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Multilayer Membrane Electrodes. III. Activity of Alkaline Earth Salts in Mixed Electrolytes

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Multilayer membranes composed of the alkaline earth salts of stearic and hexadecylsulfuric acids act as reversible electrodes to these cationic species only in mixed electrolytic solutions with even large excesses of alkali metal cations when the membrane is maintained at nearly constant volume by the imposition of a high pressure. Mixed electrolytic solutions of calcium or barium chloride with sodium or potassium chloride were studied at ionic strengths from 0.0003 to 1.5; these obeyed Harned's rule with slopes of zero at ionic strengths <0.1 , rising to -0.08 at ionic strength 1.5. Thus, thermodynamic activity coefficients of 2-1 electrolytes in mixed solutions with 1-1 salts were measured directly.

Introduction

Previous papers in this series^{2,3} have described the preparation of multilayer membrane electrodes in some detail, as well as their use in double concentration cells. These electrodes were found to be reversible to only the cationic species in the presence of calcium or barium salts in the ionic strength (μ) range from 3×10^{-4} to 15, or even higher. They were not reversible in mixed electrolytic solutions containing appreciable amounts of alkali metal cations. Improved procedures which result in electrodes reversible to the divalent cations solely in the presence of even large excesses of the monovalent cations are described in this communication, which also lists numerical values for mean activity coefficients of alkaline earth halides in mixed electrolytic solutions with alkali metals.

Experimental

Procedures.—The general procedure was to split ordinary microscope slides in half, plate out about 50 monomolecular layers of the calcium or barium salt of a long-chain fatty acid, and cement the two halves together with appropriate side arms for electrolytic solutions so that potential-determining cations could diffuse across the multilayer membrane in a direction *normal* to the axis of orientation of the long-chain acids. Three electrode systems were employed in this study, a Y-type barium stearate multilayer plated from a phosphate buffer substrate at pH 7 with a plating pressure of 30 dynes cm^{-1} (electrode A), a Y-type calcium stearate multilayer cast from the same buffer at 37 dynes cm^{-1} (electrode B) and Y-type barium hexadecylsulfate multilayer cast from the same buffer at 10 dynes cm^{-1} (electrode F). The reader is referred to the previous papers^{2,3} and the thesis⁴ for details not presented here.

The following solution chain was examined

Reference electrode	Soln. (1) MeCl ₂ (<i>m</i> _A)	Membrane	Soln. (2) MeCl ₂ (<i>m</i> _B) Me'Cl (<i>m</i> _C)	Reference electrode
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where Me was calcium or barium, Me' was sodium or potassium and where subscripts A, B and C designated the appropriate salts. When sodium or potassium chlorides were added to these electrode systems up to a molar ratio of univalent to divalent cations of 10:1, stable potentials were obtained; further, potentials measured on chains containing saturated calomel electrodes agreed well with values calculated on the basis of the extended Debye-Hückel theory⁵

(1) Based on a portion of the Dissertation of Harold Schonhorn, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the Polytechnic Institute of Brooklyn, June, 1959.

(2) H. P. Gregor and H. Schonhorn, *J. Am. Chem. Soc.*, **79**, 1507 (1957).

(3) H. P. Gregor and H. Schonhorn, *ibid.*, **81**, 3911 (1959).

(4) H. Schonhorn, Dissertation, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., June, 1959.

(5) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., New York, N. Y., 1952.

when the molal concentration of non-potential determining ions was twice that of barium or calcium.

Since the entrance of sodium or potassium into the crystal structure of the electrode would cause it to swell and finally disrupt due to the osmotic activity of ions which do not form insoluble stearates, means were investigated to keep the volume of the system as nearly constant as possible by the imposition of a high pressure. From a thermodynamic point of view, this makes the standard chemical potential of sodium or potassium stearate in the membrane so high as to reduce its mole fraction therein to insignificant levels. The problem was to maintain a high pressure (estimated to be 100 to 300 atmospheres) on both sides of a crystal in a crack 2500 Å. wide between two glass slides. Further, the "piston" must have pores of molecular dimensions, ones permeable to alkaline earth cations and essentially impermeable to stearate anions.

