Lawrence Berkeley National Laboratory
Recent Work

Title
THE EXTRACTION OF HClO4, BY TRILAURYL AMINE I. AROMATIC DILUENTS

Permalink
https://escholarship.org/uc/item/63b1d908

Authors
Bucher, J.J.
Diamond, R.M.

Publication Date
1964-09-01
THE EXTRACTION OF HC10 4 BY TRILAURYL AMINE
I. Aromatic Diluents

Berkeley, California
This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
THE EXTRACTION OF HClO₄ BY TRILAURYL AMINE

I. Aromatic Diluents

J. J. Bucher and R. M. Diamond

September 1964
THE EXTRACTION OF HClO₄ BY TRILAURYL AMINE

I. Aromatic Diluents

J. J. Bucher and R. M. Diamond

Lawrence Radiation Laboratory
University of California
Berkeley, California.

September 1964

Abstract

The role the organic diluent plays in the extraction of HClO₄ and HReO₄ into dilute solutions of trilauryl amine (TLA) has been studied, and the nature of the extracted complexes determined. With the exception of tetrachloroethylene, the diluents used in the present study (benzene, mesitylene, sym-triethylbenzene, chlorobenzene, anisole, o-dichlorobenzene, nitrobenzene, and tetrachloroethylene) were aromatic. Their dielectric constants covered a range from 2.3 to 35. It was found that the extraction can be correlated roughly with dielectric constant, but is also dependent upon the basic properties of the diluent. Inference is made that these solvents interact with the hydrogen of the ammonium cation by means of their π-electron system and also through specifically basic groups when present in the molecule. With nitrobenzene as the solvent, the predominant species in the organic phase was dissociated TLAH⁺ and ClO₄⁻ ions; with chlorobenzene, anisole and o-dichlorobenzene, it was a simple ion pair of TLAH⁺ClO₄⁻; and for the remaining low-dielectric solvents, electrostatic polymers were found in the relatively concentrated solutions (up to 0.1 M TLA·HClO₄), and ion pairs only in very dilute concentrations.
Introduction

Among the prominent organic extractants, the trialkyl amines are the most basic, and hence the best extractants for acids. In recent years they have become of particular interest in the extraction of inorganic species.\(^2\)

Before studying the more complex metallo-acid extraction systems, we are investigating the distribution of simple acids. In all such systems of an acid, basic extractant, and solvent, the extraction or distribution can be considered a competition among the organic extractant, water, diluent, and the anion for solvating (coordinating with) the proton. With moderately basic extractants such as tributyl phosphate (TBP), water captures the proton to form the hydronium ion, and may also predominate in the first coordination shell. The resulting hydrated H\(_3\)O\(^+\) is then hydrogen-bonded to TBP molecules, forming the relatively bulky complex cation H\(_3\)O\(^+\)·xH\(_2\)O·3TBP, with 0 ≤ x ≤ 3, in the organic phase.\(^3\)

With the more basic extractant, trioctyl phosphine oxide (TOPO), the water molecules around the H\(_3\)O\(^+\) ion are displaced to yield the H\(_3\)O\(^+\)·3TOPO cation.\(^4\)

The still more basic trialkyl amines can take the proton itself away from the water molecule of the H\(_3\)O\(^+\) ion to form an ammonium ion, R\(_3\)NH\(^+\), with little co-extracted water. It might then be expected that such a system would be relatively simple in behavior. But the smaller size of the presumably uncomplexed R\(_3\)NH\(^+\) ion compared to the large TBP or TOPO complexes of H\(_3\)O\(^+\) may allow electrostatic ion aggregation in the low-dielectric-constant organic phase; and the effect of the co-extracted anion and the influence of the organic diluent must also be considered. For example, the infrared spectra of alkylammonium salts with various anions\(^5\) show a regular progression of the N-H stretching frequency which can, at least roughly, be correlated with the expected order of anion basicity. A similar progression is observed in NMR spectra.\(^5\) Obviously such a cation-anion interaction influences the distribution of the various acids.
In the present paper we are interested in illustrating and discussing the role the organic diluent plays in the extraction, and how its chemical (basic) and its dielectric (coulombic) properties influence the extraction. Only aromatic diluents and a related π-electron containing solvent, tetrachloroethylene, were employed; a later paper will take up the more complicated case of the poorer (less basic) aliphatic solvents.

Experimental

Reagents. Tri-n-lauryl amine, obtained from the Archer-Daniels-Midland Company, Minneapolis, Minnesota, was converted to the hydrochloride salt, purified by recrystallization, and then stored as the salt. The HClO₄ solutions were prepared by dilution of G. F. Smith reagent-grade HClO₄ with conductivity water and standardized by titration with standard base to the phenolphthalein end point. The benzene used was Baker and Adamson reagent-grade; nitrobenzene, anisole, chlorobenzene, and o-dichlorobenzene were white-label reagents of Eastman Kodak Co. The tetrachloroethylene was obtained from Matheson, Coleman, and Bell and had a small amount of alcohol present to act as a stabilizer. Mesitylene also was obtained from Matheson, Coleman, and Bell. The triethylbenzene used was fractionally distilled from material supplied by the organic division of Dupont.

The ReO₄⁻ tracer (mostly Re¹⁸⁶ and a little Re¹⁸⁸) was prepared by irradiating KReO₄ (Varlacid Corp., New York, N. Y.) with neutrons at the Livermore Pool-Type Reactor.

