U.D.C. 541.8:547.333

THE SOLUBILITY OF AMINE SALTS IN SOLVENTS OF LOW POLARITY AND THE INFLUENCE OF DILUENTS ON THE EXTRACTION PROPERTIES OF AMINE SALTS

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I. INTRODUCTION

Amine salts have found extensive application for the extraction of acids and metal salts from aqueous solutions[1]. Since the amine salts are viscous substances and in some instances even solids, they are used, like many other extractants, as solutions in solvents of low polarity, immiscible with water. Being substances of polar structure, amine salts are in many cases relatively sparingly soluble in such diluents, and their extractive power is greatly influenced by several of the latter. Thus the selection of a suitable diluent for the amine salts, i.e. a diluent in which the amine salts are readily soluble and do not lose their extractive properties, is an important task, and the investigation of the regular features relating the structures and properties of the amine salts and the diluents to their mutual solubility and the extractive power of the solutions is of considerable practical importance.

The regular features of the solubility of amine salts in various diluents and the influence of the diluents on the extractive power of the dissolved salts are closely related to one another, since they are determined by the same factors. The most important of these factors is the ratio of the energies of interaction of the molecules of the extractant and the compound being extracted with one another and with the molecules of the diluent[2]. The ratio of the energies of these interactions also determines the state of the molecules of the salt in solution, and this determines to a considerable extent the extractive power and solubility of these salts[3,4]. A particularly marked influence on the extractive power and solubility of amine salts is shown by the specific solvation of the positively and negatively charged parts of their molecules: this solvation results from the formation of hydrogen bonds or donor–acceptor bonds with the solvent, and leads to binding of the extractant or to a marked change in its properties[5].

A large amount of experimental data has now been published on the solubilities of amine salts in various diluents and on the influence of diluents on the extractive properties of these salts. The aim of the present review is to systematise these data and to explain the observed regular features. Since the nature of these regularities and the approach to their explanation may depend on whether specific solvation of the molecules of the amine salt by the molecules of the diluent takes place, it is convenient to examine separately the phenomena taking place in systems with and without specific solvation. To explain the phenomena observed in systems without specific solvation, thermodynamic methods are chiefly used, since the mechanism of the relatively weak intermolecular interactions in these systems has as yet been comparatively little studied. For systems in which specific solvation is observed, the regular features of the solubility and the influence of the diluent on the extractive power of amine salts with various structures can be explained qualitatively on the basis of published information on the reactions of the diluent molecules with the molecules of the amine salts. The present review first gives data on the state of amine salts in solvents of low polarity, necessary for an understanding of the mechanism of these interactions.

II. THE STATE OF AMINE SALTS DISSOLVED IN SOLVENTS OF LOW POLARITY

Amine salts capable of extracting acids and metal salts are usually polar substances[5]. The dipole moments of their molecules[6] may reach 10–12 D. The factors determining the structures of these salts have been examined in detail[5,7-11].

In non-solvating solvents of low polarity, because of the low dielectric constant of the medium, dissolved amine salts are present almost completely in the undissociated state[8-16]. Moreover, the molecules of the salts in these solutions are usually appreciably associated (polymerised). It is appropriate in the present review to examine in detail data on the association of amine salts, since the degree of association of a dissolved substance is directly related to its solubility. When the size of the associated complexes of dissolved molecules reaches a definite limit, formation of a new phase takes place†. It is to be expected that all the factors facilitating a decrease in the association of an amine salt in solution should lead to an increase in its solubility.

The degree of association is determined by the ratio of the energies of interaction of the polar molecules (ion pairs) of the salt with one another and with the molecules of the solvent. It is evident that the interaction of the molecules of the salt with one another facilitates association, whereas interaction with the medium hinders it.

The interaction of the polar molecules or ion pairs of a solute with one another and with the medium is determined by a number of forces of different kinds[17-22]—electrostatic forces and dispersion forces—and an important part may also be played by weak donor–acceptor interactions,

† Voyutskii[3] points out that "... association complexes form the nuclei of a new phase in the old, so that here we have a striking example of a quantity-quality transition".

leading to the formation of charge-transfer complexes of low stability. In some instances hydrogen bonds or relatively strong donor–acceptor bonds are formed by the solute molecules with one another or with the solvent molecules. These main forms of interaction are characterised briefly below, and their influence on the association of molecules of amine salts having different structures in diluents of low polarity is examined.

The electrostatic interaction energy of the cation and the anion of the salt with the solvent is determined according to Born[23] by the relationship

$$A = \frac{Z^2e^2}{2r}\left(1 - \frac{1}{D}\right) \quad (1)$$

(where Ze and r are the charge and the radius of the ion respectively, and D is the dielectric constant of the medium) and it follows that the electrostatic interaction energy of the ions with the medium decreases with decrease in the dielectric constant of the medium. In non-polar solvents or solvents of low polarity (saturated hydrocarbons, benzene, its alkyl derivatives, etc.), this energy is extremely low. The same is true of the dipole–dipole interaction energy between solute and solvent molecules. According to Keesom[24], the mean energy of attraction between dipoles is given by the formula

$$A = -\frac{2\mu_1^2\mu_2^2}{3r^6kT}, \quad (2)$$

where μ_1 and μ_2 are the dipole moments of the ion pairs or molecules, r is the distance between them, k Boltzmann's constant, and T the absolute temperature. It is evident that dipole–dipole interaction between the dipoles of a salt and the molecules of a non-polar solvent can take place only as a result of the production of induced dipoles in the molecules, and for non-polar solvents whose molecules are only slightly polarisable, this interaction should also be small. According to formula (2), the electrostatic interaction of the polar molecules of the salt with one another should be relatively large. This interaction is intensified with increase in the dipole moments of the molecules, with decrease in the distance between the dipoles (i.e. with decrease in the size of the salt molecules), and also with fall in the temperature.

Since in non-polar, non-solvating solvents the interaction of salt molecules with the medium is small, while their interaction with one another is considerable, appreciable association of the salts is observed in these systems. With increase in the polarity of the solvent we should expect an intensification of the electrostatic interaction of the molecules of the salt with the solvent and a decrease in the association.

The interaction of the molecules of amine salts with the molecules of non-polar organic solvents is determined to a considerable extent by dispersion forces, which increase with increase in the electronic polarisability of these molecules[25,26]. These forces oppose the association of the dissolved salts, but since they are relatively weak, they can bring about a significant decrease in association only when the electrostatic interaction of the salt molecules with one another is reduced as a result of marked screening of their charges by long hydrocarbon chains in the salt.

