

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-Skinner equation for associated and dissociated electrolytes and limiting equivalent conductance (Λ_0), ion-size parameter (\hat{a}) 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: $\text{Me}_4\text{N}^+ > \text{Et}_4\text{N}^+ > \text{HPy}^+ > \text{Bu}_4\text{N}^+ > \text{Ph}_4\text{As}^+ > \text{Ph}_4\text{P}^+$; $\text{Cl}^- > \text{SO}_3\text{Cl}^- > [\text{N}(\text{SO}_2\text{Cl})_2]^- > \text{HSO}_4^-$.

NITROMETHANE is an important solvent which has suitable physical properties (dielectric constant¹, 35.94; dipole moment², 3.44 D; density¹, 1.1312 g ml⁻¹; viscosity¹, 0.627 $\times 10^{-2}$ P and specific conductance¹, 0.5-2.0 $\times 10^{-8}$ ohm⁻¹ cm⁻¹; all at 25°) for studies of electrolyte solutions. Though a number of physico-chemical studies³⁻⁹ have been carried out in nitromethane yet a study of the behaviour of some salts of strong acids is lacking in this solvent. Presently, conductances 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 reported⁴ 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°; η^{25} , 0.627×10^{-2} cp and d_0^{25} , 1.131 g ml⁻¹.

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

Tetramethylammonium, tetrabutylammonium and tetraphenylarsonium salts of imidobis(sulphuryl chloride) were prepared by the reaction of corresponding chlorides with imidobis(sulphuryl chloride) in equimolar quantities under dry nitrogen atmosphere 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 spectra¹⁰.

Tetraethylammonium and pyridinium chlorosulphates were prepared as follows: tetraethylammonium chloride and pyridine were taken in nitromethane 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 compounds obtained were washed with dry ether, recrystallized from dichloromethane ether mixture and were then characterized by their analysis and IR spectra¹¹.

Conductance measurements — Conductances were measured at 25° \pm 0.01° with the help of a precision measuring bridge type WBR No. 108 with logarithmic indicator amplifier type TAV I KC No. 034 (Wissenschaftlich Technische Werkstätten Weilheim/Oby, Germany). The procedure for measuring conductances was essentially the same as reported earlier¹². The cell constant of a dip type cell was determined by the standard method¹³ (0.1048 ± 0.0002 cm⁻¹) and was periodically checked. Some of the measurements were rechecked with the help of Flask type (Shedlovsky) conductance cell¹⁴ with cell constant = 1.3823 cm⁻¹.

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Results and Discussion

Conductances of various electrolytes have been measured in the concentration range $10 \times 10^{-4} M$ to $95 \times 10^{-4} M$ and the data are presented in Table 1.

The conductance data have been analysed by the Fuoss-Onsager-Skinner equation¹⁵ (1)

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + E'CY \ln(6E_1'CY) + LC\gamma - K_A CY^2 \Lambda \dots(1)$$

for associated electrolytes and by Eq. (2)

$$\Lambda = \Lambda_0 - SC^{1/2} + E'C \ln(6E_1' C) + (L - A\Lambda_0)C \dots(2)$$

for dissociated electrolytes, in which the symbols have the usual meanings; $S = \alpha \Lambda_0 + \beta$ and $E' = E_1' \Lambda_0 - E_2'$. The constants α , β , 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 a IBM 1620 computer using a programme in Fortran I. The least-square method has been used for the evaluation of the parameters Λ_0 , L and K_A (for associated electrolyte) following the logarithm given by Fuoss *et al.*¹⁵.

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 Cunningham⁷ have shown from conductance measurements that electrolytes having big ions such as tetraisoamylammonium, tetraisoamylboride, tetrabutylammonium, 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 observations⁷. However, positive association constant (22.9 ± 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 PyHSO_3Cl). 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-

