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Abstract

The extraction of $HClO_4$ by dilute solutions of 1-decanol, ROH, in isooctane and in 1,2-dichloroethane has been studied. In both cases the central solvation unit of the cation is believed to be the hydronium ion, which is coordinated to three molecules of alcohol. In isooctane the extracted species was the ion pair $H_3O^+ \cdot 3ROH \cdot xH_2O \ldots ClO_4^-$ over the entire range of concentrations observed. Depending upon the concentration of extracted acid and water activity in the aqueous phase, x takes values between 1 and 1.5. In the organic solvent of higher dielectric constant, 1,2-dichloroethane, the same hydration numbers were observed, but at concentrations of extracted acid below 0.001M, the predominant species in the organic phase are the dissociated ions $H_3O^+ \cdot 3ROH \cdot xH_2O$ and ClO_4^-.

Introduction

The distribution of an inorganic acid between an aqueous phase and a solution of a basic extractant in an organic diluent depends upon a competition between the extractant, water, and the anion to solvate the proton, and upon the need of the anion for solvation. Previous distribution studies of $HClO_4$ with dilute CCl_4 solutions of tributylphosphate,[3] TBP, and trioctylphosphine oxide,[4] TOPO, have suggested that the cationic species is a hydronium ion, around which three molecules of extractant are coordinated at the three sites of positive charge. Lower coordination numbers are also possible, depending upon the nature of the "inert" diluent and upon the concentration and basic strength of the extractant.[5] The more basic the extractant, the stronger its coordination to the cationic species, and the smaller may be the number of such bonds of superior strength which suffice to solvate the hydronium ion. Conversely, the maximum number of extractant molecules coordinated to the hydronium ion should obtain for extractions by a weak base. So extractions of $HClO_4$ by solutions of 1-decanol were investigated to see whether this weaker base would show a limiting coordination number of three as expected for the hydronium ion.

Furthermore, it is of interest to examine the role of the diluent in such systems. The diluent is never inert, but its interaction with an ion is expected to be small when a saturated hydrocarbon is used. In this case the lack of chemical solvation should again promote attainment of the maximum coordination (alcoholation) number in the extracted cationic complex. But the low dielectric constant leads to a positive electrostatic free energy of transfer and thus hinders the partition of ionic species into the organic phase. Those ions which do extract may be expected to associate to ion pairs in order to lose some of this electrostatic free energy. The extraction should be improved by the use of a diluent

of higher dielectric constant, and the resulting decrease in the attractive force between a pair of oppositely charged ions in the organic phase may result in their dissociation over a limited concentration range. To examine these effects, the extraction of perchloric acid into dilute solutions of 1-decanol in 2,2,4-trimethylpentane (isooctane, $\epsilon = 1.94$, 20°) and 1,2-dichloroethane ($\epsilon = 10.2$, 20°) was studied.

Experimental

Reagents.—Stock solutions of 1-decanol (Matheson, Coleman and Bell, White Label) were prepared, 0.3M in isooctane (Matheson, Coleman, and Bell, spectroscopic grade), and 0.5M in 1,2-dichloroethane (Matheson, Coleman, and Bell, spectroscopic grade). All other solutions of extractant were prepared, as required, by volumetric dilution. Solutions of perchloric acid were prepared by dilution of the 70% product (G. F. Smith, reagent grade) and were standardized with sodium hydroxide, using methyl red as indicator. A premixed, stabilized solution of Karl Fischer reagent (Matheson, Coleman, and Bell) was used for water determinations and the methanol used for its blank was an electronic grade (Baker and Adamson).

Procedure.—Solutions of 1-decanol in isooctane and in 1,2-dichloroethane (0.02-0.3M) were equilibrated with solutions of perchloric acid (0.01-6M) containing between 10 and 30 μl of $K^{186}ReO_4$ tracer, using a volume ratio, organic phase: aqueous phase, of unity for experiments in dichloroethane and 10:1 in isooctane. Equilibrium was attained in less than 1 hour for extractions into 1,2-dichloroethane. In the isooctane systems, results could not be reproduced unless 12 hours were allowed for equilibration. The safer limit of 24 hours was, therefore, observed

for all partition experiments in this medium. After equilibration, both phases were transferred to glass cones and centrifuged for 1 minute. Two 3 ml aliquots were then removed from the organic phase and γ-counted in a well-type Na(Tl)I scintillation counter with a 2" × 2" crystal. A small sample of the original tracer ($t_{1/2}$ = 3.9d) was also counted at a 10,000-fold dilution. Hence, the total number of counts added to the two-phase system could be computed, and the concentration of extracted acid is then determined as the product of the macro-concentration of $HClO_4$ and the fraction of the total counts in the organic phase. Actually, there is a difference between the true organic-phase concentration of ClO_4^- and that calculated by use of the ReO_4^- tracer. This arises from the slightly different extractability of ReO_4^- and ClO_4^-. The slope analyses of the data presented in this paper are independent of this difference, but at high concentrations of extracted acid, where corrections for that fraction of extractant complexed to the proton are necessary, a more precise knowledge of the actual concentration of $HClO_4$ is required. Fortunately, at such higher extracted acid concentrations, direct determination of the concentrations of acid by two-phase titrations with standardized sodium hydroxide could be made. Such experiments indicate that in this region of high concentration of extracted acid, the ratio of distribution coefficients of $[ClO_4^-]/[ReO_4^-]$ is of the order of 0.85.

The extraction of water alone into the alcoholic media was investigated by equilibrating solutions of 1-decanol (0.03-0.3M in isooctane, 0.02-0.5M in 1,2-dichloroethane) with water. The organic-phase concentration of water was then determined by the Karl Fischer method with a dead-stop end-point.

The water extraction was also studied as a function of water activity. Alcohol solutions of fixed concentration (0.3M in isooctane, 0.5M in 1,2-dichloroethane) were vapor-phase equilibrated with aqueous solutions of sulphuric acid in

a closed shaking system. Samples from the organic phase were quickly withdrawn after a 24 hour period, and were titrated for their water content.

The amount of water coextracted with perchloric acid was investigated by equilibrating aqueous perchloric acid (2-8M) with 0.3M solutions of 1-decanol in isooctane and with 0.1M and 0.3M solutions of 1-decanol in 1,2-dichloroethane. The organic-phase concentration of acid was determined by a direct two-phase titration against standardized base, and a sample was also analyzed for its total water content by the Karl Fischer method.

All extraction experiments were performed at 22 ± 2°.

