

CHAPTER - VII

Conductances of the tetraalkylammonium bromides
in 1,2-dimethoxy ethane at 25°C

1,2-dimethoxyethane is a potential solvent now-a-days for use in non-aqueous batteries and its application in organic synthesis and electrochemical studies¹ have been widely stressed. These necessitate the study of the transport properties of ions in this aprotic media. The conductometric method is well known to give valuable information regarding ion-solvent interactions. Although a number of studies have been made in DME dealing mainly with the alkali metal halides²⁻⁴, but literature provides no information regarding the conductometric behaviour of the tetraalkylammonium halides in pure DME as solvent media.

In this chapter conductance measurements are reported for Hex₄NBr and Hept₄NBr in 1,2-dimethoxyethane (DME) at 25°C (lower homologues are insoluble in DME) in the concentration range of 5.0×10^{-2} to 1.0×10^{-4} mol. dm⁻³. The conductance data have been analyzed by the Fuoss-Kraus theory yielding values for the ion-pair and triple ion formation constants. Analysis of the data indicates that the electrolytes are mainly associated in the form of ion-pairs ($K_p \approx 10^6 \text{ M}^{-1}$). A small amount of triple ions were also detected for these salts at $0.01 \text{ M} < C < 0.05 \text{ M}$, the maximum concentration where the data have been analyzed.

Experimental

1,2-Dimethoxyethane (Fluka, Purum) was first shaken with FeSO_4 (AR, BDH) for 1-2 hours, decanted and then distilled. The distillate was then successfully refluxed for 12 hours and distilled over metallic sodium. The b.p and density compared fairly well with the corresponding values in the literature⁵ (b.p = 83.5°C , $d_4 = 0.86261 \text{ g cm}^{-3}$ at 25°C). The specific conductance of DME was found to be $0.81 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C .

Tetraalkylammonium bromides were of Fluka's puriss or purum grade. Tetrabutylammonium bromide and tetrapentylammonium bromide were recrystallized from acetone and ether mixture and dried in vacuo at 60°C for two days. Tetrahexylammonium bromide and tetraheptylammonium bromide were washed with ether and dried in vacuo at room temperature for two days.

Conductance measurements were made by a Pye Unicam PB 9509 conductivity meter at a frequency of 2000 Hz using a di-type cell of cell constant 0.731 cm^{-1} . The measurements were made in an oil bath maintained at $25 \pm 0.005^\circ\text{C}$.

Densities were measured with an Ostwald-Sprengel type pycnometer of about 25 ml capacity. The dielectric constant of DME ($\epsilon = 7.075$) was taken from the literature⁶.

Results and Discussion

The equivalent conductance data (\wedge) vs. the concentration (c) of the electrolytes in DME at 25°C have been recorded in

Table 1. Fig. 1 reports the plot of Λ vs. C in a log-log plot for the electrolytes. A minimum is clearly visible in every case.

The conductance data have been treated by the Fuoss-Krauss theory⁷ for the triple-ion formation (eq. 1)

$$\Lambda_3(c) c^{1/2} = \frac{\Lambda_0}{K_P^{1/2}} + \frac{\Lambda_0^T K_T}{K_P^{1/2}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad \dots(1)$$

where $g(c)$ is a factor that combines together all the interionic interaction terms, Λ_0 and Λ_0^T are the limiting equivalent conductances of R_4NBr and of two possible triple-ions $R_4N(Br)_2^-$ and $(R_4N)_2Br^+$ respectively. K_P and K_T are the ion-pair and triple-ion formation constants respectively. The symmetrical approximation of considering the two possible formation constants of triple-ions equal to each other has been considered⁴.

The term $g(c)$ is of the following form (2)

$$g(c) = \frac{\exp\left[-\frac{\beta'}{\Lambda_0^{1/2}} (c\Lambda)^{1/2}\right]}{\left(1 - \frac{S}{\Lambda_0^{3/2}} (c\Lambda)^{1/2}\right) \left(1 - \frac{\Lambda}{\Lambda_0}\right)} \quad \dots(2)$$

where β' is the Debye-Huckel activity co-efficient term and S the limiting Onsager Coefficient. Neglect of $\frac{\Lambda}{\Lambda_0}$, $\frac{S}{\Lambda_0^{3/2}} (c\Lambda)^{1/2}$ and the assumption of $\epsilon \pm = 1$ leads to $g(c) = 1$ and we get

$$\Lambda(c)^{1/2} = \frac{\Lambda_0}{(K_P)^{1/2}} + \frac{\Lambda_0^T K_T}{(K_P)^{1/2}} \cdot c \quad \dots (3)$$

For the present data, it was found that the Eq. (3) is inadequate, the data showing a downward curvature when plotted as $\Lambda c^{1/2}$ vs. C (a representative plot for Hex_4NBr is shown in Fig. 2A). On the contrary equation (1) gives reasonably straight line (Fig. 2B), the curvature having almost disappeared.