Charge-transfer complexes may be formed in the reactions of many compounds, including non-polar compounds[21,27-43]. In these complexes, one of the compounds acts as a Lewis acid and the other as a base. The stability constants of these complexes usually do not exceed a few units, and the interaction energy does not exceed 0.5–1 kcal mole^{-1}.[40] Nevertheless, these interactions can apparently have a marked influence on the state of certain salts in solution[44]. The ability of many aromatic hydrocarbons to form charge-transfer complexes has been reported[41,45-48]. In most instances the aromatic hydrocarbons in these complexes act as bases, but examples of their behaviour as Lewis acids have also been described[49,50]. The salts of primary and secondary amines in such complexes can in principle act as Lewis acids if the interaction takes place through the cation of the salt, or as bases if the interaction takes place through the anion of the salt. The salts of long-chain tertiary alkylamines, unlike the salts of secondary and primary amines, apparently cannot act as Lewis acids, since the positive charge of the cation in these compounds is strongly screened by the alkyl groups, and the compounds can act only as bases. The stability of charge-transfer complexes in which the aromatic diluent acts as a base increases with increase in its basic character, which can be assessed from data on the inductive effects of substituents in the benzene ring[25]. The formation of charge-transfer complexes between the molecules of amine salts and diluents would evidently oppose association in these systems. It should be noted, however, that the formation of charge-transfer complexes cannot always alter significantly the association of the amine salt, since the energy of bonding in these complexes is low.

The strongest interactions of the molecules of an amine salt with the molecules of a solvent and with one another are produced when hydrogen bonds are formed between these molecules. Hydrogen bonds may be formed between the anions of amine salts (which exhibit electron-donating properties[5]) and the molecules of the solvent if the latter contain electropositive hydrogen atoms‡. Hydrogen bonds may also be formed between the cations of amine salts, which contain electropositive hydrogen atoms, and the molecules of solvents which are electron donors§[14,15,52-60]. These bonds are so stable (energy 4–6 kcal mole^{-1}) that in many cases they have a decisive influence on the association of salts in solutions[61]. In systems with specific solvation of this type, the dissolved salts of tertiary amines are usually present in the monomeric state.

The most stable association complexes of salt molecules are produced when hydrogen bonds are formed between the anions of some molecules of the amine salt and the cations of other molecules of this salt. Such aggregates can obviously be formed chiefly in solutions of salts of primary amines, whose cations contain electropositive hydrogen atoms which are not screened by a large number of alkyl chains.

It follows from the foregoing that in non-solvating solvents of low polarity the interaction of the polar molecules of amine salts with one another, and hence their association, should increase with increase in the dipole moments of these molecules, and should decrease with increase in the dimensions of the latter and with increase in temperature. The association of the salts should decrease with increase in the polarity of the diluent and in its ability to form charge-transfer complexes or hydrogen bonds with the salt, and should increase when bonds of these types are

‡ Examples of these solvents are alcohols, acids, chloroform, etc.[21,25].

§ Examples of these solvents are ketones, ethers, esters, aromatic compounds containing mobile π-electrons, nitro-compounds, nitriles, etc.[21,25].

formed by the salt molecules with one another. Published data on the influence of some of these factors on the association of amine salts in solutions are given below.

1. Influence of the Polarity of the Molecules of Dissolved Amine Salts on Their Association in Solution

For a series of salts with similar structures, whose molecules have dipole moments of 0.29, 1.20, 1.66, and 2.67,[64-66] the degree of association in benzene solutions has the values 9, 12, 20, and 60 respectively[62,63]. The degree of association of amine salts also increases with increase in the polarity of their molecules[67-71]. Comparison of published data shows that in benzene solutions the degree of association of trioctylammonium salts varies in the sequence—perchlorate[72] > hydrogen sulphate[73-77] > nitrate[68,69] > sulphate[78]—in accordance with the order of their polarity. The association of tridodecylammonium halides in benzene, carbon tetrachloride, and cyclohexane varies in the order—iodide > bromide > chloride[79]—again in accordance with the change in polarity of these salts.

2. Influence of the Dimensions and Shape of the Molecules of Dissolved Amine Salts on Their State in Solution

Increase in the length of the alkyl chains in amines leads to a decrease in the association of their nitrates[6,52,68,80-87]. The degree of association of decyldimethylammonium, tri-n-octylammonium, tri-n-decylammonium, and tri-n-dodecylammonium nitrates at the same concentrations in *p*-xylene has the values ~12, 3–4, 2, and 2 respectively[68]. Tri-n-alkylammonium nitrates with hydrocarbon chains longer than C_{10} in solvents of the xylene and benzene type apparently do not form aggregates larger than the dimers[68,88,89]. The tendency of amine sulphates to undergo association also decreases with increase in the length of their alkyl chains[90].

The salts of some secondary amines are more extensively associated in solvents of low polarity than are the salts of the corresponding tertiary amines, formed with the same acids[91,92]. This can be attributed to the lower steric hindrance to the approach and mutual attraction of the dipole molecules for the salts of secondary amines compared with the salts of tertiary amines¶.

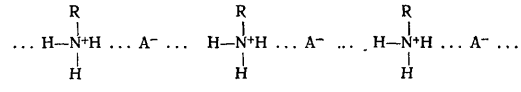
A decrease in the association of many salts containing organic radicals[62,63,93], including amine salts[9], is facilitated by the presence of double bonds in the hydrocarbon chains of their molecules, since the double bonds increase the rigidity of the chains and hence increase the steric hindrance to mutual approach of the salt molecules.

The degree of association of amine salts in non-polar solvents may depend on their concentration in the solutions[69,71], the nature of the dependence being different for salts with different structures[9]. The association of most salts of tertiary amines increases with increase in their concentration, passes through a maximum, and then decreases with further increase in the salt concentration[9,69]. For salts of tertiary amines with large anions the degree of association at moderate concentrations increases in conformity with the law of mass action[67,71,72,75,79,94]. For salts with relatively small anions[9], e.g. tri-n-octylammonium nitrate[95-97], tri-n-hexylammonium nitrate[98,99], tribenzylammonium halides[9], and various other salts having similar structures[100], the association increases with concentration more slowly than is required by the law of mass action†.

Highly associated salts are unique: their polymerisation is due to the formation of intermolecular hydrogen bonds. These salts are extensively associated at all concentrations.

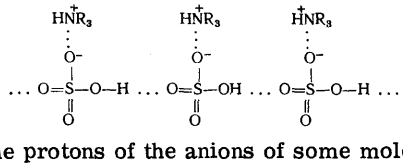
3. Influence of Intermolecular Hydrogen Bonding in Amine Salts on Their State in Solution

The formation of intermolecular hydrogen bonds is most characteristic of salts of primary amines, since the cations of these salts each contain three electropositive hydrogen atoms capable of taking part in the formation of these bonds[4,53-60,100-107]. On the other hand, the anions of amine salts may act as proton acceptors[5]. It is therefore suggested[5,51,68] that hydrogen bonds may be formed between cations and anions in different molecules of the salt of a primary amine, with the formation of relatively large and stable aggregates of the type



The salts of tertiary amines, particularly amines with long chains, cannot form such bonds because of steric hindrance and the smaller number of electropositive hydrogen atoms. With the salts of secondary amines, in view of the lower steric hindrance, the formation of intermolecular hydrogen bonds is more likely. Cryoscopic studies[68] show, however, that the nitrates of secondary amines are not associated much more extensively than are the nitrates of tertiary amines. The formation of intermolecular hydrogen bonds is apparently not characteristic of salts of secondary amines having long alkyl chains.

