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J. Christopher Peiper, and Kenneth S. Pitzer

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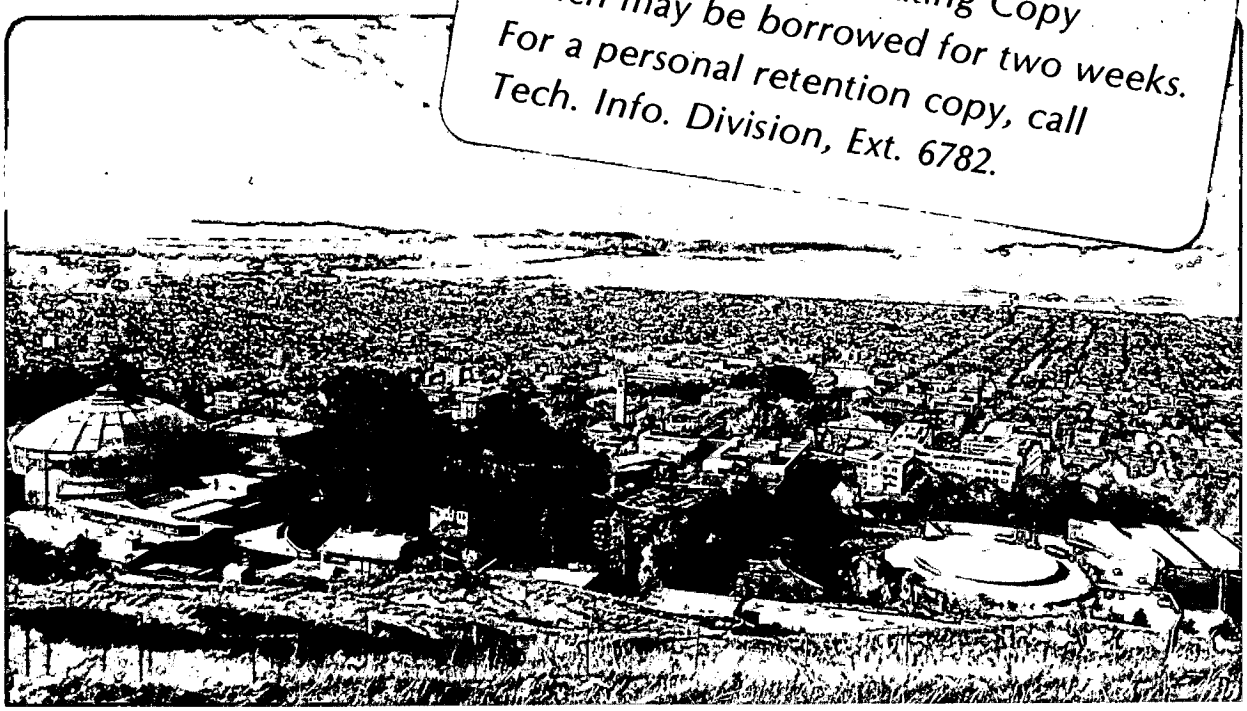

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Thermodynamics of the Unsymmetrical Mixed Electrolyte $HCl-LaCl_3$

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Abstract

The contribution of higher-order electrostatic terms (beyond the Debye-Hückel approximation) has been investigated for the system (H^+,La^{3+},Cl^-,H_2O). E.m.f. measurements were carried out on solutions at temperatures from 288.15 K to 318.15 K, and at ionic strengths from 0.1 to 5.0 mol kg^{-1}, using hydrogen and silver-silver chloride electrodes. From these measurements it is possible to determine the Pitzer mixing coefficients ${}^{s}\theta_{H,La}$ and $\psi_{H,La,Cl}$ as a function of temperature. They are well-represented by linear equations yielding temperature-invariant estimates of $\partial({}^{s}\theta_{H,La})/\partial T$ and $\partial(\psi_{H,La,Cl})/\partial T$. These estimates may be used to predict the relative apparent molal enthalpy for aqueous solutions containing H^+, La^{3+} and Cl^- with reasonable confidence. A brief table of the enthalpy and the activity coefficients is included.

Introduction

At finite concentration the properties of an electrolyte solution are complex functions of short-range forces between solute ions and of long-range (electrostatic) forces. The theory of Debye and Hückel assumes only the latter, together with a uniform hard-core repulsion, and leads to a knowledge of the limiting behavior of such solutions. "Higher-order" limiting laws arising from purely electrostatic effects may also be developed from a more complete theory; Friedman[1] discusses these, including a law for unsymmetrical mixing of ions of the same sign. Since short-range interionic forces have substantial effect on solution properties at rather low concentration, it is not easy to isolate the purely electrostatic terms in treating experimental measurements. It was shown by Pitzer[2] that the limiting law for unsymmetrical mixing could be extended to an expression valid at finite concentration and that the inclusion of this term resolved an anomaly in the properties of the system $HCl-AlCl_3$. The importance of this electrostatic function for unsymmetrical mixing was demonstrated impressively by Harvie and Weare[3] in their calculations on mineral solubility in the system Na^+, K^+, Mg^{++}, Ca^{++}, Cl^-, $SO_4^=$, H_2O at 25°C. The present study extends our understanding of unsymmetrical mixing effects by very precise measurements over a range of temperature on the system $HCl-LaCl_3$.