The Karl Fischer reagent for water determination was Matheson, Coleman, and Bell stabilized premixed single solution. The methanol used in the Karl Fischer blank was Baker and Adamson Electronic Grade, < 0.1% H₂O content, kept over molecular sieves.
The analytical techniques used were as follows: 1) The amine concentration was determined by titration with HClO₄ in glacial acetic acid, using methyl violet as an indicator, to a clear blue end point. The titrant was standardized against a known potassium phthalate – glacial acetic acid solution. 2) The alkylammonium salt was determined by titration with NaOCH₃ in a 50-50 mixture of benzene and methanol using thymol blue as an indicator. The sample diluent was N,N-dimethylformamide and the end point was again a clear blue color. NaOCH₃ was standardized against benzoic acid in a 50-50 mixture of methanol and benzene. 3) HClO₄ acid solutions were either standardized by titration with known NaOH solutions to the phenolphthalein end point or prepared by dilution from a standard HClO₄ solution.

Procedure. An approximately 0.1 molar amine solution in the appropriate solvent was converted to the perchlorate-salt form by equilibration with a known, usually 0.2 molar, HClO₄ solution to which had been added a small amount of high-specific-activity ReO₄⁻ tracer. After equilibration, the 0.1 molar active ammonium salt solution was separated, and dilutions of it made to cover the concentration range 0.1 M to 0.001 M or 0.00001 M. Samples of each of these diluted solutions were then shaken (back-extracted) with an equal volume of conductivity water until equilibrium was attained. Duplicate 2-ml aliquots of each centrifuged phase were taken for γ counting in a well-type Na(Tl)I scintillation counter. At the same time an aliquot of the original stock solution of known ClO₄⁻ concentration was counted to provide a conversion factor from c/m to equivalents of ClO₄⁻ in each phase (assuming ReO₄⁻ extracts identically to ClO₄⁻; but see later discussion) from the known total initial ClO₄⁻ concentration. All counts were corrected for background.

For the benzene-TLA system, the individual acid and amine dependencies were examined by keeping either the TLA or HClO₄ concentration fixed and varying
the other. After shaking, centrifugation, and counting of the added perrhenate tracer, the equilibrium concentrations were again calculated from the known initial ClO₄⁻ concentration and the total amount of ReO₄⁻ tracer used.

Attainment of equilibrium was checked by varying the time of shaking and the direction of tracer passage (i.e., organic phase to the aqueous in the back-extraction, aqueous to organic in the forward extraction). Shaking for 1 hour was found to be sufficient time to come to equilibrium for the cases discussed in this paper. All work was performed at 22 ± 1°C.

Measurements of the freezing points of the more concentrated TLA·HClO₄ solutions in benzene and nitrobenzene were made. The apparatus used for the benzene solutions consisted of a resistance bridge, one arm of which was a thermistor (Yellow Spring Instrument Co., Yellow Springs, Ohio; nominal 100 ohms resistance at room temperature); a zener-diode voltage regulator which supplied the signal, and a D.C. amplifier tied to a chart recorder which provided a permanent record of the small, temperature-dependent voltage changes. The voltage versus temperature change was calibrated with solutions of carbon tetrachloride and of TLA of known molality in benzene. To avoid the problem of varying amount of water impurity, the standards were water-equilibrated. The actual TLA·HClO₄ benzene mixtures measured were prepared in the same manner as already described for the back-extraction procedure, except no perrhenate tracer was added. Similarly, we measured the freezing points of solutions of TLA·HClO₄ in water-saturated nitrobenzene, but used a Beckmann thermometer rather than a thermistor and a resistance bridge.

The vapor pressure at 25°C of the more concentrated TLA·HClO₄ solutions in benzene were measured with a model 301-A vapor-pressure osmometer (Mechrolab, Inc., Mountain View, California). Known solutions of TLA in benzene were used to calibrate the apparatus.

Water titrations were performed by the Karl Fischer method, using a direct visual endpoint.
Results

As is evident from the literature of extraction of hydrochloric and nitric acids by tertiary aliphatic amines, conditions exist (high acid concentration in the aqueous phase) where more than one acid molecule extracts per amine molecule. To determine the situation with respect to the extraction of perchloric acid, solutions of 0.1 M TIA in benzene, o-dichlorobenzene, and nitrobenzene were contacted with HClO₄ solutions of various concentrations and the extracted acid determined (Table I). The acid blank for benzene in contact with 10 M HClO₄ was < 10⁻¹⁴ M; the corrections for acid extraction into pure nitrobenzene are listed in Table I. It is evident only simple alkylammonium salt formation occurs even at rather high HClO₄ concentrations. This is in agreement with data on the extraction of HClO₄ by trioctyl amine in CCl₄ where the ratio is nearly one up to an aqueous-phase acid normality of 10. Certainly in this present study, where the acid concentrations employed are not over 0.2 M, there is no possibility for excess acid extraction.

Table I
Ratio HClO₄/TLA in organic phase.

