JOURNAL OF THE TENNESSEE ACADEMY OF SCIENCE
Volume 44, Number 3, July, 1969

ELECTROMOTIVE FORCE STUDIES IN AQUEOUS SOLUTIONS AT ELEVATED TEMPERATURES. XI. THE THERMODYNAMIC PROPERTIES OF HCl - LiCl SOLUTIONS[1]

M. H. LIETZKE AND R. W. STOUGHTON

Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee

Previous papers in this series have described the thermodynamic properties of HCl-NaCl[1], HCl-KCl[2], HCl-RbCl[2], and HCl-CsCl[2] mixtures. The present paper completes the series describing the properties of mixtures of HCl and the alkali metal chlorides. Measurements of the cell Pt-H_2 (p=1) | HCl (m_2), LiCl (m_3) | AgCl, Ag have been combined with measurements of the activity coefficient of LiCl to calculate the thermodynamic properties of both HCl and LiCl in the HCl-LiCl mixtures.

EXPERIMENTAL

The experimental apparatus and the preparation of electrodes and solutions were the same as described prviously.[3] In all cases the emf measurements were carried out in the temperature range 25-175° in solutions of total ionic strength 0.5 and 1.0 in which the ratio of HCl to LiCl was varied. No drift of emf with time was observed after three to five hours. In general, the values were more reproducible in the solutions containing a higher fraction of acid, and values taken at the same temperature were reproducible to at least ± 0.5 mv.

RESULTS AND DISCUSSION

The treatment of the results in the present paper was the same as that followed in the study of the HCl-NaCl mixtures.[1] Each emf value was corrected to 1.00 atm. of hydrogen pressure by subtracting $(RT/2\mathcal{F}) \ln f_{H_2}$, where the hydrogen fugacity, f_{H_2} was taken equal to the hydrogen pressure. The corrected emf values E at each ionic strength were plotted as a function of temperature and the values corrected to the round values of temperature, 25, 60, 90, 125, and 175°. These values are given in Table I.

The activity coefficient $\gamma\pm$ of HCl at each temperature and set of concentrations in the mixtures was evaluated by using the Nernst equation and previous values[4] of the standard potential E° of the Ag, AgCl electrode.

$$E = E^{o} - \frac{RT}{\mathcal{F}} \ln [m_2(m_2 + m_3)] - \frac{2RT}{\mathcal{F}} \ln \gamma\pm \qquad (1)$$

In this equation m_2 and m_3 are the molalities of HCl and LiCl, respectively, while T is the absolute temperature, R the gas content, and $\mathcal{F}$ the Faraday.

[1] Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Plots of $\ln \gamma\pm_{HCl}$ *vs.* the ionic strength fraction of salt were made at each temperature and total ionic strength for each of the three systems. In all cases the plots were linear within experimental error and within the deviations of the ionic strength from the "constant value" in conformity with Harned's rule, as previously observed in the case of the HCl-NaCl mixtures.

Expressions for $\gamma\pm$ of HCl and LiCl in the Mixtures. The activity coefficients of HCl were smoothed as to HCl and LiCl concentrations and temperature in the same manner as described previously.[1] Hence the logarithm of the activity coefficient of the HCl was assumed to be given by

$$\ln \gamma_2 = -\mathcal{S} \rho^{1/2} \sqrt{I}/(1 + 1.5\sqrt{I}) + 2I\,[B_{22} + (B_{23} - B_{22})\,X_3] + 3I^2\,[C_{222} + 2\,(C_{223} - C_{222})\,X_3], \qquad (2)$$

while the corresponding equation for the LiCl was assumed to be

$$\ln \gamma_3 = -\mathcal{S} \rho^{1/2} \sqrt{I}/(1 + 1.5\sqrt{I}) + 2I\,[B_{33}\,(B_{23} - B_{33})\,X_2] + 3I^2\,[C_{333} + 2\,(C_{233} - C_{333})\,X_2 + (C_{333} + C_{223} - 2C_{233})\,X_2^2], \qquad (3)$$

where S is the Debye-Hückel limiting slope, ρ is the density of water, and I is the total ionic strength. In these equations, B_{ij} and C_{ijk} are interaction coefficients, while the subscript $_2$ refers to the HCl and the subscript $_3$ to the LiCl. Note that in equation (2) there is no term involving X^2_3 corresponding to the term involving X_2^2 in equation (3), since Harned's rule was observed to hold for the HCl in the mixtures. Hence $C_{222} + C_{233} - 2C_{223} = 0$.