The measurements are treated in the system of equations[4-6] for electrolyte properties based on a Debye-Hückel term plus virial coefficients (or interaction coefficients) for short-range interionic interactions. Pair and triplet interactions usually suffice, but the second virial coefficients are functions of ionic strength in an electrolyte. The higher order electrostatic function for unsymmetrical mixing is easily included as a contribution to the second virial coefficient.

The temperature derivative of the mixing parameters for the Gibbs energy

is related to the heat of mixing, and in an accompanying paper[7] the experimental data on the heat of unsymmetrical mixing are treated. That paper reviews the basic theory and the related thermodynamics, hence those aspects will not be repeated here.

Experimental

Potentials for the cell

$$Pt,H_2(g)|HCl(m_1),LaCl_3(m_2)|AgCl,Ag \qquad (1)$$

were measured at 288.15, 298.15, 308.15, and 318.15 K, and at ionic strengths from 0.1 to 5.0 mol kg^{-1}. Solutions were prepared from reagent-grade hydrochloric acid, which was twice distilled to azeotropic composition, and reagent-grade lanthanum chloride, which was recrystallized three times from aqueous solution. Analyses of stock solutions of these reagents were carried out gravimetrically by precipitation of silver chloride. The molalities of HCl and $LaCl_3$ were determined to within ±0.01 per cent and ±0.02 per cent., respectively. Sample solutions were prepared by mass dilution of the stock solutions. Electrode preparation,[8,9] purification of hydrogen gas, cell design, temperature contol and stability (±0.02 K), and other experimental details have been given elsewhere.[10,11]

Measurements of the e.m.f. were made using a Leeds and Northrup type K-5 potentiometer in conjunction with a Leeds and Northrup model 9829 D.C. null detector. Stable, drift-free readings were always obtained, even in the most concentrated solutions. Equilibrium was assumed to have been attained when the e.m.f. remained constant (to well within 0.1 mV) for 30 min. at ionic strengths below 1.0 mol kg^{-1}, and for 15-20 min. above 1.0 mol kg^{-1}. All data are listed in Table I.

As a check on technique, standard potentials of all Ag-AgCl electrodes were determined at all experimental temperatures. Cell 1 was used with $m_1 = 0.01$ mol kg^{-1} and $m_2 = 0$ mol kg^{-1}, as suggested by Bates, et al.[12] The standard potentials thus obtained were in excellent agreement with previously published values.[13]

Theory and Equations

The Nernst equation for cell 1 is

$$E = E^{\circ}(Ag,AgCl) - \frac{RT}{F} \ln\left[\frac{m(H^+)\gamma(H^+)m(Cl^-)\gamma(Cl^-)}{m_0^{\,2}} \left(\frac{P_0}{P(H_2)}\right)^{\frac{1}{2}}\right] \qquad (2)$$

Herein: $E^{\circ}(Ag,AgCl)$ is the standard potential for the silver-silver chloride electrode, F is the Faraday and R,T retain their usual meanings. The ionic activities are given by the product $m_i\gamma_i$, where m has dimension mol kg^{-1}. The hydrogen fugacity may be assumed equal to the hydrogen pressure $P(H_2)$ in this work. The quantities m_0 and P_0 are included to ensure dimensional correctness and have the values 1.0 mol kg^{-1} and 1 atm = 0.101325 MPa, respectively. In light of the results of Bates, et al.,[12] concerning the behavior of silver-silver halide electrodes, values for $E^{\circ}(Ag,AgCl)$ were taken from reference 10. All physical constants were taken from reference 14.

The activity coefficient of HCl appearing in equation 2 is given for a mixed electrolyte by Pitzer and Kim[5] (their equation 15) and more recently by Pitzer[2] (his equations 26-30). For ease of reference, we reproduce those equations here. The activity coefficient of HCl in a solution containing $LaCl_3$ is given by

$$\ln(\gamma_{HCl}) = f^{\gamma} + (m_H + m_{Cl})(B_{H,Cl} + m_{Cl}C_{H,Cl})$$

$$+ m_{La}(B_{La,Cl} + m_{Cl}C_{La,Cl} + \theta_{H,La})$$

$$+ m_H m_{Cl}(B'_{H,Cl} + C_{H,Cl})$$

$$+ m_{La}m_{Cl}(B'_{La,Cl} + C_{LaCl} + \tfrac{1}{2}\,\psi_{H,La,Cl})$$

$$+ m_H m_{La}(\theta'_{H,La} + \tfrac{1}{2}\,\psi_{H,La,Cl}); \qquad (3)$$

$$f^{\gamma} = -A_{\phi}\left[\frac{I^{\frac{1}{2}}}{1+bI^{\frac{1}{2}}} + \frac{2}{b}\ln(1+bI^{\frac{1}{2}})\right]; \qquad (3a)$$

