HARNED/ÅKERLÖF EQUATIONS AND THE SOLUBILITY OF NaCl IN HCl–WATER SYSTEM

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Abstract. The solubilities of sodium chloride in water in the presence of hydrochloric acid have been calculated with Akerlof equation and these values are compared with experimental results. B_c and α_c constants for sodium chloride are also calculated with this equation, which are comparable with their corresponding values, obtained by Harned and Robinson. α_c and B_c values vary betwee the limits —0.053 to 0.0548 and —0.087 to —0.0910 respectively, which indicate their independence of total ionic strength. The decrease in solubility of sodium chloride with increase in acid concentration is explained by the change in activity coefficients and by the concept of hydration of the ions.

The behaviour of electrolytic solution in aqueous media has been of considerable interest from the thermodynamic as well as molecular point of view. In this connection, the work on the solubilities of sodium chloride[1] and other electrolytes[2] in water in the presence of hydrochloric acid and other acids[3,4] have been thoroughly studied. The solubilities of salts in electrolytic solutions vary with the changes in pH of the solution. The effect has mainly been attributed to the presence of 'common ion', and where this has not been the case, the hydronium ion played the predominant role. In solutions where both were present the total effect is a mixture of the two effects and is best understood in terms of changes in the activity coefficients of one component in the presence of other components. The behaviour of electrolytic solutions has been described by Harned equation (1 and 2) and where these equations are found inadequate the equations (3a and 3b) are known to hold reasonably. More complicated equations describing solubilities of electrolytic solutions are due to Åkerlof (equation 8) and Åkerlöf and Thomas (equations 5, 6 and 7). These equations contain empirical coefficients and isothermal constants which are interpretable by way of molecular and ionic interactions in solutions.[5]

In the present article work on the solubilities of sodium chloride in water in the presence of hydrochloric acid has been described. A fixed volume of saturated solution of sodium chloride was mixed with hydrochloric acid solutions of various concentrations and amount of sodium chloride precipitated and hence the amount remaining in solution was calculated.[6] The amount (m_c*) of sodium chloride remained in solution has been plotted against m_B. This has been compared with the theoretically calculated values obtained through Åkerlöf equation shown also in Fig. 1.

Notation—Subscripts B refer to HCl an C to NaCl; m_B, molatity of HCl; γ_B activity coefficient of HCl in the system; $\gamma_B°$, value of γ_B when $m_B, = 0; m = m_B + mc$; P_C, solubility product of NaCl; and $B_C, =$ isothermal constant; α_c and β_c are the empirical coefficient of NaCl in this system.

Harned and Åkerlöf Equations.

The activity coefficient γ_B of HCl in a solution containing sodium chloride, can be defined by the equation

$$\log \gamma_B = \log \gamma°_B — \alpha_B m_C \qquad (1)$$

and it was believed (Harned rule) that a similar equation, i. e.

$$\log \gamma_c = \log \gamma°_c — \alpha_C m_B \qquad (2)$$

is also exact in defining the activity coefficient γ_C of sodium chloride in a solution containing hydrochloric acid, but it was latter on shown[1], that a small quadratic term is necessary to describe the activity coefficient of sodium chloride, i. e,

$$\log \gamma_B = \log \gamma_B° — \alpha_B m_C — \beta_B m_C{}^2 \qquad (3a)$$

$$\log \gamma_c = \log \gamma_c° — \alpha_C m_B — \beta_C m_B{}^2 \qquad (3b)$$

where parameter α_c and β_c have negative values and the equation indicates that γ_C increases with the addition of hydrochloric acid.

$\log \gamma_C$ is also related to ionic activity product (K_c) and solubility product (P_c) in the NaCl solution containing hydrochloric acid, through an equation
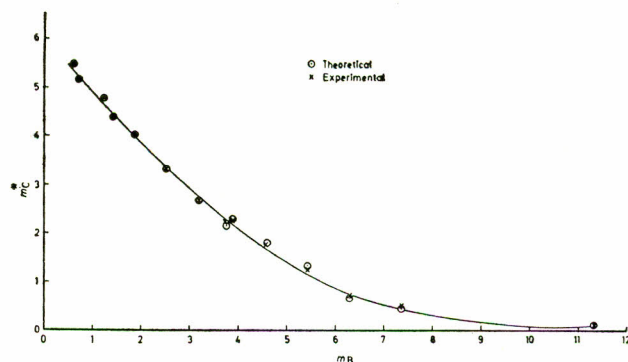

Fig. 1. Molality $m*_c$ of NaCl in solution as a function of acid concentration m_B

$$\frac{1}{\nu_c} \log K_c = \frac{1}{\nu_c} \log P_c + \log \gamma_c - \frac{1}{\nu_c} \log P_c{}^\circ + \gamma_c{}^\circ \quad (4)$$

combining equations 3 and 4

$$\frac{1}{\nu_c} \log K_c = \frac{1}{\nu_c} \log P_c + \log \gamma^\circ{}_c - \alpha_c \, m_B - \beta_c m_B{}^2 \quad (5)$$

According to Åkerlöf and Thomas[7]

$$\log \frac{\gamma^\circ{}_c}{\gamma^\circ{}_B} = B_c m \quad (6)$$

Therefore

$$\frac{1}{\nu_c} \log K_c = \frac{1}{\nu_c} \log P_c + \log \gamma^\circ{}_B + B_c m - \alpha_c m_B$$
$$- \beta_c m_B{}^2 \quad (7)$$

The equation that makes possible the solubiliy calculations of sodium chloride in hydrochloric acid has the following modified form due to Åkerlöf.[8]

$$\frac{1}{\nu_c} \log K_c = \frac{1}{\nu_c} \log P_c + \log \gamma^\circ{}_B - \tfrac{1}{2} \log m + B_c m$$
$$- \alpha_c m - \beta_c m_B{}^2 \quad (8)$$

The equation has been employed for solubility calculation in systems such as HCl–NaCl–H$_2$O and HCl–KCl–H$_2$O. For HCl–NaCl system at 25°C, the solubility calculations use values of — 0.0875, — 0.0530 and — 0.0005 for B_c, α_c and β_c respectively.

