Mean Ionic Activity Coefficients and Dissociation Constant of HCl in the System HCl–H₂SO₄–H₂O at 298 K

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Abstract—The mean ionic activity coefficients of HCl (γ₁⁺) in the system HCl–H₂SO₄–H₂O at 298 K were calculated by the Mikulin and MacKay–Perring methods and were then used for calculating the mixed thermodynamic dissociation constant of HCl (Kₘ). The mean value of the constant proved to be equal to that found previously for aqueous solution of HCl, and deviations from the mean value are most likely due to the fact that, when calculating Kₘ, incompleteness of dissociation of both electrolytes was neglected. The γ₁⁺ values calculated by the MacKay–Perring and Mikulin methods virtually coincide, within the determination and calculation errors, with the published data. This result confirms the suitability of the previously suggested procedure for determining the strictly thermodynamic mixed dissociation constants from the experimental data on the vapor pressure in combination with the mean ionic activity coefficients.

Incompleteness of electrolytic dissociation significantly affects the results of calculating the activity coefficients of components in solutions containing two or more electrolytes [1]. In most cases, the developed calculation procedures are based on the assumption that the dissolved electrolytes dissociate completely [2, 3]. Apparently, the use of such methods at any concentrations is possible only when the salting-out effect of strong electrolytes, which suppresses dissociation of the second component, is taken into account. The system HCl–H₂SO₄–H₂O offers the possibility of checking the effect of the salting-out agent on the calculation results.

Hydrochloric acid in water is a strong acid [4]; for its dissociation constant Kᵦ, contradictory values were reported, with the most probable value, apparently, lying in the range from 1.48 [5] to 217 [6]. Since we found no data on the degree of HCl ionization in the presence of other electrolytes, we made an attempt [7] to find from the experimental values for 298 K the mixed dissociation constant of HCl in the system HCl–H₂SO₄–H₂O by extrapolation to infinite dilution of the “semiconcentration” constants Kᵦ = mᵦ/aᵦ (where mᵦ is the concentration of the ionic electrolyte species, aᵦ = pᵦ/T is the activity of the nondissociated electrolyte species in solution, pᵦ is the partial pressure of HCl, and T is the fugacity of vapor over anhydrous liquid HCl). We showed in [7] that Kᵦ noticeably depends on the content of H₂SO₄ and HCl and, when the concentrations of both H₂SO₄ and HCl tend to zero, approaches the value found for aqueous solutions of HCl (6.25 × 10⁻⁷) [6].

At the same time, the thermodynamic constants [Eq. (1)] calculated from the vapor pressures and mean ionic activity coefficients should be independent of the concentration, which allows extrapolation to be obviated (here aᵦ = mᵦ/aᵦ):

\[ Kᵦ = aᵦ^{2/3} \]  

(1)

We have calculated the mean ionic activity coefficients γ₁⁺ of HCl in the system HCl–H₂SO₄–H₂O by two independent methods. The first, simpler procedure was based on using the MacKay–Perring formula [8] modified by Mikulin [9]:

\[ γ₁⁺ = 2m₁γ₂⁺/(2m₁ + 3m₂). \]  

(2)

Here the activity coefficients of the electrolytes are determined by their concentration ratio in mixed solutions (m₁ and m₂ are the molal concentrations of HCl and H₂SO₄, respectively, in mixed solution; m₁ and γ₂⁺ are, respectively, the molal concentration and mean ionic activity coefficient of the isopiestic aqueous solution of HCl).

The second, more sophisticated procedure is based on Mikulin formulas [2] which correlate the activity coefficients of electrolytes with the activity of the solvent (water in our case) in electrolyte solutions.

We solved these equations analytically, and not graphically as proposed in [10]. First, following the procedure in [10], we calculated from experimental data the relative molar decrease in the vapor pressure ρ:

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Here, as in formula (2), \( m_1 \) and \( m_2 \) are the molal concentrations of the electrolytes in a mixed solution (subscript 1 refers to HCl, and subscript 2, to H_2SO_4); \( a_w \) is the activity of water. The activities of water were taken from the classical paper [11] devoted to critical examination of the liquid–vapor equilibrium in the system of interest. Additionally, we performed measurements for the region of small HCl concentrations [7]. The experimental procedure and measurement results are given elsewhere [7, 12].

