509. *Solvent Extraction Studies. Part V.*[1] *The Relative Extractability of Acids into Basic Organic Solvents.*

By D. G. Tuck.

The factors which can affect the distribution of an acid between its aqueous solution and an organic solvent are discussed in terms of the various acid–base phenomena involved. This approach emphasises the strong influence of the basicity of the organic solvent, and of the hydrophilic (or hydrophobic) properties of the anion. Such factors govern both the distribution coefficient and the nature of the species in the organic phase. Experimental results with a variety of acids, and published records, are shown to be in agreement with these concepts.

Some of the factors which govern the solvent extraction of small covalent molecules have been discussed by Diamond and Tuck,[2] who have emphasised the importance of the size and hydration of the partitioning species. It is believed that the solvent extraction of acids can be explained qualitatively in similar terms; the extraction of a series of simple mineral acids has been studied to investigate the effect of acid strength, molecular size, hydration, etc.

Species in the Organic Phase.—The quantity obtained experimentally, the distribution coefficient, can be written as

$$D_{\mathrm{H}} = \frac{\text{Total concn. of all acidic species in the organic phase}}{\text{Total concn. of all acidic species in the aqueous phase}}.$$

Of the possible acidic species, the bare proton cannot exist in aqueous solution because of its high solvation energy,[3] and the simplest species generally considered is H_3O^+, though

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[1] Part IV, *Trans. Faraday Soc.*, 1961, **57**, 1297.

[2] Diamond and Tuck, *Progr. Inorg. Chem.*, 1961, **2**, 109.

[3] Bell, " The Proton in Chemistry," Methuen, London, 1959, p. 24.

there is both experimental[4] and theoretical[5] evidence for the stability of the trihydrated hydronium ion, $H_9O_4^+$, in aqueous solution. It seems a reasonable assumption that the most stable acidic species in the organic phase are (solvated) HX, H_3O,X, and H_9O_4,X. The work of Brown and Mathieson[6] implies that association processes in the organic phase can be ignored with basic solvents.

What determines which acidic species predominates in the organic phase? If a bare (*i.e.*, unsolvated) proton is placed at the interface of a two-phase system S–H_2O, together with, but separate from, an anion X^-, the solvation energy of the proton will be dissipated by interaction with the three competing bases, S, H_2O, and X^-. The basicity of X^- is given by $-pK_{HX}$, so that the stronger an acid is HX, the more will H^+ interact with S and H_2O. For a given organic base then, strong acids will take more water into the organic phase than do weak acids (see Results). With very strong bases the proton may be completely neutralised by S ($+ X^-$), and anhydrous S,HX will then predominate in the organic phase. More than one species may, however, exist in the organic phase in certain solvents, and there seems no reason to deny that all hydration numbers between 0 and 4, representing the appropriate average of S,HX, S,H_3O,X, and S,H_9O_4,X, are possible.[7]

Factors Affecting the Distribution Coefficient D.—The extraction of an acid HX implies the successful competition of S against H_2O at the interface, so that values of the distribution coefficient D should only be compared where the acids have the same solvation state in the organic phase. From the model above, three important factors affecting D can be identified: (i) Acid strength. Weak acids should be extracted better than strong acids, for two reasons. First, the H^+–X^- affinity is obviously stronger with weak acids; secondly, the greater is the tendency to form neutral HX molecules in the aqueous phase, the more does the aqueous phase reject HX (see below). (ii) Anion hydration. If X^- is strongly hydrated, ($H^+ + X^-$) must tend to go into the aqueous phase, thus reducing D. This assumes that anions are not solvated in the organic phase; evidence in favour of this has been discussed in ref. 4. If HX is a weak acid, hydration will be minimal and the aqueous phase will reject the acid, giving high values of D. (iii) Anion size. Insertion of X^- into the aqueous phase requires energy for the formation of a hole in the water structure, and this process is clearly size-dependent.

EXPERIMENTAL

Materials.—All the acids used were of "AnalaR" grade. Water was ion-exchanged water. Tri-n-butyl phosphate was purified by the method described elsewhere.[8] Di-isopropyl ketone was shaken with chromatographic alumina and then fractionally distilled, the fraction of b. p. at 123—125° being collected. This had the recorded value for η_D^{20}; vapour-phase chromatography showed that any impurities present amounted to $<0{\cdot}3\%$. Di-isopropyl ether and Dibutylcellosolve were as described elsewhere.[4,9]

The experimental methods were those described in earlier papers.[8,10]

RESULTS AND DISCUSSION

In order to extend the results in the literature, measurements have been carried out with tributyl phosphate (TBP), as a fairly strong organic base, and with di-isopropyl ketone (DIPK) and Dibutylcellosolve (DBS). The last two are less strongly basic (see Gordy and Stanford[11]), and were chosen in preference to other ethers and ketones because of their low mutual miscibility with water.

