Electromotive Force Studies in Aqueous Solutions at Elevated Temperatures

XV. The Thermodynamic Properties of Aqueous HCl–LaCl$_3$ Solutions to Ionic Strength 5.0

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The activity coefficient of HCl in aqueous HCl–LaCl$_3$ mixtures has been studied from 25–75°C to a total ionic strength of five using the emf technique. The activity coefficient of LaCl$_3$ in the mixtures was calculated by using the parameters describing this variation and those for the variation of the activity coefficient of LaCl$_3$ with ionic strength in pure LaCl$_3$ solutions. As a result of the extension of the measurements to the higher ionic strength, the calculated values of log γ_{LaCl_3} are now consistent with those observed for the salt in HCl–NaCl and HCl–BaCl$_2$ mixtures.

In a previous paper (*5*) in this series we reported the results of a study of the thermodynamic properties of aqueous HCl–LaCl$_3$ mixtures in the temperature range 25–175°C in solutions of total ionic strength 0.5 and 1.0. Recently we have made a study of the HCl–NaCl–LaCl$_3$ system to $I = 5$ over the temperature range 25–75°C. In connection with this latter study we found it desirable to extend the measurements in the HCl–LaCl$_3$ system to $I = 5$ but only in the temperature range 25–70°C. Using the new data we have recalculated the activity coefficient of both the HCl and the LaCl$_3$ in the mixtures. Although at $I = 1$ the values of log γ_{HCl} were affected but little, inclusion of the data at the higher ionic strengths resulted in considerable change in the values of log γ_{LaCl_3} at the higher fractions of acid. Hence it seems desirable to report separately our recent results on the HCl–LaCl$_3$ system to $I = 5$. As before, emf measurements of the cell

$$\text{Pt-H}_2(p = 1)|\text{HCl}(m_2),\ \text{LaCl}_3(m_3)|\text{AgCl, Ag}$$

have been combined with values of the activity coefficient of LaCl$_3$ obtained isopiestically (*6*) to compute the thermodynamic properties of both HCl and LaCl$_3$ in the HCl–LaCl$_3$ mixtures.

EXPERIMENTAL

The experimental apparatus and the preparation of the electrodes were the same as used previously (*1*). The e.m.f. measurements were carried out in the range 25–75°, using a water bath controlled to better than ± 0.1°C, on solutions of total ionic strength 3 and 5. At each total ionic strength solutions were prepared containing 0.75, 0.50, and 0.25 ionic strength fraction of HCl. Duplicate measurements using new electrodes and new samples of the solutions were reproducible to within a few tenths of a millivolt.

RESULTS AND DISCUSSION

The experimental data were treated as before (*5*). Each emf value was corrected to 1.00 atm of hydrogen pressure. The solubility of AgCl was neglected and the ionic strength of the solutions was taken to be equal to $m_{HCl} + 6\ m_{LaCl_3}$. The corrected emf values E for each data point as well as deviations of the emf values calculated from smoothed activity coefficients are given in Table I.

The activity coefficient $\gamma_\pm$ of HCl corresponding to each data point in Table I was calculated by using the Nernst equation and previous values (*3*) of the standard potential E^0 of the Ag, AgCl electrode.

$$E = E^0 - \frac{RT}{F} \ln\,[m_2(m_2 + 3\ m_3)] - \frac{2\,RT}{F} \ln \gamma_\pm \tag{1}$$

In this equation, m_2 and m_3 are the molalities of HCl and LaCl$_3$, respectively, while the remaining quantities have their usual significance.

