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ABSTRACT

The extraction of tetrahexyl and tetrapentyl ammonium hydroxides into solutions of alcohols in benzene and of tetrabutyl and tetrapropyl ammonium hydroxides into dilute solutions of alcohols in nitrobenzene has been studied. The variation of the extraction into benzene as a function of the aqueous base concentration at a fixed alcohol concentration indicated that the extracting ions associate as ion pairs. The dependence of the extracting species on alcohol concentration at a fixed aqueous base concentration indicated that 3 molecules of alcohol are complexed by each extracted ion pair of the base. A similar study with a solution of benzyl alcohol in nitrobenzene of fixed concentration indicated that the extracted species in such a high dielectric constant solvent is in the form of two dissociated ions. The extractions of the smaller substituted ammonium bases into varying concentrations of alcohols in nitrobenzene also showed that 3 alcohol molecules are bound in the extracted hydroxide as observed with the associated systems in benzene. It is suggested that the OH^- ion alone provides the three sites for hydrogen bonding to the alcohol molecules, and a structure for the extracted species is proposed. The tri-coordination of the OH^- ion is considered similar to that of the hydronium ion which has been established in earlier studies.

THE EXTRACTION OF TETRAALKYL AMMONIUM HYDROXIDES AND THE SOLVATION OF THE HYDROXIDE ION*

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INTRODUCTION

The nature of the solvation of the hydroxide ion has received relatively little attention[1,2] compared to the discussions in the literature[3-10] on the hydration of the hydronium ion, H_3O^+. For the latter ion, the existence of three sites of partial positive charge (the protons) leads quite natrually to a model in which three water molecules are hydrogen-bonded tightly in the first hydration shell. Additional water molecules are bound in further shells, less and less tightly as the distance from the ion increases, until the structure far enough out merges into that of ordinary water. The hydronium ion (and its tri-hydrate) is probably pyramidal, but an indication of the strength of the hydrogen-bonding of the three waters in the first shell is given by the calculations of Grahn[11] for a planar hydronium ion model. He calculates that the hydrogen-bond holding each of these three water molecules to the H_3O^+ ion has an energy of ~45 Kcal., far larger than the ordinary water-water bond of ~6 Kcal.

Similar considerations suggest that the hydroxide ion in aqueous solution also might hold a first shell of three water molecules by unusually strong hydrogen bonds and so be tri-solvated too. Ackermann,[1] from a comparison of the specific heats of dilute solutions of strong acids and bases has suggested such a model, and Frank[2] has made a similar proposal on the basis of the similarity of the broad Raman bands of HCl and KOH solutions, the relation to each other of the single ion partial molal entropies of H^+ and of OH^-, and the rates of proton transfer in acidic and basic solutions.

The present authors hoped that experimental verification of the tri-solvation of the OH^- ion could be obtained from solvent extraction studies by

a method similar to that used recently to investigate the solvation of the hydronium ion.[10,12] In this latter work, the extraction of strong acids from aqueous solutions into dilute solutions of tributyl phosphate (TBP) or trioctyl phosphine oxide (TOPO) in octane, CCl_4, or xylene, etc., was measured as a function of the (small) TBP or TOPO concentration in the organic phase. All other components were either held constant or corrected to a constant value. From the power of the extractant dependence, it was shown that three TBP molecules are involved in the extracted complexes of the strong acids $HClO_4$, $HReO_4$, HBr, $HAuCl_4$, and $HAuBr_4$, and that three TOPO molecules are bound to extracted $HClO_4$, $HReO_4$, and $HAuCl_4$. With the $HClO_4$ and HBr systems, it was possible to show further that a minimum of one water molecule (to form the H_3O^+ ion) is involved in the complex.

To apply the same sort of technique to study the solvation of the OH^- ion, conditions for the successful extraction of a strong base into a dilute solution of an extractant in an "inert" diluent had to be found. A necessary requirement for the extractant molecule is that it be weakly acidic so that it contains a hydrogen atom capable of (hydrogen-) bonding to the hydroxide ion, but not so strongly acidic so as to react to form a salt and water. The large water-insoluble alcohols seemed likely candidates, and were, in fact, successfully used.

Two important conditions on the bases used are that the cation of the base be as hydrophobic as possible, in order to promote the distribution into the dilute organic extractant solution from the aqueous phase, and that the cation not be capable of bonding to the extractant molecules. The latter requirement is necessary so that the observed dependence of the extraction on the alcohol concentration would be due only to the solvation of the OH^-, and not to solvation of both the cation and OH^- ion. The tetraalkyl ammonium ions seemed the best choice, and were used in the present study.

EXPERIMENTAL

Reagents. Tetrapropyl ammonium hydroxide, TPrAH, was obtained from Eastman Organic Chemicals and standardized against hydrochloric acid using neutral red as indicator. Tetrabutyl ammonium hydroxide, TBAH, was prepared from the bromide salt (Eastman Organic Chemicals) by passing an aqueous solution of the latter through a column of strongly basic anion exchange resin (Dowex AG1-X8, 100-200 mesh, Bio-Rad Laboratories, Richmond, California) in the hydroxide form. It was standardized in the same way as the TPrAH. Tetrapentyl ammonium hydroxide, TPAH, and tetrahexyl ammonium hydroxide, THAH, were prepared by shaking suspensions of their iodides (Eastman Organic Chemicals) in water with freshly prepared silver oxide. These were standardized using phenol red as indicator. Benzyl alcohol (Cl free) and 4-methyl cyclohexanol (both from Eastman Organic Chemicals) were dissolved in nitrobenzene (Eastman Organic Chemicals) to give stock solutions of 0.100 M and 0.400 M concentration respectively. Other solutions were prepared by dilution. Similarly, stock solutions of 0.10 M decyl alcohol (Matheson Coleman and Bell) and of 0.15 M benzyl alcohol were prepared in benzene (Allied Chemicals, New York) and less concentrated solutions obtained by volumetric dilution.

Procedure. Two ml of the base, when using TPrAH and TBAH solutions, were added to 20 ml of the dilute alcohol solutions in the organic solvent. When TPAH and THAH solutions and benzene solutions of the alcohol were used, the ratio of the volumes of the base to the organic phase was 5 to 15. The mixtures were shaken for an hour on a mechanical shaker; shaking for a longer period (up to 12 hours) did not change the results indicating that equilibrium had already been achieved. Then the mixture was centrifuged and the two phases were separated. Two 5 ml aliquots of the organic phase were shaken with 2 ml of water for about 15 minutes and titrated against 0.0100 N HCl. Similar extractions were performed with no alcohol present in the organic phase in order to determine the correction for the extractions into the solvent alone.

All experiments were done at room temperature, 22 ± 2°C.

RESULTS

The data for the extraction of the OH^- ion into the organic phase when varying concentrations of THAH were added to 0.100 M benzyl alcohol in benzene are given in Table I. Explanations for the corrections made in order to arrive at the results listed in columns 3 and 4 of Table I are given in the discussion section. Similarly, the data for the extraction of varying concentrations of THAH into 0.100 M decyl alcohol in benzene are given in Table II, for THAH into 0.075 M benzyl alcohol in benzene in Table III, and for TPAH into 0.100 M benzyl alcohol in benzene in Table IV. There was negligible extraction of TPAH and of THAH into pure benzene.

The extractions of OH^- into the organic phase when a given volume of a fixed initial concentration of THAH or TPAH was added to varying concentrations of benzyl alcohol in benzene are given in Table V (initial concentration of THAH equals 0.162 M), Table VI (initial concentration of TPAH equals 0.305 M), and Table VII (initial concentration of THAH equals 0.061 M).