<table>
<thead>
<tr>
<th>HClO₄ molarity</th>
<th>Ratio in benzene</th>
<th>Ratio in o-dichlorobenzene</th>
<th>Ratio in nitrobenzene corrected for HClO₄ extraction</th>
<th>Nitrobenzene correction molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.495</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>--</td>
</tr>
<tr>
<td>0.991</td>
<td>1.00</td>
<td>--</td>
<td>1.00</td>
<td>--</td>
</tr>
<tr>
<td>3.92</td>
<td>1.00</td>
<td>--</td>
<td>1.00</td>
<td>0.002</td>
</tr>
<tr>
<td>6.37</td>
<td>1.00</td>
<td>1.00</td>
<td>1.03</td>
<td>0.008</td>
</tr>
<tr>
<td>10.00</td>
<td>1.10</td>
<td>--</td>
<td>1.07</td>
<td>0.130</td>
</tr>
</tbody>
</table>
Figures 1, 2, and 3 show the results obtained for the extraction (actually from the back-extraction) of HClO₄ by TLA in anisole, benzene, 1,3,5-trimethylbenzene, 1,3,5-triethybenzene, o-dichlorobenzene, chlorobenzene, tetrachloroethylene, and nitrobenzene. For Figs. 1 and 2 the logarithmic plots are of the organic alkylammonium salt concentration vs. the product of the concentrations of the organic amine, aqueous hydrogen ion, and aqueous perchlorate ion. Concentrations of TLA·HClO₄ in the organic phase were determined by counting the ReO₄⁻ in an aliquot and using the conversion constant; the product

$$[\text{H}^+] [\text{ClO}_4^-] [\text{R}_3\text{N}]_{(o)}$$

is similarly obtained from the aqueous phase aliquot with the assumption that all perchloric acid in that phase comes from dissociation of the alkylammonium salt in the back-extraction and leaves an equal amount of free amine in the organic phase, that is

$$\text{R}_3\text{NH}^+ \cdot \text{ClO}_4^-_{(o)} \rightleftharpoons \text{R}_3\text{N}^1_{(o)} + \text{H}^+ + \text{ClO}_4^-$$  \hspace{1cm} (1)

As is discussed later, this appears to be experimentally valid for the systems studied, with the exception of o-dichlorobenzene.

The dotted lines for each of the curves in Figs. 1 and 2 are the results of determining the aqueous-phase acid concentrations by titration. This direct determination, instead of using the ReO₄⁻ tracer data, is necessary only in the more concentrated ammonium salt region and is the result of the difference in extraction between HReO₄ and HClO₄ which becomes greatly exaggerated in the region of organic-phase aggregation. Figure 3 has a log-log plot of the mean alkylammonium salt activity, \(\gamma^+_1(\text{R}_3\text{NH}^+)_{(o)}\), as well as of the organic-phase ammonium-ion concentration vs. the product \([\text{H}^+] [\text{ClO}_4^-] [\text{R}_3\text{N}]_{(o)}\).

Figures 4 and 5 illustrate for the benzene system the dependence of the extraction on amine and acid concentration individually. The solid lines are
for the initial concentrations; the dashed lines are data points corrected to a constant equilibrium amine or acid concentration, as will be discussed later.

Table II gives the result of freezing-point measurements of TLA·HClO₄ in nitrobenzene. Column three of this table lists the apparent molality obtained from the standard expression, $\Delta t = \theta \phi m$; $\theta$ is the molal freezing-point constant, and the value used, 6.72, was experimentally obtained from measurements of naphthalene in water-saturated nitrobenzene. In column three, the value of $\phi$, the molal osmotic coefficient, is assumed to be one. In column five, "apparent corrected molality from freezing point," the values of $\phi$ listed in column four were employed; how they were obtained will be discussed later.

Table II

<table>
<thead>
<tr>
<th>Initial molality, TLA·HClO₄</th>
<th>$\Delta t$, °C</th>
<th>Apparent molality from freezing point</th>
<th>$\phi$</th>
<th>Apparent corrected molality from freezing point</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00424</td>
<td>0.057</td>
<td>0.0085</td>
<td>0.92</td>
<td>0.0092</td>
</tr>
<tr>
<td>0.00850</td>
<td>0.118</td>
<td>0.0176</td>
<td>0.90</td>
<td>0.0194</td>
</tr>
<tr>
<td>0.0439</td>
<td>0.404</td>
<td>0.0601</td>
<td>0.83</td>
<td>0.0733</td>
</tr>
</tbody>
</table>

Table III gives the results of the freezing-point measurements for TLA·HClO₄ in benzene; Table IV lists the vapor-pressure measurements on this same solvent system. The "calculated from extraction data" columns for each table will be discussed later.

Water-titration data for TLA·HClO₄ solutions in benzene, chlorobenzene and anisole are presented in Fig. 7. These are corrected for the solubility of water in the solvents alone. In Table V, water data for amine and ammonium salt solutions in water-saturated tetrachloroethylene are tabulated.
Table III

Freezing-point data of TLA·HClO$_4$ in benzene.

