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ABSTRACT

The extraction of tetrabutylammonium nitrate into dilute solutions of 1-decanol, ROH, in 1,2-dichloroethane has been studied and the nature of the extracted species has been determined. Over the entire accessible concentration range, the organic-phase species is an ion pair of the tetrabutylammonium cation and the monosolvated nitrate ion, $NO_3^- \cdot ROH$. These results have been compared to those for tetraheptylammonium fluoride where substantial differences in solvation arise.

INTRODUCTION

Two previous papers(2,3) have shown the applicability of a solvent extraction method for determining the coordination number of small anions towards slightly acidic molecules such as alcohols and phenols. The use of larger anions poses two difficulties: larger anions are structure-breakers in water and poorly hydrated so that they have a greater tendency to distribute into the organic diluent even in the absence of extractant molecules, leading to large blank corrections; their coordination to the extractant molecules may be weaker, which will lead to poorly defined complexes of lower average coordination number. However, there is interest in determining the coordination number of the nitrate ion. It may coordinate through one or two of its oxygens(4), and in one form of solid $Cu(NO_3)_2$ it appears to bond weakly through the third oxygen also(5). The possibility exists that it might even symmetrically complex three acidic species to its three oxygens, somewhat as the hydronium ion can coordinate three basic molecules to its three sites of positive charge. The most favorable situation for this behavior would seem to be when coordinated to weakly acidic species. Therefore, in this work, the extraction of tetrabutylammonium nitrate from water into dilute solutions of 1-decanol in 1,2-dichloroethane has been investigated. Because of the structure and large size of the tetrabutylammonium cation, any evidence for coordination of alcohol to the extracted salt should be due to the nitrate ion alone.

EXPERIMENTAL

Reagents

1-decanol was obtained as a White Label product from Matheson, Coleman and Bell. The 1,2-dichloroethane was of spectroscopic grade from the same source. A stock solution of 1-decanol in 1,2-dichloroethane (0.524 M) was made, and solutions of lower alcohol concentration were prepared, as required, by volumetric dilution. Tetra-n-butylammonium iodide (White Label, Eastman Organic Chemicals) was partly converted to the nitrate by stirring a small excess of the iodide as an aqueous slurry with silver nitrate. The small quantity of iodide which remained in the filtrate from the previous step was converted to the nitrate by passing the solution through an anion exchange column (Bio-Rad AG3-X4) in the nitrate form. The Karl Fischer reagent used for water determinations was the stabilized, premixed solution available from Matheson, Coleman and Bell. The methanol used in the Karl Fischer blank was Baker and Adamson Electronic Grade (water content < 0.1%) kept over molecular sieves.

Procedure

Solutions of 1-decanol over the concentration range 0.05 M to 0.5 M in 1,2-dichloroethane were shaken with aqueous solutions of tetrabutylammonium nitrate, TBAN, varying in concentration from 0.003 M to 0.14 M. A volume ratio of organic phase to aqueous phase of 1:5 was used. When equilibrium was reached, samples of the organic phase were withdrawn and back-extracted with a measured volume of water in excess of the organic aliquot. The resultant aqueous concentrations of nitrate ion were determined by a spectrophotometric method(6). The extraction of TBAN into 1,2-dichloroethane alone was similarly studied as a function of aqueous concentration of TBAN.

Attainment of equilibrium for the extraction and back-extraction was checked by varying the time of shaking in each of the two steps. Shaking for 1 hour was found to be more than sufficient for the initial extraction and so was chosen as a convenient interval, while for the back-extraction, equilibrium was reached in less than 15 minutes. All experiments were performed at 22 ± 2°.

RESULTS

The extraction of water alone by the alcohol in 1,2-dichloroethane is shown in Fig. 1 for the range of alcohol concentrations 0.02-0.5 M. The data have been corrected for the extraction of water into the diluent itself; found in this work, 0.095M, literature value(7), 0.104M.

Data for the extraction of TBAN into 0.209 M and into 0.524 M solutions of 1-decanol in 1,2-dichloroethane are shown in Tables 1 and 2. The corrections which appear in columns 4 and 5 will be explained below. Activities of the dilute solutions of TBAN in water were computed from the equilibrium aqueous concentrations and from activity coefficients approximated by the Debye-Hückel expression

$$\log y_{\pm} = - \frac{A|Z_1 Z_2|C^{1/2}}{1 + B\mathring{a}C^{1/2}} \qquad (1)$$

where the values of A and B are those appropriate to water at 22° and a value of 6Å was chosen for the distance of closest approach, $\mathring{a}$.

