

Solvent Properties of Dichloromethane. V. Density and Partial Molar Volume of Tetraalkylammonium, Tetraphenylarsonium and Bis(triphenylphosphine)iminium Salts in Dichloromethane

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The volumetric behaviour and the density of several onium salts in dichloromethane have been studied in the 10^{-3} – 10^{-1} M concentration range at 25.00°C. The salts studied were R_4NClO_4 ($R = Et, Pr, Bu, Hex, Oct$ and Dec), Bu_4NBr , Bu_4NI , Bu_4NBBu_4 , Bu_4NSCN , Bu_4NBPh_4 , Hex_4NI , Dec_4NBr , Ph_4AsX ($X = Cl, Br, I, SCN$ and ClO_4) and $[PNP]X$ ($X = Cl, SCN$ and ClO_4); $[PNP]^+$ is an abbreviation for $[(Ph_3P)_2N]^+$.

The density–concentration plots for the R_4N^+ salts are strictly linear and the effect of the ions upon the density of the solutions seems additive. Based upon the assumption of equal contributions by Bu_4N^+ and Bu_4B^- , the density effect of the various ions has been calculated. The d - c plots for the Ph_4As^+ and the $[PNP]^+$ salts are distinctly curved.

The V_ϕ - $c^{1/2}$ plots for the R_4N^+ salts, except for Bu_4NBPh_4 and Bu_4NBBu_4 , are also linear. The curvature of the plot for Bu_4NBBu_4 prevents the partial molar volume of this salt from being determined by extrapolation. The ionic contributions to the partial molar volumes have been determined on the basis of the additivity rule, using the value $V_\phi(Bu_4N^+) = 269(1) \text{ cm}^3 \text{ mol}^{-1}$ determined by the correspondence method. The V_ϕ - $c^{1/2}$ plots for the Ph_4As^+ salts, the $[PNP]^+$ salts and Bu_4NBPh_4 are slightly curved, suggesting the volume change for association to be approx. $5 \text{ cm}^3 \text{ mol}^{-1}$.

Results of volumetric studies do not seem to be conclusive with regard to the possible presence of larger species such as triple ions, quadrupoles or larger aggregates in solutions which contain large amounts of free ions and ion pairs.

In a previous paper in this series we reported a study of the molar conductivity, Λ , of several onium salts in dichloromethane in the 10^{-3} – 10^{-1} M concentration range.¹ As observed in similar studies in solvents of low dielectric constant ($\epsilon < 12$),^{2–5} several irregularities in the Λ - $c^{1/2}$ plots were detected. Depending upon the structure and the size of the cation and the anion, a minimum and a maximum or only an inflection was observed.¹

Neglecting these minor features in the Λ - $c^{1/2}$ plots, the molar conductivities were found to be almost constant over a considerable concentration range, viz. $\sim 5 \times 10^{-3}$ – $\sim 2 \times 10^{-1}$ M. The mo-

lar conductivities of electrolytes in solvents of low ϵ are difficult to estimate, even when the association constant in very dilute solutions, K_A , the molar conductivity at infinite dilution, Λ° , and other relevant parameters are available.⁶ The constancy of Λ , however, can only be explained by an increase in the fraction of conducting species with increasing concentration.

Two views have been forwarded to account for the high Λ of concentrated salt solutions in solvents of low ϵ . According to Fuoss and Kraus,^{3,4} conducting ions are formed from non-conducting ion pairs;⁷ for a comprehensive survey see Ref. 8. The results of numerous conductivity^{3,4,9–12} and

spectroscopic studies¹³ have been considered as evidence in favour of this hypothesis. The alternative explanation is based upon the fact that ϵ of this solvent class is highly dependent upon the salt concentration.^{1,14-16} Since K_A is a function of ϵ ,¹⁷ the high Λ may rather be due to a larger fraction of dissociated ions than in dilute solutions.

This problem can probably not be illuminated by further conductivity studies, and alternative experimental techniques must be looked for. Studies of apparent and partial molar volumes have proved to be important for obtaining an improved description of electrolytes.¹⁸⁻²⁶ Since no detailed studies of the volumetric behaviour of salts in weakly dissociating media are available, it was of interest to see whether this approach is equally valuable. In this paper we report on the concentration dependence of densities and apparent molar volumes of several onium salts in dichloromethane at 25.00 °C. It was of particular interest to examine whether the irregularities in the Λ - $c^{1/2}$ plots could be detected by this technique. The measurements were performed in the same concentration range as in the conductivity study, viz. $\sim 1 \times 10^{-3}$ – $\sim 2 \times 10^{-1}$ M,¹ whenever possible.

Experimental

Materials. Tetrabutylammonium tetrabutylborate, Bu₄NBBu₄ (a commercial sample from Ventron, Karlsruhe), was dissolved in acetone; the solution was filtered and the salt was precipitated slowly by addition of water.²⁷ This procedure was repeated twice. The salt was dried in vacuum at ~ 50 °C to constant weight and was finally recrystallized twice from ethyl acetate/hexane. The other onium salts and dichloromethane were purified as described previously.^{6,28}

Measurements. All solutions were made up by weighing. The salts were generally studied up to ~ 0.2 M, exceptions being Ph₄AsClO₄, Et₄NClO₄ and Bu₄NBPh₄ with solubilities of 1.1×10^{-2} M, 6.5×10^{-2} M and 9.4×10^{-2} M, respectively, at 25.0 °C. These compounds were studied up to only ~ 80 % of the saturation concentrations to ensure solution homogeneity. In order to check the results for Bu₄NBBu₄, a different batch from Ventron was purified and all measurements repeated.

The densities of the solutions were determined using a Paar DMA 601 density meter with a reproducibility better than 3×10^{-6} g cm⁻³. The apparent molar volumes, V_ϕ , were calculated according to eqn. (1), where d_o and d represent the

$$V_\phi = \frac{1000(d_o - d)}{m d_o d} + \frac{M_2}{d} \quad (1)$$

densities of the solvent and the solution, respectively, M_2 is the molecular weight of the solute and m is the molality of the solution. For concentrations above ~ 0.02 M the apparent molar volumes were generally determined with an accuracy of from ~ 0.2 cm³ mol⁻¹ to ~ 1 cm³ mol⁻¹. In more dilute solutions the uncertainty in V_ϕ was considerably larger, particularly for some of the Ph₄As⁺ salts, all the [PNP]⁺ salts and Et₄NClO₄; this was due to the small difference between d_o and d for these salts [cf. eqn. (1)]. Only the salts with the steepest density-concentration plots could be studied down to ~ 0.003 M, when a maximal uncertainty in V_ϕ of ~ 3 cm³ mol⁻¹ was considered acceptable.

The temperature during the density studies was 25.00 °C, controlled to better than 0.01 °C with a Hewlett-Packard quartz thermometer.