For evaluation of K_P and K_T values from Eq. (1), the average $\Lambda_0 \eta_0$ values of the salts at 25°C were taken from the work of Krungalz^B. The viscosity of 1,2-DME is $\eta_0 = 0.004129$ poise. Therefore, from Walden's rule we calculate Λ_0 values of the electrolytes in 1,2-DME at 25°C (Table 3). Linear regression analysis of Eq. (1) give determination co-efficient r^2 , intercept and slope (Table 2). From the above results and arbitrary position $\Lambda_0^T = \frac{2}{3} \Lambda_0$, K_P and K_T values are calculated (Table 3).

Table 3 shows that the major portion of the electrolytes exist as ion-pairs with only a minor proportion as triple-ions (Neglecting quadruples). The K_P and K_T values change in a zig-zag fashion with cationic size from Bu_4N^+ to Hex_4N^+ but decreases

sharply for Pent_4NBr . This probably happens due to the result of spherical interaction⁹ (forming 'clathrate-like' structure around their hydrocarbon side chains) of the tetraalkylammonium ions with solvents in general. With the above values of K_p and K_T (Table 3), the ion-pair concentrations, c_p of the electrolytes have been calculated⁴ (Table 4) at a concentration of $c = 0.03M$. The results indicate that a very small fraction of the electrolytes are present as triple ions even at such a high concentration.

Table 1 : Equivalent Conductances of the Tetraalkylammonium Bromides in 1,2-Dimethoxyethane at 25°C

$10^4 \kappa$ (mol l ⁻¹)	\wedge (ohm ⁻¹ cm ² mol ⁻¹)	$10^4 \kappa$ (mol l ⁻¹)	\wedge (ohm ⁻¹ cm ² mol ⁻¹)	$10^4 \kappa$ (mol l ⁻¹)	\wedge (ohm ⁻¹ cm ² mol ⁻¹)	$10^4 \kappa$ (mol l ⁻¹)	\wedge (ohm ⁻¹ cm ² mol ⁻¹)
Et ₄ NBr		Pent ₄ NBr		Hex ₄ NBr		Hept ₄ NBr	
1.0102	11.401	29.9798	2.801	5.9989	2.916	19.9989	2.025
1.9976	7.011	49.9899	2.541	8.0019	2.487	22.0019	1.902
4.0028	4.799	70.0101	2.414	9.9989	2.141	24.9998	1.611
5.9879	3.817	99.9897	2.341	12.4999	1.976	30.0210	1.367
8.0201	3.375	129.9851	2.323	14.9879	1.793	35.0111	1.289
9.9989	3.161	159.9895	2.341	18.0019	1.677	39.9959	1.223
20.0091	2.369	199.9969	2.369	20.0109	1.580	64.9981	1.156
40.0011	2.021	219.9899	2.381	24.9985	1.462	99.9989	1.151
59.9969	1.933	289.2401	2.458	30.0017	1.379	150.0119	1.227
80.0019	1.901	300.0109	2.466	35.0105	1.337	199.9791	1.283

Contd..

Table I (Contd..)

100.0101	1.919	39.9879	1.305	249.9986	1.379
149.9992	2.013	64.9987	1.244	300.0101	1.456
159.9891	2.044	99.8998	1.279	350.0091	1.514
250.0112	2.476	149.9899	1.333		
300.0091	2.691	199.9981	1.405		
		250.0107	1.464		
		300.0105	1.513		
		499.9899	1.682		

Table 2 : Values of the Coefficients from Regression Analysis

Salt	r^2	Intercept	Slope
Bu ₄ NBr	0.96845	8.9485×10^{-2} (± 0.0078)	15.9634 (± 0.8319)
Pent ₄ NBr	0.99950	12.5304×10^{-2} (± 0.0018)	18.0405 (± 0.1177)
Hex ₄ NBr	0.99691	9.6500×10^{-2} (± 0.0021)	9.8174 (± 0.1398)
Hept ₄ NBr	0.99429	8.7854×10^{-2} (± 0.0055)	8.8998 (± 0.3390)

