[April, 1981] © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 951—956 (1981) 951

Hydration of Quaternary Phosphonium Bromides, $Bu_{4-n}Ph_nPBr$, in Chloroform[1)]

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(Received January 5, 1980)

Studies have been carried out on the hydration of quaternary phosphonium bromides, $Bu_{4-n}Ph_nPBr$(n=0—4), in the chloroform phase by means of distribution equilibrium and ^{1}H NMR spectroscopy, in order to clarify the difference between the alkyl- and aryl-substituted ions in ion–water interactions. The hydration constant for these bromides in the chloroform phase increases gradually from Bu_4PBr to Bu_2Ph_2PBr, and then rapidly to $BuPh_3PBr$ and to Ph_4PBr. The free energy of transfer from water to chloroform was evaluated for the non-hydrated species of the phosphonium bromides in the chloroform phase, the lowest being that for Bu_2Ph_2PBr. From ^{1}H NMR spectra for water in the chloroform phase, it is concluded that the hydrated water molecule is hydrogen bonded with the anion of the onium salts. In the case of phenyl-rich cations such as $BuPh_3P^+$, Ph_4P^+, and Ph_4As^+ the water molecule occupies a site so close to the central atoms that it undergoes diamagnetic effects of phenyl groups. With phenyl-rich cations such hydration will play a certain role in their aqueous solutions.

The ion–water interactions of the so-called hydrophobic ions, considerably large organic ions, have been widely investigated over the past two decades. Differences between the alkyl- and aryl-substituted ions in their interactions with water have been recognized.[2—4)] In a similar way to those of hydrocarbons, the interactions of alkyl-substituted ions with water are tentatively explained by the concept of a structure-making effect on the solvent water, though not completely established so far.

On the other hand, with tetraphenyl ions such as Ph_4M^+ (M=P, As, Sb) and BPh_4^-, their interactions with water might be more complicated, due to some effects not present in the case of benzene such as the delocalized charges on the phenyl groups[8,9)] and the hydration of the central atoms. Tetraphenyl borate is known to interact with water in a different way from Ph_4M^+ ions.[4—7)] The penta-coordinate state of the central atom was suggested for Ph_4As^+ in water, but not for Ph_4P^+, by Orenberg *et al.*[10)] who studied laser-Raman spectra. From a study of ^{1}H NMR for Ph_4M^+ and BPh_4^- ions in various solvents, Coetzee and Sharpe[7)] concluded that the screening of the central atoms by essentially flat phenyl rings is not sufficient for elimination of the solvation effects. The effects are related to the failure to classify the ions as structure makers or structure breakers.[12)]

An approach to the hydration of aryl-substituted ions would be to examine systematically the ions with mixed substituents of alkyl and aryl groups besides the tetraalkyl and tetraphenyl ions. Only tetraphenyl ions have been used as aryl-substituted ions, with only one exception.[11)] A series of studies[13—15)] deal with some quaternary phosphonium ions, $Bu_{4-n}Ph_nP^+$.

The hydration of these phosphonium ions might be influenced by two factors: (a) influence on the structure of the solvent water and (b) the interaction between the central atoms and water separated from the bulk of water. The effect of (b) might depend upon the nature of substituents as well as that of the central atom.

The present work was undertaken anticipating that the interaction with water separated from the bulk water would become conspicuous in a system containing water dissolved in a non-aqueous solvent. The methods used in this study are distribution equilibrium and ^{1}H NMR spectroscopy.

Experimental

Materials. All the phosphonium salts were synthesized from the phosphines except for commercial Ph_4PCl (DOTITE) and Ph_4AsCl. The synthesis, purification and purity of these salts are similar to those reported.[13)] Water was redistilled after ion exchange. Chloroform was distilled just before use after being treated with aqueous solution of Na_2CO_3 and then with water. The other chemicals were all of G.R. grade.