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[4] See Tuck and Diamond, *J. Phys. Chem.*, 1961, **65**, 193, for a review.

[5] Grahn, *Arkiv Fys.*, 1961, **19**, 147; 1963, **21**, 1, 13.

[6] Brown and Mathieson, *J. Phys. Chem.*, 1954, **58**, 1057.

[7] McKay, *J. Inorg. Nuclear Chem.*, 1957, **4**, 375.

[8] Tuck, *J.*, 1958, 2783.

[9] Tuck, *Analyt. Chim. Acta*, 1959, **20**, 159.

[10] Tuck, *J.*, 1957, 3202.

[11] Gordy and Stanford, *J. Chem. Phys.*. 1939, **7**, 93; 1940, **8**, 170; 1941, **9**, 204, 215.

The nature of the extracted species in these solvents has been previously discussed,[4] and in summary is denoted by the following species.

TBP,HNO_3
$TBP.CCl_3{\cdot}CO_2H$
$DBS.H_3O.NO_3$
$DBS,H_3O.CCl_3{\cdot}CO_2H$
$TBP.H_9O_4.Br$
TBP,H_9O_4,Cl
$TBP.H_9O_4.ClO_4$
$DIPK.H_9O_4.ClO_4$
$DBS.H_9O_4.ClO_4$

Fig. 1 shows that in di-isopropyl ketone, the species extracted from aqueous nitric acid solution has $\Delta V = 0{\cdot}050$ ml. per mmole of nitric acid extracted, so that the ratio $HNO_3 : H_2O$ in the extracted species is 1 : 0·93. Within the accuracy of the experiment then, one can say that the species in the organic phase are $DIPK,H_3O,NO_3$ and $DIPK,HNO_3$, in ~20 : 1 ratio. This shows close agreement with the result for Dibutylcellosolve[4] and with the $1 : 1$ $HNO_3 : H_2O$ ratio found for Dibutylcarbitol.[10] With trichloroacetic acid the ΔV graph gives a slope of 8·34 mmoles/ml., to be compared with that of 8·95 found with Dibutylcellosolve,* so that here again this ether and ketone behave similarly, with $H_2O : CCl_3{\cdot}CO_2H = {\sim}0{\cdot}9 : 1$. All these results then agree with the model proposed.

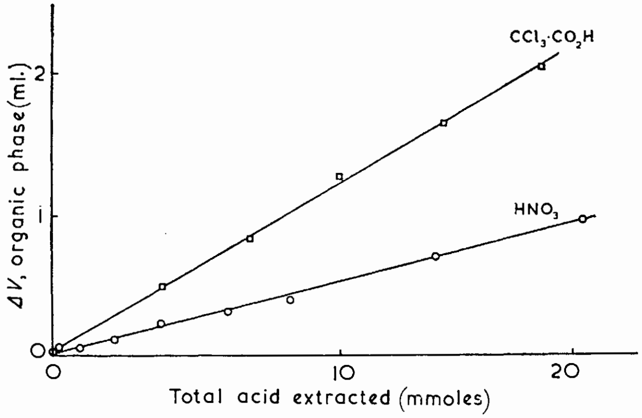

FIG. 1. Volume changes in di-isopropyl ketone due to the extraction of trichloroacetic and nitric acid.

The number of solvent molecules attached to strong acids in the organic phase is assumed to be unity at high acid concentration but may well be concentration-dependent. The structure of the $H_9O_4^+$ cation is such that a maximum of three large basic organic molecules can be hydrogen-bonded to it, so that if the concentration of H_9O_4,X in the organic phase is sufficiently low, one finds the species $(TBP)_3H_9O_4,X$. Such a complex has indeed been identified in the extraction of tetrachloroauric(III) and other strong acids.[12-15] In fact, however, there must be three equilibria:

$$3TBP + H_9O_4^+ + X^- \rightleftharpoons (TBP)_3H_9O_4,X$$
$$2TBP + H_9O_4^+ + X^- \rightleftharpoons BP)_2H_9O_4.X$$
$$TBP + H_9O_4^+ + X^- \rightleftharpoons TBP,H_9O_4.X$$

Without a knowledge of the mass-action constants K, the proportion of each solvate cannot be determined, but it is clear that as the $HX : TBP$ ratio increases, the lower solvates must be increasingly favoured. This situation will not, of course, apply where the species in the organic phase is S,HX.