$$B_{i,j} = \beta^{(0)}_{i,j} + \frac{2\beta^{(1)}_{i,j}}{\alpha^2 I}\,[1-(1+\alpha I^{\frac{1}{2}})\exp(-\alpha I^{\frac{1}{2}})]; \qquad (3b)$$

$$B'_{i,j} = -\frac{2\beta^{(1)}_{i,j}}{\alpha^2 I^2}\,[1-(1+\alpha I^{\frac{1}{2}} + \tfrac{1}{2}\alpha^2 I)\exp(-\alpha I^{\frac{1}{2}})]; \qquad (3c)$$

$$C_{i,j} = \frac{C^{\phi}_{i,j}}{2|z_i z_j|^{\frac{1}{2}}}; \qquad (3d)$$

$$\theta_{H,La} = {}^{E}\theta_{H,La} + {}^{S}\theta_{H,La};\ \theta'_{H,La} = {}^{E}\theta'_{H,La} \qquad (3e)$$

Herein: f^{γ} is the Debye-Hückel function for the activity coefficient with parameter A_{ϕ}. Values of A_{ϕ}, of dimension $kg^{\frac{1}{2}}\ mol^{-\frac{1}{2}}$, are given by Bradley and Pitzer.[15] The parameter b has the standard value 1.2 $kg^{\frac{1}{2}}\ mol^{-\frac{1}{2}}$. The molality of ion i is given by m_i and the ionic strength by I, both have dimension mol kg^{-1}. The second and third virial coefficients for a pure electrolyte ij are $B_{i,j}$ and $C_{i,j}$, and have dimension kg mol^{-1} and $kg^2\ mol^{-2}$, respectively. The second virial is assumed to have some dependence upon the ionic strength, as represented above with an equation in two adjustable parameters, $\beta^{(0)}_{i,j}$ and $\beta^{(1)}_{i,j}$.

These parameters have the same dimension as $B_{i,j}$; α has the value 2.0 $kg^{\frac{1}{2}}\ mol^{-\frac{1}{2}}$. B'_{ij} is the ionic strength derivative of $B_{i,j}$ with dimension $kg^2\ mol^{-2}$. The ionic charges, in protonic units, enter into the formula for the third virial as z_i and z_j and relate C_{ij} to the parameter $C^{\phi}_{i,j}$ which was originally defined for the osmotic coefficient and is normally tabulated. The mixing coefficients $\theta_{H,La}$ and $\psi_{H,La,Cl}$ arise from the difference in interaction between H^+ and La^{+3} from the appropriate mean for $H^+ - H^+$ and $La^{+3} - La^{+3}$, and are defined in several papers.[2-6]

Using the notation of Pitzer,[2] $\theta_{H,La}$ may be decomposed into electrostatic and short-range contributions ${}^{E}\theta_{H,La}$ and ${}^{S}\theta_{H,La}$. The term ${}^{E}\theta_{H,La}$ has an ionic strength derivative ${}^{E}\theta'_{H,La}$; the corresponding term for short range forces ${}^{S}\theta_{H,La}$ is assumed to be independent of I. The electrostatic terms ${}^{E}\theta_{i,j}$ and ${}^{E}\theta'_{i,j}$ may be calculated <u>a priori</u> from formulae given by Pitzer.[2,7]

$$ {}^{E}\theta_{i,j} = \frac{z_i z_j}{4I} [J(x_{i,j}) - \tfrac{1}{2}J(x_{i,i}) - \tfrac{1}{2}J(x_{j,j})] \tag{4a} $$

$$ {}^{E}\theta'_{i,j} = - \frac{{}^{E}\theta_{i,j}}{I} + \frac{z_i z_j}{8I^2} [x_{i,j}J'(x_{i,j}) - \tfrac{1}{2}x_{i,i}J'(x_{i,i}) - \tfrac{1}{2}x_{j,j}J'(x_{j,j})] \tag{4b} $$

where z_i, z_j and I have been defined above. The univariant function J (and its derivative, J') is obtained from cluster-integral theory with omission of short-range forces. The variable $x_{i,j}$ is defined by

$$ x_{i,j} = 6 z_i z_j A_{\phi} I^{\frac{1}{2}}. \tag{5} $$

The functions J and J' are given by Pitzer[2,7] in integral and series form. The latter is useful only for $x_{i,j} \leq 0.10$, which, fortuitously, is the region where numerical integration is difficult. Dropping for the moment the subscripts on x, one obtains

$$J(x) = -\sum_{p=3} (\ln x + K_p) \frac{x^{p-1} p^{p-3}}{p!(p-3)!} \quad . \tag{6}$$

