A STUDY OF THE SOLVENT PROPERTIES
OF ANHYDROUS NITRIC ACID

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A STUDY OF THE SOLVENT PROPERTIES OF ANHYDROUS NITRIC ACID

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To my wife
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The solubilities of selected salts in anhydrous nitric acid were determined by evaporation of the solvent, conversion of the nitrate to the sulfate and recovery of the sulfate, or flame photometry. The methods were compared for salts of low and high concentration. The solubilities determined were in the order $Sr(NO_3)_2 < LiNO_3 < Ba(NO_3)_2 \ll KClO_4 < NaNO_3 < KNO_3$. The results for $LiNO_3$ agreed with reported data while the results for $NaNO_3$ and KNO_3 were higher than results obtained by other investigators. These differences might be due to the expected increase of non-ideality for concentrated solutions. Potassium perchlorate was less soluble than KNO_3, probably due to a difference in anion solvation. The differences in the solubilities of the nitrate salts investigated may be attributed to differences in cation solvation which has been proposed as being related to ionic potential of the cations.

The Cl^-, F^-, and MnO_4^- ions were found to be reactive in ANA. The reactivity of these ions has been explained as being due to the presence of both an oxidizing and reducing species in the acid.

CHAPTER I

INTRODUCTION

Anhydrous nitric acid (hereafter referred to as ANA) is a water-white liquid with a freezing point of -42°C, a density of 1.5630 ± 0.0002 g ml^{-1} at -10°C, and a specific conductance of 0.0348 ± 0.0003 ohm^{-1} at -10°C (17). At temperatures above its freezing point ANA decomposes according to the following equation:

$$2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \tfrac{1}{2}O_2$$

where NO_2 represents an equilibrium mixture of nitrogen dioxide, NO_2, and dinitrogen tetroxide, N_2O_4. Owing to its instability, special precautions must be taken to prepare and preserve pure nitric acid. Several methods have been used to prepare ANA in the laboratory. Treating anhydrous alkali metal nitrates with 100% sulfuric acid and condensing the volatilized nitric acid product (10), fractional crystallization of ANA from concentrated nitric acid (2), and distillation of ANA from a mixture of concentrated nitric acid and 95 - 100% sulfuric acid (1) (14) have been used. The ANA employed in the herein described investigation was prepared by the third method.

The large electrical conductivity of ANA suggested that the compound is extensively self-ionized and has led to the investigation of the mechanism of self-ionization (9)(11)(13)(28).

The currently accepted method of self-ionization, substantiated by cryoscopic measurements (9)(11) and by detection of the NO_2^+ and NO_3^- ions in Raman (12)(15), infrared (21)(22), and nuclear magnetic resonance (23) spectra, is represented by the following equation:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

Water, H_2O, has been detected in ANA by identification of the hydrogen-bond solvate bonds (5). The equilibrium constant for the ionization process has been determined (17) as follows:

$$K_x = \frac{(X_{NO_2^+})\ (X_{NO_3^-})\ (X_{H_2O})\ (\gamma\pm)\ (\gamma_{H_2O})}{(X_{HNO_3})^2\ (\gamma_{HNO_3})^2}$$

where X and γ are the mole fractions and activities, respectively, for the species shown. The addition of the product(s) reverses the equilibrium of the self-ionization reaction shown (15)(21).

ANA apparently does not react with water, in the normal manner, to yield hydronium ions, H_3O^+, in solutions containing up to 10% water. This is evidenced by lower measured conductivity for solutions of water as compared to pure ANA (4)(8)(27).

The products of self-ionization are strongly solvated as indicated by cryoscopic and viscometric measurements (7)(11)(16)(18)(19)(20). Based on these measurements, the nitrate ion and nitronium ion have each been assigned a solvation number of 2; in other words, these ions have two molecules of undissociated HNO_3 associated with each ion. In nitric acid, containing up to 5% added water, water has been assigned a solvation number of 1. Data recently obtained (4)(20) indicates that the properties of the above solutions cannot be completely interpreted in terms of the solvation effects cited above nor in terms of ideal solutions. The vapor pressure lowering of ANA by alkali nitrates was explained by the formation of hydrogen-bond solvated complexes of the form $(NO_3^-) \cdot HNO_3$ (16).