Results

The log-log plot of organic-phase water concentration vs. alcohol concentration is shown in Fig. 1 for the two diluents at a water activity of unity. The amount of water extracted by the diluent alone, calculated as the product of the molar solubility in the diluent and the volume fraction of diluent in the organic medium, was subtracted from the total water concentrations (water solubility in isooctane, 0.0021M; literature value,[6] 0.002; water solubility in 1,2-dichloroethane, 0.094M, literature value,[7] 0.104M).

The dependence of the extraction of water on water activity, after correction for diluent uptake, is shown as a log-log plot in Fig. 2 for the two systems. All the data shown as open circles have been corrected to a fixed (initial) equilibrium concentration of alcohol, 0.523M in 1,2-dichloroethane and 0.314M in isooctane.

The relationship between the organic-phase concentration of acid and coextracted water is shown in Figs. 3 and 4 for the isooctane and 1,2-dichloroethane systems, respectively. The difference between the organic-phase water concentration

when the acid is present and that which extracts into equivalent solutions of alcohol alone (but corrected to the appropriate water activity) is what is plotted as $[H_2O]_o$ in Figs. 3 and 4.

The log-log plots in Fig. 5 are of organic-phase concentration of acid vs. aqueous activity of acid times the water activity to the appropriate power (described below) at initial concentrations of 0.0262, 0.105, and 0.314M 1-decanol in isooctane. Similar plots are shown in Fig. 7 for extractions by 0.0209 and 0.105M 1-decanol in 1,2-dichloroethane.

Figures 6 and 8 show the log-log dependence of organic-phase acid concentration on concentration of alcohol in the isooctane and 1,2-dichloroethane systems, respectively, for fixed aqueous acid activity.

Discussion

Alcohol-water.—The equilibrium for the distribution of water into a dilute organic solution of extractant is considered to be maintained independently of other extraction equilibria, and its equation may be written

$$nROH(org) + mH_2O = mH_2O \cdot nROH(org) \qquad (1)$$

For the low concentration of water brought into the organic phase in the present studies, the extracted species is expected to be a monohydrate. The unit slope shown in Fig. 2 for the log-log plots of $[H_2O]_o$ vs. water activity at a fixed concentration of 1-decanol proves that, indeed, the extracted species is a monohydrate for the two diluent systems considered here. Then, with the assumption that the organic-phase activity coefficient ratio is a constant, the equilibrium constant for water extraction may be expressed

$$K_{H_2O} = \frac{[H_2O \cdot nROH]_o}{[ROH]_o^n \, (H_2O)} \tag{2}$$

where brackets represent concentrations and parentheses, activities. Furthermore, since the partition of 1-decanol into water is negligible from either diluent, the water activity will remain very close to unity. Equation 2 suggests then that a log-log plot of organic-phase water concentration vs. alcohol concentration should generate a line of slope n, where n is the number of alcohol molecules complexed to each extracted water molecule. If we consider first the data in Fig. 1 for the isooctane system, it will be noticed that the points lie on a curve whose slope at the lowest concentrations of water is very close to two. On this basis the initial alcohol concentrations at the upper end of the curve may be corrected for the amount of alcohol bound to water, that is, to their equilibrium values, $[ROH]_o$, by means of equation 3:

$$[ROH]_o = [ROH]_{initial} - 2[H_2O \cdot 2ROH]_o \tag{3}$$

This has the effect of shifting the points at high concentration also onto the line of slope 2.0, which result shows that two alcohols are complexed to each extracted water molecule, and $K_{H_2O} = 0.25$.

For the corresponding system in 1,2-dichloroethane, the accuracy is much poorer, because the diluent itself extracts so much water, leaving the result as the small difference between two relatively large numbers. But a line drawn through the original data has a slope only slightly greater than unity, suggesting a 1:1 complex. The apparent slight increase in slope at the more concentrated end may only be due to the inaccuracy of the low points, or it may be real, indicating that the organic-phase activity coefficient ratio is not constant, or that

a dialcoholate of water is beginning to be formed. However, over most of the range of concentration of alcohol used in this study (below 0.3M), a unit slope is approximated. So using a correction to equilibrium concentrations of alcohol of the form,

$$[ROH]_o = [ROH]_{initial} - [H_2O \cdot ROH]_o \tag{4}$$

we obtain $n \approx 1$ and $K_{H_2O} \approx 0.15$.

Alcohol-Perchloric Acid-Water.—The equation for the extraction of perchloric acid from aqueous solution by a dilute solution of alcohol can be written

$$H^+ + ClO_4^- + mH_2O + nROH(org) = H^+ \cdot mH_2O \cdot nROH \ldots ClO_4^-(org) \tag{5a}$$

or

$$H^+ + ClO_4^- + mH_2O + nROH(org) = H^+ \cdot mH_2O \cdot nROH(org) + ClO_4^-(org) \tag{5b}$$

depending upon whether the organic-phase species is associated as ion pairs or is dissociated. The corresponding equilibrium constants are, for case (a)

$$K^a = \frac{[H^+ \cdot mH_2O \cdot nROH \ldots ClO_4^-]_o y_o}{[ROH]_o^n y_o^n \, (H_2O)^m (HClO_4)} \tag{6a}$$

and, for case (b)

$$K^d = \frac{[H^+ \cdot mH_2O \cdot nROH]_o [ClO_4^-]_o y_\pm^2}{[ROH]_o^n y_o^n \, (H_2O)^m (HClO_4)} \tag{6b}$$

where y represents the molar activity coefficient.

Let us first consider the isooctane system. If we assume, as is likely, that the extracted acid is associated in this medium, equation 6a should hold. At the low concentrations considered here, the ratio of organic-phase activity coefficients is likely to remain constant; this assumption has been tried elsewhere and justified by the results obtained,[3,4,8] as will also be seen in the present work. If, furthermore, the organic-phase acid concentration is written as $[H^+]_o$, then equation 6a reduces to

$$K^a = \frac{[H^+]_o}{[ROH]_o^n \, (H_2O)^m (HClO_4)} \tag{7}$$

Provided the extracted acid is an ion pair, equation 7 suggests that a log-log plot of $[H^+]_o$ vs. $a'_{HClO_4} \equiv (HClO_4)(H_2O)^m$ at a fixed initial concentration of 1-decanol should give a line of unit slope. At high aqueous concentrations of acid where the water activity is no longer unity, the reduced value must be included, raised to the appropriate power m. The value of m at a given organic-phase acid concentration is a measure of the hydration number of the proton, and may be interpolated from the gradient of the graph in Fig. 3; $m \approx 2$ over the range of concentrations employed.