With the salts of secondary and tertiary amines intermolecular hydrogen bonding can be expected only when they are acid salts of dibasic or polybasic acids[76,108]. We can then assume the formation of aggregates of the type



in which the protons of the anions of some molecules of the salt interact with the electron-donating atoms of the anions of other molecules of the salt. It has in fact been shown that tri-n-octylammonium hydrogen sulphate[74-78,108] and hydrogen oxalate[109] are more extensively associated than are the corresponding normal salts of these acids. The more extensive association of the acid salts, however, may be due, not only to the formation of intermolecular hydrogen bonds between their molecules, but also to the higher polarity of these salts[78], resulting from the asymmetry of their structure.

It is to be expected that the association of amine salts may be influenced by the formation of hydrogen bonds between the anions of these salts and water molecules, when

¶ Another reason for the weaker association of salts of tertiary amines is the absence of intermolecular hydrogen bonds between the molecules of the salts of these amines.

† For the association of these salts the law of mass action is probably observed only at very low concentrations.

the latter are present in the system. Barrow and his coworkers[103] showed that the presence of water may lead to the dimerisation of amine salts with the formation of compounds of the type AmineHA... H–O–H... AHAmine, where HA is the acid forming the salt. Vdovenko and his coworkers[88] and also Högfeldt[104] had previously established that tri-n-octylammonium nitrate forms hydrates in the presence of water. Work by others[68,69], however, shows that the influence of water on the association of trialkylammonium nitrates is slight.

When hydrogen bonds are formed between the molecules of an amine salt, the association of the salt may be diminished significantly only as a result of specific solvation of the molecules of the salt by solvent molecules: non-solvating solvents have relatively little influence on the state of the salt in solution. If, however, the association of the amine salt takes place only as a result of dipole–dipole interactions, the nature and properties of a non-solvating solvent (dielectric constant, etc.) have a considerable influence.

4. Influence of the Dielectric Constant of the Medium on the State of Amine Salts in Solution

The influence of the properties of solvents on the association of the molecules of amine salts in solution has been investigated by a number of authors in studies of the electrical conductivities of these salts[8,9,80–86,100–112], and also in studies of the extraction of acids and metal salts by amine salts[68,69,73–77,79,87,98,113–116]. Sukhotin[8] and Kraus and his coworkers[6,9,80–86] have shown that the salts of tertiary amines and quaternary ammonium bases, which are present in the monomeric state in polar solvents (e.g. nitrobenzene), are associated in benzene and other non-polar solvents. Fomin and his coworkers[69,74], Shmidt and Shesterikov[68], Frolov and Sergievskii[77], Vdovenko, Chaikhorskii, and their coworkers[88,98], and others[70,79,87,113,115,116] have studied the state of the salts of various tertiary alkylamines in *p*-xylene, benzene, and toluene, and have shown that the amine salts are appreciably associated in these solvents of low polarity. The increase in the degree of association observed with decrease in the dielectric constant of the medium is consistent with the decrease in the strength of electrostatic interaction of the salt molecules with the medium, following from formulae (1) and (2).

5. Association of Salt Molecules in Various Non-Polar Solvents

The dielectric constant is not the only property of a solvent determining the association of a salt dissolved in that solvent. For example, the association of trialkylammonium nitrates in octane[113] is much greater than the association of these salts in benzene and *p*-xylene[68], although the dielectric constants of all these solvents are similar and the dipole moments of their molecules are zero[117]. According to Palit's data[118], the degree of association in benzene and in cyclohexane has the values ~ 5 and ~ 10 respectively for dodecylammonium propionate, and ~ 3 and 10 respectively for dodecylammonium oleate, although the molecules of both these solvents are non-polar. The degrees of association of tridodecylammonium halides are also different for these solvents of equal polarity[79].

These differences in the degree of association of salts in different non-polar solvents are due to differences in the strength of the non-Coulombic interactions (dispersion interactions, etc.) of these non-polar solvents with the dissolved amine salts, and also, apparently, to the formation of unstable charge-transfer complexes between the amine salts and certain solvents. For a rough estimate of the influence of these interactions on association, we can use the values of the Hildebrand parameter δ, characterising the strength of the interaction of the molecules of each component of the solution with one another[2,19,45,119,120]. The greater the difference in the force fields of the molecules of the various components of the solution, i.e. the greater the difference between the parameters δ characterising these components, the greater should be the tendency for identical molecules to associate‡. The values of δ for amine salts are usually much greater than those for most non-polar diluents, and amount to 10–14 $cal^{1/2}\ cm^{-3/2}$.[121,122] For solvents of low polarity, the values of δ lie in the range 7–9 $cal^{1/2}\ cm^{-3/2}$ (see Table). The difference in the values of δ for the salt and the solvent increases on going from aromatic to aliphatic hydrocarbons (see Table), in agreement with published data on the association of amine salts in these solvents. The Table also shows that the value of δ for cyclohexane is lower than that for benzene. This agrees with the observed more extensive association of mono- and tri-dodecylammonium salts in cyclohexane compared with benzene[118]. Published data[123] indicate that the degree of association of trioctylammonium chloride is greater in cyclohexane than in toluene, and this again agrees with the higher value of δ for toluene. The degree of association of these salts has its highest values in open-chain saturated hydrocarbons, whose δ-values are much less than those for cyclic hydrocarbons and differ to the greatest extent from the values of δ for amine salts[113]. Amine salts are less associated in carbon tetrachloride than in cyclohexane[79], since the former solvent has the higher value of δ. The data in the Table also suggest that the association of salts dissolved in alicyclic hydrocarbons should decrease on going from cyclopentane to cyclo-octane.

The force of interaction between the molecules of different substances in solution depends also on their molar volumes[45]. Thus within a given class of solvents, satisfactory correspondence between the values of δ and the degree of association of salts is observed only when solvents having similar molar volumes are compared.

6. Association of Salts and Their Solubility

On the basis of the above data on the influence of the properties of salts and solvents on association, it is possible to reach preliminary conclusions regarding the influence of these properties on the solubility of amine salts in non-polar diluents and those of low polarity. Since diminished association of a salt leads to an increase in its solubility, it may be expected that the solubility of amine salts should increase with decrease in the dipole moments of their molecules, with increase in the number and length of the alkyl chains in the molecules, with the introduction of double bonds into the alkyl chains, with increase in the dielectric constant of the solvent, and (for non-solvating non-polar solvents having similar molar volumes) with increase in the parameters δ for these solvents, as well as

‡ This argument will obviously be completely valid only in the absence of specific interactions between solvent and solute.

TABLE. Parameters δ for various solvents[19,45,119,124-126].