Data for the extraction of TBAN from an initial aqueous solution of 0.0140 M into varying concentrations of alcohol are given in Table 3. The organic-phase concentrations of TBAN listed in column 3 of Tables 1, 2 and 3

have all been corrected for distribution into the diluent alone. Concentrations listed in column 4 of Table 3 are those corrected to a constant aqueous activity of TBAN, $a = 1.34 \times 10^{-4}$ or $C = 1.29 \times 10^{-2}$ M.

DISCUSSION

Alcohol-water System

The equation for the extraction of water into a solution of an alcohol, ROH, in a diluent is

$$mH_2O + nROH(org) = mH_2O \qquad (2)$$

With a small number of additional assumptions discussed in another paper(8) and justified by the results therein, an equilibrium expression can be written

$$K_{H_2O} = \frac{[H_2O \cdot nROH]_o}{(H_2O)[ROH]_o^n} \qquad (3)$$

where brackets indicate molar concentration and parentheses, acitivity. Additionally, the water activity can be ignored, since it will not depart appreciably from unity on the grounds of the low solubility of the extractant in the water phase. Experimentally, the log-log plot of organic-phase water concentrations vs initial concentration of alcohol has a slope of approximately unity, Fig. 1, although rising to a somewhat higher value (~1.3) for decyl alcohol concentrations between 0.2 and 0.5M. It may be that a dialcoholate of water is beginning to form in the more concentrated solutions, but

it seems to use more likely that the increase in slope is due to the change in the nature of the organic phase from the dichloroethane diluent to a mixture of decyl alcohol and dichloroethane. That is, the ratio of the activity coefficients in the organic phase does not remain a constant. In any case, the plot is closest to a slope of unity, suggesting that n=1. For each initial concentration of alcohol the equilibrium value $[ROH]_o$ can be computed then as

$$[ROH]_o = [ROH]_{init} - n[H_2O \cdot nROH]_o \qquad (4)$$

Using the preliminary value of unity for n, the data plotted against these equilibrium values (Fig. 1) fall on a line of slope n~1, with a value 0.20 for K_{H_2O}.

<u>TBAN-H_2O-ROH</u>

The partition of a tetraalkylammonium nitrate between an aqueous phase and the organic phase can be expressed by the equation

$$R_4N^+ + NO_3^- + mH_2O + nROH(org) = R_4N^+ \ldots NO_3^- \cdot mH_2O \cdot nROH(org) \qquad (5a)$$

or

$$R_4N^+ + NO_3^- + mH_2O + nROH(org) = R_4N^+(org) + NO_3^- \cdot mH_2O \cdot nROH(org) \qquad (5b)$$

depending on whether the extracted species is an ion pair or a pair of dissociated ions. As shown elsewhere(3), the formal expression for the equilibrium constant can be simplified, for constant water activity and a constant ratio of organic-phase activity coefficients, to

$$K = \frac{[NO_3^-]_o^z}{[ROH]_o^n (R_4N^+)(NO_3^-)} \tag{6}$$

in which z=1 for case (a), and z=2 for case (b). The aqueous activity coefficients of TBAN were estimated, in the absence of experimental data, from the Debye-Hückel expression. The osmotic coefficients of tetraethyl and tetrapropylammonium nitrates are very close to those predicted from the Debye-Hückel formalism below 0.1 m, and so it may be expected that Equation (1) will fairly well reproduce activity coefficients for TBAN over the concentration range 0.002-0.08 M.

Inspection of Equation (6) suggests that if the equilibrium concentration $[ROH]_o$ is held constant, a log-log plot of $[NO_3^-]_o$ vs $(R_4N^+)(NO_3^-)$ should give a line of slope 1/z. Figure 2 shows that at aqueous activities below 5×10^{-4} for extractions by 0.209 and 0.524M 1-decanol, such a plot has a slope of unity. At activities higher than these, an increasingly large fraction of the alcohol is complexed with the extracted nitrate thereby causing serious departures from the condition of a constant equilibrium concentration, $[ROH]_o$. This necessitates a correction back to the initial concentration by means of Equation (7).