<table>
<thead>
<tr>
<th>Initial molarity, TLA·HClO$_4$</th>
<th>$\Delta t, ^\circ$C</th>
<th>Apparent molarity, freezing point</th>
<th>Free amine</th>
<th>Monomer</th>
<th>Dimer</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00102</td>
<td>0.0059</td>
<td>0.0010</td>
<td>0.00051</td>
<td>0.00049</td>
<td></td>
<td>0.0010</td>
</tr>
<tr>
<td>0.00508</td>
<td>0.0248</td>
<td>0.0046</td>
<td>0.00086</td>
<td>0.00233</td>
<td>0.00099</td>
<td>0.0042</td>
</tr>
<tr>
<td>0.0102</td>
<td>0.0393</td>
<td>0.0076</td>
<td>0.00100</td>
<td>0.00370</td>
<td>0.00250</td>
<td>0.0072</td>
</tr>
<tr>
<td>0.102</td>
<td>0.210</td>
<td>0.0558</td>
<td>0.00159</td>
<td>0.0141</td>
<td>0.0361</td>
<td>0.0518</td>
</tr>
</tbody>
</table>

Table IV

Vapor-pressure measurements of TLA·HClO$_4$ in benzene at 25$^\circ$C.

<table>
<thead>
<tr>
<th>Initial molarity, TLA·HClO$_4$</th>
<th>Apparent molarity</th>
<th>Calculated from extraction data at 22$^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Free amine</td>
</tr>
<tr>
<td>0.0200</td>
<td>0.0142</td>
<td>0.00115</td>
</tr>
<tr>
<td>0.102</td>
<td>0.0510</td>
<td>0.00159</td>
</tr>
</tbody>
</table>

Table V

Water extraction data in C$_2$Cl$_4$ at 22$^\circ$C.

<table>
<thead>
<tr>
<th>System</th>
<th>Organic phase water molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$Cl$_4$</td>
<td>$5.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.01 M TLA, C$_2$Cl$_4$</td>
<td>$5.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.1 M TLA, C$_2$Cl$_4$</td>
<td>$6.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.01 M TLA·HClO$_4$, C$_2$Cl$_4$</td>
<td>$5.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.1 M TLA·HClO$_4$, C$_2$Cl$_4$</td>
<td>$2.5 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
Discussion

The extraction of a strong acid by a solution of a tertiary amine is an acid-base reaction in which the amine molecule takes the proton away from the aqueous $H_3O^+$ ion:

$$R_3N(\text{o}) + H_3O^+ \rightleftharpoons R_3NH^+(\text{o}) + H_2O.$$  

(2)

But even if the anion is a very weak base, it still plays a part in the extraction, as also does the "inert" diluent of the organic phase.\(^7\)

The influence of the anion comes both through its aqueous-phase and its organic-phase behavior. Since the proton can be captured and extracted by the amine only if an anion goes along to preserve electroneutrality, the hydrophobic or hydrophilic nature of the anion helps determine the degree of extraction. That is, one must consider how strongly the anion is bound into the aqueous phase by polar groups and by hydrogen bonds, and how badly its hydrophobic parts break up the water structure and so help in its extraction (ejection) from the aqueous phase. For simple spherical or pseudo-spherical monovalent anions such as the halide ions, the tetra-oxygenated complex ions, $\text{ClO}_4^-$, $\text{ReO}_4^-$, $\text{TeO}_4^-$, $\text{MnO}_4^-$, and the tetra- and hexa-halogenated metal complex ions, $\text{FeCl}_4^-$, $\text{GaBr}_4^-$, $\text{SbCl}_6^-$, etc., this behavior depends upon the size and basicity of the anions,\(^8\) as has been discussed for the somewhat related case of anion exchange with a solid ion-exchange resin.\(^9\)

The anion also plays a role through its organic-phase behavior, even neglecting any possible specific interaction with the solvent molecules, because, again depending upon its basicity and size, it can interact (hydrogen bond or Bjerrum-type ion pair) with the $R_3NH^+$ cation to influence the degree of extraction. Specifically, such interactions help determine the degree of association.
of the alkylammonium salt in the organic phase (this will be discussed more fully in a later report).

In this work we have chosen to study only the extraction of the large and very weakly basic anions \( \text{ClO}_4^- \) and \( \text{ReO}_4^- \) in order to minimize their interactions, particularly of the hydrogen bonding type, with the ammonium cation. We are concerned mainly with the influence of the diluent or solvent. The diluent can interact with the extracted salt through the effect of its dielectric properties on the charged ions, and/or by direct short-range chemical interactions.

The first effect is easy to understand. A relatively large positive electrostatic free energy obstructs the transfer of ions from a medium of high dielectric constant (water) to one with a lower dielectric constant. This is perhaps most readily seen by applying the Born charging expression \(^{10}\) to the transfer of a pair of (dissociated) monovalent ions from water to the organic phase,

\[
\Delta F_{\text{aq.} \rightarrow \text{org.}} = N_{0} \left( \frac{e^2}{2r_{+}} + \frac{e^2}{2r_{-}} \right) \left( \frac{1}{\varepsilon_{\text{org.}}} - \frac{1}{\varepsilon_{\text{aq.}}} \right).
\]

Although such a simple expression based upon a continuum model cannot be expected to compare quantitatively with real systems, the extraction of real systems might be expected to follow at least qualitatively, i.e., the higher the dielectric constant of the organic phase, the better the extraction of a particular acid to form an amine salt. Thus, in the present study, extraction of \( \text{HClO}_4^- \) and \( \text{HReO}_4^- \) is greater into nitrobenzene \( (\varepsilon = 34.8)^{11} \) solutions of trilauryl amine (TLA) than into any other solvent system observed (all with \( \varepsilon < 35 \)).

