

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

## Multilayer Membrane Electrodes. IV. Activity of Magnesium and Strontium Salts in Mixed Electrolytes

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Magnesium stearate and strontium stearate multilayer membrane electrodes were prepared. Inserted in solution chains (at concentrations up to 3-4 molal) of the corresponding chloride salts between reversible electrodes, they gave potentials which agreed within experimental error with those calculated from thermodynamic data. Magnesium stearate multilayer electrodes were also employed to measure the activity coefficient of magnesium chloride in a mixed electrolytic solution with potassium chloride; good agreement with Harned's rule was observed at a total ionic strength of 1.0. Using appropriate electrodes, the activities of the chlorides of magnesium and strontium were measured in mixtures of these two salts, and again Harned's rule was observed, with the values of the two slopes being in agreement with derived thermodynamic relationships.

This contribution is another in a series which describes the preparation and properties of membrane electrodes reversible to a metallic ion which forms an insoluble multilayer with a long-chain acid.

### Experimental

The procedures employed by Schonhorn and Gregor<sup>2,3</sup> were employed, unless noted otherwise. For further details, reference is made to the theses of Schonhorn<sup>4</sup> and Glatz.<sup>5</sup> The materials employed were of reagent grade. The stearic acid (Fisher reagent grade) melted in the range 68-69° and required no further purification. The cation-exchange membranes used were of commercial origin, and included the CTI-TNO membrane C-60 (an almost identical material is now available from the American Machine and Foundry Co. under the same designation) and the Asahi Chemical Industries membrane. The porous matrices were of ceranic (Selas 015, with a pore diameter of 0.7  $\mu$ ) and glass (Corning Vycor No. 9730, with a pore diameter of 4  $\mu$ ) and were used in plates 0.16-cm. thick. The plating trough substrate was the  $5 \times 10^{-4}$  M phosphate buffer at pH 7.21 previously employed, which was  $10^{-4}$  M in the alkaline earth cation.<sup>2</sup>

In plating the stearates of the alkaline earth cations, one finds that the ease of plating and firmness of the film decrease with decreasing atomic weight. In general, during the plating of Y-type layers, downward motion of the hydrophobic slide causes the monolayer meniscus to be markedly depressed with deposition of a hydrophilic layer; upward motion of the hydrophilic slide resulted in deposition of a hydrophobic layer with a markedly convex meniscus. The slide emerges quite dry and free of droplets when proper plating is being effected. The rate of plating customarily employed was 3 cm. min.<sup>-1</sup>.

The plating of the soft magnesium stearate film presented certain problems. First, the two half-slides were rubbed with ferric stearate to render them hydrophobic. The optimum plating pressure was determined by plating slides, assembling them, and determining their cationic selectivity (or lack of it) in solutions of magnesium chloride only. With magnesium stearate, the collapse pressure was found to be 61.5 dynes cm.<sup>-1</sup>. No plating occurred at 14 dynes cm.<sup>-1</sup>; at 17.7 and at 28.8 dynes cm.<sup>-1</sup> plating occurred but with rather shallow meniscus variations, and the electrodes proved to be reversible for but a few minutes before decaying rapidly to free diffusion potentials and low ( $10^6$  ohm) resistance readings. At a surface pressure of 35.9 dynes cm.<sup>-1</sup>, the meniscus variations were proper, and the electrodes were selective for magnesium chloride at concentrations less than 0.2 *m* (molal) but decayed when subjected to more concentrated solutions. At 43.0 dynes cm.<sup>-1</sup> the plating operation proceeded properly and electrodes ideally selective in concentrations at least as high as 4.6 *m* were obtained. At this plating pressure (43.0 dynes cm.<sup>-1</sup>) the plating rate was reduced to 2 cm. min.<sup>-1</sup> to obtain more consistent results; about two-thirds of all slides thus plated were found to be usable as electrodes. When the pressure was increased to 49.0 dynes cm.<sup>-1</sup>, as the glass slides were lowered and raised through the monolayer no plating was observed except that the slide was rendered hydrophilic on the first downward stroke. At 43.0 dynes cm.<sup>-1</sup>, magnesium electrodes were also prepared from behenic acid [CH<sub>3</sub>(CH<sub>2</sub>)<sub>20</sub>COOH, Archer-Daniels-Midland Co., m.p. 69.5-74.0°]; these were indistinguishable from the corresponding stearate electrodes.