These comments are relevant to a discussion of the different interpretations placed on

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* There is a misprint in ref. 4, where this slope is given as 9·95 mmoles/ml.

[12] Tuck, *J. Inorg. Nuclear Chem.*, 1959, **11**, 164.
[13] Diamond and Tuck, UCRL-8897 (1959).
[14] Diamond, personal communication.
[15] Tuck and Walters, *J.*, 1963, 1111.

similar results for the TBP–HCl and TBP–HBr systems by Tuck and Diamond[4] and by Kertes and Kertes.[16] The latter authors measured the increase in the volume of the organic phase, and from the results identified the formation of species $(TBP)_2HX(H_2O)_6$ (X = Cl or Br) at low organic phase acidities and $TBP,HX(H_2O)_3$ at high acidities. The TBP disolvate is reasonably explained in terms of the above argument. In the view of the present author, however, the accuracy of the volume-change method is not high enough to justify the straight-line plots drawn by Kertes and Kertes, especially since the sharp changes in hydration which these plots imply have no apparent physical justification in terms of known behaviour of organic or aqueous phases. It is true, of course, as Tuck and Diamond[4] pointed out, that with increasing acid concentration in the aqueous phase, the amount of available water eventually falls below that required for complete hydration of H^+ $(+ X^-)$, and at this stage the ratio H_2O : HX in the organic phase must fall below 4 : 1; tributyl phosphate may even enter the primary hydration shell of the hydronium ion, giving organic-phase species of the type $[(TBP)_n(H_2O)_{3-n}H_3O]^+X^-$, etc. There is, however, no unique point at which this type of solvation takes over sharply from the more usual behaviour. Kertes's explanation of the experimental results is, therefore, not believed to be justified, and that given previously[4] by us is still preferred.

The Order of Extraction of Acids.—Fig. 2 shows results for the extraction of trichloroacetic, nitric, perchloric, hydrobromic, hydrochloric, orthophosphoric, and sulphuric acid into the di-isopropyl ketone. Similar data for Dibutylcellosolve are shown in Fig. 3; with this solvent, a second organic phase is formed with hydrogen chloride and bromide at all those acid concentrations where extraction from the aqueous phase is detectable. It might be argued that activities in the aqueous phase should be plotted instead of concentrations, but, since the activity coefficients are not known for either the acid species or the solvent in the organic phase, this would in fact give no greater insight into the problem.

For the weaker acids studied, the order of extraction is clearly $CCl_3{\cdot}CO_2H > HNO_3 > H_3PO_4$ in all three solvents. For the stronger acids, extraction into di-isopropyl ketone gives $HClO_4 > HBr > HCl > H_2SO_4$. With the more basic tributyl phosphate (Fig. 4), there is a general rise in the extraction of those acids which are extracted only poorly into the ketone. In terms of the model of acid-base interactions, we can see this as a " levelling effect " which tends to overcome the effects of anion size and hydration. The general order is, however, still maintained, with $CCl_3{\cdot}CO_2H > HNO_3 > H_3PO_4$ for the weaker acids, and $HClO_4 > HBr > HCl > H_2SO_4$, at low values of D. With increasing extraction, the values of D converge (and even change order), but this occurs only when the aqueous phase has become so concentrated that the simple model used breaks down. This limitation apart, the order of extraction shows the general effect of increasing anion size, except where this is overcome by anion hydration (H_2SO_4, H_3PO_4). Thus, for the three weaker acids, the molar volumes (taken simply from $M/d_{\text{liq.}}$) are 101, 42, and 53·5 ml. for trichloroacetic, nitric, and phosphoric acid, respectively; if the anions are written as $CCl_3{\cdot}CO_2^-$, NO_3^-, and $PO_2(OH)_2^-$, the presence of two potentially strong hydrogen-bonding hydroxyl groups emphasises the hydrophilic nature of the phosphate. Results in the literature (see below) also show that hydration is more important than size in this respect.

