

CHAPTER-V

A Study on the Ion-Solvent Interactions of Tetraphenyl-
arsonium, Tetraphenylphosphonium and Some Common Ions
from Viscosity and Conductance Data

The viscosity measurements have been widely used¹⁻⁴ as an important experimental tool to provide information on the nature of ion-solvent interactions and the structural modifications of solvents by ions in solution. Although for a long time much attention has been paid to the viscosity B co-efficients of ions in aqueous solutions, measurements of B co-efficients in non-aqueous solutions are still scarce⁵. Similarly, conductance data also provides us valuable information regarding the ion-solvent interactions of electrolytes⁶ in aqueous, non-aqueous and mixed solvents. The potentiality of propylene carbonate (PC) as a solvent for a variety of applications of technological importance has already been mentioned in Chapters I and III. Moreover, the salts such as Ph_4AsCl , Ph_4PBr containing tetraphenyl ions play a very important role in Solution Chemistry and are often recommended as reference electrolytes^{2,7-10}. Thus, in the present chapter an attempt has been made to reveal the nature of ion-solvent interactions of Ph_4AsCl , Ph_4PBr and NaBPh_4 in propylene carbonate (PC) from their viscosity and conductance data. The viscosities have been measured at three different temperatures while conductance measurements were done at 25°C only. As the electrolytes are found to be unassociated in this medium, the viscosity data have been analysed using the Jones-

Dole equation in the form of unassociated electrolytes and the viscosity B co-efficients have been evaluated. Ionic B values have been derived on the basis of the reference electrolyte ' Bu_4NBPh_4 '. The conductance data are analysed by the Fuoss (1978) conductance equation and the limiting equivalent conductances have been evaluated. The single ion conductances have been derived by using two reference electrolytes ' Bu_4NBBu_4 ' and ' Bu_4NBPh_4 ' and the results have been compared.

Experimental

The purifications of the electrolytes have been described in Chapters II and IV. Freshly distilled solvent was always used for each experiment solvent properties of propylene carbonate (PC) at 25, 35 and 45°C have been mentioned earlier (Chapter - IV, Part - B).

For viscometric study, the concentrations of the salt solutions generally varied in the range 0.01-0.08 mol dm⁻³ and the solutions were prepared by weight dilution of the stock solution (ca 0.1 mol dm⁻³). The kinematic viscosities were measured at the desired temperature (accuracy $\pm 0.01^\circ\text{C}$) using a suspended Ubbelohde-type viscometer. Densities were measured using an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm³. The precisions of density and viscosity measurements were $\pm 3 \times 10^{-5}$ gcm⁻³ and 0.05% respectively.

For conductance measurements, ten to thirteen solutions of different concentrations ranging from 0.05-0.005 mol dm⁻³ were prepared for each salt. The electrical conductances were measured at 25°C with a Pye Unicam PW 9509 conductivity meter at a frequency of 2000 Hz. The details of experimental procedure have been given in Chapters II and IV.

Results

The density and viscosity data for the electrolytes at 25, 35 and 45°C have been recorded in Table 1.

The experimental viscosity data have been analysed by the Jones-Dole equation¹¹

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad (1)$$

where, η and η_0 are the viscosities of the solution and the solvent respectively, c is the molar concentration and the other terms have their usual significance.

The plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ against \sqrt{c} for the electrolytes are linear (Fig. 1) and the experimental A values at 25, 35 and 45°C have been calculated using the least squares method. The A co-efficients were also calculated theoretically at 25°C from the

physical properties of the solvent and the limiting ionic equivalent conductances by using the Falkenhagen and Vernon equation¹²:

$$A_{\text{theo}} = \frac{0.2577 \Lambda_0}{\eta_0 (\epsilon T)^{1/2} \lambda_+^+ \lambda_-^-} \left[1 - 0.6863 \left(\frac{\lambda_+^+ - \lambda_-^-}{\Lambda_0} \right)^2 \right] \quad (2)$$

These A_{theo} values have been used for analysis of the viscosity data. In view of the weak temperature dependence of the A coefficients and non-availability of limiting ion-conductance values at different temperatures, A_{theo} values at 25°C have been utilized at the other two temperatures also. Theoretical A coefficients obtained from eqn. 2 along with the experimental A values are reported in Table 2.