The derivation of the equations used for expressing log γ_{HCl} and log γ_{LaCl_3} in the HCl–LaCl$_3$ mixtures has been given previously (*5*) and will not be repeated here. As before, the expression used for the excess activity coefficient of HCl—i.e., excess over the Debye-Hückel term, was taken to be

$$\log \gamma_2^e = 2\,I\left[B_{22} + \left(\frac{B_{23}}{6} - B_{22}\right)X_3\right] + 3\,I^2\left[C_{222} + \left(\frac{C_{223}}{3} - 2\,C_{222}\right)X_3 + \left(C_{222} + \frac{C_{233}}{36} - \frac{C_{223}}{3}\right)X_3^2\right] \tag{2}$$

while the corresponding expression for the LaCl$_3$ was

$$\log \gamma_3^e = I\left[\frac{B_{33}}{6} + \left(B_{23} - \frac{B_{33}}{6}\right)X_2\right] + \frac{I^2}{2}\left[\frac{C_{333}}{12} + \left(C_{233} - \frac{C_{333}}{6}\right)X_2 + \left(\frac{C_{333}}{12} + 3\,C_{223} - C_{233}\right)X_2^2\right] \tag{3}$$

In Equations 2 and 3, X represents the ionic strength fraction of the designated component in the mixture and I represents the total ionic strength of the solution. Since, even at the higher ionic strengths, Harned's rule appears to hold for the HCl in the mixtures, the coefficient in parentheses of the X_3^2 term in Equation 2 is zero.

The total log γ values are obtained by adding a Debye-Hückel term to Equations 2 and 3. This term was assumed to be $S_T\rho^{1/2}I^{1/2}/(1 + 1.5\,I^{1/2})$ for the HCl and $3\,S_T\rho^{1/2}/(1 + 1.5\,I^{1/2})$ for the LaCl$_3$, where S_T is the limiting slope for a univalent electrolyte at temperature T and ρ is the density of water which corrects the ionic strength to a volume basis as required by the Debye-Hückel theory.

The activity coefficients of HCl in the HCl–LaCl$_3$ mixtures (including both the present and former data) were fitted by the method of least squares using Equation 2 with the coefficient of

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Table I. Observed Values of the Emf in Volts for Cell Pt, $H_2(p = 1)|HCl(m_2), LaCl_3(m_3)|AgCl, Ag$ and Deviations[a] of the Emf Values Calculated from Smoothed Activity Coefficients

m_2	m_3	Temperature, °C					
		24.4	32.2	40.2	55.3	62.4	70.5
2.2953	0.1386	0.1678	0.1630	0.1573	0.1468	0.1429	0.1362
		0	−2	−9	−11	0	−5
		24.5	32.3	39.9	54.9	62.1	70.5
1 5010	0.2929	0.1873	0.1831	0.1781	0.1689	0.1649	0.1591
		−10	−9	−12	−10	−2	−3
		24.2	32.3	40.2	54.8	62.2	70.5
0.6931	0.3847	0.2238	0.2206	0.2153	0.2067	0.2035	0.1978
		+3	+13	+3	0	+10	+2
		24.6	32.3	40.2	55.1	62.3	70.4
3.9484	0.2967	0.1126	0.1076	0.1021	0.0913	0.0863	0.0805
		+27	+22	+16	+4	+3	+1
		25.0	32.2	40.0	55.1	62.2	70.4
2.5121	0.4820	0.1405	0.1356	0.1305	0.1205	0.1156	0.1106
		−10	−11	−10	−9	−11	−6
		24.2	32.2	40.1	54.9	62.2	70.3
1.2181	0.6398	0.1796	0.1755	0.1701	0.1605	0.1561	0.1507
		−3	+5	+2	+4	+6	+2

[a] The deviations are given below each emf value as observed value less the value calculated from the smoothed activity coefficients.

the X_3^2 term set to zero. With the wide range of total ionic strength covered it was possible to express the temperature dependence of both the B and C coefficients with equations of the type

$$B_{iq} = B_{iq}' + B_{iq}''/T + B_{iq}''' \log T \qquad (4a)$$

and

$$C_{ijq} = C_{ijq}' + C_{ijq}''/T + C_{ijq}''' \log T \qquad (4b)$$

The form of these equations gives rise to excess enthalpies varying linearly with temperature and excess entropies varying linearly with log T.

