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THE STRUCTURE AND EXTRACTIVE POWER OF AMINES AND THEIR SALTS

V. S. Shmidt and E. A. Mezhov

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I. INTRODUCTION

In recent years a large number of papers have been published dealing with the use of amines of high molecular weight as extractants. The extraction of acids with amines and amine salts has attracted the greatest attention[1-40]; the extraction of metal salts by amine salts from hydrochloric-acid[1,17,23,41-84], sulphuric-acid[85-96], and nitric-acid[8,22,97-132] solutions and other media[133-144] has also attracted attention.

High-molecular-weight amines extract acids because, being bases, they are neutralised on contact with aqueous solutions of acids, and the amine salts formed pass into the organic phase.

In the presence of a sufficient excess of acid, the amines are almost completely present as the corresponding salts. Therefore, in the extraction of acids and salts from acid solution, the part of extractant is played in the majority of cases not by the amines themselves, but by their salts.

The relation between the structure of amines and the extractive power of their salts has attracted great attention. The possibility of predicting the extractive properties of amine salts is of great practical importance in the selection of extractants for different purposes. A considerable number of experimental results on the extractive power of amine salts have now been published. The object of the present review is to systematise these results and to interpret them from the point of view of information in the literature on the structure of amine salts. Extraction by amine salts may take place by different mechanism. Therefore, possible mechanisms for the extraction of acids and metal salts by amine salts are first briefly considered.

II. BRIEF INFORMATION ON THE MECHANISM OF EXTRACTION OF ACIDS AND METAL SALTS BY AMINE SALTS

The extraction of acids by amine salts may proceed with the formation of addition products or by anion-exchange mechanism. The extraction of nitric acid with tri-n-octyl-[3], di-n-octyl-,[4] tri-n-nonyl-,[8] tri-n-decyl-[8], or tri-n-dodecyl-ammonium[129] nitrates is an example of extraction by an addition mechanism; the reaction is of the type†

$$\text{AmineHNO}_3\,\text{org} + \text{H}^+_{\text{aq}} + \text{NO}^-_{3\,\text{aq}} \rightleftharpoons [\text{AmineHNO}_3]\text{HNO}_{3\,\text{org}}. \qquad (1)$$

Examples of the anion-exchange mechanism are provided by the extraction of oxalic acid by tri-n-octylammonium nitrate[6,7]

$$\text{AmineHNO}_3\,\text{org} + \text{HC}_2\text{O}^-_{4\,\text{aq}} \rightleftharpoons \text{AmineH}_2\text{C}_2\text{O}_4\,\text{org} + \text{NO}^-_{3\,\text{aq}}, \qquad (2)$$

the extraction of nitric acid by an amine perchlorate[106]

$$\text{AmineHClO}_4\,\text{org} + \text{NO}^-_{3\,\text{aq}} \rightleftharpoons \text{AmineHNO}_3\,\text{org} + \text{ClO}^-_{4\,\text{aq}}, \qquad (3)$$

and the extraction of technetium(VII)[34] by the reaction

$$\text{AmineHNO}_3\,\text{org} + \text{TcO}^-_{4\,\text{aq}} \rightleftharpoons \text{AmineHTcO}_4\,\text{org} + \text{NO}^-_{3\,\text{aq}}. \qquad (4)$$

Metal salts MA_m are extracted by amine salts AmineHA because compounds are formed that pass into the organic phase; their composition may be expressed by the formula $(\text{AmineHA})_n.MA_m$.[100]‡ The structure of these compounds is more closely represented by the formula $(\text{AmineH})_n[MA_{n+m}]$, since interaction of the molecules of amine with the metal atom is not effected directly but through the system AmineH–A–M, and the absorption spectra indicate the presence of the complex anions MA^{n-}_{n+m} in the molecules of the extracted compounds[97,99,106]. The sum $n+m$ is usually equal to the coordination number of the central atom M.

The formation of the extractable compounds of metal salts may be represented by the addition reaction

$$MA_{m\,\text{aq}} + n(\text{AmineHA})_{\text{org}} \rightleftharpoons (\text{AmineH})_n[MA_{n+m}]_{\text{org}}, \qquad (5)$$

by the anion-exchange reaction

$$MA^{n-}_{n+m\,\text{aq}} + n(\text{AmineHA})_{\text{org}} \rightleftharpoons (\text{AmineH})_n[MA_{n+m}]_{\text{org}} + nA^-_{\text{aq}}, \qquad (6)$$

or by a number of simultaneous addition and anion-exchange reactions

$$MA^{(m-i)+}_{i\,\text{aq}} + n(\text{AmineHA})_{\text{org}} \rightleftharpoons (\text{AmineH})_n[MA_{n+m}]_{\text{org}} + (i-m)A^-_{\text{aq}}, \qquad (7)$$

where the minimum value of i is 0 and the maximum corresponds to the coordination number of the ion M^{m+}.[60,99,100]

Since for reactions (5)–(7), corresponding to different values of i, the reaction product is identical but the metal compounds in the aqueous phase are in dynamic equilibrium with one another, the position of the extraction equilibrium for any given composition of the phases does not depend on the reaction by which the compound is formed. For this reason, in spite of the extensive experimental information available on extraction equilibria, there were until recently no convincing arguments in the literature on how to find out by which of the above reactions the extraction of metal salts by amine salts occurs in any individual case.

Investigation of the mechanism of the extraction of uranyl sulphate by an ^{35}S-labelled amine sulphate showed that, under conditions such that anionic uranyl complexes predominate in the aqueous solution, extraction occurs mainly by an anion-exchange mechanism; but when anionic complexes are not present in solution, extraction by addition reactions predominates[145]. This rule appears to be valid also for the extraction of salts of other metals by amine salts with like anions.

The ability of amine salts to extract acids and metal salts by an addition mechanism depends on the stability of the extractable addition compounds formed by their interaction. The ability of amine salts to extract anions by an anion-exchange mechanism, however, depends on the relation between the stability of the initial amine salt and of the compound formed after anion exchange. If the amine salt is to have the properties of a strong extractant, it is also necessary that this salt and the extracted compound should, as far as possible, be slightly soluble in the aqueous phase, and on extraction should go practically completely into the organic phase. It is usual to employ amine salts with a quite high molecular weight. Compounds of these amines pass practically completely into the organic phase during extraction, and therefore extractive power is largely determined by the stability of the compound extracted.

In this review the main factors connected with the structure of amines that determine the extractive power of their

† The initial amine salt and the addition product may be present in the solutions as polymers[5,19,36-38].

‡ The compound extracted may be solvated by solvent molecules including AmineHA molecules[117].

salts are considered. Since the extractive power of amine salts insoluble in water is determined by the stability of the extractable compounds that they form, the relation between the stability of these compounds and the structure of the amine salts used as extractants will first be considered.

III. THE EFFECT OF THE STRUCTURE OF AMINE SALTS ON THE STABILITY OF THE COMPOUND EXTRACTED BY DIFFERENT EXTRACTION MECHANISMS

1. Extraction of Acids by an Addition Mechanism

A large number of addition products of acids and salts have been described in the literature[146-162]. In 1908 a product of the addition of HCl to tetramethylammonium chloride $(CH_3)_4NCl.HCl$ was isolated[147,148]. There are other reports of the preparation of compounds of this type[149-154]. After these reports, many papers appeared on the formation of acid–salt addition products in solution. It was established that molecules of the acids combine with anions of the salts; on dissociation of the latter this leads to the formation of complex anions of the type FHF^-,[155,156] $ClHCl^-$,[157-159] $PiHPi^-$ [160] (Pi = picrate ion), and $HSO_4^-.H_2SO_4$.[161,162] Van Looy and Hammett found that the sulphates of some amines, dissolved in nitromethane, can add on molecules of sulphuric acid with the formation of compounds $(AmineH_2SO_4).2H_2SO_4$, in which these molecules are linked by hydrogen bonds to oxygen atoms of the anions[146]. Frolov and Sergievskii have reported the probable formation of an addition product of sulphuric acid with an amine hydrogen sulphate, $(TOA.H_2SO_4)H_2SO_4$ [163] [TOA = = tri-n-octylamine (Ed. of Translation)]. Recently the addition of hydrohalic acids to anions of halide salts has been studied in detail by McDaniel and Vallee[164], Harmon and Gebauer[165], and Lipovskii and Nikitina[166], who show that the addition of acid molecules to salt anions is due to the formation between them of hydrogen bonds involving the protons of the acid.