$$[NO_3^-]_o' = [NO_3^-]_o \, [ROH]_o'/[ROH]_o \tag{7}$$

where primed quantities refer to this (initial) condition, and unprimed quantities refer to experimental values. The equilibrium concentration $[ROH]_o$ in Equation (7) is that concentration of alcohol not complexed by water nor by the nitrate ion, and can be computed from Equation (8)

$$[ROH]_o = [ROH]_{init} - [ROH \cdot H_2O]_o - n[NO_3^-]_o \tag{8}$$

with n = 1. These equilibrium concentrations of alcohol are listed in column 4 of Tables 1 and 2, and the corrected conentration of TBAN(org), $[NO_3^-]_o'$, is given in column 5. Direct experimental justification for the form of Equations (7) and (8) will emerge below. Their immediate application to the data in Fig. 2 clearly raises all points at high aqueous activities onto the line of unit slope extended from data at low activities where the correction is insignificant. The unit gradient for 1/z, or the value z=1, permits the conclusion that, over the accessible range of concentration, TBAN is associated as ion pairs in the organic phase.

If the aqueous activity of TBAN is held constant, then Equation (6) suggests that a log-log plot of $[NO_3^-]_o$ vs $[ROH]_o$ should generate a line of slope n, the number of alcohol molecules which solvate the nitrate ion. Such a plot was constructed first for the organic-phase salt concentrations, corrected in column 4 of Table 3 to a constant aqueous TBAN activity of 1.34×10^{-4}, against the initial concentration of alcohol. The line that passes through these points is linear and has unit slope. This strongly suggests that the extracted species has only 1 alcohol per nitrate ion. Thus, the correction of the initial alcohol concentrations to their equilibrium values, $[ROH]_o$, may be made through Equation (8) with n=1, and these latter are listed in column 5 of Table 3. The corrected points, shown in Fig. 3, fall onto a line which parallels the original, of slope 1.0. This value of unity for the alcoholation number validates the use of the ratio $[ROH]_o'/[ROH]_o$ to the first power in Equation (7), and gives a value for K, in Equation (6), of 1.5×10^2.

An attempt was also made to determine the amount of water coextracted with TBAN into the organic phase. Solutions of 1-decanol (0.524 M) were equilibrated with aqueous solutions of TBAN up to a concentration of 0.028M,

and the water content of the organic phases were determined at equilibrium by the method of Karl Fischer. The results are shown in Table 4, where in columns 2 and 3 are given the organic-phase concentrations of TBAN uncomplexed and complexed with the alcohol, respectively, and in column 4 are listed the concentrations of water after correction for that distributing into the solvent alone. In column 5, are given, without parentheses, the excess water concentrations left after correcting column 4 for the water uptake by the equilibrium concentration of uncomplexed 1-decanol. These water concentrations increase with organic-phase salt concentration, a result which suggests that the nitrate is hydrated in the organic phase. However, we have ignored water that might be coextracted with TBAN distributing into the diluent itself (column 2). Separate water data obtained for the latter are shown in Table 5, indicating something more than one water molecule extracted per uncomplexed nitrate. The amount of this water associated with the blank concentrations of TBAN in column 2 of Table 4 may then be interpolated from the data in Table 5, and are shown in parentheses in column 5 of Table 4. The result which emerges from subtracting these numbers from those not in parentheses and comparing with the TBAN concentrations in column 3 is that about one water molecule seems to co-extract with each nitrate-alcohol complex. However, it should be noted that these final water concentrations are not very accurate as they are the result of a number of subtractions, and so within the experimental errors involved the extracted nitrate complex could be anhydrons or have up to two water molecules co-extracted.

The presence and extent, or the absence, of hydration of anions in the organic phase is determined by a balance between opposing effects. On the grounds that a water molecule is more acidic than a molecule of 1-decanol, and further, that water may well be able to approach an anion to within a

