**Dynamics of Ion Pairing in Dilute Aqueous HCl Solutions by Spectroscopic Measurements of Hydroxyl Radical Conversion into Dichloride Radical Anion**

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1. The first order rate constants of the formation of Cl_2•−.

Table S1. The first-order rate constants $k_{obs} \times 10^{-6}$ fitted\(^a\) to the growth of absorbance measured at 340 nm, being the absorption maximum of Cl_2•−.

| $m_{HCl}$[mol·kg\(^{-1}\)] | 288.15 K | 298.15 K | 313.15 K | 323.15 K | 333.15 K | 343.15 K | 373.15 K |
|---------------------------|---------|---------|---------|---------|---------|---------|---------|
| 0.002                     | 0.20 ± 0.01 | 0.28 ± 0.01 | 0.29 ± 0.03 | -       | 0.30 ± 0.05 | 0.32 ± 0.05 | -       |
| 0.005                     | 0.52 ± 0.05 | 0.69 ± 0.02 | 0.86 ± 0.05 | -       | 0.95 ± 0.10 | 0.94 ± 0.07 | -       |
| 0.008                     | -        | -        | -        | -       | 2.04 ± 0.09 | 3.01 ± 0.08 | -       |
| 0.01                      | 1.82 ± 0.13 | 1.82 ± 0.03 | 2.26 ± 0.19 | 2.24 ± 0.19 | 2.5 ± 0.3   | 2.8 ± 0.4   | 2.9 ± 0.5 |
| 0.015                     | -        | -        | -        | -       | 5.4 ± 0.3   | 6.2 ± 0.4   | -       |
| 0.02                      | 4.8 ± 0.6 | 7.5 ± 0.3 | 9.5 ± 0.8 | 8.3 ± 0.4 | 8.6 ± 0.5   | 9.1 ± 0.5   | -       |
| 0.03                      | -        | 15.7 ± 0.6 | 23 ± 4   | 27 ± 4   | 26 ± 3     | -          | -       |
| 0.04                      | -        | 35 ± 3   | -        | -       | 38 ± 2     | -          | -       |
| 0.05                      | 32 ± 4   | 38.4 ± 1.9 | -       | 45 ± 5   | 44 ± 4     | 44 ± 5     | -       |
| 0.1                       | 100 ± 40 | 119 ± 6  | -        | 130 ± 30 | 125 ± 16   | 160 ± 20   | -       |

\(^a\) Non-linear curve fitting procedure using Levenberg-Marquardt iteration algorithm employed in OriginLab 2019; $k_{obs}$ represent average of 3 – 5 profiles; uncertainty corresponds to root mean squared error of the fitted values; the determination coefficient $R^2$ ranged from 0.9048 to 0.9997, except for the data in italic where $0.7840 < R^2 < 0.8843.$
2. Kinetics of Cl$_2^-$ formation

Taking into account the steady state approximation for \((H_3O^+ \cdot \cdot OH \cdot Cl^-)\) in reaction (3b), and assuming \(k_3 >> k_4[^*OH], k_6[Cl^-] >> k_6\), the differential rate equations for a simplified scheme involving equilibrium (3a) and reactions (3b-c) are:

\[
\frac{d[(Cl^- \cdot H_3O^+)\}}{dt} = k_3[H_3O^+][Cl^-] - k_{-3}[(Cl^- \cdot H_3O^+)] \quad (S1)
\]

\[
\frac{d[^*OH]}{dt} = -k_4[(Cl^- \cdot H_3O^+)][^*OH] \quad (S2)
\]

\[
\frac{d[Cl^*]}{dt} = k_4[(Cl^- \cdot H_3O^+)][^*OH] - k_6[Cl^*][Cl^-] \quad (S3)
\]

\[
\frac{d[Cl_2^-]}{dt} = k_6[Cl^*][Cl^-] \quad (S4)
\]

Solution of eq. (S1)

\[
[(Cl^- \cdot H_3O^+)] = \frac{k_2}{k_{-3}} [H_3O^+][Cl^-](1 - e^{-k_{-3}t}) \quad (S5)
\]

Substituting solution of eq. (S1) into eq. (S2) one obtains:

\[
\frac{d[^*OH]}{dt} = -\frac{k_4k_3}{k_{-3}} [H_3O^+][Cl^-][^*OH](1 - e^{-k_{-3}t}) \approx -\frac{k_4k_3}{k_{-3}} [H_3O^+][Cl^-][^*OH] \quad (S6)
\]

Where \(e^{-k_{-3}t} \approx 1\) taking into account the time span of measurements and \(k_{-3} > 10^9 \text{ s}^{-1}\) as expected.