Results

The density of the solutions. Fig. 1 shows the density of the solutions of the R₄N⁺ salts as a function of the concentration. By coincidence, the d - c plots for Bu₄NBBu₄ and Dec₄NBr are superimposable. The density of aqueous solutions of salts can generally be determined with high accuracy by means of the Root equation [eqn. (2)].²⁹ S_v^\dagger is the experimental slope in the Masson

$$d = d_o + 10^{-3}(M_2 - d_o V_\phi^\circ)c - 10^{-3} S_v^\dagger d_o c^{3/2} \quad (2)$$

equation,³⁰ i.e. the relationship between V_ϕ and $c^{1/2}$ [eqn. (3)]. V_ϕ° in eqns. (2) and (3) is the partial

$$V_\phi = V_\phi^\circ + S_v^\dagger c^{1/2} \quad (3)$$

molar volume at infinite dilution. An alternative density equation, eqn. (4), may be derived from

$$d = d_o + 10^{-3}(M_2 - d_o V_\phi^\circ)c - 10^{-3} S_v^\dagger d_o c^{3/2} - 10^{-3} b_v d_o c^2 \quad (4)$$

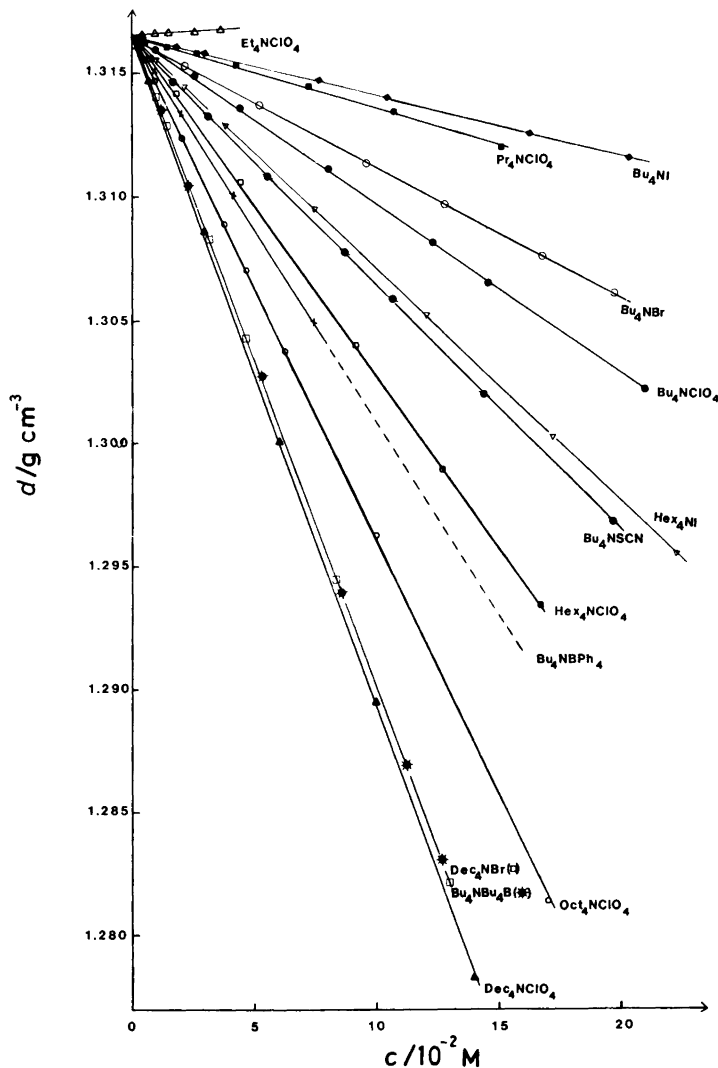


Fig. 1. Density-concentration plots for solutions of R_4N^+ salts in dichloromethane at 25.00°C.

the Redlich-Meyer equation [eqn. (5)]¹⁹, in which

$$V_\Phi = V_\Phi^\circ + S_v c^{1/2} + b_v c \quad (5)$$

S_v is the theoretical slope calculated using the Debye-Hückel limiting law, while b_v serves as a measure of the deviation from this law.

The excellent linearity of the d - c plots for all R_4N^+ salts (Fig. 1) shows that the densities of solutions of this class of salts in dichloromethane are satisfactorily described by the first two terms in eqns. (2) and (4). For convenience one may substitute $10^{-3}(M_2 - d_0 V_\Phi^\circ)$ in these two eqns. by

k_d , leading to eqn. (6). S_v^\dagger in eqn. (2) is distinctly

$$d = d_0 + k_d c \quad (6)$$

positive for all the salts studied, viz. from ~ 10 to $\sim 20 \text{ cm}^3 \text{ mol}^{-3/2}$ [cf. the plots according to eqn. (3) described below]. The anticipated curvature, i.e. decreasing slope with increasing concentration due to the last term in eqn. (2), apparently cannot be detected by our procedure for R_4N^+ salts at concentrations up to $\sim 0.2 \text{ M}$.

Fig. 2 shows a plot of the slopes in Fig. 1, k_d , versus the number of carbon atoms in the R_4N^+

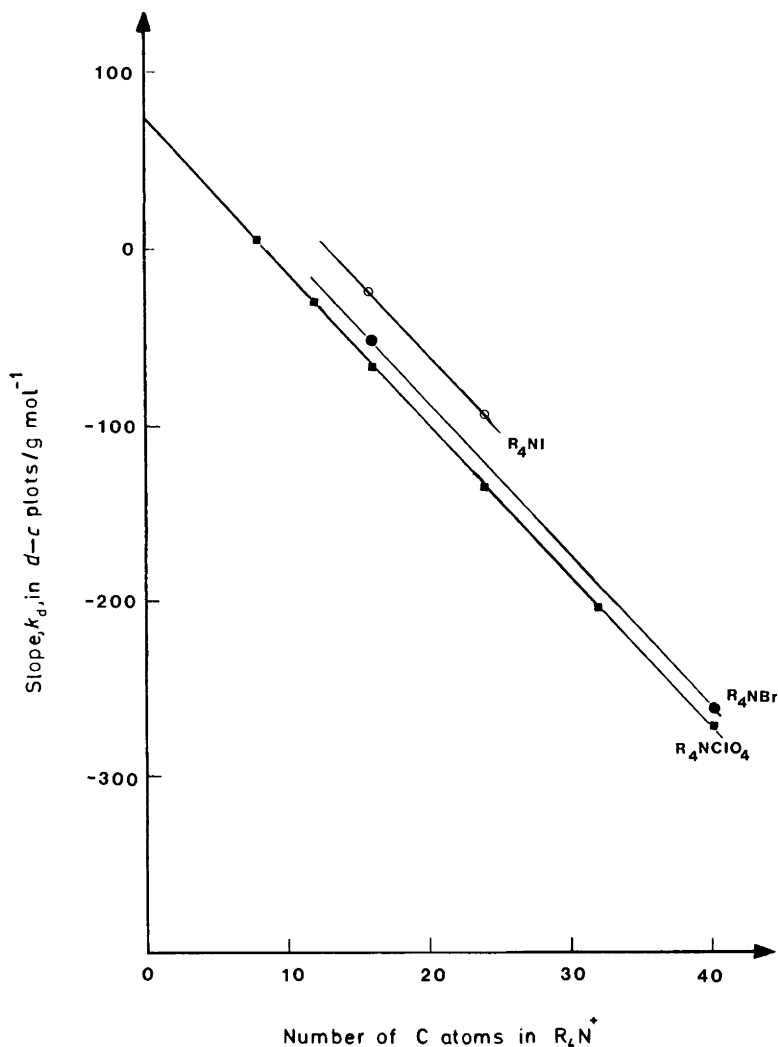


Fig. 2. Slopes of the density-concentration plots, k_d , for R_4NClO_4 , R_4NI and R_4NBr vs. the number of carbon atoms in the R_4N^+ cations.

cations. Although only two iodides and two bromides were examined, the plot in Fig. 2 indicates that the effect of the cation and the anion upon the density of the solutions is additive. By assuming equal contributions from Bu_4N^+ and Bu_4B^- to the density of solutions of Bu_4NBBu_4 [eqn. (7)] the effect of the various ions upon the

$$k_d(Bu_4N^+) = k_d(Bu_4B^-) = \frac{1}{2} k_d(Bu_4NBBu_4) \quad (7)$$

density of the salt solutions could be calculated using the additivity rule. The results are listed in Table 1. The validity of the assumption was tested for Hex_4NI and Bu_4NBr : The calculated slopes

for these salts were $-0.093(1)$ and $-0.060(1)$ $g\ cm^{-3}\ M^{-1}$, respectively, which was, indeed, observed experimentally.