Table VIII gives the extraction of the OH^- ion into the organic phase when varying concentrations of TBAH are added to 0.075 M benzyl alcohol in nitrobenzene. Blank determinations were made of the extraction of the various concentrations of the base into pure nitrobenzene and the concentrations listed in column 2 are those obtained after subtracting the blanks. Explanations for the corrections made in order to arrive at the results given in columns 3, 4, and 5 are given later.

The data for the extraction of OH^- into the organic phase when a fixed volume of a given initial concentration of TBAH or TPrAH is added to varying concentrations of benzyl alcohol in nitrobenzene are given in Tables IX and X respectively. Determinations were made of the extraction of TBAH and TPrAH into pure nitrobenzene and the equilibrium concentrations given in column 2 are those obtained after subtracting these blanks. The corrections made to arrive at the values given in columns 3, 4, 5 and 6 are discussed later. Similarly, the data for

the extraction of a solution of TBAH, initially 0.437 M, into varying concentrations of 4-methyl cyclohexanol in nitrobenzene is given in Table XI.

DISCUSSION

The equation for the extraction of a tetraalkyl ammonium hydroxide by a dilute solution of an alcohol in an "inert" solvent can be written as

$$nROH_{(o)} + R_4N^+ + OH^- = R_4N^+ \ldots\ldots OH^- \cdot nROH_{(o)} \qquad (1)$$

$$R_4N^+_{(o)} + OH^- \cdot nROH_{(o)} \qquad (1')$$

where eq. (1) represents creation of an ion-pair in the organic phase, while eq. (1') shows the formation of a pair of dissociated ions. Which expression is correct in a given case depends upon the conditions, particularly upon the dielectric constant of the solvent. The possible influence of water on the extraction has not been shown as it was not determined in the present study, but all aqueous solutions used were dilute (<0.5 M) so that no appreciable changes in water activity occurred during these experiments.

The corresponding equilibrium constants are

$$K = \frac{(R_4N^+ \ldots OH^- \cdot nROH)}{(ROH)^n (R_4\overset{+}{N})(OH^-)} \qquad (2)$$

$$K = \frac{(R_4N^+)\ (OH^- \cdot nROH)}{(ROH)^n (R_4N^+)(OH^-)} \qquad (2')$$

To determine which is the correct expression, the extraction of the base can be studied as a function of the equilibrium aqueous tetraalkyl ammonium

hydroxide concentration, keeping the equilibrium alcohol concentration in the organic phase constant. Under this condition, eqs. (2) and (2') simplify to

$$K' = \frac{[R_4N^+ \ldots OH^- \cdot nROH]\gamma}{(R_4N^+)(OH^-)} = \frac{[OH^-]_{(o)}\gamma}{(R_4N^+)(OH^-)} \qquad (3)$$

$$K' = \frac{[R_4N^+][OH^- \cdot nROH]\gamma_\pm^2}{(R_4N^+)(OH^-)} = \frac{[OH^-]^2_{(o)}\gamma_\pm^2}{(R_4N^+)(OH^-)} \qquad (3')$$

where brackets signify concentration and parentheses indicate activities, and $[OH^-]_{(o)}$ is the concentration of the hydroxide species in the organic phase.

Similarly, to determine the number of alcohol molecules coordinated in the extracting species, the equilibrium aqueous phase base concentration can be held fixed and the extraction studied as a function of the equilibrium alcohol concentration in the organic phase. With this condition, eqs. (2) and (2') simplify to

$$K'' = \frac{[R_4N^+ \ldots OH^- \cdot nROH]\gamma}{(ROH)^n} = \frac{[OH]_{(o)}\gamma}{(ROH)^n} \qquad (4)$$

$$K'' = \frac{[R_4N^+][OH^- \cdot nROH]\gamma_\pm^2}{(ROH)^n} = \frac{[OH^-]^2_{(o)}\gamma_\pm^2}{(ROH)^n} \qquad (4')$$

In the majority of the experiments performed in this study only low concentrations of alcohol were used, and so it was not necessary to take into account the possible organic phase dimerization of the large alcohol molecules employed.[13] Furthermore, only a small fraction of these alcohol molecules were involved in the extracted complex, so that the organic phase essentially retained the properties

of the diluent. Changing the concentration of the alcohol should then have only a small effect on its activity coefficient, permitting alcohol concentrations to be substituted for activities in eqs. (4) and (4').

Benzene Systems. In a solvent with as low a dielectric constant as benzene ($\epsilon = 2.3$), it might be expected that the extracting ions associate as ion-pairs.[14,15] To prove that this was the case, the extraction was studied as a function of the aqueous tetraalkyl ammonium hydroxide concentration at a fixed alcohol concentration. Assuming for the moment that activities can be replaced by concentrations, it can be seen that eq. (3) requires a second power dependence of $[OH^-]_{(o)}$ on the aqueous phase tetraalkyl ammonium hydroxide concentration while eq. (3') requires a first power dependence. Figure 1 shows a log-log plot of $[OH^-]_{(o)}$ vs aqueous tetrahexyl ammonium hydroxide, THAH, for the extraction by 0.10 M benzyl alcohol in benzene. It can be seen that a slope of 2 is indicated for the more dilute aqueous solutions, but these data must be corrected to a constant equilibrium concentration of uncoordinated benzyl alcohol in order to satisfy the requirement of eqs. (3) and (3'). This has been done in column 4 of Table I by calculating a corrected organic phase hydroxide concentration, $[OH^-]'_{(o)}$, by means of the expression $[OH^-]'_{(o)} = [OH^-]_{(o)}[ROH]'^3/[ROH]^3$, where the primed quantities refer to the condition of constant alcohol concentration and the unprimed quantities are the experimental values actually determined (constant initial alcohol concentration, rather than a constant value at equilibrium). This third power relationship comes from the results described in a later paragraph. The corrected values, $[OH^-]'_{(o)}$ are also plotted in Fig. 1, and a straight line of slope 2.0 is drawn through them. It can be seen that the points follow this line up to about 0.07 M base, after which the points start to level off and increasingly fall below the line.

The fact that the corrected points determine a line of slope 2.0 indicates that the extracting THAH-alcohol complex is an ion-pair, as expected. The fall-off in the extraction at higher aqueous concentrations seems to us to suggest the

onset of micelle formation by the THAH in the water solution. Once the critical micelle concentration is passed and micelles form, the activity coefficient of the aqueous THAH decreases and extraction should deviate from the slope determined by the more dilute solution. To show, in fact, that this deviation in extraction behavior is an aqueous phase effect, the extraction was repeated at a lower initial benzyl alcohol concentration, and also with a different alcohol. Figure 1 shows the experimental points for the extraction with 0.10 M decyl alcohol and Fig. 2 shows the data for 0.075 M benzyl alcohol. Again the corrected values of the organic phase hydroxide concentration, $[OH^-]'_{(o)}$, for aqueous concentrations below 0.07 M, determine straight lines of slope 2.0 in the log-log plots, indicating an ion-paired species. But again the points deviate beyond that concentration, and in a parallel manner, even though the magnitude of extraction and the organic phase base concentrations are quite different.

As a final indication that this fall-off in extraction at high aqueous tetraalkyl ammonium hydroxide concentration is due to micelle formation in that phase, and to observe the effect of cation size on the extraction, a similar set of extractions were performed using tetrapentyl ammonium hydroxide, TPAH, and 0.10 M benzyl alcohol. The corrected values of $[OH^-]'_{(o)}$ from column 4, Table IV are plotted vs aqueous TPAH concentration in Fig. 2, and again a straight line of slope 2.0 can be drawn through the points. Aqueous phase micelle formation with the smaller TPAH would be expected to occur only at a higher aqueous concentration than with THAH, and only above an aqueous concentration of 0.2 M do the points begin to deviate.

