Response of the Ag-AgCl Electrode to Chloride Ion in Water and Water–Ethyl Alcohol Mixed Solvents

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The potential response of the Ag-AgCl electrode to chloride ion at ionic strength of 2 in aqueous solution has been determined by potential measurements of the cells $Ag\text{-}AgCl/MCl_{(x)}$, $MClO_{4(2-x)}//LiClO_{4(s)}$ or $NaClO_{4(s)}//NaCl_{(s)}//NaCl_{(s)}/Hg_2Cl_2\text{-}Hg$ for M=H, Na, and Li, and at ionic strength of 2 in water–ethyl alcohol mixed solvents by potential measurements of the cells $Ag\text{-}AgCl/LiCl_{(x)}$, $LiClO_{4(2-x)}$, X% ETOH//$LiClO_{4(s)}$, X% EtOH//$LiClO_{4(s)}//NaCl_{(s)}/Hg_2Cl_2\text{-}Hg$. The deviation from Nernst behavior in aqueous solution was appreciable, and was of the same direction (ΔE per decade $< RT/nF$) for all solute pairs. The deviation for the mixed solvents decreased as the alcohol content increased, until at 80% EtOH the ΔE per decade $> RT/nF$. Correction factors giving the variation of activity coefficients are tabulated for these systems from 0.1 to 1.5 molar MCl.

IN THE determination of formation constants of inorganic complex ions, a constant ionic strength system is frequently employed wherein the ligand concentration is varied in opposition to the concentration of a noncomplexing ligand. In some cases (*2*, *5*), it has been advantageous to use a constant ionic conductance system instead of a constant salt content system. In all cases, the author assumed that activity coefficients of all species remain constant as the ligand concentration is changed. However, at high strengths or in partially nonaqueous solvents where the dielectric constant is reduced considerably compared with dilute aqueous solution (*4*), there is reason to doubt the verity of this assumption.

In the course of research on the formation of cadmium-chloride complex ions in water–ethyl alcohol mixed solvents, it became necessary to evaluate the ranges of perchlorate substitution with chloride over which the activity coefficient of the chloride was constant. Apparently, this information would be furnished by potential measurements of the cells:

$$\text{I. } Ag\text{-}AgCl/NaCl_{(x)}, NaClO_{4(2-x)}//LiClO_{4(s)}//NaCl_{(s)}//NaCl_{(s)}/Hg_2Cl_2\text{-}Hg$$

$$\text{II. } Ag\text{-}AgCl/LiCl_{(x)}, LiClO_{4(2-x)}, X\%\ EtOH//LiClO_{4(s)}, X\%\ EtOH//LiClO_{4(s)}, H_2O//NaCl_{(s)}/Hg_2Cl_2\text{-}Hg$$

The use of saturated salt bridges minimizes fluctuation of junction potential as the ligand concentration is varied. Therefore, the cell e.m.f. should be dependent principally upon the activity of the metal chloride, and the plot of e.m.f. *vs.* log chloride concentration should be linear with a Nernst slope of RT/nF. At low substitution of perchlorate with chloride, the medium is essentially unchanged, and the Nernst slope should be obtained. At high replacement, the medium is changed substantially, and departure from linearity would be anticipated.

In this paper, an attempt is made to estimate the activity coefficient variation of HCl, NaCl, and LiCl in aqueous solution and LiCl in water-ethyl alcohol mixed solvent up to 80% by volume ethyl alcohol.

EXPERIMENTAL

Sodium and lithium perchlorates free of chloride contamination were obtained from the G.F. Smith Chemical Co. Silver chloride used for saturation of the solutions was prepared fresh by careful reaction of equivalent amounts of silver nitrate and sodium chloride, except for $HCl\text{-}HClO_4$ solutions where finely divided commercial reagent (Fisher) was used. All other chemicals were reagent grade.

The Ag-AgCl electrodes were prepared by deposition of AgCl on Ag wire by anodic oxidation in dilute hydrochloric acid (*1*). Two electrodes were prepared, and in several experiments potentials of both electrodes were measured. The electrodes were stored in the dark and never allowed to dry completely. An *H*-type cell with two intermediate compartments was used in all experiments. Corning ultrafine sintered glass frits were used in the construction of the cell compartments. A Leeds and Northrup potentiometer No. 7552 in conjunction with a Leeds and Northrup galvanometer No. 4230C was used for potential measurements. The cell assembly was thermostatically controlled at 27° C. by means of a water bath.