In Fig. 3 the equilibrium extraction data for \( \text{HReO}_4^- \) tracer out of macro \( \text{HClO}_4^- \) into TLA in nitrobenzene is presented as a log-log plot of the concentration of \( \text{R}_2\text{NH}^+ \) vs. the concentration product \( [\text{H}^+][\text{ClO}_4^-][\text{R}_2\text{N}]_{(c)} \). Such a plot should
yield a slope of one-half or one, depending upon whether the organic-phase species is a dissociated or an associated (ion-paired) salt, respectively. The equations for these two cases are

\[ R_2N(o) + H^+ + ClO_4^- \leftrightarrow R_2NH^+(o) + ClO_4^-(o) \]  

and

\[ R_2N(o) + H^+ + ClO_4^- \leftrightarrow R_2NH^+\cdot ClO_4^-(o). \]  

The usual assumption is made that, for the relatively dilute solutions under study, the activity coefficients of the neutral molecules and ion-paired species in the organic phase are unity. Since the aqueous-phase acid concentrations are so low, concentrations can be substituted for activities within the accuracy of the measurements. Then the equilibrium constant expressions for the above reactions are

\[
K_0 = \frac{[R_2NH^+]_o[ClO_4^-]_o\gamma_\pm^2}{[R_2N]_o[H^+][ClO_4^-]} \]  

and

\[
K_1 = \frac{[R_2NH^+\cdot ClO_4^-]_o}{[R_2N]_o[H^+][ClO_4^-]}. \]  

As can be seen in Fig. 3, the slope of the plot is approximately one-half, indicating the presence of dissociated ions in the organic phase. The change in slope above the value one-half as the concentration was raised was felt to arise from the increase in the interionic attractions of the ammonium salt with increasing concentration. To approximately correct for this effect,
values of $\gamma^\pm (0)$ have been calculated using a Debye-Hückel expression with a
distance-of-closest-approach parameter of 4.0 Å. \textsuperscript{12} The resulting values of
$\gamma^\pm (0)[R_jNH^+] (0)$ are shown in Fig. 3 connected by a dashed line, and it can be
seen that the straight line of slope 1/2 obtained experimentally at low con-
centrations ($\gamma^\pm (0) \to 1$) is continued up to 0.1 M by the corrected data.
Admittedly this treatment is not accurate, since ion association at the higher
concentrations has not been taken into account, but a more detailed calculation
by the method of Mayer and Poirier, \textsuperscript{13} which does include some of the effect of
ion pairing, does not differ significantly from the plotted results (for a dis-
tance-of-closest approach of 5 Å). The plot in Fig. 3, then, leads to a value
for $K_o$ of $2.8 \times 10^7$.

Confirmation of the result that free ions of $R_jNH^+$ and $ClO_4^-$ exist in
the dilute (up to 0.05 M) nitrobenzene solutions comes from the freezing-point
measurements. To provide an approximate correction to the freezing-point
measurements as was done for the extraction data, the molal osmotic coefficient,$\phi$, was calculated by the relationship, \textsuperscript{14}

$$\phi = 1 - 0.7676 f(x) \sigma \sqrt{c}. \quad (6)$$

As seen in Table II, the highest concentration shows a 20% deviation from the
molality calculated assuming complete ionization; but is closer to the molality
calculated as independent ions than as ion pairs.

Let us next consider the sequence of diluents—benzene, sym-trimethyl-
benzene, sym-triethylbenzene. With the back-extraction technique largely used
in this study, a simultaneous variation of both the amine and acid concen-
trations occurs, providing an exacting test of any postulated model. Figure 1
shows that the log-log plot of $[R_jNH^+] (0)$ vs. the product $[H^+][ClO_4^-][R_jN] (0)$
for the system using benzene as the diluent has a slope of unity for an organic-phase ammonium salt concentration range of $1 \times 10^{-7}$ to $7 \times 10^{-4}$ M. This region conforming to eq. 5' is thus interpreted as having the salt exist predominantly as a molecule or as an electrostatic ion pair in the organic phase. The first of these two possibilities is unlikely; almost certainly the salt exists as an ion pair. The result can also be checked by studying the dependence of the extraction on the amine and on the acid concentration individually, when holding the other concentration variable constant. Figures 4 and 5 show that the amount of extracted acid does indeed obey eq. 5' in the range of concentrations under study when corrected to a constant equilibrium concentration of aqueous acid and of organic-phase amine, respectively. These corrections are made by assuming eq. 5' to hold over the small region of extrapolation necessary for the correction; the fact that the corrected points fall on the line whose slope is determined by points where no corrections are needed indicates the validity of the method.

Thus, slope analyses of both forward and backward extractions suggest that the organic-phase perchlorate-salt species in benzene up to a concentration of $7 \times 10^{-4}$ M is an ion pair. From the various sets of data, the value of $K_1$ from eq. 5' can be calculated under these conditions: $K_1 = 3.7 \times 10^6$. It should be realized that this constant actually-expresses the extraction of tracer $\text{HReO}_4$ out of macro $\text{HClO}_4$, not of $\text{HClO}_4$ out of $\text{HClO}_4$. The difference between the two systems is small in the region considered; the constant for pure $\text{HClO}_4$ would be slightly smaller.