Strontium stearate multilayer electrodes were prepared in a

similar manner. Here, the collapse pressure was 43.0 dynes cm.<sup>-1</sup>. At 38.1 dynes cm.<sup>-1</sup>, plating could be effected but without proper meniscus movements, and the electrodes were not even initially reversible to strontium. At 35.0 dynes cm.<sup>-1</sup>, pronounced meniscus movements were observed, and the electrodes proved to be reversible in solutions of strontium chloride at concentrations at least as high as 3.0 *m*.

The assembly of plated glass slides followed the earlier procedures<sup>2,3</sup> but with some improvements. Prior to the plating procedure, the two glass half-slides were placed in a clamp (Brown and Sharp Vice and Clamp No. 752) which permitted the application of a lateral pressure perpendicular to the crack in the glass. As pressure was applied, the cracked edge portion was viewed under a microscope at 440 $\times$  to ensure proper alignment. Pressure was applied by thumb and finger on the vice barrel to the point of maximum torque. At this point the width of the crack was observed on the scale of the microscope eyepiece. After the multilayer had been plated, the glass half-slides were realigned in the clamp which was tightened until the crack width was the same as before plating. This procedure gave a lateral pressure which produced usable electrodes consistently. The clamped half-slides were then fixed together by four glass tabs cemented over the upper and lower portions of the crack. The multilayer in the crack was exposed by wiping the plane surfaces vigorously with filter paper.

For the initial screening of electrodes prior to being "protected," the cemented half-slides were mounted vertically on an insulating block and placed in a grounded metal box. Strips of filter paper were soaked in the two electrolytic solutions being employed, with one end placed on a side of the electrode, the other in a small beaker containing the solution in question and the reference electrode. In this manner one could avoid cementing solution side arms to the electrode. Steady initial potential readings were obtained in about 5 min. The asymmetry potentials were usually in the 0-3-inv. range, with a daily variation of  $\pm 0.5$  inv.

The potentials measured were in the range 0-70 mv., and the resistance of a reversible multilayer electrode was usually in the range  $1-50 \times 10^7$  ohms. A Keithley Model 200 B vacuum tube voltmeter in conjunction with a Keithley Model 2008 decade shunt was employed.

### Results and Discussion

With solutions of but a single electrolyte, unprotected electrodes yielded stable, reproducible potentials. Since these mean activity coefficients are known, it was possible to compare experimentally determined potentials with calculated values; data on these systems are given in Tables I and II. When mixed electrolytic solutions were employed, protected electrodes also gave stable and reproducible potentials, but here there was no basis for comparison with theoretical values or ones obtained by other methods. The solution chain employed was:

reference electrode	soln. (1) MCl <sub>2</sub> ( <i>m</i> <sub>A</sub> )	multilayer membrane	soln. (2) MCl <sub>2</sub> ( <i>m</i> <sub>B</sub> ) M'Cl or M''Cl <sub>2</sub> ( <i>m</i> <sub>C</sub> )	reference electrode
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where M is the alkaline earth cation also present in the multilayer, M' an alkali metal cation, and M'' a different alkaline earth cation.

Four criteria for a reversible potential value were employed. The first was that prior to and immediately after each individual measurement on mixed electrolytes solution 2 was replaced by one containing only MCl<sub>2</sub>

(1) Based on a portion of the Dissertation of Alfred C. Glatz, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the Polytechnic Institute of Brooklyn, June, 1961.

(2) H. P. Gregor and H. Schonhorn, *J. Am. Chem. Soc.*, **81**, 3911 (1959).

(3) H. Schonhorn and H. P. Gregor, *ibid.*, **83**, 3576 (1961).

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

(5) A. C. Glatz, Dissertation, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., June, 1961.

TABLE I

POTENTIALS WITH MAGNESIUM STEARATE MULTILAYER MEMBRANE ELECTRODES				
Chain: Ag   AgCl		MgCl <sub>2</sub>   multilayer   MgCl <sub>2</sub>		AgCl   Ag
soln. (1)		membrane		soln. (2)
MgCl <sub>2</sub> soln. (1), <i>m</i>	MgCl <sub>2</sub> soln. (2), <i>m</i>	E. m. f. measd., mv.		E. m. f. calcd., mv.
0.0001	0.00001	(37.0)		87.80
.001	.0001	83.2		85.68
.002	.001	24.0		25.19
.004	.001	50.1		49.76
.004	.002	24.5		24.57
.008	.002	47.7		48.70
.010	.004	32.0		31.84
.010	.008	7.2		7.72
.010	.002	55.2		56.41
.200	.100	22.8		23.68
1.000	.500	32.4		33.24
2.000	1.000	50.4		50.34
4.630	2.000	122.4		119.39