Procedure. Distribution equilibria were attained by shaking chloroform solution of known concentration of phosphonium bromide with an equal volume of an aqueous solution of sodium bromide in an air-thermostat, the temperature being regulated to 25±0.5 °C. The concentration of NaBr was 0.08 and/or 0.125 mol dm^{-3}. The initial concentration of the phosphonium salts in chloroform phase was in the range 5×10^{-3}—2×10^{-1} mol dm^{-3}. The shaking time was 45 min, the same results being obtained by shaking for 20 min. The aliquots of the equilibrated chloroform phases were subjected to measurements for water content and ^{1}H NMR of water in the phase. The aqueous phases were analyzed for phosphonium salts. An aliquot of the aqueous phase was diluted and a part of it was transferred to a neutral aqueous solution containing sodium bromide (0.1 mol dm^{-3}) and Methyl Orange in a large excess in comparison with the phosphonium bromide (below 5×10^{-5} mol dm^{-3}). Phosphonium ion was then extracted into a fresh chloroform phase in a form of 1 : 1 ion-pair with the anion of Methyl Orange. The molar absorption coefficient of the ion-pair at 415 nm is around 2.6×10^5 dm^3 mol^{-1} cm^{-1} in chloroform for all the phosphonium salts examined. Lambert-Beer's law holds. All the phosphonium ions seemed to be almost quantitatively extracted into chloroform. For the sake of confirmation the standard solutions of each phosphonium salt were treated under the same conditions for calibration.

Measurement. The water contents in the chloroform phases were determined by Karl Fischer's method with a Hirama Rika recording automatic titrator.

The ^{1}H NMR spectra were obtained on a Hitachi R-20 (90MHz) spectrometer, equipped with a temperature controller. All the solutions were measured at 25±0.5 °C with the probe temperature established by a standard methanol calibration. Tetramethyl silane (TMS) was used as an internal standard at a concentration of 0.3% (v/v). The chemical shift for each solution is the mean from a minimum of three scannings for each solution.

Solubility of NaBr in Chloroform. The solubility of NaBr in chloroform was tested as follows: A 50 cm^3 volume of chloroform was shaken with 0.125 mol dm^{-3} aqueous solution of NaBr, 30 cm^3 of the chloroform phase being separated and evaporated at room temperature in the dark, no residue remained. After adding of 10 cm^3 water titration was carried out with silver nitrate solution. No titrant was consumed.

Results

Water Content in Chloroform Phase. For all the onium salts examined, the water concentration in the organic phase increases linearly with increase in the analytical concentration of a given onium salt in the phase. Examples for Bu_2Ph_2PBr and Ph_4PBr, the ionic strength of aqueous phase being 0.125 (NaBr), are shown in Fig. 1. The linear relation between water concentration in the organic phase and the salt concentration indicates two kinds of water species, (a) free water dissolved in the solvent and (b) hydrated water accompanied by the onium salt. The average hydration number of the phosphonium salt is constant and nearly independent of its concentration in the organic phase. The average hydration number, α, for some onium salts (Table 1) was determined from the slopes of the straight lines in Fig. 1. For both aqueous phases of ionic strength of 0.08 and 0.125, the α values agree with each other within experimental error as expected, since the water activities for both ionic strengths are nearly the same, *i.e.*, 0.997 and 0.996 for aqueous solutions of NaBr of 0.08 and 0.125 mol dm^{-3}, respectively, evaluated from osmotic coefficients of NaBr at 25 °C in water.[16]

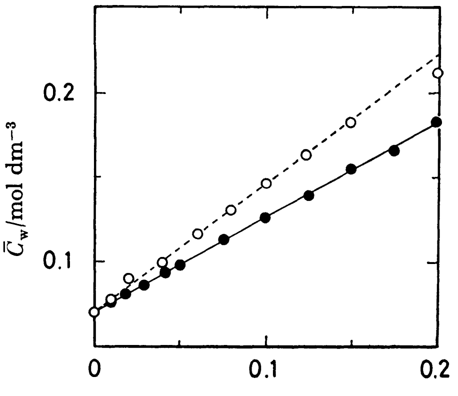

Fig. 1. The water concentration, $\bar{c}_w$, in chloroform phase equilibrated with aqueous phase of an ionic strength of 0.125 (NaBr), as a function of the analytical concentration of phosphonium bromide, $\bar{c}_{RBr}$, in the organic phase, at 25 °C. The open circles are for Ph_4PBr and closed circles, for Bu_2Ph_2Br.

