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The Activity Coefficient of Hydrochloric Acid in Concentrated Aqueous Higher Valence Type Chloride Solutions at 25°. II. The System Hydrochloric Acid–Strontium Chloride

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The activity coefficient of hydrochloric acid in strontium chloride solutions has been determined at 1, 3, 5 ionic strengths. The rule of linear variation of the logarithm of the activity coefficient of the acid at these total constant ionic strengths is verified. Following a procedure which employs the Gibbs–Duhem equation and cross differentiation relations, the thermodynamics of the system has been developed.

Previous results obtained by us[1] for the system hydrochloric acid–barium chloride–water were carried out at 1, 2, and 3 total ionic strengths. In this communication we have taken advantage of the fact that strontium chloride has a higher solubility than barium chloride and have extended this type of study over the wider concentration range of 1 to 5 total ionic strengths.

Experimental Data

The observed electromotive forces of the cells designated are recorded in Table I. Each value represents the mean of three results which were found on the average to agree within 0.05 mv.

TABLE I

ELECTROMOTIVE FORCES IN ABSOLUTE VOLTS OF THE CELL: H_2 (1 ATM.) | HCl ($\mu_1 = m_1$), $SrCl_2$ (μ_2) | AgCl–Ag at AT 25° AT 1, 3 AND 5 TOTAL IONIC STRENGTHS

	$\mu = 1$		$\mu = 3$		$\mu = 5$
m_1	E	m_1	E	m_1	E
1.0	0.23322	3.0	0.15183	5.0	0.09519
0.9	.23760	2.7	.15752	4.5	.10227
.8	.24206	2.4	.16346	4.0	.10964
.7	.24714	2.1	....	3.5	.11734
.6	.25264	1.8	.17685	3.0	.12575
.5	.25908	1.5	.18458	2.5	.13495
.4	.26655	1.2	.19339	2.0	.14514
.3	.27569	0.9	.20400	1.5	.15707
.2	.28809	.6	.21765	1.0	.17213
.1	.30782	.3	.23875	..	....

Test of the Linear Variation Rule for the Logarithm of the Activity Coefficient of the Acid Component at 1, 3 and 5 Constant Total Ionic Strengths.—In Table II, the activity coefficients of hydrochloric acid computed by the equation

$$E = E^0 - 0.05915 \log \gamma_1{}^2 m_1(m_1 + 2m_2) \qquad (1)$$

are recorded. The value of 0.22246 absolute volts for $E^{0(1)}$ was employed in this calculation. The molalities of the acid and salt are represented by m_1 and m_2, respectively. The numerical equations used to test the linear variation of the logarithm of the activity coefficient of the acid are given at the top of the table. In the columns designated by $\Delta\gamma_1$, the deviations from the linear relationship are recorded. Since a deviation of 0.1 per cent. corresponds to 0.05 millivolt, it is evident that the linear relationship is closely obeyed. This agreement is particularly apparent by examination of the results at the highest total concentration of 5μ.

Thermodynamic Calculations.—The following computations are based on the thermodynamic development given in detail in our earlier communication.[1] Having shown that the linear variation rule holds for the acid component, the assumption is made that a similar relation is valid for the other electrolyte component. Thus

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12}\mu_2 \qquad (2)$$

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21}\mu_1 \qquad (3)$$

$$\mu = \mu_1 + \mu_2 = \text{constant} \qquad (4)$$

where γ_1 and γ_2 are the activity coefficients of hydrochloric acid and strontium chloride in the mixtures, $\gamma_{1(0)}$ and $\gamma_{2(0)}$ their activity coefficients in water, μ_1, and μ_2 their concentrations expressed as ionic strengths, and α_{12} and α_{21}, are the linear constants at the given ionic strengths.