In Fig. 5, log-log plots of $[H^+]_o$ vs. a'_{HClO_4} have been so constructed for extractions by 0.0262, 0.105 and 0.314M (initial concentrations) 1-decanol in isooctane. At low concentrations of extracted acid, all the points lie on a line of unit slope, suggesting, indeed, that the organic-phase is associated as ion pairs. At higher concentrations where curvature becomes pronounced, an increasingly large fraction of alcohol is complexed with the extracted acid. Since such alcohol is no longer free, this represents a serious departure from the condition of a fixed, equilibrium concentration of extractant. The organic-phase concentrations of acid must be corrected back to this condition, by means of equation 8.

$$[H^+]_o' = [H^+]_o \, [ROH]_o'^{\,n}/[ROH]_o^n \tag{8}$$

where primed quantities refer to the condition of a fixed (initial) equilibrium concentration, and unprimed quantities denote experimental values, among which the value of $[ROH]_o$ can be obtained from the relationship

$$[ROH]_o = [ROH]_{init} - 2[H_2O{\cdot}2ROH]_o - n[H^+]_o \tag{9}$$

Using the value n = 3, the origin of which is justified below, application of equations 8 and 9 to the data in Fig. 5 clearly raises all the points on the curved portions of the graphs onto the lines of slope 1.0, extended from a region where such corrections were not necessary.

Having established that the data are entirely consistent with the initial assumption of ion pairs, it remains to determine the value of n, the number of alcohol molecules complexed per proton. Equation 7 suggests that this value is accessible if the log-log dependence of $[H^+]_o$ on $[ROH]_o$ is investigated at a constant aqueous concentration of perchloric acid. Such graphs were constructed for extractions from 0.473M and 0.950M aqueous perchloric acid over the range of initial alcohol concentrations 0.025-0.3M, and the data are shown in Fig. 6. The two lines which pass through the points at low concentrations of alcohol, where corrections are insignificant, have slopes of 3, which suggests that three molecules of alcohol are complexed to the proton. At higher concentrations, the correction to equilibrium concentrations of alcohol may now be made through equation 9 on the basis of the preliminary result, that n = 3. All the points corrected thereby, are then, at a given aqueous concentration of perchloric acid, accomodated by a single line of slope 3.0, indicating trialcoholation of the proton. This result is the origin of the cubic indices in equation 8 to correct for variation in extractant concentration.

The system using 1,2-dichloroethane as diluent was similarly investigated. Log-log graphs of $[H^+]_o$ vs. a'_{HClO_4} were plotted for initial concentrations of 0.0209M and 0.105M 1-decanol in 1,2-dichloroethane. The slopes of these graphs, however, are closer to 0.5 than to unity, Fig. 7, suggesting dissociated ions, equation 6b. If the organic-phase activity coefficient of the alcohol is assumed to be unity, then

$$K^d = \frac{[H^+]_o^2 \, y_\pm^2}{[ROH]_o^n (H_2O)^m (HClO_4)} \tag{10}$$

and a log-log graph of $[H^+]_o \, y_\pm$, rather than $[H^+]_o$ alone, vs. a'_{HClO_4} should, at a fixed concentration of alcohol, generate a line of slope 0.5. Mean ionic activity coefficients calculated in media of $\epsilon \sim 10$ are, at best, tenuous approximations. However, using a value of $\epsilon = 10.5$ and 5Å for the distance of closest approach, the inclusion of the first six terms of the Mayer-Poirier expression[9] for $y_\pm$ satisfied the conditions of convergence and allowed values of $y_\pm$ to be computed for each experimentally measured organic-phase concentration of perchloric acid. Furthermore, the application to the original data in Fig. 6 does lower the points at the higher concentrations onto a line of slope 0.5, while the points at lower concentrations, where the correction is very small, already lie on that line. Thus, we conclude that the species is dissociated into independent ions in the 1,2-dichloroethane medium over the range of concentrations studied.

Inspection of equation 10 shows that at a constant aqueous concentration of perchloric acid, a log-log plot of $[H^+]_o \, y_\pm$ vs. $[ROH]_o$ should generate a line of slope 0.5n. Such graphs are shown in Fig. 8 at constant aqueous concentrations of 0.105M and 0.983M $HClO_4$. The lines that pass through the corrected points

have slopes of 1.5, indicating that, over the range of alcohol concentrations 0.02-0.3M, the alcoholation number is, as before, 3. Experiments conducted at alcohol concentrations higher than 0.3M show that thereafter, the concentrations of extracted acid begin to rise more rapidly than would be predicted on this basis. While any explanation of this tendency is, at this stage, speculative, there are a number of sources from which such behavior might arise. One possibility is that at such concentrations of alcohol, the gross nature of the diluent is changing from that of 1,2-dichloroethane to a mixture of 1-decanol and 1,2-dichloroethane, and this mixture may provide enhanced extraction without changing the nature of the extracted species. That is, the ratio of organic-phase activity coefficients may not remain constant, as may also have been indicated by the water data. Any explanation which supposes the change in slope reflects the creation of a new extracted species would require, from the slope analysis, as many as 6 alcohols per proton, which seems most unlikely.

There appears to be little difference between the solvation spheres, primary and secondary, of the proton in the isooctane and 1,2-dichloroethane media. For both diluents, in the range of concentrations studied, the average hydration number is 2 to 2.5. In both systems the central unit is most likely the hydronium ion, with the three molecules of alcohol coordinated to the three sites of positive charge. The additional water probably bridges between the alcohols and the hydronium ion, although we have not shown that the perchlorate anion is anhydrous and so not involved. The value of K^a for perrhenate tracer out of perchloric acid solutions is 2.2×10^{-2} for the isooctane system, and the value of K^d for perrhenate tracer out of perchloric acid solutions for the 1,2-dichloroethane system is 1.3×10^{-6}. These constants cannot be directly compared, but contrary to what was expected, the diluent of higher dielectric constant

does not give greatly enhanced extraction in the region studied, although below 1M $HClO_4$ and 0.1M decanol, extraction into 1,2-dichloroethane is better than into isooctane. A possible explanation is that the dipolar dichloroethane interacts strongly enough with 1-decanol to cut down the effective concentration of alcohol. However, the interionic attractions between the weakly basic perchlorate ion and the large, solvated hydronium ion are lowered sufficiently in dichloroethane that, over the concentration range investigated, the extracted species exists predominantly as free ions.

