Physico-chemical Studies in Non-aqueous Solvents: Part XV—
Conductance Studies of Some Uni-univalent Electrolytes in
Nitromethane at 25°

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Conductances of tetraalkylammonium, tetraphenylphosphonium and tetraphenylarsonium
chlorides and chlorosulphates, pyridinium chlorosulphate and a few other similar salts of
imidobis(sulphuryl chloride) have been measured in nitromethane at 25°. The conductance
data have been analysed by the Fuoss-Onsager-Björnner equation for associated and dissociated
electrolytes and limiting equivalent conductance ($\Lambda_o$), ion-size parameter ($\xi$) and association
constant ($K_A$) (where appropriate) have been calculated. All the salts (except pyridinium
chlorosulphate) are fully dissociated in this solvent. Ionic mobilities, solvated and corrected
ionic radii of the electrolytes have also been computed. The following order of increasing
mobility of ions in nitromethane has been observed: Me₄N⁺>Et₄N⁺>HPy⁺>Bu₄N⁺>Ph₄As⁺>Ph₄P⁺;
Cl⁻>SO₄Cl⁻>[N(SO₄Cl)₂]⁻>HSO₄⁻.

NITROMETHANE is an important solvent which has suitable physical properties
(dielectric constant, 35.94; dipole moment, 3.44 D; density, 1.1312 g ml⁻¹; viscosity, 0.627
× 10⁻² P and specific conductance, 0.5-2.0 × 10⁻⁸ ohm⁻¹ cm⁻¹; all at 25°) for studies of electrolyte
solutions. Though a number of physico-chemical studies have been carried out in nitromethane
yet a study of the behaviour of some salts of strong acids is lacking in this solvent. Presently, conduc-
tances of tetraalkylammonium, tetraphenylphosphonium and tetraphenylarsonium chlorides
and chlorosulphates, pyridinium chlorosulphate and of similar salts of imidobis(sulphuryl chloride)
have been measured and the data have been used for the estimation of limiting equivalent conductances,
limiting ionic mobilities and effective ionic radii.

Materials and Methods

Nitromethane (Fluka) was purified by the method already reported and stored over molecular sieves
(4 Å) in the dark. For each experimental run, the solvent was passed through a column packed with
dry alumina, distilled under vacuum; sp. cond., 2.5 × 10⁻⁸ ohm⁻¹ cm⁻¹ at 25°; $\eta^{25}$, 0.627 × 10⁻² cp
and $d^0$, 1.131 g ml⁻¹.

Tetraphenylphosphonium chloride and tetraethyl-
ammonium hydrogen sulphate (AR, E. Merck) were
dried in vacuum for 3-4 hr before use. Tetraphenyl-
arsonium chloride monohydrate (AR, E. Merck)
was heated in vacuum to 70° over phosphorous(V)
oxide to render it anhydrous.

Tetramethylammonium, tetraethylammonium and
tetraphenylarsonium salts of imidobis(sulphuryl chloride) were prepared by the reaction of corres-
ponding chlorides with imidobis(sulphuryl chloride) in equimolar quantities under dry nitrogen at-
mosphere and keeping the reaction temperature below 80°. HCl was produced during the reaction. After
the reaction, the products were washed with ether and recrystallized from ether-dichloromethane. These
were finally dried in a current of dry nitrogen and were characterized by their analysis and IR spectra.

Tetraethylammonium and pyridinium chlorosul-
phates were prepared as follows: tetraethylammo-
nium chloride and pyridine were taken in nitro-
methane separately and equimolar quantities of
chlorosulphuric acid were added in each case. The
reaction mixture was kept for few hours and then
the solvent removed under vacuum. The compo-
unds obtained were washed with dry ether, recrystal-
lized from dichloromethane ether mixture and
were then characterized by their analysis and
IR spectra.

Conductance measurements — Conductances were
measured at 25°±0.01° with the help of a precision
measuring bridge type WBR No. 108 with loga-
rithmic indicator amplifier type TAV 1 KC No. 034
(Wissenschaftlich Technische Werkstatten Weilheim/
Oby, Germany). The procedure for measuring conductances was essentially the same as reported
earlier. The cell constant of a dip type cell was determined by the standard method (0.1048 ±
0.0002 cm⁻³) and was periodically checked. Some of the measurements were rechecked with the help
of Flask type (Shedlovsky) conductance cell with
cell constant = 1.3823 cm⁻¹.
Results and Discussion

Conductances of various electrolytes have been measured in the concentration range \(10^{-4} \text{M}\) to \(95 \times 10^{-4} \text{M}\) and the data are presented in Table 1. The conductance data have been analysed by the Fuoss-Onsager-Skinner equation \(^1\)

\[
\Lambda = \Delta_0 - S(C)'^{1/2} + E'C \ln(6E'_1 C') + L C' + K_A C' + \Lambda
\]

(1)

for associated electrolytes and by Eq. (2)

\[
\Lambda = \Delta_0 - S(C)'^{1/2} + E'C \ln(6E'_1 C') + (L - \Delta_0) C
\]

(2)

for dissociated electrolytes, in which the symbols have the usual meanings; \(S = \alpha \Delta_0 + \beta)\) and \(E' = E'_1 \Delta_0 - E'_1\). The constants \(\alpha, \beta, E'_1\), and \(E'_2\), obtained from the physical properties of the solvent, have the values 0.7174, 125.8, 2.25 and 57.80 respectively. All the calculations have been carried out on an IBM 1620 computer using a programme in Fortran I. The least-square method has been used for the evaluation of the parameters \(\Lambda_0, L\) and \(K_A\) (for associated electrolyte) following the logarithm given by Fuoss et al. \(^8\).