A study of the solubility of alkali metal and alkaline earth nitrates was undertaken in an effort to relate the solvation of the cations to physical measurements. Nitrate salts of these elements were chosen because of the common ion (NO_3^-) whereby changes in the solvation could be expected to be related to the cations without the interference of an anion solvation effect.

CHAPTER II

EXPERIMENTAL INVESTIGATION OF SOLVENT PROPERTIES OF ANHYDROUS NITRIC ACID

I. MATERIALS AND EQUIPMENT USED

J.T. Baker fuming nitric acid (90% HNO_3) and Fisher Commercial Grade concentrated H_2SO_4 were used in preparing the ANA. All salts used in preparation of solutions were Fisher Certified Reagent Grade without further purification. All glassware was standard, calibrated Pyrex glassware.

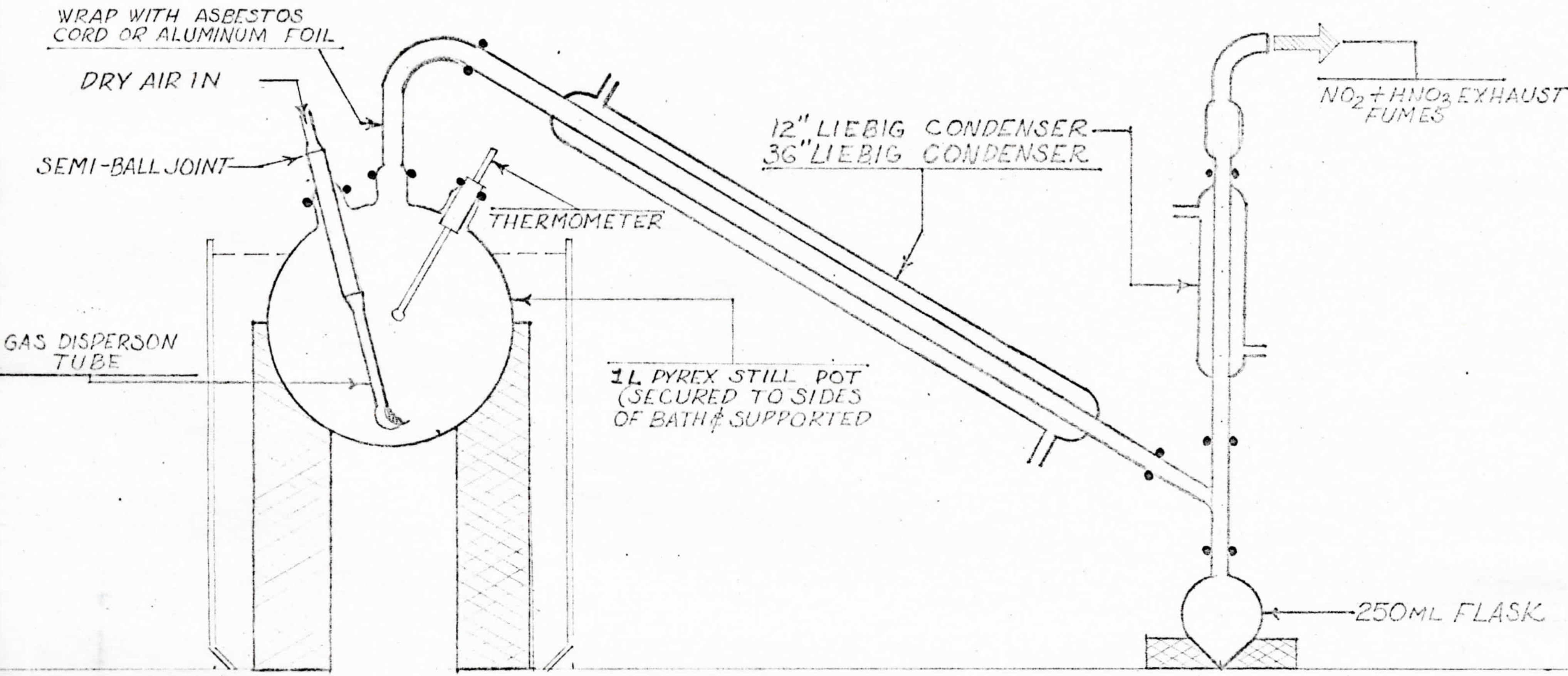
The emission flame spectrophotometer used in the flame analyses was the Beckman Model B Spectrophotometer with the Beckman B9125 Flame Attachment.