Now that it has been established that eq. (1), rather than (1'), represents the reaction for the extraction into systems using benzene as a diluent, the dependence of the extracting species on alcohol can be determined. Equation (4) shows that a log-log plot of the organic phase tetraalkyl ammonium hydroxide concentration vs the equilibrium (uncomplexed) organic phase alcohol concentration should give a straight line whose slope yields n, the number of alcohol

molecules involved in the complex. Table V gives the data necessary for such a plot for benzyl alcohol and an initial aqueous THAP concentration of 0.162 M. But since a varying amount of the base extracts, these results must be corrected to a constant equilibrium value of the aqueous base concentration in order to satisfy the requirement of eq. (4). This can be done directly from the curves in Figs. 1 and 2, and the corrected values of $[OH^-]_{(o)}$ are given in column 4 of Table V and are plotted in Fig. 3. (Because the extraction does not vary much with aqueous THAH concentration in the region around 0.16 M THAH, these corrections are negligible in this case.) It can be seen that this line leads to a value of n = 2.6, suggesting that three alcohol molecules are involved per OH^-. But if so, the amount of alcohol corresponding to three times the extracted base concentration should be subtracted from the initial alcohol concentration at each point to give the true equilibrium alcohol concentration in the organic phase. These corrected equilibrium concentrations, are given in column 5 of Table V, and are plotted as solid triangles in Fig. 3. This final set of points satisfies the conditions for eq. (4) and yields a slope of n = 2.94.

Similarly, Fig. 3 also shows a plot of extracted base vs organic phase benzyl alcohol concentration for 0.305 M TPAH, and Fig. 4 shows the plot for benzyl alcohol in benzene and 0.062 M THAH. In both of these cases, a slope of 3.0 is obtained when the data are corrected to the equilibrium concentration of uncomplexed alcohol, again indicating that three molecules of alcohol are complexed by each extracted ion-pair of the base.[16] It should be noted that no extraction of the bases was observed into pure benzene, and that eq. (4) with n = 3 is the origin of the third-power correction to a constant alcohol concentration used earlier.

Nitrobenzene systems. In order to show that this ratio of three alcohols per OH^- is valid for a wider class of base-solvent systems, and, in particular, to observe the extraction into a solvent of relatively high dielectric constant where the ionic complex may dissociate, the extraction into nitrobenzene (ϵ = 35)

was studied. As will be discussed later, such a high dielectric constant not only causes the dissociation of the extracted complex, but also increases the extraction tremendously over that into a low dielectric constant solvent such as benzene. This makes possible the use of smaller substituted ammonium cations, and, in fact, requires their use, as extraction into the solvent alone becomes appreciable with cations as large as THA and TPA. So the extraction of tetrapropyl ammonium hydroxide, TPrAH, and mainly of tetrabutyl ammonium hydroxide, TBAH, was studied, and even with these a correction for extraction into the pure solvent had to be applied.

With nitrobenzene we might expect eqs. (1'),(2'), (3') and (4') to apply; to test whether the extracted species is indeed dissociated, the extraction of TBAH was studied as a function of the aqueous base concentration, holding the initial organic phase benzyl alcohol concentration constant at 0.075 M. The plot of the raw data given in columns 1 and 2 of Table VIII and shown as open circles in Fig. 5 has a slope of 1 over the entire range of concentration studied as required by eq. (3'), and suggesting that the extracted ions are indeed dissociated. But to strictly comply with the requirements of eq. (3') these data must be corrected to a constant equilibrium concentration of uncomplexed alcohol, and the change in aqueous phase and organic phase activity coefficients for the base must also be considered. The correction to a constant equilibrium alcohol concentration can be made from the expression

$$[OH^-]'_{(o)} = [OH^-]_{(o)}[ROH]'^{3/2}/[ROH]^{3/2},$$

obtained in a following paragraph (eq. (4') with n = 3), and the organic base concentrations so obtained are listed in column 4 of Table VIII. The corrections for the activity coefficients are more difficult, since no experimental data are available for either phase. In the range of concentrations of TBAH in nitrobenzene used, around 10^{-3} M, certainly the most important effect on an ion is that of the surrounding ion environment, and so an extended Debye-Hückel expres-

$$\log y^{\pm} = -\frac{A|Z_1Z_2|\sqrt{I}}{1 + B\,\mathring{a}\sqrt{I}} - \log\left[1 + 0.001\,\frac{M}{d_o}\,(\nu W_A - W_B)\right]$$

might be expected to give a fair approximation to the mean ion activity coefficient. In this expression, I is the ionic strength, Z_1 and Z_2 are the ionic charges, $A = \frac{1.82 \times 10^6}{(\epsilon T)^{3/2}}$ (mole/l)$^{-1/2}$(deg K)$^{3/2}$, $B = \frac{50.29}{(\epsilon T)^{1/2}}$ Å^{-1}(mole/l)$^{-1/2}$(deg K)$^{3/2}$, W_A is the molecular weight of the solvent and W_B that of the solute, M is the molarity of the solute, ν is the number of moles of ions formed per formula weight of the solute, d_o is the density of the nitrobenzene (and is also assumed to be the density of the dilute solutions used) and $\mathring{a}$ is the distance of closest approach parameter.[17] For nitrobenzene, $\epsilon = 35.6$ and $T = 295$, and so the values of A and B are 1.70 and 0.490 respectively. The difficulty is in estimating the value of $\mathring{a}$ to use. In any case the result is to partially overcome the increase due to the correction to a constant equilibrium alcohol concentration. For a not unreasonable value of $\mathring{a}$ (but perhaps too small a one), $\mathring{a} = 4.0$ Å, the alcohol correction is almost exactly compensated for. Column 5 of Table VIII lists the corrected equilibrium mean base activity in the organic phase and these are plotted as filled circles in Fig. 5. It can be seen that they are not greatly different from the open circles of column 2, the uncorrected equilibrium base concentrations.

The effect of aqueous phase activity coefficients for TBAH is more difficult to estimate, as in the range of concentration employed, 10^{-2}-10^{0} M, the activity coefficient is most likely not a monotonically decreasing function of the concentration. But the changes are probably not very large in this range; the coefficient decreases slightly (about 15%) from 2×10^{-2} M to a concentration of a few tenths molar and then increases.[18] All of the corrections taken together just about cancel each other, and so the final result, is this case at least, must be similar to the original data given in columns 1 and 2 of Table VIII. Certainly the conclusion that a slope of unity is obtained and that the extracted species is in the form of two dissociated ions is beyond change by the corrections.

This means that eq. (4') should be used to determine the value of n, the

of the extraction on alcohol concentration in nitrobenzene. In Table IX are the experimental data for the extraction of TBAH from an initially 0.437 M aqueous solution into various dilute benzyl alcohol solutions in nitrobenzene. But again these data must be corrected to a constant equilibrium value of the aqueous base concentration to satisfy the requirement of eq. (4'). This has been done assuming the first power dependence of $[OH^-]_{(o)}$ on aqueous $[OH^-]$ indicated in Fig. 5, and the results are listed in column 4 of Table IX and shown as open circles in the log-log plot of Fig. 6. It can be seen in that figure that a line of slope 1.5 passes through the points, again indicating, as with the benzene extractions, that three alcohol molecules are bound in the extracted complex per hydroxide; the factor 3/2 rather than 3 comes from the result, already established in the preceding paragraphs, that the species is dissociated into two ions, rather than being an ion-pair as in the benzene solutions of lower dielectric constant. But to rigorously fulfill the conditions necessary for the application of eq. (4') the equilibrium organic phase alcohol concentrations, rather than the initial concentration, should be used, and the organic phase activity coefficients for TBAH should be used. The correction to the unbound alcohol concentration is easily made by subtracting three times the organic base concentration from the initial alcohol concentration, and is listed in column 5 of Table IX. The organic phase TBAH activity coefficients may again be approximated by a Debye-Hückel expression, and the final corrected mean activity, $y_{\pm M}$, (for an $\mathring{a}$ of 4.0 Å) is listed in column 6 of Table IX. A log-log plot of this mean organic phase TBAH activity vs the equilibrium organic alcohol concentration is also shown in Fig. 6 as filled circles, and a slope of 1.5 remains.