shorter distance than can an alcohol molecule, it might be supposed that an anion would be hydrated in the organic phase. However, in the aqueous phase water can be accomodated in a highly organized hydrogen-bonded structure, and it tends to be coextracted into the organic phase only when strong anion-water interactions obtain in that phase. With small ions, where hydration in the aqueous phase is very considerable and partition into the organic phase is strongly hindered, the ions that do extract require extensive solvation. For example, the extraction of the fluoride ion(3) by 1-decanol in tolene requires four molecules of 1-decanol and, additionally, just over two molecules of water per anion. Water is displaced from the fluoride ion solvation sheath only when the acidity of the extractant, and hence its solvating ability, is raised greatly above that of the alcohols, as was found in experiments using phenols as extractants. The nitrate ion, because of its size and structure, does not require extensive solvation. Various evidence(9,10), particularly relaxation studies(11), suggest that the nitrate ion is a pronounced structure-breaker in water and is not highly hydrated. Thus, the nitrate ion can extract reasonably well, even without the extractant, and does not seem to coordinate strongly with alcohol in the organic phase. Only a 1:1 complex with 1-decanol has been observed in the present study, in contrast to the 3:1 alcohol complex found with hydroxide ion(2) and the 4:1 complex observed with fluoride(3). But because of the uncertainty as to whether or not a water molecule is also carried along, and if so, whether it is bridging between the alcohol and the anion, we cannot conclude if the extracted nitrate is monodentate, or bidentate as is the usual case when coordinated to a metal cation.

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Table 1. Extraction of TBAN into 0.209 M 1-decanol in 1,2-dichloroethane.

Equil. concn. TBAN(aq)	Activity TBAN(aq)	Equil. Concn. TBAN(org)	Equil. alcohol concn.	Corr. equil. concn. TBAN(org)
8.57×10^{-2}	4.80×10^{-3}	8.00×10^{-2}	9.5×10^{-2}	1.47×10^{-1}
7.16×10^{-2}	3.40×10^{-3}	7.04×10^{-2}	1.05×10^{-1}	1.18×10^{-1}
4.98×10^{-2}	1.65×10^{-3}	3.83×10^{-2}	1.37×10^{-1}	4.91×10^{-2}
3.32×10^{-2}	7.6×10^{-4}	1.56×10^{-2}	1.60×10^{-1}	1.71×10^{-2}
2.31×10^{-2}	3.8×10^{-4}	1.05×10^{-2}	1.65×10^{-1}	1.12×10^{-2}
1.25×10^{-2}	1.26×10^{-4}	3.9×10^{-3}	1.72×10^{-1}	3.9×10^{-3}
1.02×10^{-2}	7.7×10^{-5}	2.2×10^{-3}	1.73×10^{-1}	2.2×10^{-3}
6.5×10^{-3}	3.2×10^{-5}	1.6×10^{-3}	1.74×10^{-1}	1.6×10^{-3}
2.9×10^{-3}	7.4×10^{-6}	3.0×10^{-4}	1.75×10^{-1}	3.0×10^{-4}

Table 2. Extraction of TBAN into 0.524 M 1-decanol in 1,2-dichloroethane.

Equil. concn. TBAN(aq)	Activity TBAN(aq)	Equil. Concn. TBAN(org)	Equil. alcohol concn.	Corr. equil. concn. TBAN(org)
7.60×10^{-2}	4.00×10^{-3}	1.79×10^{-1}	2.67×10^{-1}	2.99×10^{-1}
6.48×10^{-2}	2.85×10^{-3}	1.33×10^{-1}	3.13×10^{-1}	1.89×10^{-1}
4.41×10^{-2}	1.35×10^{-3}	8.26×10^{-2}	3.63×10^{-1}	1.01×10^{-1}
3.61×10^{-2}	9.2×10^{-4}	6.79×10^{-2}	3.78×10^{-1}	8.02×10^{-2}
2.06×10^{-2}	3.15×10^{-4}	2.65×10^{-2}	4.19×10^{-1}	2.82×10^{-2}
1.19×10^{-2}	1.05×10^{-4}	7.3×10^{-3}	4.39×10^{-1}	7.4×10^{-3}
9.7×10^{-3}	7.0×10^{-5}	5.1×10^{-3}	4.41×10^{-1}	5.1×10^{-3}
6.3×10^{-3}	3.0×10^{-5}	2.6×10^{-3}	4.43×10^{-1}	2.6×10^{-3}
2.6×10^{-3}	5.1×10^{-6}	9.5×10^{-4}	4.44×10^{-1}	9.5×10^{-4}

Table 3. Extraction of 0.0140 M TBAN into 1-decanol in 1,2-dichloroethane.