The procedure followed for potential measurements of cell I-type systems was to prepare stock solutions of MCl and $MClO_4$ of exactly the same molarity and saturate with AgCl slightly above room temperature. A series of measurements was started by equilibrating the stock solutions for 12 to 24 hours at 27° C., adding 50.00 ml. of $MClO_4$ stock to the test compartment, withdrawing a small quantity, and replacing with an equal amount of chloride stock solution. Increasing amounts of perchlorate solution were withdrawn and replaced with chloride solution, the potential being measured after each addition. At least 10 minutes was allowed for equilibration. More time was allowed if the potential drift was greater than 0.3 mv. in 10 minutes.

The procedure followed for potential measurements of type II cells was to prepare stock solutions of LiCl and $LiClO_4$ of the same concentration and alcohol content. The water of hydration of $LiClO_4$ was taken into account in preparation of the stock solutions. Volume contractions for the mixed solvents were compensated for by addition of diluents of the same alcohol content. Approximately 10 minutes was allowed to reach equilibrium after each addition, as was done for type I cells. Potential drift was checked periodically to ensure that equilibrium measurements were obtained. Except for 80% ethyl alcohol where identical response was obtained for both series, at least three sets of measurements were taken at each alcohol content. The amount of substitution of chloride was pur-

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posely varied so as to minimize the effect of accumulative error of substitution. Each set included measurements in the dilute chloride region where Nernst behavior was anticipated. The sets for each alcohol content were then normalized by equating potentials at 0.1*M* LiCl to compensate for long term potential drift of the reference electrode-salt bridge system.

RESULTS AND DISCUSSION

Cell potentials of type I cells, as a function of chloride concentration, for the various solute pairs are given in Figures 1 to 3. Included in Figure 2 are the potentials for the NaCl-NaClO$_4$ system *vs.* NaClO$_{4(s)}$//NaCl$_{(s)}$//NaCl$_{(s)}$/Hg$_2$Cl$_2$-Hg reference electrode. Three facts can be drawn from these data: The deviation from Nernst behavior is the same for each solute pair, ΔE per decade less than RT/nF; the limiting slope for NaCl-NaClO$_4$ system is theoretical (59.72 mv. per decade) only at very low concentrations of NaCl; and there is some difference in the potential response at high chloride concentrations with the salt bridge system employed for the NaCl-NaClO$_4$ system. Consideration of the nature of the junctions between the solutions and reference electrode-salt bridges leads to the assumption that the change in junction potential with substitution of chloride for perchlorate should be extremely small for all the systems studied (3). From the Hendersen equation, one can estimate a maximum junction potential of 2 mv. between 2*M* NaCl and 2*M* NaClO$_4$. With a saturated perchlorate salt bridge in the salt bridge system, the junction potential should be considerably reduced. The situation is analogous to the cell NaCl$_2$//NaClO$_{4(s)}$ or LiClO$_{4(s)}$//NaClO$_{4(2)}$. The difference in electrode response for the two salt bridges might result from chemical changes in the junction itself. However, quiescent junctions between 2*M* NaCl and NaClO$_{4(s)}$, 2*M* NaCl and LiClO$_{4(s)}$ showed no evidence of chemical reactions (such as precipitate formation). The reason for the difference in the two response curves for this system is therefore unknown. Thus, activity coefficient factors showing the deviation of NaCl activity coefficient are computed for both sets of data.

Table I gives the activity coefficient correction factors as a function of chloride concentration. These factors were derived from expanded plots of the data shown in Figures 1 to 3 and, when multiplied by the corresponding chloride concentrations, give parameters proportional to chloride activities. The change in chloride activity with chloride concentration may thus be readily computed.

Table I. Activity Coefficient Correction Factors

MCl, Concn. Moles/Liter	2.304*M* NaCl[a]	2.304*M* NaCl[b]	1.890*M* HCl
0.10	0.920	0.920	1.00
0.20	0.875	0.875	0.970
0.30	0.863	0.863	0.956
0.40	0.852	0.845	0.945
0.50	0.840	0.822	0.928
0.60	0.833	0.803	0.916
0.70	0.828	0.790	0.904
0.80	0.822	0.778	0.896
0.90	0.819	0.762	0.886
1.00	0.815	0.751	0.880
1.10	0.811	0.739	0.858
1.20	0.810	0.728	0.852
1.30	0.804	0.712	0.824
1.40	0.800	0.702	0.808
1.50	0.793	0.687	0.794
1.60	0.793	0.675	0.782
1.70	0.791	0.665	0.770
2.00	0.788	0.656	

[a] Saturated NaClO$_4$ salt bridge. [b] Saturated LiClO$_4$ salt bridge.

One observation that bears on the problem of difference in potential response for the NaCl-NaClO$_4$ system is that the activity coefficients decrease rapidly with increase in chloride concentration in dilute chloride solution. For the saturated LiClO$_4$ salt bridge, the activity coefficients continue to decrease as the chloride concentration increases, but for the NaClO$_4$ bridge, the decrease is nearly insignificant above 1*M* NaCl. The cause of the rapid decrease in activity coefficient at low chloride concentrations ought likewise to be operative at high chloride concentrations. Thus, the data obtained with the LiClO$_4$ bridge are taken to be the most representative of the system.