TABLE 1 — CONDUCTANCE DATA FOR NITROMETHANE SOLUTIONS AT $25^\circ \pm 0.01^\circ$

$C \times 10^4$ M	Λ	$C \times 10^4$ M	Λ
Ph ₄ PCl			
15-639	83-423	63-924	79-449
41-077	80-984	92-228	78-126
47-545	80-592	95-403	77-813
60-549	79-743	—	—
Ph ₄ As[N(SO ₂ Cl) ₂]			
15-772	73-524	46-298	70-476
21-664	72-801	51-894	70-111
22-834	72-646	58-584	69-658
24-000	72-521	61-974	69-379
29-877	71-963	65-257	69-275
43-903	70-674	68-752	68-942
Me ₄ N[N(SO ₂ Cl) ₂]			
18-677	96-678	34-585	94-534
23-030	96-029	58-782	92-293
26-245	95-503	63-040	91-792
30-431	95-049	66-033	91-603
33-604	94-616	—	—
Bu ₄ N[N(SO ₂ Cl) ₂]			
18-678	75-545	45-289	72-250
20-326	75-332	61-755	70-956
35-223	73-370	64-949	70-765
36-953	73-193	71-407	70-209
38-555	73-029	84-693	69-271
41-747	72-722	94-669	68-696
Ph ₄ AsCl			
23-682	83-713	77-877	79-987
55-318	81-113	81-993	79-683
57-979	81-014	95-200	79-029
61-952	80-915	—	—
Et ₄ NSO ₃ Cl			
41-369	90-617	66-805	88-000
47-157	89-805	72-497	87-490
55-577	89-030	78-603	86-514
61-091	88-683	—	—
HPySO ₃ Cl			
31-382	84-679	74-683	75-593
38-156	83-028	85-962	73-905
45-185	81-306	97-441	72-513
63-609	77-084	—	—
Et ₄ NHSO ₄			
15-413	88-659	42-105	82-894
29-890	85-298	51-919	81-365
32-419	84-613	71-352	78-827
37-270	83-720	—	—

TABLE 2 — CONDUCTANCE PARAMETERS FOR NITROMETHANE SOLUTIONS AT $25^\circ \pm 0.01^\circ$

Electrolyte	Λ_0	L	K_A	\bar{a}	$\sigma\Lambda$
Ph ₄ PCl	90.10 ± 0.35	969.1 ± 50.2	—	5.48 ± 0.12	0.31
Ph ₄ AsCl	92.57 ± 0.16	968.3 ± 33.9	—	5.44 ± 0.07	0.19
Ph ₄ As[N(SO ₂ Cl) ₂]	80.39 ± 0.09	886.1 ± 22.9	—	5.49 ± 0.05	0.12
Me ₄ N[N(SO ₂ Cl) ₂]	105.13 ± 0.09	874.7 ± 21.5	—	5.07 ± 0.04	0.11
Bu ₄ N[N(SO ₂ Cl) ₂]	84.10 ± 0.08	524.7 ± 8.0	—	4.55 ± 0.02	0.27
Et ₄ NSO ₃ Cl	102.87 ± 0.24	637.5 ± 41.1	—	4.66 ± 0.08	0.11
Et ₄ NHSO ₄	97.10 ± 0.07	218.2 ± 16.9	—	4.02 ± 0.05	0.18
HPySO ₃ Cl	99.69 ± 0.67	196.7 ± 44.6	22.9 ± 3.4	4.77 ± 0.03	0.43

photriamide. Moreover, the standard deviations of the individual parameters in nitromethane are slightly larger than those in other solvents¹⁶⁻¹⁸. This may be attributed to slight instability of some of these salts in nitromethane. This is in accord with an earlier report¹⁹.

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

$$L - A\Lambda_0 = E'_1\Lambda_0 H(b) - E'_2G(b) - 6E'K(b) \quad \dots(3)$$

$$\hat{a} = \frac{567.4}{bD} \quad (\text{at } 25^\circ) \quad \dots(4)$$

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

$$L = 2E'_1\Lambda_0 (1.603 - \ln b) \quad \dots(5)$$

A perusal of results (Table 2) reveals that the ion-size parameter for all the salts (except Et_4NHSO_4) is equal to $5.0 \pm 0.5 \text{ \AA}$ in nitromethane. These values compare favourably with those reported by Coetzee and Cunningham⁷ 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 lower⁶ than the present values. This may be due to incomplete dissociation of these ions in nitromethane^{4,5}.