Viscosity B coefficients obtained at 25, 35 and 45°C by using the least squares method have been recorded in Table 2.

Viscosity data have also been analysed on the basis of the transition state treatment of the relative viscosity of electrolyte solutions as suggested by Feakins et al¹³

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000} \left(\frac{\Delta \nu_2^{M^\ddagger} - \Delta \nu_1^{M^\ddagger}}{RT} \right) \quad (3)$$

In the above equation, \overline{V}_1^0 and \overline{V}_2^0 are the partial molar volumes of propylene carbonate and solute respectively. $\Delta \mu_2^\ddagger$, the contribution per mole of solute to the free energy of activation for viscous flow of the solution, has been determined from the above relationship and the values have been reported in Table 3. $\Delta \mu_1^\ddagger$ is the free energy of activation per mole of pure solvent¹⁴.

Ionic B co-efficients along with the ionic $\Delta \mu_2^\ddagger$ values at three different temperatures are presented in Table 4.

Table 5 deals with the ionic radii and solvation numbers of ions at 25°C.

The measured equivalent conductances and the corresponding molarities for Ph_4AsCl , Ph_4PBr and NaBPh_4 in PC are given in Table 6. The conductance data were analysed with the help of the Fuoss conductance equation^{15,16} as described earlier (Chapter - IV).

The values of Λ_0 , K_A and R are recorded in Table 7.

The limiting ionic conductances (λ_0^\pm) based on the reference electrolytes viz. Bu_4NBBu_4 and Bu_4NBPh_4 (Λ_0 values taken from Chapter - IV) are given in Table 8, the λ_0^\pm value of Cl^- ion was taken from the literature¹⁷. The Walden products and Stokes radii of ions are also recorded in Table 8.

Discussion

The A coefficients reported in Table 2 are found to be small and positive for all the electrolytes and the observed A coefficients for Ph_4AsCl and NBPh_4 at 25°C agree very well with the theoretical ones. For Ph_4PBr , the experimental A coefficient at 25°C differs from the theoretical A value. Similar differences between theoretical and experimental A coefficients, however, have been observed in other systems⁷ also.

Viscosity B coefficients (Table 3) are large and positive and the values decrease in the order $B(\text{Ph}_4\text{AsCl}) > B(\text{NBPh}_4) > B(\text{Ph}_4\text{PBr})$. Viscosity B coefficients for Ph_4AsCl and Ph_4PBr in PC are greater than those in water (1.08 and 0.98 for Ph_4AsCl and 1.05 and 0.95 for Ph_4PBr at 25 and 35°C respectively)⁴. Viscosity B value for Ph_4PBr in PC at 25 and 35°C are smaller than the corresponding values in DMSO⁷ (viz. 1.356 and 1.270 at 25 and 35°C respectively). With the rise of temperature, the B values decrease in general (though it has a very weak temperature dependence), indicating that the tetraphenyl salts behave as structure makers in the solvent. This behaviour is similar to those observed in aqueous system⁴ and in other dipolar aprotic solvents like acetonitrile^{5,18}, dimethylsulphoxide^{7,19} and sulfolane²⁰.

The ionic B values were calculated by eqn. (4) using Bu_4NBPh_4 as the reference electrolyte^{8,9}

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{N}^+) + B(\text{Ph}_4\text{B}^-) \quad (4)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \left(\frac{5.35}{5.00} \right)^3 \quad (5)$$