In the di-isopropyl ketone series, both hydrochloric and hydrobromic acid are extracted an order of magnitude less than perchloric, and in view of the comments on the series $CCl_3{\cdot}CO_2H > HNO_3 > H_3PO_4$, it seems likely that hydration is important here too. The primary hydration numbers derived by Glueckauf,[17] namely, ClO_4^- 0·3, $Br^- \approx Cl^- =$ 0·9, support this view, as does the following experiment. With Dibutylcellosolve, both hydrochloric and hydrobromic acid readily form a " third phase " whenever appreciable

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[16] Kertes, *J. Inorg. Nuclear Chem.*, 1960, **14**, 104; Kertes and Kertes, *Canad. J. Chem.*, 1960, **38**, 612.

[17] Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 1235.

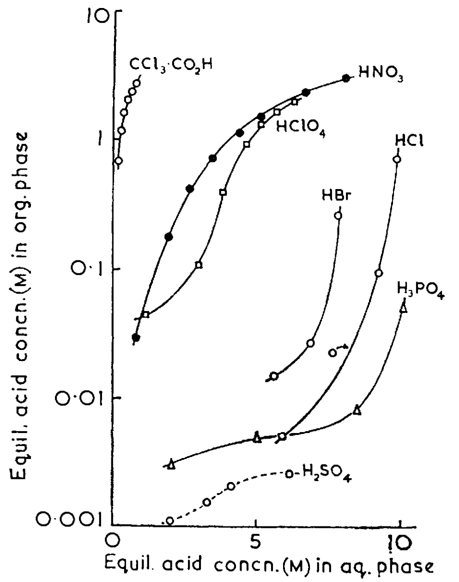

FIG. 2. Extraction of acids into di-isopropyl ketone.

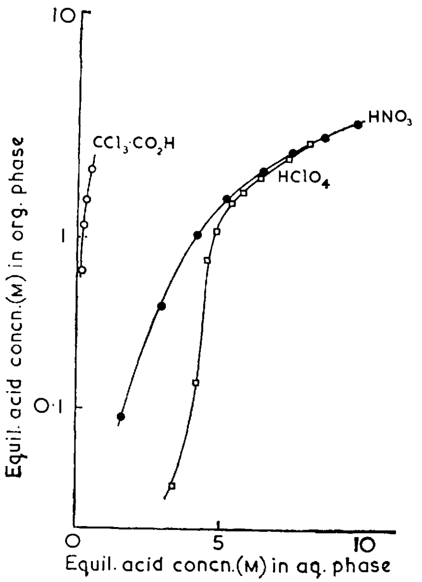

FIG. 3. Extraction of acids into Dibutylcellosolve.

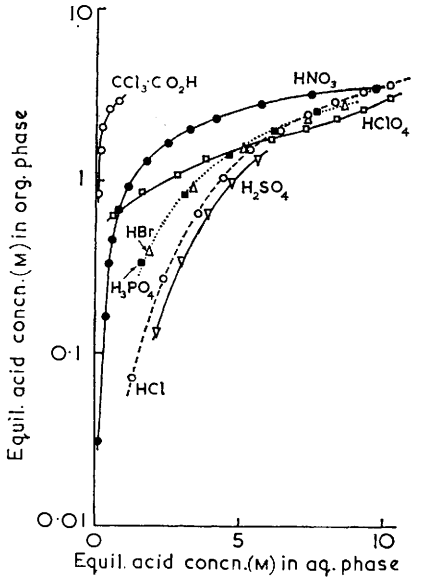

FIG. 4. Extraction of acids into tri-n-butyl phosphate. Only one curve has been drawn through the results for HBr (. . . △ . . .) and H_3PO_4 (. . . ■ . . .).

extraction occurs (8·2M-HBr, 10·1M-HCl). Concentrated hydrochloric acid and an equal volume of solvent were shaken together, and the third phase just dissolved by dropwise addition of water to the system. Solid calcium chloride (~1 g.) was then added and the system re-equilibrated; the third phase now constituted ~40% of the total organic volume. This is ascribed to the lowering of the activity of water, which leads to a smaller amount of water available for hydration, on addition of the salt; the appearance of the third phase merely represents a sharp increase in the amount of acid removed from the aqueous phase as a result of this hydration.

