Activity Measurements of Bivalent Cations Singly and in Mixture with Resin Membrane Electrodes in Aquo-Organic Media

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Synopsis

Cation exchange resin membranes were used as electrodes for activity measurements in aquo-propanolic media for bivalent ions, e.g., Ca, Mg, Cu, Zn, either singly or in a mixture of two. From the results it may be concluded that ion exchange resin membranes can be satisfactorily utilized for measurement of these ions in such media when present singly or in a mixture.

INTRODUCTION

Measurement of activities of cations in aqueous and nonaqueous solutions with the help of clay membranes is an established fact.[1-3] In such measurements, it was assumed that the activity of cation in one compartment is known and is comparable to that of the theoretical value obtained using the Debye-Hückel limiting law equation. The present work involves the measurements of activities of bivalent cations, singly and also in mixtures, with the help of different cation exchange resin membranes in aquo-*n*-propanolic solvent.

Theoretical

The cell set up for measurement of single ionic activity is as follows:

$$\text{calomel, } A_1(a_1) \mid \mid A_1(a_2), \text{ calomel}$$
$$\text{membrane}$$
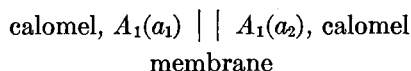
where a_1 = activity of A_1, a_2 = activity of A_2, and A = any bivalent cation. In this system the cell potential E is due to a drop in cation activity across the membrane and is

$$E = \frac{RT}{2F} \ln \frac{a_1}{a_2}. \tag{1}$$

When the membrane separates, unlike cations having the same valence state in such a cell arrangement, the cell EMF, E_1, is given as
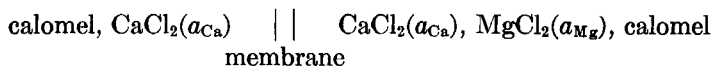
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$$E_1 = \frac{RT}{2F} \ln \frac{a_1(A_1)}{a_2(A_2)} \cdot \frac{UA_1}{UA_2} \qquad (2)$$

where A = any bivalent cation and UA_1/UA_2 = mobility ratio.

The mobility ratio acts as a correction term of the Nernst equation. It probably arises from the difference in speed of the ions inside a permeable membrane[2] or from the difference in the exchangeability of ions on the electrodes surface.[5] In a mixture of two ions in solution, e.g., Ca and Mg ions, the relative effect of the ions on electrode surface is assumed to be determined by their mobility ratio. The activity of ions in a mixture was determined with the help of the mobility ratio previously determined and applying the cell EMF value

$$E = \frac{RT}{2F} \ln \frac{a_{Ca}}{a_{Ca} + a_{Mg} \dfrac{U_{Mg}}{U_{Ca}}} \qquad (3)$$

for the following cell arrangement:

calomel, $CaCl_2(a_{Ca})$ $|\,|$ $CaCl_2(a_{Ca})$, $MgCl_2(a_{Mg})$, calomel
                                    membrane

In this connection the statement of McLean et al.[5] regarding the accuracy of the determination of mobility ratio in mixtures is to be kept in mind.

Individual activity of any bivalent ion in a mixture is calculated using the Debye-Hückel (D.H.) equation, and it is assumed that the solvent changes the dielectric constant of the medium and in turn the activity of an ion. Further, we have assumed that in dilute solutions activity of a bivalent ion remains unchanged whether another bivalent ion is present or not, except for the change due to ionic strength. In determining the activity of an ion in one compartment, it is assumed that activity of the ion in the other compartment is the theoretical value obtained from D.H. equation.

EXPERIMENTAL

Resin membranes were prepared from a mixture of finely powdered (200 mesh) exchange resin and similarly powdered polystyrene at 130°–155°C and 4000 psi pressure in a steel mold. The membranes were cut into suitable size and affixed to one end of a Pyrex glass tube. They are then exchanged both inside and outside with the particular cation whose activity is to be measured. In case of mobility ratio determinations, they are exchanged on two sides with two different cations whose mobility ratio is to be determined.