Initial alcohol concn.	Equil. concn. TBAN(aq)	Equil. concn. TBAN(org)	Corr. equil. concn. TBAN(org)	Corr. alcohol concn.
5.24×10^{-1}	1.19×10^{-2}	7.3×10^{-3}	8.5×10^{-3}	4.39×10^{-1}
4.19×10^{-1}	1.21×10^{-2}	6.0×10^{-3}	6.8×10^{-3}	3.45×10^{-1}
3.14×10^{-1}	1.23×10^{-2}	4.5×10^{-3}	4.9×10^{-3}	2.57×10^{-1}
2.62×10^{-1}	1.24×10^{-2}	4.0×10^{-3}	4.3×10^{-3}	2.15×10^{-1}
2.09×10^{-1}	1.25×10^{-2}	3.9×10^{-3}	4.1×10^{-3}	1.72×10^{-1}
1.57×10^{-1}	1.27×10^{-2}	2.7×10^{-3}	2.7×10^{-3}	1.30×10^{-1}
1.05×10^{-1}	1.28×10^{-2}	1.8×10^{-3}	1.8×10^{-3}	0.86×10^{-1}

Table 4. Coextraction of water into 0.524 M 1-decanol in 1,2-dichloroethane.

Equil. concn. TBAN(aq)	Concn. uncomplexed TBAN(org)	Equil. concn. complexed TBAN(org)	Concn. Water	Concn. Excess Water
0	0	0	0.94×10^{-1}	0
8.0×10^{-3}	1.6×10^{-3}	0.45×10^{-2}	1.00×10^{-1}	$0.7\ (0.2) \times 10^{-2}$
1.35×10^{-2}	4.7×10^{-3}	1.03×10^{-2}	1.06×10^{-1}	$1.4\ (0.57) \times 10^{-2}$
2.15×10^{-2}	1.17×10^{-2}	2.35×10^{-2}	1.30×10^{-1}	$4.1\ (1.50) \times 10^{-2}$

Table 5. Coextraction of water into 1,2-dichloroethane (no decanol).

Equil. concn. TBAN(aq)	Concn. TBAN(org)	Concn. Excess water
0	0	0
9.0×10^{-3}	0.2×10^{-2}	0.25×10^{-2}
2.50×10^{-2}	1.6×10^{-2}	2.0×10^{-2}

FIGURE CAPTIONS

Fig. 1. Variation of organic-phase water content (1,2-dichloroethane diluent) with concentration of 1-decanol: ● initial concentration of 1-decanol; o, equilibrium concentration.

Fig. 2. Dependence of nitrate extraction on aqueous activity of TBAN at a fixed concentration of 1-decanol ■, 0.524 M and ●, 0.209 M 1-decanol; □, o, data corrected to constant equilibrium concentrations of 1-decanol.

Fig. 3. Dependence of nitrate extraction on concentration of 1-decanol at a constant equilibrium aqueous TBAN activity of 1.34×10^{-4} (0.0129 M); o, equilibrium concentration of 1-decanol.