II. EXPERIMENTAL PROCEDURES

Preparation of ANA. ANA was distilled from a 4:1 mixture of fuming nitric acid and concentrated H_2SO_4. A diagram of the distillation apparatus is shown in Figure 1.

One hundred twenty-five milliliters of H_2SO_4 was placed in the 1000 ml. three necked flask, followed by 600 milliliters of fuming nitric acid. If the ambient temperature exceeded 25°C the mixture was cooled. All ground glass joints were

FIGURE I
DISTILLATION APPARATUS FOR PREPARATION
OF ANHYDROUS NITRIC ACID



NOTE: A "GLASS-COL" HEATING MANTLE OR A CONSTANT WATER LEVEL HEATING BATH MAY BE USED FOR TEMPERATURE CONTROL.

NOTE: ALL CONNECTIONS ARE ₸ 24/40

greased with Kel-F grease. Dry air was then blown through the mixture at a very moderate rate for 24 hours to remove dissolved NO_2. The temperature of the Glass-col heating mantle was raised to 60°C and the acid was carried over on the dry air stream. The yields of ANA varied from 50 - 70% depending on the efficiency of the reflux condenser. If the temperature significantly exceeded 60° some NO_2 discolored the product; however, with proper temperature control a water-white product could be obtained.

Sample Preparation. Saturated solutions of the salts were prepared by adding ANA to portions of the dried salts contained in small volumetric flasks. After addition of the ANA, the flasks were stoppered to prevent absorption of moisture from the air and stored at -10°C to effect saturation. From time to time the flasks were shaken to insure saturation. When saturation appeared complete, the flasks were transferred to an ice bath, 0±0.5°C. The flasks were held at this temperature for about three hours with frequent shaking to effect equilibrium and, if necessary, additional dry salt added before removal of samples for analysis. Five milliliter samples for analysis were transferred to weighing bottles or weighed volumetric flasks, as appropriate, and weighed. An all-glass hypodermic syringe, permanently affixed to the 5 milliliter pipette, was used to remove the samples, to prevent contamination, and enhance safety in handling. After the samples were weighed, they were diluted with demineralized water.

Flame Analysis for Li , Na^+, K^+, Ba^{2+}, Sr^{2+}. The relative emissions, as % transmittance, for each of the above volumetrically diluted samples was determined (26). Concentration of the alkali or alkaline earth metal ions was determined from a calibration curve previously obtained from standard solutions varying in concentration from 0 - 100 micrograms of cation per milliliter of solution. The wavelengths used for the analyses and the detection limits for each ion are shown in Table I.

Analysis of $LiNO_3$, $NaNO_3$, and KNO_3 by Evaporation. The samples were evaporated to constant weight in a hood by means of a heat lamp. The temperature was kept below boiling to prevent loss of the nitrates through bumping or spattering.

EDTA Analysis for Sr^{2+} and Ba^{2+}. The volumetrically diluted samples of strontium nitrate and barium nitrate were titrated with EDTA (disodium ethylenediamine tetraacetic acid) in a buffered solution of pH 12.5 using MTB (methyl thymol blue) as the indicator (25). The results were inaccurate due to a dragging endpoint and, in an effort to minimize this effect, a screened indicator was prepared by the tri-stimulus method of Reilly and Sawyer (26). The titration was performed again and, as before, the results were inaccurate. For this reason,

TABLE I

EMISSION SPECTRA OF

Ba, Li, K, Na, and Sr

Element	Wavelength $m\mu$	Emission Sensitivity $\mu g\ ml^{-1}\ (\%\ T)^{-1}$
Barium	455.5 553.6	3.0 1.0
Lithium	670.8	.067
Potassium	404.4 767	1.7 .02
Sodium	590.0	.001
Strontium	460.7	.06

flame analysis was used in determining Sr^{2+} and Ba^{2+} although the EDTA is more precise at moderate concentrations.

CHAPTER III

DISCUSSION OF RESULTS

The literature contains references to the solubility of several salts in ANA (20)(24), a summary of which is given in Table II. Since these determinations were made by extrapolation of vapor pressure data or the method was not specified, an attempt was made to verify several of these determinations by the direct determination of the salt present in the solution. In an attempt to relate cation solvation effects to solubility, the solubilities of some heretofore unreported metal nitrate salts were determined. The results obtained for the above measurements and the methods of analysis used in the determinations are given in Table III.

