Activity Coefficients of HCl, NaCl, and KCl in Several Mixed Electrolyte Solutions at 25°C

Peter G. Christenson
Scripps Institution of Oceanography, La Jolla, Calif. 92037

The mean ionic activity coefficients of HCl, NaCl, and KCl in aqueous $MgCl_2$, $CaCl_2$, $BaCl_2$ and in mixtures of these divalent chlorides were calculated from emf measurements at 25°C, all at a total ionic strength of 1. Experimentally determined values in the three-salt systems agree to within 1% with those predicted by applying simple additivity equations to parameters derived from two-salt systems.

In concentrated solutions of two unassociated aqueous electrolytes, the mean ionic activity coefficient of one or both electrolytes often obeys the empirical linear relationship:

$$\log \gamma_1 = \log \gamma_1{}^\circ - \alpha_{12} y_2 I \tag{1}$$

at constant total ionic strength. This relationship is usually referred to as Harned's rule (6, 12). Gieskes (4) found that the activity coefficient of NaCl in a multicomponent artificial seawater solution was correctly predicted by the following simple extension of this relationship:

$$\log \gamma_1 = \log \gamma_1{}^\circ - \sum_{i=2}^{N} \alpha_{1i} y_i I \tag{2}$$

Lerman (8) also used this extension to calculate activity coefficients in Dead Sea brines. Åkerlöff (1, 2) showed that equations of type 2 can be used to calculate solubilities of salts in multicomponent electrolyte solutions.

Curvature in a plot of $\log \gamma_1$ vs. y_2 is often fitted by adding a quadratic term to Equation 1:

$$\log \gamma_1 = \log \gamma_1{}^\circ - \alpha_{12} y_2 I - \beta_{12} y_2{}^2 I^2 \tag{3}$$

Extending Equation 3 to multicomponent systems results in

$$\log \gamma_1 = \log \gamma_1{}^\circ - \sum_{i=2}^{N} \alpha_{1i} y_i I - \sum_{i=2}^{N} \beta_{1i} y_i{}^2 I^2 \tag{4}$$

The purpose of this study was to further test the validity of Equations 2 and 4. This was accomplished by comparing experimental activity coefficient data for the systems XCl (y_1) − YCl$_2$ (y_2) − ZCl$_2$ (y_3) with that predicted from Equations 2 and 4 by use of the parameters α_{12}, β_{12} derived from the simpler systems XCl (y_1) − YCl$_2$ (y_2) and XCl (y_1) − ZCl$_2$ (y_2). In the three-salt mixtures the divalent chlorides were present in a 1:1 ionic strength ratio ($y_2 = y_3$), and in all mixtures the total ionic strength was unity. Divalent rather than univalent chlorides were used as background electrolytes since they negligibly affect the response of the glass electrodes to univalent cations.

Experimental

Reagents. Deionized, doubly distilled water was used in all solutions. All salts were recrystallized from water after treating the aqueous solutions with chlorine gas to remove trace impurities of Br$^-$ and I$^-$. HCl, approximately 6m, was treated similarly by bubbling chlorine through it, then boiling to remove Cl_2, Br_2, and I_2, and

then diluting to approximately 1m. It was then titrated with dried Mallickrodt primary standard Na_2CO_3 and diluted to exactly 1m. The 1m NaCl and KCl were made up by weight. The 0.3333m $MgCl_2$, $CaCl_2$, and $BaCl_2$ were analyzed for Cl$^-$ with $AgNO_3$ with dichlorofluorescein as an adsorption indicator. The three or four replicates of each analysis agreed to better than 0.1%. Stock solutions containing two divalent chlorides in 1:1 ratio were made up by weight from the single electrolyte solutions. The pH of all stock salt solutions was greater than 5.2.

Method. The procedure for obtaining potentials was identical to the one used earlier (3). Temperature was maintained at 25.000 ± 0.007°C. Ag–AgCl electrodes were prepared electrolytically from Beckman No. 39261 silver electrodes according to Ref. 11. Corning No. 476025 triple purpose pH electrodes were used in those solutions containing HCl, Beckman No. 39278 sodium ion electrodes in those containing NaCl, and Beckman No. 39137 cationic electrodes in those containing KCl. More than one pair of electrodes were used to collect data on each of the mixed electrolyte systems to get a true estimate of the precision of the method. The cell potentials were measured with a Leeds and Northrup K-5 potentiometer connected to a Keithley 640 electrometer and 370 recorder.