The coefficients B_{ij} and C_{ijk} are, of course, temperature dependent. If the coefficients are expressed as

$$B_{iq} = B'_{iq} + B''_{iq}/T \text{ and } C_{ijq} = C'_{ijq} + C''_{ijq}/T, \qquad (4)$$

they are consistent with temperature-independent excess free enthalpies and entropies, i.e., excess over the molality and Debye-Hückel parts. If the coefficients are expressed as

$$B_{iq} = B'_{iq} + B''_{iq}/T + B'''_{iq} \log T \qquad (5)$$

and

$$C_{ijq} = C'_{ijq} + C''_{ijq}/T + C'''_{ijq} \log T, \qquad (5')$$

then they give rise to excess enthalpies varying linearly

TABLE I

Observed Values of the Emf in Volts for the Cell Pt—($_2$ (p=1) | HCl (m_2), LiCl (m_3) | AgCl, Ag and Deviations[a] of the Emf Values Calculated from Smoothed Activity Coefficients

		t°C					
m_2	m_3	25	60	90	125	150	175
.3762	.1274	.2781	.2592	.2429	.2171	.1977	.1742
		−3	−28	−9	−8	+8	+4
.2518	.2611	.2881	.2725	.2542	.2303	—	—
		−4	−6	−16	−9		
.1254	.3880	.3076	.2943	.2778	.2560	.2383	.2156
		+9	+9	+1	+8	+15	−9
.7678	.2717	.2399	.2180	.1985	.1696	.1484	.1239
		+2	−6	+11	+2	+8	−5
.5064	.5110	.2513	.2322	.2105	.1838	.1648	.1444
		+4	+13	−4	−7	+9	+23
.2530	.7756	.2676	.2500	.2326	.2072	.1890	.1682
		−7	−1	+7	−2	−3	−14

[a] The deviations are given below each reported emf as observed emf values less the values calculated from smoothed activity coefficients. Thus, a positive deviation indicates that the emf reported here is algebraically larger.

with temperature and excess entropies varying linearly with ln T. It was found that when equation (2) was used to describe the variation of $\ln \gamma\pm_{HCl}$ in the HCl-LiCl mixtures, it was possible to express the B_{12} as in equation (5) and the C_{ij2} as in equation (4). Convergence difficulties in the least squares fit were encountered when an attempt was made to use both equation (5) and (5'). This probably means that in the ionic strength range studied (to 1.0*m*) the contribution of the B terms is much more important than that of the C terms (hence the difficulty in determining as many parameters in the C coefficients). This same behavior was reported in the case of the HCl-NaCl mixtures.

The value of B'_{22}, B''_{22}, B'''_{22}, B'_{23}, B''_{23}, B'''_{23}, C'_{222}, C''_{222}, $C'_{223}{}'$, and C''_{223} were obtained directly by the least squares fit of equation (2) while the values of C'_{233} and C''_{233} were obtained by the application of Harned's rule: $C_{222} + C_{233} - 2C_{223} = 0$. The additional parameters needed for calculating the $\ln \gamma_3$ values (equation (3)), namely the coefficients B_{33} and C_{333} for the pure LiCl solutions, were evaluated by the method of least squares using activity coefficient data[5] on these solutions at 25°.

The parameters for calculating the various B and C coefficients are given in Table II. As mentioned before, the activity coefficient of HCl in the HCl-LiCl mixtures obeys Harned's rule, i.e., varies linearly with the ionic strength fraction of salt in the mixtures, just as observed previously in the case of HCl-NaCl mixtures. Since plots of the activity coefficient of HCl in the mixtures calculated using the parameters in Table II are similar to those in the HCl-NaCl mixtures, they are not shown here.