Chemical Shift of Water Proton in Chloroform Phase. Single resonance of water proton is found in the ^1H NMR spectra of organic solutions of onium salts equilibrated with aqueous phase. Equilibrium is established in the organic phase between free water and hydrated water through a rapid exchange reaction in the NMR time scale. The observed chemical shifts are obtained for averaged proton by the process

$$H_2O(\text{hydrated}) \rightleftharpoons H_2O(\text{free})$$

and we thus have

$$\delta = x_f\delta_f + x_h\delta_h, \tag{1}$$

where δ is the observed chemical shift, x_f the fraction of the free water, δ_f the chemical shift of free water proton and subscript h refers to the hydrated water.

The chemical shift of free water proton in the presence of phosphonium salt would differ from that in the absence of the salt. The salt effect on the ^1H chemical shift can be expressed by

$$\delta_f = \delta_f^\circ + F(\bar{c}), \tag{2}$$

where $F(\bar{c})$ is a function of the gross concentration of a given salt and δ_f° the chemical shift of free water proton in the absence of the salt. In order to understand the F-function, the chemical shifts of water proton in chloroform phase were measured in the presence of hexane, butyl bromide, benzene, and chlorobenzene. The water concentration in these solutions was 0.0665 mol dm^{-3}, the same for all runs, the ratio to water solubility being *ca.* 0.9. The results are shown in Fig. 2.

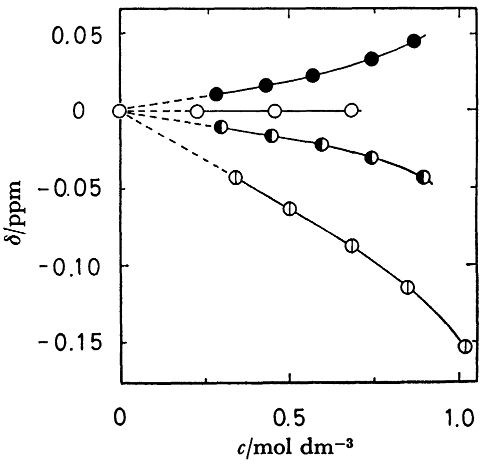

Fig. 2. Chemical shift of water proton in chloroform solutions of some solutes; butyl bromide (●), hexane (○), chlorobenzene (◐), and benzene (⦶), as a function of solute concentration, at 25°C. The shifts are relative to that of water in pure chloroform at a concentration of 0.0665 mol dm^{-3}.

The ^1H chemical shifts of water are expressed by the relative value to that of water proton in pure chloroform measured against internal TMS. A linear relation with respect to the solute concentration holds for each solution, at least up to near 0.7 mol dm^{-3}. Equation 2 can thus be simplified to

$$\delta_f = \delta_f^\circ + \beta\bar{c}, \tag{3}$$

where β is a constant for a given salt. The hydrated water concentration is given by $\alpha\bar{c}$, x_h being equal to $(1-x_f)$ by definition. Combining Eqs. 1 and 3, we have

$$\delta = x_f\delta_f^\circ + (1-x_f)\left(\delta_h + \frac{\beta}{\alpha}\bar{c}_0\right), \tag{4}$$

where $\bar{c}_0$ is the solubility of water in chloroform (0.072 mol dm^{-3}, 25 °C). Since the last term in the second brackets is a constant for a given onium salt by the