With the boundary condition \[^*OH](t = 0) = c_0\) at low dose being of the order of \(10^{-6} \text{ M}\) and thus implying \([H_3O^+][Cl^-] = \text{const}\), solution of eq. (S6) is

\[
[^*OH] = c_0e^{-\alpha t} \text{, where } \alpha = \frac{k_4k_3[H_3O^+][Cl^-]}{k_{-3}} \quad (S7)
\]

Thus solution of eq. (S3) with the boundary condition \([Cl^*](t = 0) = 0\) is

\[
[Cl^*] \approx c_0 \frac{\alpha}{\alpha - k_6[Cl^-]} (e^{-k_6[Cl^-]t} - e^{-\alpha t}) \quad (S8)
\]

\[
= \frac{\alpha}{\alpha - k_6[Cl^-]} \{ e^{-(\alpha + k_6[Cl^-])t} - 1 \}[^*OH]
\]
Since \( k_6 \) and \( k_4 \) are of similar order, \( k_3/k_4 < 1 \), \([\text{HCl}] \leq 0.1 \text{ M} \) and \( t < 10^{-6} \text{ s} \), one can neglect \( \alpha \) as small compared to \( k_6[\text{Cl}^-] \) and neglect the exponential term \( \exp\{-(\alpha+k_6[\text{Cl}^-])t\} \). Then \([\text{Cl}^*]\) substituted to eq. (S4) gives

\[
\frac{d[\text{Cl}_2^*]}{dt} \equiv \alpha[\text{•OH}] = - \frac{d[\text{•OH}^\prime]}{dt} \equiv \frac{k_4k_3}{k_3-3}[\text{H}_3\text{O}^+] [\text{Cl}^-][\text{•OH}]
\] (S9)

3. Density of aqueous HCl solution in dependence of temperature \( T \)

To describe the temperature dependence for the density \( \vartheta \) of aqueous HCl solution Clegg and Wexler [S1] used the following polynomial expression:

\[
\vartheta(T) = \sum_{k=0}^{q} p_k c_{\%(w/w)}^k + (T - T_0) (q_1 - q_2 T_0) + q_2 (T^2 - T_0^2)/2
\] (S10)

where \( T_0 = 283.15 \text{ K} \), \( q_1 = r_1 + r_2 c_{\%(w/w)}^{r_3}, \ q_2 = r_4 + r_5 \sqrt{c_{\%(w/w)}} + r_6 c_{\%(w/w)} \), \( c_{\%(w/w)} \) is the mass fraction of HCl in solution, and \( p_{k=0,...,9} r_1, r_1, \ldots, r_6 \) are fitting parameters to the experimental data collected in Table S2. The calculated densities are given in Table S3.

Table S2. Adjustable parameters for eq. (S10) obtained in this work using OriginPro 2021 nonlinear fitting procedure.

| \( k \) | \( r_k \) | \( p_k \) |
|------|-------|-------|
| 0    |       | 0.99707 |
| 1    | -3.71636144·10^{-4} | 4.91·10^{-3} |
| 2    | -2.097063856·10^{-3} | -1.57213·10^{-5} |
| 3    | 1.8829510589 | 1.32583·10^{-6} |
| 4    | -1.7085424103·10^{-5} | -3.81277·10^{-8} |
| 5    | 5.1656343322·10^{-5} | 5.67147·10^{-10} |
| 6    | -3.4570919219·10^{-5} | -3.16067·10^{-12} |
| 7    |       | -7.86698·10^{-14} |
| 8    |       | 1.16366·10^{-15} |
| 9    |       | -4.21105·10^{-18} |
Table S3. Density of aqueous solution of HCl given in kg·m\(^{-3}\) calculated from eq. (S10). Data for pure water given in the first row are from ref. [S2].