The quantities K_p are constants given as sums involving Euler's constant, lnp and integral fractions; the first few values are $K_3 = 0.41970$, $K_4 = -0.292608$, $K_5 = -0.369464$ and $K_6 = -3.00381$. From eq (6) one may obtain

$$J'(x) = -\sum_{p=3}^{\infty} [1+(p-1)(\ln x + K_p)] \frac{x^{p-2} p^{p-3}}{p!(p-3)!} \quad . \tag{7}$$

The error in truncating either series at P = 6 for x = 0.10 is less than 0.5 percent., which was calculated by comparison to the direct numerical result.

For x > 0.10, numerical methods are most precise. The integrals given by Pitzer[2,7] may be rearranged <u>via</u> variable substitution to yield:

$$J(x) = \frac{x}{4} - 1 + \int_0^1 \frac{\ln t}{q} (1-e^q) dt \tag{8a}$$

$$J'(x) = \frac{1}{4} + \int_0^1 \frac{t}{q^2} [1-(1-q)e^q] dt \tag{8b}$$

$$q = \frac{xt}{\ln t} \quad . \tag{8c}$$

A variety of numerical techniques may be used to compute these integrals; the authors prefer a 200-point Gauss-Legendre method.

The temperature dependence of ${}^{E}\theta_{H,La}$ and ${}^{E}\theta'_{H,La}$ derives solely from that of A_ϕ, as indicated in eq (5). This knowledge, plus precise e.m.f. measurements interpreted <u>via</u> eq (2) and (3), allows the determination of ${}^{S}\theta_{H,La}$ and $\psi_{H,La,Cl}$ as functions of temperature. This analysis assumes that the virial coefficients appearing in eq (3) are known over the temperature range of interest. This is in fact the case if it may be assumed that, e.g.,

$$\beta^{(0)}_{La,Cl}(T) = \beta^{(0)}_{La,Cl}(298.15\ K) + (T-298.15\ K)\left(\frac{\partial\beta^{(0)}_{La,Cl}}{\partial T}\right)_{298.15K},$$

and similarly for the remaining pure-electrolyte parameters. Table II gives values for all HCl and $LaCl_3$ parameters, and their temperature derivatives, at 298.15 K. Thus, only the mixing parameters ${}^{S}\theta_{H,La}$, and $\psi_{H,La,Cl}$ remain unknown.

The excess enthalpy of HCl-$LaCl_3$ mixtures may be calculated from the excess Gibbs energy[6,7] by the usual differentiation. For these mixtures H^{ex} is given by

$$\frac{H^{ex}}{n_w RT} = f_H - 2\,T\,m_H m_{Cl}\left[\frac{\partial}{\partial T}B_{H,Cl} + m_{Cl}\frac{\partial}{\partial T}C_{H,Cl}\right]$$

$$- 2\,T\,m_{La}m_{Cl}\left[\frac{\partial}{\partial T}B_{La,Cl} + m_{Cl}\frac{\partial}{\partial T}C_{La,Cl}\right]$$

$$- 2T\,m_H m_{La}\left[\frac{\partial}{\partial T}\theta_{H,La} + \frac{1}{2}m_{Cl}\frac{\partial}{\partial T}\psi_{H,La,Cl}\right] \qquad (9)$$

$$f^H = \frac{A_H I}{RTb}\ln(1+bI^{\frac{1}{2}}) \qquad (9a)$$

Here, f^H is the Debye-Huckel function for the enthalpy, with parameter A_H (of dimension J $kg^{\frac{1}{2}}$ $mol^{-3/2}$) as defined by Bradley and Pitzer.[15] Once more the mixing parameter $\frac{\partial}{\partial T}\theta_{H,La}$ may be separated into electrostatic and short-range effects

$$\frac{\partial}{\partial T}\theta_{H,La} = \frac{\partial}{\partial T}{}^{E}\theta_{H,La} + \frac{\partial}{\partial T}{}^{S}\theta_{H,La}. \qquad (10)$$

The electrostatic contribution may be calculated from eq (4a)

$$\frac{\partial}{\partial T}\left({}^{E}\theta_{i,j}\right) = \frac{z_i z_j}{4I}\left[J'(x_{i,j})\frac{\partial x_{i,j}}{\partial T} - \tfrac{1}{2}J'(x_{i,i})\frac{\partial x_{i,i}}{\partial T} - \tfrac{1}{2}J'(x_{j,j})\frac{\partial x_{j,j}}{\partial T}\right] \qquad (11)$$

From eq (5) one obtains

$$\frac{\partial x_{i,j}}{\partial T} = \frac{3z_i z_j}{2RT^2} A_H I^{\frac{1}{2}} \tag{12}$$

Results and Discussion

Linear least-squares procedures were used to fit eqs (2) and (3) to the experimental data. Only isothermal fits were performed. All points were given equal weight as measurements of E. The pure-electrolyte parameters were taken from references 16-18. For each isothermal fit, the only unknown parameters were ${}^{S}\theta_{H,La}$ and $\psi_{H,La,Cl}$.