It is to be expected that the stability of the hydrogen bond between a given acid and a salt anion will increase with increasing electron-donor properties (basicity) of the atoms forming the anion[167]. Obviously, the electron-donor properties of each anion increase with the displacement of the negative charge of the salt towards this anion, i.e. with the polarity of the salt of which the anion forms part. McDaniel and Vallee[164] determined the free energies and heats of formation of the addition products of HCl, HBr, and HI with corresponding halide salts of the type R_4NHal(R = alkyl) of different polarity. The results show, as would be expected, that more polar salts form more stable addition products with acids. For example, the value of $-\Delta H$ for the compound of HCl with the least polar of the salts $(CH_3)_4NCl$ was 11.3 kcal mole^{-1}, for the more polar $(C_2H_5)_4NCl$ the value was 13.7, and for the still more polar $(C_4H_9)_4NCl$ it was 14.2 kcal mole^{-1}.

From the data presented it would be expected that, in the extraction of acids by amine salts by the addition mechanism, the stability of the extracted compounds (AmineHA)HA will also increase when amines whose salts are more polar are used; and, therefore, in a series of salts of different amines with the same anions, greater extractive power will be shown by salts of more polar structure.

2. Extraction of Metal Salts by an Addition Mechanism

The extraction of metal salts by an addition mechanism is due to the formation of complex compounds of the type $(AmineH)_n[MA_{n+m}]$ when an amine salt AmineHA interacts according to Eqn. (7) with various molecules or ions $MA_i^{(m-i)+}$ $(i \leq m)$ present in aqueous solution. In reactions of this type, of which reaction (5) is a particular case, a necessary condition for the formation of the compound to be extracted is the addition to the central atom M of the $M^{(m-i)+}$ group of supplementary anions A^- of the amine salt in quantity sufficient to form the complex anion MA_{n+m}^{n-}. The addition of anions of the amine salt to the given central atom M with the formation of a coordinate bond will occur more readily the higher the electron-donor power (basicity) of these anions. As has been noted, the basicity of the anion increases with increasing polarity of the amine salt containing the anion. It could therefore be expected that, as in the extraction of acids, the stability of the extracted compounds of metal salts with amine salts should increase, in a series of salts having the same anion, in the sequence of salts of increasingly polar structure.

After formation of the complex being extracted, the substituted ammonium cation that has entered into the composition of the amine salt occurs in the external coordination sphere. Outer-sphere cations may have considerable influence on the stability of the complex anions linked with them and of the compound as a whole[168-173]. Recently, Sinitsyn and Zvyagintsev made a detailed study of the effect of the properties of outer-sphere cations on the stability of the complex anions linked to them[174]; as an example they used compounds of the type $K_2[RuCl_5NO]$, where K is a singly charged cation. They showed that the stability of the bond to Cl ions in the complex anion increases in the order $Na^+ < K^+ < NH_4^+ < Rb^+ < Cs^+$. For the compounds $(AmineH)_2[RuCl_5NO]$ the effect of the outer-sphere cations increases in the order: primary amine < secondary amine < tertiary amine. Sinitsyn and Zvyagintsev note that an increase in the stability of the Ru–Cl bonds occurs because of a redistribution of electron density in the compounds and particularly because of a displacement of electron density along the line $K \ldots Cl \rightarrow Ru$ in the direction of the Ru atom. Obviously, the more polar the K–Cl bond, the greater will be the displacement towards the Ru atom. This kind of bond may also be expected for compounds of those amines, the salts of which $AmineH^+Cl^-$ are also more polar.

It follows from the foregoing that in a series of amine salts with the same anions, salts of a more polar structure should have a greater extractive power for metal salts by an addition mechanism, as in the extraction of acids.

3. Extraction by an Anion-Exchange Mechanism

In extraction by an anion-exchange mechanism, represented by Eqns. (2)–(4) and (6), "ready made" and mostly stable anions take part in the reactions, and the effect of outer-sphere substituted ammonium cations on the stability of the complex anions that form the compounds extracted usually has no material effect on the stability of these compounds. In this case, the stability of the extracted compound is mainly determined by the stability of the bond between the cation and the anion. Factors affecting the stability of such bonds have been widely described[175-185]; they include ionisation potentials, electron affinity and

charge of cation and anion, the sizes of cation and anion, their polarisability, and the energy of interaction with the surrounding medium. The extraction equilibrium depends on the relation between the stability of the initial amine salt and that of the salt formed by exchange of anions.

A special feature of extraction by the anion-exchange mechanism is that the stability of the initial amine salt and that of the amine salt formed after extraction are connected with the properties not only of the cation but also of the anion. In this case, when the two exchanging anions have similar properties, a change in the structure of the amine can affect to the same degree the stability of the salts formed by both anions, and therefore will not materially affect the extraction equilibrium.

A considerable influence of the structure of the amine on the anion-exchange equilibrium may be observed when the stability of the salts of different anions undergoing exchange changes in a different way when the structure of the amine changes. Such different behaviour of anions may be observed in the presence of specific factors affecting the structure and stability of the salts, including steric factors, differences in the power of anions to form hydrogen bonds with different cations, etc. These factors are described in greater detail in the following Section, on the dependence of the structure of amine salts on the nature of the amines. Also, since the polarity of amine salts has a great effect on extraction by an addition mechanism, we shall first consider structural factors of amines that determine the polarity of their salts.

IV. PRINCIPAL STRUCTURAL FACTORS OF AMINES DETERMINING THE STRUCTURE OF THEIR SALTS

The interaction of amine salts with acids leading to the formation of salts is connected with the presence on the nitrogen atom of an unshared pair of electrons capable of forming a coordinate bond with electron-acceptor atoms and ions[189-191]. A coordinate bond of the nitrogen atom with positive hydrogen ions, which are strong acceptors of a pair of electrons, is particularly easily formed. This explains the basic properties of amines and their ability to form compounds with acids.

The structure of compounds formed by amines with acids depends on the properties of the acid, the base, and the medium in which interaction occurs[192-199]. The structure of amine salts has been studied by many workers in the field of acid–base theory and also by those studying the electrical conductivity of non-aqueous solutions. When sufficiently strong acids and bases (amines) interact, there is complete transfer of a proton from the acid to the base and salts with a polar structure $AmineH^+ \ldots A^-$ are formed[194,198-204]. When the amine is a weak base, i.e. has only a slight tendency to add on protons, or if the acid is relatively weak, i.e. liberates a hydrogen ion with difficulty, interaction between them to form an addition product may involve merely the formation of a hydrogen bond between the amine nitrogen atom and the acid, without transfer of the proton from the acid to the nitrogen atom. The structure of such a product may be schematically represented by the formula Amine ... HA. It has been shown by infrared spectroscopy, by conductivity and dielectric constant measurements, and also by measurements of refraction and dipole moments that e.g. the following compounds have such a structure — tribenzylamine with picric acid[205,206], pyridine with acetic acid[207], aniline with phenol[208], aniline and *p*-nitroaniline with acetic and formic acids[209], hexamethylenetetramine with phenol[199], and ethylamine with *m*-nitrophenol, *p*-nitrophenol, pentachlorophenol, and 2-bromo-5-nitrophenol[210].

