Interpretation of Ion-Ion & Ion-Solvent Interaction Patterns in Aquo Hydrochloric Acid System on the Basis of Diffusion Studies

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Integral diffusion coefficient, \( \bar{D} \), for the system HCl-H\(_2\)O has been determined experimentally using modified diaphragm cell technique. Failure of the equations based on classical ion-ion and ion-solvent interactions is explained by the use of irreversible thermodynamics. A kinetic model for the system is also proposed to explain anomalous behaviour of H\(^+\) and Cl\(^-\) in the system.

As specific ion effects become important in concentrated solutions, it is clear that the flow of an ion must be influenced by the other ions present and the gradient of their properties as well. The macroscopic framework necessary to cover this complex situation is provided by thermodynamics of irreversible processes\(^1\).

Assuming local equilibrium and using balances of mass, energy and momentum, the entropy produced irreversibly, \( \sigma \), for an isothermal electrolytic system is given by the equation,

\[
\sigma = \sum J_i X_i
\]

where \( J_i \) is the flow of ions and solvent in mol cm\(^{-2}\) sec\(^{-1}\) and \( X_i \) is the force, in terms of electrochemical potential gradient, of these ions.

It is necessary to have independent \( J_i \) and \( X_i \) for the Onsager's reciprocity relation (ORR) to be valid. Consequently, contribution due to solvent \( X_a \) is eliminated using Gibbs-Duhem equation and \( J_i \)'s are referred to a solvent-fixed reference frame. For this choice, the linear relations are,

\[
J_i = \sum_i l_{ij} X_j
\]

And according to ORR,

\[
l_{ij} = l_{ji}
\]

Miller\(^1\) has shown that values of \( l_{ij} \) for a 1:1 electrolyte in a neutral solvent like water may be calculated from a knowledge of equivalent conductance, transference number and thermodynamic diffusion coefficient \( (D)_v \), which in turn is related to \( (D)_o \), the volume fixed diffusion coefficient; the value of \( (D)_o \) can be obtained from experimental integral diffusion coefficient \( (\bar{D}) \). If the distinction between \( l_i \) and \( l_i^b \) (the cell transference number and Hittorf transference number respectively) is omitted, which actually means the validity of ORR, the three \( l_i \)'s can be calculated from the equation,

\[
l_{ij}/N = \frac{l_{ij} A}{1000 F^2} + \frac{(D)_o}{1000 \times 2RT (1 + cd\ln y/dc)}
\]

An inverse description of transport process using friction coefficients \( (R_{ij}) \) can also be used where,

\[
X_i = \sum_{j=1,2} R_{ij} J_i
\]

\( R_{ij} \) can also be determined from the equation given by Miller\(^1\).

Integral diffusion coefficient \( \bar{D} \) for the system HCl-H\(_2\)O was measured over the concentration range 0.01 M-3.0 M using a modified diaphragm cell at 25°C as described earlier\(^2\).

An azeotropic mixture of HCl-H\(_2\)O was initially prepared from A R grade HCl by distillation. Later, the stock solution was used to prepare all dilute solutions. The concentrations (initial and after diffusion run of both compartments) were determined both by conductometric titrations (using a DIGISUN digital conductimeter bridge, model 909) and by potentiometric titrations (using a Systronic Expanded pH metre, 331) against standard NaOH solution. In all the cases conductivity water (specific conductance less than 1 micromho per cm) was used. The densities of the solutions were measured by Ostwald modification of the Sprengel pyknometer (having 50 ml capacity) and viscosities were measured by an Ostwald viscometer (having 12 cm long capillary with 0.06 cm internal diameter). The temperature was maintained at 25°C ± 0.1°C with the help of a thermostat.

A comparison of the \( (D)_h \) values given in Table 1 (columns 10 and 11, obtained either by the Onsager and Fuoss relation\(^3\) or by Stokes' self-consistent equation\(^3\), with the \( (D)_s \) values (Table 1, column 5) obtained from \( D \) values (Table 1, column 4) shows that values obtained using Stokes' self-consistent equation agree well with the experimental values upto 0.1 M (error, \( \pm 1\% \)) after which disagreement becomes prominent with increase in concentration.

