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Acidity Functions for Acid-Salt Mixtures: $HCl-AlCl_3$ and HCl-KCl

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THROUGH STUDIES of electron transfer reactions in acid solutions (*1*) we have become interested in measuring the acidity function, H_o, (*2*) in acid-salt mixtures. To begin with we selected HCl-KCl and $HCl-AlCl_3$ mixtures, at several ionic strengths, because acid activities in these mixtures are known and because these mixtures conform to Harned's rule (*3*, *5*).

EXPERIMENTAL

Stock solutions of constant boiling hydrochloric acid were used as the source of HCl in preparing the acid-salt mixtures. Weighed portions of these solutions were analyzed by titration with 0.1*N* sodium hydroxide solutions, which were first standardized against potassium acid phthalate.

Stock solutions of aluminum chloride were prepared from reagent grade $AlCl_3 \cdot 6H_2O$ and then weighed portions of solutions were analyzed by potentiometric titration with standard silver nitrate solutions. The aluminum content was taken as one-third the chloride content.

The potassium chloride stock solution was prepared from reagent grade KCl and was standardized gravimetrically by precipitation of AgCl from a weighed portion of the stock solution.

Two indicators, 4-nitroaniline and 2-nitroaniline, were purchased from Aldrich Chemical Co. Solutions of these indicators in HCl were prepared, and the HCl content was determined by titration of weighed samples with standardized NaOH.

The solutions of acid-salt mixtures were prepared from the stock solutions by delivering weighed amounts of each stock solution, including the indicator, and an appropriate weight of water to make solutions of the desired ionic strength and (molal) concentration of each component.

Acidity functions of the mixtures were then determined by means of a Beckman, model DU, spectrophotometer. Readings were made at the maxima corresponding to the basic forms of the indicators: 4-nitroaniline and 380 mμ; 2-nitroaniline, 410 mμ. The acidity functions of the solutions were calculated as

$$H_o = pK + \log \frac{(D - D_{BH^+})}{(D_B - D)}$$

where pK refers to the appropriate indicator and D, D_{BH^+} and D_B are the absorbancies of the mixture, tha acid and basic forms of the indicator (at equal total indicator concentrations), respectively. Measurements were made at 25.5 ± 0.5°. The solutions were stored in a water bath, and the cell compartment of the spectrophotometer was controlled by circulation of the water from the thermostated bath through the thermospacers.

RESULTS AND DISCUSSION

Results from measurements of the acidity functions of $AlCl_3$-HCl mixtures are given in Table I. Mixtures at two ionic strengths (1 and 3) were studied. In Table II, the results obtained for KCl-HCl, with $\mu = 3$, are recorded.

For all solutions studied, graphs of H_o *vs.* log (H^+) or *vs.* log $(H^+)\ \gamma_\pm$ gave good straight lines. All three of these systems obey Harned's rule for mixed electrolytes (*4*). In preliminary studies made by means of a Dubosq colorimeter, $BiCl_3$-HCl mixtures and $SrCl_2HCl$ mixtures (μ =

Table I. The Acidity Function, H_o for $AlCl_3$-HCl Mixtures at 25° C.

(μ = 1.00, Indicator = 4-nitroaniline)

HCl, molal	$-H_o$	$\gamma_\pm$ for HCl (*3*)
0.1037	-1.047	0.719
0.1864	-0.74	0.728
0.3141	-0.48	0.741
0.4046	-0.35	0.750
0.5050	-0.24	0.760
0.6960	-0.09	0.781
0.8179	-0.00	0.793
0.9203	+0.05	0.803
1.0080	0.10	0.810
(μ = 3, Indicator = 2-nitroaniline)		
1.176	0.36	1.011
1.298	0.47	1.030
1.453	0.51	1.054
1.799	0.64	1.108
1.912	0.69	1.127
2.140	0.75	1.163
2.449	0.83	1.212
2.618	0.92	1.240
2.742	0.88	1.261

Table II. The Acidity Functions, H_o, for KCl-HCl Mixtures at 25° C.

(μ = 3.00. Indicator = 4-nitroaniline)

HCl, molal	$-H_o$	$\gamma_\pm$ for HCl1 (*5*)
0.879	0.14	0.945
1.216	0.39	0.988
1.381	0.40	1.110
2.007	0.65	1.116
2.268	0.78	1.166
2.311	0.78	1.174
2.673	0.85	1.236
2.842	0.87	1.253
3.347	1.02	1.370

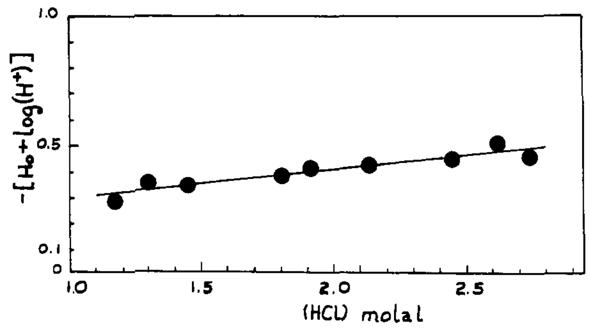

Figure 1. $-[H_o + \log(H)]$ vs. (HCl) for HCl-$AlCl_3$ mixtures μ = 3.0

1.00, 3.00, and 5.00) were also examined. Precision of these measurements was poor but graphs of H_o *vs.* log (H^-) and log (H^-) $\gamma_\pm$ were rectilinear to within the precision the measured H_o values.

The acidity function, H_o, may be written

$$H_o = -\log a_{\bar{H}} \frac{\gamma_B}{\gamma_{BH^\cdot}} = -\log(H^-) - \log \frac{\gamma_H + \gamma_B}{\gamma_{BH^\cdot}} \tag{1}$$

rearranging, one obtains,

$$H_o + \log(H^-) = -\log \frac{\gamma_{H^\cdot} \gamma_B}{\gamma_{BH^\cdot}} \tag{2}$$

For the systems and conditions studied, graphs of $-[H_o + \log(H^-)]$ *vs.* (HCl) give good straight lines (Figure 1). Since these solutions conform to Harned's rule, one can also represent log $\gamma_\pm$ for HCl as a linear function of HCl. Thus both log $\gamma_\pm$ for HCl and log $\gamma_{H^\cdot} \cdot \gamma_B / \gamma_{BH}$ can be described as linear functions of the same variable, HCl. Furthermore, in the preliminary studies with $BiCl_3$-HCl and $SrCl_2$-HCl mixtures, the same relationship seemed to apply.

It seems likely that for acid-salt mixtures which follow Harned's rule it will be possible to write

$$-[H_o + \log(H^-)] = \log \frac{\gamma_{\cdot H^\cdot} \gamma_{\cdot B}}{\gamma_{BH^\cdot}} = c(\mathrm{HCl}) + b \tag{3}$$

One may, perhaps, even be able to infer conformity to Harned's rule from validity of Equation 3 for a binary acid-salt mixture. A considerable body of additional data may be required, however, before this last hypothesis can be established.

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