Comparable Published Results.—Attention has already been drawn[2] to the results obtained by Pagel and McLafferty[18] with tributyl phosphate and a series of carboxylic acids. These experiments show quite clearly: (i) the effect of molecular size, (*a*) $C_4H_9{\cdot}CO_2H > C_3H_7{\cdot}CO_2H > C_2H_5{\cdot}CO_2H > CH_3{\cdot}CO_2H$, (*b*) $C_2H_4(CO_2H)_2 > CH_2(CO_2H)_2$, (*c*) $CH_2Cl{\cdot}CO_2H > CH_3{\cdot}CO_2H$, and (*d*) $HO{\cdot}CHPh{\cdot}CO_2H > HO{\cdot}CH_2{\cdot}CO_2H$; (ii) the effect of hydroxyl, or a second carboxyl group, in increasing the affinity for the aqueous phase, despite the increase in molecular volume involved in replacing hydrogen by hydroxyl, (*a*) monobasic > dibasic, (*b*) $CH_3{\cdot}CO_2H > HO{\cdot}CH_2{\cdot}CO_2H$, and $C_2H_5{\cdot}CO_2H > CH_3{\cdot}CH(OH){\cdot}CO_2H$, and (*c*) $HO_2C{\cdot}C_2H_4{\cdot}CO_2H > HO_2C{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H > HO_2C{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO_2H$.

A similar series of extractions of simple carboxylic acids into di-isopropyl ether[19] gave $C_3H_7{\cdot}CO_2H > C_2H_5{\cdot}CO_2H > CH_3{\cdot}CO_2H$, which has also been found with isobutyl methyl ketone.[20]

An interesting study[21] of the separation of formic and sulphuric acid with methyl ethyl, diethyl, isopropyl methyl, and isobutyl methyl ketone, and with diethyl ether, showed that with M-solutions the coefficient *D* is always larger for formic acid (by a factor varying from 54 with ethyl methyl ketone to $4{\cdot}25 \times 10^3$ with isobutyl methyl ketone). The two factors favouring formic acid are acid strength and the hydration of $SO_2(OH)^-$; the molecular volumes do not differ markedly, and in fact that of sulphuric acid is the larger.

Extraction studies with long-chain amines (either as the pure amine[22] or in chloroform solution[23]) reveal the same effects. Thus Smith and Page[22] found that acetic, chromic, hydrochloric, nitric, oxalic, sulphuric, and toluene-*p*-sulphonic acid were extracted almost completely from dilute solution. The complete extraction of hydrochloric or sulphuric acid is not surprising in view of the high basicity of amines.[11] The following acids were incompletely extracted from dilute solution by methyldioctylamine:

	Residue (%) in aq. phase		Residue (%) in aq. phase		Residue (%) in aq. phase
$HO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	11	$PO(OH)_3$	44	$NH_2{\cdot}CH_2{\cdot}CO_2H$	98
$CH_3{\cdot}CH(OH){\cdot}CO_2H$ ...	16	Gluconic	88	$HO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$	100

Comparable results with 0·2N-acid, and 5% of methyldioctylamine in chloroform[23] include the following:

	Residue (%) in aq. phase		Residue (%) in aq. phase		Residue (%) in aq. phase
$H{\cdot}CO_2H$ ...	10	$CH_3{\cdot}CO_2H$...	24	$HO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$	99
HF	13	$PO(OH)_3$ ...	24	$HO_2C{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$	100

Here again the effect of both size and structure can be seen. A result which emphasises the importance of hydrogen-bonding of the anion to water is that an amino-group (in place of hydrogen) lowers the extraction more than does hydroxyl. It should be noted that with amines, acid strength may have an effect not noted hitherto, namely, that if a salt R_3NHX is easily hydrolysed back to $R_3N_{(o)}$ and $HX_{(aq)}$, extraction must be reduced.