Saturated solutions of ANA and lithium, sodium, barium, and strontium nitrates were prepared. Samples of each of these solutions were taken and the solubility determined by evaporation of the solvent. During evaporation a white film formed on the surfaces of the weighing bottles which was assumed to be due to the reaction of the vapors with some atmospheric contaminant; therefore, the results obtained were unreliable. In a redetermination of the $LiNO_3$ solution and, also, of other salts in subsequent determinations by the same method, the occurrence of the white film was prevented by

TABLE II

SOLUBILITY OF SELECTED SALTS IN ANHYDROUS NITRIC ACID AT 0°C, DETERMINED BY EXTRAPOLATION OF VAPOR PRESSURE DATA (20)

Substance	Solubility	
	g per 100g of HNO_3	g per 100g solution
KNO_3	35.0	25.9
$NaNO_3$	9.2	8.4
NH_4NO_3	26.7	21.1
NH_4ClO_4	3.7	3.6
KH_2PO_4	<45	<31

NOTE: The data of Potier and co-workers (24) is given in the form of a curve from which no reliable values could be obtained, although the solubilities of the alkali nitrates follows the order $Li \ll Na < Rb < Cs < K$ at 0°C.

TABLE III

SOLUBILITIES OF SELECTED SALTS IN ANHYDROUS NITRIC ACID AT 0°C, DETERMINED BY MEASUREMENT OF THE CONCENTRATION OF THE SALT OR ITS CATION

Substance	Solubility g per 100g of solution	Average Deviation %	Method of Analysis
KNO_3	47.80	± 0.69	Evaporation
$NaNO_3$	11.4	± 6.5	Flame Photometry
	12.88	± 2.85	Evaporation
$LiNO_3$	0.023	± 3.9	Evaporation
	0.023	± 14.6	Conversion to Sulfate
	0.028	± 1.5	Flame Photometry
$Sr(NO_3)_2$	0.0137	± 1.2	Flame Photometry
$Ba(NO_3)_2$	0.0773	± 2.3	Flame Photometry
$KClO_4$	1.75	± 1.1	Flame Photometry

carrying out the evaporation in a hood arranged for maximum air flow rate. Despite the improved reliability, the high possible error inherent in such low values for the solubility as that of $LiNO_3$ led to the use of flame photometric analyses for subsequent determinations where the solubility is low.

Lithium nitrate was analyzed by the two above cited techniques and, in addition, by evaporation after the conversion of the nitrate to the sulfate with H_2SO_4 in an attempt to reduce decomposition of the nitrate salt. The three methods are compared in Table IV. It may be noted from Table IV that the results are in good agreement in all three cases, from which it was concluded that any of the three methods investigated would be applicable in subsequent work. It may also be noted that these results confirm the reported observation (24) that lithium nitrate has a relatively low solubility in ANA.

The solubility of $NaNO_3$ in ANA was determined by analysis of the nitric acid-$NaNO_3$ solutions (after dilution with demineralized water) for the sodium ion by the flame photometric method. The results of these analyses are shown in Table V. The large average deviation, as shown in the table, was attributed to the high $NaNO_3$ concentration present in the nitric acid-$NaNO_3$ solutions. Because of the high solubility, the $NaNO_3$ solutions were also analyzed by the evaporation

TABLE IV

DETERMINATION OF THE SOLUBILITY OF $LiNO_3$ IN ANHYDROUS NITRIC ACID AT 0°C AND COMPARISON OF THREE METHODS OF ANALYSIS

Sample	Solubility g per 100g of solution	Deviation	Method
1	0.0275	0.0007	Flame Photometry
2	0.0288	0.0006	
3	0.0282	0.0000	
Average	0.0282	0.00043 (±1.5%)	Flame Photometry
1	0.0212	0.0014	Evaporation
2	0.0236	0.0010	
3	0.0229	0.0003	
Average	0.0226	0.0009 (±3.8 %)	Evaporation
1	0.0189	0.0043	Conversion to Sulfate
2	0.0298	0.0066	
3	0.0209	0.0023	
Average	0.0232	0.0044 (±14.6%)	Conversion to Sulfate