Class of compound	Solvent	δ	Class of compound	Solvent	δ
Saturated open-chain hydrocarbons	Neopentane	6.2	Aromatic hydrocarbons	n-Butylbenzene	8.6
	Isopentane	6.8		n-Propylbenzene	8.6
	n-Pentane	7.1		Ethylbenzene	8.8
	n-Hexane	7.3		Toluene	8.9
	n-Heptane	7.4		Benzene	9.2
	n-Octane	7.5		o-Xylene	9.0
	n-Nonane	7.6		m-Xylene	8.8
	n-Decane	7.7		p-Xylene	8.8
	n-Dodecane	7.8		Mesitylene	8.8
	n-Tetradecane	7.9		Styrene	9.3
	n-Hexadecane	8.0		Naphthalene	9.9
	2,2,4-Trimethylpentane	6.8		Nitrobenzene	10.0
	Isopentane [sic]	6.6	Halogenated hydrocarbons	Bromobenzene	10.0
		7.3		o-Dichlorobenzene	11.0
		7.6		Chlorobenzene	9.5
Unsaturated hydrocarbons	Hex-1-ene	7.7		CCl_4	8.6
	Oct-1-ene			$CHCl_3$	9.3
	Hexa-1,5-diene	8.2		$CHBr_3$	10.5
				CH_2Cl-CH_2Cl	9.0
Saturated cyclic hydrocarbons	Cyclopentane	8.5		CH_2Br-CH_2Br	9.6
	Cyclohexane	8.6			
	Cycloheptane	7.8	Other compounds	Nitromethane	12.6
	Cyclo-octane			Carbon disulphide	10.0
	Methylcyclohexane			Dioxan	10.0
				Pyridine	10.7
				Acetonitrile	11.9
				Methyl ether	8.8

with rise in temperature. The formation of intermolecular hydrogen bonds or donor–acceptor and charge-transfer complexes between the molecules of the amine salt should decrease its solubility (as a result of which the salts of primary amines and the acid salts of polybasic acids have a low solubility), whereas the formation of corresponding bonds with the diluents should increase the solubility. The published regular features of solubility show good agreement with these conclusions.

III. THE INFLUENCE OF THE STRUCTURES AND PROPERTIES OF AMINES AND DILUENTS ON THE SOLUBILITY OF AMINE SALTS IN SYSTEMS WITHOUT SPECIFIC SOLVATION

Many of the conclusions regarding the regular features of the solubility of amine salts in diluents of low polarity, reached above from an examination of the state of these salts in solutions, can be reached also by thermodynamic methods. In some instances it is possible to predict the solubility quantitatively.

From the thermodynamic viewpoint, solubility may be determined by factors of two different types—(1) factors independent of the nature of the solvent and determined entirely by the nature of the solute, and (2) factors depending on the properties not only of the solute but also of the solvent.

For systems obeying the laws governing ideal solutions, the solubility of solids is independent of the nature of the liquid solvent. Liquids in ideal systems are miscible in all proportions.

For many real systems, the mutual solubility of liquids is restricted, and the solubility of solids in the liquids depends not only on their properties but also on the nature of the solvent. When real systems obey the laws of regular solution[19], the solubility values can be calculated from the parameters δ of solute and solvent. For solutions whose behaviour differs from that predicted by the theory of regular solutions, quantitative prediction of the solubility is difficult. Large changes in solubility on passing from one system to another, however, can be predicted qualitatively on the basis of this theory with allowance for the deviations expected on the basis of data on specific interactions in these systems. It is therefore of interest to examine the correspondence between solubility data for amine salts and the regular features expected for ideal and regular solutions.

1. Solubility in Ideal Systems

In ideal systems the solubility of solids is given by Shreder's equation[127,128]

$$\ln N = -\frac{\Delta H_f\,(T_f - T)}{RT_f\,T} \qquad (3)$$

where N is the mole fraction of the solute in a saturated solution, ΔH_f the heat of fusion of the solute, T_f the melting point of the solute, and T the temperature of the system.

It follows from Eqn. (3) that the solubility of solids in ideal liquid systems decreases with increase in the melting point and the heat of fusion, and increases with rise in the temperature of the system. This equation also shows that at the melting point the solubility is unlimited: i.e. ideal liquids are miscible in all proportions. The experimental data show good agreement with Shreder's equation for solutions of various non-polar substances in non-polar diluents[129]. It is evident that even qualitative conclusions regarding the solubility of amine salts in diluents of low polarity can be reached from Eqn. (3) only for amines of high molecular weight containing very large organic radicals, which screen the dipole moments of the salts, so that their behaviour and properties approach those of non-polar hydrocarbons.

The salts of tertiary amines with sufficiently high molecular weights are solids, and their melting points increase with increase in molecular weight. The salts of amines with very long hydrocarbon chains are sparingly soluble even in relatively polar solvents, in agreement with conclusions reached from Eqn. (3). From this it follows that the increase in the solubility of amine salts in non-polar solvents with increase in the length of the hydrocarbon chains of the amines, expected from considerations related to association of the salts, should be observed only within definite limits. The salts of amines with extremely long alkyl chains are sparingly soluble because of the increase in their melting point.

2. Solubility in Systems Obeying the Laws Governing Regular Solutions

Regular solutions are those in which the distribution of the components is completely homogeneous and disordered, the force fields of the molecules are symmetrical, and the molecular volumes of the molecules do not differ greatly from one another[19]. Solutions of non-polar substances in non-polar solvents correspond most closely to this definition and show the closest agreement with the rules derived for regular solutions[45,119,120]. For regular solutions the solubility differs from the ideal solubility, but quantitative allowance can be made for this deviation by means of equations containing the parameters δ. The solubility of solids

in regular solutions is determined[45] by the equation

$$\ln a^{i}_{\text{solid}} = \ln \varphi_2 + \varphi_1\left(1 - \frac{V_2}{V_1}\right) + \frac{V_2\varphi_1^2(\delta_2 - \delta_1)^2}{RT}, \qquad (4)$$

where a^{i}_{solid} is the ideal solubility, calculated from Eqn. (3), φ_1 and φ_2 are the volume fractions of solvent and solute in the saturated solution, V_1 and V_2 the molar volumes of these substances, and δ_1 and δ_2 their solubility parameters.

It follows from Eqn. (4) that, other conditions being equal, the solubility should be greater, the smaller the difference $\delta_2 - \delta_1$. Hildebrand[130-132] points out that Eqn. (4) is approximate and that caution must be exercised in using this equation to calculate the solubilities of polar substances[19], despite the fact that values of δ for a large number of polar substances have been published[133]. Although amine salts are polar substances, the principles of the theory of regular solutions are observed for many polar substances containing a bulky hydrocarbon portion, with an accuracy which is greater, the greater the volume of the non-polar radicals in the molecules of these substances[134]. The first attempt to apply the theory of regular solutions to the determination of the solubility of amine salts in non-polar solvents was made by Kertes[121,122], who determined the values of δ for a number of tertiary, secondary, and primary alkylammonium chlorides from their solubilities in various solvents. Similar values of δ were obtained for each salt in different solvents, indicating that the characteristic features of regular solutions are observed (approximately at least) with solutions of long-chain alkylamines. For primary, secondary, and tertiary alkylammonium chlorides the values of δ[121,122] are ~ 13–14, ~ 11–12, and 10.5–10.6 respectively, in agreement with the higher solubility of tertiary amine salts in solvents of low polarity. In accordance with Eqn. (4) and the values of δ given in the Table, the solubility of amine salts in saturated hydrocarbons is much less than that in aromatic hydrocarbons or in carbon tetrachloride. It may be expected that the regular features of solubility in non-solvating solvents will be analogous for other amine salts.