Fig. 3 shows the $d-c$ plots for the Ph_4As^+ and $[PNP]^+$ salts (the scales in Figs. 1 and 3 are identical). Characteristic for these salts, particularly the $[PNP]^+$ salts, is a distinct deviation from linearity, i.e. decreasing slope with increasing concentration. The plots for the Ph_4As^+ salts are almost linear for concentrations above $\sim 0.03\ M$ but no abrupt change in the slopes at some particular concentration is evident. From the fairly linear part of the plots in Fig. 3, the ionic contributions of Ph_4As^+ , Cl^- and $[PNP]^+$ could be esti-

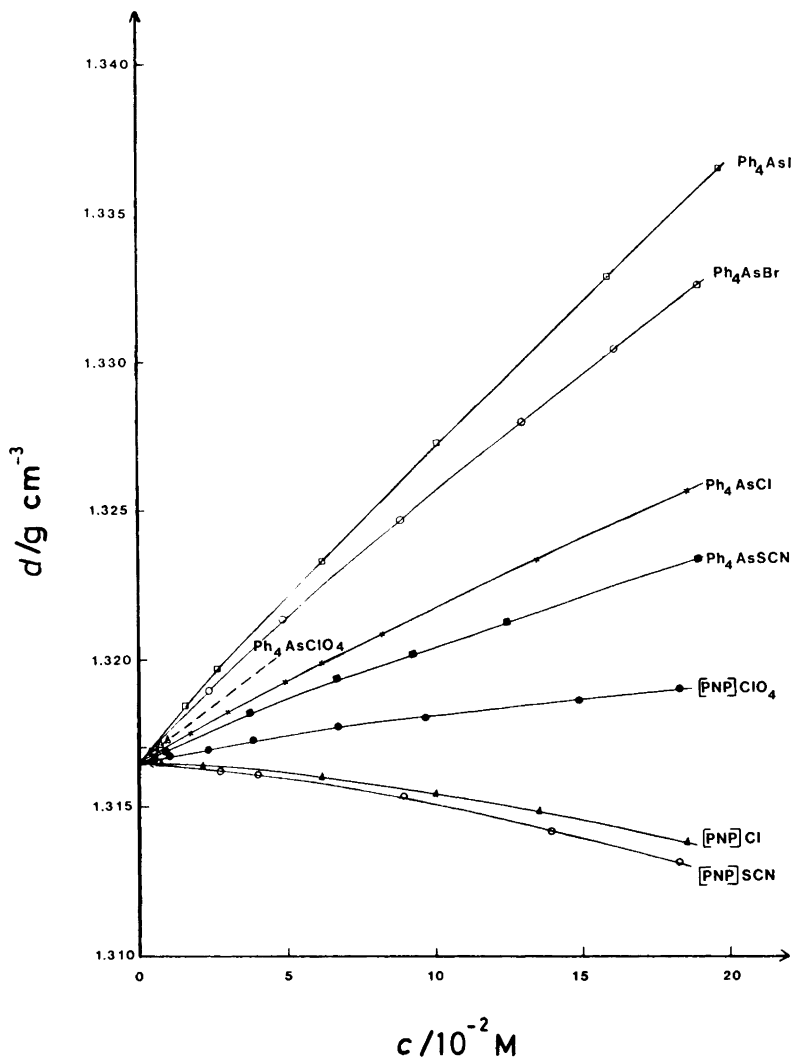


Fig. 3. Density-concentration plots for Ph_4As^+ and $[\text{PNP}]^+$ salts in dichloromethane.

mated with some certainty. The results are listed in Table 1 together with the various values of k_d arrived at from the analysis for the R_4N^+ salts. The effect of the Ph_4As^+ ion is seen to be negligible, while the Ph_4B^+ ion causes a small density reduction. This difference is as anticipated, taking into account the similar van der Waals volumes of the two ions.³¹ The $[\text{PNP}]^+$ ion causes a density reduction comparable to that of the Et_4N^+ ion. In this respect the $[\text{PNP}]^+$ ion resembles a number of uncharged aromatic compounds.³²

Apparent and partial molar volumes. Apparent molar volumes, V_ϕ , are generally extrapolated to infinite dilution using the Redlich-Meyer equation [eqn. (5)].¹⁹ The Debye-Hückel limiting law, however, cannot be used for salts dissolved in dichloromethane.¹ Furthermore, S_v in this solvent cannot be calculated since this requires a knowledge of the pressure dependence of ϵ which is not presently available. One thus has to apply Masson's equation [eqn. (3)], which according to Choi and Criss³³ may result in an error in V_ϕ° of from 2 to 3 $\text{cm}^3\text{ mol}^{-1}$.

Table 1. The ionic contributions to the slopes, k_d , in the density-contribution plots according to eqn. (6).

Ion	$k_d/g\text{ cm}^{-3}\text{ M}^{-1}$
Et_4N^+	-0.058(3)
Pr_4N^+	-0.096(2)
Bu_4N^+	-0.132(1) ^a
Hex_4N^+	-0.202(1)
Oct_4N^+	-0.268(1)
Dec_4N^+	-0.336(1)
Ph_4As^+	-0.005(5) ^b
[PNP] ⁺	ca. -0.060 ^b
Cl^-	0.050(5) ^c
Br^-	0.072(1)
I^-	0.109(1)
SCN^-	0.034(1)
ClO_4^-	0.065(1)
Bu_4B^-	-0.132(1) ^a
Ph_4B^-	-0.023(1)

^a $k_d(\text{Bu}_4\text{N}^+) = k_d(\text{Bu}_4\text{B}^-) = 1/2 k_d(\text{Bu}_4\text{NBBu}_4)$. ^bBased upon the linear part of the d - c plots in the 0.05–0.2 M concentration range. ^cBased only upon Ph_4AsCl .

The V_ϕ - $c^{1/2}$ plots for the R_4N^+ perchlorates are shown in Fig. 4, while those for the remaining R_4N^+ salts (except Bu_4NBBu_4 and Bu_4NBPh_4) are shown in Fig. 5. In the case of $\text{Oct}_4\text{NClO}_4$, Dec_4NBr and $\text{Dec}_4\text{NClO}_4$, i.e. the salts of highest molecular weight and with steepest d - c plots, the linearity of the V_ϕ - $c^{1/2}$ plots could be verified experimentally down to ~ 0.003 M. The slopes S_v^+ , are independent of the anion but range from $\sim 12\text{ cm}^3\text{ l}^{1/2}\text{ mol}^{-3/2}$ for Et_4NClO_4 and Pr_4NClO_4 to $\sim 20\text{ cm}^3\text{ l}^{1/2}\text{ mol}^{-3/2}$ for the perchlorates of the larger cations. Slopes of a similar order of magnitude have been observed in volumetric studies of R_4N^+ salts in methanol,³⁴ ethanol³⁵ and N,N -dimethylformamide.³⁵ The significantly smaller slopes of V_ϕ - $c^{1/2}$ plots for R_4N^+ salts in water³⁶ have been proposed to be due to the higher ϵ of this solvent.³⁷ The extrapolated values at infinite dilution in dichloromethane, V_ϕ^∞ , are listed in Table 2. Fig. 6 shows a plot of $V_\phi^\infty(\text{R}_4\text{NClO}_4)$ versus the number of carbon atoms in the cations. The plot is perfectly linear with a slope of $17.2(1)\text{ cm}^3\text{ mol}^{-1}$; this is the increment usually observed