The analysis of data by Eq. (1) gives negative values of association constants for all the electrolytes (except pyridinium chlorosulphate) suggesting thereby complete dissociation of these electrolytes in this solvent. The data have thus been analysed using Eq. (2). Schiff et al. \(^4,5\) have measured conductances of some quaternary ammonium halides in nitromethane and have shown that the tetramethyl salts are slightly associated and the association decreases with the increase in the size of the cation. Coetzee and Cunningham \(^7\) have shown from conductance measurements that electrolytes having big ions such as tetraisoamylammonium, tetraisoamylboride, tetraisoamylammonium, tetraphenylboride, etc., are completely dissociated in this solvent. Since most of the electrolytes used here are constituted of relatively big ions, their complete dissociation in nitromethane is in agreement with the above observations. However, positive association constant \((22.9 \pm 3.4)\) for pyridinium chlorosulphate shows it to be slightly associated in this solvent. All the relevant data along with standard deviations are recorded in Table 2.

It may further be pointed out that Eq. (1) gives the best fit in all the cases, though it also gives negative association constants (except for PyHSO₄Cl). This is without any physical meaning and thus the parameters reported in Table 2 are obtained from Eq. (2). Monica et al. \(^16\) have also reported a similar observation in hexamethylphos-
photothriamide. Moreover, the standard deviations of the individual parameters in nitromethane are slightly larger than those in other solvents\textsuperscript{16-18}. This may be attributed to slight instability of some of these salts in nitromethane. This is in accord with an earlier report\textsuperscript{19}.

**Ion-size parameter** — Ion-size parameter ($\delta$) of fully dissociated electrolytes has been obtained using Eqs. (3) and (4):

$$ L - \Delta \gamma_0 = E(b) - G(b) - 6E'K(b) \quad \ldots \quad (3) $$

$$ d = \frac{2E'K(b)}{\gamma} \quad \ldots \quad (4) $$

where $H(b)$, $G(b)$ and $K(b)$ have their usual meanings and $D$ is the dielectric constant of the solvent. For pyridinium chlorosulphate, $d$ has been calculated from Eq. (5):

$$ L = 2E'K_0 (1.603 - ln b) \quad \ldots \quad (5) $$

A perusal of results (Table 2) reveals that the ion-size parameter for all the salts (except Et\textsubscript{4}N\textsuperscript{+}HSO\textsubscript{4}\textsuperscript{-}) is equal to 5.0 ± 0.5 Å in nitromethane. These values compare favourably with those reported by Coetzee and Cunningham\textsuperscript{9} for electrolytes constituted of large ions in the same solvent. However, the values obtained for the electrolytes of relatively smaller ions in the solvent are lower\textsuperscript{6} than the present values. This may be due to incomplete dissociation of these ions in nitromethane\textsuperscript{4,5}.

**Single ion conductances** — Kay et al.\textsuperscript{6}, on the basis of experimental transference number measurements, have computed the mobility of chloride ion to be 62.52 ohm\textsuperscript{-1} cm\textsuperscript{2} mol\textsuperscript{-1} in nitromethane. This value as well as that of Et\textsubscript{4}N\textsuperscript{+} ion (which in turn has been obtained from chloride ion mobility from Et\textsubscript{4}NCl) have been used to calculate ionic mobilities of the various ions studied here, employing Kohlrausch's law of independent ion migration. Though the mobilities of Me\textsubscript{4}N\textsuperscript{+} and Bu\textsubscript{4}N\textsuperscript{+} ions obtained here differ by 2.0 ± 0.3 ohm\textsuperscript{-1} cm\textsuperscript{2} mol\textsuperscript{-1} from the literature values\textsuperscript{6}, yet in view of the slight instability of chlorosulphosphate\textsuperscript{19} and imidodihydrouracil chloride) anions in nitromethane\textsuperscript{20}, ionic mobility values reported here may be taken as the best approximations. All the values are recorded in Table 3.

The data in Table 3 give the following order of decreasing mobilities of ions: Me\textsubscript{4}N\textsuperscript{+} > Et\textsubscript{4}N\textsuperscript{+} > PyH\textsuperscript{+} > n-Pr\textsubscript{4}N\textsuperscript{+} > n-Bu\textsubscript{4}N\textsuperscript{+} > Ph\textsubscript{4}As\textsuperscript{+} > Ph\textsubscript{4}P\textsuperscript{+}; Cl\textsuperscript{-} > SO\textsubscript{4}Cl\textsuperscript{-} > [N(SO\textsubscript{4}Cl)\textsubscript{2}]\textsuperscript{-} > HSO\textsubscript{4}\textsuperscript{-}.

