

# Notes

## Variations of Bi-ionic Potentials on Counterion Concentrations

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An explanation for the variation of bi-ionic potentials with concentrations of electrolytes is furnished on the basis of Harned's rule.

THE possibility of rapid determination of mean activity of an electrolyte in a mixture of electrolytes was facilitated with the advent of glass<sup>1</sup>, ion-exchange resin<sup>2</sup> and clay<sup>3</sup> membrane electrodes. These membranes had the unique property of generating an electric potential difference (membrane potential), when interposed between solutions of unequal concentrations of an electrolyte. With the glass electrode used for pH measurement, the potential difference was found to be a function of the activity of only H<sup>+</sup> ion in a mixture of ions. The same condition does not hold good for ion-exchange resin and clay membrane electrodes. Non-specific behaviour of the latter seemed most plausible in the light of theories concerning membrane potentials<sup>4</sup>. Determination of activity of an ion in the presence of another is possible from membrane potential measurements provided the bi-ionic potential for the ion-pair is known. Ghosh and Mukherjee<sup>5</sup> observed dependence of bi-ionic potential on ionic proportions in a mixture of two electrolytes in contact with a membrane surface. In the present note an explanation for the aforesaid variation is furnished on the basis of applicability of Harned's rule<sup>6</sup> in the membrane phase.

For counterions of equal valence ( $Z_A = Z_B = 1$ ), the membrane potential (bi-ionic potential),  $E_M$  for the cell (A),

SCE	Solution of AY having mean activity ( $= a'_A$ )	Cation exchanger membrane not permeable to CO-ion and free from convection current	Solution of BY having mean activity ( $= a''_B$ )	SCE
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Cell — A (where AY = HCl and BY = NaCl)

can be expressed by Eq. (1)

$$E_m = \frac{RT}{F} \ln \frac{\bar{D}_A}{\bar{D}_B} \cdot \frac{a'_A}{a''_B} \cdot \frac{\bar{f}_B}{\bar{f}_A} \quad \dots(1)$$

where  $\bar{D}_A/\bar{D}_B$  and  $\bar{f}_B/\bar{f}_A$  are respectively, the mobility and activity coefficient ratios in the membrane phase.

When the left hand compartment of cell (A) contains a mixture of AY and BY having mean activities  $a''_A$  and  $a'_B$  respectively, the membrane po-

SCE	AY+ BY having mean activities $a''_A$ and $a'_B$ respectively	Cation exchanger membrane not permeable to CO-ion and free from convection current	Solution of BY having mean activity $a''_B$	SCE
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Cell — B (where AY = HCl and BY = NaCl)

tential,  $E'_m$ , for the cell (B) is given by Eq. (2)

$$E'_m = \frac{RT}{F} \ln \frac{\bar{D}_A}{\bar{D}_B} \cdot \frac{\bar{f}_B}{\bar{f}_A} \cdot \frac{a'_B + a''_A \bar{D}_B \bar{f}_B / \bar{f}_A}{a''_B} \quad \dots(2)$$

Details of membrane preparation and allied procedure are described elsewhere<sup>7</sup>. All chemicals used are of AR grade. Potential measurements have been performed with a Leeds Northrup K-2 type potentiometer in conjunction with a Leeds Northrup galvanometer. Tiny calomel electrodes differing at best by 0.2 mV and having saturated KCl-agar bridge at the tip were used as reference electrodes. Temperature was maintained at  $25^\circ \pm 0.5^\circ$ . Mean activity coefficients of electrolytes were obtained either from literature (only for pure HCl solutions)<sup>8</sup> or calculated according to Debye-Hückel equation (both for the other pure electrolyte solution as also for both the electrolyte components in the mixed solutions).

Results from measurements in cell A (Table 1) show that the quantity  $\bar{D}_A/\bar{D}_B \cdot \bar{f}_B/\bar{f}_A$  is more or less constant with an average value 5.55. With strong acid cation exchangers it has been shown by Boyd<sup>9</sup> that the ratio  $\bar{f}_B/\bar{f}_A \approx 1$  for the pair Na<sup>+</sup>/H<sup>+</sup> for about 50% conversion of one form into another. So it is reasonable to assume the same result for the present case also, i.e.,  $\bar{f}_B/\bar{f}_A = 1$ , particularly because of the equal activity of the electrolytes AY and BY in the bulk, on the two sides, as per the condition

TABLE 1 — MEASUREMENTS OF  $\bar{D}_A/\bar{D}_B \cdot \bar{f}_B/\bar{f}_A$  FROM EMF MEASUREMENTS OF CELL-A

[Membrane — Jabalpur Mg form (cationic exchanger) clay (montmorillonite); membrane heated to  $(450^\circ \pm 10^\circ\text{C})$ ; thickness — 0.1-0.2 mm. specific resistance =  $1.3 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>; range of applicability of Nernst's equation = 0.003-0.018 m; experimental accuracy was within  $\pm 0.2$  mV with saturated calomel electrodes at  $25^\circ \pm 0.5^\circ$ ]

[HCl] or [NaCl]	$E'_m$ (mV)*	$\frac{\bar{D}_A}{\bar{D}_B} \cdot \frac{\bar{f}_B}{\bar{f}_A}$
0.003	45.00	5.76
0.006	42.60	5.25
0.009	45.70	5.78
0.018	43.40	5.42
		Av. 5.55

\*Average of five separate readings not differing from each other by more than 0.2 mV.