In a similar manner the extraction of TBAH into various concentrations of 4-methyl cyclohexanol in nitrobenzene was determined. The original data recorded in Table XI have been corrected as in the benzyl alcohol extractions, and the final corrected results, the filled circles in Fig. 7 again give a slope of 1.5 and again are not very different from the original data.

system, the extraction of TPrAH by several concentrations of benzyl alcohol was also determined. The results are given in Table X, and again the original data in the first three columns must be corrected to a constant equilibrium aqueous base concentration (column 4), to the unbound alcohol concentration (column 5), and for the organic phase activity coefficient of TPrAH (column 6). The results are shown in Fig. 6, and it can be seen that a slope of 1.5 results, and that the extraction is less than that for TBAH by a little more than an order of magnitude. This is a smaller drop with a decrease in size of four-CH_2-groups than was observed in the benzene case.

Thus it can be seen that an alcohol to base ratio of 3 to 1 is obtained in each case for both benzene and nitrobenzene systems. As mentioned in the introduction, it is most unlikely that the tetraalkyl ammonium cations can bind the alcohol molecules, and so it is strongly suggested that the complex is built around the hydroxide ion. In fact, it is reasonable to assign this role to the OH^- ion, as it has three (negative) sites of electrons available for hydrogen-bonding to the alcohol molecules, and these bonds should be far stronger than usual hydrogen-bonds because of the influence of the negative charge on the ion. This is exactly analogous to the enhanced strength of the hydrogen-bonds formed by the H_3O^+ ion as discussed elsewhere.[8,11] The result is a structure for the extracted hydroxide species shown in Fig. 8a. Since the water content of the species was not determined, it is not known whether water molecules occur as bridges between the OH^- ion and the three alcohol molecules, Fig. 8b, as has been suggested for the extraction of the hydronium ion with TBP.[10] Such a trisolvated hydroxide ion is similar to the aqueous phase species suggested by Frank,[2] but differs from the earlier proposal by Ackermann,[1] in not having one of the hydrogen-bonded solvent molecules (H_2O) bound to the hydroxide hydrogen, but only to the three sites of negative charge.

The results of the extraction of TBAH and of TPAH into benzene solutions of alcohol, and of TPrAH and TBAH into nitrobenzene solutions of alcohol show the influence of cation size on the extraction. A larger

cation would be expected to extract better for two reasons. One is that the large hydrophobic cations interfere with the hydrogen-bonded water structure and so tend to be ejected from it into the less structured organic solvent. This effect, the interference of the hydrophobic ion with the water-water interactions, is greater, the larger the ion, for then the greater the interference. The other reason is due primarily to an ion-solvent interaction; the electrostatic free energy opposing the transfer of an ion from a high dielectric constant medium such as water into a low dielectric constant solvent such as benzene will be less the larger the ion. This can be seen most simply from the Born expression[19] for the electrostatic free energy of transfer of ions of charge Z_+ and Z_- and size r_+ and r_- from water into an organic solvent,

$$\Delta F_{elect.} = -\frac{e^2}{2}\left(\frac{Z_+^2}{r_+} + \frac{Z_-^2}{r_-}\right)\left(\frac{1}{\epsilon_W} - \frac{1}{\epsilon_o}\right) \qquad (5)$$

The larger the cationic radius, r_+, the smaller is the positive value of $\Delta F_{elect.}$. Although this positive free energy is partially compensated for by ion-pairing of the cation and anion in low dielectric constant media, the compensation is only partial, and the effect remains.

The magnitude of the increase in extraction into benzene with the addition of four $-CH_2-$groups in going from TPAH to THAH found in this work is about 100, in agreement with the factor 3 per $-CH_2-$group found by Collander for the extraction of a wide variety of organic species from water into diethyl ether.[20]

On the other hand, the present results for the extraction into nitrobenzene media show a smaller effect per $-CH_2-$group. The difference between TPrAH and TBAH is about a factor of 15, or a factor of 2 per $-CH_2-$group. However, this smaller effect is to be expected from eq. (5), as the much larger dielectric constant of nitrobenzene, $\epsilon = 35$, makes the magnitude of $\Delta F_{elect.}$ and the effect of a change in ion size about 30 times smaller than for benzene, $\epsilon = 2.3$.

from water into nitrobenzene rather than into benzene also is the reason for the much better extraction of the bases into nitrobenzene than into benzene solutions. In fact the bases of the larger cations, THAH and TPAH, extract well enough into pure nitrobenzene, without any alcohol present, to make difficult the study of their extraction by the method used in this report; the necessary blank correction for their extraction into the pure solvent becomes too large. But as has been pointed out before,[8] such high dielectric constant media make very good extraction solvents for large ion systems.

In summary it can be said that the present work has established the tri-coordinate nature of the hydroxide ion, similar to that of the hydronium ion. It remains for further studies to determine whether a tri-hydrated species can actually be isolated in the extraction.

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FOOTNOTES AND REFERENCES

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15a) C. A. Kraus and R. M. Fuoss, J. Am. Chem. Soc. 55, 21 (1933).

15b) R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. 55, 1019 (1933).

16. It should be noted that the correction to uncomplexed equilibrium alcohol concentration is not the cause of the value n = 3.0. Making the correction by assuming 2 or 4 molecules of alcohol tied up per hydroxide ion extracted does not lead to slopes of 2.0 or 4.0 respectively, but only to values slightly different from 3.0.

17. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," (Butterworths Scientific Publications, London, 1955).

18. Such an approximate estimate of the bahavior is obtained by extrapolation from the known behavior of the coefficients of CsCl, CsOH, and tetrabutyl ammonium chloride.

19. M. Born, Z. Physik, 1, 45 (1920).

20. R. Collander, Acta Chem. Scand. 3, 717, (1949).

Table I.

Extraction of TMAH into 0.100 M benzyl alcohol in benzene.

Equil. base conc. (aq.)	Equil. base conc. (org.)	Equil. alcohol conc.	Corrected equil. base conc. (org.)
1.36×10^{-1}	8.60×10^{-3}	7.42×10^{-2}	2.11×10^{-2}
9.50×10^{-2}	8.80×10^{-3}	7.36×10^{-2}	2.21×10^{-2}
6.00×10^{-2}	6.96×10^{-3}	7.91×10^{-2}	1.41×10^{-2}
4.50×10^{-2}	5.28×10^{-3}	8.42×10^{-2}	8.85×10^{-2}
3.10×10^{-2}	3.16×10^{-3}	9.05×10^{-2}	4.26×10^{-3}
1.70×10^{-2}	1.10×10^{-3}	9.67×10^{-2}	1.22×10^{-3}
1.39×10^{-2}	7.60×10^{-4}	9.77×10^{-2}	8.06×10^{-4}
9.20×10^{-3}	3.80×10^{-4}	9.89×10^{-2}	3.93×10^{-4}

Table II.