The values of B_{22}', B_{22}'', B_{22}''', B_{23}', B_{23}'', B_{23}''', C_{222}', C_{222}'', C_{222}''', C_{223}', C_{223}'', and C_{223}''' were obtained directly by the least-squares fit. The additional parameters needed for calculating log γ_3^e by Equation 3 were obtained as follows. The value of C_{233} was obtained by the application of Harned's rule: $C_{222} + C_{223}/36 - C_{223}/3 = 0$, while the values of B_{33} and C_{333} were evaluated by the method of least squares using activity coefficient data on pure $LaCl_3$ solutions (*6*). Since the activity coefficient of $LaCl_3$ has been measured only at 25°C, the values of B_{33}, C_{333}, and C_{233} were determined at this temperature only. Hence it was possible to compute the activity coefficient of $LaCl_3$ in the HCl–$LaCl_3$ mixtures only at 25°C.

The parameters for calculating the various B and C coefficients (on a common logarithm basis) are given in Table II. These parameters for the smoothed activity coefficients and the previously determined E^0 values were used to calculate emf values for each experimental point. The algebraic differences between the observed E values and those calculated are given below the observed E values in Table I. Plots of log γ_{HCl} vs. fraction of $LaCl_3$ in the mixtures at constant total ionic strength are very similar to those given before (*5*) at $I = 0.5$ and 1.0. At all total ionic strength values and temperatures in the range investigated, the log γ_{HCl} values become more negative as the fraction of $LaCl_3$ in the mixture increases.

Table II. Parameters of *B* and C Coefficients (Equations 2 and 3) for the HCl–$LaCl_3$ System over the Range 25–75°C to Total Ionic Strength of 5

$B_{22}' = 0.425636$ $B_{22}'' = -4.80492$ $B_{22}''' = -0.142033$
$B_{23}' = 19.5252$ $B_{23}'' = -838.275$ $B_{23}''' = -6.70742$
$C_{222}' = -0.143550$ $C_{222}'' = 8.87139$ $C_{222}''' = 0.0461840$
$C_{223}' = 0.421340$ $C_{223}'' = -17.0198$ $C_{223}''' = -0.146019$

At 25°C

$B_{33} = 0.290756$
$C_{333} = 0.0309296$
$C_{233} = 0.0178843$

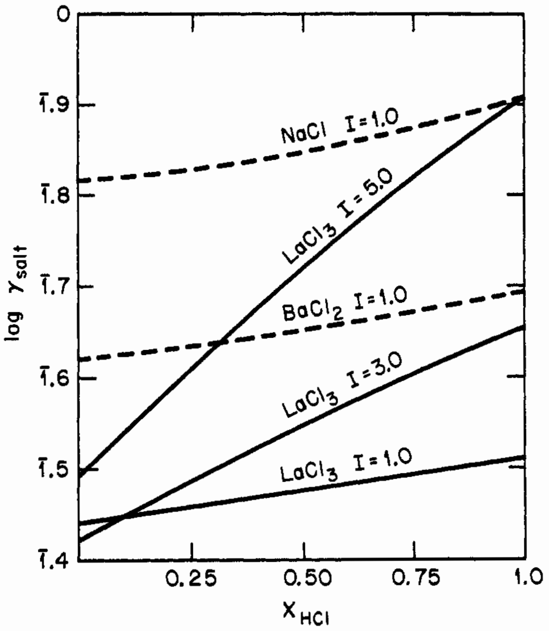

Figure 1. Plots of log γ_{LaCl_3} vs. X_{HCl} in HCl–$LaCl_3$ mixtures

As mentioned above, inclusion of data on the HCl–$LaCl_3$ mixtures to a total ionic strength of five results in a considerable change in the values of log γ_{LaCl_3} previously reported (*5*) when data only at $I = 0.5$ and 1.0 were available. The values of log γ_{LaCl_3} calculated from the parameters in Table II are plotted in Figure 1 vs. the fraction of acid in the mixtures. As the fraction of HCl increases in the mixtures at constant total ionic strength, the log γ_{LaCl_3} values increase (become less negative), the effect being greater the higher the total ionic strength. For comparison plots of log γ_{NaCl} in HCl–NaCl mixtures (*2*) and log

γ_{BaCl_2} in HCl-$BaCl_2$ mixtures (*4*), both at $I = 1.0$, are also shown in the figure. As can be seen, the plot of the log γ_{LaCl_3} in HCl-$LaCl_3$ mixtures is now consistent with the corresponding plots in the other two systems.

