Behaviour of Solutions of Tetraalkylammonium Salts in Ethyl Bromide as Liquid Membranes

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Solutions of tetraheptylammonium bromide, iodide, nitrate, or perchlorate in ethyl bromide behave as anionic liquid membranes with ideality degrees close to 100%. In the cases of tetraheptylammonium fluoride, or chloride, the ideality degrees are about 80%. A picture of the characteristics and structures of this class of membranes is given.

Preliminary results[1] showed that solutions of tetraheptylammonium bromide in ethyl bromide (EtBr) behave as quasi-ideal anionic membranes with respect to the Br^- ion. It is the aim of the present work to give a picture of the properties of EtBr-based liquid membranes.

The physico-chemical requirements to be satisfied by the system, solvent + salt, of which a liquid membrane consists, are:

(i) The solvent should be immiscible with water (hence, the use of low-dielectric-constant organic compounds, whose solubilities in water are generally small).

(ii) The salt should be insoluble in the water phase but highly soluble in the organic phase. This high ratio of solubilities is easily obtained by using salts having large ions with organophilic character such as alkyl-substituted ammonium cations[1–4] (for anionic membranes), or anionic substituted phosphoric esthers[5] and naphthalene sulfonates[6–8] (for cationic membranes).

(iii) The electrolytic conductivity of the organic phase should be good.

(iv) The solvent-salt interactions should be such that one of the two ions of the salt stands in the liquid as "trapped charge", a concept analogous to the „fixed charge" in solid state membranes.

As a solvent for these purposes, EtBr has appropriate characteristics[9]: 1) Solubility of EtBr in H_2O at 25 °C is 0.06 mol/litre; 2) Solubility of H_2O in EtBr is 0.06 mol/litre; 3) No salting-in effect is noticed in aqueous solutions of inorganic acids[9].

The system, EtBr + Quaternary Ammonium Salt R_4NX ($X = F^-, Cl^-, Br^-, I^-, ClO_4^-, NO_3^-$; while the radical R is an aliphatic chain with a number of C atoms varying from 1 to 7), has then been investigated in order to ascertain the conditions for this system to work as a liquid membrane.

Experimental

The materials used were as follows. Aqueous acid solutions were prepared from triply distilled water and reagent-grade Carlo Erba HF, HCl, HBr, HI, HNO_3, and $HClO_4$. Ethyl bromide (Carlo Erba) was distilled before use. $(C_7H_{15})_4NCl$, $(C_7H_{15})_4NBr$, and $(C_7H_{15})_4NI$ were from Eastman Kodak. $(C_6H_{13})_4NClO_4$, $(C_7H_{15})_4NClO_4$, $(C_7H_{15})_4NNO_3$, $(C_7H_{15})_4NF$ were prepared according to

$$AgX + R_4NI \rightarrow R_4NX + AgI$$

(where $X = NO_3$, ClO_4, F; and $R = C_6H_{13}$, C_7H_{15}) in ethanolic solution. The AgI precipitate was filtered; the residual solution was treated with H_2O, thus R_4NX precipitated; the latter was subsequently filtered, frequently washed with water and recrystallised. The

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other tetraalkylammonium salts in Table 1 were normally available (Carlo Erba, Merck, Fischer, BDH, Schuchardt, Aldrich) with the required degree of purity, and were used as received, without further purification. Conductivity measurements were carried out by means of a conductivity bridge LKB type 3216 B equipped with Wagner earth, and using LKB conductivity cells. E. m. f. measurements were carried out with a Leeds & Northrup K 3 potentiometer having a type 602 Keithley electrometer (10^{14} Ohm input impedance) as a null-point detector.

All measurements were carried out at 25.00 ± 0.02 °C in a specially designed air-thermostat.

Results and Discussion

Table 1 summarizes solubility and conductivity data for various tetraalkylammonium (TAA) salts in EtBr; solubilities of TAA salts (from $C=4$ to $C=7$) in water are also quoted.

Table 1. Solubility and conductivity data for solutions of tetraalkylammonium salts in ethyl bromide and in water, at 25 °C.