| \(m_{\text{HCl}}[\text{mol·kg}^{-1}]\) | 288.15 K | 298.15 K | 313.15 K | 323.15 K | 333.15 K | 343.15 K | 373.15 K |
|---------------------------------|----------|----------|----------|----------|----------|----------|----------|
| 0                              | 999.2    | 997.0    | 992.2    | 988.0    | 983.2    | 977.7    | 958.4    |
| 0.002                          | 1001.0   | 997.4    | 995.4    | 991.0    | 985.9    | 980.3    | 974.1    |
| 0.005                          | 1002.1   | 997.8    | 995.6    | 991.1    | 986.3    | 981.3    | 976.1    |
| 0.008                          | 1003.2   | 998.2    | 995.7    | 990.6    | 985.6    | 980.4    | 975.3    |
| 0.01                           | 1003.9   | 998.4    | 995.7    | 990.2    | 984.8    | 979.4    | 974.0    |
| 0.015                          | 1005.6   | 998.8    | 995.5    | 988.9    | 982.5    | 976.1    | 969.9    |
| 0.02                           | 1007.1   | 999.1    | 995.2    | 987.5    | 980.0    | 972.6    | 965.3    |
| 0.03                           | 1009.6   | 999.6    | 994.7    | 985.0    | 975.4    | 966.0    | 956.8    |
| 0.04                           | 1011.7   | 1000.0   | 994.2    | 982.8    | 971.6    | 960.5    | 949.6    |
| 0.05                           | 1013.3   | 1000.2   | 993.8    | 981.0    | 968.4    | 955.9    | 943.6    |
| 0.1                            | 1018.0   | 1000.9   | 992.4    | 975.5    | 958.7    | 942.0    | 925.4    |

4. Relative permittivity of solution in dependence of acid concentration and temperature

These dependencies were obtained using the scaling procedure proposed by Artemov et al. [S3] who assumed that the hypothetical electrophoretic effect results from intrinsic high concentration of hydronium cations in HCl solution:

\[
\varepsilon(T) = (\Delta\varepsilon + \varepsilon_{\infty}) \cdot \frac{\varepsilon_{\text{H}_2\text{O}}(T)}{\varepsilon_{\text{H}_2\text{O}(298K)}} \tag{S11}
\]

where \(\varepsilon_{\text{H}_2\text{O}}\) is the relative permittivity of water, \(\Delta\varepsilon\) is the concentration dependent correction resulting from the presence of HCl, and \(\varepsilon_{\infty}\) is the high frequency dielectric constant, assumed to be 5 at 25 °C.
Table S4. The relative permittivity of aqueous HCl solution calculated as a function of temperature and acid concentration using extrapolated data from refs. [S3,S4] and the temperature dependence for $\varepsilon_{H_2O}$\textsuperscript{a)} from ref. [S5].

| $m_{HCl}$ [mol·kg$^{-1}$] | 288.15 K | 298.15 K | 313.15 K | 323.15 K | 333.15 K | 343.15 K | 373.15 K |
|---------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 0                         | 82.15     | 78.40     | 73.11     | 69.78     | 66.61     | 63.59     | 55.32     |
| 0.002                     | 82.23     | 78.48     | 73.18     | 69.85     | 66.68     | 63.65     | 55.38     |
| 0.005                     | 82.20     | 78.45     | 73.15     | 69.82     | 66.65     | 63.63     | 55.36     |
| 0.008                     | 82.16     | 78.42     | 73.12     | 69.80     | 66.63     | 63.60     | 55.33     |
| 0.01                      | 82.14     | 78.40     | 73.10     | 69.78     | 66.61     | 63.58     | 55.32     |
| 0.015                     | 82.09     | 78.34     | 73.05     | 69.73     | 66.56     | 63.54     | 55.28     |
| 0.02                      | 82.03     | 78.29     | 73.01     | 69.69     | 66.52     | 63.50     | 55.25     |
| 0.03                      | 81.93     | 78.19     | 72.91     | 69.59     | 66.43     | 63.42     | 55.17     |
| 0.04                      | 81.82     | 78.09     | 72.81     | 69.50     | 66.34     | 63.33     | 55.10     |
| 0.05                      | 81.71     | 77.98     | 72.72     | 69.41     | 66.26     | 63.25     | 55.03     |
| 0.1                       | 81.17     | 77.47     | 72.24     | 68.95     | 65.82     | 62.83     | 54.66     |