Finally, even though conditions were picked so as to favor the maximum coordination number for the extracted proton—use of a weak base, 1-decanol, and of poorly (chemically) solvating diluents—the only coordination number observed was three. This result lends support to the idea that the distributing species is the hydronium ion whenever the extractant is not so powerful a base as to be able to take the proton away from a water molecule. As a consequence, it is suggested that such a hydronium ion core is also involved when not too concentrated solutions of ethers and ketones and other relatively weak oxygenated bases are used as extractants for strong acids. For such weak bases, the maximum coordination number, three, might also be expected to be observed, and has been found in a few cases, as for example Refs. 10 and 11.

Acknowledgments

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Footnotes and References

(1) This work has been supported by the U. S. Atomic Energy Commission.

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Figure Captions

Fig. 1. Variation of organic-phase water concentration with concentration of 1-decanol in 1,2-dichloroethane (upper) and in isooctane (lower): open symbols, total concentration of 1-decanol; solid symbols, equilibrium concentration of 1-decanol.

Fig. 2. Variation of water extraction with water activity for 0.523M 1-decanol in 1,2-dichloroethane (upper) and 0.314M 1-decanol in isooctane (lower): ●, raw data; o, data corrected to a fixed (initial) equilibrium concentration of 1-decanol.

Fig. 3. Variation of organic-phase water content with extracted acid for 0.314M 1-decanol in isooctane. $[H_2O]_o$ does not include H_2O dissolved in diluent nor that complexed with alcohol.

Fig. 4. Variation of organic-phase water content with extracted acid: ●, 0.314M 1-decanol in 1,2-dichloroethane; ▲, 0.105M 1-decanol in 1,2-dichloroethane. $[H_2O]_o$ does not include water dissolved in diluent nor that complexed with alcohol.

Fig. 5. Dependence of acid extraction on aqueous acid and water activities at fixed concentrations of 1-decanol in isooctane: ●, 0.314M, ▲, 0.105M, ■, 0.0262M 1-decanol; o, △, □, data corrected to equilibrium concentrations of alcohol. $a'_{HClO_4} \equiv (HClO_4)(H_2O)^m$.

Fig. 6. Dependence of acid extraction on alcohol concentration in isooctane at constant equilibrium aqueous concentrations of acid: ●, 0.950M, ■, 0.473M; o, □, data corrected to equilibrium concentrations of alcohol.

Fig. 7. Dependence of acid extraction on aqueous acid and water activities at fixed concentrations of 1-decanol in 1,2-dichloroethane: ●, 0.105M, and , 0.0209M 1-decanol; o, □, data corrected for organic-phase activity coefficient of extracted acid. $a'_{HClO_4} \equiv (HClO_4)(H_2O)^m$.

Fig. 8. Dependence of acid extraction on alcohol concentration in dichloroethane at constant equilibrium aqueous concentrations of acid: ●, 0.105M, and ■, 0.983M; ○, □, data corrected for organic-phase activity coefficient of extracted acid.