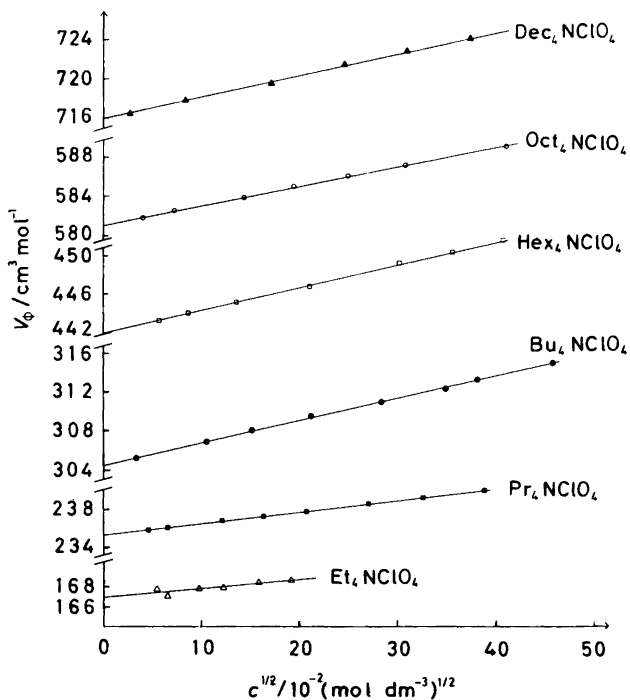


Fig. 4. The apparent molar volume, V_ϕ , of R_4NClO_4 in dichloromethane vs. the square-root of the concentration, $c^{1/2}$.

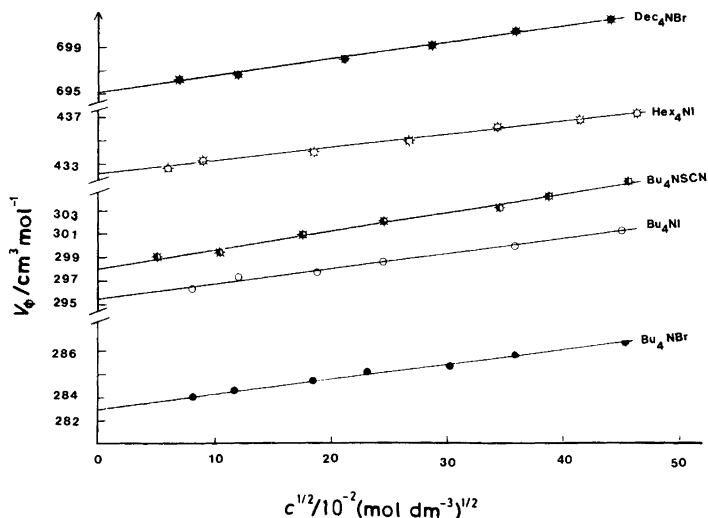


Fig. 5. V_{ϕ} - $c^{1/2}$ plots for Dec₄NBr, Hex₄NI, Bu₄NSCN, Bu₄NI and Bu₄NBr.

for a CH₂ group in non-aqueous solvents.^{26,38,39}

The calculated values of $V_{\phi}(\text{Bu}_4\text{NBPh}_4)$ for concentrations below $\sim 8 \times 10^{-3}$ M indicated a

Table 2. Partial molar volumes, V_{ϕ}° , of electrolytes in dichloromethane at 25.00 °C.

Electrolyte	$V_{\phi}^{\circ} / \text{cm}^3 \text{ mol}^{-1}$
Et ₄ NCIO ₄	167
Pr ₄ NCIO ₄	235.5
Bu ₄ NCIO ₄	304.5
Hex ₄ NCIO ₄	442
Oct ₄ NCIO ₄	581
Dec ₄ NCIO ₄	716
Bu ₄ NBr	283
Bu ₄ NI	295
Bu ₄ NBBu ₄	538 ^b
Bu ₄ NSCN	297
Bu ₄ NBPh ₄	532
Hex ₄ NI	432
Dec ₄ NBr	692
Ph ₄ AsCl	271
Ph ₄ AsBr	277
Ph ₄ AsI	292
Ph ₄ AsSCN	294
Ph ₄ AsCIO ₄	303
[PNP]Cl	436
[PNP]SCN	453
[PNP]CIO ₄	464

^aMaximum uncertainty is 2 cm³ mol⁻¹ for R₄N⁺ salts and 5 cm³ mol⁻¹ for Ph₄As⁺ and [PNP]⁺ salts (see text). ^bEstimated to be equal to $2 \times V_{\phi}^{\circ}(\text{Bu}_4\text{N}^+)$ (see text).

curvature of the V_{ϕ} - $c^{1/2}$ plot. The limits of error, however, prevented a definite conclusion to be reached as to whether this curvature was real or not. The larger negative slope in the d - c plot for Bu₄NBBu₄ (Fig. 1) allowed V_{ϕ} to be determined with some certainty down to $\sim 3 \times 10^{-3}$ M. Although the limits of error in V_{ϕ} at low concentrations were considerable, the calculated values of $V_{\phi}(\text{Bu}_4\text{NBBu}_4)$ gave a V_{ϕ} - $c^{1/2}$ plot which was distinctly curved. For concentrations above $\sim 2 \times 10^{-2}$ M the plot was linear with a slope as for the other Bu₄N⁺ salts. The linear part of the V_{ϕ} - $c^{1/2}$ plot indicated a V_{ϕ}° value for Bu₄NBBu₄ of

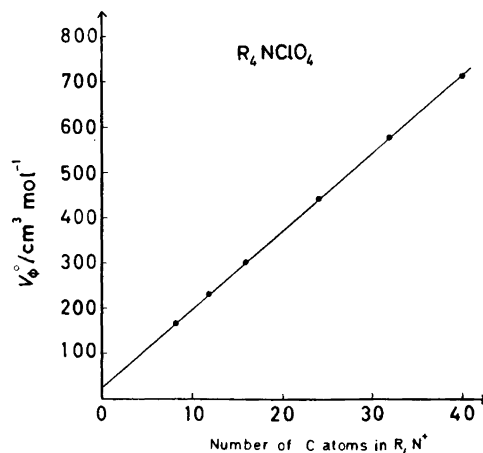


Fig. 6. The partial molar volume, V_{ϕ}° , of R₄NCIO₄ in dichloromethane vs. the number of carbon atoms in the R₄N⁺ cations.

$\sim 560 \text{ cm}^3 \text{ mol}^{-1}$. The curvature of the plot, however, suggested this value to be too large. Apparently, V_ϕ° for Bu_4NBBu_4 and Bu_4NBPh_4 in dichloromethane cannot be determined with certainty by extrapolation to infinite dilution according to Masson's equation [eqn. (3)].