Spin-State Equilibrium in LuCoO<sub>3</sub>

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TABLE 2 — MEASUREMENTS OF  $\bar{D}_A/\bar{D}_B \cdot \bar{f}_B/\bar{f}_A$  FROM EMF  
MEASUREMENTS OF CELL-B

Conc. of HCl + NaCl (m)	(HCl) (m)	$E'_m$ (mV)*	$\frac{\bar{D}_A}{\bar{D}_B} \cdot \frac{\bar{f}_B}{\bar{f}_A}$	$\frac{\bar{f}_B}{\bar{f}_A}$
0.002 + 0.004	0.006	31.45	8.18	1.47
0.003 + 0.003	0.003	55.35	7.81	1.41
0.004 + 0.002	0.0045	50.10	7.50	1.35

\*Average of five separate readings not differing from each other by 0.2 mV.

of measurements using cell-A. This implies that with cell-A it will be possible to get the value of  $\bar{D}_A/\bar{D}_B$ . If one assumes  $\bar{D}_A/\bar{D}_B$  to be constant throughout<sup>10</sup>, then the variation in the value of the quantity  $\bar{D}_A/\bar{D}_B \cdot \bar{f}_B/\bar{f}_A$  in measurements with cell-B will mainly be due to changes in  $\bar{f}_B/\bar{f}_A$ . The variation in  $\bar{f}_B/\bar{f}_A$  with composition of the solution in the left hand compartment of cell B (Table 2) reveals that as the mole-fraction of AY in the constant total molality mixture increases  $\bar{f}_B/\bar{f}_A$  decreases. This decrease is systematic and is independent of the concentration change of BY on the other side of the membrane.

The glass-gel surface in glass electrodes has been considered as a mixed-electrolyte phase, and accordingly the Harned-rule has been applied successfully to interpret the so-called alkali error for glass electrodes both at high and low  $pH$ s<sup>10,11</sup>. Thus, for one particular glass the equation found applicable is  $\log f_{Na^+}^g = -\alpha N_{H^+}^g$ , where  $f_{Na^+}^g$  is the activity coefficient of sodium ion in gel layer and  $N_{H^+}^g$  is the mole-fraction of H<sup>+</sup> in the gel layer. In such a situation, for high acid activities in the bulk electrolyte mixture, the proportion of H<sup>+</sup>-glass in the glass-gel surface would obviously increase over that of Na<sup>+</sup>-glass. Accordingly the Na<sup>+</sup> activity in the glass-gel surface  $f_{Na^+}^g$  would decrease.

If we assume a somewhat similar situation in the present case then the decrease of  $\bar{f}_B/\bar{f}_A$  with increasing acid concentration becomes easily explicable.

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In LuCoO<sub>3</sub>, low spin Co<sup>III</sup> ions partially transform to the high spin Co<sup>3+</sup> ions up to about 450K above which temperature the proportion of the two spin states remain constant. There appears to be no electron-transfer between the two spin-states as also evidenced by the low resistivity of this material.

**S**TUDIES on the transport and magnetic properties of lanthanum and other rare earth cobaltates<sup>1-5</sup> employing variety of techniques including Mossbauer spectroscopy show that at low temperatures, the cobalt ions exist predominantly in the low-spin state (Co<sup>III</sup>,  $t_{2g}^6 e_g^0$ ) and transform partially to the high-spin state (Co<sup>3+</sup>,  $t_{2g}^4 e_g^2$ ) up to a temperature  $T_1$ , the magnitude of  $T_1$  varying with the cobaltate. The two spin seems to order themselves on unique crystallographic sites around  $T_1$ . In the case of the lighter rare earth cobaltates, electron transfer from Co<sup>3+</sup> to Co<sup>III</sup> takes place at temperatures above  $T_1$  and gives rise to Co<sup>II</sup> ( $t_{2g}^6 e_g^1$ ) and Co<sup>IV</sup> ( $t_{2g}^4 e_g^1$ ) states<sup>4,5</sup>. Such electron transfer provides the mechanism of conduction in the cobaltates. In the case of HoCoO<sub>3</sub> and ErCoO<sub>3</sub>, however, Co<sup>3+</sup> and Co<sup>III</sup> are found to be equally populated above  $T_1$  and there is no evidence of electron transfer<sup>6,7</sup>. This has been attributed to the small size of Ho<sup>3+</sup> and Er<sup>3+</sup> and consequent increase in acidity of these central A ions in the perovskites of the type ABO<sub>3</sub> (where A is a trivalent rare earth ion or Y<sup>3+</sup>, and B is a trivalent transition metal ion). Accordingly, YCoO<sub>3</sub>, where Y<sup>3+</sup> is slightly larger than Ho<sup>3+</sup> shows evidence for electron transfer from Co<sup>3+</sup> to Co<sup>III</sup> above  $T_1$ . In order to confirm that the populations of two spin-states of trivalent cobalt ion and electron transfer between them were indeed controlled by the size of the rare earth ion, we have now investigated the extreme case of LuCoO<sub>3</sub>. Lu<sup>3+</sup> besides being the smallest of rare earth ions is also diamagnetic and would, therefore, not cause complications due to any magnetic interactions.

LuCoO<sub>3</sub> was prepared by the decomposition of the corresponding cobalticyanide at 1000 K and the stoichiometry confirmed by thermogravimetric analysis. It has orthorhombic structure ( $a = 5.017 \text{ \AA}$ ,  $b = 5.341 \text{ \AA}$ ,  $c = 7.295 \text{ \AA}$ ) as found by X-ray diffraction. The inverse magnetic susceptibility curve of LuCoO<sub>3</sub> shows a plateau around 450 K although not as distinct as in LaCoO<sub>3</sub> and other cobaltates (Fig. 1). The plateau is indicative of the ordering of the two spin states of cobalt in LuCoO<sub>3</sub> around this temperature. Accordingly, unit cell parameters and volume also show changes in slope around 500K. The plot of  $\chi_g T$  versus  $T$  (Fig. 1), shows essentially constant value beyond 450K just