The occurrence of ion pairs in the region studied does not tell anything about the nature of the species transferring across the interface; it is not necessary for the ion pair to first form in the aqueous phase. Nor is the formation of an ion pair a requirement for good extraction. On the contrary,
the formation of an ion pair (or higher association) indicates that the solvent has too low a dielectric constant to support dissociated ions, and so is a poor solvent for the extraction of ionic species. The ion-pairing process compensates for some of the electrostatic free energy gained in the transfer from water to the low-dielectric-constant solvent, but simplified calculations indicate that the latter dominates, so that the lower the dielectric constant, the poorer the extraction, and the greater the ion association.

For TIA·HClO₄ concentrations higher than 7 × 10⁻⁴ M in benzene, the extraction data of Fig. 1 indicate a progressively increasing aggregation of the salt. Almost certainly this is an electrostatic polymerization.² By subtracting the amount of ammonium perchlorate ion pair (calculated from the value of K₁ obtained at lower concentrations) from the total organic-phase perchlorate, we can obtain the amount of perchlorate in the more highly associated species. Figure 6 is a log-log plot of this excess versus the product [R₃N]⁻¹[H⁺][ClO₄⁻]. As is evident from Fig. 6, a line of slope two best fits the points and suggests that the electrostatic polymers are principally ion quadrupoles (dimers), with K₂ = [R₃NH⁺·ClO₄⁻]²[ClO₄⁻][H⁺]². The value of K₂ from the plot is 2.5 × 10⁻⁵. The experimental points used for this evaluation of K₂ were those from the titration data, the dotted curve on the back-extractions in Fig. 1, and not the curve given by using ReO₄⁻ tracer. As already mentioned there is a small difference between the extraction of HReO₄ and HClO₄. The result of this difference in the region where the ion quadrupoles (dimers) predominate shows up principally in the value of the aqueous phase HClO₄ concentrations, and is magnified six-fold in the product [R₃N]²[H⁺][ClO₄⁻]². As can be seen, the HClO₄ titration curve converges into the HReO₄ tracer curve at fairly high amine-salt concentrations; it is only at the highest concentration that the difference between the two becomes important.
Further evidence for a quadrupolar species comes from the freezing-point and vapor-pressure measurements. The "apparent molarities" obtained from the freezing points listed in Table III, agree fairly well with the sum of the molarities of free amine, monomer (ion-pair), and dimer as calculated from extraction data up to a value of 0.01 M TIA·HClO₄. The smaller molarity obtained from the freezing-point measurement with 0.1 M TIA·HClO₄ may reflect a real increase in aggregation for the more concentrated solutions with the lowering in temperature from 22°C to the freezing point of benzene. It is evident in Table IV that the "apparent molarities" determined from the vapor-pressure measurements of these more concentrated amine-salt:solutions at 25°C, and the calculated molarities from the 22°C extraction data agree quite well (when only free amine, monomer, and dimer are used in the calculation) even for 0.1 M TIA·HClO₄.

It is interesting to note that agreement between these freezing-point and vapor-pressure values and the extraction data is obtained by ignoring any excess water in the organic phase, even though the Karl Fischer data indicate some water uptake in the range 0.01 to 0.1 TIA·HClO₄ in benzene (Fig. 7). This agreement in the value of "apparent" and total calculated molarities suggests to us that the excess water must not be osmotically active; inclusion of this water in the calculation would lead to the result that the TIA·HClO₄ is extremely highly aggregated under these conditions, in great disagreement with the extraction results. But it is not clear what role this "bound" water is playing in these and similar systems. As is evident from Table V, and in surprising contrast to other less basic extractants such as tributyl phosphate or trioctyl phosphine oxide, the trilauryl amine itself extracts even less water than TIA·HClO₄, remaining essentially unhydrated in the organic diluents investigated.
There is an indication that the aggregation of TIA·HClO₄, which occurs in benzene, is not as large as might be expected to occur with such a low-dielectric-constant medium. Studies with aliphatic hydrocarbons, of not much lower dielectric constants, as diluent show much higher aggregation. A possible explanation is that the π-electrons of the aromatic molecule interact with the hydrogen of the ammonium cation, thus helping to stabilize the salt in the organic phase. To study this possibility, we have measured the extraction of HClO₄ and tracer HReO₄ into trimethylbenzene and triethylbenzene solutions of TIA; these molecules might be expected to show a steric hindrance to such a π-electron interaction. It can be seen from Fig. 1 that the extraction behavior in these two solvents is generally similar to that in benzene. At low concentrations the slope of the log-log plots is unity, indicating ion pairs, and at higher concentrations the plots turn up, suggesting higher aggregation.

But the values of the constant, K₁, for extraction of the ion pair decrease in the order 3.7 × 10⁶, 1.8 × 10⁵, and 2.4 × 10⁴ for benzene, trimethylbenzene, and triethylbenzene, respectively, and the concentrations of TIA·HClO₄ at which the curves rise above a slope of unity similarly decrease from 7 × 10⁻⁴ to 1 × 10⁻⁴ to 1 × 10⁻⁵. Since all three solvents have about the same dielectric constant ε = 2.3 at 25°C, the differences in behavior are best explained as due to the increasing steric blocking posed by the alkyl groups of the alkyl interaction of the π-electrons with the ammonium cation. The larger the alkyl groups, the greater the hindrance, and the weaker the interaction. As a result, the extraction will be poorer, but the need for electrostatic solvation will be greater. So electrostatic aggregation will occur at a lower concentration, as is observed.