Similar difficulties with a probable curvature of the $V_\phi-c^{1/2}$ plots at low concentrations were encountered for the Ph_4As^+ and $[\text{PNP}]^+$ salts. As for Bu_4NBBu_4 and Bu_4NBPh_4 , as described above, the plots were linear for concentrations above $\sim 2 \times 10^{-2} \text{ M}$ with slopes, S_v° , of $20 \text{ cm}^3 \text{ l}^{1/2} \text{ mol}^{-3/2}$ for the Ph_4As^+ salts and slightly less, $\sim 15 \text{ cm}^3 \text{ l}^{1/2} \text{ mol}^{-3/2}$, for the $[\text{PNP}]^+$ salts. For lower concentrations, the apparent molar volumes, V_ϕ , were repeatedly found to be smaller than expected on the basis of the linear part of the $V_\phi-c^{1/2}$ plots.

The $d-c$ plots for $[\text{PNP}]\text{Cl}$ and $[\text{PNP}]\text{SCN}$ (Fig. 3) show that the densities of dilute solutions are almost equal to the density of the pure solvent. V_ϕ° for $[\text{PNP}]\text{Cl}$ and $[\text{PNP}]\text{SCN}$, both salts of high molecular weight, may therefore be approximated by the last term in eqn. (1), M_2/d_0 . The values of V_ϕ° arrived at in this way were generally about $5 \text{ cm}^3 \text{ mol}^{-1}$ smaller than the extrapolated partial molar volumes. This reduction in V_ϕ° of $\sim 5 \text{ cm}^3 \text{ mol}^{-1}$ was then assumed to apply for all Ph_4As^+ and $[\text{PNP}]^+$ salts, leading to the $V_\phi-c^{1/2}$ plots shown in Figs. 7 and 8. Numerous density studies of solutions of Ph_4AsI and

Ph_4AsBr , the salts with the steepest $d-c$ plots, seemed to confirm this assumption. The partial molar volumes of the Ph_4As^+ and the $[\text{PNP}]^+$ salts arrived at in this way are listed in Table 2 together with V_ϕ° for the R_4N^+ salts. It is to be emphasized that the uncertainty in $V_\phi^\circ(\text{Ph}_4\text{AsX})$ and $V_\phi^\circ([\text{PNP}]\text{X})$ may amount to at least $3-4 \text{ cm}^3 \text{ mol}^{-1}$.

Fig. 9 shows the $V_\phi-c^{1/2}$ plots for Bu_4NBPh_4 and Bu_4NBBu_4 . As outlined above for the Ph_4As^+ and $[\text{PNP}]^+$ salts, $V_\phi^\circ(\text{Bu}_4\text{NBPh}_4)$ was assumed to be $5 \text{ cm}^3 \text{ mol}^{-1}$ smaller than the extrapolated value. The value of $V_\phi^\circ(\text{Bu}_4\text{NBBu}_4)$, $538(2) \text{ cm}^3 \text{ mol}^{-1}$, was based upon the assumption of equal contributions from anion and cation and using a V_ϕ° value for Bu_4N^+ of $269(1) \text{ cm}^3 \text{ mol}^{-1}$ determined by indirect methods (see Discussion). This value of $V_\phi^\circ(\text{Bu}_4\text{NBBu}_4)$ is no less than $\sim 22 \text{ cm}^3 \text{ mol}^{-1}$ smaller than that obtained by extrapolation of the $V_\phi-c^{1/2}$ plot for concentrations above $2 \times 10^{-2} \text{ M}$. Although the two values of $V_\phi^\circ(\text{Bu}_4\text{NBBu}_4)$ are subject to some uncertainty, the discrepancy appears real and may serve as a confirmation of the exceptional curvature of the $V_\phi-c^{1/2}$ plot for this salt.

Discussion

When an ionic compound, A^+B^- , is dissolved in a solvent of low ϵ , such as dichloromethane, a number of species may be present in the solution:

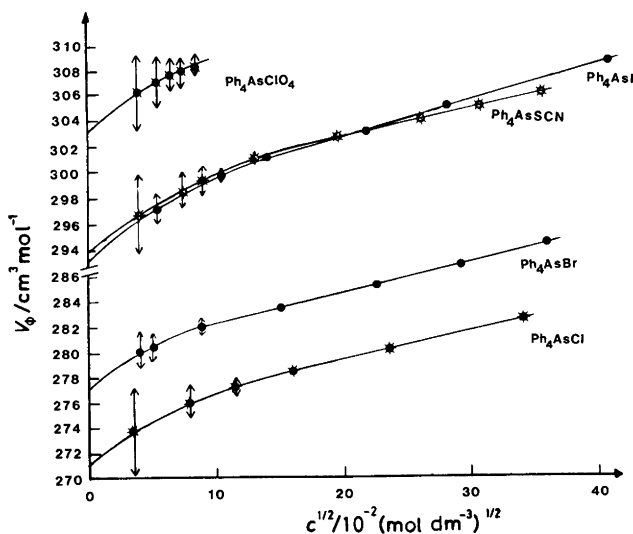
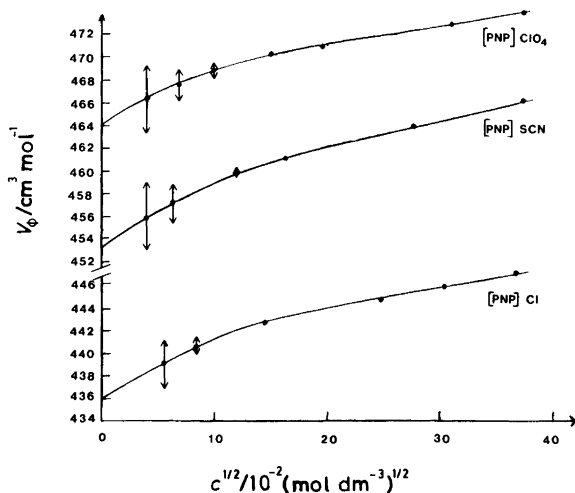


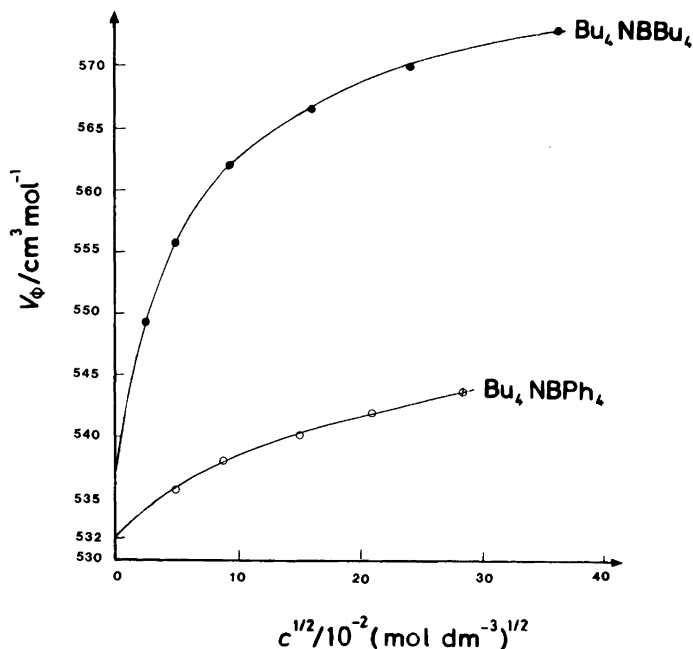
Fig. 7. $V_\phi-c^{1/2}$ plots for Ph_4As^+ salts.

Fig. 8. V_ϕ - $c^{1/2}$ plots for [PNP]⁺ salts.