The Nernst slope, S, of each pair of electrodes was determined by making several successive dilutions of a 1m XCl solution with water. This slope was checked before and often after a mixed electrolyte was run, and agreement was always within 0.3%. Activity coefficients for these XCl solutions were taken from Ref. 12. Only electrode pairs which gave an average Nernst slope of 118.3 ± 0.5 mV were accepted. These slopes are listed in tables deposited with the ACS Microfilm Depository Service.

Several successive dilutions of the 1m univalent chloride with the divalent chloride solution were then made. From these dilutions and the resulting changes in cell potential, the mean ionic activity coefficient of the univalent chloride was calculated from

$$\log [\gamma_1]_{i+1} = \Delta E/S - \frac{1}{2} \log \left(\frac{[m_x m_{cl}]_{i+1}}{[m_x m_{cl} \gamma_1{}^2]_i} \right) \tag{5}$$

Response time of the electrodes varied from 5 to 15 min, after which the drift became linear with time and less than 60 μV/hr. The true potential was obtained by extrapolating along the constant drift line to the time of the dilution. Overall precision of the emf measurements is about ±20 μV.

Results and Discussion

Results are tabulated in terms of m_x, m_{cl}, y_2 (or $y_2 + y_3$), ΔE, and $-\log \gamma_1$ and are available from the ACS Microfilm Depository Service. These results are also plotted in Figures 1–3, together with data from other investigators.

Two-salt systems. Data in the tables for two-salt systems were fitted to Equations 1 and 3 by the method of least squares to obtain parameters α_{12}, β_{12}. In this procedure the intercept was fixed, and the points were
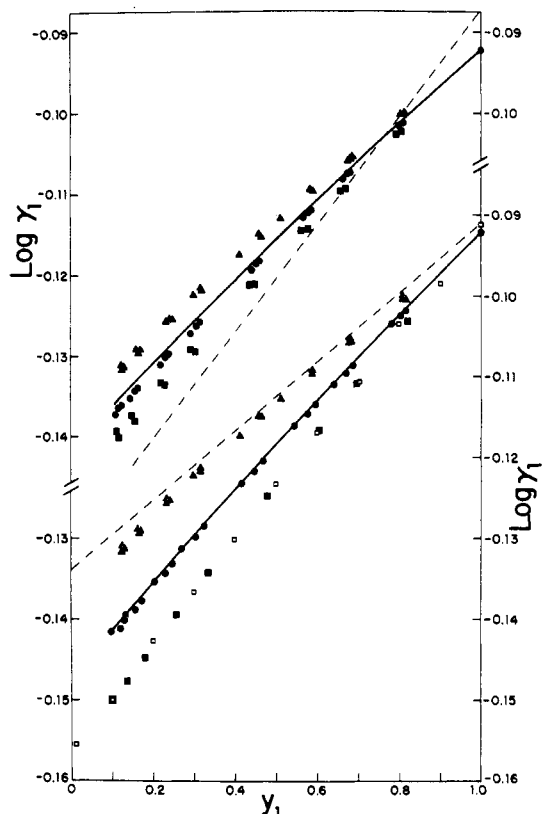
Figure 1. Mean ionic activity coefficients of HCl
Upper portion:
▲ HCl–MgCl$_2$–H$_2$O
■ HCl–CaCl$_2$–H$_2$O
● HCl–MgCl$_2$–CaCl$_2$–H$_2$O
Solid line: HCl–MgCl$_2$–CaCl$_2$–H$_2$O, predicted
Dashed line: HCl–CaCl$_2$–H$_2$O, Lietzke and O'Brien (10)
Lower portion:
▲ HCl–MgCl$_2$–H$_2$O
■ HCl–BaCl$_2$–H$_2$O
● HCl–MgCl$_2$–BaCl$_2$–H$_2$O
Solid line: HCl–MgCl$_2$–BaCl$_2$–H$_2$O, predicted
Dashed line: HCl–MgCl$_2$–H$_2$O, Lietzke and O'Brien (10)
□ HCl–BaCl$_2$–H$_2$O, Harned and Gary (5)