EMFs were measured with the help of two tiny calomel electrodes (as reference) and recorded within ± 0.1 mV in Leeds-Northrup K_2-type potentiometer as described earlier.[3,4] Only those membranes showing no or negligible asymmetric potentials, i.e., ± 0.1 mV, were used. The calculations of mobility ratio were done in the range of activities in which the

membrane electrode registers theoretical readings and obeys Nernst's equation.

RESULTS AND DISCUSSION

Results of measurements are given in Tables I to VI. Close scrutiny of the results (theoretical and observed) in Tables I, II, III, and IV reveals the fact that the resin membranes perform well in the low concentration range of salts (usually up to .0081M) where the Nernst equation is valid

TABLE I
Activity Measurement of Mg Ions[a]

| | | Membrane potential, mV | | | | |
Solvent	Molality ratio	Zeo-Karb-225	Amber-lite IRC-120	Dowex 50WX8	Amber-lite IRC-50	Theor. EMF, mV
20% Propanol–water	.0009/.0001	25.4	24.8	25.5	24.8	25.6
mixture	.0081/.0009	19.3	20.0	19.5	19.2	20.0
	.0027/.0003	23.9	22.8	23.6	23.8	23.5
	.0243/.0027	14.2	14.3	14.0	14.1	13.6
40% Propanol–water	.0009/.0001	23.8	25.0	24.0	24.6	24.3
mixture	.0081/.0009	15.3	15.8	15.9	14.8	16.2
	.0027/.0003	20.9	21.8	21.3	20.7	21.4
	.0243/.0027	8.6	13.2	7.8	12.5	6.75
60% Propanol–water	.0009/.0001	21.6	23.5	22.1	20.9	21.7
mixture	.0081/.0009	12.6	10.1	8.9	9.4	8.3
	.0027/.0003	17.9	17.8	17.2	18.0	16.9

[a] Salt used, $MgCl_2$; temp., 28°C.

TABLE II
Activity Measurement of Ca Ions[a]

| | | Membrane potential, mV | | | | |
Solvent	Molality ratio	Zeo-Karb-225	Amber-lite IRC-120	Dowex 50WX8	Amber-lite IRC-50	Theor. EMF, mV
20% Propanol–water	.0009/.0001	25.4	24.8	25.2	23.9	25.6
mixture	.0081/.0009	19.5	19.2	19.8	18.9	20.0
	.0027/.0003	22.8	24.0	23.4	22.9	23.5
	.0243/.0027	7.0	12.2	9.6	10.5	13.6
40% Propanol–water	.0009/.0001	23.9	24.1	23.9	24.4	24.3
mixture	.0081/.0009	14.5	17.1	14.8	13.9	16.2
	.0027/.0003	20.8	22.5	21.2	19.4	21.4
	.0243/.0027	8.0	10.2	9.9	9.5	6.75
60% Propanol–water	.0009/.0001	21.2	20.9	21.4	21.0	21.7
mixture	.0081/.0009	10.4	12.2	12.5	11.3	8.3
	.0027/.0003	15.4	17.0	15.9	13.2	16.9

[a] Salt used, $CaCl_2$; temp., 28°C.

TABLE III
Activity Measurement of Zn Ions[a]

Solvent	Molality ratio	Membrane potential, mV				Theor. EMF, mV
		Zeo-Karb-225	Amber-lite IRC-120	Dowex 50WX8	Amber-lite IRC-50	
20% Propanol–water mixture	.0009/.0001	24.6	25.7	24.5	24.8	25.1
	.0081/.0009	18.2	17.9	18.4	17.7	18.6
	.0027/.0003	22.5	22.9	22.7	22.0	22.9
	.0243/.0027	12.5	13.5	12.6	14.6	11.4
40% Propanol–water mixture	.0009/.0001	23.2	23.7	23.5	22.5	23.7
	.0081/.0009	13.0	13.7	14.3	10.0	14.2
	.0027/.0003	19.4	21.1	21.2	18.5	20.2
	.0243/.0027	11.6	10.4	8.0	12.6	3.86
60% Propanol–water mixture	.0009/.0001	20.1	22.5	19.5	18.5	20.8
	.0081/.0009	14.0	15.4	13.4	13.9	5.25
	.0027/.0003	14.6	14.6	14.9	19.0	14.95
	.0243/.0027	—	—	—	—	—

[a] Salt used, ZnSO$_4$; temp., 28°C.