\textsuperscript{a)} $\varepsilon_{H_2O}(T) = 5321 \cdot T^{-1} + 233.76 - 0.9297 \cdot T + 0.1417 \cdot 10^{-2} \cdot T^{2} - 0.8292 \cdot 10^{-6} \cdot T^{3}$

5. Mean activity coefficient in dependence of acid concentration and temperature

Debye-Hückel and Pitzer-Hückel models of electrolyte solutions treat the solvent as a dielectric continuum and an electrolyte as an ubiquitous solute. Under these assumptions, the activity of the electrolyte depends on the concentration and the activity coefficient $\gamma_{\pm}$, describing the interaction energy of ions in solution. To calculate $\gamma_{\pm}$ we have selected the two most commonly used expansions for 1:1 electrolyte, respectively given by eqs. (S12) and (S13).

\[
\ln(\gamma_{\pm}) = -\frac{3A_{\phi}\sqrt{m}}{1 + B\sqrt{m}} + h_1 \frac{m}{m^o} + b_2 \left(\frac{m}{m^o}\right)^2 + b_3 \left(\frac{m}{m^o}\right)^7 - \ln\left(1 + 2M_{H_2O}m\right). \tag{S12}
\]

\[
\ln(\gamma_{\pm}) = f^r + B^r \cdot \frac{m}{m^o} + \frac{3}{2} C^\phi \left(\frac{m}{m^o}\right)^2. \tag{S13}
\]
where \( m \) is the molality, expressed in \( \text{mol} \cdot \text{kg}^{-1} \), \( m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1} \), \( M_{\text{H}_2\text{O}} \) is the molar mass of water expressed in \( \text{kg} \cdot \text{mol}^{-1} \). The osmotic coefficient, \( A_\Phi(T) = \frac{e^3}{12\pi} \sqrt{\frac{N_A \theta}{2(\varepsilon \varepsilon_0 k_B T)^2}} \), where \( e \) is the elementary charge, \( N_A \) is the Avogadro’s number, \( \varepsilon_0 \) is the permittivity of free space, and \( k_B \) is the Boltzmann constant, should be expressed in \( (\text{mol} \cdot \text{kg}^{-1})^{-1/2} \). For HCl concentration less than 5 \( \text{mol} \cdot \text{kg}^{-1} \), the parameters \( B = 1.4 \ (\text{mol} \cdot \text{kg}^{-1})^{-1/2} \), \( b_2 = 6.0 \cdot 10^{-3} \), \( b_3 = -9.7 \cdot 10^{-5} \) are temperature independent, and \( h_1 = 0.33866 - 1.2837 \cdot 10^{-3} (T - 298.15) \) depends linearly on \( T \) [S6]. The formulae for \( f^\gamma, B^\gamma, C^\Phi \) were derived from the calorimetric data reported by Saluja \textit{et al.} [S7], and Holmes \textit{et al.} [S8], and later tested by Partanen \textit{et al.} [S6]. The activity coefficients calculated from eq. (S12) and eq. (S13) using the formulae for \( f^\gamma, B^\gamma, C^\Phi \) from refs. [S6-S8], differ by less than 2 %. The values presented in Table S5 represent the arithmetic mean.