Extraction of THAH into 0.100 M decyl alcohol in benzene.

Equil. base conc. (aq.)	Equil. base conc. (org.)	Equil. alcohol conc.	Corrected equil. base conc. (org.)
1.53×10^{-1}	3.18×10^{-3}	9.05×10^{-2}	4.29×10^{-3}
1.10×10^{-1}	3.48×10^{-3}	8.96×10^{-2}	4.83×10^{-3}
7.45×10^{-2}	2.18×10^{-3}	9.35×10^{-2}	2.67×10^{-3}
3.87×10^{-2}	6.00×10^{-4}	9.82×10^{-2}	6.32×10^{-4}
1.58×10^{-2}	1.20×10^{-4}	9.96×10^{-2}	1.21×10^{-4}

Table III.

Extraction of THAN into 0.075 M benzyl alcohol in benzene.

Equil. base conc. (aq.)	Equil. base conc. (org.)	Equil. alcohol conc.	Corrected equil. base conc. (org.)
1.49×10^{-1}	4.40×10^{-3}	6.18×10^{-2}	7.87×10^{-3}
1.08×10^{-1}	4.64×10^{-3}	6.11×10^{-2}	8.57×10^{-3}
6.92×10^{-2}	3.94×10^{-3}	6.32×10^{-2}	6.59×10^{-3}
5.24×10^{-2}	2.88×10^{-3}	6.64×10^{-2}	4.16×10^{-3}
3.57×10^{-2}	1.60×10^{-3}	7.02×10^{-2}	1.95×10^{-3}
1.86×10^{-2}	4.80×10^{-4}	7.36×10^{-2}	5.08×10^{-4}
1.52×10^{-2}	3.20×10^{-4}	7.40×10^{-2}	3.53×10^{-4}

Table IV.

Extraction of TPAH into 0.100 M benzyl alcohol in benzene.

Equil. base conc. (aq.)	Equil. base conc. (org.)	Equil. alcohol conc.	Corrected equil. base conc. (org.)
5.64×10^{-1}	1.90×10^{-3}	9.43×10^{-2}	2.26×10^{-3}
3.00×10^{-1}	1.82×10^{-3}	9.45×10^{-2}	2.15×10^{-3}
2.24×10^{-1}	1.38×10^{-3}	9.59×10^{-2}	1.57×10^{-3}
1.51×10^{-1}	7.80×10^{-4}	9.77×10^{-2}	8.38×10^{-4}
1.13×10^{-1}	5.00×10^{-4}	9.85×10^{-2}	5.23×10^{-4}
7.53×10^{-2}	2.40×10^{-4}	9.93×10^{-2}	2.45×10^{-4}
5.07×10^{-2}	1.00×10^{-4}	9.97×10^{-2}	1.01×10^{-4}

Table V.

Extraction of 0.162 M THAH into benzyl alcohol in benzene.

Alcohol conc.	Equil. base conc. (org.)	Equil. base conc. (aq.)	Corrected equil. base conc. (org.)	Corrected alcohol conc.
1.50×10^{-1}	2.04×10^{-2}	1.01×10^{-1}	1.8×10^{-2}	8.90×10^{-2}
1.00×10^{-1}	8.60×10^{-3}	1.36×10^{-1}	7.9×10^{-3}	7.42×10^{-2}
7.50×10^{-2}	4.50×10^{-3}	1.48×10^{-1}	4.35×10^{-3}	6.15×10^{-2}
5.00×10^{-2}	1.76×10^{-3}	1.57×10^{-1}	1.7×10^{-3}	4.47×10^{-2}
3.50×10^{-2}	7.60×10^{-4}	1.60×10^{-1}	7.5×10^{-4}	3.27×10^{-2}
2.50×10^{-2}	3.60×10^{-4}	1.61×10^{-1}	3.6×10^{-4}	2.39×10^{-2}

Table VI.

Extraction of 0.305 M TPAH into benzyl alcohol in benzene.

Alcohol conc.	Equil. base conc. (org.)	Equil. base conc. (aq.)	Corrected equil. base conc. (org.)	Corrected alcohol conc.
1.50×10^{-1}	5.40×10^{-3}	2.89×10^{-1}	5.88×10^{-3}	1.34×10^{-1}
1.00×10^{-1}	1.88×10^{-3}	2.99×10^{-1}	1.93×10^{-3}	9.44×10^{-2}
7.50×10^{-2}	1.00×10^{-3}	3.02×10^{-1}	1.01×10^{-3}	7.20×10^{-2}
5.00×10^{-2}	3.60×10^{-4}	3.04×10^{-1}	3.60×10^{-1}	4.89×10^{-2}

Table VII.

Extraction of 0.061 M THAH into benzyl alcohol in benzene.

Alcohol conc.	Equil. base conc. (org.)	Equil. base conc. (aq.)	Corrected equil. base conc. (org.)	Corrected alcohol conc.
1.50×10^{-1}	9.34×10^{-3}	3.30×10^{-2}	3.19×10^{-2}	1.22×10^{-1}
1.00×10^{-1}	5.04×10^{-3}	4.60×10^{-2}	8.92×10^{-3}	8.50×10^{-2}
7.50×10^{-2}	2.90×10^{-3}	5.23×10^{-2}	3.97×10^{-3}	6.63×10^{-2}
5.00×10^{-2}	1.26×10^{-3}	5.72×10^{-2}	1.44×10^{-3}	4.62×10^{-2}
3.00×10^{-2}	3.80×10^{-4}	5.99×10^{-2}	3.94×10^{-4}	2.89×10^{-2}

Table VIII.

Extraction of TBAH into 0.075 M benzyl alcohol in nitrobenzene.

Equil. base conc. (aq.)	Equil. base conc. (org.)	Equil. alcohol conc.	Corrected equil. base conc. (org.)	Corrected equil. mean base activity (org.)
3.70×10^{-1}	6.70×10^{-3}	5.49×10^{-2}	1.08×10^{-2}	8.42×10^{-3}
2.76×10^{-1}	5.02×10^{-3}	5.99×10^{-2}	7.02×10^{-3}	5.61×10^{-3}
2.09×10^{-1}	3.60×10^{-3}	6.64×10^{-2}	4.32×10^{-3}	3.54×10^{-3}
9.24×10^{-2}	1.66×10^{-3}	7.01×10^{-2}	1.84×10^{-3}	1.64×10^{-3}
3.69×10^{-2}	6.80×10^{-4}	7.36×10^{-2}	7.00×10^{-4}	6.51×10^{-4}
1.85×10^{-2}	3.40×10^{-4}	7.40×10^{-2}	3.49×10^{-4}	3.28×10^{-4}

Table IX.
Extraction of 0.437 M TBAH into benzyl alcohol in nitrobenzene.

Alcohol conc.	Equil. base conc. (org.)	Equil. base conc. (aq.)	Corrected equil. base conc. (org.)	Corrected alcohol conc.	Corrected equil. mean base activity (org.)
1.00×10^{-1}	9.40×10^{-3}	3.43×10^{-1}	1.20×10^{-2}	7.18×10^{-2}	9.00×10^{-3}
7.50×10^{-2}	6.70×10^{-3}	3.70×10^{-1}	7.91×10^{-3}	5.49×10^{-2}	6.17×10^{-3}
5.00×10^{-2}	3.95×10^{-3}	3.77×10^{-1}	4.58×10^{-3}	3.82×10^{-2}	3.76×10^{-3}
2.50×10^{-2}	1.40×10^{-3}	4.23×10^{-1}	1.44×10^{-3}	2.10×10^{-2}	1.30×10^{-3}
1.00×10^{-2}	4.00×10^{-4}	4.33×10^{-1}	4.04×10^{-4}	8.80×10^{-3}	3.80×10^{-4}

Table X.