Ionic B coefficients obtained from the above relationships have been recorded in Table 4. Viscosity B coefficient for the reference electrolyte, Bu_4NBPh_4 , has been taken from Chapter - IV. An attempt was made to measure the B coefficient of $\text{Ph}_4\text{AsBPh}_4$ in PC so that the internal consistency could be maintained for ionic B values. But owing to the poor solubility of $\text{Ph}_4\text{AsBPh}_4$ in PC, the experiment could not be performed. For this reason, ionic B value of Cl^- ion at 25°C was calculated by taking the B value of Et_4N^+ ion ($B_+ = 0.258$) from Chapter - IV and that of Et_4NCl ($B = 0.51$) from the literature²¹ assuming that the rule of additivity also holds too in this case. Table 4 shows that the ionic B values decrease in the order : $\text{Ph}_4\text{As}^+ > \text{Ph}_4\text{P}^+ > \text{Na}^+$ and $\text{Ph}_4\text{B}^- > \text{Br}^- > \text{Cl}^-$. With the increase of temperature the B_{\pm} values decrease in general indicating that these ions behave as structure makers in this solvent. Ionic free energies of activation of viscous flow based on the division of Bu_4NBPh_4 have also been presented in Table 4. $\Delta \int_2^{\mu^{\circ\ddagger}}$ for Ph_4As^+ and Cl^- ions could not be calculated owing to the non-availability of ionic contributions of any one of these two ions. Values of $\Delta \int_2^{\mu^{\circ\ddagger}}$ for the other ions are in the order : for cations, $\text{Ph}_4\text{P}^+ > \text{Na}^+$ and for anions $\text{Ph}_4\text{B}^- > \text{Br}^-$. It may be noted that $\Delta \int_2^{\mu^{\circ\ddagger}}$

values for all the ions are positive and thus the formation of transition state is less favourable in the presence of these ions.

Ionic B_{\pm} co-efficients have also been analysed on the basis of Einstein's equation²²

$$B_{\pm} = 2.5 \frac{4}{3} \pi \frac{R_{\pm}^3 N}{1000} \quad (6)$$

where the terms have their usual significance. The number of solvent molecules (n_s) bound to the ion in the primary region can be calculated by the combination of the Jones-Dole equation with that of Einstein²³

$$B_{\pm} = \frac{2.5}{1000} (V_1 + n_s V_s) \quad (7)$$

where, V_1 represents the bare ion molar volume and is related to the crystallographic radius r_c of the ion. V_s is the solvent molar volume. The values of R_{\pm} and n_s are shown in Table 5. It can be seen that for cations, R_{\pm} values are in the order : $\text{Ph}_4\text{As}^+ > \text{Ph}_4\text{P}^+ > \text{Na}^+$. Comparison with their ionic radii indicates that the tetraphenyl ions are scarcely solvated in propylene carbonate. However, R_{\pm} value for Na^+ ions is about four times of its crystallographic radius indicating that this ion is highly solvated in this medium. Amongst the anions, although the ionic radius of BPh_4^- ion is larger than its crystallographic radius by a small amount but the ionic radii for Cl^- and Br^- ions are much greater than their crystallographic radii indicating that these two ions are solvated

in this medium. Similar observation for solvation of Br^- ion in PC has been reported by Yeager et al²⁴ from spectroscopic studies. It should be noted that from conductance studies of Br^- ion in PC (Chapter - IV) poor solvation was predicted. However, similar observation was also made by others¹⁷.

Table 7 shows that the limiting equivalent conductance (Λ_0) of the tetraphenyl salts decrease in the order $\text{Ph}_4\text{PBr} > \text{Ph}_4\text{AsCl} > \text{NaBPh}_4$. Since, ionic radii of Ph_4P^+ and Ph_4As^+ are close to each other and both of them are large enough, it appears that the higher mobility of Br^- ion compared to Cl^- ion is primarily responsible for the larger Λ_0 value of Ph_4PBr .

The association constants (K_A) in Table 7 show that these salts are almost unassociated ($K_A < 10$) in this solvent medium. This is quite expected owing to the high dielectric constant of PC, very large size of the tetraphenyl salts and their low charge density values.