When the strength of the base or the acid is increased, a more stable bond is formed between the proton of the acid and the amine nitrogen atom, the link with the anion of the acid is weakened[194,209,211], and the polarity of the salts formed increases. For example, the dipole moments of compounds of pyridine with acetic, chloroacetic, and trichloroacetic acids are respectively 2.98, 4.67, and 7.78 D: i.e. the polarity of these compounds increases appreciably with the strength of the acid[198]. In contrast to the weak acetic acid, hydrochloric acid forms a polar salt with *p*-nitroaniline involving complete transfer of the proton of the acid to the nitrogen atom of the amine[209]. In contrast to the very weak acid *m*-nitrophenol, the stronger acids 2,4-, 2,5-, and 2,6-dinitrophenols form ion-pairs with triethylamine; these contain the $O^- \ldots HN^+$ bond. The weaker base pyridine forms compounds with these phenols without the transfer of a proton to the nitrogen atom[210]. The polarity of the compound of a relatively strong base, tri-n-butylamine, with a strong acid, $HClO_4$, is much higher than the polarity of the compound of a weak base, aniline, with the relatively weak picric acid[192,208]. Detailed information on the effect of the strength of acids and bases on the polarity of the salts formed is given in Shatenshtein's book[194].

In many cases in which the acid proton is transferred to the amine nitrogen atom, the bond between the cation and the anion does not remain purely ionic, and in addition to electrostatic interaction between them, non-coulombic forces may also play a part. For example, in many alkyl- and aryl-ammonium halides the substituted ammonium ions are linked to the anions not only by ionic bonds but also by hydrogen bonds[212-219]. Sato, who studied the infrared spectra of tri-n-octylammonium nitrate $R_3NH^+ \ldots NO_3^-$ in different solvents, found that the frequency of the N^+-H stretching vibrations was strongly displaced towards the long-wave side[32]; he explains this by the presence of a strong hydrogen bond between the cation and the anion of the amine salt.

Hydrogen bonds of substituted ammonium cations are most easily formed with anions of weak acids; they are formed with far greater difficulty with the anions of strong acids[216,217]. The possibility of the formation of a hydrogen bond by a substituted ammonium cation and an anion in compounds of amines with complex salts is greatly reduced, since the negative charges are displaced from the peripheral atoms of the complex anions towards the central atom of the latter[216-219]. Nevertheless, the existence of intramolecular hydrogen bonds has been noted in salts of some complex acids, for example $(R_3NH)[UO_2(NO_3)_3]$ and $(R_3(NH)_2[PuO_2Cl_4]$, and in compounds containing other complex anions of the actinide elements[220-227].

The relation between the dipole moments of salts and the structure of the amines forming them has not been systematically investigated. A considerably greater amount of systematic information has accumulated on the study of the relation between the basicity of amines and their structure[188]. Since it has been established that the polarity of amine salts increases with their basicity, data on the basicity of amines may be used within certain limits to predict how the polarity of amine salts will depend on their structure. However, the basicity of an amine determined in some solvent is not a universal quantitative characteristic of the ability of the amine to form polar

salts with acids under any conditions; for the basicity depends on the nature of the solvent, and the order of basicity of amines of different structure may change with change of solvent[193-196]. It is therefore more rational to consider (using quantitative data obtained in the determination of the basicity of amines of different structure) factors connected with the structure of amines that directly influence the structure (polarity) of their salts. The most important of these factors are the electron-donor power of amines, the formation of intramolecular hydrogen bonds in the amine salt molecules, the solvation of amine salt cations and anions by molecules of solvent, steric factors, and the effect of "inert" non-solvating solvents.

1. Electron-Donor Power of Amines

From the point of view of electronic theory, the power of amine molecules to coordinate protons and form polar compounds with acids depends on the mobility of the unshared electron pair on the nitrogen atom[176,177,186-189].

The greater the displacement of electron density in the amine molecule towards the nitrogen atom, the greater will be the mobility of the electron pair of the nitrogen atom capable of forming a donor–acceptor bond. The shift in electron density towards the nitrogen atom depends on the inductive effects of the radicals attached to this atom. Aliphatic radicals have a positive inductive effect, or a greater power of repelling electrons compared with the hydrogen atom. For this reason, the mobility of electrons of the nitrogen atom is greater in alkylamines than in ammonia.

When the number of identical substituents on the nitrogen atom increases, their total inductive effect increases. For the aliphatic amines this leads to an increase in the electron-donor properties of nitrogen in the order — primary < secondary < tertiary amines — which corresponds to a decrease in the ionisation potentials of the amines in this order. Values of the ionisation potentials, which indicate the mobility of the unshared pair of electrons on the nitrogen atom, determined[228,229] for some alkylamines, show (Table 1) that, when the number of alkyl substituents or their length is increased, the ionisation potentials are reduced.

Because of the negative inductive effect of the aryl radicals in aromatic amines, the electron density is displaced from the nitrogen atom in the direction of these radicals, and the unshared pair of electrons on the nitrogen atom is less mobile than in ammonia[215]. The general inductive effect of the substituents in aromatic amines also increases in the order — primary < secondary < tertiary — which reduces the electron-donor power of the nitrogen atom (and the ability of the amines to form polar salts) in the same order.

As mentioned above, the power of amines to form polar salts parallels their power of adding protons (their basicity). Much has been published on the determination of basicity, which confirms how substituents on the nitrogen atom affect the electron-donor power of the amines and their ability to form polar compounds with acids[188]. For aqueous solutions the basicity is expressed quantitatively by the basicity constant

$$K_b = \frac{[\text{AmineH}^+][\text{OH}^-]}{[\text{Amine}]}. \quad (8)$$

For organic systems in aprotic solvents the basicity constant directly characterises the power of the amine to form a polar salt on reaction with an acid. For such solutions this value is given by the formula

$$K_b = \frac{[\text{AmineH}^+ \ldots \text{A}^-]}{[\text{Amine}][\text{HA}]}. \quad (9)$$

The quantities necessary for the calculation of K_b in aqueous solution are mainly determined by means of indicators or by potentiometric and other methods connected with the measurement of hydrogen-ion concentration[232]. The degree of conversion of HA to A^-, necessary for the determination of K_b in aprotic solvents, is usually determined spectrophotometrically[210].

The basicity constants of some alkylamines determined in water are given in Table 2. In aqueous solutions, because of the effect of other factors besides electron-donor power of amines (mainly solvation of cations), the expected dependence of K_b on the number of substituents is not observed throughout the series of alkylamines with different substituents. However, Table 2 shows that the basicity of all alkylamines is greater than that of ammonia. The basicity of primary and secondary amines changes little as the length of the alkyl chain is increased; in the tertiary amine series there is a tendency for the basicity to increase as the alkyl chain in lengthened. The basicity constants of the dialkylanilines increase with the length of the alkyl chain. For example, the value for dimethylaniline is 4.5×10^{-10}, and that for diethylaniline 165×10^{-10}.[234] The basicity of aromatic amines is lower than that of ammonia, and decreases as the number of aromatic substituents increases. The basicity constant of aniline in water is 3.8×10^{-10}; that of diphenylamine is 7.6×10^{-14}.[234]

In aprotic organic solvents, in contrast to aqueous solution because of the relatively weak solvation effect the basicity of amines is in many cases determined by the electron-donor power of the nitrogen atom alone, and the order of basicity expected from the inductive effects of

TABLE 1. Ionisation potentials (eV) of amines[228] (ammonia, 10.15 eV).

No. of C in alkyls	Primary amines	Secondary amines	Tertiary amines
1	CH_3NH_2—8.97	$(CH_3)_2NH$—8.24	$(CH_3)_3N$—7.82
2	$C_2H_5NH_2$—8.86	$(C_2H_5)_2NH$—8.01	$(C_2H_5)_3N$—7.50
3	$C_3H_7NH_2$—8.78	$(C_3H_7)_2NH$—7.84	$(C_3H_7)_3N$—7.23
4	$C_4H_9NH_2$—8.71	$(C_4H_9)_2NH$—7.69	

TABLE 2. Basicity constants of some alkylamines in water[233,234] at 25° (ammonia $\sim 1.8 \times 10^{-5}$).