Figure 1 shows how the log γ_{LiCl} varies with total ionic strength and fraction of acid at 25° for the various mixtures. The log γ values are lower at I = 1.0 in the pure salt solutions and then cross the I = 0.5 curve. This same behavior was also observed in the other HCl-alkali metal chloride systems.[2]

Values of the emf E were calculated, using the previously determined $E°$ values and the B and C values for the smoothed activity coefficients (Table II), for each experimental point. The algebraic difference between the observed E values and those calculated are given below the observed E values in Table I.

The relationship between the B and C coefficients as

TABLE II

Parameters of the B and C Coefficients (equations 2 and 3) on a Common Logarithm Basis

$B'_{22} = 4.80663$	$B''_{22} = -192.292$	$B'''_{22} = -0.716243$
$B'_{23} = 7.87968$	$B''_{23} = -370.094$	$B'''_{23} = -1.15556$
$B_{33} = 0.0184969$ at 25°		
$C'_{222} = 0.0481675$	$C''_{222} = -20.0283$	
$C'_{223} = 0.0247978$	$C''_{223} = -10.3258$	
$C'_{233} = 0.0014281$	$C''_{233} = -\ 0.6233$	
$C_{333} = 0.0009198$ at 25°		

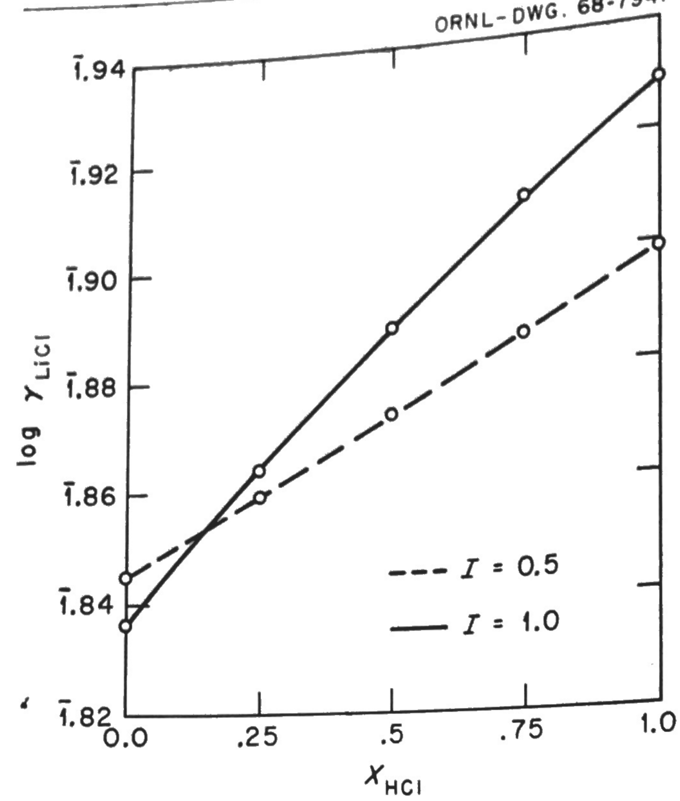

Fig. 1. Plots of log γ_{LiCl} *vs.* ionic strength fraction of HCl at 25° for HCl-LiCl mixtures.

defined by equations 2 and 3 and the α-coefficient of Harned's rule as well as the expressions for the partial molal free energy G_q, the partial molal enthalpy H_q, and the partial molal entropy S_q for component q may be calculated using the expressions previously reported[6] in the study of HBr-KBr mixtures. In a future paper actual values of these thermodynamic quantities will be compared, not only for the mixtures discussed in this paper but for mixtures of HCl with salts of higher valance type as well.

The authors would like to express their sincere appreciation to John T. Turk, a co-op student from the University of Tennessee, for performing the experimental measurements.

LITERATURE CITED

1. M. H Lietzke, H. B. Hupf, and R. W. Stoughton, J. Phys. Chem. *69,* 2395 (1965).
2. M. H. Lietzke and H. A. O'Brien, Jr. ibid., in press.
3.: R S. Greeley, W. T. Smith, Jr., R. W. Stoughton, and M. H. Lietzke, ibid., *64,* 652 (1960).
4. M. H. Lietzke and R. W. Stoughton, J. Phys. Chem. *68,* 3043 (1964).
5. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press Inc., New York, N.Y., 1955, Appendix 8.10.
6. M. H. Lietzke and R. W Stoughton, J. Phys. Chem. *67,* 2573 (1963).