Table 3 : Ion-pair and Triple-ion Formation Constant of the Electrolytes in DME at 25 °C

Salt	$\Lambda_0 / \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	$K_p \times 10^{-6} / (\text{mol} \cdot \text{dm}^{-3})^{-1}$	$K_T / (\text{mol} \cdot \text{dm}^{-3})^{-2}$
Bu ₄ NBr	138.37	2.3908	267.5855
Pent ₄ NBr	132.76	1.1225	192.0191
Hex ₄ NBr	128.61	5.1815	260.6404
Hept ₄ NBr	125.93	4.7376	230.7455

Table 4 : Ion-pair Concentration, c_p^a , for the Electrolytes
 in DME at 25°C at C = 0.03M

Electrolyte	$c_p \times 10^4$
Bu ₄ NBr	271.9020
Pent ₄ NBr	270.1120
Hex ₄ NBr	281.3890
Hept ₄ NBr	282.6880

$$^a c_p = c(1 - \alpha - 3\alpha_T) ; \alpha = 1 / (k_p^{\frac{1}{2}} c^{\frac{1}{2}}) ;$$

$$\alpha_T = (k_T / k_p^{\frac{1}{2}}) c^{\frac{1}{2}}$$

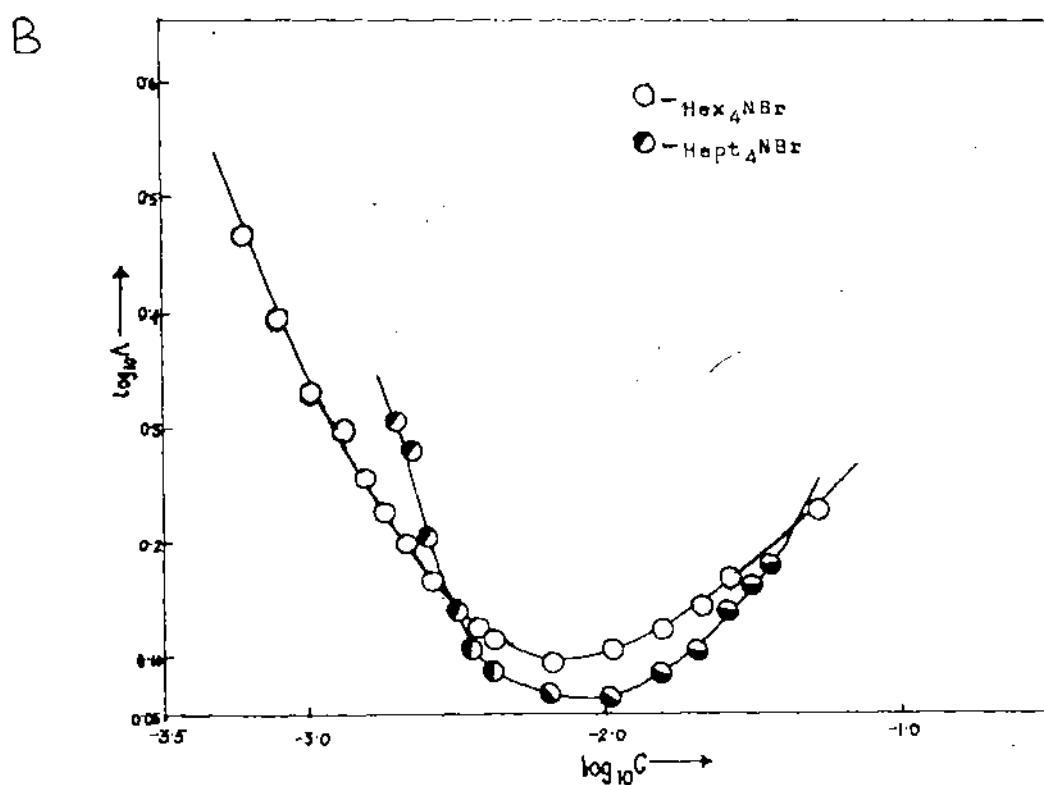
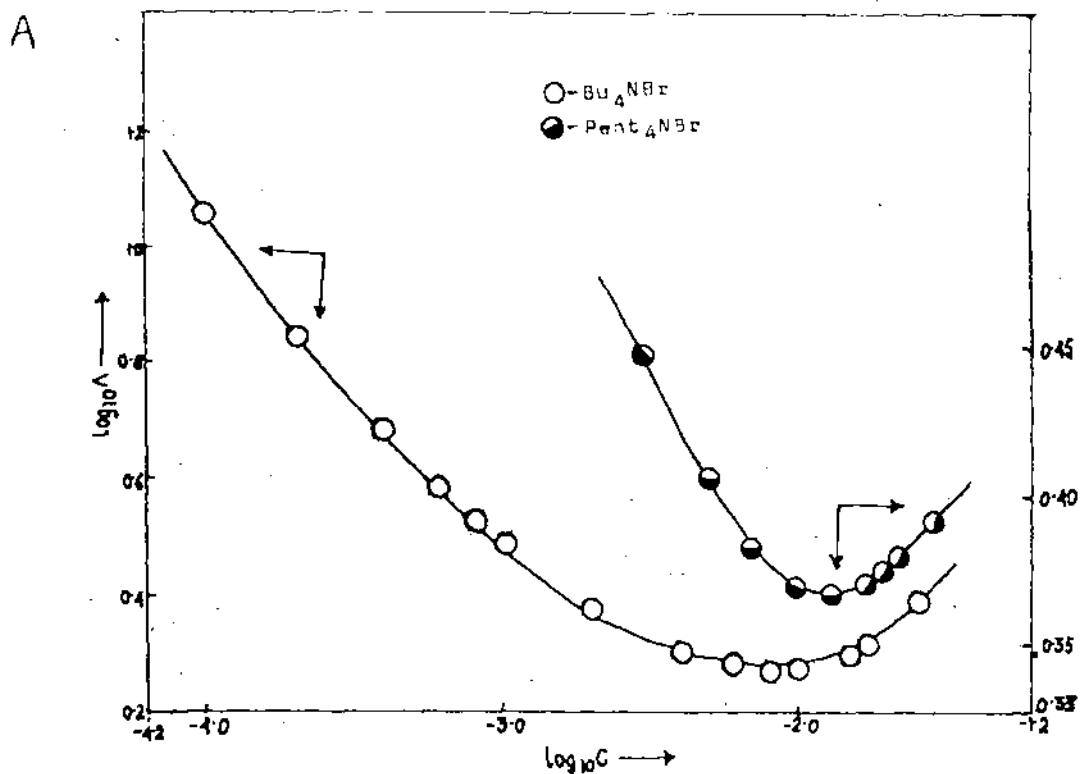
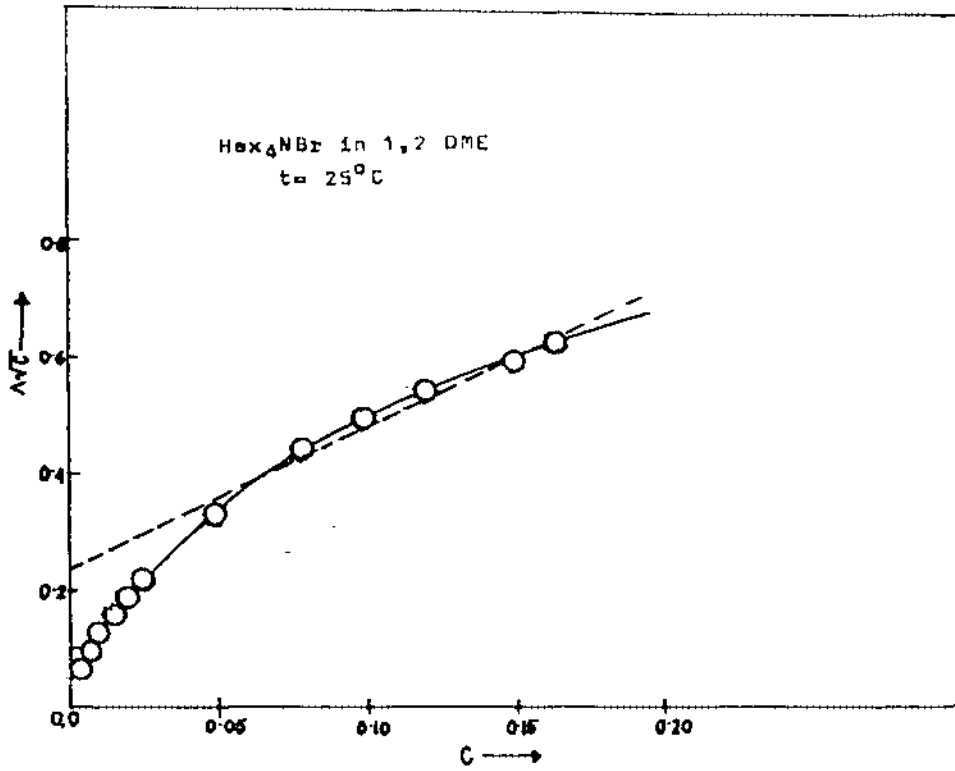