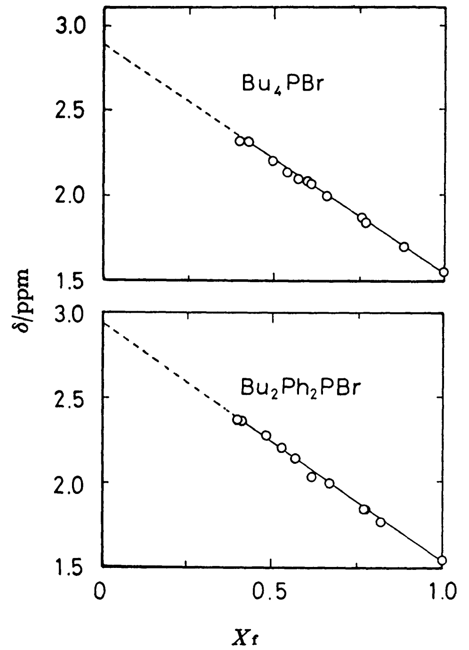

Fig. 3. ^1H chemical shifts of water in chloroform solutions of phosphonium bromides against internal TMS as a function of the fraction of free water to the total of water in the solution, at 25 °C.

TABLE 1. THE ^1H CHEMICAL SHIFTS OF WATER SOLVATED TO PHOSPHONIUM SALTS IN CHLOROFORM, AT 298 K

Salts	δ'_h/ppm[a)]	α[b)]
Bu_4PBr	2.89	0.50
Bu_3PhPBr	2.90	0.52
Bu_2Ph_2PBr	2.92	0.55
$BuPh_3PBr$	2.85	0.67
Ph_4PBr	2.79	0.77
Ph_4PNO_3[c)]	3.01	0.84
Ph_4PCl[d)]	3.10	1.09
Ph_4AsBr	2.75	0.79

a) Average chemical shifts from protons of hydrated water, measured against internal TMS (see text). b) Average hydration number. c) Ionic strength of aqueous phase was adjusted by $NaNO_3$ (0.125). d) Ionic strength of aqueous phase was adjusted by NaCl(0.125).

above assumption, the plots of the observed chemical shifts against the free water fraction should give straight lines. Some of the plots are shown in Fig. 3, in which linearity holds. The values for the second brackets in Eq. 4 are obtained from the intercepts of these straight lines with the ordinate (Table 1).

The resonance of water proton, in the absence of salt in the chloroform phase, shifts gradually to high-field by dilution, *viz.*, 1.55, 1.54, and 1.51 ppm (relative to internal TMS) at water concentrations of 0.072, 0.036, and 0.014 mol dm^{-3}, respectively. It seems that the free water slightly associates in chloroform at the free water concentration of 0.072 mol dm^{-3}.

Distribution Ratios of Phosphonium Bromides at Zero Concentration. The distribution ratio, D, of a phosphonium bromide is defined by

$$D = \frac{\bar{c}_{RBr}}{c_{RBr}}, \quad (5)$$

where $\bar{c}_{RBr}$ and c_{RBr} are the analytical concentrations of the salt in the chloroform phase and in the aqueous phase, respectively. As an example, the distribution ratios of Bu_4PBr and Ph_4PBr are shown as a function of $\bar{c}_{RBr}$ in Fig. 4, where the ionic strength of aqueous phase is 0.125, adjusted by NaBr. From these curves the distribution ratios at zero concentration of the phos-