No. of C in alkyls	Primary amines	Secondary amines	Tertiary amines
1	$CH_3NH_2 \sim 4.4 \cdot 10^{-4}$	$(CH_3)_2NH \sim 5.2 \cdot 10^{-4}$	$(CH_3)_3N \sim 5.4 \cdot 10^{-5}$
2	$C_2H_5NH_2 \sim 3.4 \cdot 10^{-4}$	$(C_2H_5)_2NH \sim 9.6 \cdot 10^{-4}$	$(C_2H_5)_3N \sim 5.6 \cdot 10^{-4}$
3	$C_3H_7NH_2 \sim 4.7 \cdot 10^{-4}$	$(C_3H_7)_2NH \sim 1.02 \cdot 10^{-3}$	$(C_3H_7)_3N \sim 5.5 \cdot 10^{-4}$
4	$i\text{-}C_4H_9NH_2 \sim 3.1 \cdot 10^{-4}$	$(i\text{-}C_4H_9)_2NH \sim 4.8 \cdot 10^{-4}$	—
5	$i\text{-}C_5H_{11}NH_2 \sim 5 \cdot 10^{-4}$	$(i\text{-}C_5H_{11})_2NH \sim 9.6 \cdot 10^{-4}$	—

the substituents is fully observed. It has been shown that in chlorobenzene the strength of amines varies in the order tributylamine > dibutylamine > monobutylamine[210,235,236]. The same order has been established for the ethylamines[237,238], methylamines[238,239], octylamines[46], decylamines[46], and some other amines. Pearson and Vogelsong, who have studied the relation between basicity and structure in the greatest detail, showed that in chlorobenzene and dichloroethane the basicities of tributyl-, triethyl-, and trimethyl-amines are higher than those of the corresponding secondary amines[240]. It has also been shown that the introduction into aromatic amines of substituents with a positive inductive effect, for example alkyl groups, also leads to an increase in basicity[219,241]. Because inductive effects of substituents in amines often have a definite influence on the polarity of salts of these amines, Hall was able to establish a quantitative relationship between the basicity constants K_b and Taft's constants, which characterise the inductive effects[242,243]. Taft proposed the use of a number of parameters (induction constants) σ^* which characterise the inductive effects of various substituents attached to a reactant atom or group, and showed that for a number of reactions the following relationship holds§

$$\log k/k_0 = \rho^*\sigma^*, \qquad (11)$$

where k is the equilibrium constant for the substituted compound, k_0 is the constant for the reference compound, and ρ^* represents coefficients constant for each type of reaction[244-250].

Hall[242,243] and also Hansson[251] have shown that this equation is applicable to the calculation of the basicity constants of amines. Logarithms of the basicity constants of 46 primary, secondary, and tertiary amines investigated by Hall (except for amines with considerable steric hindrance round the nitrogen atom) depend linearly on $\Sigma\sigma^*$, i.e. the sum of Taft's induction constants for all the substituents attached to the nitrogen atom. A number of other primary, secondary, and tertiary amines show an analogous linear dependence[242,252,253].

Therefore, the order of the basicity of amines of different structure has been confirmed in a great number of cases by consideration of the influence of the inductive effects of substituents on the mobility of the unshared electron pair of the amine nitrogen atom¶. Therefore values of σ^*, which characterise these inductive effects, may be used to estimate the probable polarity of salts formed by amines of different structure. Values of σ^* for some substituents are given in Table 3.

The use of Taft's induction constants to calculate the effect of bulky substituents, e.g. long alkyl chains, is limited by steric effects; apparently they are most successfully applied to evaluate the polarity of primary alkylamine salts.

TABLE 3. Values of Taft's induction constants σ^* for some substituents[250,251,255].

Substituent	σ^*	Substituent	σ^*
NO_2	+5.3	$O_2N(CH_2)_2$	+0.50
Cl_3C	+2.65	H	+0.430
CH_3OOC	+2.00	$(C_6H_5)_3CH$	+0.405
Cl_2CH	+1.94	$(C_6H_5)(C_6H_4)CH$	+0.040
CH_3CO	+1.65	CH_3	0.000
HO	+1.55	cyclo-$C_6H_{11}CH_2$	−0.060
$ClCH_2$	+1.050	C_2H_5	−0.100
$BrCH_2$	+1.030	n-C_3H_7	−0.115
$C_6H_5OCH_2$	+0.850	n-C_4H_9	−0.130
$C_6H_5(OH)CH$	+0.765	i-C_4H_9	−0.125
CH_3COCH_2	+0.600	t-$(C_4H_9)CH_2$	−0.140
C_6H_5	+0.600	i-C_3H_7	−0.200
$C_6H_5CH_2$	+0.225	$(C_6H_5)_2CH$	−0.225
$(C_6H_5)(CH_3)_2$	+0.020	t-$(C_4H_9)CH_2CH$	−0.285
$HOCH_2$	+0.555	t-(C_4H_9)	−0.320
CH_3OCH_2	+0.520		

TABLE 4. Values of the constants σ in Hammett's equation for some substituents in the *para*-position[255,256].

	Substituent	σ		Substituent	σ
Amino- -groups	NH_2	−0.660	Hydroxy- and alkoxy- -groups	OH	−0.357
	$NHCH_3$	−0.592		OCH_3	−0.268
	$N(CH_3)_2$	−0.600		OC_2H_5	−0.250
	$NHNH_2$	−0.550		OC_3H_7	−0.268
	NHOH	−0.339		$OCH(CH_3)_2$	−0.286
Carboxy- -groups	COOH	+0.265		OC_4H_9	−0.320
	$COOC_2H_5$	+0.522		OC_5H_{11}	−0.340
	CHO	+0.216		$O(CH_2)_5CH(CH_3)_2$	−0.265
	$COCH_3$	+0.516		$OCH_2C_6H_5$	−0.415
	COC_6H_5	+0.459		OC_6H_5	−0.028
	COO^-	+0.132	Alkyl groups	CH_3	−0.170
	CN	+0.628		C_2H_5	−0.151
Other groups	NO_2	+0.778		C_3H_7	−0.126
	NO	+0.123		$CH(CH_3)_2$	−0.151
	F	+0.062		C_4H_9	−0.161
	Cl	+0.227		$CH_2CH(CH_3)_2$	−0.115
	Br	+0.232		$CH(CH_3)C_2H_5$	−0.148
	I	+0.276		$C(CH_3)_3$	−0.198
	CF_3	+0.551		$(CH_3)_2CH(CH_2)_2$	−0.225
	CH_2Cl	+0.184		$C(CH_3)_2C_2H_5$	−0.190

The effect of nuclear substituents in aromatic amines is determined by Eqn. (11) with the aid of Hammett's σ constants[254-257], which are less sensitive to steric hindrance if the substituent is in the *para*- or *meta*- position. Values of σ for some substituents are given in Table 4. Values of ρ^* for calculating the basicity constants from Eqn. (11) are negative. It may therefore be concluded from the data in Table 3 that all amines in which there are substituents on the nitrogen atom with positive values of σ^*, exceeding the value of σ^* for H, must have a lower electron-donor power (basicity) than ammonia. These amines are less likely to form polar salts with acids. It cannot therefore be expected that salts of amines containing these substituents (Cl_3C, CH_3COO, CH_3CO, $CNCH_2$, C_6H_5, etc.) would form stable extraction compounds with acids and metal salts where extraction is by an addition mechanism. Replacement of hydrogen atoms in ammonia by substituents with a value of σ^* less than 0.430 should lead to increased electron-donor power and to increased basicity. Values of σ^* for substituents having negative inductive effects decrease considerably when a CH_2 group comes between them and the nitrogen atom. It follows from the data in Table 3 that the polarity of salts should increase in the order $C_6H_5NH_2 < C_6H_5CH_2NH_2 < C_6H_5[CH_2]_3NH_2$; the polarity of salts of this last amine and the stability of the compounds extracted should be comparable with the stability and polarity of alkylamine salts. It also follows from the data in Table 3

§ A similar relationship

$$\log k/k_0 = \rho\sigma \qquad (10)$$

was previously proposed by Hammett for calculating the effect of substituents in aromatic rings on the reaction constants of different functional groups attached to these rings[254].