The procedure for the preparation of "protected" multilayer electrodes followed the original procedure³ through the cementing together of the two coated half-slides. Then the plane surfaces were wiped with filter paper to remove the multilayer there, and a square (2×2 cm.) of a cation-permeable membrane was laid onto each face. Interpolymer membranes of polystyrenesulfonic acid and Dynel in a 1:3 ratio cast from a dimethylformamide solution were used⁶; other cation-permeable membranes of high selectivity will also serve provided they do not become impermeable irreversibly upon drying. Directly over the selective membranes were placed $2 \times 2 \times 0.3$ cm. pieces of porous glass or unglazed porcelain; Corning Porous Vycor No. 7930 having an average pore diameter of 40 Å. or Sels Micro-porous Filter Media with an average pore diameter of 4 μ was used.

Plastic polymethyl methacrylate blocks with holes cut for the entrance of solutions and electrodes were placed outside the porous matrix and the whole clamped in a strong vise or "C" clamp. Pressure was applied by hand and maintained throughout the life of the cell. An epoxide cement was applied to the periphery of the cell, joining the faces of the glass half-slides with the exposed surface of the porous glass or ceramic plates to seal the unit and prevent lateral swelling.

A necessary condition for good electrode construction is that the pores in the supporting matrix (glass or ceramic) be small; materials having pores 100 μ in diameter did not appear to be usable. It appeared too that the finer the pores, the greater the life time of the electrodes but with a longer time for equilibration.

Electrical measurements were made using a Keithley vacuum tube voltmeter, potential readings were accurate to within $\pm 0.4\%$. Saturated calomel and silver-silver chloride reference electrodes were employed with appropriate corrections for their asymmetry and the asymmetry potential of the multilayer electrode itself (< 2 mv.). Potentials were measured at room temperature and corrected to 25°. Protected electrodes had resistances of 10^7 to 10^8 ohms, requiring appropriate shielding. The time required to attain constant potential readings varied with the nature of the porous matrix and the cation-permeable membranes used. Starting with a dry cell, about 1 hr. was required to attain constant values. If the composition of the solution was changed but slightly (going from 0.01 to 0.02 *m*) about

(6) H. P. Gregor, H. Jacobson, D. M. Wetstone and R. C. Shair, *J. Phys. Chem.*, **61**, 141 (1957).

10 minutes were required for constant potentials; large changes in composition led to longer times of response.

With reversible reference electrodes, theoretical potentials (setting the transport number of divalent cations equal to unity) of double concentration cells with alkaline earth salts could be calculated exactly; the appropriate mean molal activity coefficient data listed by Harned and Owen⁷ and Robinson and Stokes⁸ were employed. When saturated calomel reference electrodes were used, the single ion activity coefficients given by Conway⁶ were employed. For more concentrated solutions not covered by the latter reference, it was assumed that the activity of the univalent anion present was the same as that in a potassium chloride solution of the same ionic strength, and single cationic activities were calculated from the mean activity.⁹ Corrections for potentials arising at liquid junctions were not made.

Results

The potential of the solution chain with silver-silver chloride electrodes at 25° is

$$E_{mv.} = 29.58 \log \frac{4m_A^3 \gamma_A^3}{m_B(2m_B + mc)^2 \gamma_B^2}$$

where γ_A and γ_B are the mean molal activity coefficients of the 2-1 electrolyte in solution (1) and in the solution of mixed electrolytes (2), respectively. When saturated calomel electrodes were employed

$$E_{mv.} = 29.58 \log \frac{m_A \gamma_A^{++}}{m_B \gamma_B^{++}}$$

where γ_A^{++} and γ_B^{++} are the molal activity coefficients of the divalent cationic species in solutions A and B. All results given here were obtained with protected electrodes, unless otherwise specified.

Tables I-III give the results of measurements on a number of solution chains. Data on the double concentration cell measurements which preceded and followed each of the tabulated values are not included. As with the unprotected electrodes,³ about 80% of all protected electrodes constructed were found to function properly. The table headings are self-explanatory; activity coefficients calculated using Harned's rule are designated γ_B^* and will be discussed later.