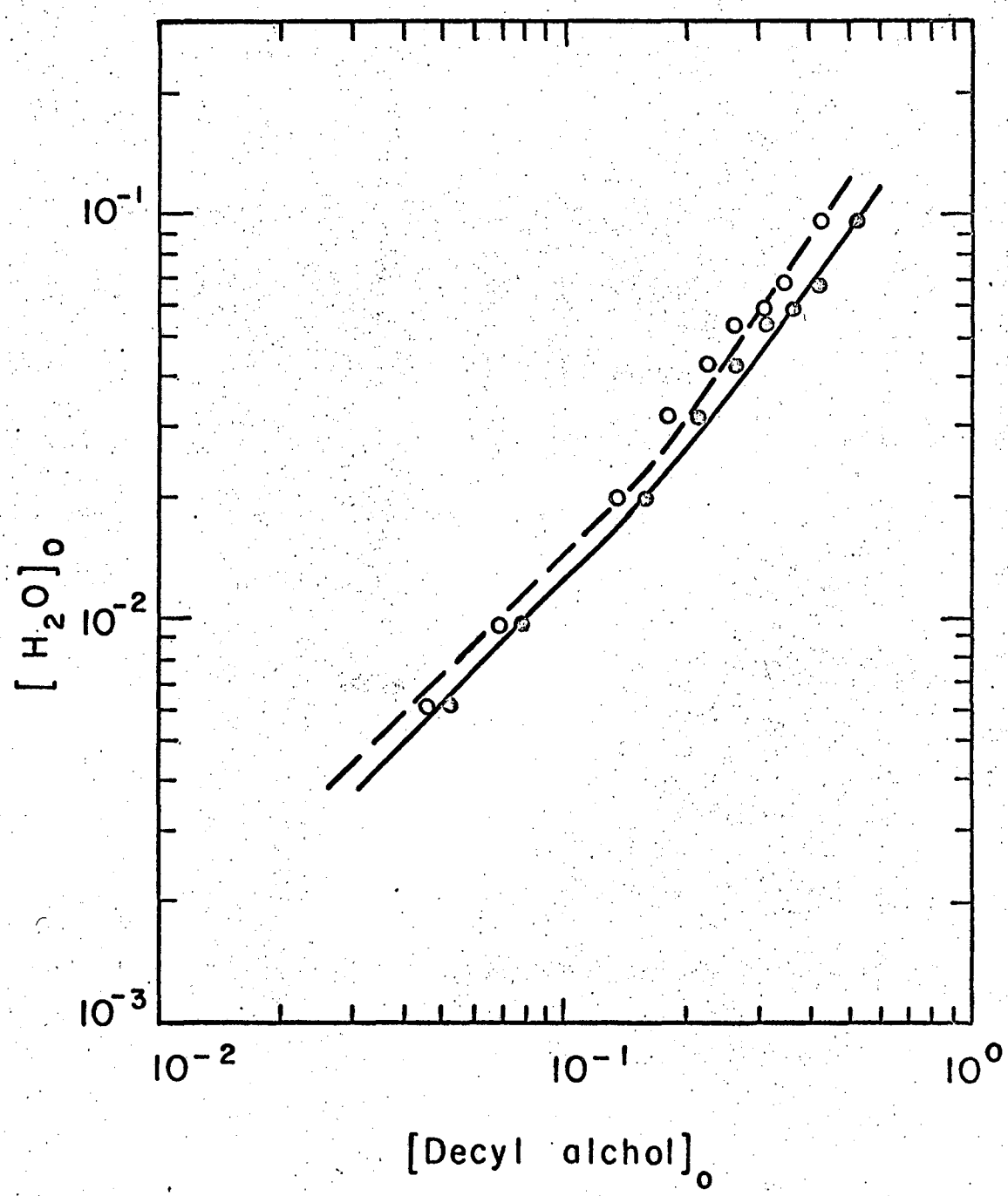

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Fig. 1

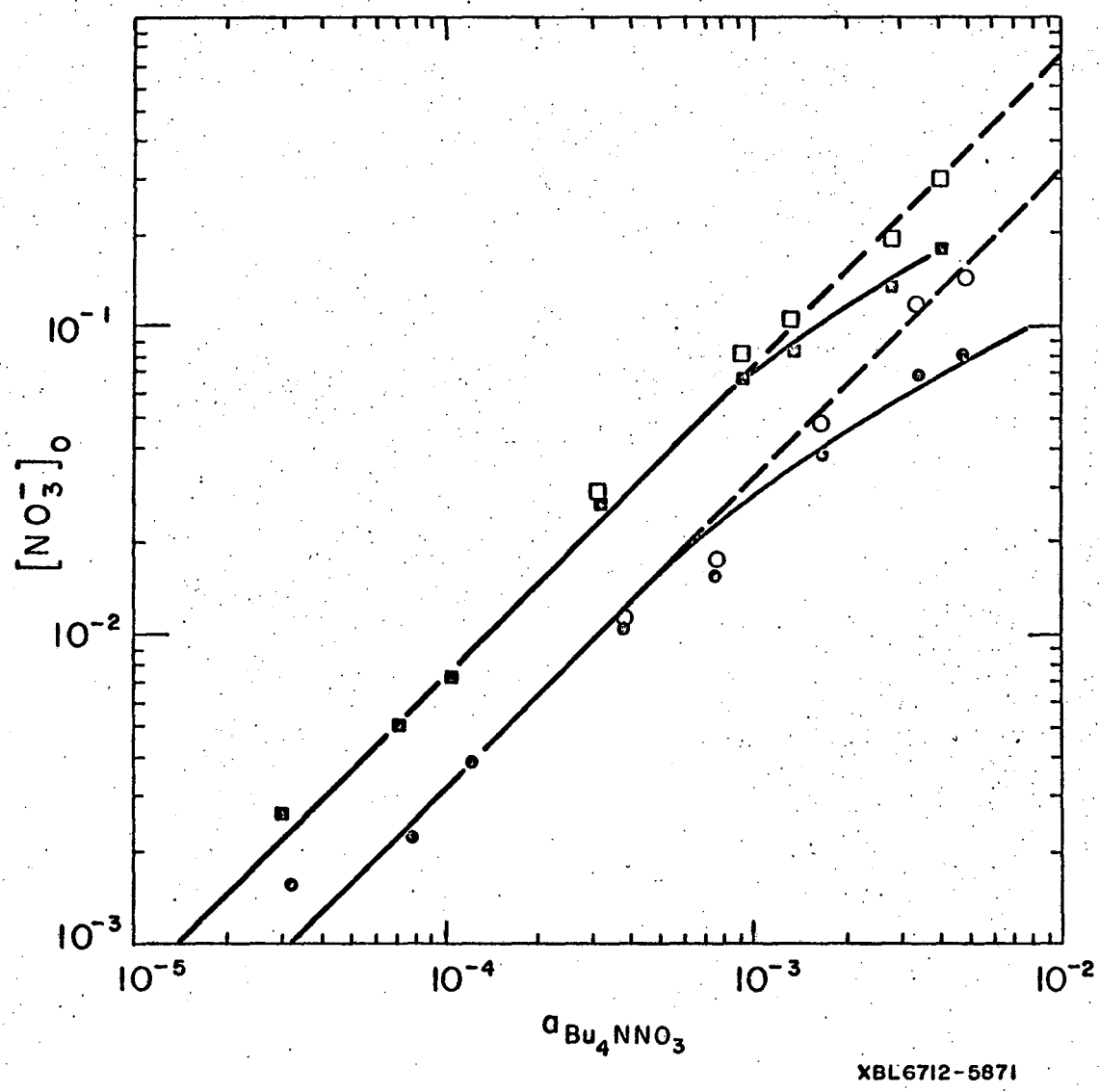