¶ In a later paper Mead also established quantitative relationships between the heats of neutralisation of some amines with trichloroacetic acid in benzene and Taft's parameters[258]. Recently Kuča, with the aid of induction constants σ^*, has established a quantitative relationship between the extractive power of a large number of organophosphorus compounds and their structure[259].

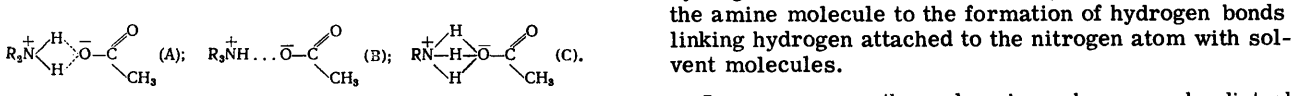
that the polarity of salts and the stability of the extracted compounds of alkylamines should increase with increase in length, number, and degree of branching of alkyl chains linked to the nitrogen atom.

The data in Table 4 show that introduction into the benzene and other aromatic groups of aromatic amines, of such substituents as Cl, NO_2, NO, and COOH should lead to a decrease in the electron-donor power (basicity) of the amines and to a reduction in the polarity of their salts. When such substituents as OH, alkoxy-groups, or alkyl groups are introduced into the *para*-position, the basicity of the aromatic amines should increase. Therefore, the polarity of their salts and the stability of compounds extracted by an addition mechanism should also increase.

The data in Tables 3 and 4 may be used for a preliminary evaluation of the probable changes in polarity and extractive power of amine salts when some substituents are replaced by others. However, the electron-donor power of amines is not the only factor that determines the structure of their salts. A number of other factors, considered below, must also be taken into account.

2. Intramolecular Hydrogen Bonding

The formation of intramolecular hydrogen bonds in amine salts may have a material effect on the structure of these salts. As has been mentioned above, the anions of weak acids show a tendency to form hydrogen bonds with the hydrogen atoms of substituted ammonium cations. The number of possible intramolecular hydrogen bonds increases with the number of hydrogen atoms attached to the nitrogen atom, the number being greater in primary amines than in secondary, and greater in secondary than in tertiary amines. Barrow and Yerger showed that in chloroform the stability constants of compounds of acetic acid with dibutylamine and diethylamine are higher than with the corresponding tertiary amines[260,261]. They explained this by an increase in the number of intramolecular hydrogen bonds in the compound of the secondary amine (A) in comparison with the compound of the tertiary amine (B). According to these authors, three intramolecular hydrogen bonds are formed in compounds of the primary amine (C):[261]



The presence of hydrogen bonds in these compounds has been confirmed by infrared spectroscopy[261]. Davis[262,263] noted that in solvents that do not solvate cations the absorption spectra of acid indicators change differently in reactions with primary, secondary, and tertiary amines. He explained these differences also by the formation of different numbers of intramolecular hydrogen bonds. Ryan, having compared the absorption spectra of the compounds $Cs_2[UO_2Cl_4]$, $[(C_4H_9)_4N]_2[UO_2Cl_4]$, and $[(C_4H_9)_3NH_2][UO_2Cl_4]$, established that the spectrum of the last compound differs from the spectra of the first two[220,221]; this can also be explained by the presence of an hydrogen bond between the cation R_3NH^+ and the anion $[UO_2Cl_4]^{2-}$. Similar spectral differences were observed in compounds of secondary amines $[(C_2H_5)_2NH_2]_2[UO_2Cl_4]$, the differences being more marked in these. According to Ryan's results, the melting points of salts of secondary amines with $[UO_2Cl_4]^{2-}$ are much lower than those of salts of the corresponding tertiary amines; in the author's opinion this also indicates the greater part played by non-coulombic forces in the bond between the anion and the secondary alkylammonium cations. A hydrogen bond is also assumed to be present in compounds of primary amines $[RNH_3]_2[UO_2Cl_4]$.[220] Similar effects, indicating the formation of internal hydrogen bonds, have also been noted in analogous chloride compounds of uranium(IV).[221] Vdovenko, Lipovskii, and coworkers have demonstrated the presence of intramolecular hydrogen bonds in a number of salts of long-chain alkylamines[166,225-227].

The formation of intramolecular hydrogen bonds promotes the approach of the anion and the cation, and therefore the polarity of the amine salt is reduced; this leads to a reduction in the dissociation constants of the amine salts in polar organic solvents and to a decrease in the electrical conductivity of solutions of these salts. According to Kraus[192] the conductivity constants of tetra-, tri-, di-, and mono-butylammonium picrates in nitrobenzene are $>2 \times 10^{-1}$, 1.9×10^{-4}, and 1.6×10^{-4} respectively; the distances between the centres of gravity of the positive and negative charges in these salts of picric acid are: tetrabutylammonium salt (intramolecular hydrogen bond) about 6.29 Å, tributylammonium salt (one hydrogen bond) 1.02 Å, dibutylammonium salt (two hydrogen bonds) 0.977 Å, and monobutylammonium salt (three hydrogen bonds) 0.992 Å. Differences in the polarity of salts of secondary and tertiary amines, due to the greater power of secondary amines of forming intramolecular hydrogen bonds with anions, have also been noted by other workers[211,212].

It follows from the foregoing that the formation of intramolecular hydrogen bonds, just like changes in the electron-donor power, leads (in the absence of other forces affecting the structure of amine salts, considered below) to the polarity of the alkylamine salts varying in the order: tertiary > secondary > primary.

The most favourable conditions for the formation of hydrogen bonds between cation and anion occur when the molecules of solvent do not form hydrogen bonds with hydrogen atoms of substituted ammonium cations. Intramolecular hydrogen bonds are therefore usually observed in such solvents as carbon tetrachloride, chloroform, benzene, xylene, etc. The formation of intramolecular hydrogen bonds is also favoured by steric hindrance in the amine molecule to the formation of hydrogen bonds linking hydrogen attached to the nitrogen atom with solvent molecules.

In some cases, the order given above may be disturbed by solvation of the cation and the effect of steric factors.

3. Solvation of Cations of Amine Salts by Solvent Molecules

An example of the effect of solvation of a substituted ammonium cation on the basicity of amines and the polarity of their salts is provided by the disturbance in aqueous solutions of the order of their basicity to be expected from the electron-donor power of the amines. Data in Table 2 show that in aqueous solutions secondary amines have a higher basicity than the corresponding tertiary amines, although tertiary amines have the higher electron-donor power. This deviation is explained in the following way. According to Izmailov's theory[197] ionisation of molecules of acids or bases takes place because of interaction with molecules of bases or acids

respectively, or because of interaction with solvent molecules. Ionisation of an amine in water may be represented by the equations

$$\text{Amine} + \text{aq.} \rightleftharpoons \text{Amine.aq.}, \quad (12)$$

$$\text{Amine.aq.} \rightleftharpoons \text{AmineH}^+\text{.aq.} + \text{OH}^- \quad (13)$$

$$\text{Amine} + \text{aq.} \rightleftharpoons \text{AmineH}^+\text{.aq.} + \text{OH}^- \quad (14)$$

From these equations it follows that the total energetic effect of the ionisation reaction and the equilibrium constant K_b that characterises it are determined, not only by the mobility of the free electron pair of the amine nitrogen atom, but also by the differences in the solvation (hydration) energies of the amine molecules and the corresponding substituted ammonium ions. The higher basicity of secondary and primary alkylamines in comparison with tertiary amines in aqueous solution is explained by the fact that the hydration energy of mono- and di-alkylammonium ions is considerably higher than that of the corresponding trialkylammonium ions[238]. At the same time, the heats of hydration of the unionised amines are considerably lower than those of the ions, and have no material effect on the energy balance of the ionisation reaction. The heats of hydration of ammonium ions are as high as 85 kcal mole^{-1}, but the heats of hydration of unionised amines do not exceed 10–11 kcal mole^{-1}.[238,264,265]