With solvents whose molar volumes have similar values, the solubility of amine salts should increase with increase in the value of δ for the solvent. The data in the Table indicate that for aromatic hydrocarbons the order of solvent power will be—nitrobenzene > chlorobenzene > benzene > toluene > xylene ≃ ethylbenzene > n-propylbenzene —which corresponds to the observed solvent power of these solvents for amine salts[135]. The observed sequence indicates that the solvent power of the diluent decreases with increase in the number and length of the alkyl substituents in benzene. An interesting parallelism is observed between the increase in the acidic properties (increase in ionisation potential[136]) of substituted benzene derivatives and their solvent power for the salts of tertiary amines. In this series of compounds the solvent power decreases with decrease in the acidic properties. If this regular feature is observed for other benzene derivatives, we may expect that all derivatives with substituents having positive inductive effects will be weaker solvents than derivatives containing substituents with negative inductive effects[137,138]. These results can be explained if we assume that the solubility of amine salts increases with increase in the acid–base interaction of the anions of the amine salts with the solvent molecules.

The data in the Table suggest that cyclohexane is a more effective solvent than open-chain hydrocarbons, but is less effective than aromatic hydrocarbons. The solubility of tri-n-octylammonium chloride in cyclohexane is in fact less than that in toluene, but much greater than that in saturated hydrocarbons[123]. In the selection of aromatic hydrocarbons for the dissolution of amine salts, compounds with a large number of long alkyl chains attached to the benzene ring should evidently be avoided as far as possible. The data in the Table show good agreement with the familiar ready solubility of amine salts in nitromethane, chloroform, and pyridine[139]. The data also suggest that the presence of naphthalene in benzene or carbon tetrachloride may increase their solvent power, and also that the solvent power of alicyclic hydrocarbons should vary in the order—cyclo-octane > cycloheptane > cyclohexane > cyclopentane > methylcyclohexane.

In the theory of regular solutions, the solubility of a liquid is determined by the relationship[19,5,119]

$$\ln N_2 = -\frac{V_2\varphi_1^2}{RT}(\delta_2 - \delta_1)^2, \qquad (5)$$

where the subscripts 2 and 1 denote quantities relating to solute and solvent respectively§. Thus for liquids also, the solubility is determined by the difference $\delta_2 - \delta_1$, and we should expect the regular features of the solubility of liquid amine salts to be analogous to those observed for the solid salts.

For a preliminary estimate of the possibility of dissolving amine salts in solvents which do not exhibit specific solvation, an equation derived from the theory of regular solutions[45], relating the consolute temperature of a mixture of liquids with the parameters δ, is of interest:

$$T_{\text{cons}} = (\delta_1 - \delta_2)^2(V_1 + V_2)/4R \qquad (6)$$

where V_1 and V_2 are the molar volumes of the components of the mixture. This equation and the value of δ for the amine salt can be used to determine approximately the solvents in which the salt will be soluble at ordinary temperatures. By substituting in Eqn. (6) the values of δ for amine salts determined by Kertes[121,122] and the known values of δ for various solvents, it can readily be established that for solutions of these salts in aromatic and chlorinated hydrocarbons the values of T_{cons} lie considerably below room temperature, whereas those for solutions in aliphatic hydrocarbons are much higher than room temperature, in agreement with the solubility data.

Thus the conclusions reached on the basis of the theory of solubility for regular solutions agree with the observed regular features of the solubility of amine salts, and the formulae of this theory, together with known values of δ, can be used to predict semi-quantitatively the solubility of the salts in various solvents.

All saturated hydrocarbons are poor solvents for amine salts. At the same time there are significant differences in the solvent power of individual saturated hydrocarbons. Thus the volume solubility of amine salts and various other polar organic compounds in hydrocarbons decreases with increase in the length of the hydrocarbon chain[121,122,140-142]. For example, the solubility of tridodecylammonium nitrate in octane is greater than that in decane[143]. At the same time, the values of δ for hydrocarbons increase slightly with increase in the chain length. Similar regular features

§ This equation is applicable when $V_2 \simeq V_1$. More complex equations are used when the difference between these volumes is large[45].

were observed in a study of the solubility of water in saturated hydrocarbons[144]. The solubility of water, expressed in mole fractions, increases slightly with increase in the length of the alkyl chains, the increase corresponding exactly to that expected from formula (5). On passing to long-chain hydrocarbons, however, the increase in molar volumes takes place so rapidly that the volume solubility of water in these hydrocarbons decreases, whereas the solubility expressed in mole fractions increases.

Thus in those instances where the values of δ change only slightly on going from one substance to another, the solubility (in volume fractions) is influenced chiefly by the change in the molar volumes, the volume solubility of the solute decreasing with increase in the molar volume of the solvent. This conclusion also agrees with the solubility rule derived by Semenchenko[145-147], according to which the mutual solubility of two substances increases with decrease in the difference in their "generalised moments" given by the ratios of the dipole moments of the molecules to their molar volumes. Since the polarity of the molecules of the amine salts is much greater than the polarity of the diluent molecules, the generalised moments of the amine salts are also greater than the generalised moments of the diluents. Thus the solubility of the salts in the diluents should increase with increase in the generalised moment of the diluent and with decrease in the generalised moment of the amine salt. When the dipole moments change little from one compound to another, the solubility should evidently be influenced chiefly by the values of the molar volumes. The solubility of a salt should increase with increase in its molar volume (since this leads to a decrease in its generalised moment) and with decrease in the molar volume of the solvent. The observed regular features of the solubility of amine salts in various solvents agree with these conclusions from Semenchenko's rule. For example, the solubilities of trialkylammonium nitrates in non-polar solvents change in the order—tridodecylamine > tridecylamine > trioctylamine[143]—and the solubilities of the sulphates change in the order—tertiary amine > secondary amine > primary amine[108,114,135].

These data also indicate that the solubility of salts of aromatic amines and amines with cyclic radicals should be less than the solubility of the salts of n-alkylamines containing the same number of carbon atoms, since the molar volumes of arylamines and cycloalkylamines are less than the molar volumes of the corresponding n-alkylamines.

Thus either Semenchenko's rule or the equations of the theory of regular solutions can be used to predict semi-quantitatively the solubility of various amine salts in diluents with different structures. The possibility of applying the theory of regular solutions for this purpose will probably increase with increase in the availability of data on the values of δ for various amine salts and diluents.

As already noted, these criteria are not valid when strong specific interaction takes place between the components of the solutions. Thus in a number of instances chloroform is a more powerful solvent than benzene, despite the fact that the value of δ for chloroform differs little from that for benzene. These deviations are due to the fact that specific solvation, which has a marked influence on solubility, takes place in amine salt–chloroform systems.