Fig.1 Plot of $\log_{10} \Delta$ vs $\log_{10} C$ for (A) Bu_4NBr & Pent_4NBr & (B) Hex_4NBr & Hept_4NBr in 1,2-DME at 25°C

A



B

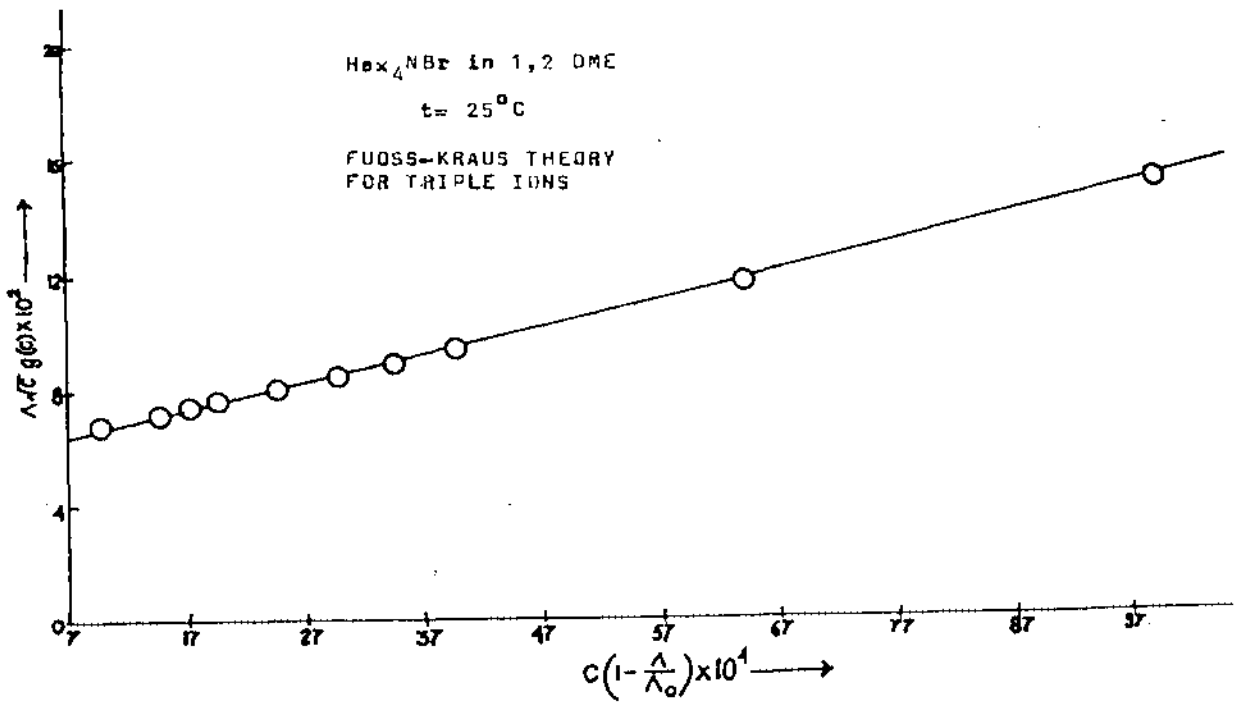


Fig. 2 A representative plot of (A) $\Lambda C^{1/2}$ vs C & (B) $g(c) C^{1/2}$ vs $C(1 - \frac{\Lambda}{\Lambda_0})$ for Hex₄NBr in 1,2-DME at 25°C.

R E F E R E N C E S

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