The increased solvation of incompletely substituted ammonium ions was established by a number of workers as early as the 1920s;[266-268] it is due to the presence in these ions of a greater number of hydrogen atoms linked directly to the nitrogen atom than in completely substituted alkylammonium ions, these hydrogen atoms being capable of forming hydrogen bonds with water molecules. It is assumed that the hydrated ions of primary, secondary, and tertiary amines in water have respectively the structures $RN(H_3O)_3^+$, $R_2N(H_3O)_2^+$, and $R_3N(H_3O)^+$.[238]

The higher solvation of mono- and di-substituted ammonium ions compared with the corresponding trialkylammonium ions makes the ionisation of hydrates of primary and secondary amines energetically more favoured than the ionisation of tertiary hydrates[268]. This rule is followed in aqueous solutions not only by amines having hydrocarbon substituents but also by other aliphatic amines, for example the derivatives of hydroxylamine NH_2OH, $NH(CH_3)OH$, and $N(CH_3)_2OH$, and also by the compounds NH_2OCH_3, $NH(CH_3)OCH_3$, and $N(CH_3)_2OCH_3$.[269]

In both organic and aqueous solvents, aliphatic amines show a number of deviations from the order to be expected on the basis of electronic interpretations, for the basicity of amines of different structure[244,270]. According to a number of authors, primary and secondary amines are the strongest in several organic solvents as well as in water. Izmailov and Mozharova showed that disturbances of the normal order of amine basicity occur in organic solvents that strongly solvate substituted ammonium cations, for example in alcohols; this can be explained, as for aqueous solutions, by solvation effects[270]. It has also been shown[240] that the addition of alcohols and other diluents capable of forming bonds with hydrogen atoms attached to amine nitrogen atoms has a great effect on basicity constants of amines in aprotic solvents, whereas the addition of alcohols has practically no effect on the basicity or the polarity of salts of tertiary amines, with no free hydrogen directly linked to nitrogen; the strongest effect is obtained with primary amines, which have two such atoms in the molecule. For example, the basicity constant of the tertiary amine $(C_2H_5)_3N$, which is 2680 in chloroform, does not change on the addition of 4–5 mole % of ethanol[240]; the basicity constant of the corresponding secondary amine increases from 1230 to 12 700 (approximately tenfold) when the same amount of alcohol is added to the solution, and the corresponding change in basicity of the primary amine is from 35 to 5830 (~150 times).

Bayles and Taylor have given detailed data (including values of ΔG°, ΔH°, and ΔS°) for the acid–base interaction of amines of different structure in different diluents[271]. As a rule, in pure alcohols the strongest bases are the primary amines, followed by the secondary and tertiary amines.

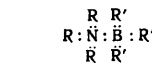
A change in the expected basicity sequence of amines occurs also because solvation of the cation prevents formation of intramolecular hydrogen bonds. In such solvents as ethyl acetate or alcohol, the oxygen atoms may form hydrogen bonds with the alkylammonium cations. The participation of hydrogen atoms linked to nitrogen in the formation of hydrogen bonds prevents the formation of hydrogen bonds between the cation and the anion. As mentioned above, the absorption spectra of some anions of substituted ammonium salts in benzene changed according to whether tertiary or primary amines were used; this was explained by the different power of the primary amines to form intramolecular hydrogen bonds. In water, however, the absorption spectra of these anions show little difference[262,263]: the hydrogen atoms which would have formed bonds with the anions now form bonds with solvent molecules. Thus, solvation of the substituted ammonium cation leads to an increase in the polarity of amine salts also by eliminating intramolecular hydrogen bonds.

Because of stronger solvation of the cations, the salts of primary amines may be more polar than the salts of secondary and tertiary amines. It is therefore to be expected that, in solvents capable of solvating ammonium cations, the compounds of primary and secondary amines extracted by an addition mechanism will be more stable than the corresponding compounds of tertiary amines. The greatest power of forming bonds with amine hydrogen atoms, and therefore of solvating cations of amine salts, is possessed by molecules of compounds that are electron donors — oxygen-containing organic solvents (alcohols, ethers, esters, ketones, phosphine oxides, alkylphosphonates, etc.)[272-275] and also organic bases (amines, nitriles of organic acids[276-280], dioxan, nitrobenzene[281], etc.).

The solvation of anions in amine salts may take place in solvents the molecules of which have electron-acceptor properties, such as alcohols and carboxylic acids, or in compounds of the chloroform type. Solvation of the anion, like that of the cation, may well lead to some increase in the polarity of the salt. But, since the molecules of extracted compounds attach themselves to the anion, solvation of the anion hinders the formation of compounds to be extracted by an addition mechanism. Solvation of the anions by alcohol molecules[282-284] appears to be the cause of the reduction in the extractive power of amine salts observed when alcohols are added to solutions of these extractants[54,129]. Similar solvation is probably also the main cause of the reduction of partition coefficients when chloroform is added to solutions of amine salts[123,285].

4. Steric Factors

Steric factors also affect the basicity of amines and the polarity of their salts. The effect of these factors on the formation of addition products with amines by acidlike compounds (in Shatenshtein's terminology[193,194]) has been studied in greatest detail. The interaction of amines of different structure with acidlike compounds of the type BR'_3 – $B(CH_3)_3$, $B(C_2H_5)_3$, etc. – which are strong electron acceptors, has been studied in detail by Brown and his coworkers[286-294]. The structure of the compounds of BR'_3 with NR_3 may be represented by the formula



To form a coordinate bond in this compound, the molecules of the two compounds must approach each other sufficiently closely; because of the relatively large volume of the BR'_3 molecules, steric factors begin to play an important part. The ability of methylamines to combine with $B(CH_3)_3$ varies in the order $NH_3 < CH_3NH_2 < (CH_3)_2NH \gg \gg (CH_3)_3N$. In this case the tertiary amine is the least basic because of steric hindrance due to the presence of three methyl groups on the nitrogen atom. The order of the strength of the other methylamines is that to be expected from the inductive effects of the substituents. The following order of basicity holds for the interaction of $B(CH_3)_3$ with ethylamines, which have more bulky alkyl groups: $NH_3 < C_2H_5NH_2 > (C_2H_5)_2NH \gg (C_2H_5)_3N$. When the volume of the molecule of acidlike compound increases (as with tributylboron), steric hindrance increases still further, and the stability of compounds of different amines varies in the order: $NH_3 < CH_3NH_2 > (CH_3)_2NH \gg (CH_3)_3N$; $NH_3 > C_2H_5NH_2 \gg (C_2H_5)_2NH > (C_2H_5)_3N$. Thus, when ethylamines react with tributylboron, the order of basicity of the amines is, because of steric hindrance, opposite to that to be expected from the inductive effects of the alkyl groups. The ability of tertiary alkylamines to form addition products with methanol decreases as the alkyl chain is lengthened[20], although the electron-donor power of the amines increases. Other examples of the effect of steric hindrance on basicity include the reducted reactivity with $B(CH_3)_3$ of 2-methylpyridine compared with pyridine itself (Brown and Taylor[286]), the diminished stability of the compound of SO_3 with triethylamine compared with the trimethylamine compound[295,296], and of the compounds of SO_3 with *o*-substituted compared with *p*-substituted aromatic amines[297], and the decreased stability of iodine complexes with aromatic amines when substituents are introduced in the *ortho*-position[298].

In the reaction of amines with proton acids, steric hindrance due to the alkyl groups is less significant because of the small volume of the proton, than in the reaction of amines with methylboron or with alcohols, and obviously could be important only with amines having sufficiently long hydrocarbon chains.

Hall noted that calculation of the basicity constants of amines on the basis of Taft's induction constants gives accurate results only when there is no steric hindrance to the reaction of the acid with the base[242]. If the alkyl groups attached to the amine nitrogen atom are considerably branched, the basicity constants of the amines are much lower than those calculated by formulae allowing only for the inductive effect of substituents.

Forman and Hume[299] evaluated the effect of steric hindrance on the basicity of amines by comparing values of the basicity calculated with the aid of Taft's induction constants with experimental values from the literature[300,301]. For primary and unbranched secondary amines the calculated values were close to the experimental. For secondary amines with sufficiently long and branched alkyl radicals, and for tertiary amines with long alkyl radicals, the experimental basicity constants were lower than the calculated values. Recently, Chremos and Zimmerman have attempted to allow for steric factors in the calculation of basicity constants by the introduction of a new scale of values for σ^*, representing both the polar and the steric effects of substituents[252].