TABLE II

POTENTIALS WITH STRONTIUM STEARATE MULTILAYER MEMBRANE ELECTRODES				
Chain: Ag   AgCl		SrCl <sub>2</sub>   multilayer   SrCl <sub>2</sub>		AgCl   Ag
soln. (1)		membrane		soln. (2)
SrCl <sub>2</sub> soln. (1), <i>m</i>	SrCl <sub>2</sub> soln. (2), <i>m</i>	E. m. f. measd., mv.		E. m. f. calcd., mv.
0.0001	0.00001	(37.8)		87.84
.001	.0001	83.5		85.66
.005	.0025	25.5		24.29
.05	.025	21.1		21.95
.10	.05	22.7		23.38
.30	.10	36.3		36.73
.50	.25	24.9		24.77
1.00	.50	28.9		29.39
2.00	1.00	41.8		41.10
3.00	1.00	78.7		76.73

with  $m_A:m_B = 2:1$ ; only when both potentials agreed with the theoretical value was the intermediate value accepted. Second, resistance measurements were made periodically and a nonfunctioning electrode was designated as one that had a resistance of less than  $10^7$  ohms. The third criterion was that functioning electrodes made at different times from different solutions gave the same experimental results. The fourth criterion was that Harned's rule was obeyed.

With mixed electrolytic solutions containing a univalent electrolyte ( $m_C$ ), the potential of the solution chain with silver-silver chloride electrodes at  $25^\circ$  is

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

where  $\gamma_A$  and  $\gamma_B$  are mean activity coefficients of the 2-1 electrolyte in solutions 1 and 2, respectively. When both electrolytes in solution 2 are 2-1, the potential is

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

Table III gives experimental results and calculated mean activity coefficients of magnesium chloride in mixed electrolytic solutions with potassium chloride and with strontium chloride, and Table IV shows values for strontium chloride in mixed electrolytic solutions with magnesium chloride and calcium chloride. In all tables, values which did not meet the four criteria for reversible electrodes are enclosed in parentheses.

With unprotected electrodes, about 5 min. of contact with the solution was required to attain the first equilibrium potential readings; thereafter, constant potentials were attained almost immediately. With electrodes protected using porous ceramic, about 3 hr. was required to attain constant potential readings initially,

TABLE III

POTENTIALS WITH MAGNESIUM STEARATE ELECTRODES IN MIXED ELECTROLYTES					
Chain: Ag   AgCl		soln. (1)		soln. (2)	
		0.333 <i>m</i>		<i>m</i> <sub>B</sub> , <i>m</i> <sub>C</sub>	
		membrane		AgCl   Ag	
MgCl <sub>2</sub> , <i>m</i>	KCl, <i>m</i>	SrCl <sub>2</sub> , <i>m</i>	E. m. f. mv.	$\gamma^{\pm}_{MgCl_2}$	
0.333	0.0000		0.0	0.507	
.316	.0526		-.6	.514	
.308	.0769		-.8	.517	
.286	.143		-1.4	.528	
.250	.250		-2.8	.554	
.200	.400		-3.4	.581	
.143	.571		-3.2	.617	
.111	.667		-4.5	.678	
.091	.726		(35.5)	(.253)	
.283		0.050	4.0	.482	
.222		.111	9.5	.455	
.167		.167	15.1	.431	
.111		.222	(8.3)	(.589)	

TABLE IV

POTENTIALS WITH STRONTIUM STEARATE ELECTRODES IN MIXED ELECTROLYTES						
Chain: Ag   AgCl		soln. (1)		soln. (2)		
		SrCl <sub>2</sub> , <i>m</i> <sub>A</sub>		<i>m</i> <sub>B</sub> , <i>m</i> <sub>C</sub>		
		membrane		AgCl   Ag		
SrCl <sub>2</sub> , <i>m</i>	SrCl <sub>2</sub> , <i>m</i>	MgCl <sub>2</sub> , <i>m</i>	CaCl <sub>2</sub> , <i>m</i>	E. m. f. mv.	$\gamma^{\pm}_{SrCl_2}$	
0.100	0.100	0.000		0.0	0.514	
.100	.0667	.0333		6.4	.495	
.100	.0500	.0500		10.5	.489	
.100	.0333	.0667		16.5	.481	
.100	.0250	.0750		20.5	.477	
.100	.0167	.0833		25.9	.474	
.100	.0091	.0909		(16.5)	(.748)	
.333	.333	.000		0.0	.437	
.333	.283	.050		2.7	.432	
.333	.222	.111		6.9	.420	
.333	.167	.167		(-7.7)	(.673)	
.100	.100	.000		0.0	.514	
.100	.0667		0.0333	6.5	.493	
.100	.0500		.0500	11.1	.482	
.100	.0333		.0667	(6.7)	(.633)	

and about 30 min. subsequently. Electrodes protected using the finer pore glass required 4 hr. for the first, constant readings, and about 1 hr. afterward. This slow time response appears to be due, in large part, to the slowness of diffusion across the ceramic or porous glass matrix, and to the appreciable capacity of the commercial ion-exchange membranes. Continuous replacement of the cell solution was required. Protected electrodes could be used continuously for over 4 days. In general, their usable life was reduced by solutions of high ionic strength.