Still another type of π-electron-containing diluent was studied, namely tetrachloroethylene. This molecule has a single pair of π-electrons, and the
liquid also has a dielectric constant of 2.3.\textsuperscript{19} As shown in Fig. 2, the equilibrium extraction curve for TLA·HClO\textsubscript{4} and TLA·HReO\textsubscript{4} in tetrachloroethylene is very similar to that in triethylbenzene; \( K_\perp = 3.3 \times 10^4 \). Apparently having only a single pair of \( \pi \)-electrons which are somewhat shielded by the chlorine atoms leads to about the same interaction as the three pairs of \( \pi \)-electrons in the sterically blocked triethylbenzene.

Figure 2 also shows the extraction curve with chlorobenzene as diluent. The shape of the plot indicates ion pairs in the organic phase up to about 0.025 M TLA·HClO\textsubscript{4} with a \( K_\perp \) of \( 4.2 \times 10^7 \). Above this concentration, aggregation apparently commences, but it is to be noted that this is at a considerably higher concentration than with benzene. The major difference between chlorobenzene and benzene is the dipole moment of the former, which leads to its significantly higher dielectric constant, \( \varepsilon = 5.6 \).\textsuperscript{20} It is probably the increased electrostatic solvation of the ions in chlorobenzene, rather than any specific chemical interaction, which is the origin of the order-of-magnitude larger value of \( K_\perp \) and the decreased degree of further aggregation, compared to extraction into benzene.

This trend is continued in going to \( o \)-dichlorobenzene (\( \varepsilon = 9.9 \))\textsuperscript{21} as a diluent, Fig. 2. The log-log plot of unit slope shows that the organic phase contains ion pairs up to a concentration of 0.01 M TLA·HClO\textsubscript{4}, and the value of \( K_\perp \) is still another order of magnitude larger, \( K_\perp = 1.8 \times 10^8 \). Again this increase is due mainly to the increase in dielectric constant, that is to the better electrostatic solvation of the ions. But beyond an organic-phase concentration of 0.01 M TLA·HClO\textsubscript{4}, a progressively increasing amount of the amine salt is transferred to the aqueous phase. The effect of this solubilization is to invalidate the assumption \( [R_3N]_0 = [H^+] = [\text{ClO}_4^-] \). By separating the aqueous phase and then re-extracting it with new solvent, the amount of ammonium
salt present in the aqueous phase could be determined and subtracted from the cube root of the original product, \([R_jN]_c([H^+][ClO_4^-])\). By this means the dotted line in Fig. 2 is obtained. With this correction, the slope of the line is unity up to 0.1 M TLA·HClO₄. The same re-extraction procedure was done for 0.1 M TLA·HClO₄ in chlorobenzene and benzene; the solubility of the ammonium salt in water out of these two solvents, however, was found to be less than \(1 \times 10^{-5}\) M. It is not obvious to us why there should be this peculiarity with \(o\)-dichlorobenzene.

The last solvent used in this study was anisole. Although it has a dielectric constant \((\varepsilon = 4.35)^{22}\) lower than that of chlorobenzene; its equilibrium extraction curve, Fig. 1, shows only ion pairs in the organic phase to 0.1 M TLA·HClO₄, and the value of \(K_1\), \(1.2 \times 10^8\), is three times that for chlorobenzene. Here, obviously, the better extraction and lack of aggregation cannot be due to electrostatic solvation, but to a more specific chemical interaction between the solvent and the cation. There are two possible sources in the anisole molecule for this interaction. The ether oxygen is basic and is the likely site of bonding, but the methoxy group also enhances the influence of the ring \(\pi\)-electrons, and both effects probably contribute.

What conclusions can we draw from the results that have been discussed? Certainly a principal reason, or driving force, for the excellent extraction of aqueous acids by amines comes from the reaction of the amine to form the ammonium cation, eq. 2. Furthermore, reference to Table VI shows that the order of increasing \(K_1\), the overall constant for the extraction of TLA·HClO₄ as an ion pair (the predominant species at lower concentrations for most of the systems studied), parallels roughly the order of increasing dielectric constant. This is not startling; it is what we intuitively expect. And the reason for this has been mentioned; it is because the positive electrostatic
free energy of transfer of the ions from water to the low-dielectric-constant medium is only partially compensated for by the act of ion-pairing (a type of electrostatic solvation).

Table VI

Comparison of order of extraction constants and dielectric constants.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$K_1$</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethylbenzene</td>
<td>$2.4 \times 10^4$</td>
<td>2.26$^{17}$</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>$3.3 \times 10^4$</td>
<td>2.30$^{18}$</td>
</tr>
<tr>
<td>Trimethylbenzene</td>
<td>$1.8 \times 10^5$</td>
<td>2.28$^{17}$</td>
</tr>
<tr>
<td>Benzene</td>
<td>$3.7 \times 10^6$</td>
<td>2.28$^{17}$</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>$4.2 \times 10^7$</td>
<td>5.62$^{19}$</td>
</tr>
<tr>
<td>Anisole</td>
<td>$1.2 \times 10^8$</td>
<td>4.33$^{21}$</td>
</tr>
<tr>
<td>$\alpha$-dichlorobenzene</td>
<td>$1.5 \times 10^8$</td>
<td>9.95$^{20}$</td>
</tr>
</tbody>
</table>