TABLE I

POTENTIALS OF SOLUTION CHAINS OF MIXED CALCIUM AND POTASSIUM CHLORIDES MEASURED WITH CALCIUM STEARATE MULTILAYER MEMBRANE ELECTRODE B AT CONSTANT TOTAL IONIC STRENGTH μ_T

Chain: Ag | AgCl | Soln. (1) | Membrane | Soln. (2) | AgCl | Ag

Soln. 2		E.m.f., mv.	γ_B^a	γ_B^{*b}
CaCl ₂ (B), m	KCl (C), m			
Soln. 1—0.00100 m CaCl ₂ ; for soln. 2, $\mu_T = 0.0003$				
0.0001000	0.0000000	85.4	0.940	
.0000833	.0000500	86.8	.945	
.0000667	.000100	88.4	.930	
.0000500	.000150	90.2	.931	
.0000333	.000200	93.5	.938	
Soln. 1—0.00100 m CaCl ₂ ; for soln. 2, $\mu_T = 0.003$				
0.00100	0.00000	0.00	0.889	
.000833	.000500	.24	.890	
.000667	.00100	.83	.887	

(7) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1958.

(8) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955.

(9) H. P. Gregor and K. Sollner, *J. Phys. Chem.*, **60**, 53 (1946).

.000500	.00150	3.05	.892
.000333	.00200	6.80	.888
.000167	.00250	13.85	.894

Soln. 1—0.0100 m CaCl₂; for soln. 2, $\mu_T = 0.03$

0.0100	0.0000	0.00	0.731
.00800	.00600	0.47	.731
.00600	.0120	1.72	.735
.00400	.0180	5.05	.732
.00200	.0240	11.75	.736

Soln. 1—0.200 m CaCl₂; for soln. 2, $\mu_T = 0.6$

0.200	0.000	0.00	0.472	0.472
.150	.150	0.18	.478	.478
.100	.300	2.01	.487	.487
.0667	.400	5.15	.491	.492
.0500	.450	6.55	.511	.494

Soln. 1—0.500 m CaCl₂; for soln. 2, $\mu_T = 1.5$

0.500	0.000	0.00	0.448	0.448
.400	.300	-1.22	.466	.462
.300	.600	-0.68	.479	.476
.200	.900	+1.30	.493	.489
.100	1.200	+7.70	.502	.503

^a γ_B calculated from measured e.m.f. ^b γ_B^* calculated from Harned's rule.

TABLE II

POTENTIALS OF SOLUTION CHAINS OF MIXED CALCIUM AND POTASSIUM CHLORIDES MEASURED WITH CALCIUM STEARATE MULTILAYER MEMBRANE ELECTRODE B

Chain: SCE || Soln. 1 | Membrane | Soln. 2 || SCE

Soln. 2		μ_T	E.m.f., mv.	$\gamma_{Ca^{++}}^a$	$\gamma_{Ca^{++}}^{*b}$
CaCl ₂ (B), m	KCl (C), m				
Soln. 1—0.00100 m CaCl ₂					
0.00100	0.00000	0.003	0.00	0.797	0.797
.000833	.000500		2.95	.812	
.000667	.00100		6.05	.796	
.000500	.00150		10.1	.776	
.000333	.00200		15.5	.766	
.000167	.00250		18.4	.770	
Soln. 1—0.00100 m CaCl ₂					
0.00100	0.00000	0.0030	0.00	0.797	0.797
.000800	.000400	.0028	2.81	.800	.802
.000600	.000800	.0026	6.36	.810	.807
.000400	.00120	.0024	11.90	.790	.813
.000200	.00160	.0022	20.70	.795	.821
Soln. 1—0.0100 m CaCl ₂					
0.0100	0.0000	0.03	0.00	0.553	0.553
.00800	.00600		2.48	.570	
.00600	.01200		6.36	.562	
.00400	.01800		11.83	.550	
.00200	.0240		20.40	.564	