TABLE V

DETERMINATION OF THE SOLUBILITY OF $NaNO_3$ IN ANHYDROUS NITRIC ACID AT 0°C AND COMPARISON OF THE METHODS OF ANALYSIS

Sample	Solubility g per 100g of solution		Method
1	11.9	0.3	Flame Photometry
2	11.1	0.5	
3	11.4	0.2	
4	13.0	1.4	
5	12.3	0.7	
6	10.2	1.4	
Average	11.6	0.75 (±6.46%)	Flame Photometry
1	13.19	0.31	Evaporation
2	12.62	0.26	
3	12.41	0.47	
4	13.31	0.43	
Average	12.88	0.367 (±2.85%)	Evaporation

method, and, as shown in Table V, the results are in good agreement with those obtained by the flame photometric method. As also shown in Table V, the solubility found exceeds the reported values. The solubilities determined in this investigation, for those salts of relatively high solubility, exceed the values previously reported in the literature obtained by extrapolation of vapor pressures. This suggests that the method based on the actual determination of the metal ion in solution could be more reliable insofar as the more concentrated solutions would be expected to exhibit less ideal behavior.

In the preparation of the KNO_3-ANA solutions, it was evident that the solubility was of such magnitude as to preclude analysis of the potassium ion by the flame photometric method. Therefore, the evaporation method was used for the analysis of the potassium ion. It was also observed that the solution of KNO_3 in ANA is a highly exothermic process, confirming an observation previously reported (6). It was also noted that the solutions became slightly yellow colored which can be explained as being due to the thermal decomposition of some ANA and the solution of the products. At the temperatures used to effect saturation, the KNO_3 solutions showed a strong tendency to form a white crystaline solid which could be due to the formation of a complex of the form $KNO_3 \cdot HNO_3$ which has been reported in the literature (16).

A volumetric method for the determination of the strontium and barium ions, employing EDTA and MTB as an indicator, has been developed which reportedly gives good results (25). An attempt was made to analyze the ANA-$Ba(NO_3)_2$ or $Sr(NO_3)_2$ solutions by this method; however, the results were unsatisfactory due to the dragging endpoint obtained. Redeterminations employing a screened indicator were equally as inconclusive. Subsequent determination by the flame photometric method indicated that a possible explanation of the dragging endpoint was the small concentration of the barium and strontium ions in the solutions. Similarly, gravimetric analyses were not performed on the barium and strontium ions for this reason.

In an effort to study the anion solvation effect on the previous solubilities, it was decided to investigate the solubilities of other metal salts in ANA.

The addition of ANA to dried NaCl produces an immediate, highly exothermic reaction yielding a brown gaseous product. No attempt was made to collect gas samples for analysis; however, it may be reasonably assumed that, in addition to NO_2 from thermal decomposition of ANA, volatile chlorine compounds, resulting from oxidation of the chloride ion, could be present.

In view of the NaCl-ANA reactions, it was decided to investigate the possible reactions between $KClO_4$ and ANA ($NaClO_4$

was not available at the time). Since the perchlorate ion (ClO_4^-) represents chlorine in its highest oxidation state, the non-observance of any reaction upon solution would indirectly support evidence for oxidation of the chloride ion in NaCl. As anticipated, no apparent reaction occurred when ANA was added to anhydrous $KClO_4$. The solubility was determined by flame photometric analysis for the potassium ion, the results of which are shown in Table III. As may be seen by comparision of the results of the KNO_3 solubility determination, $KClO_4$ is significantly less soluble.

Since the fluoride ion is known to be more stable with respect to chemical oxidation than the chloride ion, it may be reasonably expected that NaF would not be reactive with ANA. However, the addition of ANA to dried NaF yielded an immediate exothermic reaction producing a pale brown gas and sufficient energy to apparently fuse the NaF remaining in the flasks. This reaction, along with the ANA-NaCl reaction, confirms the extreme reactivity of ANA. As with the NaCl reaction, no attempt was made to collect or analyze the products of the reaction and no explanation as to the course of the reaction can therefore be proposed.