If we consider that a major reason for the deviation in concentrated solutions is the modification of various viscous forces by the presence of a large number of ions, then by Agar equation\(^3\) the plot of
Table 1—Experimental Values and Verification of Classical Theories

<table>
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<tr>
<th>C (g mol/l)</th>
<th>ρ (centipoise)</th>
<th>(\dot{D}\times10^5) (cm² sec⁻¹)</th>
<th>(D_0\times10^5) (cm² sec⁻¹)</th>
<th>(D_{TH}\times10^5)</th>
<th>(D_{TH}^*\times10^5)</th>
<th>(\eta/\eta^0)</th>
<th>(f(D)\eta/\eta^0)</th>
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</table>

\(f(D)\eta/\eta^0 = 1 + 0.036 m (\dot{D}_{H_2O}/D_0 - h)\).

†Using the relation \(D_{TH} = (D_0 + \Delta_1 + \Delta_2) \times (1 + cdlny/dc)\)

‡Using the relation \(D_{TH} = (D_0 + \Delta_1) \times (1 + cdlny/dc)\).

\[\eta/\eta^0 f(D) \text{ vs } m \text{ should be linear with a slope of 0.036 (} \dot{D}_{H_2O}/D_0 - h) \text{ where,}\]

\[f(D) = \frac{D_{obs}}{[(D_0 + \Delta_1 + \Delta_2)(1 + m(dlny/dm))]},\]

and \(h\) is hydration number. A plot of values in column 9 (Table 1) against \(m\) gives a negative hydration number for hydrochloric acid which makes the applicability of the equation doubtful.

Failure of the classical approach may be attributed to ion association, alteration in the solvent structure, short range ion-ion interactions and the specific ion effects. These effects can be considered in the \(lij\) terms; diffusion coefficient turns out to be combined effect of the \(lij\)'s. Consequently, a systematic study of \(lij\) as a function of concentration of electrolyte solution should lead to a better understanding of transport mechanism in the system.

An examination of \(lij/N\) values (Table 2, columns 9 and 11) shows that the relative deviation of \(lij/N\) from its limiting value at \(C = 0\) is not large up to 0.08 M concentration. In solutions of moderate concentrations, at least the magnitude of \(lij/N\) should be determined largely by interaction of ion \(i\) with the solvent. \(lij/N\) will also be affected by long range coulombic interaction, ion association and alteration in solvent structure due to ions. The slow decline of the values with concentration suggests an increasing negative \(i-i\) coulombic contribution.

Most interesting is the rapid rise of \(l_{12}/N\) with concentration (Table 2, column 10). This rise is responsible for both the rapid decline of the conductance and the catastrophic failure of the Nernst-Hartley equation with increasing concentration. \(l_{12}/N\) is a measure of the degree of coupling between the motion of ions 1 and 2 and is a function of long range coulombic ion-ion interactions, ion-solvent interactions and specific short range ion-ion interactions which may be interpreted in terms of ion pair formation. So the increase in the values of \(l_{12}/N\) (Table 2, column 10) indicates an increase in the ion pair formation.

A theoretical calculation of \(lij/N\) shows that \(l_{12}/N\) value should contain a factor \(\eta^n\) where \(n\) is more negative than \(-2\). According to Frank (cited in ref. 1), this means that the effect is essentially relaxational. However, it has also been observed earlier that a theoretical calculation of \(lij/N\) from a Debye-Huckel ion atmosphere model shows that specificities in \(lij/N\) may also result from the relaxation effect and ion pair formation effects which are results of nonzero anion-cation interaction. The failure of the classical Onsager-Fuoss theory is possibly due to non-inclusion of the ion pair term.

In translational diffusion, the ions will form ion-water cluster shell either by building up a water cluster shell around an ion or by forming water cluster shell first and then capturing an ion. The latter appears to be more
probable in view of the relaxational effect that arises due to continuous formation and destruction of shell. The difference in diffusion pattern of H\(^+\) ion from that of Cl\(^-\) ion suggests different mechanisms of diffusion of the two ions. It seems that at first H\(_3\)O\(^+\) ion is formed and then solvation sheath is built up around it so that the diffusion mechanism of H\(^+\) ions is governed by the jumps of the H\(_3\)O\(^+\) ion from one shell to another and by the movement of H\(_3\)O\(^+\) ion with solvation shell. The low charge density has relatively weak electrostatic field and thereby causes a net decrease in hydrogen-bonded water cluster structure. So, a series of proton jumps will be involved (of course, water molecules close to a proton are not arrival points for another proton after one of its jumps).

In the Cl\(^-\) ion transport mechanism, the high charge density will lead to a net structural increase around the ion. So, movement of the ion with formation and destruction of ion-cluster shell and the ion with the solvation shell around it become controlling factors in diffusion, and at higher concentrations ion pair formation plays an important role in the diffusion mechanism.

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References