^a $\gamma_{Ca^{++}}$ is the single ion activity for calcium calculated from the e.m.f. measurement. ^b $\gamma_{Ca^{++}}^{*}$ is the value given by Conway.⁵

Discussion

A discussion of activity coefficients in mixed electrolytic solutions commences properly with the applicability of Harned's rule. Using the notation of Robinson and Stokes⁸

$$\log \gamma_B = \log \gamma_{(B)} + \alpha_{B\mu} = \log \gamma_{B(0)} - \alpha_{B\mu}$$

where γ_B is the mean activity coefficient of the 2-1 electrolyte, $\gamma_{(B)}$ the mean activity coefficient of the 2-1 electrolyte extrapolated to zero concentra-

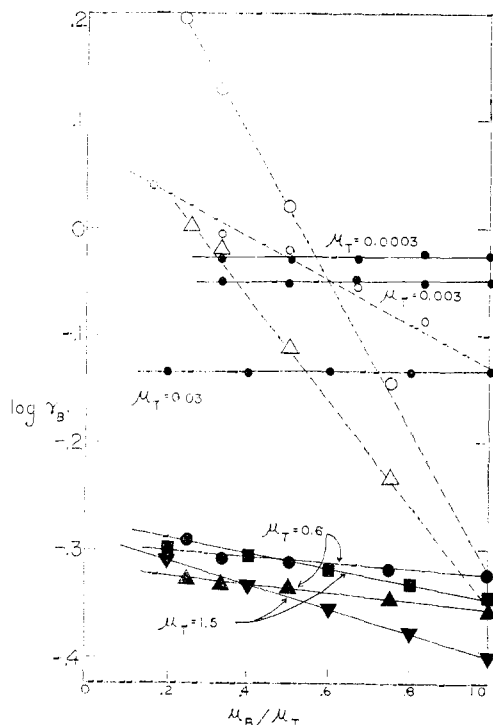


Fig. 1.—Harned's rule plots of the logarithm of the mean activity coefficients of calcium chloride (●, ■) and barium chloride (△, ▼) in the presence of potassium chloride at different total ionic strength μ_T . The ionic strength due to the alkaline earth salt is μ_B . All measurements were made with "protected" electrodes A and B, except for those values designated by open symbols and dotted lines, which were obtained with "unprotected" electrodes.

tion in the 1-1 electrolyte, μ_B the ionic strength due to the 2-1 electrolyte and α_B the slope of the Harned's rule plot; or, $\gamma_{B(0)}$ is the mean activity coefficient of the pure 2-1 electrolyte (at zero

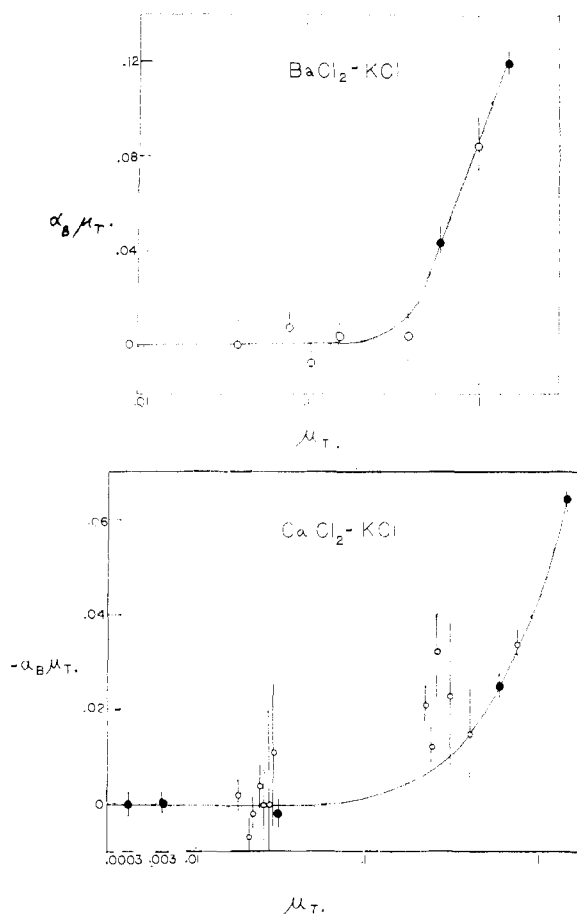


Fig. 2.—Slopes of modified Harned's rule plots for calcium chloride-potassium chloride and barium chloride-potassium chloride mixed electrolytic solutions. The vertical bars show the average deviation for single (○) and sets (●) of measurements at each ionic strength.

