chloride solutions through the barium-form membranes into initially inactive barium chloride solution. This may be deduced from the smallness of the ratio(C''/C') of tracer counts in the initially inactive solution (C'') to those of the active solution (C') ($\leqslant 0.03$, even after several hundred hours) [9]. Nevertheless, in counts of the membranes, there is a continued uptake of ^{133}Ba with time (Table 5).

TABLE 5

^{133}Ba uptake [9] by eight membranes containing Ba$_{2.5}$.Antarox CO.880.TPB$_5$ (0.04 g) plus 2-nitrophenylphenyl ether (0.36 g) in PVC (0.17 g)
Active solution: 10^{-3}M ^{133}BaCl$_2$. Inactive solution: 10^{-3}M BaCl$_2$.
Series: 32

Membrane no.	Time (h)	C''/C'	C_{act}/C_{inact}	Uptake of ^{133}Ba by membrane (%)
1	2	—	3.2	1.0
2	4	0.01	2.4	1.8
3	6	—	3.1	2.4
4	24	0.01	2.1	4.0
5	48	0.02	1.4	5.6
6	72	0.01	1.8	6.6
7	144	0.01	1.6	6.6
8	503	0.03	1.4	Not counted

The uptake of ^{133}Ba by the membranes (last column of Table 5) and the small degree of permeation (C''/C') suggests that the stabilization of ions by the polyethoxylate ligand is important in relation to selective electrode response in addition to the simple availability of pathways for primary ion transport through the membrane [9]. The values of C_{act}/C_{inact} (Table 5), namely, the ratio of counts on the active side of the membrane to those on

the inactive side, are consistent with the diffusion with time of ^{133}Ba into the membranes, or away from the radioactive solution/membrane interface. Such diffusion does not occur within membranes of 2-nitrophenylphenyl ether alone in PVC and occurs at a very much reduced level when the PVC with 2-nitrophenylphenyl ether contains Antarox CO-880 instead of Ba$_{2.5}$. Antarox CO-880.TPB$_5$.

Experiments under applied potential

These have been carried out [10] on PVC (0.17 g) matrix membranes containing either

(i) Ba$_{2.5}$ Antarox CO-880.TPB$_5$ (0.04 g) plus 2-nitrophenylphenyl ether (0.36 g);

(ii) Orion 92-20-02 calcium liquid ion-exchanger (0.4 g). In these cases, potentials were applied from a purpose-built potentiostat to electrodes placed in solutions on each side of the membrane.

Membranes (i) were unable to maintain stable current flows. For example, for applied potentials of 2 V, the currents of 15 μA decayed to 7 μA in 4 h, recovered on reversal of the polarity and fell to $<5\ \mu$A in the next 4 h. There was no further evidence of significant recovery of current upon further potential reversals [10].

Membranes (ii), on the other hand, are characterised by stable current flows over prolonged periods and over successive polarity reversals. For example, at an applied potential of 10 V the current was steady for the tested 24 h at 5 - 6 μA, according to membrane; the current continues at this value for successive tested periods of 25 h for repeated polarity reversals [10].

In radiotracer experiments [10], applied potentials did not promote permeation of ^{133}Ba through membranes (i) into the initially inactive solution. For membranes (ii) ^{45}Ca did not permeate against the potential gradient, but on reversal of the polarity, permeation into the inactive counter solution occurred to a far greater extent than in the absence of any applied potential.

Conclusion

Radiotracer and applied potential studies confirm the selective permeability to counter-ions of membranes made from phosphate based calcium liquid ion-exchangers contained in PVC. The migration of calcium ions through such membranes can be explained in terms of the availability of membrane pathways (which, of course, provide the means for ionic conduction as opposed to the electronic conduction of glass membranes). This migration is seen to be selective for calcium ions from among alkaline earth metal ions unless there is a blockage of the exchange sites, as with beryllium, which is preferred by the liquid ion-exchanger.

For applications in batteries and electrochemical storage systems, there will be greater interest with respect to transition metal ions and to condi-

tions of high alkalinity or acidity. While neither extreme conditions of pH nor permeation of transition metal ions have been assessed, it is possible that phosphate-based membranes containing the copper-form liquid ion-exchanger may, on the evidence of electrode selectivity coefficients [18], be worthy of investigation. Other ions, such as nickel and zinc, may behave similarly by suitable choice of solvent mediator. The polyethoxylate-based PVC membranes do not permeate ions and are also unable to withstand polarity reversals under conditions of applied potential. They are, therefore, most unlikely to have any scope as separators.

In the studies described here, attention has been focussed on the sensor providing the mechanism for ion-exchange and ion-transfer. The role of the solvent mediator cannot be overlooked, however, and proper choice of this could lead to functional separator membranes for phosphate sensors. It has been implied that the solvent mediator partly solvates the cation as well as fulfilling the role of solvent for the ion-sensor [20]. Solvent mediators also act as PVC plasticisers and can participate in selective membrane permeability of ions by solvent extraction principles in the manner discussed in the patent literature [21 - 23] for dialysis and electrodialysis using PVC membranes with plasticising mediators of organophosphorus components con-

taining the $-\overset{\textstyle |}{\underset{\textstyle \|}{\text{P}}}-$ group, or with grafted functional groups as in poly(vinyl-
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chloroethylether), poly(epichlorhydrin), poly(methylvinylketone), etc.

Acknowledgement

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