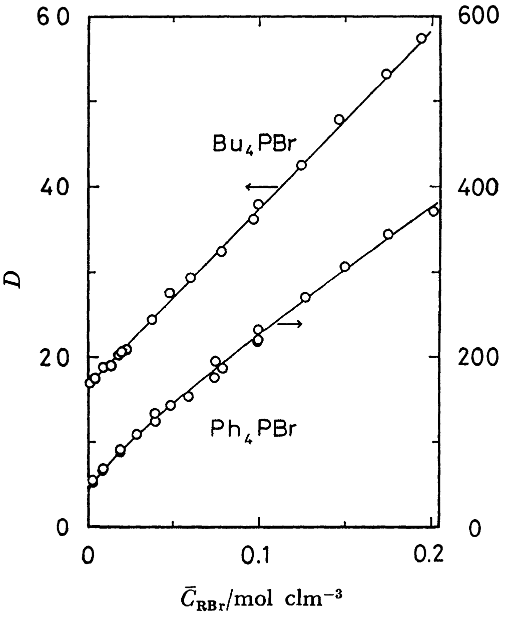

Fig. 4. Distribution ratios of phosphonium bromides between chloroform phase and aqueous phase of an ionic strength of 0.125 (NaBr) as functions of the analytical concentration of the salts in the organic phase, $\bar{c}_{RBr}$, at 25 °C.

TABLE 2. HYDRATION CONSTANTS OF PHOSPHONIUM BROMIDES IN CHLOROFORM PHASE AND DISTRIBUTION CONSTANTS BETWEEN CHLOROFORM AND WATER AT 298 K

		Hydration constant	Distribution constant				
			I=0.125(NaBr)		I=0.08(NaBr)		Mean value
Salts	α	K_h	D_0	$K_D\times10^{-2}$	D_0	$K_D\times10^{-2}$	$K_D\times10^{-2}$
Bu_4PBr	0.50	1.0_0	16.5	1.3	11.5	1.3	1.3
Bu_3PhPBr	0.52	1.0_8	28	2.1	18	1.9	2.0
Bu_2Ph_2PBr	0.55	1.2_2	42	3.0	30	3.0	3.0
$BuPh_3PBr$	0.67	2.0_3	41	2.1	29	2.1	2.1
Ph_4PBr	0.77	3.3_4	44	1.6	31	1.6	1.6

phonium bromides, D_o, are obtained by graphical extrapolation. These results are given in Table 2.

The D_o value is considered to be the distribution ratio for the undissociated and monomer species of the phosphonium bromide in the organic phase. The possible species in the organic phase are the dissociated ions, hydrated and non-hydrated monomer, and the aggregated species. The activity coefficients of RBr in aqueous phase are expected to be constant because of constant ionic strength in the aqueous phase. Hence, the increase in D with increase in $\bar{c}_{RBr}$ is attributed to the decrease in the activity coefficient of RBr in the chloroform phase, probably due to the aggregation of RBr[17-19]. The aggregation effect on D can be subtracted by extrapolation of D to zero concentration of RBr, the dissociation effect on D being considered insignificant. This can be judged from the behavior of D in the low concentration range of RBr. A tendency of increase in D toward zero concentration, which should be seen if the dissociation is significant, was not observed. An estimation for the degree of dissociation of RBr in chloroform phase saturated with water also supports the view. If we apply Bjerrum's equation,[20] the dissociation constant is estimated to be *ca.* 2×10^{-7} for phosphonium bromides. In the estimation the distance of closest approach is taken as 6.5 Å[21] and the dielectric constant of chloroform solution saturated with water, 5.[22] The dissociation constant thus obtained gives the degree of dissociation of the order of 0.01 at $\bar{c}_{RBr}$ of 0.001 mol dm^{-3}, which is lower than the lowest concentration examined. For dichloromethane as organic phase, the degree of dissociation is estimated as 0.14 even at 0.01 mol dm^{-3}. In fact, an increase in D for Ph_4PBr was found[25] at lower concentrations in dichloromethane.

It is reasonable concluded that the D_o values given in Table 2 are the overall distribution ratios for monomer species of hydrated and non-hydrated RBr in chloroform phase at zero concentration of RBr.