When the length of the hydrocarbon chains of amines increases beyond a certain limit it is to be expected that the ability of the amines to add on protons and to form polar compounds with acids will be reduced; the length of the alkyl chain (or volume of other substituent having a positive inductive effect), corresponding to maximum polarity of the salts formed and maximum stability of the compounds extracted, is probably greater for primary than for secondary and tertiary amines.

In considering the effect of steric factors on the polarity of amine salts, it must be noted that these factors affect also the interaction of amines with the solvent, especially the solvation of the cations, and this in turn affects the basicity. It has been noted that, with long-chain primary and secondary amines, solvation of the substituted ammonium cations by alcohol molecules (especially higher alcohols) is made difficult by the formation of hydrogen bonds with hydrogen atoms attached to the amine nitrogen atom[242]. It is to be expected that the role of the solvation of substituted ammonium cations and its effect on the basicity of amines and the polarity of their salts will decrease as the hydrocarbon chains of the amine become longer.

5. Effect of "Inert" Solvents

At present, the field of study of "inert" solvents has considerably contracted, because it has been shown that most solvents investigated are not inert, but are capable of specifically solvating cations or anions of dissolved salts[281,302-304]. As has been shown above, the solvation of cations and anions of amine salts by molecules of solvent has a considerable effect on the structure of these salts, and therefore on their extractive power. Here we shall consider as "inert" non-polar solvents the molecules of which have no fundamental groups capable of forming stable hydrogen bonds with cations or anions of amine salts and also cannot appreciably solvate molecules and ions of amine salts by dipole–dipole interaction, but they may solvate them mainly by dispersion forces[304]. Pearson and Vogelsong established that in non-polar "inert" solvents of the n-heptane type the order of basicity of primary, secondary, and tertiary amines is changed in a similar way to that described above for solvents that solvate the cation[238,240]. Thus, in n-heptane the polar compounds of tri-n-butylamine with the acid indicator 2,4-dinitrophenol are formed with greater difficulty than the corresponding compounds of di-n-butylamine. It is assumed that this order for non-polar solvents which do not form bonds with the cation and anion of the salt may be explained as follows. The energy of interaction of molecules of amine salts with such non-polar solvents is much lower than with the analogous moderately polar solvents, and

apparently far lower than the energy of interaction of the amine molecules themselves with these non-polar solvents[82]. It may therefore be assumed that the difference in the solvation energies of the amines and their salts in such solvents is determined for various amines largely by the differences in the energies of solvation of the amines themselves. In such a case it may be expected that the greater the energy of solvation of the amine molecule, the more energetically unfavourable will be the formation of a polar salt by interaction of the amine with the acid. Because of the greater number of hydrocarbon chains, the energy of interaction of molecules of tertiary aliphatic amines with non-polar hydrocarbon solvents is higher than the energy of solvation of molecules of the corresponding secondary and primary amines[240]. It has been suggested that, on the basis of the variation in solvation energy, the formation of polar salts of tertiary amines in hydrocarbon solvents is less favoured than the formation of such salts of the corresponding secondary and primary amines[240]. The influence of opposing factors — solvation and the inductive effects of the alkyl groups of the amine — is probably the cause of secondary amines having a greater power of forming polar salts than have tertiary amines in non-polar aprotic solvents. When the alkyl chains are lengthened it is probable that the differences in the solvation energies of secondary and tertiary amines in such solvents will decrease, and the main factors determining the structure of the amine salt may be the inductive effect of substituents and steric factors.

Up to now, few papers have been published on the study of amine salts in solvents of this type, because of the very slight solubility of most amines in such solvents, which makes such systems of little practical importance.

V. THE EFFECT OF THE STRUCTURE OF AMINES ON THE EXTRACTIVE POWER OF THEIR SALTS WITH EXTRACTION BY AN ADDITION MECHANISM

In the extraction of acids and metal salts by the addition mechanism the stability of the compounds being extracted should increase when the structure of the amine is altered in such a way that the polarity of the amine salts is increased. When the structure of an amine changes, there should be a corresponding change in extractive power. When the effect of the various factors mentioned above is taken into account, it is possible to explain published results on the extractive power of amines of different structure.

A number of papers contain data that enable the extractive power of primary, secondary, and tertiary amines to be compared. Shevchenko and his coworkers showed that the nitrate of a tertiary amine (tri-n-octylamine) extracts nitric acid much more strongly than does the nitrate of the secondary amine (di-n-octylamine)[3,4]. These results were confirmed by Skavdahl and Mason[18]. Sinitsyn, Zvyagintsev, and their coworkers showed that the extraction of ruthenium nitroso-complexes by amines from hydrochloric-acid[65,174] and nitric-acid[104] solutions increases when the number of alkyl chains in the amine is increased. Laskorin and Yuzhin established that chlorides of tertiary amines extract gallium(III) better from hydrochloric-acid solutions than do those of secondary amines[49]. Winchester and Maraman showed that the extraction of Pu^{IV}, U^{VI}, and Th^{IV} from nitric-acid solutions by amine nitrates is greater with secondary and tertiary than with primary alkylamines[98]. Good and his coworkers, having systematically studied the dependence of the extractive power of amines on their structure, found that the extraction of Fe^{II}, Co^{II}, Ga^{III}, and In^{III} by solutions of amine chlorides in benzene is also greater on passing from primary to secondary and then to tertiary alkylamines[61-63,68,305,306]. The same order was established for the extraction of a number of other elements[73,125]. Nemodruk showed that the extraction of uranyl acetate by solutions of amine acetates in a solvent that does not solvate cations is greater with dialkylaniline than with aniline[307]. The order established for the extractive power of primary, secondary, and tertiary amines is in agreement with the order of increasing polarity of salts of these amines and stability of the compounds extracted, which are formed by an addition mechanism.

A deviation from the usual order of the extractive power of primary, secondary, and tertiary amines is observed when solvents capable of solvating cations are used. For example, it was shown[307] that replacement of the non-solvating solvent by isobutyl methyl ketone, which solvates alkylammonium cations, led to a significant increase in the extraction of uranyl from acetic solutions of the primary amine, aniline; as a result, in this solvent aniline became a stronger extractant than the tertiary amine dialkylaniline. This increase in the extractive power of the primary amine may be explained by solvation of the cation of the amine salt by solvent molecules, leading to an increase in the polarity of the amine salt and in the stability of the extracted compound.

Many workers have noted[138] that the introduction into the amines of substituents with negative inductive effects leads to a reduction in extractive power. Thus, amines with aromatic substituents directly attached to the nitrogen atom are relatively weak extractants. This also agrees with the data given above on the reduction of the polarity of salts and the stability of compounds when such substituents are introduced. According to the data in Table 3, the value of σ^* is lower for the cyclohexyl and benzyl groups than for the aryl group C_6H_5, and even lower than for a hydrogen atom. This explains the relatively high extractive power of benzylamines[44,72,309] and cyclohexylamines[309].

The effect of the length of alkyl chains on the extractive power of symmetrical tertiary n-alkylamines was studied by Wilson, who observed an increase in the extraction of plutonium from nitric-acid solutions when the number of carbon atoms in the alkyl chain was increased to eight[97]. This is in agreement with what would be expected from increased inductive effects in the substituents. With further increase in the chain length the extractive power of the alkylamines begins to decrease. Zvyagintsev and Frolov[26,33,40], Zvyagintsev and Sinitsyn[104,174], Timoshev[275], Baroncelli[310], and their coworkers have described a similar dependence of the extractive power of amines on the length of the alkyl chains. The increase in the extractive power of the trialkylamines when the number of carbon atoms in the chain increases to eight is in agreement with the increase, mentioned above, in the inductive effect of alkyl chains when their length is increased. Timoshev points out that one of the causes of the increase in extractive power with increasing alkyl chain length in amines of low molecular weight is also the reduction in the solubility of the extracted compound in the aqueous phase[275]. The reduction in extractive power with further increase in chain length appears to be due to steric hindrance, which becomes the main factor determining the structure and stability of the extracted compounds[311-313].