The unknowns ${}^{S}\theta_{H,La}$ and $\psi_{H,La,Cl}$ may also be estimated by a graphical procedure. This procedure defines the quantity $\Delta\ln\gamma_{HCl}$ as the difference between the experimental value of $\ln\gamma_{HCl}$, calculated from (2) and that calculated from eq (3) with ${}^{S}\theta_{H,La}$ and $\psi_{H,La,Cl}$ zero. This yields

$$(\Delta\ln\gamma_{HCl})/m_{La} = {}^{S}\theta_{H,La} + \frac{1}{2}(m_H + m_{Cl})\,\psi_{H,La,Cl} \qquad (13)$$

so that a plot of $(\Delta\ln\gamma_{HCl})/m_{La}$ vs $\frac{1}{2}(m_H + m_{Cl})$ should give a straight line with intercept ${}^{S}\theta_{H,La}$ and slope $\psi_{H,La,Cl}$. Figure 1 shows at the top a plot of this type for the data at 298.15 K. Care must be exercised when using this procedure, since a constant uncertainty in the measured e.m.f. leads to an uncertainty in $(\Delta\ln\gamma_{HCl})/m_{La}$ which is greatly magnified for small La^{3+} molalities. However, we recommend construction of such plots as a visual check on the least-squares calculations.

The quality of the measurements and of the fit is better judged from the deviation of measured from calculated values of E shown on the lower part of Figure 1. When the ${}^{E}\theta$ and ${}^{E}\theta'$ terms are included (solid circles), the deviations are randomly positive and negative and rarely exceed 0.5 mV.

Also plotted on Figure 1 are the results (as triangles) if the higher order electrostatic terms are omitted. The systematic departures are apparent, primarily for dilute solutions.

The values are given in Table III of ${}^{S}\theta_{H,La}$, $\psi_{H,La,Cl}$, and the standard deviation of fit determined at each temperature *via* the least-squares procedure, and Figure 2 presents the temperature dependence of the results graphically. The errors bars correspond to the standard deviations of the parameters as determined by the fitting procedure. Also included in Table III are values of the standard deviation and of $\theta_{H,La}$ and $\psi_{H,La,Cl}$ determined without ${}^{E}\theta_{H,La}$ and ${}^{E}\theta'_{H,La}$; inclusion of the higher-order electrostatic terms is clearly indicated by the standard deviation values as well as by Figure 1. The mixing parameters are well represented by the equations

$$ {}^{S}\theta_{H,La} = 0.281 + 0.0018\ (T - 298.15) $$

$$ \psi_{H,La,Cl} = 0.006 - 0.0025\ (T - 298.15) \qquad (14) $$

The temperature coefficients of these parameters are then

$$ \frac{\partial}{\partial T}\left({}^{S}\theta_{H,La}\right) = 0.0018 \pm 0.0007 $$

$$ \frac{\partial}{\partial T}\left(\psi_{H,La,Cl}\right) = -0.0025 \pm 0.0003 \qquad (15) $$

where, again, errors were determined *via* the least-squares fitting procedure.

Most of the earlier measurements[19-21] for this system are not sufficiently precise to contribute to those aspects considered here. The most recent study that of Khoo, *et al.*,[22] reports data with precision comparable to the present study but only for 25°C and only to I = 3 mol kg^{-1}. They used slightly different pure-electrolyte parameters and there are small differences in the reported E values for pure HCl. In general, the results and conclusions of Khoo, *et al.*, for 25°C are the same as those of this investigation.

The activity coefficients of HCl and $LaCl_3$ and the excess enthalpy were calculated by eqs (3) and (9-11), and are presented in

Table IV. The enthalpy of mixing is the difference between the next to last column (y = 0.5) and the average of the adjoining columns (y = 0,1). These calculations are reasonably straightforward; hence we have not made efforts to provide extensive tables.