Extraction of 0.475 M TPrAH into benzyl alcohol in nitrobenzene.

Alcohol conc.	Equil base conc. (org.)	Equil. base conc. (aq.)	Correct equil. base conc. (org.)	Corrected alcohol conc.	Corrected equil. mean base activity (org.)
8.84×10^{-1}	2.21×10^{-2}	3.53×10^{-1}	2.98×10^{-2}	8.18×10^{-1}	1.95×10^{-2}
4.65×10^{-1}	8.35×10^{-3}	4.31×10^{-1}	9.19×10^{-3}	4.38×10^{-3}	6.98×10^{-3}
2.37×10^{-1}	3.35×10^{-3}	4.58×10^{-1}	3.48×10^{-3}	2.27×10^{-1}	2.89×10^{-3}
9.62×10^{-2}	8.50×10^{-4}	4.71×10^{-1}	8.58×10^{-4}	9.36×10^{-2}	7.89×10^{-4}

Table XI.

Extraction of 0.437 TBAH M into 4-methyl cyclohexanol in nitrobenzene.

Alcohol conc.	Equil. base conc. (org.)	Equil. base conc. (aq.)	Correct equil. base conc. (org.)	Corrected alcohol conc.	Corrected equil. mech base activity (org.)
4.00×10^{-1}	5.60×10^{-3}	3.81×10^{-1}	6.44×10^{-3}	3.83×10^{-1}	5.13×10^{-3}
3.00×10^{-1}	3.80×10^{-3}	3.99×10^{-1}	4.18×10^{-3}	2.89×10^{-1}	3.43×10^{-3}
2.00×10^{-1}	2.06×10^{-3}	4.16×10^{-1}	2.16×10^{-3}	1.94×10^{-1}	1.91×10^{-3}
1.00×10^{-1}	8.00×10^{-4}	4.29×10^{-1}	8.16×10^{-4}	9.76×10^{-2}	7.42×10^{-4}
5.00×10^{-2}	2.80×10^{-4}	4.34×10^{-1}	2.82×10^{-4}	4.92×10^{-2}	2.62×10^{-4}

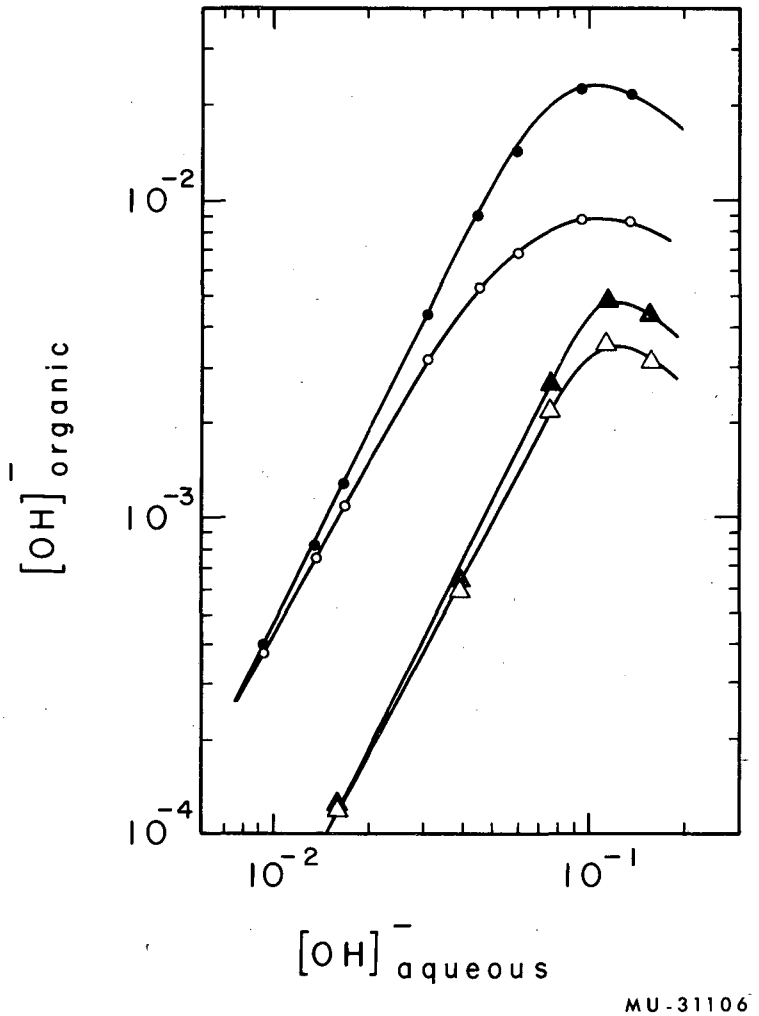

Fig. 1. Extraction of OH^- into benzene from varying concentrations of THAH: O initial benzyl alcohol conc. of 0.100 M, ● corrected values for an equilibrium benzyl alcohol conc. of 0.100 M; △ initial decyl alcohol conc. of 0.100 M, ▲ corrected values for an equilibrium decyl alcohol conc. of 0.100 M.

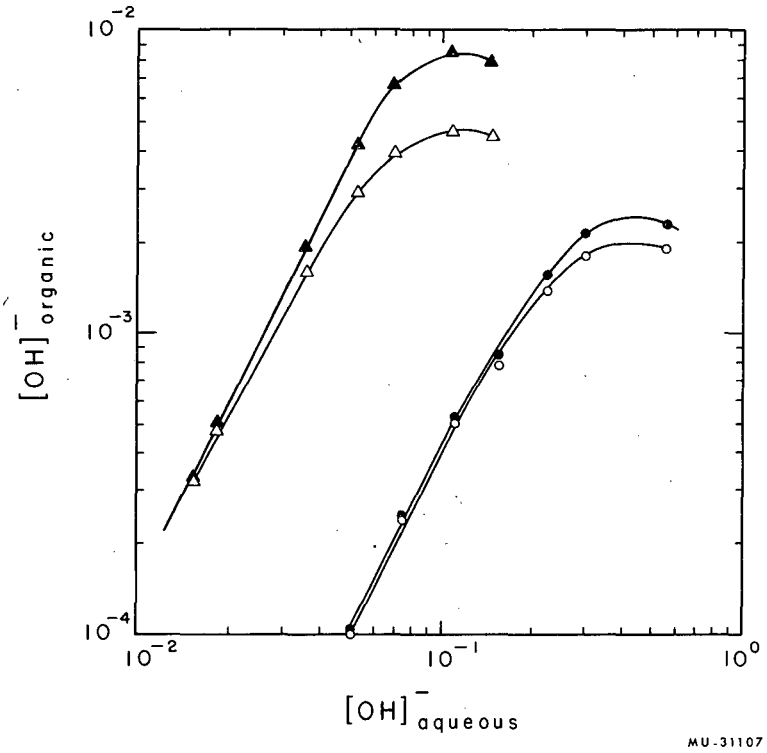

Fig. 2. Extraction of OH^- into benzene from varying concentrations of TPAH and THAH; O TPAH and an <u>initial</u> benzyl alcohol conc. of 0.100 M, ● TPAH and corrected values for an <u>equilibrium</u> benzyl alcohol conc. of 0.100 M; △ THAH and an <u>initial</u> conc. of benzyl alcohol of 0.075 M, ▲ THAH and corrected values for an <u>equilibrium</u> benzyl alcohol conc. of 0.075 M.