TABLE III

POTENTIAL OF SOLUTION CHAINS OF MIXTURES OF BARIUM CHLORIDE AND SODIUM CHLORIDE OR POTASSIUM CHLORIDE MEASURED WITH BARIUM STEARATE MULTILAYER MEMBRANE ELECTRODE A

Chain:	Ag AgCl Soln. 1 Membrane Soln. 2 AgCl Ag						
Soln. 1 BaCl ₂ (A)	BaCl ₂ (B)	(C)	μ_T	E.m.f.	γ_B	γ_B^*	
0.0200	0.0100	0.00250 NaCl	0.0325	21.7	0.715		
.0200	.0100	.00500 NaCl	.035	19.4	.709		
.0200	.0100	.0100 NaCl	.040	14.7	.708		
.0200	.0100	.0100 KCl	.040	14.7	.709		
.0200	.0100	.0500 KCl	.080	-4.30	.660		
.500	.250	.250 KCl	1.00	12.90	.427	0.426	
.00500	.00250	.150 KCl	0.158	-49.0	.556	.553	
.00200	.00100	.100 KCl	.103	-62.6	.613	.622	
.200	.150	.150 KCl	.60	-0.50	.450	.450	
.200	.100	.300 KCl	1.33	.461	.461	.461	
.200	.0500	.450 KCl	6.80	.472	.472	.473	
.500	.400	.300 KCl	1.50	-1.75	.418	.417	
.500	.300	.600 KCl	-	2.40	.441	.441	
.500	.200	.900 KCl	-	1.33	.466	.465	
.500	.100	1.200 KCl	-	3.58	.492	.491	

concentration of the 1-1 electrolyte) and μ_C the ionic strength contribution of the 1-1 electrolyte. Systems which obey Harned's rule give constant values of α at constant ionic strength, or where

$\mu_B + \mu_C = \mu_T$. Figure 1 shows Harned's rule plots for some of the data collected. Since the ionic strength varied widely, the abscissa is normalized by the plot of μ_B/μ_T , the fraction of the total ionic strength contributed by the 2-1 electrolyte. The slope in Fig. 1 is not equal to α_B but to $\alpha_B\mu_T$.

Inspection of Fig. 1 and Tables I and III shows that at $\mu_T < 0.1$ the slope of Harned's rule plot is essentially zero or that the activity coefficient of the 2-1 electrolyte (γ_B) is a function of solely the ionic strength. The simple Debye-Hückel expression without a term for the distance of closest approach gives $\gamma_B = 0.67$ at $\mu_T = 0.03$ while the experimental value is 0.73. The distance of closest approach is calculated to be 5.1 Å. At $\mu_T > 0.1$, γ_B increases as the 1-1 salt replaces the 2-1 salt in the mixed electrolytic solution. Figure 2 shows a plot of $\alpha_B\mu_T$ as a function of μ_T for these systems with the vertical lines representing the limits of the average deviation being determined by the error in the voltmeter with its magnitude depending also upon the ratio μ_T/μ_C , the apparent error being magnified when the ratio is large. When a number of points at constant μ_T were measured, Fig. 2 shows the average error which is smaller. This plot makes use of another form of Harned's rule,

$$\log \gamma_B = \log \gamma_{B(0)} - \alpha_B \mu_T (\mu_C/\mu_T)$$

because the actual measurement gives $\alpha_B \mu_C$ rather than α_B .