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Enthalpies of Ternary System Pentane–Cyclohexane–Benzene

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A flow calorimeter was used to measure enthalpy differences for the ternary system *n*-pentane–cyclohexane–benzene. The results are presented for three compositions with temperatures up to 600°F and pressures extending to 1400 psia.

The results of enthalpy measurements for the binary systems *n*-pentane–cyclohexane (*8*), *n*-pentane–benzene (*7*), and cyclohexane–benzene (*6*) have been published, but the enthalpy values for the ternary mixture of pentane–cyclohexane–benzene have not previously been reported. Three compositions of this ternary mixture of a paraffin, naphthalene, and aromatic have been studied, one rich in pentane, one an equimolar mixture, and the third, rich in benzene. Table I shows the exact compositions of the mixtures. The mixtures were prepared by weighing the pure components for samples of 5000 grams. All the hydrocarbons were obtained from the Phillips Petroleum Co. and their purity established with the use of a Loenco chromatograph. The *n*-pentane had only a trace of isopentane present with a purity of 99.96%, and density at 75°F of 0.6219 g/cc, with refractive index of $\eta^{20}\mathrm{D} = 1.3757$. The benzene density was 0.8730 g/cc, with refractive index of $\eta^{20}\mathrm{D} = 1.50030$, and a purity of 99.87%. The cyclohexane had a purity of 99.5%, with density of 0.7749 g/cc, and $\eta^{20}\mathrm{D} = 1.42604$. The uncertainty of the mixture compositions due to weighing errors was less than 0.2%.

The enthalpy of the mixtures was obtained with a flow calorimeter that measured the isobaric change in enthalpy between a relatively high inlet temperature and an outlet temperature of 75.0°F. As the hydrocarbon mixture flowed through the calorimeter, the enthalpy was transferred to saturated liquid Freon-11. By measuring the volumetric flow rate of both the hydrocarbon and the Freon-11, the enthalpy lost by the hydrocarbon mixture was determined. The details of this apparatus have been presented (*9*). Repeated studies (*5*, *7–9*) performed by comparing the results with published values for *n*-pentane (*2–4*) and liquid water (*11*) have shown that the accuracy of measurement is within 1.5 Btu/lb.

Table I. Properties of Liquid Phase at 75°F and 1 Atm

n-Pentane		Benzene			Heat of mix-	H needed for
Mol %	Wt %	Mol %	Wt %	Density, g/cc	ing, Btu/lb	−200°F basis, Btu/lb
60.1	57.3	20.0	20.5	0.6944	3.6	114.5
33.3	30.8	33.3	33.3	0.7449	4.1	103.4
20.0	18.5	59.8	59.8	0.7920	5.3	100.1

A total of 573 measurements was made on the ternary mixtures of pentane, cyclohexane, and benzene. These results, presented relative to the liquid state at 75°F and the pressure of measurement, have been tabulated and deposited with the ACS Microfilm Depository Service. These measured values were converted to a zero enthalpy basis of −200°F and the saturated liquid condition of the pure components, corresponding to the base level used by the API data book (*1*). As a first step in performing this conversion, the measured values are corrected to account for the change in enthalpy with increasing pressure at 75°F in the liquid phase. This was done using the thermodynamic equation of state (*9*), and amounted to a maximum change of 3.4 Btu/lb at 1400 psia. This correction was made with greater preciseness than the accuracy of measurement.

The enthalpy value needed to convert the enthalpy values of the pure components from 75° to −200°F has already been established for *n*-pentane (*9*), cyclohexane (*8*), and benzene (*5*). For the mixtures, the number needed to convert the data to the −200°F basis is a weight average of the conversion numbers for the pure components plus the heat of mixing at 75°F in the liquid phase. The heat of mixing was computed using the procedure presented by Tsao and Smith (*12*). Table I shows the computed heats of mixing, and also the enthalpy needed to convert the enthalpy values relative to 75°F and the saturated liquid phase to the −200°F basis.

The computed heats of mixing are similar to the corresponding values measured by Mathiesen and Thynne (*10*) for the hexane–cyclohexane–benzene system. The measured en-

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