TABLE IV
Activity Measurement of Cu Ions[a]

Solvents	Molality ratio	Membrane potential, mV				Theor. EMF, mV
		Zeo-Karb-225	Amber-lite IRC-120	Dowex 50WX8	Amber-lite IRC-50	
20% Propanol–water mixture	.0009/.0001	24.8	25.2	25.0	24.5	25.1
	.0081/.0009	17.9	19.0	18.4	17.5	18.6
	.0027/.0003	22.3	23.4	22.7	22.0	22.9
	.0243/.0027	13.6	14.9	12.8	14.3	11.4
40% Propanol–water mixture	.0009/.0001	23.2	23.9	23.7	22.5	23.7
	.0081/.0009	13.9	14.9	14.3	12.2	14.2
	.0027/.0003	19.6	21.1	20.5	18.4	20.2
	.0243/.0027	9.5	10.3	8.7	12.4	3.86
60% Propanol–water mixture	.0009/.0001	20.3	21.6	20.5	19.3	20.8
	.0081/.0009	13.3	14.2	9.6	12.1	5.25
	.0027/.0003	14.1	15.6	14.8	16.1	14.95
	.0243/.0027					

[a] Salt used, CuSO$_4$; temp., 28°C.

and eq. (1) can be used in aquopropanolic media. The maximum deviation from the theoretical EMF in case of membranes other than Amberlite IRC-50 is found to be ±0.8 mV in 20% propanol at comparatively low salt concentration. However, as the salt concentration increases or the percentage of n-propanol in the medium increases, the deviation becomes larger and larger, and its pronounced effect is to be noticed from the tables. With 60% propanol, the deviation in some cases is high even in lower salt concentrations. This may be due to the increase in dielectric constants of

TABLE V
Measurement of Mobility Ratios of Ca and Mg Ions[a]

Solvent	Membrane	.0009/.0009[b]		.0027/.0027[b]	
		EMF, mV	Mobility ratio (U_{Ca}/U_{Mg})	EMF, mV	Mobility ratio (U_{Ca}/U_{Mg})
20% Propanol–water mixture	Zeo-Karb-225	3.0	1.26	3.1	1.27
	Amberlite IRC-120	3.8	1.34	4.6	1.42
	Dowex 50WX8	5.5	1.53	6.2	1.62
	Amberlite IRC-50	1.3	1.10	3.2	1.28
40% Propanol–water mixture	Zeo-Karb-225	2.7	1.23	2.4	1.20
	Amberlite IRC-120	4.2	1.38	3.8	1.34
	Dowex 50WX8	5.8	1.56	5.3	1.50
	Amberlite IRC-50	2.7	1.23	2.5	1.21
60% Propanol–water mixture	Zeo-Karb-225	1.5	1.12	1.8	1.15
	Amberlite IRC-120	3.5	1.31	6.2	1.62
	Dowex 50WX8	5.5	1.53	5.4	1.52
	Amberlite IRC-50	1.2	1.10	1.2	1.10

[a] Salt used, $CaCl_2$ and $MgCl_2$; temp., 28°C.
[b] Molality ratio.

the media, which change ionic conductances enormously. The erratic behavior of Amberlite IRC-50 in some cases cannot be explained, but a possible explanation may be given on the basis of the membrane material itself. Dowex 50, Zeo-Karb 225, and Amberlite IRC-120 are all nuclear sulfonic (styrene-based) resins, whereas Amberlite IRC-50 is a carboxylic (acrylic) resin. Although the exchange capacity of the latter is comparable to that of the former three, the latter probably retains on its surface more of the exchangeable ions in nonexchangeable form under the influence of the particular media concerned, and as a result the membrane potential becomes less. It may be said from such a study that these carboxylic-type resins may not be suitable membrane material to study the electrochemical properties of ions in aquo-organic media.