The reaction of ANA with $KMnO_4$ had been reported to yield MnO_2 as a reaction product (3). In order to confirm this observation, ANA was added to dried $KMnO_4$. There was no apparent immediate reaction and the solution took on the purple color characteristic of the permanganate ion. Shortly thereafter, however, reaction occurred as was evidenced by the appearance of black MnO_2 in the reaction vessel. Since MnO_2 represents a lower oxidation state of manganese than permanganate, it may thus be concluded that ANA can, under specific circumstances, act as either an oxidizing or reducing agent.

CHAPTER IV

SUMMARY AND CONCLUSIONS

The solubility of selected salts in ANA was determined in an attempt to relate solubility to cation solvation effects. In this investigation the solubilities were determined by direct measurement of the salt or the salt cation in solution whereas previously reported data was obtained by extrapolation of data obtained by measurements of the colligative properties of ANA-salt solutions (20). Three methods of analysis for the salt concentration were employed in this investigation; (1) recovery of the salts in solution by evaporation of the ANA solvent, (2) flame photometric determination of the metal ion in solution, and (3) conversion of nitrates to sulfates by H_2SO_4 and subsequent recovery of the sulfate salt. The results obtained are shown in Table III and, as can be noted, are in the following order: $Sr(NO_3)_2 < LiNO_3 < Ba(NO_3)_2 \ll KClO_4 < NaNO_3 < KNO_3$. The data for $LiNO_3$ agrees with the previously reported data (24); however, as seen by comparison of Table II with Table III, there is a significant difference in the data obtained in this investigation and that previously reported for $NaNO_3$ and KNO_3. In those cases of high solubility, for example $NaNO_3$ and KNO_3, it may be reasonably expected that deviations from ideality would be greater and that the direct measurement of the salt, or its cation, in solution would be more reliable than those results obtained by measurements of properties influenced by the ideality of the solution. The difference in solubility, and related solvation effects, between a number of salts, all with the same anion, may be related to differences in ionic potential. Ionic potential is defined as the ratio of ionic charge (in esu) to crystal radius (in A^o) from which it may be seen that the ionic potential decreases with increasing atomic number within periodic groups or increases with increasing charge on the ion. In Figure II, wherein the solubility versus ionic potential is plotted for the cations investigated, the influence of ionic potential on solubility can be seen. The higher heat of solution of KNO_3 in ANA, also observed in previous investigations, would likewise tend to support the inference of greater solvation effects for the larger ions.

The effect of the anion on solubility and solvation was investigated for selected salts in which the cation was maintained constant. As previously noted in the Discussion of Results, both NaCl and NaF reacted with the solvent in some as yet unexplained manner. In the case where no apparent reaction occurred, the solubilization of $KClO_4$ in ANA was investigated. The decreased solubility of $KClO_4$ with respect to KNO_3 may possibly be attributed to the lesser