Salt	Solubility in EtBr (mol/litre)	Specific Conductivity in EtBr (ohm^{-1} cm^{-1})	Solubility in water (mol/litre)
$(CH_3)_4NCl$	$< 10^{-3}$	$< 10^{-7}$	higlyh soluble
$(CH_3)_4NBr$	$< 10^{-3}$	$\simeq 10^{-7}$	highly soluble
$(C_2H_5)_4\ddot{U}Cl$	$< 10^{-3}$	$\simeq 10^{-7}$	highly soluble
$(C_2H_5)_4NBr$	$< 10^{-3}$	$\simeq 10^{-7}$	highly soluble
$(C_2H_5)_4NI$	$< 10^{-3}$	$\simeq 10^{-7}$	highly soluble
$(C_2H_5)_4NClO_4$	$< 10^{-3}$	1×10^{-6}	highly soluble
$(C_2H_5)_4NPF_6$	$< 10^{-3}$	1×10^{-5}	highly soluble
$(C_3H^7)_4NI$	$< 10^{-3}$	8×10^{-6}	highly soluble
$(C_3H_0)_4NPF_6$	6×10^{-3}	3×10^{-5}	highly soluble
$(C_3H_0)_4NBF_4$	4×10^{-3}	2×10^{-5}	highly soluble
$(C_4H_4)_4NBr$	0.6	1.2×10^{-4}	> 5.0
$(C_4H_0)_4NI$	0.2	1.3×10^{-4}	0.03
$(C_4H_4)_4NClO_4$	> 3.0	2.2×10^{-4}	4×10^{-3}
$(C_4H_4)_4NPF_6$	> 4.0	2.5×10^{-4}	1×10^{-3}
$(C_5H_{11})_4NBr$	0.3	1.5×10^{-4}	0.3
$(C_5H_{11})_4NI$	0.3	1.7×10^{-4}	traces
$(C_6H_{13})_4NBr$	> 2.0	1.3×10^{-4}	2×10^{-3}
$(C_6H_{13})_4NI$	0.6	1.4×10^{-4}	1×10^{-3}
$(C_6H_{13})_4NClO_4$	2.0	3.4×10^{-4}	traces
$(C_0H_{15})_4NCl$	> 3.0	1.3×10^{-4}	7×10^{-4}
$(C^7H_{15})_4NBr$	0.8	1.3×10^{-4}	4×10^{-4}
$(C^7H_{15})_4NI$	0.5	1.3×10^{-4}	traces
$(C_0H_{15})_4NClO_4$	0.5	3.0×10^{-4}	traces
$(C^7H_{15})_4NNO_3$	1.0	2.5×10^{-4}	1×10^{-4}

The conductivities quoted for the CH_3-, C_2H_5-, and C_3H_7-salts are those of the saturated solutions; for the C_4H_9-, C_5H_{11}-, C_6H_{13}-, and C_7H_{15}-salts, those of the 0.05 M solutions.

These data enable to select the compounds most suitable for our purpose. It is apparent that the solubilities of TAA salts in EtBr depend on the number of C atoms in the aliphatic chain R: for $C \leqq 3$ these solubilities are very poor and in the same range as inorganic salts. But for $C \geqq 4$ the solubilities abruptly increase by two or three orders of magnitude. Inorganic salts (alkali- and alkali-earth halides and perchlorates) are practically insoluble in EtBr ($< 10^{-3}$ mol/l), and their saturated solutions show very poor conductivities ($\leqq 10^{-7}$ mhos /cm). Conductivities of TAA salts with $C \geqq 4$ in EtBr are conspicuous and do not, in practice, cause any difficulty.

This behaviour is probably due to dispersion forces between the aliphatic chains in the TAA^+ ions and in EtBr, an effect which increases with ionic size, steric phenomena being probably also involved when passing from $C=3$ to $C=4$. As a matter of fact, similar results have been observed studying the salting-in effect of TAA^+ ions on EtBr: the effect is absent when $C=1$, very smal when $C=2$, and conspicuous [9] for $C=4$.

The solubility behaviour of TAA salts in water is opposite to that in EtBr. Up to $C=5$ significant solubilities may be observed. With $C=6$ and $C=7$ the TAA salts are practically insoluble in water.

These observations make it evident that only these latter salts – amongst those studied here – are suitable for use in EtBr as liquid membranes, as the solubility ratio, organic phase to aqueous phase, agrees with the requirements mentioned above.

The degree of ideality in the behaviour of the present system as a membrane has been studied by measuring the e.m.f. of the cell

$$H_2(1\ \text{atm})/\underset{a_1}{HX,\ \text{aq.}}/A/\underset{a_2}{HX,\ \text{aq.}}/H_2(1\ \text{atm}) \quad (1)$$

where $X = F^-$, Cl^-, Br^-, I^-, NO_3^-, or ClO_4^-, and A denotes the liquid anionic membrane ($EtBr + R_4NX$) being studied, responsive to the X^- anion of the aqueous HX acid. Using this kind of cell eliminates any liquid-unction potential which could arise if one uses saturated calomel electrodes, as is frequently done. The hydrogen electrodes in the cell (1) were of the capillary-imbibition type as described by BIANCHI and coworkers [10–12]. In the case of HF,

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palladium-hydrogen electrodes [13, 14] were used instead of hydrogen electrodes. Cell (1) was simply U-shaped (see Fig. 1) as suggested by the high density of EtBr (1.45 kg/l at 25 °C). The anionic membrane A in cell (1) consists of a 0.015 to 0.002 molal $(C_7H_{15})_4NX$ solution in EtBr, and separates two aqueous HX solutions whose mean molal activities are a_1 (fixed) and a_2 (variable), respectively. The measured e.m.f.'s E are collected in Table 2, for each of the characteristic anions X^-. The mean molal activities of the aqueous acids HX in Table 2 were obtained from the corresponding molalities by using activity coefficients interpolated from those available in the literature [15–17].