The single ion conductances were calculated on the basis of reference electrolytes viz. Bu_4NBBu_4 ^{7,25} and Bu_4NBPh_4 ²⁶ by using the following relationships:

$$\lambda(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Bu}_4\text{B}^-) \quad (8)$$

$$\frac{\lambda_0(\text{Bu}_4\text{N}^+)}{\lambda_0(\text{Ph}_4\text{B}^-)} = \frac{r_{\text{Ph}_4\text{B}^-}}{r_{\text{Bu}_4\text{N}^+}} = \frac{5.35}{5.00} = 1.07 \quad (9)$$

The reason behind the choice of Bu_4NBBu_4 as the reference electrolyte lies in the fact that the cation and anion in this electrolyte are symmetrical in shape and have almost equal van der Waals volume.

The Λ_0 value for Bu_4NBBu_4 was taken from our earlier work (Chapter - IV) and the λ_0^\pm values thus calculated are presented in Table 8. The limiting ion conductances based on eqn. (9) have also been recorded in Table 8. It can readily be seen that the limiting ionic conductances obtained from the above relationships are in very close agreement with each other, suggesting that either of the above two reference electrolytes may be used for the division of Λ_0 values into ionic components in this medium. We also made an attempt to measure the limiting equivalent conductance of $\text{Ph}_4\text{AsBPh}_4$ so that the ionic λ_0 values for all the ions could be exclusively evaluated from the experimental results. However, due to the poor solubility of $\text{Ph}_4\text{AsBPh}_4$, the idea was discarded. The limiting ionic equivalent conductance for Ph_4As^+ ion was calculated by taking λ_0 value of Cl^- ion (15.90) from the literature¹⁷. Table 8 shows that the λ_0 values for the ions decrease in the order : $\text{Ph}_4\text{As}^+ > \text{Ph}_4\text{P}^+ > \text{Na}^+$ and $\text{Br}^- > \text{Cl}^- > \text{Ph}_4\text{B}^-$. The λ_0^\pm values for Na^+ and Br^- ions obtained by us are in good agreement with the values reported by Takeda et al [$\lambda_0(\text{Na}^+) = 10.45$ and $\lambda_0(\text{Br}^-) = 18.70$]¹⁷. Results indicate that the mobility of Br^- ion is greater than that of Cl^- ion.

The Walden product ($\lambda^{\pm} \eta$) and Stokes radii (r_s) of the ions have also been given in Table 8. From the table we can see that the Stokes radii of tetraphenyl ions are much less than the corresponding crystallographic radii (Table 5) and this shows that these ions are scarcely solvated in this solvent system. However, for Na^+ ion, the Stokes radius is much greater than its crystallographic radius (0.95 Å) indicating that this ion is substantially solvated in this solvent medium. This is also in consistent with the result obtained from the present viscometric study. Moreover, the Stokes radius of Na^+ ion in PC obtained by us (3.09 Å) is in excellent agreement with the literature value (3.10 Å)¹⁷. Table 8 further shows that the Br^- ion has the highest ionic mobility amongst the anions. The lower mobility of Cl^- ion than Br^- ion may be due to its enhanced ion-solvent interactions in this medium which effectively increases the size of this ion in solution. Larger Stokes radius of Cl^- ion compared to Br^- ion also supports the above view point. On the other hand it appears that large sizes of tetraphenyl ions, their low charge density values and the high relative permittivity of PC render these ions to be free, unassociated and almost unsolvated in this solvent medium.

Table 1. Concentration, c /(mol dm⁻³), density, ρ /(gcm⁻³) and relative viscosity, η_r of Ph₄AsCl, Ph₄PBr and NaBPh₄ in PC at 25, 35 and 45°C