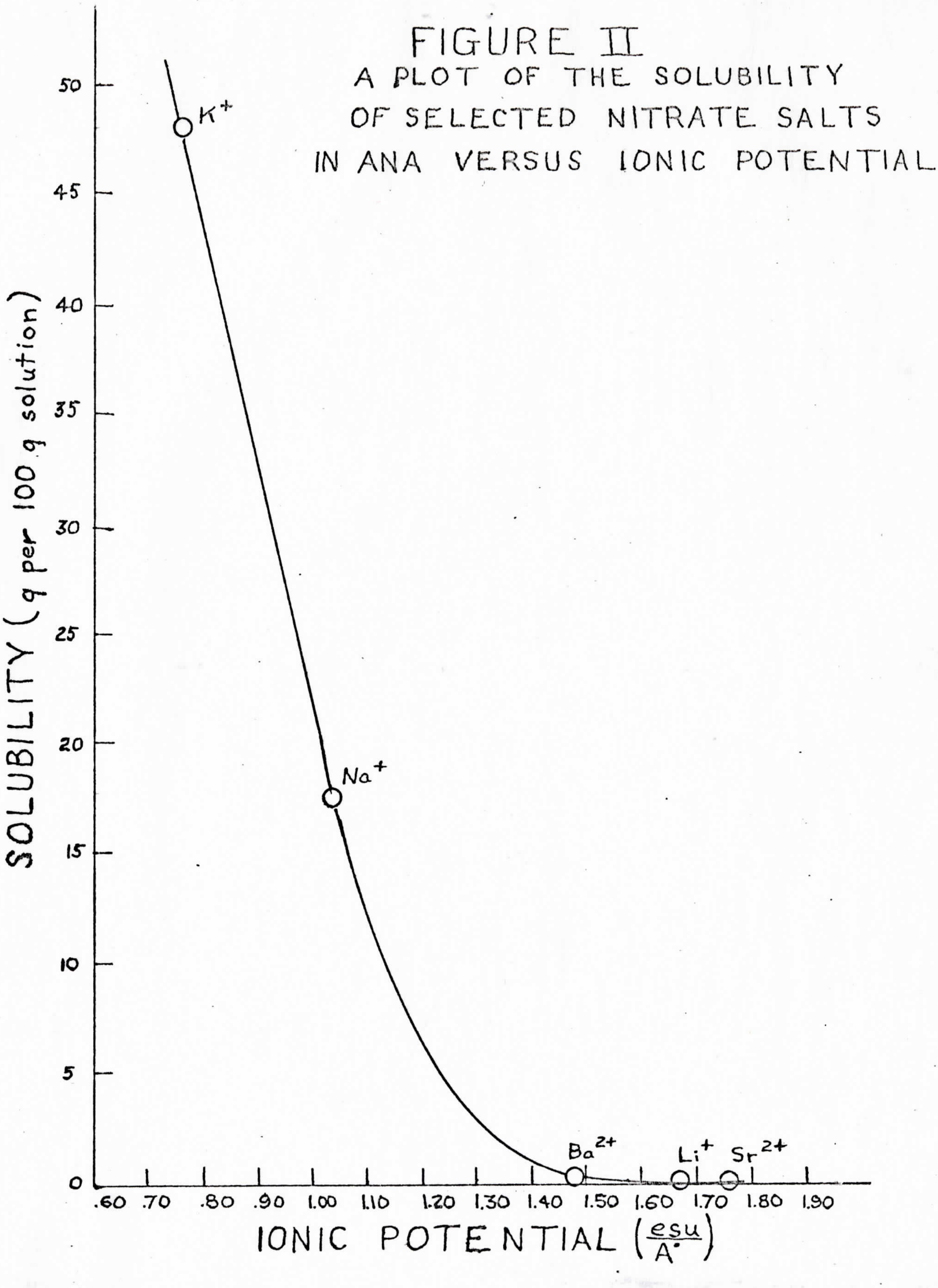


FIGURE II
A PLOT OF THE SOLUBILITY OF SELECTED NITRATE SALTS IN ANA VERSUS IONIC POTENTIAL

solvation of the perchlorate ion. Insofar as the pursuit of the investigation of cationic solvation effects is concerned, the selection of anions is limited as is indicated by the reaction of the permanganate ion, MnO_4^-, with the solvent to yield manganese dioxide, MnO_2.

The reaction of the Cl^-, F^-, and MnO_4^- ions with ANA can only be explained as being due to the presence of both an oxidizing and a reducing species in the solvent. The equilibrium set up by self-ionization of the solvent, as shown below:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

may be interpreted as yielding an oxidizing species, NO_3^-, and a reducing species, NO_2^+, on the basis of which ANA may be reasonably expected to exhibit both oxidizing and reducing properties, dependent upon the conditions of reaction.

Table IV compares the three methods of determination previously mentioned for the solubility of $LiNO_3$. From this comparison, it may be concluded that for salts of low solubility in ANA the flame photometric method is the most reliable.

In Table V, the evaporation method and the flame photometric method are compared for a salt of reasonably high solubility, NaCl. As may be noted, the evaporation method gives more reliable results, probably due to the large inherent error introduced in the dilution of the solutions to the concentration range applicable for the determination by the flame photometer.

This investigation has shown that determinations of Ba^{2+} and Sr^{2+}, at the concentration levels produced in ANA solutions, cannot be made by methods involving the titration of these ions by EDTA.

As noted previously, changing the anion changes the solubility due to a difference in solvation of the anions. Therefore, by assuming a point of zero solvation for an anion, the solvation due to the cation may be calculated and related to thermodynamic properties. Further investigation is planned whereby this line of pursuit is followed for salts of differing anions which are stable in ANA. Electrical conductivity measurements would accompany these investigations so as to relate ionic characteristics of the solution to solvation effects.

As shown above, both oxidizing and reducing species must be present in ANA. Further work to prove the oxidizing and reducing species present is a necessary step toward predicting the reactivity of ANA and a specified reactant.

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