Discussion

Hydration Constant. The distribution equilibria in the present systems can be expressed as

$$H_2O \rightleftharpoons \overline{H_2O} \qquad \text{(a)}$$

$$R^+ + Br^- \rightleftharpoons \overline{RBr} \qquad \text{(b)}$$

$$\overline{RBr} + \overline{H_2O} \rightleftharpoons \overline{RBr\cdot H_2O}, \qquad \text{(c)}$$

where R^+ stands for the phosphonium ion, the bar indicating the species in chloroform phase. The aggregation process is neglected, the fact that the average hydration number is less than unity for all RBr examined being taken into account.

The hydration constant in chloroform phase, K_h, corresponding to the equilibrium (c), is given by

$$K_h = \frac{\alpha}{1-\alpha}\,\frac{1}{\bar{a}_w}\,\frac{\bar{y}_h}{\bar{y}_{RBr}}, \qquad (7)$$

where $\bar{a}_w$ is the water activity in chloroform phase, $\bar{y}_i$ the activity coefficient of species i in chloroform phase, referred to the concentration scale of mol dm^{-3}, and subscript h denotes the hydrated phosphonium bromide. With pure water chosen as a standard state for water in chloroform phase, $\bar{a}_w$ is equal to a_w. Since the water activity is close to unity, $\bar{a}_w$ is taken as unity. At infinite dilution of $\overline{RBr}$, the last factor in Eq. 7 becomes unity, and we obtain the hydration constant simply by replacing α with the numerical values given in Table 1. The hydration constants in chloroform phase at 25 °C are given in Table 2.

The K_h value increases gradually from Bu_4PBr to Bu_2Ph_2PBr and rapidly to $BuPh_3PBr$ and to Ph_4PBr. This suggests that the hydrated water molecule is stabilized through interactions with phenyl-rich cations ($n \geq 3$) to a greater extent than butyl-rich cations ($n \leq 1$).

Free Energy of Transfer of RBr from Water to Chloroform. In order to examine the effects of the substituent of phosphonium bromides upon distribution equilibria, it is essential to split the distribution constant, K_D, (equilibrium (b)), from the overall distribution ratios, D_o. Since the distribution ratio for the non-hydrated species of RBr in chloroform phase is given by $(1-\alpha)\,D$, we have

$$K_D = \frac{\bar{a}_{RBr}}{a_R a_{Br}} = \frac{(1-\alpha)D}{c_{Br}}\,\frac{\bar{y}_{RBr}}{\gamma^2_{RBr(NaBr)}}, \qquad (8)$$

where $\gamma_{RBr(NaBr)}$ is the mean activity coefficient of RBr in the aqueous phase in molality in the presence of NaBr, the small difference between the two concentration scales in aqueous solution being ignored. At zero concentration of RBr in the organic phase, we have

$$K_D = \frac{(1-\alpha)D_o}{c_{Br}}\,\frac{1}{\gamma^2_{(0)RBr}}, \qquad (9)$$

where $\gamma_{(0)RBr}$ is the activity coefficient of RBr at zero concentration in the presence of NaBr at the ionic strength of 0.08 and/or 0.125, in aqueous solution. In order to obtain the values for $\gamma_{(0)RBr}$, we need parameters, either the interaction parameters for mixed electrolyte solutions[26] or Harned's coefficients,[27] α_{ij}. So far they do not seem to have been reported. For the present purpose we can use the equation[27,28]

$$\log \gamma_{(0)MX} = \log \gamma_{(0)NX} = \frac{1}{2}\log \gamma_{MX(0)}\cdot\gamma_{NX(0)}, \qquad (10)$$