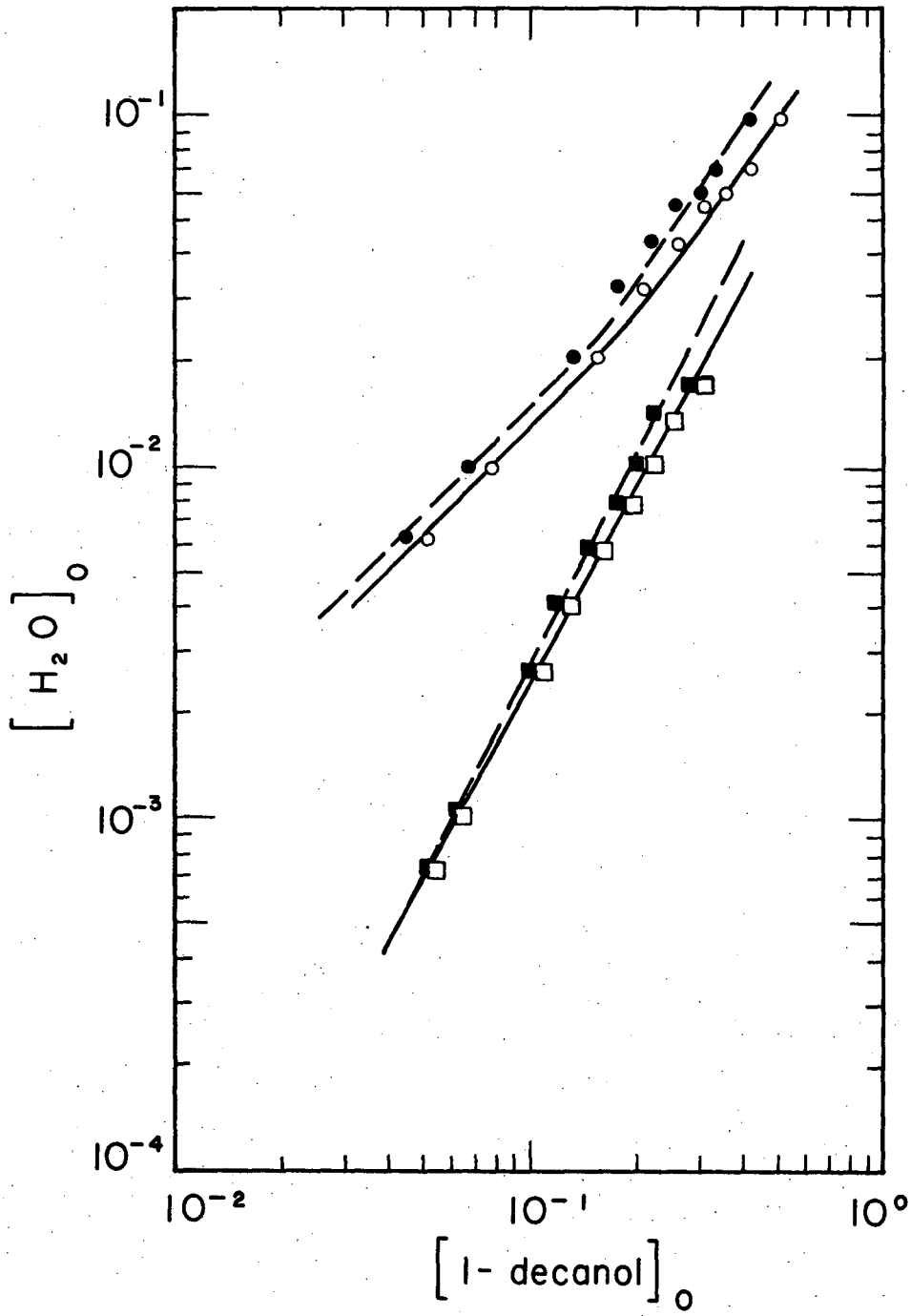

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Fig. 1

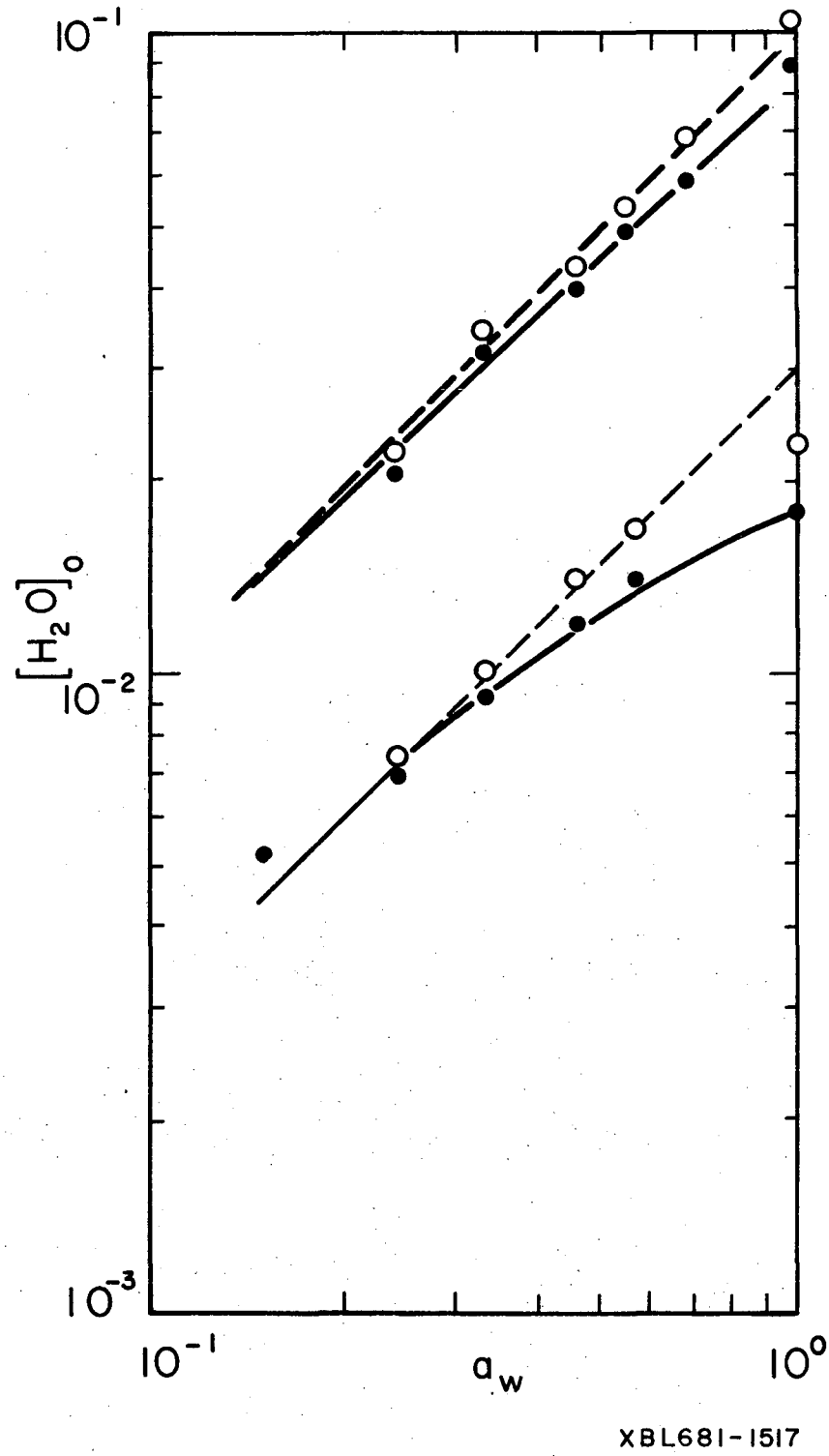
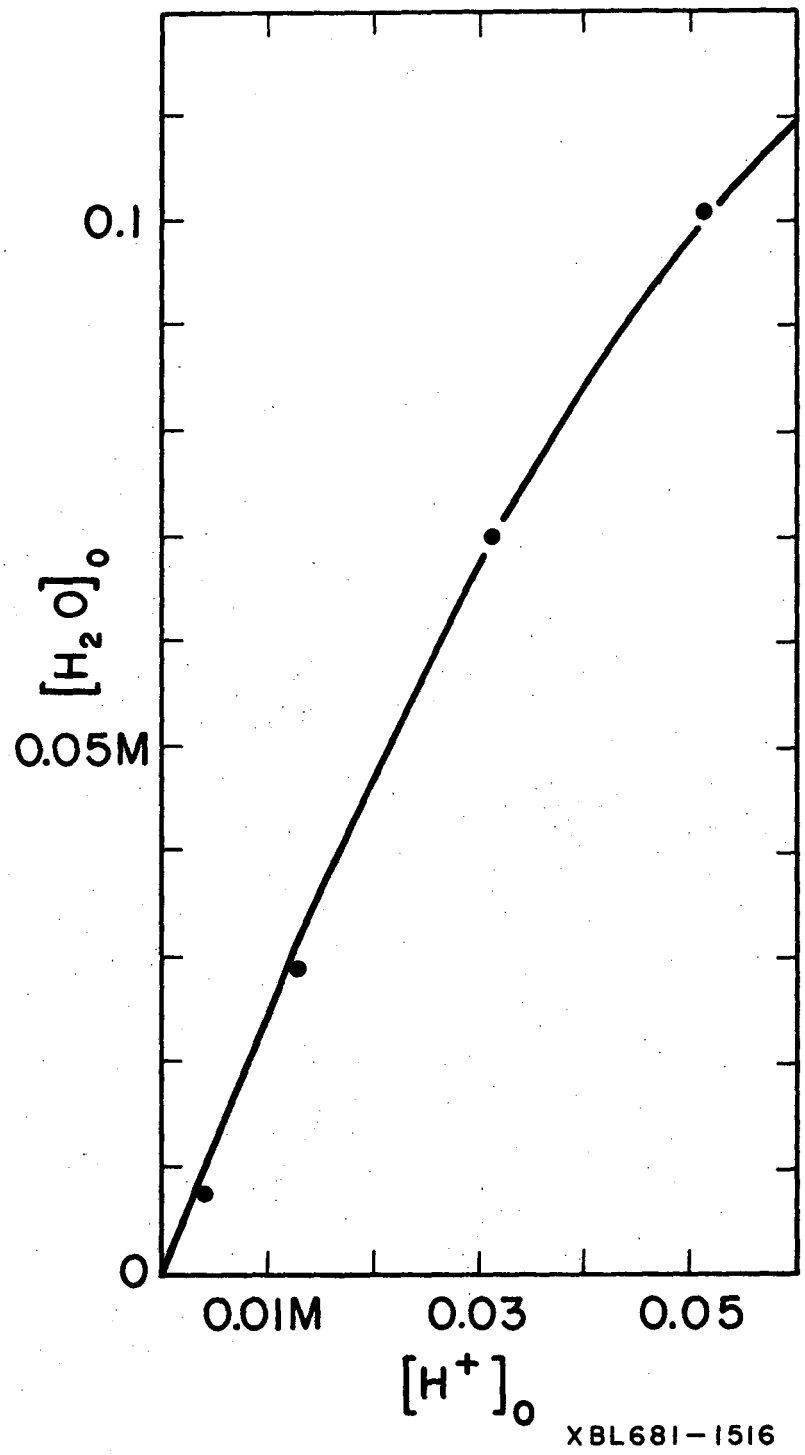