c	ρ	η_r	c	ρ	η_r
Ph ₄ AsCl 25°C			Ph ₄ PBr 25°C		
0.01374	1.19953	1.0174	0.01512	1.19967	1.0195
0.02762	1.20023	1.0348	0.03001	1.20049	1.0373
0.03255	1.20046	1.0404	0.03993	1.20104	1.0492
0.03753	1.20074	1.0465	0.05506	1.20188	1.0668
0.04249	1.20099	1.0523	0.06994	1.20270	1.0841
0.05260	1.20150	1.0644			
NaBPh ₄ 25°C			Ph ₄ AsCl 35°C		
0.01003	1.19896	1.0134	0.01353	1.19019	1.0168
0.02506	1.19915	1.0342	0.02740	1.19069	1.0334
0.04010	1.19936	1.0505	0.03229	1.19087	1.0394
0.05013	1.19946	1.0625	0.03723	1.19105	1.0452
0.05982	1.19958	1.0744	0.04214	1.19123	1.0510
0.08020	1.19982	1.0988	0.05217	1.19159	1.0631

Table 1 (Contd..)

Ph ₄ PBr 35°C			NaBPh ₄ 35°C		
0.01501	1.19041	1.0180	0.01044	1.18998	1.0104
0.02977	1.19111	1.0346	0.02832	1.19040	1.0308
0.03962	1.19158	1.0455	0.04541	1.19081	1.0485
0.05462	1.19228	1.0621	0.05702	1.19109	1.0605
0.06938	1.19298	1.0786	0.06790	1.19135	1.0717
			0.09133	1.19191	1.0957
Ph ₄ AsCl 45°C			Ph ₄ PBr 45°C		
0.01350	1.17825	1.0164	0.01486	1.17857	1.0170
0.02712	1.17854	1.0325	0.02948	1.17917	1.0329
0.03196	1.17865	1.0382	0.03922	1.17957	1.0433
0.03684	1.17875	1.0438	0.05406	1.18018	1.0593
0.04171	1.17886	1.0496	0.06867	1.18078	1.0750
0.05162	1.17907	1.0614			

Contd..

Table 1 (Contd..)

	NaBPh ₄ 45°C	
0.00985	1.17832	1.0121
0.02464	1.17886	1.0297
0.03943	1.17939	1.0469
0.04930	1.17975	1.0584
0.05885	1.18010	1.0696
0.07893	1.18083	1.0930

Table 2. Theoretical A values and experimental A co-efficients, $A_{\text{obs}}/\text{dm}^{3/2}\text{mol}^{-1/2}$ at 25, 35 and 45°C

Salts	A_{theo} (25°C)	A_{obs}		
		25°C	35°C	45°C
Ph_4AsCl	0.0112	0.0111	0.0066	0.0066
Ph_4PBr	0.0106	0.0207	0.0149	0.0126
NaBPh_4	0.0154	0.0166	0.0134	0.0081

Table 3. Viscosity B co-efficients, $B/\text{dm}^3\text{mol}^{-1}$ and $\Delta/\mu^{\circ\pm}/\text{kJ mol}^{-1}$ values in propylene carbonate at different temperatures

Salts	25°C		35°C		45°C	
	B	$\Delta/\mu^{\circ\pm}$	B	$\Delta/\mu^{\circ\pm}$	B	$\Delta/\mu^{\circ\pm}$
Ph_4AsCl	1.176±0.007	56.22	1.166±0.003	57.42	1.146±0.003	58.27
Ph_4PBr	1.150±0.003	55.78	1.087±0.001	55.25	1.049±0.001	55.28
NaBPh_4	1.175±0.001	55.31	1.158±0.004	55.46	1.130±0.002	55.41

Table 4. Ionic B co-efficients^a, $B_{\pm}/\text{dm}^3\text{mol}^{-1}$ and ionic $\Delta\mu_{\pm}^{\ddagger}/\text{kJ mol}^{-1}$ values in PC at different temperatures

Ion	25°C		35°C		45°C	
	B_{\pm}	$\Delta\mu_{\pm}^{\ddagger}$	B_{\pm}	$\Delta\mu_{\pm}^{\ddagger}$	B_{\pm}	$\Delta\mu_{\pm}^{\ddagger}$
Ph_4As^+	0.924	-	-	-	-	-
Ph_4P^+	0.692	33.44	0.659	32.96	0.638	32.84
Na^+	0.458	18.60	0.452	17.98	0.438	17.46
Cl^-	0.252	-	-	-	-	-
Br^-	0.458	22.34	0.428	22.29	0.411	22.44
BPh_4^-	0.717	36.71	0.706	37.48	0.692	37.95