Calculation of K_c and P_c: Equation (4)

$$\frac{1}{\nu_c} \log K_c = \frac{1}{\nu_c} \log P^\circ{}_c + \log \gamma^\circ{}_c \text{ is used to calculate}$$

K_c, here log $\gamma^\circ{}_c$ is replaced by the relationship (equation 6)

log $\gamma^\circ{}_c$ = log $\gamma^\circ{}_B$ + $B_c m$ to give

$$\frac{1}{\nu_c} \log K_c = \frac{1}{\gamma_c} \log P^\circ{}_c + \log \gamma^\circ{}_B + B_c m$$

which, for HCl–NaCl–H$_2$O system is

$\tfrac{1}{2} \log K_c = \tfrac{1}{2} \log P^\circ{}_c + \log \gamma^\circ{}_B + B_c m = 0.78952$

here $P^\circ{}_c$ is the solubility product of NaCl for its saturated aqueous solution and $\gamma^\circ{}_B$ is the activity coefficient of HCl in water at a m molal concentration. B_c = —0.0875 calculated from the equation:

$$\alpha_B - \alpha_c = B_c$$

for the values given by Harned and Robinson[9] for HCl–NaCl system at 20°C when m = 3, the approximation being valid in this case. The solubility of NaCl in its saturated solution at 20°C was observed as 35.7g 100 g H$_2$O (6.108 M).

Results and Discussion

In Table 1 are given molalities of hydrochloric acid (m_B) and sodium chloride (m_c), in the unmixed state.

TABLE 1. SOLUBILITY OF SODIUM CHLORIDE IN HYDROCHLORIC ACID

(A value of β_c was assumed to be –0.0006)

m_B	m_c	m	$-\alpha_C$	$-B_C$	m_{ppt} Expt	m_{ppt} Calc
0·61	5·497	6·107	0·0541	0·889	0·0171	0·0168
0·71	5·497	6·207	0·0537	0·089	0·344	0·3444
1·23	4·886	6·116	0·0534	0·0893	0·133	0·1334
1·44	4·886	6·326	0·0532	0·091	0·496	0·4964
1·866	4·276	6·142	0·0530	0·08922	0·243	0·243
2·519	3·665	6·184	0·0534	0·0887	0·305	0·3046
3·189	3·054	6·243	0·0541	0·0875	0·361	0·3617
3·761	3·054	6·815	0·05305	0·0911	0·897	0·890
3·878	2·443	6·321	0·0541	0·088	0·181	0·1809
4·587	1·832	6·419	0·0548	0·087	0·055	0·055
5·443	1·832	7·275	0·05306	0·0906	0·577	0·5766
6·333	1·832	8·165	0·0535	0·0883	1·127	1·129
7·40	1·222	8·622	0·0532	0·089	0·713	0·715
11·332	0·611	11·943	0·053	0·0890	0·503	0·5032

The table also shows values for α_c, B_c and the values for the sodium chloride precipitate obtained experimentally and calculated theoretically (through equation 8. Fig. 1 shows the agreement between the experimental and the theoretical values to be rather good. In all cases the agreement is better than 2%. This shows the validity of equation 8 over a wide range of acid and salt concentrations.

In the present calculations log $\gamma^\circ{}_B$ values, at m molality, were taken from Åkerlöf and Teare.[10] β_c was kept constant at a value of —0.0006 for all calculations. This value was selected in view of its values at 25°C (—0.0005) and at 20°C (—0.0008) for 3 molal total concentration.[9] Though the selection appears arbitrary, yet it can be taken to be reasonable because it gave nearly constant values of α_c and B_c; these vary between the limits —0.053 to — 0.0548 and — 0.087 to —0.091 respectively. The values are comparable with their corresponding values at 1, 2 and 3 molal total cocentrations.[9] These were obtained through successive approximation, which gave best coincidence between observed and calculated amounts of precipitates. Moreover, values for α_c and B_c also indicate that these are constant and independent of total ionic strength. This is in accordance with the observations of Harned.[11]

In Fig. 1 is plotted moles ($m^*{}_c$) of sodium chloride remaining in solution as the acid concentration is increased. The curve becomes asymptotic with the acid concentration axis at higher concentrations, namely at 10–11 M. The decrease in solubility of sodium chloride, as the acid concentration in solution rises, has been explained by the changes in their activity coefficients.[1] For example the activity coefficient of hydrochloric acid in its own solution is 1.316 at 3M and 25°. After mixing with a solution of sodium chloride when concentration of both is 1.5 M, it is lowered to 1.187. When the solution contains only 3M sodium chloride the activity coefficient is 1.069 in the limit. This and the data on trace activity coeffiincient of hydrochloric acid in salt solution has been explained, at least qualitatively,[12] by the concept of hydration of the ions. It turns out that hydration reduces the 'free water' effective as solvent

which increases the 'effective' concentration of acid. Attempt has also been made to give a quantitative significance to hydration.[5]

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