Fig. 2

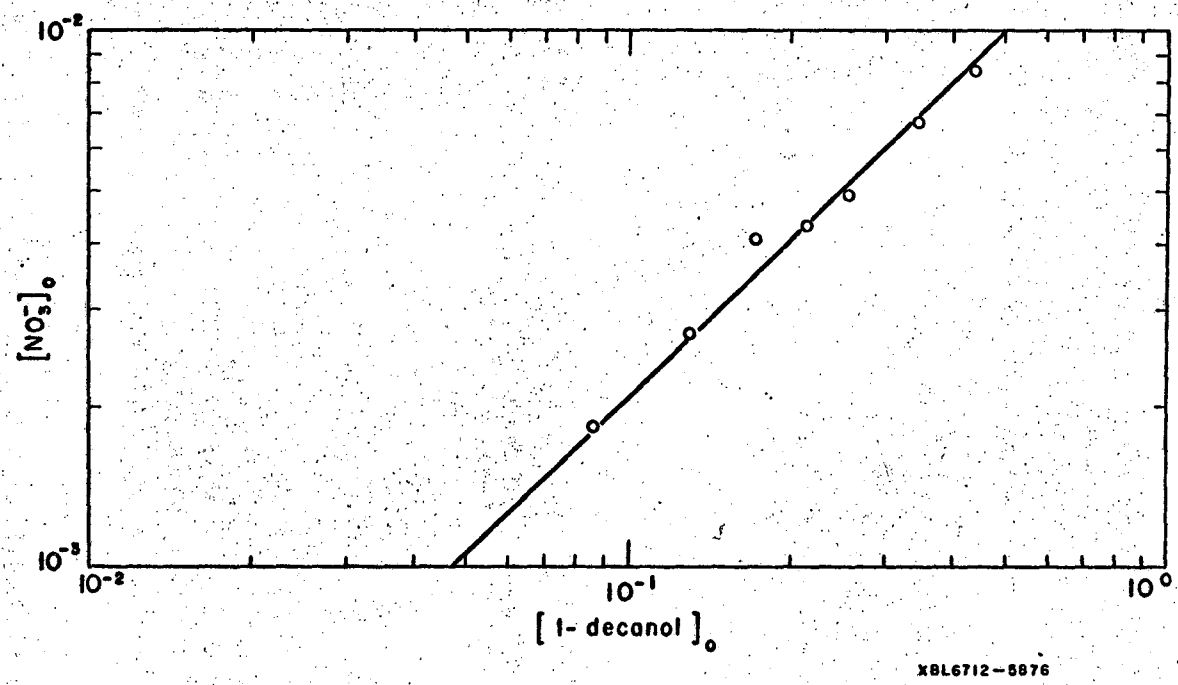

Fig. 3

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