Figure 2. Mean ionic activity coefficients of NaCl
Upper portion:
▲ NaCl–MgCl$_2$–H$_2$O
■ NaCl–CaCl$_2$–H$_2$O
● NaCl–MgCl$_2$–CaCl$_2$–H$_2$O
Solid line: NaCl–MgCl$_2$–CaCl$_2$–H$_2$O, predicted
△ NaCl–MgCl$_2$–H$_2$O, Lanier (7)
□ NaCl–CaCl$_2$–H$_2$O, Lanier (7)
Lower portion:
▲ NaCl–MgCl$_2$–H$_2$O
■ NaCl–BaCl$_2$–H$_2$O
● NaCl–MgCl$_2$–BaCl$_2$–H$_2$O
Solid line: NaCl–MgCl$_2$–BaCl$_2$–H$_2$O, predicted
△ NaCl–MgCl$_2$–H$_2$O, Lanier (7)
□ NaCl–BaCl$_2$–H$_2$O, Lanier (7)

weighted according to their scatter by the weighting function

$$W_j = 10^{-5}/[0.0005 + 0.0015\ y_2 I_{(j)}]^2 \tag{6}$$

where the denominator represents an estimate of the variance of the jth point, and the numerator normalizes the weights to values near unity. Values of the parameters so obtained are listed in Table I, together with their standard deviations. Systems fit best by Equation 3 have their parameters listed for this equation as well as for Equation 1, since for many uses, the more approximate Equation 1 is probably sufficient and slightly more convenient.

Figure 1 indicates that the activity coefficients of HCl appear to display small curvature in all systems studied and so are best fit by Equation 3. However, the significance of this curvature is questionable since it is within the error limits imposed by the ±20 μV precision of the emf measurements. Figure 2 indicates that the activity coefficients of NaCl follow Equation 1, except for those in the system NaCl–BaCl$_2$–H$_2$O which display small curvature. KCl data, shown as dashed lines in Figure 3, was reported earlier (3).

Three-salt systems. The solid lines in Figures 1–3 are those predicted by use of Equations 2 or 4, depending upon whether the two-salt systems required a β_{12} term.
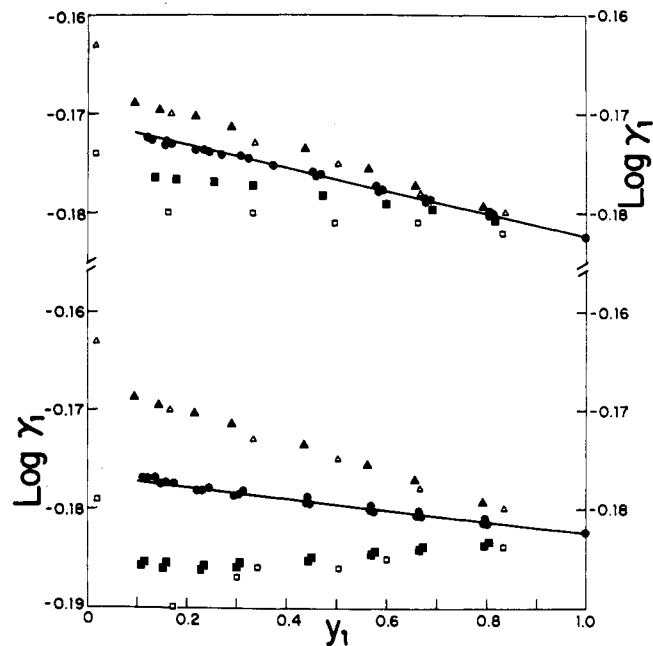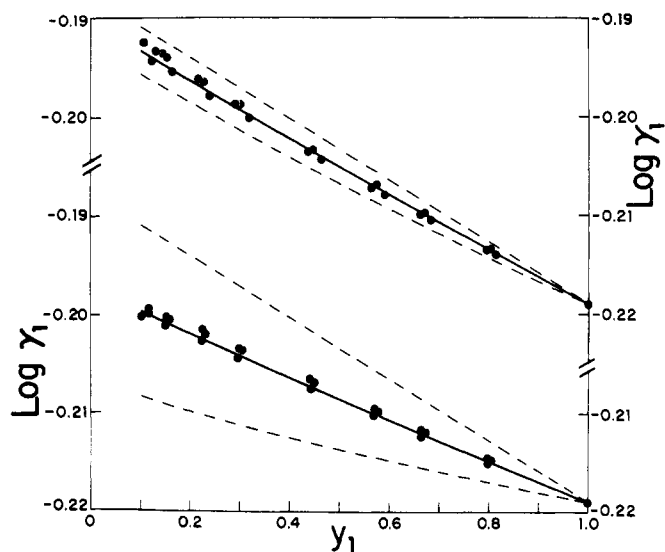