Comparison of data on the extraction of nitric acid and uranyl nitrates by tertiary n-alkylamines with more than eight carbon atoms in the chain shows that their extraction is reduced by increasing the length of the amine alkyl chains[8,24,129]. The effect of steric factors also appears in the reduction of the extractive power of amine salts with alkyl chains which branch near the nitrogen atom; this has been observed by many workers[138].

From the foregoing it is clear that the extractive power of amine salts in extraction by an addition mechanism is determined by a number of the same factors as effect their polarity. With substituents of relatively small volume and solvents that do not solvate cations, the extractive power changes with changes in the inductive effect of the substituents. When diluents that solvate cations are used, the effect of cation solvation and rupture of intramolecular hydrogen bonds becomes evident. When very bulky substituents are introduced into the amine molecule, steric factors begin to play a predominating part.

VI. THE EFFECT OF THE STRUCTURE OF AMINES ON THE EXTRACTIVE POWER OF THEIR SALTS WITH EXTRACTION BY AN ANION-EXCHANGE MECHANISM

Up to now little information has been published on the effect of amine structure on the extraction of simple acids with amine salts by an anion-exchange mechanism. Data on the extraction of metal salts by an anion-exchange mechanism[94,96,308,314] show that the rules governing the effect of the structure of amines on the extractive power of their salts cannot materially differ from the rules governing extraction by an addition mechanism.

The extraction of thorium by tri-n-octylammonium sulphate from aqueous sulphate solutions, in which thorium is present as anionic complexes, is an example of the extraction of a metal salt by an anion-exchange mechanism[90,91]. As previously noted, when an extractable compound is formed in such cases, factors affecting the stability of the complex anion in this compound play a secondary part, and factors that determine the strength of interaction of the cation and the anion are of greater significance. It has been found that thorium is extracted from sulphuric-acid solutions better by primary than by secondary amines, and better by secondary than by tertiary amines. The same behaviour is observed in the extraction of Zr, U^{IV}, and Fe^{III}, which also readily form anionic complexes in sulphate solutions[68]. This behaviour may be explained in terms of steric concepts. Steric hindrance to the approach of relatively bulky anionic sulphate complexes to monoalkylammonium cations is obviously less than to their approach to di- and tri-alkylammonium cations. To form an extractable compound the complex anion must displace the SO_4^{2-} anion from the amine sulphate molecule. Since the SO_4^{2-} anion is smaller than the complex sulphate anions of Th, U^{IV}, and Zr, the differences between primary, secondary, and tertiary amines in relation to steric hindrance to this anion are less important than for complex anions. From this it follows that the sulphate ion will be replaced by a complex sulphate ion more easily in salts of primary amines than in salts of tertiary amines. This probably explains the greater extractive power of primary amines (in comparison with secondary and tertiary amines) in the extraction of Th, Zr, and U^{IV} from sulphate solutions.

The same order of extractive power of amines would obviously also be expected for the extraction of other elements from media in which they form stable anionic complexes greatly exceeding in size the anion of the amine salt which acts as extractant. When the complex anions, although predominating in the aqueous phase, are formed with greater difficulty than in the case considered (Th, Zr, U^{IV}), other factors — governing stabilisation of the anion and interaction of cation and anion — may be important at the same time. In view of the opposing effects of these factors, when less stable anionic complexes are formed in the aqueous phase, the differences in extractive power between primary, secondary, and tertiary amine salts may decrease in extraction by an anion-exchange mechanism, and in some cases the extractive power of amines with different numbers of alkyl groups may be practically the same[143]. In these cases it appears that the increase in steric hindrance on passing from primary to tertiary amines is probably compensated for by the increase in the stabilising action of the cation on the complex anion. When the length or volume of the alkyl chains increases, steric factors begin to play a predominating part. Thus, Sato[309,313] has shown that with cyclohexyl- and benzyl-alkylamines (C_{12} alkyl) the extraction of U^{VI} from sulphuric-acid solution decreases when additional alkyl chains are introduced into the amine, i.e. in the order primary > secondary > tertiary. Clearly, all the considerations mentioned above still hold good if the extraction of Th, Zr, U, and Fe sulphates proceeds by an addition mechanism, since the great volume of the complex sulphate anions formed in the extraction can probably give rise to steric hindrance in this case also.

Laskorin and his coworkers have shown[308,314] that triisooctylamine is a much weaker extractant of V^V and Mo^{VI} ions than is tri-n-octylamine. This may be explained by the greater steric hindrance to the approach of anion and cation in the case of triisooctylamine.

A more thorough investigation into the structure of amine salts could make possible a more complete elucidation of the principles of extraction by amine salts and the prediction of the relative extractive power of amines of different structure.

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CHEMILUMINESCENCE AND THE KINETICS OF CHEMICAL REACTIONS

V. I. Papisova, V. Ya. Shlyapintokh, and R. F. Vasil'ev

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I. INTRODUCTION

Chemiluminescence — the emission of light accompanying chemical reactions — is closely connected with the kinetics and the mechanism of the reaction.

The appearance of excited states in a reaction zone is due to the occurrence of exothermic elementary acts. The measured intensity of emission is proportional to the rate of the elementary process in which energy is evolved, and hence is related to the kinetic parameters of the reaction. Investigation of the kinetics, the temperature dependence, and the spectra of the emission may give much valuable information for an understanding both of the reaction mechanism and of the actual phenomenon of chemiluminescence — of the ways in which chemical energy is transformed into radiation.

It must be emphasised that a study of chemiluminescence divorced from the mechanism of the corresponding reaction can hardly provide a fruitful approach. For example, the weakening of emission accompanying the introduction of a new component into the reaction mixture can be equally well explained by its retarding effect on the reaction velocity or by its quenching action on excited states which appear at the same rate as before. In the absence of information on the rate of the chemical reaction and of the influence of the additive on it, no choice can be made between these fundamentally different effects.

The present review surveys the relationship between the chemiluminescence and the kinetics of reactions. From the considerable number of papers on chemiluminescence, those have been selected which report either the investigation of chemiluminescence in reactions whose mechanism has been reliably established or the parallel study of a reaction by chemiluminescence and chemical kinetic methods.

Special attention has been paid to the prospects for using chemiluminescence as a method for the quantitative investigation of reaction kinetics.

The main information has been divided into three parts — (1) gas-phase reactions (hot and cold flames, reactions of atoms obtained in high concentrations from electric discharges), (2) liquid-phase reactions (oxidation of cyclic hydrazides and of acridine compounds) accompanied by bright chemiluminescence, and (3) reactions accompanied by very weak chemiluminescence, which do not differ fundamentally from the previous reactions, but comprise a wide range of both scientific and practical interest, and therefore are discussed as a separate group.

II. CHEMILUMINESCENCE OF FLAMES

The intensity of the emission from many flames exceeds the equilibrium value corresponding to the temperature of the flame. In particular, the glow from cold and dilute flames is purely chemiluminescent. The radiation from low-temperature flames is to a greater or lesser extent chemiluminescent[1,2]. The non-equilibrium character of the radiation can be shown by comparing its absolute intensity with the intensity of the radiation from a black body having the same temperature as the flame. Thus according to Kondrat'ev[1] the intensity of the radiation from an oxygen–hydrogen flame at 10 mmHg and 1000°K exceeds the equilibrium value by a factor of 10^{12}, while the corresponding factor for the $2CO + O_2$ flame at 100 mmHg and 1400°K is 10^{10}.

The character of the radiation can be assessed also from measurements of the intensity distribution in the emission spectrum. The non-equilibrium character of radiation is indicated by a difference between the true temperature of the flame and the rotational temperature of individual species: in the oxygen–acetylene flame at 1 atm, for example, the true temperature is 3400°K, while the rotational temperature of hydroxyl is 5400°K, and that of C_2 is 4700°K.[3] Finally, departures from equilibrium can