The mobilities of the ions decrease with increase in their size. However, Ph\textsubscript{4}P\textsuperscript{+} and HSO\textsubscript{4}\textsuperscript{-} are exceptions to this order. Although HSO\textsubscript{4}\textsuperscript{-} may be slightly solvated (probably through hydrogen bonding), the decrease in mobility of Ph\textsubscript{4}P\textsuperscript{+} is surprising.

**Stokes radii** ($r_s$) of various ions have been calculated using Robinson-Stokes equation\textsuperscript{10},

$$ r_s = \frac{F(\gamma \pm) z^+}{6\pi \eta \lambda N} \quad \ldots \quad (6) $$

In the Robinson and Stokes method the tetraalkylammonium ions are assumed to be unsolvated because of their low charge density. But it has been found that the Stokes radii obtained from Eq. (6) are smaller in contrast to the estimated crystallographic radii ($r_c$) of these ions\textsuperscript{10}. Thus the Stokes radii obtained above have been corrected following the suggestion of Nightingale\textsuperscript{21}. The calibration curve (Fig. 1) has been constructed by plotting $r_c$ vs $r_s$ for tetraalkylammonium ions in solution and the corrected radii ($r_cor$) of the ions are obtained from the above plot corresponding to their respective $r_s$ values. It is clear from Fig. 1 that except for the tetramethylammonium ions, all other ions lie on a linear plot, indicating that the tetramethylammonium ion may be slightly solvated in nitromethane. A similar behaviour has been observed in dimethylsulphoxide\textsuperscript{22}, hexamethyolphosphothriamide\textsuperscript{16}, N,N-dimethylacetamide\textsuperscript{17} and tetramethyleurea\textsuperscript{23}.

Table 3 records the solvated and corrected radii of the various ions. A comparison of solvated radii of monovalent anions in this and other solvents\textsuperscript{24} shows that the solvated radius decreases with the increase in size of anion in methanol and acetonitrile and is almost constant in formamide, dimethylformamide and dimethylacetamide. However, in nitromethane it increases with increase in size of anion and this behaviour is similar to one observed in sulpholane\textsuperscript{24}. The conductance behaviour

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**Table 3** — Ionic Mobilities ($\lambda^{+}$), Stokes ($r_s$) and Corrected ($r_cor$) Radii of Various Univalent Ions in Nitromethane at 25°C ± 0.01°C

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\lambda^{+}$</th>
<th>$r_s$ (Å)</th>
<th>$r_cor$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me\textsubscript{4}N\textsuperscript{+}</td>
<td>54-79</td>
<td>2.39</td>
<td>3.47</td>
</tr>
<tr>
<td>Et\textsubscript{4}N\textsuperscript{+}</td>
<td>46-62</td>
<td>2.75</td>
<td>4.00</td>
</tr>
<tr>
<td>Pr\textsubscript{4}N\textsuperscript{+}</td>
<td>37-14</td>
<td>3.34</td>
<td>4.52</td>
</tr>
<tr>
<td>Bu\textsubscript{4}N\textsuperscript{+}</td>
<td>33-76</td>
<td>3.87</td>
<td>4.94</td>
</tr>
<tr>
<td>Ph\textsubscript{4}P\textsuperscript{+}</td>
<td>27-58</td>
<td>4.74</td>
<td>5.70</td>
</tr>
<tr>
<td>Ph\textsubscript{4}As\textsuperscript{+}</td>
<td>30-05</td>
<td>4.35</td>
<td>5.35</td>
</tr>
<tr>
<td>HPy\textsuperscript{+}</td>
<td>44-43</td>
<td>2.94</td>
<td>4.16</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>62-52</td>
<td>2.09</td>
<td>3.47</td>
</tr>
<tr>
<td>SO\textsubscript{4}Cl\textsuperscript{-}</td>
<td>55-26</td>
<td>2.37</td>
<td>3.68</td>
</tr>
<tr>
<td>[N(SO\textsubscript{4}Cl)\textsubscript{2}]\textsuperscript{-}</td>
<td>50-34</td>
<td>2.60</td>
<td>3.87</td>
</tr>
<tr>
<td>HSO\textsubscript{4}\textsuperscript{-}</td>
<td>49-49</td>
<td>2.64</td>
<td>3.92</td>
</tr>
</tbody>
</table>

*Values from ref. 6.
of nitromethane solutions of these uncommon electrolytes has also been found to show some resemblance with sulpholane solutions. A perusal of Table 3 also reveals that the sum of the Stokes cationic and anionic radii for all the electrolytes is greater than the Fuoss-Onsager-Skinner ion size parameter (\(\bar{\alpha}\)) as has been observed in tetramethylurea.

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References


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