Figure 3. Mean ionic activity coefficient of KCl
Upper portion:
Top dashed line: KCl–MgCl$_2$–H$_2$O, Christenson and Gieskes (3)
Bottom dashed line: KCl–CaCl$_2$–H$_2$O, Christenson and Gieskes (3)
● KCl–MgCl$_2$–CaCl$_2$–H$_2$O
Solid line: KCl–MgCl$_2$–CaCl$_2$–H$_2$O predicted
Lower portion:
Top dashed line: KCl–MgCl$_2$–H$_2$O, Christenson and Gieskes (3)
Bottom dashed line: KCl–BaCl$_2$–H$_2$O, Christenson and Gieskes (3)
● KCl–MgCl$_2$–BaCl$_2$–H$_2$O
Solid line: KCl–MgCl$_2$–BaCl$_2$–H$_2$O, predicted

Table I. Parameters for Equations 1 and 3

System	Parameters for Equation 1			Parameters for Equation 3			
	$-\log \gamma_1$	α_{12}	$\sigma\alpha_{12}$	α_{12}	$\sigma\alpha_{12}$	$\dot{\beta}_{12}$	$\sigma\beta_{12}$
HCl–MgCl₂–H₂O	0.09205	0.0434	0.0002	0.0398	0.0002	0.0054	0.0004
HCl–CaCl₂–H₂O	0.09205	0.0527	0.0002	0.0501	0.0005	0.0039	0.0007
HCl–BaCl₂–H₂O	0.09205	0.0634	0.0004	0.0601	0.0001	0.0050	0.0002
NaCl–MgCl₂–H₂O	0.1824	−0.0155	0.0001				
NaCl–CaCl₂–H₂O	0.1824	−0.0077	0.0003				
NaCl–BaCl₂–H₂O	0.1824	0.0044	0.0001	0.0054	0.0003	−0.0016	0.0005

For these three-salt systems in which the divalent chlorides are present in a 1:1 ratio, the parameters describing the solid lines are simply the arithmetic average of those from the composing two-salt solutions.

As can be seen from Figures 1–3, Equations 2 and 4 predict the activity coefficients in these three-salt systems very well. The worst prediction is in the system HCl–MgCl₂–CaCl₂, where the predicted trace $\log \gamma_1$ is about 1% too positive.

Thus, simple additivity schemes, as represented by Equations 2 and 4, apply to these and a variety of other systems (*1, 2, 4, 8*). These simple schemes do not appear to be universally applicable, however, as shown by the HCl–CsCl–BaCl₂–H₂O data of Lietzke et al. (*9*). These investigators found that in this three-salt system, the $\log \gamma_1$ plot of HCl displays curvature and falls below the straight lines of the composing two-salt systems.

Acknowledgment

The author thanks J. M. Gieskes for his encouragement and valuable discussions.

Nomenclature

ΔE = change in cell potential in millivolts resulting from changing $[m_x m_{cl}]_i$ to $[m_x m_{cl}]_{i+1}$

γ_1 = mean ionic activity coefficient of XCl

γ_1° = Mean ionic activity coefficient of XCl in pure XCl solution

I = total ionic strength on molality scale

m = molality, mol solute/kg H₂O

N = number of electrolytes in solution

S = Nernst slope of electrode pair in millivolts

σ = standard deviation of a parameter computed by least squares

W_j = weight assigned to the jth point

X = H⁺, Na⁺, or K⁺

y_i = ionic strength fraction of ith salt

Y, Z = Mg²⁺, Ca²⁺, or Ba²⁺

Literature Cited

(1) Åkerlöf, G., *J. Amer. Chem. Soc.*, **56**, 1439 (1934).
(2) Åkerlöf, G., *J. Phys. Chem.*, **41**, 1053 (1937).
(3) Christenson, P. G., Gieskes, J. M., *J. Chem. Eng. Data*, **16**, 398 (1971).
(4) Gieskes, J. M. T. M., *Z. Phys. Chem., N. F.*, **50**, 78 (1966).
(5) Harned, H. S., Gary, R., *J. Amer. Chem. Soc.*, **76**, 5924 (1954).
(6) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolyte Solutions," 3rd ed., Chap. 14, Reinhold, New York, N.Y., 1958.
(7) Lanier, R. D., *J. Phys. Chem.*, **69**, 3992 (1965).
(8) Lerman, A., *Geochim. Cosmochim. Acta*, **31**, 2309 (1967).
(9) Lietzke, M. H., Hupf, H. B., Stoughton, R. W., *J. Inorg. Nucl. Chem.*, **31**, 3481 (1969).
(10) Lietzke, M. H., O'Brien, Jr., H. A., *J. Phys. Chem.*, **72**, 4408 (1968).
(11) McBryde, W. A. E., *Analyst*, **94**, 337 (1969).
(12) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions," 2nd ed., Chap. 15 and Appendix 8.10, Butterworths, New York, N.Y., 1959.