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TABLE I. Experimental Potentials for the Cell Pt, $H_2|HCl(m_1), LaCl_3(m_2)|$ AgCl, Ag. I is the Ionic Strength and B.P. is the Barometric Pressure

$I \approx 0.10$ mol kg^{-1}

10^3 m_1/mol kg^{-1}	100.00	69.559	50.020	29.831	19.904	9.805	B.P./kPa
10^3 m_2/mol kg^{-1}	0	5.073	8.330	11.695	13.349	15.032	
E(288 K)/mV	-	367.14	378.42	395.07	407.23	427.32	95.72
E(298 K)/mV	351.85	365.93	377.74	394.90	407.47	428.16	95.64
E(308 K)/mV	-	363.69	375.81	393.61	406.54	427.95	95.67
E(318 K)/mV	-	361.07	373.43	391.64	404.97	427.14	95.64

$I \approx 1.0$ mol kg^{-1}

10^3 m_1/mol kg^{-1}	1000.0	702.43	494.96	293.03	187.974	106.98	B.P./kPa
10^3 m_2/mol kg^{-1}	0	49.595	84.174	117.83	135.34	148.84	
E(288 K)/mV	-	252.15	265.67	283.47	297.14	313.89	95.67
E(298 K)/mV	232.17	247.34	261.38	279.77	294.20	311.48	95.63
E(308 K)/mV	-	242.39	256.38	275.46	290.00	307.97	95.67
E(318 K)/mV	-	236.38	250.99	270.63	285.51	304.18	95.63

$I \approx 2.0$ mol kg^{-1}

10^3 m_1/mol kg^{-1}	2000.0	1371.7	991.63	585.02	386.84	190.39	B.P./kPa
10^3 m_2/mol kg^{-1}	0	104.72	168.06	235.83	268.86	301.60	
E(398 K)/mV	185.08	203.99	218.32	238.95	253.45	275.32	95.64

TABLE I (continued)

$I \approx 3.0$ mol kg^{-1}

10^3 m_1/mol kg^{-1}	3000.0	2079.5	1466.0	898.01	597.15	317.67	B.P./kPa
10^3 m_2/mol kg^{-1}	0	153.42	255.66	350.33	400.48	447.06	
E(288 K)/mV	-	177.65	195.56	215.59	230.70	250.05	95.76
E(298 K)/mV	150.64	171.65	189.82	210.22	225.87	246.12	95.66
E(308 K)/mV	-	164.84	183.46	204.46	220.75	241.14	95.76
E(318 K)/mV	-	157.46	176.67	198.08	214.89	235.69	95.76

$I \approx 4.0$ mol kg^{-1}

10^3 m_1/mol kg^{-1}	4000.0	2827.2	2047.1	1269.5	839.74	384.33	B.P./kPa
10^3 m_2/mol kg^{-1}	0	195.47	325.49	455.09	526.71	602.61	
E(288 K)/mV	-	151.02	168.00	189.86	206.06	231.99	95.38
E(298 K)/mV	120.70	144.30	161.60	184.15	200.86	227.70	95.37
E(308 K)/mV	-	-	155.26	178.30	195.09	222.60	95.38
E(318 K)/mV	-	129.86	147.54	170.97	188.45	216.73	95.38

$I \approx 5.0$ mol kg^{-1}

10^3 m_1/mol kg^{-1}	5000.0	3435.8	2354.2	2092.4	1580.4	1106.1	B.P./kPa
10^3 m_2/mol kg^{-1}	0	260.70	440.97	484.60	569.93	648.89	
E(288 K)/mV	-	127.68	150.22	155.67	169.20	184.53	95.34
E(298 K)/mV	93.44	120.62	143.68	148.99	163.31	178.91	95.34
E(308 K)/mV	-	113.97	137.15	143.03	156.73	172.85	95.29
E(318 K)/mV	-	106.48	129.85	135.35	149.78	166.30	95.30

TABLE II. Ion-interaction Parameters at 298.15 K

	HCl	$LaCl_3$
$\beta^{(0)}$	0.1775[a]	0.5889[b]
$\beta^{(1)}$	0.2945[a]	5.60[b]
C^{ϕ}	0.00080[a]	-0.02383[b]
$\frac{\partial\beta^{(0)}}{\partial T} \times 10^4$	-3.081[c]	2.5267[b]
$\frac{\partial\beta^{(1)}}{\partial T} \times 10^4$	1.419[c]	79.80[b]
$\frac{\partial C^{\phi}}{\partial T} \times 10^4$	0.6213	-3.7144[b]

[a] From reference 16.

[b] From Reference 17.

[c] From Reference 18.

TABLE III. Mixing Parameters from Isothermal Fits to Data of Table I

	T/°C			
	15	25	35	45
	(with $^{E}\theta$ and $^{E}\theta'$ included)			
$S_{\theta_{H,La}}$/kg mol^{-1}	0.265 ± .013	0.278 ± .009	0.296 ± .010	0.319 ± .015
$\psi_{H,La,Cl}$/kg^2 mol^{-2}	0.030 ± .006	0.009 ± .004	-0.019 ± .005	-0.045 ± .007
σ_{fit}/mV	0.49	0.41	0.37	0.62
	(without $^{E}\theta$ and $^{E}\theta'$)			
$\theta_{H,La}$/kg mol^{-1}	-0.305 ± .022	-0.324 ± .017	-0.296 ± .021	-0.284 ± .030
$\psi_{H,La,Cl}$/kg^2 mol^{-2}	0.129 ± .010	0.118 ± .008	0.084 ± .010	0.059 ± .015
σ_{fit}/mV	0.71	0.72	0.86	1.15

TABLE IV. Activity Coefficients and Excess Enthalpies for the System (H^+, La^{3+}, Cl^-, H_2O) at Ionic Strength Fraction y of $LaCl_3$. The Trace Activity Coefficients of HCl and $LaCl_3$ are given in Columns 4 and 5, respectively. The Excess Enthalpy is Given for a Quantity of Solution Containing 1.0 kg Water.