Free and solvated ions, A^+ and B^- , contact ion pairs, $[AB]$, various types of solvent-separated ion pairs, $[A|B]$, triple ions, $[A_2B]^+$ and $[AB_2]^-$, quadrupoles, $[AB]_2$, and higher aggregates, $[AB]_n$. The possible presence of all these species, together with the variations in their concentrations, has to be taken into account when the results described here are considered.

Unfortunately, no relationships of any proven

reliability are available which allow the concentrations of the various species to be calculated. In the recent conductivity study of several onium salts in dichloromethane, it was found that the degree of dissociation, α , given by Λ/Λ° , is almost constant in the concentration range $\sim 5 \times 10^{-3} - \sim 2 \times 10^{-1}$ M. α was found to be ~ 0.11 for most R_4N^+ salts (~ 0.25 for Bu_4NBBu_4 and Bu_4NBPh_4),³² ~ 0.32 for the Ph_4As^+ salts and

Fig. 9. V_ϕ - $c^{1/2}$ plots for Bu_4NBBu_4 and Bu_4NBPh_4 .

~ 0.40 for the $[\text{PNP}]^+$ salts. This constancy is less pronounced for Bu_4NBPh_4 , Bu_4NBBu_4 , $\text{Oct}_4\text{NClO}_4$, $\text{Dec}_4\text{NClO}_4$ and the $[\text{PNP}]^+$ salts, i.e. the salts for which no minimum or maximum but only an inflection is seen in the $\Lambda-c^{1/2}$ plots.

For concentrations well below the minimum (inflection) in $\Lambda-c^{1/2}$ plots (in dichloromethane, at $\sim 3 \times 10^{-2} \text{ M}$)¹ it is reasonable to assume that only free ions and ion pairs are present in the solutions.^{3,4} The constancy of α therefore allows one to consider the slopes of the $d-c$ plots of Fig. 1 to be those for these species only [eqn. (8)].

$$k_d = \alpha k_d (\text{free ions}) + (1-\alpha)k_d (\text{ion pairs}) \quad (8)$$

For concentrations around 10^{-3} M , where α is known to vary considerably,¹ no curvature of the $d-c$ plots could be detected, even when greatly expanded scales were employed. Furthermore, no deviation from linearity could be observed for concentrated (10^{-2} – 10^{-1} M) solutions of the R_4N^+ salts, including Bu_4NBBu_4 , Bu_4NBPh_4 and the salts of the larger R_4N^+ cations for which α is known to be dependent upon the concentration.¹ Apparently, free ions and ion pairs from R_4N^+ salts in dichloromethane influence the density of the solutions to the same extent. The validity of the additivity law for the ionic contributions to the density of the solutions (Fig. 2 and Table 1) favours this conclusion. The excellent linearity of the $d-c$ plots of Fig. 1 may therefore be considered as evidence against the presence of species other than free ions and ion pairs for concentrations of R_4N^+ salts in dichloromethane up to $\sim 2 \times 10^{-1} \text{ M}$. However, since the effects of free ions and ion pairs upon the density of the solutions are essentially equal, it is reasonable to believe that the effect of triple ions or larger aggregates will not be significantly different from the average effect of an ion pair and the free ions. The results of density studies, despite the extreme accuracy with which such measurements are performed, are therefore not conclusive with regard to the possible presence of other species in the solutions. It is notable, however, that none of the features of the $\Lambda-c^{1/2}$ plots, including the presence of a minimum and a maximum or an inflection,¹ i.e. those features which are the basis for the triple ion assumption,^{3,4} can be recognized in the $d-c$ plots for the R_4N^+ salts.

The non-linearity of the $d-c$ plots for the Ph_4As^+ and $[\text{PNP}]^+$ salts (Fig. 3) may have its ori-

gin in the structure of the ion pairs. A Bjerrum treatment¹⁷ of conductivity data for dichloromethane has revealed that the ion pairs from salts of these two cations can be considered as solvent-separated ion pairs in very dilute solutions.¹ Based upon the expression for the ion atmosphere,¹ one may conclude that as the concentration increases, the solvent-separated ion pairs will gradually be transformed into ion pairs of the contact type. The same conclusion has been arrived at in a recent study on the dielectric properties of solutions of Ph_4AsI and $[\text{PNP}]\text{ClO}_4$ in dichloromethane.¹⁶ Presumably, ion pairs of small charge separation cause a more pronounced disruption of the solvent structure.

As outlined above for the slopes of the $d-c$ plots, one may consider the apparent molar volumes, V_ϕ , as average volumes for the dissociated ions and the ion pairs [eqn. (9)]. The excellent

$$V_\phi = \alpha V_\phi (\text{free ions}) + (1-\alpha)V_\phi (\text{ion pairs}) \quad (9)$$

linearity of the $V_\phi-c^{1/2}$ plots in Figs. 4 and 5 indicates that V_ϕ for ion pairs from most R_4N^+ salts is equal to the sum of the volumes of the free ions. The linearity of the plot of $V_\phi^\circ(\text{R}_4\text{NClO}_4)$ versus the number of carbon atoms in the cations, C_N (Fig. 6), seems to substantiate this conclusion. However, a plot such as that shown in Fig. 6 will also be observed if the volume change that accompanies the ion pair formation between R_4N^+ and ClO_4^- ions, ΔV_ϕ° , is non-zero but independent of the size of the cation (eqn. (10)). V_ϕ° is a constant which, according to

$$V_\phi^\circ = V_\phi^\circ + \Delta V_\phi^\circ + 17.2 C_N \quad (10)$$

the extrapolation method of Jolicoeur and co-workers,²³ represents $V_\phi^\circ(\text{ClO}_4^-)$. The volume change for association, ΔV° , is positive for most liquids.⁴⁰ This is the expected behaviour, since when ions associate to form a neutral pair there is a release of the solvent molecules which had been oriented by the free ions. Since R_4N^+ and ClO_4^- ions are essentially unsolvated in dichloromethane,^{6,26} it is reasonable that the volume change that accompanies ion pair formation from this class of ions in dichloromethane is small. A negligible ΔV_ϕ° for all R_4N^+ perchlorates in this solvent can thus be the cause of the linearity of the plot shown in Fig. 6.

The slopes of the $V_\phi-c^{1/2}$ plots for the R_4N^+ per-

chlorates (Fig. 4) increase with the size of the cation. Since the ion pairs from the salts of the larger cations start to associate to larger aggregates at lower concentrations than for Et_4NClO_4 and Pr_4NClO_4 ,¹⁶ the contribution of the volumes of these species to the measured apparent molar volumes at lower concentrations will increase with the increase in the size of the cation. If one assumes that the volume change occurring upon association of two ion pairs to one quadrupole is positive, the different slopes in the plots of Fig. 4 can be accounted for.

The slight, but distinct non-linearity of the $V_\phi\text{-}c^{1/2}$ plots for the Ph_4As^+ salts (Fig. 7) the $[\text{PNP}]^+$ salts (Fig. 8) and Bu_4NBPh_4 (Fig. 9) can probably be explained by the fairly open structure of ions containing several phenyl groups and by the ability of these groups to interact with dichloromethane. Upon association to ion pairs, particularly contact ion pairs, the attendant release of solvent molecules will cause the volume change to be positive. The volume change, which is $\sim 5 \text{ cm}^3 \text{ mol}^{-1}$ for salts of these types of ions in dichloromethane, may partly or mainly be due to the formation of solvent-separated ion pairs from free ions or due to the formation of contact ion pairs from solvent-separated ion pairs.