^a Division on the basis of Bu_4NBPh_4

Table 5. R_{\pm}° and solvation number (n_s) of ions in PC at 25°C

Ion	$r_c^* / \text{\AA}$	R_{\pm}	n_s
Ph_4As^+	6.40 ^a	5.27	-8.55
Ph_4P^+	6.30 ^a	4.79	-9.05
Na^+	1.17 ^b	4.18	2.12
Cl^-	1.64 ^b	3.42	0.89
Br^-	1.80 ^b	4.17	1.78
BPh_4^-	4.20 ^c	4.84	-0.28

r_c^* = Crystallographic radii

^a C.V. Krishnan and H.L. Friedman, *J. Phys. Chem.*, **73**, 3934, 1969.

^b B.S. Gourary and F.J. Adrian, *Solid State Phys.*, **10**, 127, 1960.

^c R.A. Robinson and R.H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1959.

Table 6. Equivalent conductances and corresponding molarities of the salts in PC at 25°C

$10^4 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{mol}^{-1}$	$10^4 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{mol}^{-1}$
Ph_4AsCl		Ph_4PBr	
526.010	20.95	503.161	22.01
424.854	21.54	425.378	22.56
375.326	21.85	390.417	22.81
325.538	22.21	352.436	23.11
276.169	22.63	300.803	23.49
226.221	22.98	271.034	23.74
175.895	23.42	240.035	24.06
125.065	23.98	210.937	24.30
90.716	24.46	191.420	24.53
51.498	25.03	152.793	24.97
		127.613	25.27
		80.867	26.03
		51.653	26.63
NaBPh_4			
495.579	13.66		
426.918	14.08		
380.736	14.36		
351.022	14.58		
298.843	14.92		
271.135	15.16		
239.549	15.41		
210.876	15.65		
189.741	15.83		
155.893	16.21		
125.704	16.51		
90.385	16.94		
52.179	17.53		

Table 7. Conductance parameters of the electrolytes in PC at 25°C

Salts	$\Lambda_{\infty}/\text{Scm}^2\text{mol}^{-1}$	$K_A/\text{dm}^3\text{mol}^{-1}$	walden product	$R/\text{\AA}$	σ
Ph_4AsCl	27.21 ± 0.02	4.57 ± 0.07	0.672	11.20	0.10
Ph_4PBr	29.01 ± 0.02	5.52 ± 0.05	0.717	9.30	0.07
NaBPh_4	19.58 ± 0.02	7.75 ± 0.08	0.484	14.00	0.09

Table 8. Limiting ionic conductances, Walden products and Stokes radii of the ions in PC at 25°C

Ion	$\lambda_{\infty}^{+a} / \text{Scm}^2 \text{mol}^{-1}$	$\lambda_{\infty}^{+b} / \text{Scm}^2 \text{mol}^{-1}$	$\lambda_{\infty}^{+\eta a} / \text{Scm}^2 \text{mol}^{-1} \text{P}$	$\lambda_{\infty}^{+\eta b} / \text{Scm}^2 \text{mol}^{-1} \text{P}$	$r_s^a / \text{\AA}$	$r_s^b / \text{\AA}$
Ph_4As^+	11.31	-	0.279	-	2.93	-
Ph_4P^+	10.77	10.79	0.266	0.267	3.03	3.06
Na^+	10.72	10.74	0.255	0.265	3.09	3.09
Cl^-	15.90 ^c	-	0.393	-	2.08	-
Br^-	18.24	18.22	0.451	0.450	1.81	1.82
Ph_4S^-	8.86	8.34	0.219	0.218	3.74	3.75

^a Calculations based on Bu_4NBBu_4 .

^b Calculations based on Bu_4NBPh_4 .