IV. THE INFLUENCE OF SPECIFIC SOLVATION ON THE SOLUBILITY OF AMINE SALTS IN DILUENTS OF LOW POLARITY

Amine salts dissolve readily in solvents which solvate their cations or anions as a result of the formation of hydrogen bonds. Thus acidic substances, capable of hydrogen bonding with the anions of amine salts[5,86,95,96,148-155] (organic acids and alcohols, and various chlorinated hydrocarbons), and also basic substances, capable of hydrogen bonding with the cations of amine salts[5,97,148,156] (ethers, ketones, nitro-compounds, and various amines), are usually effective solvents for amine salts and are miscible with them in all proportions. These substances prevent the association of amine salts by forming compounds with them, bringing them into solution¶. Basic diluents are more effective solvents for the salts of primary and secondary amines than for the salts of tertiary amines, since, as noted above, the formation of hydrogen bonds with these substances is least characteristic of the cations of the salts of tertiary amines. Acidic diluents dissolve the salts of tertiary amines more effectively than the salts of primary amines.

Substances which solvate amine salts are capable of dissolving these salts even when they are not used in the pure form; the addition of small quantities of many of these substances to amine salts increases considerably the solubility of the latter in non-solvating solvents of low polarity, e.g. in saturated aliphatic hydrocarbons[95,135,157-164]. The marked influence of various substances, added as a third component, on the mutual solubility of liquids and the solubility of solids in liquids was described at an early date. The action of a third component which increases solubility, known as solubilisation, was noted by Alekseev as early as 1879.[165] Timmermans[166] established that a third substance is able to increase the mutual solubility of two other substances if it is soluble in both of them. It is evident that an increase in the solubility of amine salts in non-solvating diluents may be achieved by the addition of substances which are capable not only of solvating the amine salts but also of dissolving in the diluents, i.e. substances of the types indicated above, whose molecules contain large hydrocarbon portions.

Several theories have been put forward to explain the mechanism and the regular features of solubilisation[167-169]. The most widespread are McBain's colloidal–adsorption theory[167], according to which the substance being dissolved passes into solution by being sorbed inside colloidal particles of the added solubilising agent, distributed in the solvent; and Winsor's solvation theory[168,169], which attributes the action of the solubilising agent to its simultaneous interaction with the substances in both the phases exhibiting negligible or limited miscibility. Experimental data obtained in recent years on the solubility of water in non-polar organic solvents[118,170,171] show more complete agreement with Winsor's theory than with McBain's theory. Apart from this, the colloidal–adsorption theory cannot be used to explain the regular features of the solubilisation of amine salts, since the solubilising agents added (alcohols,

¶ An example of the complete absence of association as a result of solvation of the anions of a salt by diluent molecules is provided by solutions of tridodecylammonium halides in chloroform[79]. In benzene these salts are appreciably associated.

ketones, and nitro-compounds) are not present in the organic solvents in colloidal form. Examination of the experimental data on the solubility of amine salts in solvents of low polarity in the presence of solubilising additives shows that these data can also be explained on the basis of the concepts of solvation theory.

1. The Use of Solvation Theory to Explain the Phenomena of the Solubilisation of Amine Salts

According to Winsor's theory[168,169], the efficiency of a solubilising agent depends on the value of the "affinity ratio" $R = A_{co}/A_{cw}$, where A_{co} measures the affinity of the solubilising agent for the phase of low polarity, and A_{cw} the affinity of the solubilising agent for the more polar phase. According to Winsor, the maximum increase in solubility per mole of solubilising agent added is reached when R is close to unity, i.e. when the affinities of the added third component for the two phases are the same. If two liquids—one polar and one non-polar—are immiscible and the value of R for an added third substance is greater than unity, this substance, when added to the system, enters the non-polar phase to a greater extent, and preferential dissolution of the polar substance in the non-polar phase takes place. When $R < 1$, the addition of the solubilising agent is accompanied by dissolution of the material of the non-polar phase in the polar phase. The quantity of solubilising agent required to homogenise the system when $R < 1$ and when $R > 1$ is greater than the quantity required when $R = 1$.

These qualitative ideas make it possible to predict the nature and the strength of the solubilising action of various additives on the solubility of amine salts in solvents of low polarity, in particular the action of alcohols having various structures.

The mechanism of the solubilising action of alcohols can be explained as follows. Alcohols are capable of solvating the anions of trialkylammonium nitrates, sulphates, chlorides, and iodides[95,96,172-175] with the formation of the relatively stable solvates $AmineHNO_3.2ROH$,[96] $[AmineH]_2SO_4.2ROH$,[172,173] $AmineHCl.ROH$,[61,174,175] and $AmineHI.ROH$.[176] This solvation leads on the one hand to breakdown of the salt aggregates to monomers[177] and on the other hand to dissolution of the salt in the solvent of low polarity, since the attachment of the alcohol molecules to the amine salt molecule leads to a decrease in the overall dipole moment of the resulting solvate and a simultaneous increase in its dimensions, including the dimensions of its hydrocarbon portion†. The number of alcohol molecules required for the solubilisation of low concentrations of tri-n-octylammonium nitrate in a non-polar diluent has recently been determined[178], and found to be 2 moles $mole^{-1}$, which agrees with the value of the solvate number found by other workers[96], who have studied the amine nitrate–alcohol system by physicochemical analysis. It also follows[178] that the dissolution of the amine nitrate in a non-polar solvent requires the formation of its solvate with the alcohol. The solvates formed by alcohols with amine salts are relatively stable. According to published data[96], the stability constants of the compounds $AmineHNO_3.2ROH$ for alcohols containing 6–12 carbon atoms in the chain are $\sim 10^3$ and differ little from one another, although the values decrease slightly with increase in the length of the alkyl chain of the alcohol. Since the interaction of alcohols with solvents of low polarity, e.g. saturated hydrocarbons, which is due entirely to van der Waals forces, is much weaker than with amine salts, the values of R in alcohol–amine salt–non-polar diluent systems are apparently much less than unity. Thus in a homologous series of alcohols a stronger solubilising action should be shown by alcohols characterised by a higher value of R, i.e. by alcohols with a higher affinity for the non-polar phase. We may thus expect that the solubilising action of aliphatic alcohols in amine salt–non-polar solvent systems will increase with increase in the length of the alkyl chains of the alcohols. This dependence of the solubilising power of alcohols on their structure was observed by Izmailov and Franke[171] and by Purnell and Bowden[179] for systems in which the bonding of the alcohol with the main material of the polar phase was much greater than that with the material of the non-polar phase.