Table S5. The average activity coefficient \( \gamma_\pm \) calculated for aqueous HCl solution in dependence of temperature and molality.

| \( m_{\text{HCl}} \ [\text{mol} \cdot \text{kg}^{-1}] \) | 288.15 K | 298.15 K | 313.15 K | 323.15 K | 333.15 K | 343.15 K | 373.15 K |
|---|---|---|---|---|---|---|---|
| 2 | 0.9532 | 0.9524 | 0.9510 | 0.9500 | 0.9489 | 0.9477 | 0.9438 |
| 5 | 0.9297 | 0.9285 | 0.9265 | 0.9249 | 0.9233 | 0.9215 | 0.9154 |
| 8 | 0.9143 | 0.9128 | 0.9103 | 0.9085 | 0.9064 | 0.9042 | 0.8967 |
| 10 | 0.9061 | 0.9045 | 0.9018 | 0.8997 | 0.8975 | 0.8951 | 0.8869 |
| 15 | 0.8897 | 0.8879 | 0.8848 | 0.8824 | 0.8799 | 0.8771 | 0.8675 |
| 20 | 0.8769 | 0.8750 | 0.8716 | 0.8690 | 0.8662 | 0.8632 | 0.8526 |
| 30 | 0.8574 | 0.8553 | 0.8516 | 0.8487 | 0.8456 | 0.8422 | 0.8304 |
| 40 | 0.8427 | 0.8405 | 0.8365 | 0.8335 | 0.8301 | 0.8265 | 0.8139 |
| 50 | 0.8309 | 0.8286 | 0.8245 | 0.8213 | 0.8178 | 0.8140 | 0.8007 |
| 100 | 0.7931 | 0.7906 | 0.7861 | 0.7825 | 0.7784 | 0.7740 | 0.7584 |
6. Lifetime of the pair (Cl-H3O⁺)

Table S6. The lifetime of the pair (Cl-H3O⁺) in ps calculated as the reciprocal of the rate constant $k_3$.

| $m_{HCl}$ [mol·kg⁻¹] | 288.15 K | 298.15 K | 313.15 K | 323.15 K | 333.15 K | 343.15 K | 373.15 K |
|------------------------|----------|----------|----------|----------|----------|----------|----------|
| 0.002                  | 106.6 ± 1.5 | 97.6 ± 1.2 | 55.6 ± 1.7 | - | 30.3 ± 1.9 | 24.8 ± 1.7 | - |
| 0.005                  | 47.5 ± 0.7 | 40.1 ± 0.2 | 28.1 ± 0.2 | - | 16.5 ± 0.3 | 12.2 ± 0.2 | - |
| 0.008                  | -         | -         | 31.1 ± 0.2 | - | 14.4 ± 0.1 | 15.0 ± 0.1 | - |
| 0.01                   | 43.7 ± 0.5 | 27.8 ± 0.2 | 19.6 ± 0.3 | 14.0 ± 0.2 | 11.4 ± 0.2 | 9.9 ± 0.3 | 4.9 ± 0.2 |
| 0.015                  | -         | -         | -         | - | 11.6 ± 0.1 | 10.0 ± 0.1 | - |
| 0.02                   | 30.5 ± 0.8 | 30.5 ± 0.3 | 22.2 ± 0.3 | 14.0 ± 0.1 | 10.8 ± 0.1 | 8.7 ± 0.1 | - |
| 0.03                   | -         | 31.9 ± 0.1 | 25.6 ± 0.1 | 21.2 ± 0.1 | 15.7 ± 0.3 | -         | - |
| 0.05                   | 36.3 ± 0.1 | 27.8 ± 0.3 | -         | 13.9 ± 0.3 | 10.2 ± 0.2 | 8.0 ± 0.2 | -         |
| 0.1                    | 30.9 ± 4.4 | 23.6 ± 0.2 | -         | 11.4 ± 0.5 | 8.3 ± 0.2 | 8.4 ± 0.2 | -         |

7. Calculated UV-Vis spectra of representative chlorine complexes

UV-Vis spectra of two representative, optimised complexes were calculated using Gaussian 09W software and time dependent (TD) DFT method coupled with UB3LYP functional and 6-311++g(3df,3pd) basis set. The polarizable continuum model with integral equation formalism (IEFPCM) was assumed for the aqueous solvent. Six excited states were considered. The calculated spectra are presented in Figure S1.
Figure S1. UV-Vis spectra of two chlorine complexes calculated using TD-DFT method: before (green) and after (blue) the concerted electron-proton transfer. Geometries of the respective complexes are also shown in the figure.

References:

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