The mobility ratio is supposed to be a characteristic quantity for a particular membrane electrode surface. Table V illustrates the variation in mobility with the nature of the resin; it is roughly about 1.2 in the case of Zeo-Karb-225 and 1.5 in the case of Dowex 50WX8. This is due to the fact that critical ions are constrained in their mobilities during their movement through the membrane, and this stems from the attraction for critical ions by the exchange sites of the pores of the ion exchange membrane. This attraction for critical ions by the exchange sites, or difference in speed inside the membrane,[2] is probably dependent on cationic properties and on the nature of the cation. Except for very slight irregular variation with concentration of cations, the mobility ratio is almost constant for a particular cation pair in solutions of varying dielectric constants. On applying these mobility ratio values (from Table V) for the measurement of unknown activities in mixtures using eq. (3), reproducible results are obtained which

TABLE VI
Activity Measurement of Ca and Mg Ions in Mixture[a]

Solvent	Membrane	$\frac{Ca + Mg}{Ca} = \frac{.0009 + .0009}{.0009}$ [b]		$\frac{Ca + Mg}{Ca} = \frac{.0027 + .0027}{.0027}$ [b]	
		Calculated activity[c]	Theoretical activity	Calculated activity[c]	Theoretical activity
20% Propanol–water mixture	Zeo-Karb-225	5.73×10^{-4}	5.67×10^{-4}	13.7×10^{-4}	12.8×10^{-4}
	Amberlite IRC-120	6.2×10^{-4}	5.67×10^{-4}	14.9×10^{-4}	12.8×10^{-4}
	Dowex 50WX8	6.28×10^{-4}	5.67×10^{-4}	14.6×10^{-4}	12.8×10^{-4}
	Amberlite IRC-50	6.25×10^{-4}	5.67×10^{-4}	14.3×10^{-4}	12.8×10^{-4}
40% Propanol–water mixture	Zeo-Karb-225	5.23×10^{-4}	4.59×10^{-4}	10.35×10^{-4}	9.04×10^{-4}
	Amberlite IRC-120	5.3×10^{-4}	4.59×10^{-4}	9.73×10^{-4}	9.04×10^{-4}
	Dowex 50WX8	4.95×10^{-4}	4.59×10^{-4}	9.82×10^{-4}	9.04×10^{-4}
	Amberlite IRC-50	5.32×10^{-4}	4.59×10^{-4}	10.1×10^{-4}	9.04×10^{-4}
60% Propanol–water mixture	Zeo-Karb-225	4.02×10^{-4}	3.02×10^{-4}	5.72×10^{-4}	4.59×10^{-4}
	Amberlite IRC-120	3.94×10^{-4}	3.02×10^{-4}	6.4×10^{-4}	4.59×10^{-4}
	Dowex 50WX8	3.8×10^{-4}	3.02×10^{-4}	5.89×10^{-4}	4.59×10^{-4}
	Amberlite IRC-50	4.00×10^{-4}	3.02×10^{-4}	6.37×10^{-4}	4.59×10^{-4}

[a] Salts used, CaCl₂ and MgCl₂; temp., 28°C.
[b] Molality ratio.
[c] From eq. (3).

are given in Table VI.   Hence it may be concluded that ion exchange resin membranes can be an important tool for the measurement of activities of ions in solution of aquo-propanolic media and that the activities so obtained are comparable to calculated activities of cations obtained from the Debye-Hückel limiting law, not taking into account ion–ion and ion–solvent interactions.

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