With change in the properties of the amine salt, however, another type of relationship is possible. If the electron-donating power of the anion of the amine salt is low or if there is steric hindrance to the solvation of the anion by the alcohol, and if as a consequence the affinity of the alcohol for the salt is so low that it is less than its affinity for the non-polar solvent and $R > 1$, an increase in the solubilising action of the alcohol will be brought about by changes in its structure which lead to a decrease in R, i.e. to an intensification of its interaction with the amine salt and a decrease in the interaction with the non-polar diluent. This will evidently be observed with decrease in the length of the alkyl chain of the alcohol, since this intensifies the interaction of the alcohol with the amine salt[96]. These regular features are probably characteristic of the solubilisation of salts having bulky anions, whose electron-donating properties are weakened considerably, for example the salts of organic acids or the compounds of various metal salts, extractable by amines. The electron-donating properties of the anions of these salts may be very weak, so that their solvation by alcohols is very weak[179].

A solubilising action with respect to amine salts in non-polar solvents may evidently be shown not only by alcohols but also by other organic compounds which are capable of solvating these salts and are readily soluble in non-polar solvents. As noted above, this ability may probably be shown not only by alcohols but also by aliphatic acids with sufficiently long alkyl chains, phenol and its derivatives soluble in non-polar diluents, and other organic compounds with a large hydrocarbon portion which are electron acceptors, i.e. which have at least weak acidic properties and hence are capable of solvating the anions of amine salts. On the basis of Winsor's theory, it may be expected that, of the solubilising agents which are readily soluble in non-polar solvents, the most effective for the solubilisation of salts whose anions exhibit significant electron-donating properties, e.g. amine nitrates and chlorides, should be substances with weaker acidic properties than alcohols. These substances may be very weak aprotic acids, interacting with the anions of amine salts by a donor–acceptor mechanism. If, however, the acidic properties of these solvents, added as solubilising agents, are so weak that $R > 1$ and the strength of the donor–acceptor interaction of these substances with anions is comparable with that of the dispersion interactions with the non-polar solvent, Winsor's theory indicates that increase in the acidic properties of the solubilising agent should lead to an increase in solubility in the system. In this connection it is of interest to

† These changes lead to a decrease in the generalised moment[145-147] of the salt.

recall that the solvent power of aromatic hydrocarbons increases with increase in their acidic properties. The existence of this relationship indicates the possibility that these "non-solvating" diluents of low polarity dissolve amine salts as a result of weak donor–acceptor interactions with the anions of these salts.

Solubilisation can apparently take place as a result of solvation not only of the anions but also of the cations of amine salts. The solvation of cations may be of greatest importance for the solubilisation of the salts of primary amines[68] and the acid salts of dibasic and polybasic acids with any anions: it prevents the polymerisation of these salts which takes place as a result of the formation of hydrogen bonds between the cations of some molecules of the salt and the anions of other molecules of the salt[51]. The solubilising influence of the solvation of cations is less with secondary and tertiary amines, since less extensive solvation takes place than with primary amines, because of the greater steric hindrance and the smaller number of acidic hydrogen atoms in these amines[97]. The ability to solvate the cations of the salts of primary amines and to solubilise these salts is shown by substances which are electron donors[180,181]—ketones, ethers, esters, amides of carboxylic acids, nitro-compounds, etc.—and the ability (albeit weak) to solubilise the salts of primary amines is also shown by various substances which have very weak basic properties, e.g. benzene.

An interesting conclusion from Winsor's ideas is the possibility of the non-additive ("synergic") solubilising action of various agents. Studies of solubilisation in water–non-polar solvent systems[118,170] established that mixtures of solubilising agents, for one of which $R < 1$ while for the other $R > 1$, have a much greater solubilising action than each agent taken separately at the same concentration. Winsor attributes this to the fact that for this synergic mixture the value of R becomes close to unity. A very marked increase in solubilising power is observed at definite ratios of these solubilising agents, corresponding to $R = 1$.[118,171] It may be expected that, with solubilisation in amine salt–non-polar solvent systems, it is also possible to select solubilising agents, one mole of a mixture of which would give a greater (synergic) solubilising effect than would one mole of either component taken separately.

2. Solubilisation of the Extractable Compound by Excess of the Extractant

Various amine salts having a bulky inorganic complex anion do not dissolve even in relatively polar solvents, in which other salts of these amines, containing smaller anions, are readily soluble[158]. In these instances the solubility of the sparingly soluble amine salt can be increased as a result of its solvation by the molecules of a more soluble salt of the amine, present in solution. The salt $[R_3NH]_2[CoCl_4]$ in *p*-xylene is solvated by molecules of the extractant R_3NHCl.[182] Solvation of extractable amine salts by an excess of the extractant is also indicated by the fact that, in order to prevent separation into layers in organic solutions of low polarity, containing salts formed during extraction such as $[AmineH]_2[Pu(NO_3)_6]$ or $[AmineH].[UO_2(NO_3)_3]$, the presence of an excess of the simple salt $AmineHNO_3$ in the solution is required[158,183]. The dissolution of the salt $[AmineH]_4[U(SO_4)_4]$ in butylbenzene[184] also requires the presence, in the solvent, of the simple salt $[AmineH]_2SO_4$ in quantities sufficient for formation of the solvate $\{[AmineH]_2SO_4\}\{[AmineH]_4[U(SO_4)_4]\}$. Smulek and Siekierski[185], in a study of the dependence of the activity coefficients of the dissolved iron(III)–$[AmineH][FeCl_4]$ complex on the concentration of the extractant (AmineHCl), established that these coefficients decrease with increase in the extractant concentration. This phenomenon also can be attributed to a decrease in the concentration of free $[AmineH][FeCl_4]$ as a result of its solvation by AmineHCl molecules. The solvation of extractable complexes by molecules of amine salts used as extractants is also indicated by published data[186–188]. As in the solubilisation of amine salts by the addition of alcohols, the efficiency of the solubilising action of the amine salt used as extractant is greater the greater its affinity for the diluent, i.e. the greater its solubility in non-polar solvents. Thus it follows from published data[158] that in those instances where the amine salt ($AmineHNO_3$) is more soluble in the diluent, the quantity required for dissolution of the insoluble salt $[AmineH]_2[Pu(NO_3)_6]$ is smaller; the quantity of amine salt required for solubilisation of the complex salt also decreases in diluents which are more effective solvents for the simple amine salt. The composition of the organic phase corresponding to the limiting solubility[158] corresponds to the solvates $[TOAH]_2[Pu(NO_3)_6]$‡ in nitromethane, $[TOAH]_2[Pu(NO_3)_6].4TOAHNO_3$ in xylene, and $[TOAH]_2[Pu(NO_3)_6].2TOAHNO_3$ in dibromomethane. In the polar nitromethane, the salt being extracted dissolves without solvation, but in the other diluents solvation by the amine salt increases with decrease in the solvent power of the diluent. Shmidt et al.[182] demonstrated the existence of a relationship between the degree of solvation of $[TOAH]_2[CoCl_4]$ by molecules of the amine salt TOAHCl and the degree of association of the latter in the diluent. In the opinion of these authors, the degree of association of the amine salt used as extractant does not change in many extraction systems when the amine salt forms extractable compounds with metal salts. Wilson's data also agree with this suggestion, since in nitromethane, in which tri-n-octylammonium nitrate is monomeric, only two molecules of $TOAHNO_3$ take part in formation of the complex, whereas in xylene, in which the degree of association[68] of $TOAHNO_3$ is ~ 3, formation of the complex $[TOAH]_2[Pu(NO_3)_6].4TOAHNO_3$ involves the participation of three times the number of amine salt molecules, i.e. six molecules.