The potential response of the Ag-AgCl electrode to chloride ion in water-ethyl alcohol mixtures using type II cells is shown in Figure 3. The corresponding activity correction factors are given in Table II. The deviation from Nernst behavior was expected to increase with decrease in dielectric

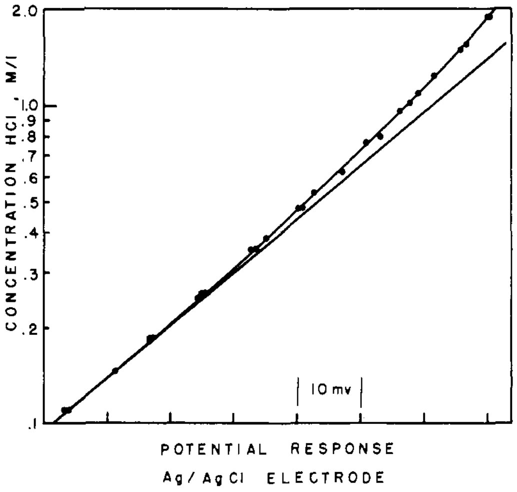

Figure 1. Potential response of the cell Ag-AgCl/HCl$_{(x)}$, HClO$_{4(1.89-x)}$//LiClO$_{4(s)}$//NaCl$_{(s)}$/Hg$_2$Cl$_2$-Hg as a function of HCl concentration

Straight line gives Nernst response extropolated from dilute solution. Potential at origin is +0.050 volt

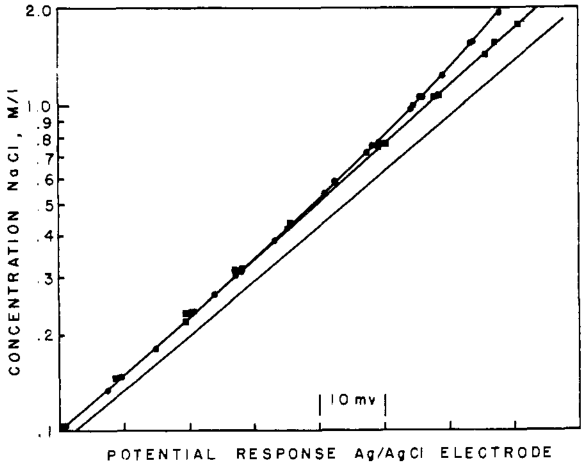

Figure 2. Potential response of the cell Ag-AgCl$_{(s)}$/NaCl$_{(x)}$, NaClO$_{4(2.30-x)}$//LiClO$_{4(s)}$//NaCl$_{(s)}$//NaCl$_{(s)}$/Hg$_2$Cl$_2$-Hg (upper curve), and the cell Ag-AgCl$_{(s)}$/NaCl$_{(x)}$NaClO$_{4(2.30-x)}$//NaClO$_{4(s)}$//NaCl$_{(s)}$//NaCl$_{(s)}$/Hg$_2$Cl$_2$-Hg as a function of sodium chloride concentration

Straight line gives Nernst response extrapolated from dilute solution. Potential at origin is +0.060 volt

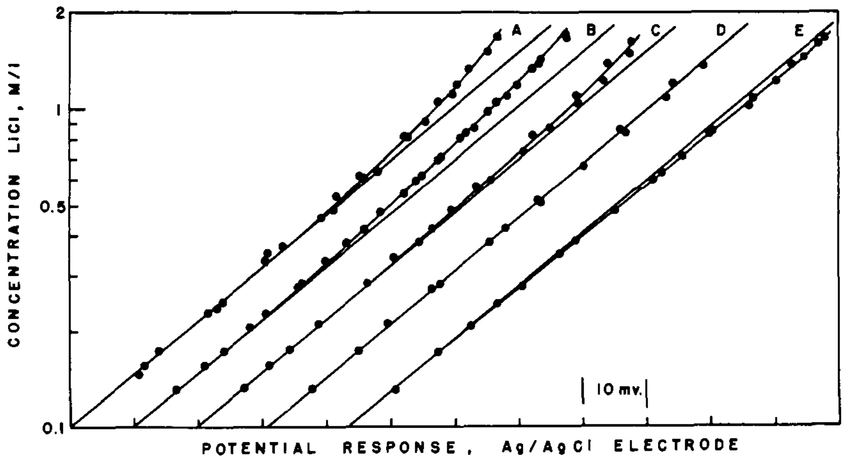

Figure 3. Potential response of the cell Ag-AgCl$_{(s)}$/LiCl$_{(x)}$, LiClO$_{4(2.0-x)}$, X% EtOH//LiClO$_{4(s)}$, X% EtOH//LiClO$_{4(s)}$/ /NaCl$_{(s)}$/Hg$_2$Cl$_2$-Hg as a function of lithium chloride concentration

Straight lines give Nernst response extrapolated from dilute solution.