I	$\gamma_\pm$(HCl)			$\gamma_\pm(LaCl_3)$			H^{ex}/RT		
mol/kg	y=0	y=.50	y=1.0	y=0	y=.50	y=1.0	y=0	y=.50	y=1.0
0.010	0.905	0.903	0.901	0.715	0.724	0.732	0.001	0.001	0.001
0.020	0.875	0.874	0.871	0.641	0.652	0.661	0.002	0.002	0.002
0.050	0.830	0.828	0.824	0.538	0.551	0.560	0.008	0.008	0.008
0.100	0.795	0.793	0.788	0.465	0.478	0.487	0.023	0.023	0.023
0.200	0.766	0.762	0.756	0.406	0.416	0.423	0.063	0.062	0.061
0.400	0.755	0.747	0.736	0.367	0.373	0.375	0.173	0.168	0.162
0.600	0.765	0.751	0.735	0.358	0.358	0.355	0.314	0.302	0.289
0.800	0.785	0.765	0.743	0.361	0.354	0.346	0.479	0.459	0.435
1.000	0.811	0.784	0.756	0.369	0.357	0.342	0.666	0.637	0.600
2.000	1.011	0.937	0.867	0.466	0.414	0.366	1.845	1.811	1.685
3.000	1.318	1.171	1.039	0.652	0.533	0.433	3.295	3.454	3.238
4.000	1.761	1.500	1.275	0.968	0.728	0.544	4.866	5.593	5.341
5.000	2.390	1.952	1.590	1.497	1.034	0.709	6.428	8.279	8.100

Figure Captions

Figure 1. The upper plot shows the composition dependence of $(\Delta \ell n\ \gamma_{HCl})/m_{La}$ at 298 K eq.(13). Data for $(m_H + m_{Cl})/2 < 0.2$ mol kg^{-1} are not shown: the uncertainties for these points are large and the deviations are negative and very large if ${}^{E}\theta_{H,La}$ and ${}^{E}\theta'_{H,La}$ are neglected (the triangles). The straight lines represent least-squares fits to the e.m.f. data. The lower plot shows the residuals $(E_{obs} - E_{calc})$ for the data at 298 K, for least-squares calculations with and without higher-order electrostatic terms, circles and triangles, respectively. Note the definite dish-shaped curvature for the fit without these terms. Obviously, the data at low ionic strength are much better represented with inclusion of ${}^{E}\theta_{H,La}$ and ${}^{E}\theta'_{H,La}$.

Figure 2. The temperature dependence of the mixing parameters ${}^{S}\theta_{H,La}$ and $\psi_{H,La,Cl}$. The fitted lines are given by eqs. (14).