Fig. 2



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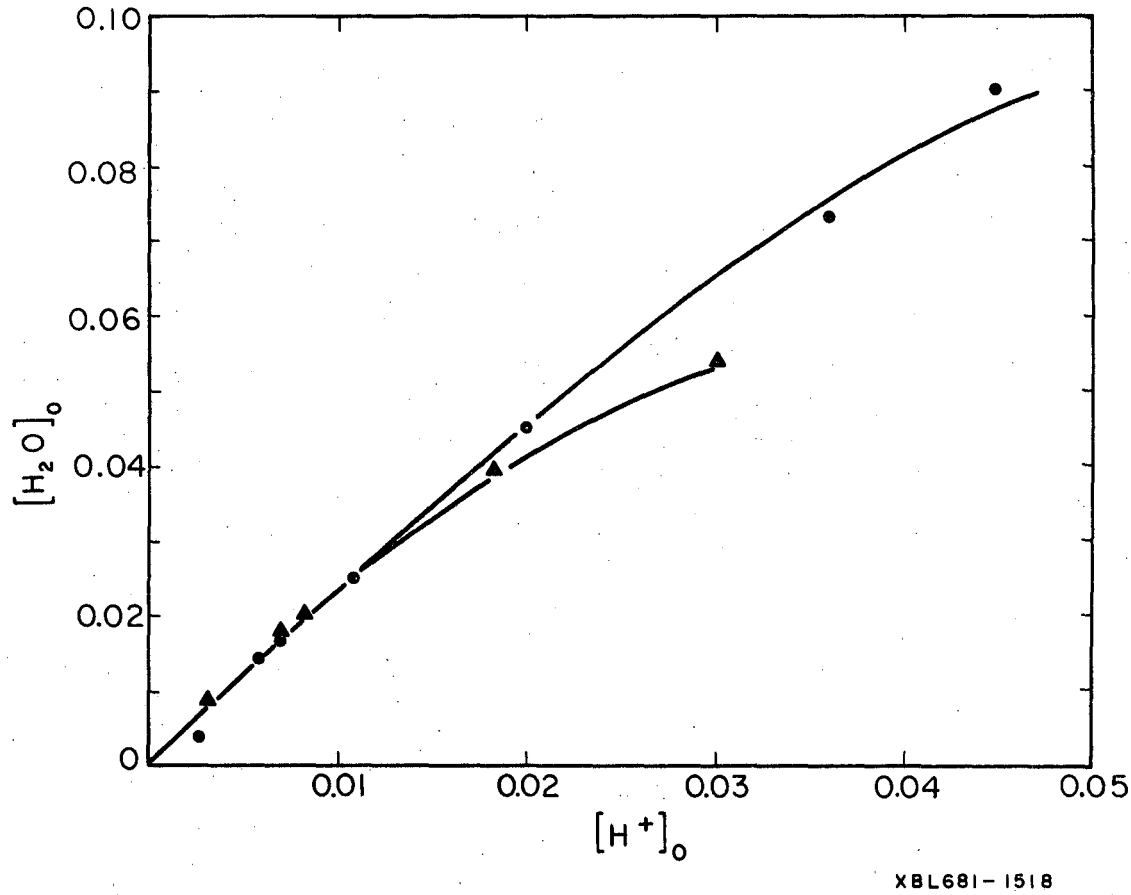

