

## The Standard Association Constant of Ion Pair $[\text{GaCl}]^{2+}$ in the System of $\text{HCl}+\text{GaCl}_3+\text{H}_2\text{O}$

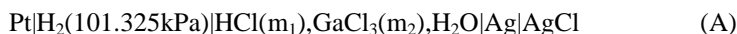
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**Abstract:** The standard association constants of ionic pair  $[\text{GaCl}]^{2+}$ ,  $K_{\text{as}}$ , were determined by emf (electromotive force) method at 278.15 to 318.15 K. The thermodynamic quantities for the ionic association process were calculated and it was pointed that the association entropy is driving force to form the ionic pair.

**Keywords:** Ion pair, association entropy, EMF,  $\text{GaCl}_3$ .

This paper reports the EMF (electromotive force) measurements of cell (A) without liquid junction at five temperatures from 278.15 to 318.15 K.



The measurements on the system  $\text{HCl}+\text{GaCl}_3+\text{H}_2\text{O}$  was carried out in an appropriate concentration of hydrochloric acid when the concentration of hydrochloric acid is not lower than 0.13 mol/kg the hydrolysis of  $\text{Ga}^{3+}$  can be avoided or eliminated<sup>1</sup>. The standard association constant,  $K_{\text{AS}}$ , in ion association process,  $\text{Ga}^{3+} + \text{Cl}^- = \text{GaCl}^{2+}$ , was determined by a linear extrapolation on the basis of extended Debye-Huckel equation. The experimental details of the cell design, purification of the hydrogen gas, *etc* have been reported in our previous publications<sup>2-4</sup>.

### Determination of the standard association constant of the ion pair

At higher hydrogen ion molality the ion association between  $\text{Ga}^{3+}$  and  $\text{Cl}^-$  becomes dominant and its standard association constant,  $K_{\text{AS}}$ , is

$$K_{\text{AS}} = a_{\text{p}} / a_{\text{Cl}} a_{\text{Ga}} \quad (1)$$

where  $a$  is activity, subscript p, Ga and Cl mean ion pair  $[\text{GaCl}]^{2+}$ ,  $\text{Ga}^{3+}$  and  $\text{Cl}^-$ , respectively. Substitution of equation (1) into Nernst's equation of cell (A) yields an extrapolation working equation for  $K_{\text{AS}}$ :

$$\begin{aligned} \ln K'_{AS} &= (E-E^0)/k + \ln (m_H m_p / m_{Ga} m^0) + 4A(I \rho / C^0)^{1/2} / [1 + B a^0 (I \rho / C^0)^{1/2}] \\ &= \ln K_{AS} - bI / m^0 \end{aligned} \quad (2)$$

where  $m_i$  is molality of species  $i$ , subscript H means  $H^+$ ,  $k = RT/F$ ,  $R$  is gas constant,  $T$  is thermodynamic temperature and  $F$  is Faraday constant,  $m^0$  is the unit molality,  $C^0$  is the unit molarity,  $I$  is the total ionic strength of the cell solution,  $\rho$  is density of water,  $b$  is the empirical parameter,  $a^0$  is the ionic size parameter, and  $A$  and  $B$  are the Debye-Hückel parameters,  $\ln K'_{AS}$  is the extrapolation function.

The least-square estimate of the intercept of the linear regression of  $\ln K'_{AS}$  against  $I/m^0$  from equation (2) was  $\ln K_{AS}$ . The standard deviation of the fit,  $S_f$ , and the values of  $\ln K_{AS}$  of different temperatures are listed in **Table 1**.

According to Fuoss theory<sup>5</sup>, the logarithm of association constant of ionic pair,  $\ln K_F$ , is inversely proportional to product of dielectric constant  $D$  and temperature  $T$  so that an empirical equation was used:

$$\ln K_{AS} = A_1 + A_2/TD \quad (3)$$

The experimental values of  $\ln K_{AS}$  at different temperatures were fitted with the calculated value equation (3). The values of parameters  $A_i$  obtained are  $A_1 = -1.4276$ ,  $A_2 = 89116.0$ , the relative coefficient  $r = 0.980$ .

The standard molar thermodynamic quantities  $\Delta G_m^0$ ,  $\Delta H_m^0$ , and  $\Delta S_m^0$ , for the ionic association reaction of the ion pair were calculated and their values are listed in table 1 also. From **Table 1**,  $\Delta H_m^0 < T \Delta S_m^0$  leads us to conclude that the association entropy is the driving force for the ionic association reaction.

**Table 1** Values of  $\ln K_{AS}$  and thermodynamic functions

T/K	278.15	288.15	298.15	308.15	318.15
$\ln K_{AS}$	2.302	2.342	2.387	2.436	2.490
$S_f \times 10^3$	9.6	9.5	9.2	9.3	9.2
$\Delta G_m^0$ (kJ.mol <sup>-1</sup> )	-5.32	-5.61	-5.92	-6.24	-6.59
$\Delta S_m^0$ (J.K <sup>-1</sup> .mol <sup>-1</sup> )	27.8	31.7	35.8	40.4	45.4
$\Delta H_m^0$ (kJ.mol <sup>-1</sup> )	2.42	3.51	4.76	6.21	7.86

## References

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