From these tables and others,⁴ values of α_B were calculated as were values of α_C , the slope of Harned's rule in terms of compound C. These were calculated using the method of Harned and Gary¹⁰ who extended Harned's rule by applying the Gibbs-Duhem equation to obtain expressions for solutions of two electrolytes of any valence type to which Harned's rule applies. For potassium and barium chlorides at $\mu_T = 0.6$, $-\alpha_B = 0.072$ and $-\alpha_C = 0.044$ while at $\mu_T = 1.5$, $-\alpha_B = 0.081$ and $-\alpha_C = 0.058$; for potassium and calcium chlorides at $\mu_T = 0.6$, $-\alpha_B = 0.042$ and $-\alpha_C = 0.047$ while $\mu_T = 1.5$, $-\alpha_B = 0.045$ and $-\alpha_C = 0.055$. A comparison with similar systems shows good agreement. The mixed electrolytic system barium chloride-hydrochloric acid was investigated by Harned and Mason.¹¹ Harned and Gary¹⁰ calculated α_B from their data; at $\mu_T = 1.5$, $-\alpha_B = 0.077$, in good agreement with our value of 0.080 obtained for the barium chloride-potassium chloride system. This may suggest that at these concentration levels some specific ion effects occur.

It must be recognized that at the present time there is no absolute proof that the protected multi-layer membrane electrodes are reversible to the divalent cations only in mixtures with 1-1 electrolytes. However, the applicability of Harned's rule, the fact that the slopes are essentially zero over a wide range of μ_B/μ_C ratios in dilute solutions and agree well with the α values obtained by others at higher concentrations indicates strongly that the electrodes are indeed quite ion-specific, *i.e.*, reversible to only the divalent cation. Radio-tracer transport experiments are in progress to verify these conclusions.

Accordingly, the activity coefficient of 1-1 or 2-1 electrolytes in a mixed electrolytic system can be calculated from its composition, the value of $\gamma_{(0)B}$ or $\gamma_{B(0)}$ and the appropriate value of α_B or α_C . These are designated as γ_B^* and are tabulated as such. An error of ± 0.2 mv. in the electrometer reading leads to an error of ± 0.002 in γ_B^* ; accordingly, the agreement found is good.

A particularly sensitive test of the ion-specificity

(10) H. S. Harned and R. Gary, *J. Am. Chem. Soc.*, **76**, 5924 (1954); **77**, 1994, 4696 (1955).

(11) H. S. Harned and C. M. Mason, *ibid.*, **53**, 3377 (1939).

of an electrode can be made by measuring solution chains between saturated calomel reference electrodes; the extra-thermodynamic values obtained have the customary uncertainty in the liquid junction potentials. Here the potential is determined directly by the activity ratio of the cation which can move across the membrane; non-permeating ions have no effect except through their influence upon the activity coefficient of the permeating cation. Table II shows a number of measurements made using mixtures of calcium chloride and potassium chloride at different concentrations. The activity coefficient of the alkaline earth cation in the pure reference solution was taken from Conway.⁵ In general, good agreement was observed in dilute solutions, although even here at $\mu_T = 0.003$ there is a trend away from the Conway values, possibly due to changes in liquid junction potentials. Similar results were obtained with the barium chloride-sodium chloride system. A number of measurements were also made with chains not at constant total ionic strength but at constant molality of the anion (chloride) or at constant total molality ($3m_B + 2m_C$); at ionic strength levels of approximately both 0.03 and 0.3 the values of γ_B were not constant.

It is interesting to note the dotted lines in Fig. 1 which represent erroneous values of γ_B calculated from data obtained using unprotected electrodes. Here one apparently obtains a bi-ionic or "mixed" potential with both cations being potential determining. The entrance of the univalent ion into the membrane lattice apparently does not lead to irreversible changes unless the ratio is quite high. The transport number of the alkali metal cation in the membrane phase increases with its concentration in the solution phase.

The molar ratio of 1-1 to 2-1 electrolytes at which the protected electrode was apparently specific for the alkaline earth cation was found to be at least 100:1; this allows one to measure calcium ion activities in many solutions of biological origin. Succeeding papers in this series will take up such measurements.

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