Fig. 4

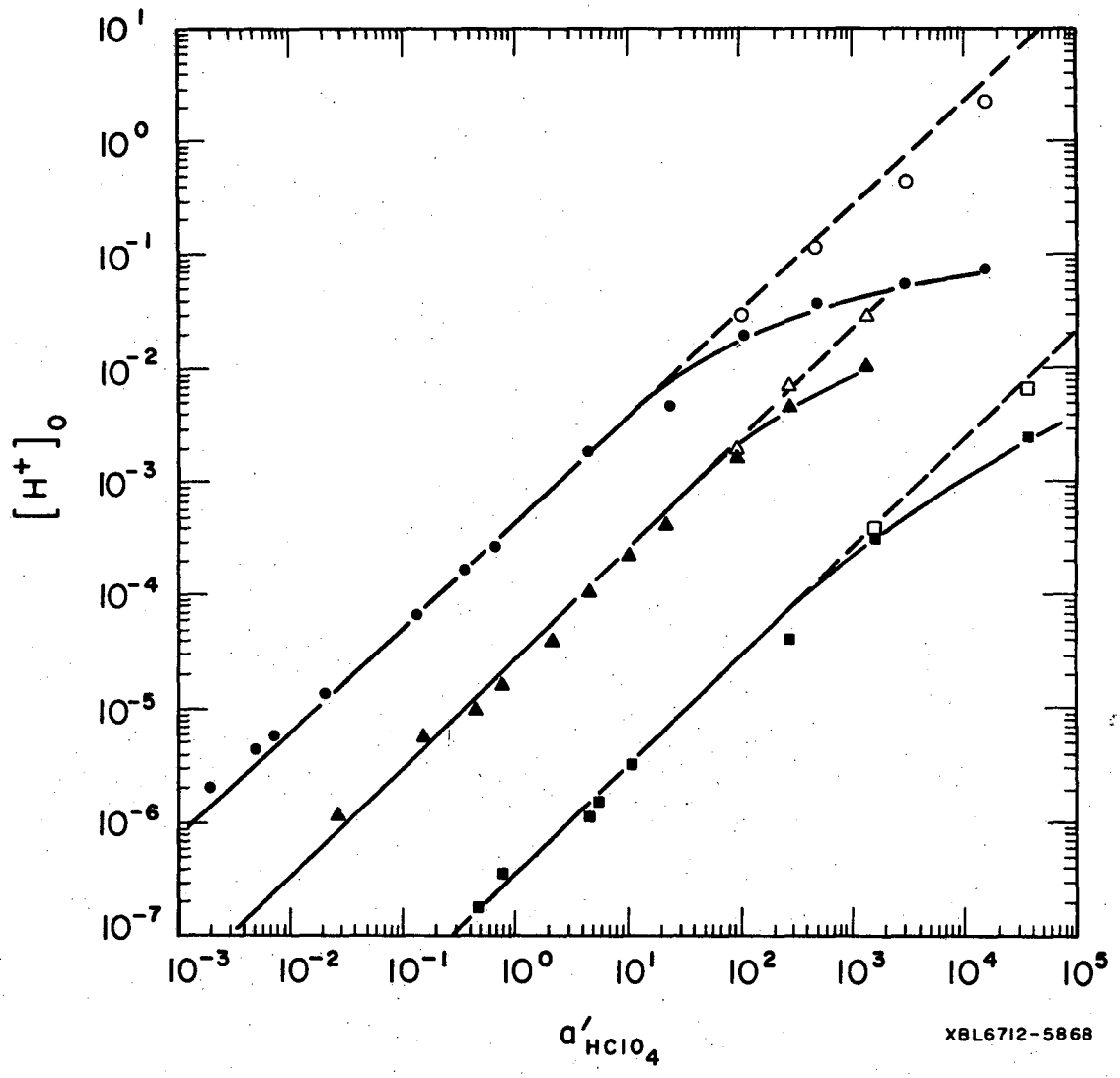
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Fig. 5

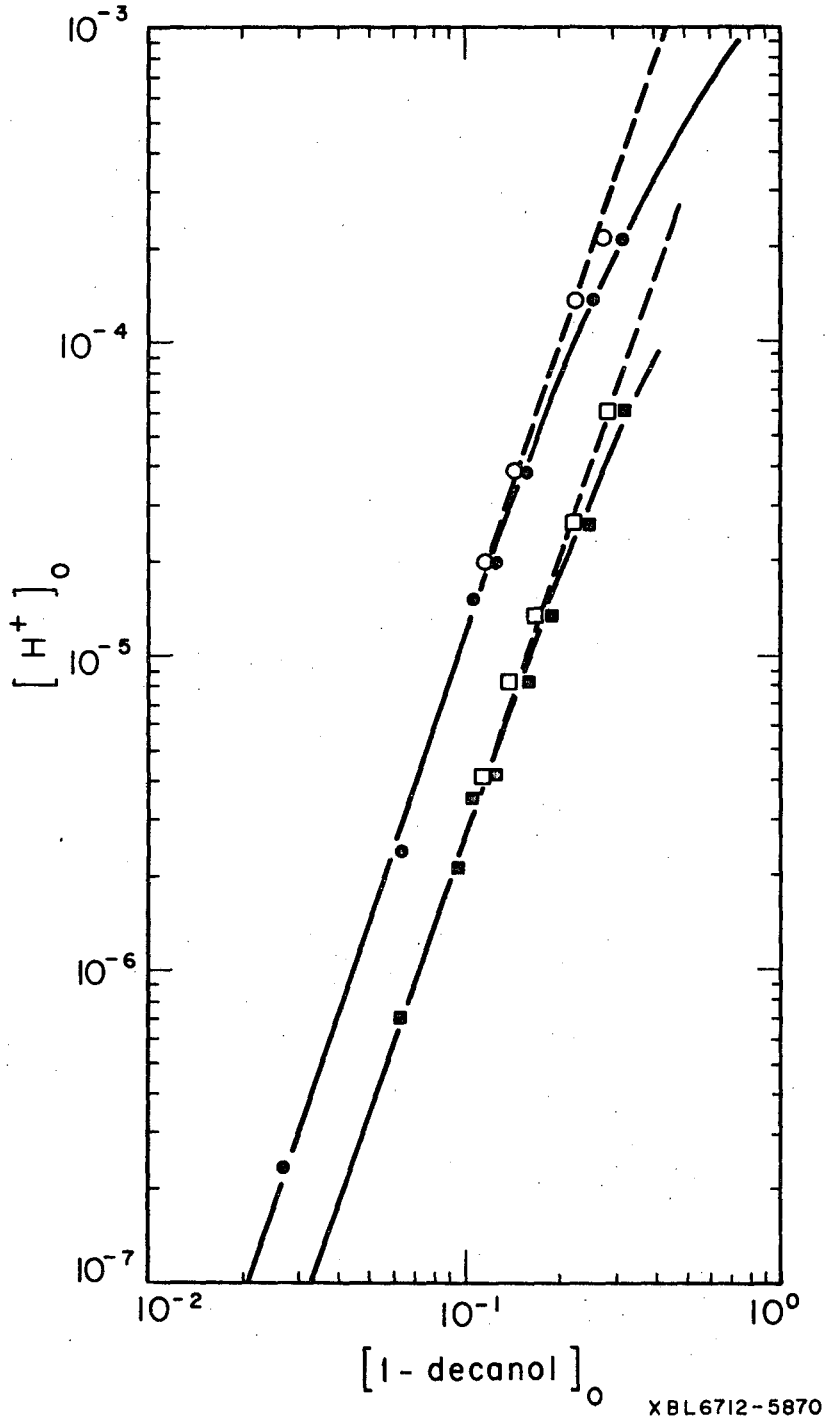
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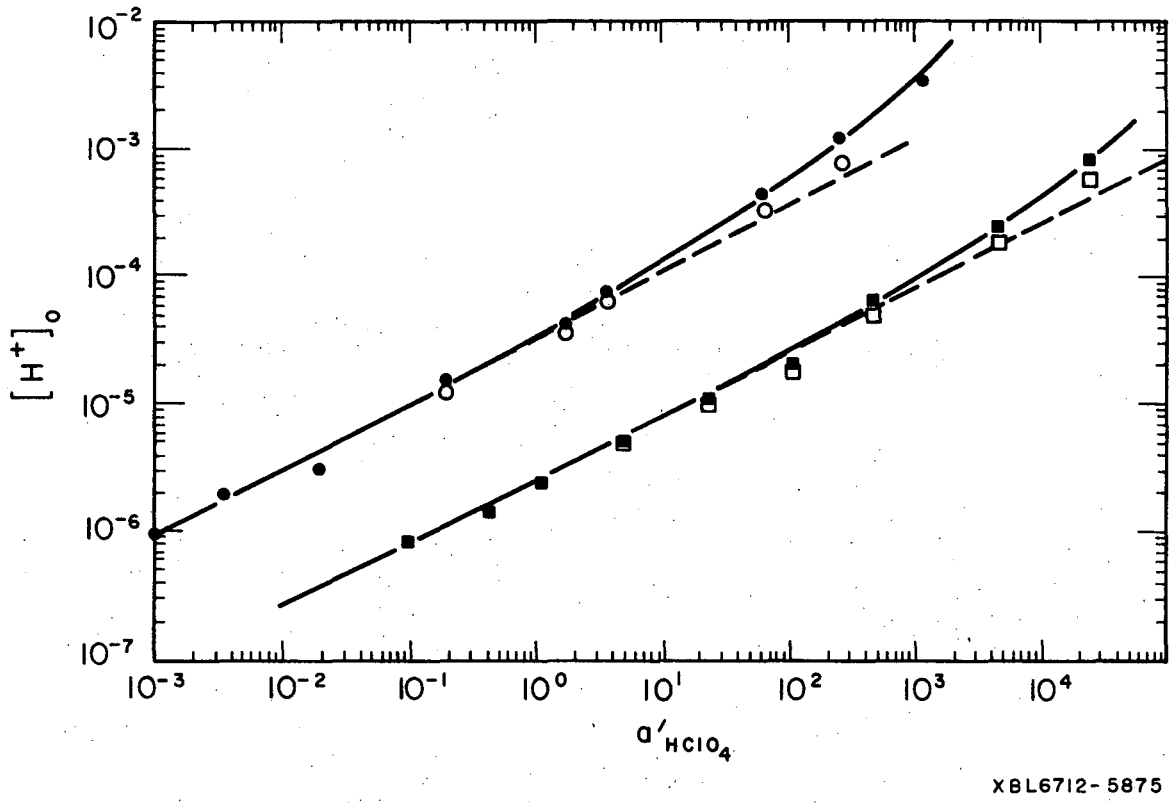
Fig. 6