A. 0% Ethyl alcohol, potential at 0.10*M* approximately +0.066 v.
B. 20% Ethyl alcohol, potential at 0.10*M* approximately +0.055 v.
C. 40% Ethyl alcohol, potential at 0.10*M* approximately +0.028 v.
D. 60% Ethyl alcohol, potential at 0.10*M* approximately +0.009 v.
E. 80% Ethyl alcohol, potential at 0.10*M* approximately −0.013 v.

Table II. Activity Correction Factors

LiCl Concn.	Ethyl Alcohol, %				
	0	20	40	60	80
0.05	1.00	1.00	1.00	1.00	1.00
0.10	1.00	1.00	1.00		1.010
0.15	1.00	1.00	1.00		1.014
0.20	1.00	0.985	1.00		1.018
0.25	1.00	0.976	1.00		1.024
0.30	0.993	0.967	1.00		1.025
0.35	0.991	0.957	0.994		1.031
0.40	0.987	0.950	0.988		1.032
0.45	0.980	0.942	0.982		1.033
0.50	0.978	0.936	0.980		1.036
0.55	0.973	0.931	0.976		1.038
0.60	0.968	0.927	0.975		1.040
0.65	0.960	0.923	0.969		1.046
0.70	0.954	0.912	0.970		1.050
0.75	0.949	0.909	0.963		1.053
0.80	0.939	0.900	0.956		1.062
0.90	0.925	0.890	0.950		1.067
1.00	0.908	0.880	0.940		1.075
1.10	0.895	0.864	0.941		1.081
1.20	0.879	0.954	0.917		1.091
1.30	0.861	0.838	0.908		1.100
1.40	0.836	0.825	0.889		1.086
1.50	0.817	0.813	0.880		1.067

constant. Interestingly, the deviation goes through a minimum at 60% ethyl alcohol, with a deviation at 80% opposite to that at lower alcohol contents. The reason for the difference is uncertain, but may be associated with the change of the difference of dielectric constants for LiCl and LiClO$_4$ solutions with alcohol content. Unfortunately, the dielectric constants of mixed solvents containing perchlorate and halide salts are not available.

The results of this work show that for the HCl-HClO$_4$ and LiCl-LiClO$_4$ systems, the response of the Ag-AgCl electrode to chloride concentration is exactly that predicted by the Nernst equation up to 0.1*M*. This is in direct contrast to the work reported by Bishop and Dhaneshwar (*1*), who observed that the Ag-AgCl electrode did not respond in a Nernst fashion in aqueous solution, but gave a continually changing response with ΔE per decade = 64.5 mv. at pCl = 1 and ΔE per decade = 0 mv. at pCl = 5. In the light of the present work, their results are apparently due to the failure to take into account the solubility of AgCl at low added chloride concentrations (accounting for ΔE per decade = 0 at pCl 75); the change in junction potential at the reference electrode–test solution interface; and the absence of a supporting electrolyte. Since no mention was made of the analysis of chloride concentration of the solutions, one can safely assume that the decrease in slope at pCl = 3 is the result of dissolution of AgCl. Incredibly, Bishop and Dhaneshwar do not mention the reference electrode–salt bridge system or the source of chloride ion used in their experiments. Even if a saturated bridge was used, there would be a small junction potential change with change in chloride concentration since the ionic strength was not held constant. In addition, a given salt in combination with different reference electrode–salt bridge combinations appears to lead to small differences in electrode response.

The results of this work bear directly on the technique for measurement of stability constants of metal complexes. It is generally assumed that at high, constant ionic strength, the activity coefficients of ionic species in solution are constant over wide substitution ranges. Simple approximation of activity coefficient variation as carried out in this work should lead to more reliable estimates of stability constants, particularly for metal-complex systems where the degree of complex formation is not extensive.

LITERATURE CITED

(1) Bishop, E., Dhaneshwar, R.G., *Analyst* 88, 424 (1963).
(2) Fritz, J.S., Waki, H., *J. Inorg. Nucl. Chem.* **26**, 865 (1964).
(3) Harned, H.S., Owen, B.B., "Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, 1958.
(4) Hasted, J.B., Roderick, G.W., *J. Chem. Phys.* **29**, 17 (1958).
(5) Marple, L.W., *J. Inorg. Nucl. Chem.* **27**, 1693 (1965).

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