The parameters of the equation of the surface \( \rho = f(m_1, m_2) \) were determined by the least-squares procedure, and the derivative \( (\partial \rho / \partial m_i)_{m_2} \) was taken. These values were used to find by Eq. (4) the intermediate quantity \( \Psi_1 = (\partial \ln \gamma_i / \partial I)_y \) required for numerical solution of integrals (5) and (6):

\[
\Psi_1 = \frac{2}{2m_1 + 6m_2} \left\{ \frac{55.51}{4a_w} \left[ \frac{1}{2} p + (2m_1 + 3m_2) \frac{\partial \rho}{\partial m_1} \right] - 1 \right\},
\]

\[
\ln \gamma_{1i} = \ln \gamma_{1i}^* + \int_0^{I=19} (\Psi_1 - \Psi_1^*) dI,
\]

\[
\ln \gamma_{1i} = \ln \gamma_{1i}^* + \int_0^{I=19} (\Psi_1 - \Psi_1^*) dI + \int_{I=19}^{I=1} \Psi_1^* dI.
\]

Here, \( \gamma_{1i} \) are the mean ionic activity coefficients of HCl in the system of interest, \( I = m_1 + 3m_2 \) is the ionic strength of the solution, \( \Psi_1^* = (\partial \ln \gamma_i / \partial I)_y \) is the value of the derivative for aqueous solution of HCl at the same ionic strength \( I = I^* \).

According to [10], Eq. (5) is suitable for finding \( \ln \gamma_{1i}^* \) at ionic strengths that do not exceed the value corresponding to the solubility of HCl in water, and at higher ionic strengths Eq. (6) is used. For numerical solution of integral (5), we found by least-squares treatment of the experimental data the parameters of Eq. (7) of the surface \( \Psi_1 = \Psi_1^* = f(I, y) \) (where \( y = 2m_1/(2m_1 + 6m_2) \)); its form was chosen in compliance with Eq. (25) in [10]. Equation (8) of the surface \( \Psi_1 = f(I, y) \), whose form is in compliance with Eq. (100) in [2], was found similarly for the range of ionic strengths above 19.

\[
\Psi_1 - \Psi_1^* = a_1 y + b_1 I + c_1 y^2 + d_1 I y + e_1 f_1 + f_1 y^2 + g_1 y^{12} + h_1 I^{12} + i_1 y^{12} + j_1 y^3 + k_1,
\]

\[
\Psi_1 = a_0 y^{12} + b_0 y^2 + c_0 y + d_0 I y + e_0 f_0 + f_0 y^2 + g_0 y^{12} + h_0 I^{12} + i_0 y^{12} + j_0 y^3 + k_0.
\]

Here, \( a_i, b_i, c_i, d_i, e_i, f_i, g_i, h_i, i_i, j_i, k_i, \) and \( l_i \) are empirical constants (see table).

Then Eqs. (7) and (8) were substituted in relationships (5) and (6), which were integrated under the condition of constant \( y \). The results (plots of \( \ln \gamma_{1i} \) vs. \( x_1 \)) are shown in Fig. 1 together with the experimental data of [1], given for comparison. It is seen that the results of calculations by methods of [2] and [8, 9] are reasonably consistent at high concentrations of HCl but noticeably differ at small \( x_1 \). Figure 2 shows the plots of \( \ln \gamma_{1i} \) (obtained by extrapolation to \( x_1 = 0 \) of the plots of \( \ln \gamma_{1i} \) vs. \( x_1 \), Fig. 1) vs. molal concentration of H_2SO_4 (\( m_2 \)). The solid curve shows the tabulated [13, 14] logarithms of the mean ionic activity coefficients of HCl in water, plotted vs. molal concentration of H_2SO_4 (\( m_2 \)). The result could be attributed to the specific features of our calculation procedures if the experimental data from [1] were not in the best agreement with the curve.

The \( \gamma_{1i} \) values for HCl in water containing H_2SO_4 were used for calculating \( k_m \) by formula (1). To calculate the mixed thermodynamic dissociation constants, we used only the \( \gamma_{1i} \) values found by Eqs. (2), (5), and (6). When calculating the numerical values of the mixed constant by formula (1), we assumed that \( m_{1x} = ((\text{H}^+ m_1)^{1/2}, [\text{H}^+] = m_1 + 2m_2, \) i.e., that the dissociation is complete. The fugacity of the vapor of pure hydrogen chloride \( f_0^{1/2} \) was taken previously [6] by the Kessler procedure [15]. The results in the form of the plots of \( \ln k_m \) vs. mole fraction of H_2SO_4 (\( x_2 \)) are shown in Fig. 3. It is seen that the mean value of \( \ln k_m \) is close to that for aqueous HCl (17.95), although the scatter of the \( \ln k_m \) data depends on the content of both H_2SO_4 (\( x_2 \))

\[
\rho = 2(1 - a_w)(2m_1 + 3m_2).
\]