where $\gamma_{(0)MX}$ is the activity coefficient of MX at zero concentration in the presence of electrolyte, MX, at a given ionic strength, $\gamma_{MX(0)}$ and $\gamma_{NX(0)}$ being the activity coefficients of MX and NX in the pure solutions of MX and NX at the same ionic strength, respectively. The equation is found to be useful for some binary mixtures, including tetraalkyl ammonium bromides, at least for dilute solutions ($I \leq 0.1$): For mixed aqueous solutions of HBr (1) and Bu_4NBr (2),[29] α_{12} are 0.3304 and 0.268 at ionic strengths of 0.1 and 0.25, respectively, which give the values 0.746 and 0.668 for $\gamma_{(0)HBr}$. Equation 10 gives the values 0.747 and 0.656, respectively. For α_{21} at ionic strength of 0.1, the reported value is -0.2057. This leads to the value 0.727 for $\gamma_{(0)Bu_4NBr}$, which is less by only 3% than the value estimated by means of Eq. 10. In the mixed solutions of KBr and $(C_3H_7)_4NBr$,[30] $\gamma_{(0)Pr_4NBr}$ values are determined to be 0.748 and 0.594 at ionic strengths of 0.1 and 0.5, respectively, Eq. 10 giving 0.736 and 0.561, respectively.

By assuming Eq. 10, we can rewrite Eq. 9 as:

$$K_D = \frac{(1-\alpha)D_\circ}{a_{\pm(\mathrm{NaBr})}} \frac{1}{\gamma_{\mathrm{RBr(0)}}}. \tag{11}$$

Since no activity coefficients for RBr in each of the pure solutions are known, some estimations must be made. Use of the activity coefficient of Bu_4NBr might be a good approximation for Bu_4PBr. The $\gamma_{\mathrm{Bu_4NBr}}$[30] in aqueous solution at 25 °C fits the Debye-Hückel limiting law up to moderate concentration; *e.g.*, the deviations from the law amount to only 0.6% at 0.1 and 5% even at 0.4 mol dm^{-3}, though the consistence is regarded as accidental.[23] Thus, we obtain the value of 1.3×10^2 for K_D, which is common to both systems with different ionic strengths. For other phosphonium bromides, the limiting law was also applied to obtain $\gamma_{\mathrm{RBr(0)}}$. The K_D values thus obtained are given in Table 2. The agreement between two values for K_D at different ionic strengths is good in spite of a considerable difference between $D_\circ$ values. This supports the validity of the assumption.

From K_D, we obtain the free energy of transfer for RBr (non-hydrated in chloroform) from water to chloroform at 25°, $\Delta G_{c\leftarrow w}$, by means of

$$\Delta G_{c\leftarrow w} = -RT \ln K_D,$$

where a hypothetical solution of 1 mol dm^{-3} in each phase is taken as the standard state for RBr.

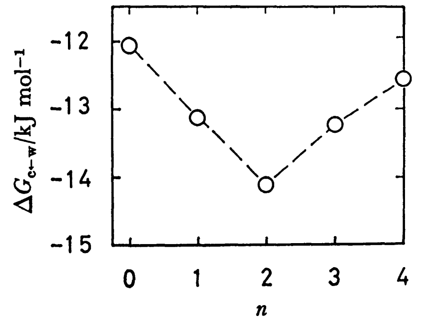

Fig. 5. The free energy of transfer for $Bu_{4-n}Ph_nPBr$ from water to chloroform as a function of *n*, at 25 °C. The standard state is taken as a hypothetical solution of 1 mol dm^{-3} of the salt.

$\Delta G_{c\leftarrow w}$ is shown as a function of *n* in Fig. 5. No additivity of group contributions to $\Delta G_{c\leftarrow w}$ is found; $\Delta G_{c\leftarrow w}$ is the lowest for Bu_2Ph_2PBr. This might be related to hydration processes in the aqueous phase, since there is no reason to expect that, of the phosphonium bromides, Bu_2Ph_2PBr interacts most effectively with the solvent chloroform. The state of cosphere water of phenyl groups differs from that of butyl groups. Different types of cospheres coexist in each cation with *n*=1—3. Thus, we find the interpretation for the variation of $\Delta G_{c\leftarrow w}$ with *n* in terms of the statement by Friedman and Krishnan:[2] adjacent cospheres interfere with each other so that the overall solvation is less energetic than one might guess from the properties of separate cospheres.