Application of the Gibbs–Duhem equation permits the calculation of α_{21} if α_{12} is known, and subsequently the osmotic coefficients, ϕ_x, and the vapor pressures of the solutions. In our nomenclature, the equations required for these calculations are

$$\frac{\alpha_{21}}{z_{2+}z_{2-}} = \frac{\alpha_{12}}{z_{1+}z_{1-}} - \frac{2}{2.3\mu}\left[\left(\frac{\phi_1}{z_{1+}z_{1-}} - \frac{\phi_2}{z_{2+}z_{2-}}\right) - \left(\frac{1}{z_{1+}z_{1-}} - \frac{1}{z_{2+}z_{2-}}\right)\right] \qquad (5)$$

and

$$\left(\frac{\nu_1}{j}\alpha_{12} + \frac{\nu_2}{k}\alpha_{21}\right)\frac{x^2}{2} + \left(\frac{\nu_1}{2.3j\mu} - \frac{\nu_2}{2.3k\mu} - \frac{\nu_2}{k}\alpha_{21}\right)x = \frac{2}{2.3\mu}\frac{\phi_2}{z_{2+}z_{2-}} + \frac{2\phi_x}{2.3\mu}\left[\frac{x}{z_{1+}z_{1-}} - \frac{(1-x)}{z_2{}^+z_{2-}}\right] \qquad (6)$$

In these expressions, the subscripts 1 and 2 refer to electrolytes 1 and 2, respectively, z_{1+}, z_{1-}, z_{2+}, z_{2-} represent the valences of the cations and anions, ν_1, ν_2 the number of ions into which the electrolyte dissociates and ϕ_1 and ϕ_2 the osmotic coefficients of the two electrolytes in the pure solvent. The valence factors j and k are defined by $\mu_1 = jm_1$, and $\mu_2 = km_2$ where m_1, m_2 are the molalities of the electrolytes. The osmotic coefficient of a solution of any composition is denoted by ϕ_x where x has all values between 0 and 1. The vapor pressure of the mixture may be computed by the equation

$$-\log a_{w(x)} = \frac{2\mu\phi_x}{(2.3)(55.5)}\left[\frac{x}{z_{1+}z_{1-}} - \frac{(1-x)}{z_{2+}z_{2-}}\right] \qquad (7)$$

Our results prove the validity of equation 2 within very narrow limits. A test of the validity of equation 3 is afforded by the result that if equation 3 is valid, the quantity, $S = \nu_1 k\alpha_{12} +$

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(1) H. S. Harned and R. Gary, THIS JOURNAL, **76**, 5924 (1954).

TABLE II

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID

$$\text{Equations used for calculations} \begin{cases} \mu = 1;\ \log \gamma_1 = -0.09076 - 0.0581\ \mu_2 \\ \mu = 3;\ \log \gamma_1 = +0.11961 - 0.0579\ \mu_2 \\ \mu = 5;\ \log \gamma_1 = +0.37651 - 0.0582\ \mu_2 \end{cases}$$

	$\mu = 1$			$\mu = 2$			$\mu = 3$	
m_1	γ_1	$\Delta\gamma_1$	m_1	γ_1	$\Delta\gamma_1$	m_1	γ_1	$\Delta\gamma_1$
1.0	0.8111	−0.0003	3.0	1.318	+0.001	5.0	2.380	0.000
0.9	.7985	− .0021	2.7	1.265	.000	4.5	2.224	− .001
.8	.7903	+ .0003	2.4	1.216	.000	4.0	2.080	− .001
.7	.7794	− .0001	2.1	....	......	3.5	1.949	+ .003
.6	.7708	+ .0017	1.8	1.123	+ .001	3.0	1.821	+ .001
.5	.7596	+ .0007	1.5	1.079	+ .001	2.5	1.701	− .001
.4	.7495	+ .0007	1.2	1.038	+ .002	2.0	1.592	.000
.3	.7401	+ .0012	0.9	0.9955	+ .001	1.5	1.489	+ .001
.2	.7281	− .0009	.6	.9557	− .0006	1.0	1.391	− .001
.1	.7179	− .0014	.3	.9175	− .0013	..	...	.....