As noted in Tables I and II, good agreement was found between activity coefficients measured and those calculated from values in the literature.<sup>6-8</sup> The unprotected electrodes showed ideal selectivity at concentrations  $10^{-4}$  *m* and greater, but gave low e. m. f. values in  $10^{-5}$  *m* solutions. Similar behavior was noted by Gregor and Schonhorn<sup>2</sup> with calcium and barium stearate electrodes. At these low concentrations, the concentration-mobility product for hydrogen ions in the solution and membrane phases is not insignif-

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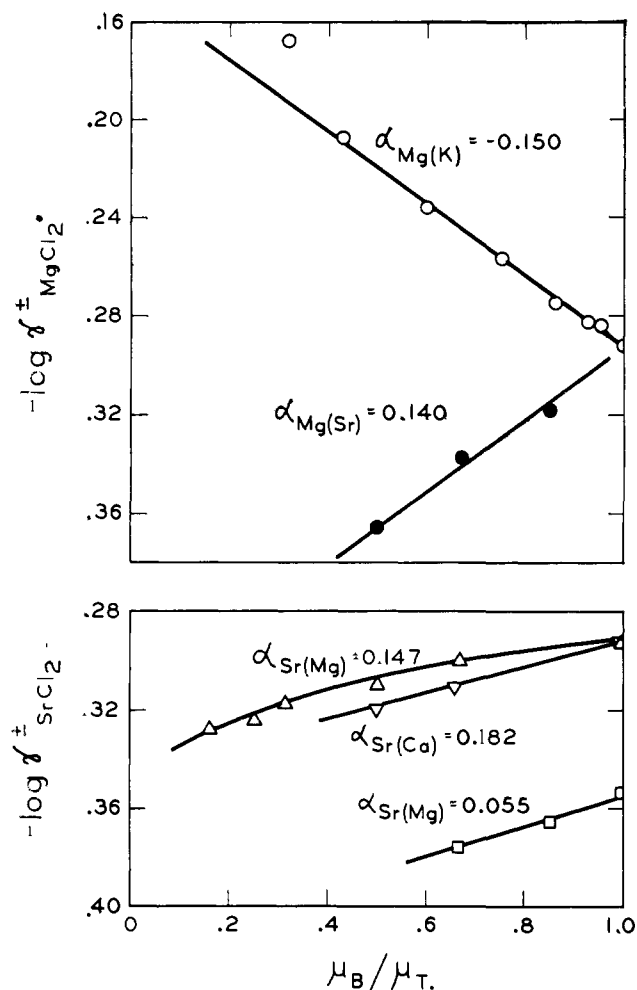


Fig. 1.—Harned's rule plot for  $\gamma_{\text{MgCl}_2}^{\pm}$  in  $\text{MgCl}_2\text{-KCl}$  solutions (○), and in  $\text{MgCl}_2\text{-SrCl}_2$  solutions (●), both at  $\mu_T = 1$ ; for  $\gamma_{\text{SrCl}_2}^{\pm}$  in  $\text{SrCl}_2\text{-MgCl}_2$  solutions at  $\mu_T = 0.3$  (△) and  $\mu_T = 1.0$  (□), and in  $\text{SrCl}_2\text{-CaCl}_2$  solutions at  $\mu_T = 0.3$  (▽).

icant relative to that of the alkaline earth cations, and appreciable hydrogen ion concentration differences can produce appreciable potential differences.