State of Hydration Water. Comparing δ'_h with the hydration number (Table 1), we find: (1) As found in a series of Ph_4PX's, δ'_h increases (low-field shift) in the order X^-, Br^-, NO_3^-, Cl^-, in accordance with that of the average hydration number; (2) with respect to a series of phosphonium bromides, the low-field shift remains nearly constant or gradually increases from Bu_4PBr to Bu_2Ph_2PBr with gradual increase in hydration number, and decreases to $BuPh_3PBr$ and to Ph_4PBr in spite of rapid increase in the hydration number (Fig. 6).

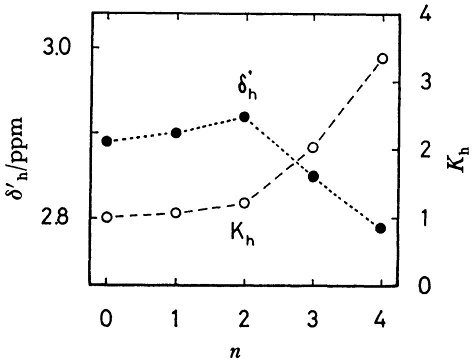

Fig. 6. ^{1}H chemical shift of water solvated to $Bu_{4-n}Ph_nPBr$ in chloroform phase and their hydration constants, as function of *n*, at 25 °C.

We infer from (1) that the hydrated water is hydrogen-bonded with anions of the phosphonium salts. Since the δ'_h values are the average values from two protons of hydrated water molecule, the chemical shift for the proton which participates in hydrogen bond, δ°_h, is roughly estimated from δ'_h by the relation

$$\delta^\circ_h = 2\delta'_h - \delta^\circ_f,$$

where assumptions are made that the chemical shift for the other proton is equal to that of non-hydrated water, the correction factor, $\bar{c}_\circ\beta/\alpha$, being relatively small as expected from Fig. 2. The values for δ°_h are, for example, 4.0, 4.4, and 4.7 ppm (against TMS), for Ph_4PBr, Ph_4PNO_3, and Ph_4PCl, respectively.

Let us examine the salt effect upon the chemical shift of free water proton: (a) polarization of free water due to the salts as electric dipoles, and (b) magnetic anisotropy due to phenyl groups and polarization of free water due to charges located on the phenyl groups. Effect (a) leads to the net low-field shift of free water proton (Fig. 2), the effect being expected to nearly the same degree for all onium bromides examined since their molal volumes are nearly the same[13] while effect (b) due to phenyl rings leads to net high-field shift. With the present onium salts, however, the phenyl groups may differ from benzene or chlorobenzene as regards their interactions with water because of geometric effects and charge delocalization effects. The π-electron donation from phenyl groups to phosphorus *d*-orbitals of quaternary phosphonium salts was shown by Gim and McFarlane.[8] The charge delocalization for Ph_4P^+ ion was estimated to be 0.18 electron unit per phenyl group.[9] When a water molecule is situated in the vicinity of the peripheries of phenyl rings, it will undergo deshielding effects due to the local magnetic field of phenyl rings as well as possible polarization induced by delocalized charges. In contrast, high-field shift should be observed when the water molecule is located so close to the central atom that the proton undergoes the diamagnetic effect due to phenyl rings. In this case, however, the water molecule is not regarded as "free," but "hydrated." Onium salts lead to deshielding free water protons.

We can conclude from (2) that the hydrated water molecule interacts not only with anions but with cations, especially with phenyl-rich cations ($n \geq 3$), as evidenced by relatively large hydration constants for these salts. Starting with Bu_4PBr, we find the most favorable site for water molecule at $BuPh_3PBr$, since it is free from steric hindrance by butyl groups. For butyl-rich salts, no sites of this kind are available and thus their hydration constants are expected to be nearly the same.

The hydration constant for Ph_4AsBr seems to be somewhat larger than that for Ph_4PBr, in accordance with the less low-field shift for the former. This is consistent with the results obtained by Orenberg *et al.*[10]

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