^c from ref. 17

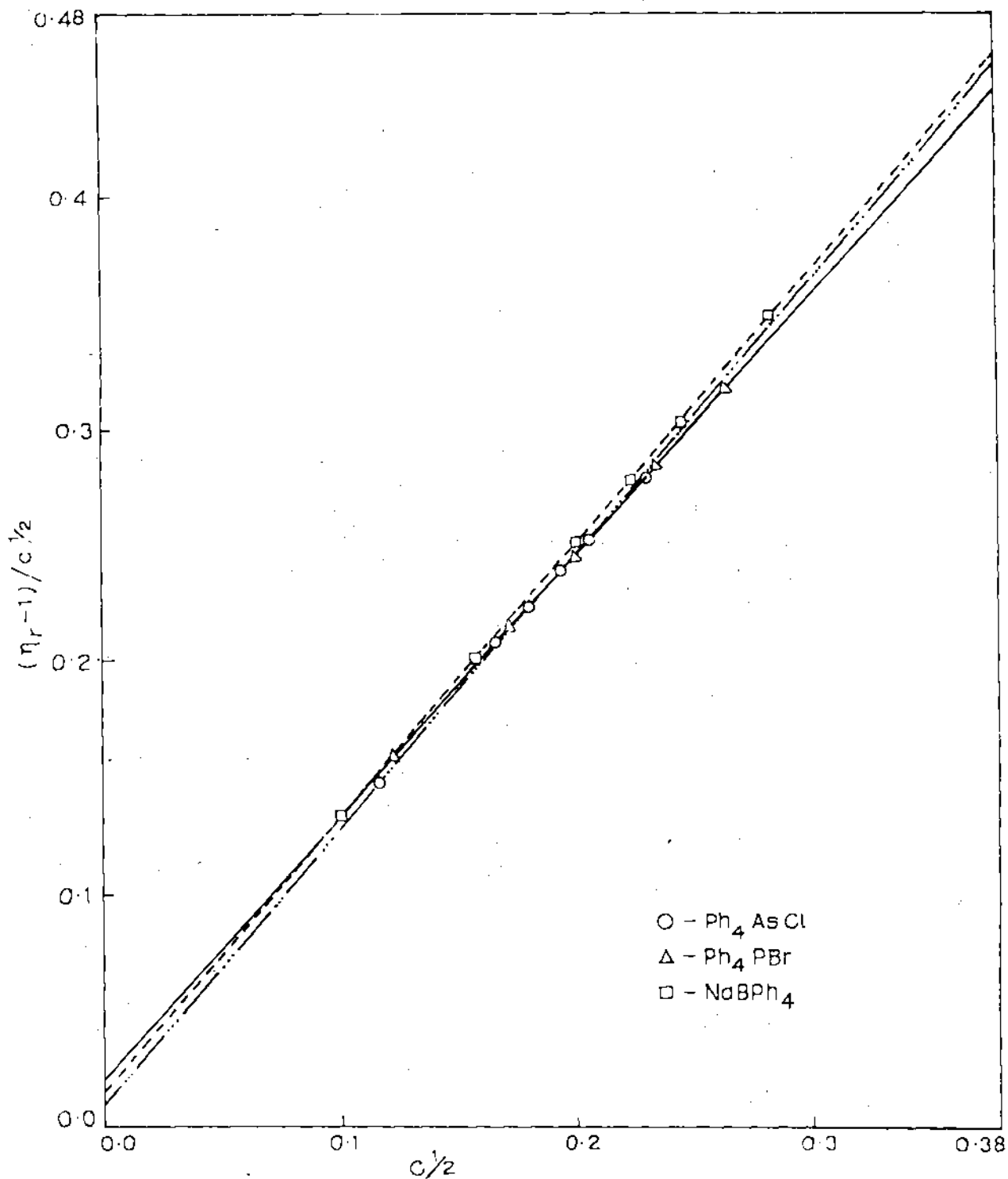


Fig. 1. Representative plot of $(\eta_r - 1)/c^{1/2}$ against $c^{1/2}$ for some electrolytes in PC at 25°C

R E F E R E N C E S

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