$\nu_{2j}\alpha_{21}$, must be a constant independent of the total ionic strength, μ. For solutions containing hydrochloric acid and a bivalent chloride $S = 6\alpha_{12} + 3\alpha_{21}$. Values of the osmotic coefficients ϕ_1, and ϕ_2 of the acid and salt, respectively, obtained from the isopiestic vapor pressure measurements of Stokes[2] and Robinson and Stokes,[3] and α_{12}, α_{21} and S are given in Table III.

TABLE III

DATA EMPLOYED IN EQUATIONS 5 AND 6

	ϕ_1	ϕ_2	α_{12}	α_{21}	S
$\mu = 1$	1.039	0.869	0.0581	−0.0646	0.155
$\mu = 3$	1.348	1.009	.0579	− .0836	.097
$\mu = 5$	1.680	1.192	.0582	− .0868	.089

It is to be observed that the value of S decreases with increase in concentration and is nearly the same at 3 and 5 μ. This result is similar to the one observed for hydrochloric acid–barium chloride–water systems and indicates that the linear relationship represented by equation 3 is not strictly valid at the lower concentrations.

TABLE IV

OSMOTIC COEFFICIENTS AND VAPOR PRESSURES AT 25° OF THE SYSTEM $HCl–SrCl_2–H_2O$ CALCULATED BY EQUATIONS 6 AND 7

	$\mu = 1$			$\mu = 3$			$\mu = 5$	
m_1	ϕx	P	m_1	ϕx	P	m_1	ϕx	P
1.0	1.039	22.88	3.0	1.348	20.53	5.0	1.680	17.55
0.9	1.027	22.94	2.7	1.325	20.73	4.5	1.646	17.92
.8	1.015	22.99	2.4	1.301	20.93	4.0	1.611	18.29
.7	1.001	23.04	2.1	1.275	21.13	3.5	1.573	18.67
.6	0.988	23.09	1.8	1.247	21.33	3.0	1.533	19.05
.5	.972	23.14	1.5	1.217	21.52	2.5	1.489	19.43
.4	.956	23.19	1.2	1.184	21.72	2.0	1.442	19.81
.3	.938	23.24	0.9	1.148	21.91	1.5	1.390	20.19
.2	.918	23.29	.6	1.107	22.11	1.0	1.332	20.57
.1	.895	23.34	.3	1.062	22.30	0.5	1.267	20.95
.0	.869	23.39	.0	1.008	22.49	0.0	1.190	21.34

Table IV contains the osmotic coefficients and vapor pressures of these mixtures calculated by equations 6 and 7.

Conclusions

(1) The linear relationship given by equation 1 is valid within very narrow limits for the system hydrochloric acid–strontium chloride–water at 1, 3 and 5 total ionic strengths.

(2) The values of α_{12} are the same at all ionic strengths investigated but α_{21} varies with the total ionic strength. This result is in accord with a similar one involving the system hydrochloric acid–barium chloride–water. The nature of the variation of S with μ indicates the linear variation of the logarithm of the activity coefficients of strontium chloride in aqueous hydrochloric solutions is not strictly valid in the more dilute solutions. At the higher concentrations both linear relationships given by equations 2 and 3 represent the behavior of the hydrochloric acid–strontium chloride–water system within narrow limits.

(3) In these studies, we have consistently employed molalities and ionic strengths. Since activity coefficients are pure numbers, it is obvious that α_{12} and α_{21}, in equations 2 and 3, have the dimensions of a reciprocal molality. This fact suggests that volume concentrations be employed in investigations of this nature rather than molalities with the prospect that the results would be more nearly in conformity with subsequent theoretical considerations.

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[2] R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

[3] R. A. Robinson and R. H. Stokes, *ibid.*, **45**, 612 (1949).