XBL6712-5875

Fig. 7

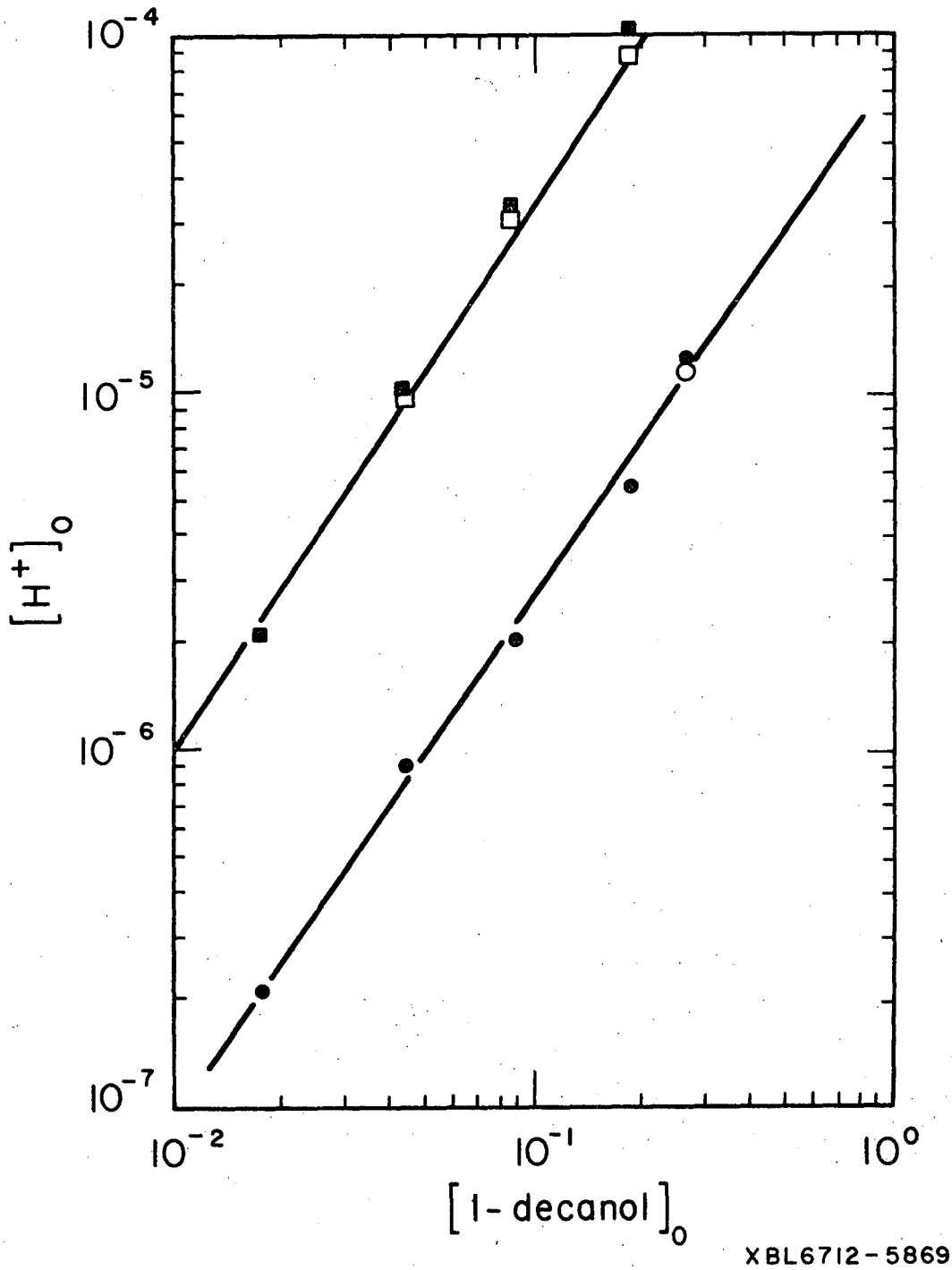


Fig. 8

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