The $V_\phi\text{-}c^{1/2}$ plot for Bu_4NBBu_4 (Fig. 9) indicates that this salt behaves exceptionally in dichloromethane. In a recent study of conductivity in dichloromethane it was found that the association constant, K_A , for this salt is significantly smaller than that observed for all other Bu_4N^+ salts.³² The calculated Bjerrum distance, a ,¹⁷ $11.0(10) \text{ \AA}$, is distinctly larger than the sum of the radii of Bu_4N^+ and Bu_4B^- , 7.8 \AA . A distance of closest approach of this magnitude indicates that the ion pairs from Bu_4NBBu_4 in very dilute solutions in dichloromethane may be considered as solvent-separated ion pairs. In this respect, Bu_4NBBu_4 differs from all other R_4N^+ salts so far studied conductometrically in this solvent.¹ Presumably, this is due to the fact that in this salt both the cation and the anion are structurally flexible species in which the alkyl groups efficiently screen the ionic charges. As the concentration increases, conformational reorganization of the alkyl groups will take place leading continuously to more compact ions and to more compact ion pairs. Gradually, less space will be available for the solvent molecules between the alkyl

groups in the ions and between the ions in the ion pairs.

The ionic contributions to V_ϕ° . Since ΔV_ϕ° for ion pair formation from dissociated R_4N^+ salts is negligible, the partial molar volumes (Table 1) may be considered to be equal to V_ϕ° for completely dissociated salts. These values may therefore be separated into their component ionic contributions. For this purpose, a reliable reference value for the partial molar volume of a particular ion is desirable.⁴¹ Unfortunately, such a reference value for $V_\phi^\circ(\text{Bu}_4\text{N}^+)$, equal to $1/2 V_\phi^\circ(\text{Bu}_4\text{NBBu}_4)$,²¹ cannot be obtained due to the distinct non-linearity of the $V_\phi\text{-}c^{1/2}$ plot for Bu_4NBBu_4 . Millero's method⁴¹ for the separation of ionic contributions to partial molar volumes is based upon volumetric studies of $\text{Ph}_4\text{AsBPh}_4$ and the assumption that $V_\phi^\circ(\text{Ph}_4\text{As}^+) = V_\phi^\circ(\text{Ph}_4\text{B}^-)$. However, the limited solubility of $\text{Ph}_4\text{AsBPh}_4$ in dichloromethane at 25.00°C , viz. $\sim 2.4 \times 10^{-4} \text{ M}$, prevents determination of V_ϕ° for this salt.

Owing to these difficulties one is left with indirect methods for the determination of the ionic contributions to $V_\phi^\circ(\text{salt})$. Of the various techniques which have been proposed over the years, the ultrasonic vibration potential (u.v.p.) method^{42,43} is presumably the most reliable one. Critical remarks to this method, however, have been made by Panckhurst²⁰ and by Krumgalz.²⁶ Since this method was not available, various extra-thermodynamic procedures had to be attempted for the evaluation of $V_\phi^\circ(\text{ion})$.

The correspondence method due to Criss and Cobble⁴⁴ is based upon the following relation [eqn. (11)]:

$$V_\phi^\circ(\text{ion})_{s_1} = a V_\phi^\circ(\text{ion})_{s_2} + b \quad (11)$$

S_1 and S_2 refer to the two different solvents, 1 and 2, while a and b are constants obtained by least-squares best fit of the $V_\phi^\circ(\text{ion})$ values for the two solvents. From the partial molar volumes in dichloromethane and in acetonitrile,⁴² $V_\phi^\circ(\text{Bu}_4\text{N}^+)$ was found to be $269.1 \text{ cm}^3 \text{ mol}^{-1}$. A similar analysis of the data for dichloromethane and for propylene carbonate⁴³ gave a value of $269.4 \text{ cm}^3 \text{ mol}^{-1}$. As a control, the V_ϕ° values for all R_4N^+ ions in acetonitrile and in propylene carbonate taken from the compilation by Zana and Yeager^{42,43} were found to obey eqn. (11) to within

Table 3. Partial molar volumes of ions in dichloromethane at 25.00 °C.

Ion	$V_{\Phi}^{\circ}/\text{cm}^3 \text{ mol}^{-1}$
Et_4N^+	130
Pr_4N^+	199
Bu_4N^+	269
Hex_4N^+	405
Oct_4N^+	544
Dec_4N^+	680
Ph_4As^+	266
$[\text{PNP}]^+$	427
Cl^-	6
Br^-	12
I^-	26
SCN^-	28
ClO_4^-	37
BBu_4	269
BPh_4	264

$1 \text{ cm}^3 \text{ mol}^{-1}$. The value of $269 \text{ cm}^3 \text{ mol}^{-1}$ was therefore selected for $V_{\Phi}^{\circ}(\text{Bu}_4\text{N}^+)$ in dichloromethane, and V_{Φ}° for other ions was calculated according to the additivity rule (Table 3). The reasonable values for $V_{\Phi}^{\circ}(\text{Ph}_4\text{As}^+)$, $266(4) \text{ cm}^3 \text{ mol}^{-1}$, and $V_{\Phi}^{\circ}(\text{Ph}_4\text{B}^-)$, $264(4) \text{ cm}^3 \text{ mol}^{-1}$, obtained in this way indicate that the suggested reference value for $V_{\Phi}^{\circ}(\text{Bu}_4\text{N}^+)$ is a reliable one. Mukerjee's method²² is based upon the assumption that $V_{\Phi}^{\circ}(\text{ion})$ depends upon the ionic radius, r .⁸ A plot of the calculated partial molar volumes of the halide ions versus r^3 is, indeed, found to be linear. This indicates once more that the selected reference value for $V_{\Phi}^{\circ}(\text{Bu}_4\text{N}^+)$ is reasonable. This agreement between the results obtained by the correspondence method⁴⁴ and by Mukerjee's method,²² however, is not entirely surprising, since the two methods for separating $V_{\Phi}^{\circ}(\text{salt})$ into the ionic contributions are essentially the same.

The extrapolation method, proposed by Conway and co-workers^{45,46} some 20 years ago and revived by Krumgalz²⁶ in recent years, was also examined. In this method, $V_{\Phi}^{\circ}(\text{X}^-)$ is obtained from a plot of $V_{\Phi}^{\circ}(\text{R}_4\text{NX})$ versus the molecular weight of the cation by extrapolation to zero molecular weight. This method applied to the R_4N^+ perchlorates led to a $V_{\Phi}^{\circ}(\text{ClO}_4^-)$ value of only $6 \text{ cm}^3 \text{ mol}^{-1}$. This unreasonably small value seems to confirm the serious doubts expressed by Conway²¹ and by Zana⁴⁷ with regard to the reliability

of the extrapolation method for organic solvents. Jolicoeur and co-workers²³ have modified this method by plotting $V_{\Phi}^{\circ}(\text{R}_4\text{NX})$ versus the number of carbon atoms in the R_4N^+ cations [cf. eqn. (10)]. From the plot in Fig. 6, however, a value of $V_{\Phi}^{\circ}(\text{ClO}_4^-)$ of only $29(1) \text{ cm}^3 \text{ mol}^{-1}$ is obtained, which is significantly smaller than that arrived at by the correspondence method, viz. $37 \text{ cm}^3 \text{ mol}^{-1}$.