Solubility of Organic Solvents.—For the systems discussed so far, the possible existence of S,HX species in the aqueous phase can be ignored.[4] The solubility of diethyl ether in aqueous perchloric, hydrochloric, sulphuric, phosphoric,[24] and nitric[25] acid is, however,

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[18] Pagel and McLafferty, *Analyt. Chem.*, 1948, **20**, 272.
[19] Werkman, *Ind. Eng. Chem.*, *Analyt.*, 1930, **2**, 302.
[20] Vogt and Geankoplis, *Ind. Eng. Chem.*, 1953, **45**, 2119.
[21] Whitehead and Geankoplis, *Ind. Eng. Chem.*, 1955, **47**, 2114.
[22] Smith and Page, *J. Soc. Chem. Ind.*, 1948, **67**, 48.
[23] Moore, *Analyt. Chem.*, 1957, **29**, 1660.
[24] Marie and Lejeune, *Monatsh.*, 1929, **53**, 69; Lejeune, *Compt. rend.*, 1939, **208**, 1225.
[25] Kirrman and Graves, *Bull. Soc. chim. France*, 1934, **1**, 1494; Sutton, AERE C/R 438 (1949).

well established. In some cases this solubility can be related to the extraction behaviour of the system. Thus the solubility of di-isopropyl ether in aqueous hydrochloric acid is markedly concentration-dependent,[9,26] and a similar result has now been found with di-isopropyl ketone, as shown in Fig. 5. Comparison with Fig. 6 shows the parallel between the solubility of the solvent in the aqueous phase, and the value of D. In such systems then, the acid–base complex (S,HX or analogue) is only formed when S,H^+ competes successfully against H_2O for the base Cl^-. Even when the competition favours the formation of S,HX, the latter species may go into either the aqueous or the organic phase; this may be related to the general deficiency of " free " water molecules in concentrated aqueous acids. This model explains why di-isopropyl ether overcomes the competitive effect of water at a lower acidity (*i.e.*, higher water concentration) than does di-isopropyl ketone, since the higher basicity [11] of the ether makes it a better competing agent—the two solvents have the same molecular volume. It is more difficult to identify the precise reason for the difference between hydrobromic and hydrochloric acid, since there are only small differences in size, basicity, hydration, etc., between Br^- and Cl^-.

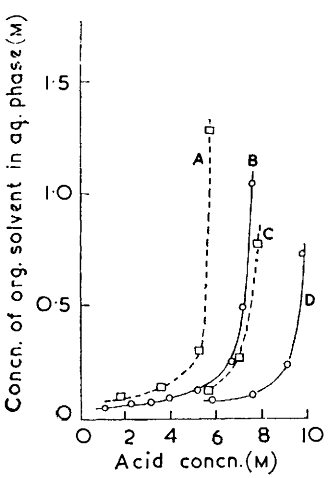

FIG. 5. Solubility of di-isopropyl ketone in aqueous solutions of hydrochloric and hydrobromic acid.
(A) HBr–Pr^i_2O. (B) HCl–Pr^i_2O (from ref. 9). (C) HBr–Pr^i_2CO. (D) HCl–Pr^i_2CO.

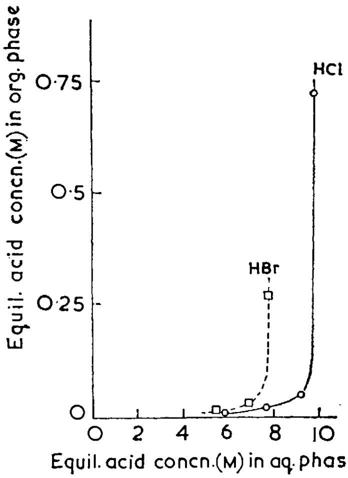

FIG. 6. Extraction of hydrochloric and hydrobromic acid into di-isopropyl ketone.

Extraction into Alcohols.—The alcohols have both strongly basic [11] and acidic properties, and therefore constitute a different class from the purely basic solvents considered so far. Their amphoteric nature enables them to compete for the solvation energy of both H^+ and X^-, and one would therefore expect that solutes with hydrophilic anions will be extracted much better into alcohols than into (say) ethers or ketones. This is confirmed by results in the literature; thus sulphuric acid had $D = 0{\cdot}15$ with butan-1-ol, compared with 0·025—0·0001 in ethers and ketones [20] (cf. also Fig. 2). Similarly hydrochloric acid has $D = 0{\cdot}66$ in the same solvent, but 0·02—0·01 in ethers and ketones.[27] It is hoped to investigate alcohol–acid extraction systems in greater detail in the future.

Dr. R. M. Diamond (University of California) is thanked for many useful discussions. The experimental work with di-isopropyl ketone was carried out at the University of Manchester during the tenure of a Turner and Newall Fellowship.

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[26] Campbell, Laurene, and Clark, *J. Amer. Chem. Soc.*, 1952, **74**, 6193.
[27] Crittenden and Hixson, *Ind. Eng. Chem.*, 1954, **46**, 265.