On the other hand, the parallelism in the order is not exact. For example, anisole with a dielectric constant of 4.33 has a larger $K_1$ than chlorobenzene with a dielectric constant of 5.62. Thus, at least one other factor is involved. Besides "electrostatic" solvation of the ions, that is, the effects of the long-range Coulomb field of the ions, there is also a "chemical" solvation, a short-range interaction. By this is meant the direct coordination of the ions with the solvent molecules. The perchlorate anion is a very weak base and as such is not expected to take much part in interactions with the weakly basic solvent molecules used in this study, but the acidic $R_3NH^+$ cation can do so via its hydrogen. This hydrogen, which is most likely the site of the cationic charge, would like to surround itself with
negative charge (i.e., the anion), with the negative end of solvent dipoles, or with any unbonded electron pairs that are available. The π-electrons of the aromatic molecules used as diluents in this study come under this classification, as do the basic electron-donating oxygen atoms of the ether, ester, keto, and nitro groups. The stronger the interaction of the ammonium cation with the π-electrons or the basic groups, the greater will be the reduction in free energy of the species in the organic phase, and the greater will be its extraction.

A similar argument holds for the order of the organic phase TIA·HClO₄ concentrations at which the salt aggregates beyond the ion pair in the different solvents. The order goes roughly as the dielectric constant, but with the same abnormalities. Again these can be explained by the same hypothesis that the stronger the complexing of the ammonium cation by the basic solvent molecules (either through π-electrons or more strongly through basic oxygen-containing groups), the less need the ions have to lower their free energy by ion aggregation. Another way of looking at this is that the stronger the complexing of the ammonium cation by the solvent molecules, the larger the dynamic size of that (solvated) cation, and hence the smaller the degree of aggregation from the usual electrostatic theory.

Finally, the appearance of steric hindrance in the cation complexing by trimethyl and triethylbenzene supports the suggested ammonium-cation solvent interaction, and the particular hypothesis of the π-electron, ammonium-cation interaction would explain the observed fact that the ion aggregation in aromatic solvents is less than that in aliphatic or saturated cyclic solvents. This latter topic will be discussed again in a paper dealing specifically with nonaromatic solvents.
FOOTNOTES AND REFERENCES

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


15. See review of G. Kraus, J. Phys. Chem. 60, 129 (1956), and references therein.


19. A. Weissberger et al., op cit., p. 207.

20. Ibid., p. 190.


22. Ibid., p. 128.
FIGURE CAPTIONS

Fig. 1. Plot of organic-phase alkylammonium salt molarity vs. the product of free amine and aqueous hydrogen and perchlorate ions concentrations, for the organic diluents (1) anisole; (2) benzene, (3) mesitylene, and (4) triethylbenzene. 0, data from $\text{ReO}_4^-$ tracer; $\Delta$, data from acid titration; $\nabla$, data from acid and amine dependencies in benzene (see Figs. 4 and 5).

Fig. 2. Plot of organic-phase alkylammonium salt molarity vs. the product $[\text{R}_3\text{N}]_0[\text{H}^+][\text{ClO}_4^-]$, for the organic diluents (1) $o$-dichlorobenzene, (2) chlorobenzene, and (3) tetrachloroethylene. 0 and $\Theta$, data from $\text{ReO}_4^-$ tracer; $\Delta$, data from acid titration; $\Theta$, see text for explanation of correction for ammonium salt solubility in the aqueous phase.

Fig. 3. Plot of organic-phase alkylammonium salt molarity 0, and mean ion activity $\Theta$, in nitrobenzene vs. the product $[\text{R}_3\text{N}]_0[\text{H}^+][\text{ClO}_4^-]$.

Fig. 4. Dependence of acid extraction on amine molarity, in benzene, at an aqueous hydrogen-ion concentration of $9.90 \times 10^{-5}$ molar. 0, constant initial acid concentration; $\Theta$, data corrected to a constant equilibrium aqueous hydrogen-ion molarity.

Fig. 5. Dependence of acid extraction on aqueous acid molarity at a constant amine concentration in benzene: (1) $[\text{R}_3\text{N}]_0=2.28 \times 10^{-4}$; (2) $[\text{R}_3\text{N}]_0=3.42 \times 10^{-5}$. 0, constant initial amine concentration; $\Theta$, data corrected to a constant equilibrium amine concentration.

Fig. 6. Concentration of organic-phase acid in excess of that as ion pairs vs. the product $[\text{R}_3\text{N}]_0[\text{H}^+][\text{ClO}_4^-]$.

Fig. 7. Variation of organic-phase water uptake as function of trilaurylammonium perchlorate concentration. $\Theta$, benzene; $\Delta$, chlorobenzene; 0, anisole.
Fig. 1
Fig. 2
Fig. 3

\[ \frac{[R_3NH]^+}{[R_3NH^+]_0} \] vs. \( [R_3N]_0 [H^+] [ClO_4^-] \)
Fig. 4
Fig. 6

$\left[ H^+ \right]_0 - \left[ H^+ \right]_{\text{monomer}}$

$10^{-3}$

$10^{-2}$

$10^{-1}$

$10^{-10}$

$10^{-9}$

$10^{-8}$

$\left[ R_3 N \right]_0$ $\left[ H^+ \right]$ $\left[ \text{ClO}_4^- \right]$
Fig. 7
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.