Tables III and IV give results with protected magnesium stearate and strontium stearate electrodes, respectively. Initially, attempts were made to measure the potentials of these mixed electrolytic solutions using unprotected electrodes; in all cases the electrode failed except where a mixture of strontium chloride and magnesium chloride was measured using a strontium stearate electrode, as will be noted later. In these tables, the values in parentheses represent the lowest concentration of added electrolyte at which the membrane electrode failed. Accordingly, the magnesium stearate electrode was reversible to the magnesium ion with potassium chloride at a molar ratio  $m_{\text{K}}/m_{\text{Mg}} \leq 6$  at total ionic strength,  $\mu_T = 1.0$ , and with strontium chloride at  $m_{\text{Sr}}/m_{\text{Mg}} \leq 1$  at  $\mu_T = 1.0$ . The strontium stearate electrode was reversible to the strontium ion with magnesium chloride at  $m_{\text{Mg}}/m_{\text{Sr}} \leq 5$  at  $\mu_T = 0.3$  and  $\leq 0.5$  at  $\mu_T = 1.0$ , while with calcium chloride it was reversible only at  $m_{\text{Ca}}/m_{\text{Sr}} \leq 1$  at  $\mu_T = 0.3$ . In the case of strontium stearate electrodes and mixed strontium-magnesium electrolytic solutions, both unprotected and protected electrodes gave the same results.

Figure 1 shows the data plotted according to Harned's rule, which in modified form is<sup>3</sup>

$$\log \gamma_B = \log \gamma_{B(O)} - \alpha_{B(C)} \mu_T (\mu_B/\mu_T)$$

where  $\gamma_{B(O)}$  is the activity coefficient of electrolyte B at

$\mu_B = \mu_T$  or where  $m_C = 0$ , and  $\alpha_{B(C)} \mu_T$  is the slope. The corresponding values of  $\alpha_{B(C)}$  for each mixed electrolyte are also given in Fig. 1.

The linear relationships expressed above are not always obeyed and in some cases (usually involving 2-1 electrolytes at high ionic strengths) expressions with higher powers of  $\mu_C$  are required in order to account for the results.<sup>9-15</sup> Harned and Gary<sup>16</sup> have shown that if Harned's rule is valid for both electrolytes B and C, then the slopes  $\alpha_{B(C)}$  and  $\alpha_{C(B)}$  are related by

$$\frac{\nu_C}{j} \alpha_{C(B)} = \frac{\nu_B}{k} \alpha_{B(C)} - \frac{2}{2.3 \mu_T} \left[ \frac{\nu_B}{k} (\Phi_B - 1) - \frac{\nu_C}{j} (\Phi_C - 1) \right]$$

where  $\Phi_B$  and  $\Phi_C$  are the osmotic coefficients of electrolytes B and C, both at  $\mu_T$ , where  $\nu_B$  and  $\nu_C$  are the numbers of ions formed by the dissociation of molecules B and C, where  $\mu_B = k m_B$  and  $\mu_C = j m_C$ . Glueckauf *et al.*,<sup>13</sup> have also shown that if Harned's rule is valid for both electrolytes B and C, then

$$\nu_B j \alpha_{B(C)} + \nu_C k \alpha_{C(B)} = S (\text{a constant})$$

The latter expression is useful in determining whether Harned's rule holds for electrolyte C when it is known for B. The value of  $\alpha_{B(C)}$  must be known for at least two values of  $\mu_T$ , and  $\alpha_{C(B)}$  can then be calculated for each value of  $\mu_T$ . These relationships have been examined<sup>16-19</sup> and have shown reasonable validity at higher ionic strength levels.

The  $\alpha_{B(C)}$  coefficient for the system  $\text{MgCl}_2\text{-KCl}$  at  $\mu_T = 1.0$  was  $-0.150$ , while the  $\alpha_{B(C)}$  coefficients for the systems  $\text{BaCl}_2\text{-KCl}$  and  $\text{CaCl}_2\text{-KCl}$  at  $\mu_T = 1.0$  as calculated by Schonhorn and Gregor<sup>3</sup> were  $-0.075$  and  $-0.043$ , respectively. A negative  $\alpha_{B(C)}$  coefficient means that the mean activity coefficient of the alkaline earth chloride increases as potassium chloride is added to the solution at constant total ionic strength. The increase in the (absolute) value of the  $\alpha_{B(C)}$  coefficient with the decreasing atomic weight of the alkali metal cation suggests that specific effects other than hydration are responsible.

For the  $\text{MgCl}_2\text{-SrCl}_2$  system, the availability of  $\alpha_{B(C)}$  and  $\alpha_{C(B)}$  coefficients at  $\mu_T = 1.0$  allows for a direct test of the Harned and Gary relationship. Using the value of  $\alpha_{B(C)} = 0.140$  for this system and the osmotic coefficients for strontium and magnesium chlorides obtained from Robinson and Stokes,<sup>8</sup> the  $\alpha_{C(B)}$  coefficient was calculated to be 0.054, compared with the experimental value of 0.055.

Figure 1 shows that strontium chloride in magnesium chloride at  $\mu_T = 0.3$  does not show the linear Harned's rule relationship shown by the same system at  $\mu_T = 1.0$ , which is in agreement with observations on similar systems.

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