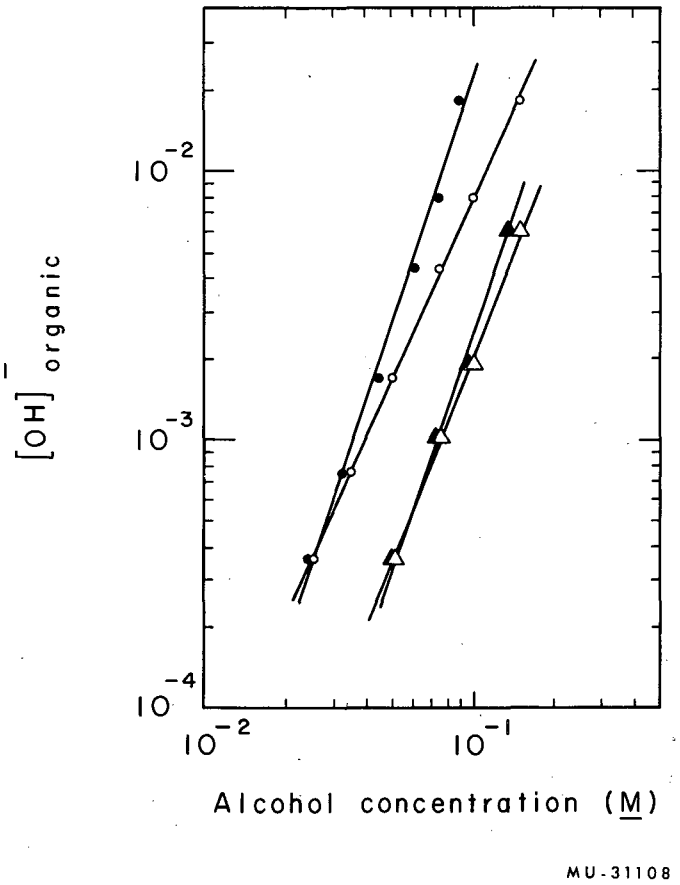

Fig. 3. Extraction of OH^- into benzene: O 0.162 M THAH and varying initial concentrations of benzyl alcohol, ● corrected to concentrations of unbound benzyl alcohol; △ 0.305 M TPAH and varying initial concentrations of benzyl alcohol, ▲ corrected to concentrations of unbound alcohol.

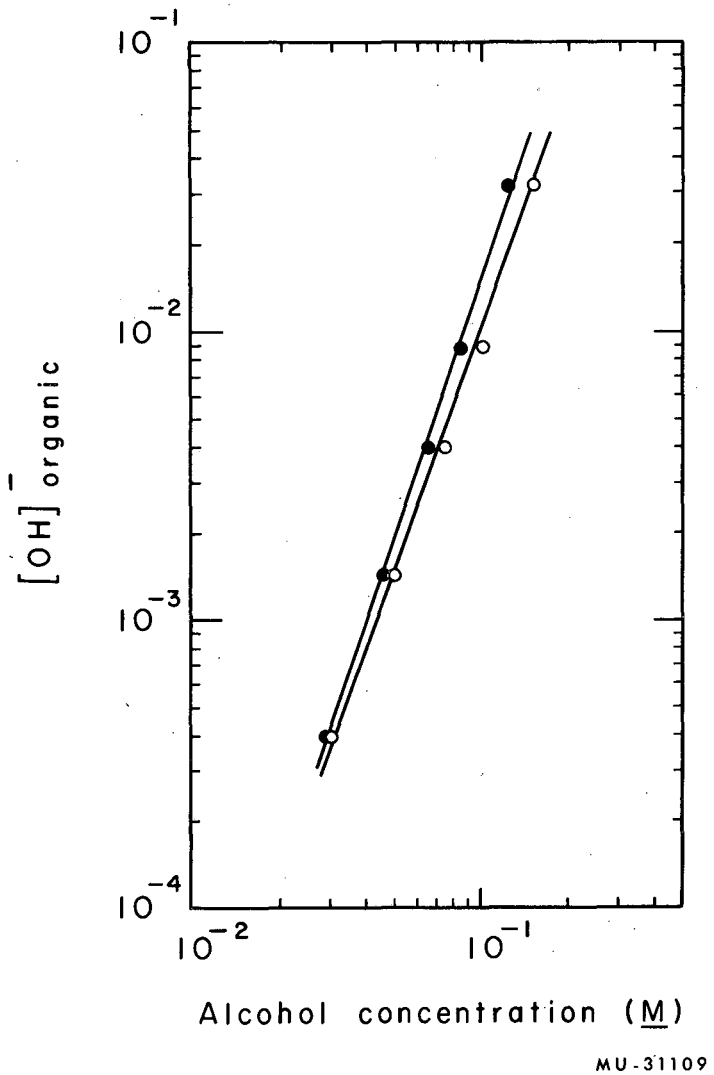

Fig. 4. Extraction of OH^- into benzene from 0.061 M THAH: O varying initial concentrations of benzyl alcohol, ● corrected to concentrations of unbound benzyl alcohol.

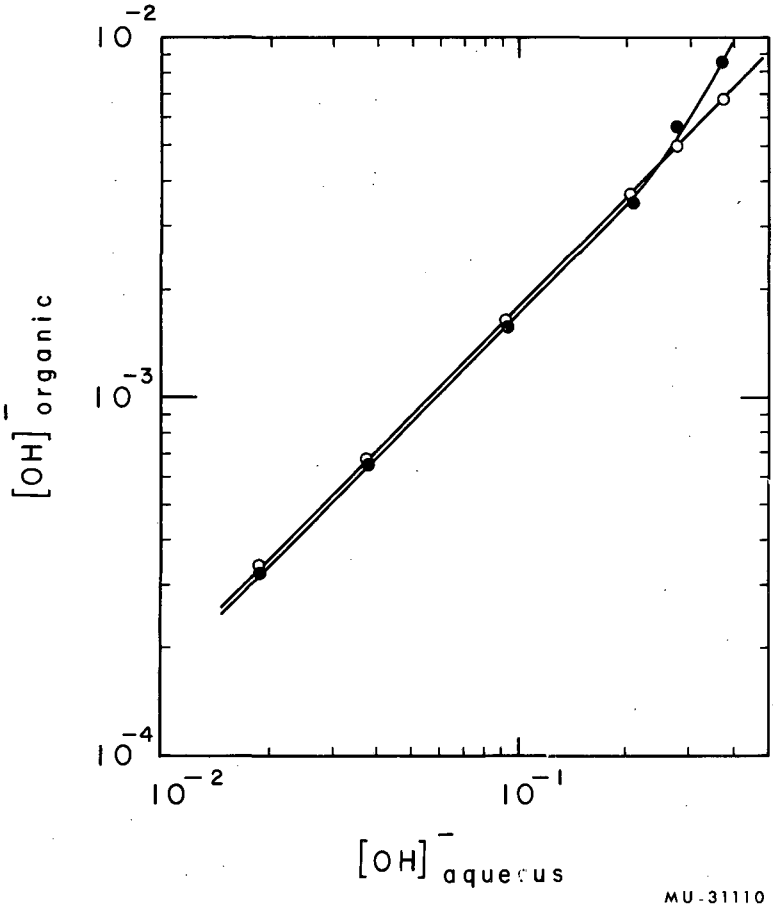

Fig. 5. Extraction of OH^- into nitrobenzene from varying concentrations of TBAH: O initial benzyl alcohol conc. of 0.075 M, ● corrected values for an equilibrium benzyl alcohol conc. of 0.075 M.