Single ion conductances — Kay *et al.*⁶, on the basis of experimental transference number measurements, have computed the mobility of chloride ion to be $62.52 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ in nitromethane. This value as well as that of Et_4N^+ ion (which in turn has been obtained from chloride ion mobility from Et_4NCl) 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_4N^+ and Bu_4N^+ ions obtained here differ by $\pm 0.33 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ from the literature values⁶, yet in view of the slight instability of chlorosulphate¹⁹ and imidobis(sulphuryl chloride) anions in nitromethane¹⁰, 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: $\text{Me}_4\text{N}^+ > \text{Et}_4\text{N}^+ >$

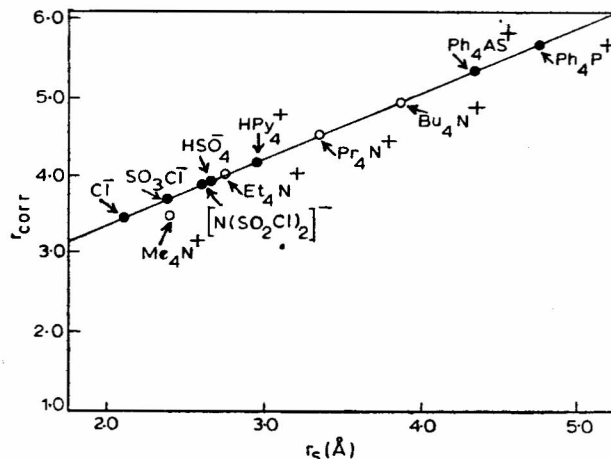


Fig. 1 — Nightingale calibration curve for determining effective ionic radii in nitromethane [Hollow circles (O) are the points for tetraalkylammonium ions and solid circles (●) refer to effective ionic radii obtained from the curve for various ions]

$\text{PyH}^+ > n\text{-Pr}_4\text{N}^+ > n\text{-Bu}_4\text{N}^+ > \text{Ph}_4\text{As}^+ > \text{Ph}_4\text{P}^+$;
 $\text{Cl}^- > \text{SO}_3\text{Cl}^- > [\text{N}(\text{SO}_2\text{Cl})_2]^- > \text{HSO}_4^-$.

The mobilities of the ions decrease with increase in their size. However, Ph_4P^+ and HSO_4^- are exceptions to this order. Although HSO_4^- may be slightly solvated (probably through hydrogen bonding), the decrease in mobility of Ph_4P^+ is surprising.

Stokes radii (r_s) of various ions have been calculated using Robinson-Stokes equation²⁰,

$$r_s = \frac{F^2|Z_{\pm}|}{6\pi\eta\lambda_{\pm}^{\circ}N} \quad \dots(6)$$

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 ions²⁰. Thus the Stokes radii obtained above have been corrected following the suggestion of Nightingale²¹. 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_{corr}) 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 dimethylsulphoxide²², hexamethylphosphotriamide¹⁶, N,N-dimethylacetamide¹⁷ and tetramethylurea²³.

Table 3 records the solvated and corrected radii of the various ions. A comparison of solvated radii of monovalent anions in this and other solvents²⁴ 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 sulpholane²⁴. The conductance behaviour

TABLE 3 — IONIC MOBILITIES (λ_{\pm}°), STOKES (r_s) AND CORRECTED (r_{corr}) RADII OF VARIOUS UNIVALENT IONS IN NITROMETHANE AT $25^\circ \pm 0.01^\circ$

Ion	λ_{\pm}°	r_s (Å)	r_{corr} (Å)
Me_4N^+	54.79	2.39	3.47
Et_4N^+	46.62*	2.75	4.00
Pr_4N^+	39.14*	3.34	4.52
Bu_4N^+	33.76	3.87	4.94
Ph_4P^+	27.58	4.74	5.70
Ph_4As^+	30.05	4.35	5.35
HPy^+	44.43	2.94	4.16
Cl^-	62.52	2.09	3.47
SO_3Cl^-	55.26	2.37	3.68
$[\text{N}(\text{SO}_2\text{Cl})_2]^-$	50.34	2.60	3.87
HSO_4^-	49.49	2.64	3.92

*Values from ref. 6.

of nitromethane solutions of these uncommon electrolytes has also been found to show some resemblance with sulpholane solutions²⁵. 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{a}) as has been observed in tetramethylurea²⁶.

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