Comments on $V_{\Phi}^{\circ}(\text{ion})$ in dichloromethane. The multitude of methods for the separation of $V_{\Phi}^{\circ}(\text{salt})$ into the ionic contributions, $V_{\Phi}^{\circ}(\text{anion})$ and $V_{\Phi}^{\circ}(\text{cation})$, combined with the limited accuracy of values for $V_{\Phi}^{\circ}(\text{salt})$ in many organic solvents, render comparisons with the numerous literature values for $V_{\Phi}^{\circ}(\text{ion})$ in the various solvents of doubtful value. As an example may be given $V_{\Phi}^{\circ}(\text{Et}_4\text{N}^+)$ in methanol, for which published values range from $125 \text{ cm}^3 \text{ mol}^{-1}$ ²⁵ to $144 \text{ cm}^3 \text{ mol}^{-1}$.³⁴ The individual ionic volumes determined by Zana and co-workers,^{24,42,43,47-49} however, seem highly consistent. The partial molar volumes of the R_4N^+ ions in dichloromethane appear to be comparable to the volumes in most other solvents determined by this group.²⁴ The notable exceptions are water and propylene carbonate, in which the ionic volumes of the R_4N^+ ions, particularly the smaller R_4N^+ ions, are significantly greater than in the usual organic solvents.²⁴ The same trend exists with regard to V_{Φ}° for Ph_4As^+ and Ph_4B^- .²³

A particular problem arises when values for V_{Φ}° of anions in the various solvents are to be compared. Since these values are generally determined by the additivity rule, their accuracy will necessarily be rather limited. Still, one may conclude that the partial molar volumes of the halide ions in dichloromethane and in acetonitrile⁴⁸ are rather similar and are distinctly smaller, by $\sim 10 \text{ cm}^3 \text{ mol}^{-1}$, than in other protic and aprotic solvents. This difference may have its origin in the fact that dichloromethane and acetonitrile act as carbon acids toward small anions. From $V_{\Phi}^{\circ}(\text{ion})$ the intrinsic radii, r_i , can be calculated [eqn. (12)].

$$r_i = \frac{3V_{\Phi}^{\circ 1/3}}{4\pi N_o} \quad (12)$$

The results are listed in Table 4 together with Stokes radii in dichloromethane, r_s ,⁶ and the

Table 4. A comparison between intrinsic radii, r_i , as calculated from the ionic partial molar volumes in dichloromethane, the Stokes' radii, r_s , in dichloromethane and the crystallographic radii, r_c .

Ion	$r_i/\text{Å}$ in CH_2Cl_2^a	$r_s/\text{Å}$ in CH_2Cl_2^b	$r_c/\text{Å}^c$
Et_4N^+	3.72	3.69	4.00
Pr_4N^+	4.28	4.97	4.52
Bu_4N^+	4.74	5.22	4.94
Hex_4N^+	5.43	6.41	5.62
Oct_4N^+	6.00	8.28	d
Dec_4N^+	6.46	10.00	d
Ph_4As^+	4.72	4.53	4.25 e
$[\text{PNP}]^+$	5.53	5.39	d
Ph_4B^-	4.71	4.53	4.25 e
Cl^-	1.34	3.11	1.81
Br^-	1.68	2.97	1.95
I^-	2.18	2.85	2.16
SCN^-	2.23	2.72	2.27
ClO_4^-	2.45	2.76	2.45 f

^aCalculated from $V_\phi^\circ(\text{ion})$ (Table 2) by eqn. (12).

^bStokes radii, r_s , calculated by the Stokes-Einstein equation.⁶

^cCrystallographic radii.⁸

^dNo estimate available.

^evan der Waals radius.

^fIonic radius.⁵⁰

crystallographic radii, r_c . In the case of I^- and ClO_4^- , i.e. the ions which are essentially unsolvated by dichloromethane,⁶ the intrinsic radii are in excellent agreement with the crystallographic ones.⁵⁰ $r_i(\text{Br}^-)$ and $r_i(\text{Cl}^-)$, however, are distinctly smaller than r_c and r_s . Previous conductivity studies have shown that Br^- and Cl^- are solvated in dichloromethane.⁶ The intrinsic radii for the R_4N^+ cations are approximately 0.2 Å smaller than the corresponding r_c . It appears that only in the case of Et_4N^+ is r_i a reasonable measure of the size of R_4N^+ cations in dichloromethane. It is notable that the agreement between the various radii for Ph_4As^+ and for Ph_4B^- is quite satisfactory.

It has become customary to separate $V_\phi^\circ(\text{ion})$ into a geometric contribution, $A r^3$, and a contribution of electrostriction, $-B/r$ [eqn. (13)].⁵¹

$$V_\phi^\circ(\text{ion}) = A r^3 - B/r \quad (13)$$

and B are constants, while the ionic radius, r , is usually represented by the crystallographic radius, r_c (see Ref. 48 for critical discussion of A and B). On the basis of the Drude-Nernst equa-

tion,⁵² which in turn is based upon the Born model⁵³ of an ion in a solvent continuum, a value of B for monovalent ions can be calculated [eqn. (14)]:^{36,47,54,55}

$$B = 6.9 \times 10^{12} \epsilon^{-1} \ln \epsilon / dP. \quad (14)$$

In this equation B is expressed in $\text{cm}^3 \text{Å} \text{mol}^{-1}$, ϵ is the dielectric constant of the solvent and P is the pressure in dyne cm^{-2} . Since $d\epsilon/dP$ for dichloromethane is not known, one may employ the isothermal compressibility, β_T ,^{54,55} as an approximate value.^{35,48} In this way a B value of $\sim 76 \text{ cm}^3 \text{Å} \text{mol}^{-1}$ is obtained, which is of the correct magnitude for R_4N^+ ions, viz. $100(20) \text{ cm}^3 \text{Å} \text{mol}^{-1}$.⁴⁸ The reasonable value for B , even for the largest R_4N^+ ions, suggests that the long alkyl chains "curl up," causing this class of ions to behave as "hard" spheres. Some derived radii for the Dec_4N^+ cation seem to confirm this conclusion: Based upon N-C and C-C distances of 1.5 Å and a C-H distance of 1.1 Å one obtains a N-H (terminal) distance of 11.1 Å, in fair agreement with the Stokes radius of 10.0 Å (see Ref. 6 and Table 4). The intrinsic radius, r_i , derived from $V_\phi^\circ(\text{Dec}_4\text{N}^+)$ [eqn. (12)] and used for the evaluation of B [eqn. (13)] is only 6.46 Å. This radius, however, is in fair agreement with the distance of closest approach, 5.8(2) Å, calculated by the Bjerrum equation¹⁷ from conductivity data for dichloromethane.¹ The conclusion that the larger R_4N^+ ions exist as "hard" spheres in this solvent has also been arrived at from viscosity studies on solutions of R_4NClO_4 .⁵⁶

It should be emphasized that R_4N^+ cations with large alkyl groups may have significantly larger intrinsic radii in solvents other than dichloromethane. Recently, Lawrence and co-workers⁵⁷ have shown that this class of ions in dimethylsulfoxide and in hexamethylphosphoric triamide have a more open configuration of the alkyl groups. This may indicate that the donor ability of the solvent is a determining factor with regard to the size and structure of R_4N^+ ions in solution. Additionally, the flexibility of the alkyl chains seems to decrease with increasing size of the solvent molecules. The relatively small molar volume, the low dielectric constant and the exceedingly low donicity of dichloromethane may be favourable for the formation of "hard" spheres of large R_4N^+ ions in this solvent.

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