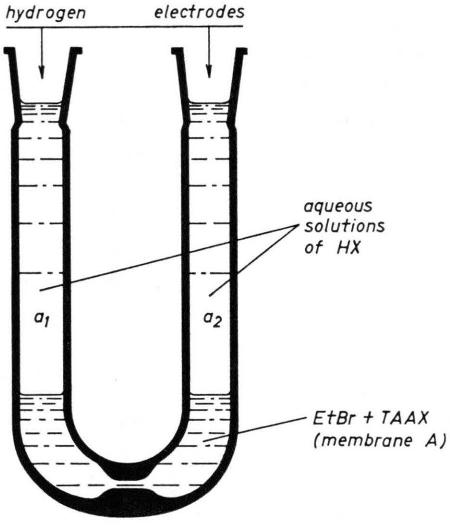

Fig. 1. Showing cell (1).

In the case of the ClO_4^- anion, the experiments with $(C_7H_{15})_4NClO_4$ completely paralleled runs with $(C_6H_{13})_4NClO_4$, which are also quoted in Table 2.

Table 2. Measured e.m.f.'s E of cell (1), in volts, as functions of the mean molal activities a_2 of different aqueous acids HX, with membranes $(C_7H_{15})_4NX + EtBr$ responsive to the anion X^-. Temperature: 25 °C.

HF ($a_1 = 0.00235$)

a_2	E
0.000896	− 0.12850
0.000230	− 0.09280
0.000579	− 0.05795
0.00119	− 0.02230
0.00235	0

HBr ($a_1 = 0.00905$)

a_2	E
0.0000968	− 0.22464
0.000946	− 0.11440
0.00905	0
0.0745	+ 0.10700
0.820	+ 0.23144
5.870	+ 0.33143

HI ($a_1 = 0.00925$)

a_2	E
0.000309	− 0.17335
0.000984	− 0.11300
0.00296	− 0.05740
0.00925	0
0.0271	+ 0.05635

HCl ($a_1 = 0.00905$)

a_2	E
0.0000988	− 0.17650
0.000294	− 0.13142
0.000966	− 0.09540
0.00283	− 0.04650
0.00905	0
0.0257	+ 0.04680
0.0799	+ 0.09210
0.228	+ 0.12860
0.828	+ 0.19068

HNO_3 ($a_1 = 0.00917$)

a_2	E
0.00976	− 0.11524
0.0000998	− 0.23235
0.000300	− 0.18570
0.00288	− 0.05690
0.00917	0
0.0259	+ 0.05520
0.0791	+ 0.10987

$HClO_4$ ($a_1 = 0.00981$)

a_2	E, in $(C_6H_{13})_4NClO_4$	E, in $(C_7H_{15})_4NClO_4$
0.000109	− 0.23928	− 0.23295
0.000300	− 0.18185	− 0.18150
0.00104	− 0.11050	− 0.11329
0.00292	− 0.05516	− 0.06199
0.00981	0	0
0.0266	+ 0.05351	+ 0.05130
0.0807	+ 0.11260	+ 0.11002
0.127	—	+ 0.13300
0.235	+ 0.16341	+ 0.16481
0.894	+ 0.22560	+ 0.22802

Conditions of non-ideality for the anionic membrane A would imply that $t_- < 1$ (t_- denoting the transference number of the X^- anion across A) and would lead to the following e.m.f. expression [18–24] for cell (1):

$$E = k \int_{a_1}^{a_2} t_- \,\mathrm{d}\log a \tag{2}$$

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where $k = 4.606\ RT/F$, $a_1 =$ constant, and water transport through A is neglected. If A behaved as an ideal anionic membrane, $t_- = 1$ so that the e.m.f. expression would be

$$E_{\max} = k \log(a_2/a_1)\,. \qquad (3)$$

The actual behaviour of A can be compared with the ideal behaviour considering the relationships between E and $\log a_2$, and between $E_{\max}$ and $\log a_2$, given by the derivatives of Eqs. (2) and (3):

$$\mathrm{d}E/\mathrm{d}\log a_2 = k\,t_- \qquad (4)$$

and
$$\mathrm{d}E_{\max}/\mathrm{d}\log a_2 = k \qquad (5)$$

respectively.