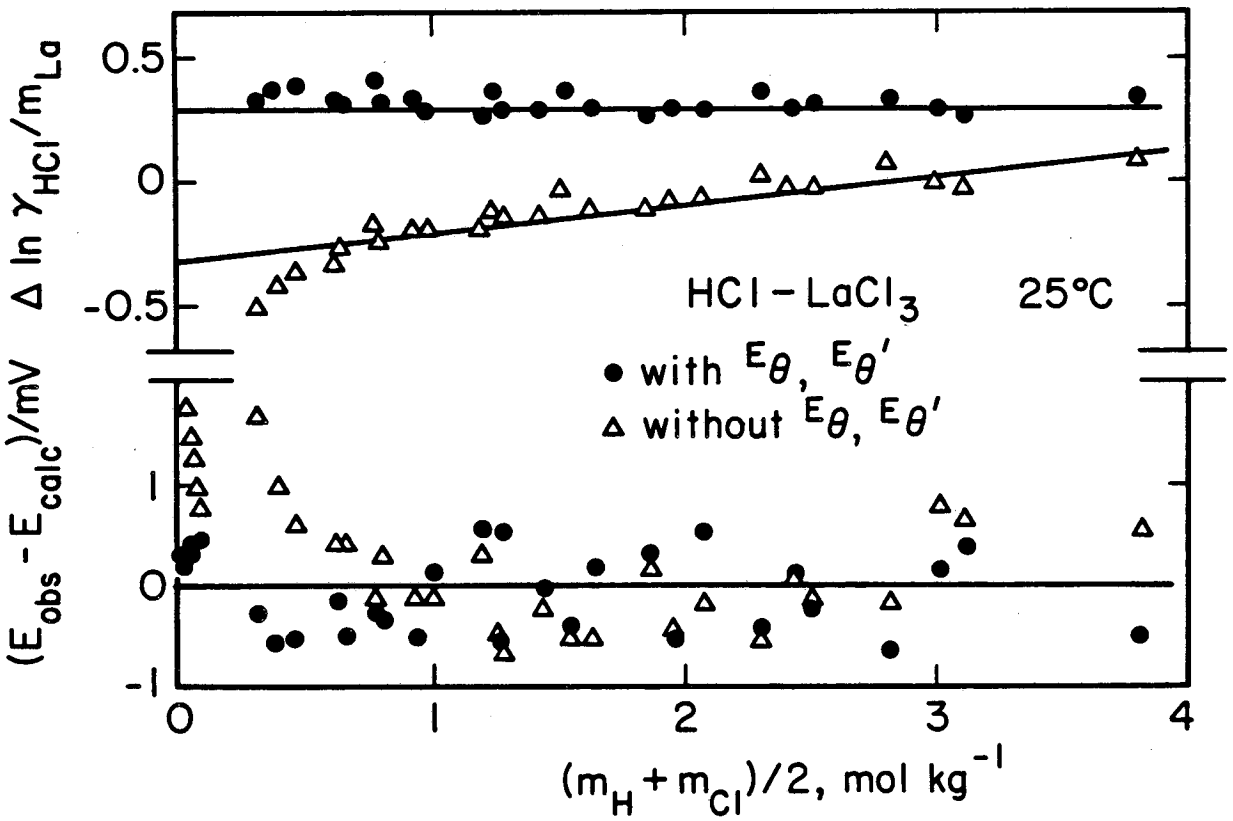
0.5
0
-0.5
Δ ln γ_HCl/m_La
HCl – LaCl3
25°C
● with Eθ, Eθ′
△ without Eθ, Eθ′
1
0
-1
(E_obs - E_calc)/mV
0
1
2
3
4
(m_H + m_Cl)/2, mol kg^-1

Figure 1

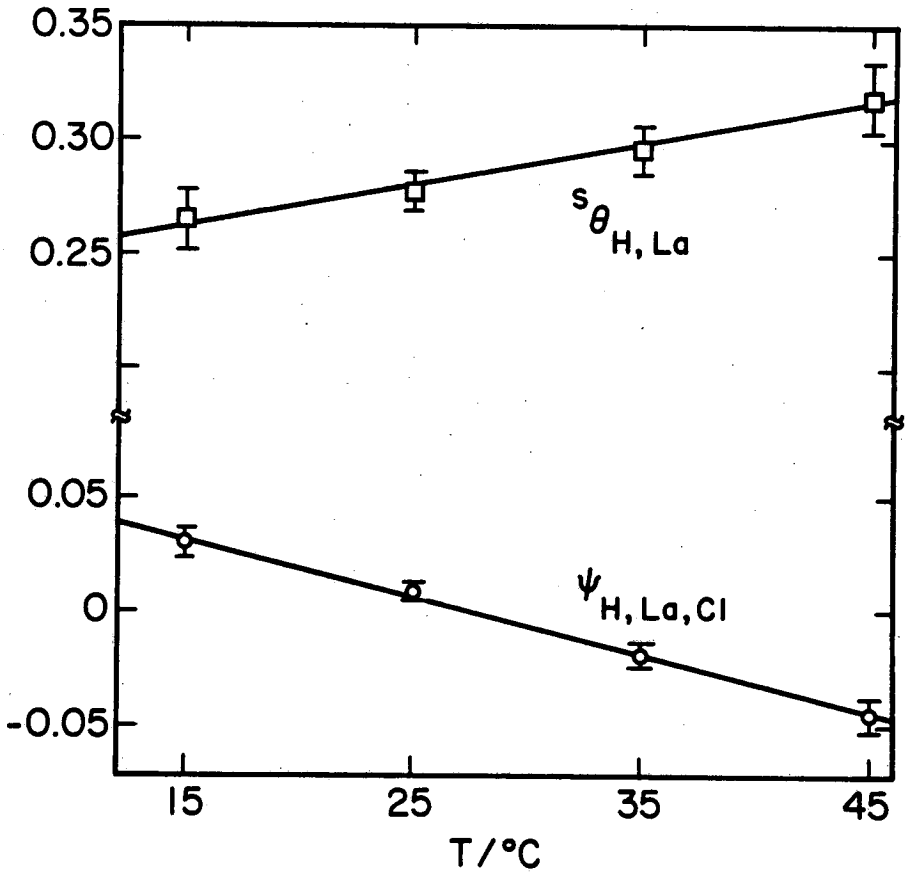

Figure 2

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