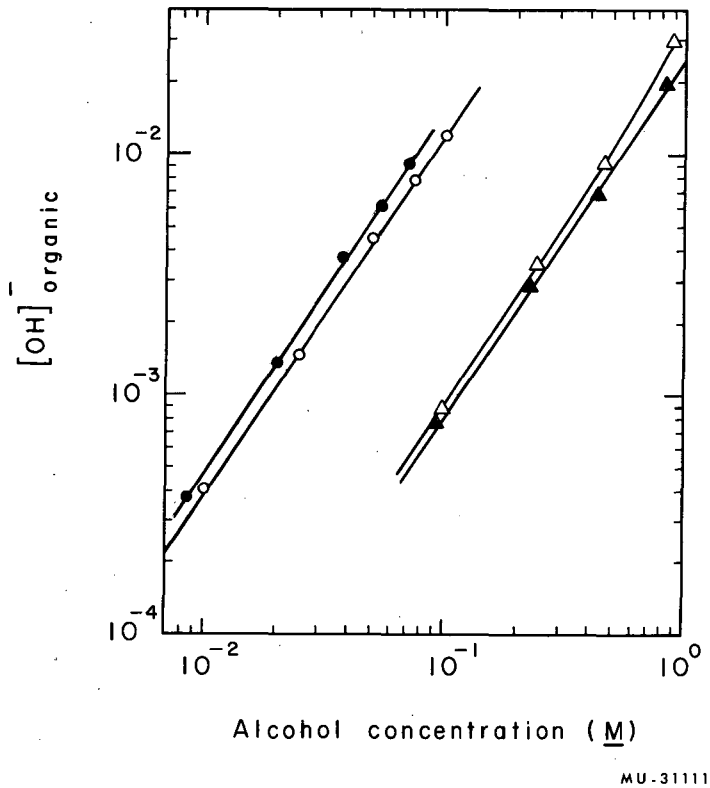

Fig. 6. Extraction of OH^- into nitrobenzene: O from 0.437 M TBAH and varying initial concentrations of benzyl alcohol, ● corrected to concentrations of unbound benzyl alcohol and for organic phase TBAH activity coefficients; △ from 0.47 M TPrAH and varying initial concentrations of benzyl alcohol, ▲ corrected to concentrations of unbound benzyl alcohol and for organic phase TPrAH activity coefficients.

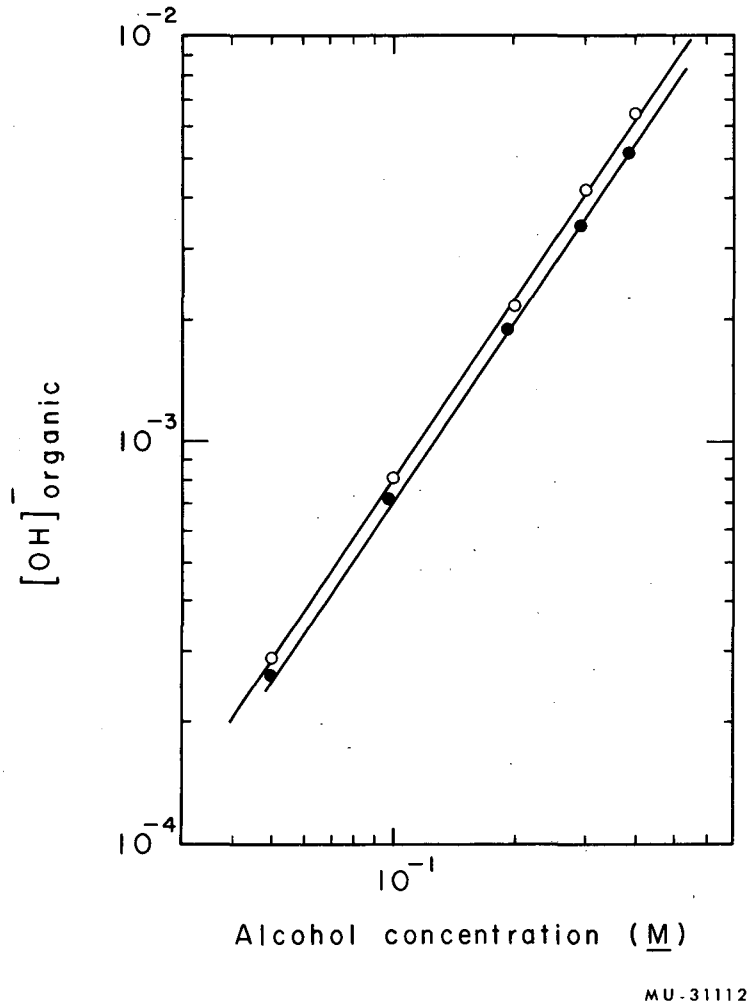

Fig. 7. Extraction of OH^- into nitrobenzene from 0.437 M TBAH: O varying initial concentrations of 4-methyl cyclohexanol, ● corrected to concentrations of unbound alcohol and for organic phase TBAH activity coefficients.

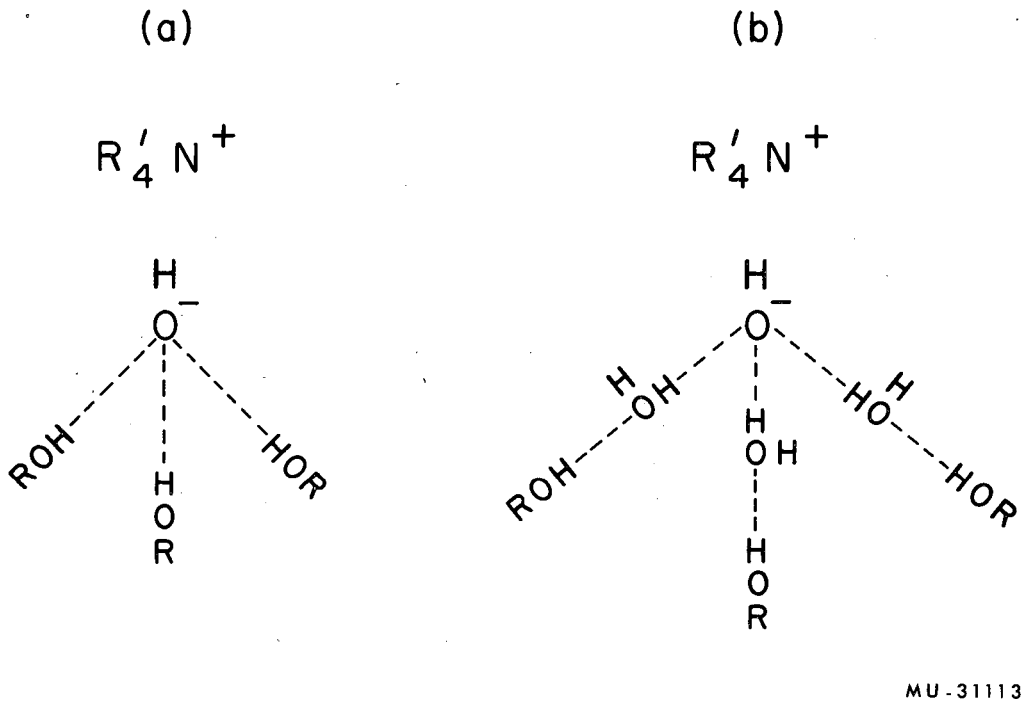

Fig. 8. (a) Suggested structure for the extracted hydroxide species, (b) structure for the extracted hydroxide if water molecules occur as bridges between OH^- ion and alcohol molecules.

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