In Fig. 2 the measured E's and the corresponding $E_{\max}$'s calculated from Eq. (3) are plotted against $\log a_2$, for the different characteristic anions X^-. All the solid lines with a slope of $k = 0.1183$ volts refer to $E_{\max}$ as a function of $\log a_2$ and represent the limiting case of ideal behaviour for A.

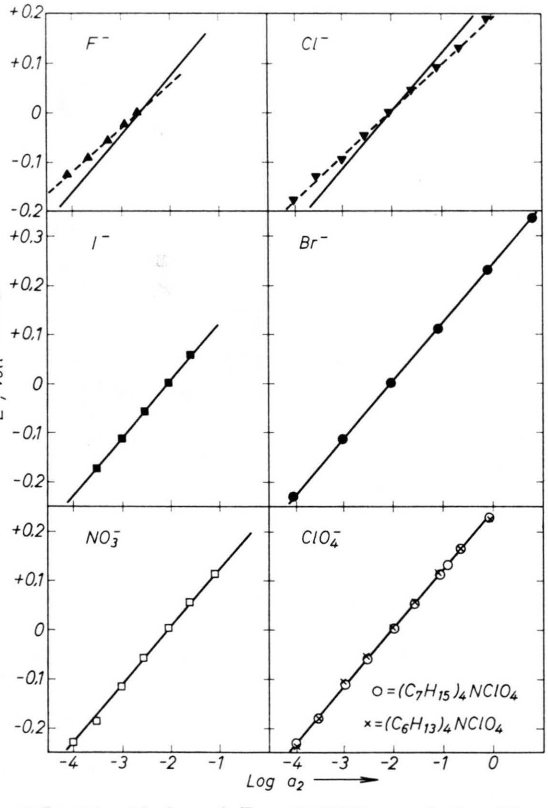

Fig. 2. Limiting ideal e.m.f. $E_{\max}$ [solid lines, calculated from Eq. (3)] compared with the measured e.m.f. E of cell (1), as a function of $\log a_2$, at 25 °C, for different characteristic anions.

It is apparent that the E's points fall on straight lines virtually coincident with the solid lines of the $E_{\max}$'s, when $X = Br^-$, I^-, ClO_4^-, NO_3^-. In these cases, actually, the least-squares slopes of the E lines approach the limiting theoretical value within 1.5 mV. From these slopes one can calculate the transference number of the X^- anion across the membrane A. It turns out that t_{X^-} is close to unity, which indicates that A behaves as an almost ideal ($\cong 100\%$) anionic membrane for the anions Br^-, I^-, ClO_4^-, and NO_3^-. This is to say, the response of the membrane A is Nernstian, at least in the HX activity range covered by the present experiments, an interval corresponding to nearly five logarithmic decades in the case of HBr.

The behaviour found in the cases of $X = Cl^-$ and $X = F^-$ shows remarkable deviations from a Nernstian ideal response (in fact, $t_{F^-} = 0.78$, $t_{Cl^-} = 0.79$), under the present experimental conditions. Yet, this behaviour is still described by straight lines (see dotted lines in Fig. 2), which makes the $(C_7H_{15})_4NF + EtBr$ and the $(C_7H_{15})_4NCl + EtBr$ membranes equally suitable for electroanalytical applications. In fact, the dotted lines for F^- and Cl^- in Fig. 2 can be considered as calibration lines.

Ideality losses of the present membranes could, in principle, be ascribed to various factors: water transport through the membrane, co-ion transport effect in the membrane due to H^+ coming from the HX acid, the organophilic cation $(C_7H_1\ )_4N^+$ not completely "trapped" in the membrane. However, the first of these hypotheses (water transport) can be considered as immaterial, for the present liquid membranes. In fact, any electroendoosmotic effect would require an appropriate porous structure, as in the case of solid membranes, and could not obviously be considered here.

Independent determinations of transference numbers both of the co-ion across the membrane and of the organophilic $(C_7H_{15})_4N^+$ cation within the membrane, would likely shed light on the transport mechanism in the present class of membranes, and call to be done.

Conclusions

The reported results indicate that EtBr solutions of TAAX salts with $C = 6$ and $C = 7$ under the present experimental conditions are nearly ideal anionsensitive liquid membranes for X = Br^-, I^-, ClO_4^-, NO_3^-, and partly ideal ones for X = Cl^- and F^-. The interesting aspects of these liquid membranes are, of course, electroanalytical [1, 25, 26] but also biological. These systems, in fact, can be taken as models for analogous biological situations where in a water-immiscible phase practically fixed ionised species of large dimensions and small and mobile counterions can be present. Systems of this kind in contact with aqueous solutions containing the same counterion show membrane characteristics and can give rise to the corresponding potentials.

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