The solubilisation of extractable compounds by an excess of the extractant is a widespread phenomenon, which is observed not only in extraction with amine salts. The dissolution of salts of dibutyl hydrogen phosphate in non-polar diluents is possible only in the presence of an excess of this acid ester[189], i.e. when the molecules of the salt are solvated by molecules of the corresponding acid. The solubility of the solid salt is proportional to the concentration of acid in the solution raised to a power corresponding to the solvate number[189]. Thus in the dissolution of the solid salt, as a result of solvation by the corresponding acid, the law of mass action is observed in accordance with the stoichiometry of the solvate. In the solubilisation of liquid amine salts as far as complete dissolution of the salt, these stoichiometric relationships are not observed, since the solvate formed usually has a higher affinity for the amine salt phase; it remains in this phase and is not transferred to the non-polar phase until almost all the insoluble liquid amine salt is converted into a solvate soluble in the non-polar phase. Homogenisation of the two-phase liquid system takes place after addition of almost the

‡ TOA = $(n\text{-}C_8H_{17})_3N$ (Ed. of Translation).

total quantity of solubilising agent required for conversion of the polar phase into the solvate.

It should be noted that stoichiometric relationships between the solubilising agent and the amine salt, corresponding to the degree of solvation under the conditions of homogenisation, are observed only at relatively low concentrations of these substances in the non-polar solvents. At higher concentrations the quantity of solubilising agent required for the transfer of one mole of the insoluble salt into the medium of low polarity decreases[190], since solubility begins to be affected not only by solvation but also by the overall increase in the dielectric constant of the solvent occurring in the presence of the solubilising agent, which is usually a more or less polar substance. Increase in the dielectric constant of the medium, as noted in Section III, leads to a decrease in the association of the molecules of the amine salts and hence to an increase in their solubility.

V. THE INFLUENCE OF NON-SOLVATING DILUENTS ON THE EXTRACTION PROPERTIES OF AMINE SALTS

The influence of non-solvating diluents on extraction has been relatively little studied. In the early work on this problem, attempts were made to establish a relationship between the partition coefficients or extraction constants and the dielectric constant of the medium or the polarisability of the diluent[191-197]. Because of the strong influence of factors additional to those studied by the authors cited, unambiguous relationships could not be established in most instances. More fruitful work has been carried out in recent years by Rozen and Khorkhorina[198], based on the molecular theory of solutions, and also by Siekierski[185,199-203] and Vdovenko et al.[204], who based their conclusions on the theory of regular solutions and used the parameters δ for the extractants, diluents, and extractable complexes to take account of the influence of the diluents.

The position of equilibrium for a reaction in solution (including extraction) and the solubility of the reactants are determined to a considerable extent by the same thermodynamic functions. Thus the higher solubility of a given substance corresponds to a decrease in its activity coefficient in solution[45]. The decrease in the activity coefficient of an amine salt dissolved in a diluent also corresponds to a decrease in its extraction properties. At the same time it is evident that a decrease in the activity coefficient of a reaction product, e.g. the compound being extracted, leads to a displacement of the equilibrium towards formation of this compound[119]. As early as 1938 Hildebrand[119], pointing out the relationship between the position of equilibrium for reactions and the values of δ for the reactants, wrote: "In general we may summarise by saying that in order to get a large amount of a certain substance in an equilibrium reached in solution, one should employ a solvent which is a good one for the substance desired and a poor one for the substance or substances on the other side of the equation of equilibrium. The quality of a solvent in this connection may be determined by any or all of the factors considered in connection with solubility in general, viz. polarity, chemical combination and internal pressure." The internal pressure, which is one of the chief factors determining solubility in non-polar solvents which do not react chemically with the solute and which obey the laws governing regular solutions, is given by the parameter δ. The influence of the values of δ on the extraction equilibrium can be seen by examining the simplest thermodynamic equations for extraction equilibria[202-204]. If the extraction of a metal salt (A) by an amine salt (E) takes place according to the equation

$$A_{aq} + n\,E_{org} \rightleftarrows A \cdot n\,E_{org} \equiv EC_{org},$$

where EC is the extractable compound of the salt A with the amine salt, the equilibrium constant for this reaction is given by the formula

$$K = \frac{[EC]\gamma_{EC}}{[A][E]^n \gamma_E^n \gamma_A}, \qquad (7)$$

where γ_{EC}, γ_E, and γ_A represent respectively the activity coefficients of the compound being extracted, the extractant, and the extractable salt. If [EC] is the concentration of the element being extracted in the organic phase, and [A] its concentration in the aqueous phase, it follows from Eqn. (7) that the distribution constant for this element α at constant composition of the aqueous phase is given by the formula

$$\alpha = K'[E]^n \frac{\gamma_E^n}{\gamma_{EC}}. \qquad (8)$$

If the concentration of the extractant also remains constant, we have

$$\alpha = K'' \frac{\gamma_E^n}{\gamma_{EC}}, \qquad (9)$$

where K'' is a constant.

It can be seen from formula (9) that, when the diluent is replaced at constant composition of the phases, the changes in α will depend on the changes in the ratio γ_E^n/γ_{EC}, for which Rozen[198] proposed the symbol *dil*. According to the theory of regular solutions[205], the activity coefficients of solutes are related to the solubility parameters by the expression

$$\ln \gamma_2 = \ln \frac{\varphi_2}{x_2} + \frac{V_2\varphi_1^2}{RT}(\delta_2 - \delta_1)^2 + \varphi_1\left(1 - \frac{V_2}{V_1}\right), \qquad (10)$$

where the subscripts 2 and 1 relate to solute and solvent respectively (x_2 is the mole fraction of solute in the solution). Smulek[195] and Siekierski[199] showed that, in complete agreement with this equation, the activity coefficients of amine salts dissolved in various diluents decrease with increase in the value of δ for the diluent. By substituting in Eqn. (9) the activity coefficients of the extractant and the complex being extracted given by Eqn. (10), Vdovenko et al.[204] obtained the following equation relating the distribution constant of the metal being extracted α_M with the values of δ and the molar volumes V of the extractant, the diluent, and the compound being extracted

$$\lg \alpha = \text{const} + \frac{0.8686}{RT}(V_{EC}\delta_{EC} - nV_E\delta_E)\,\delta_{dilt} + 0.4343\,(nV_E - V_{EC})\left(\frac{\delta_{dilt}^2}{RT} - \frac{1}{V_{dilt}}\right), \qquad (11)$$

where the subscripts EC, E, and dilt denote quantities relating to the compound being extracted, the extractant, and the diluent respectively. Analysis of Eqn. (11) shows[204] that the dependence of α_M on δ_{dilt} for a constant value of V_{dilt} should in general pass through an extremal value. Differentiation of Eqn. (11) with respect to δ_{dilt} shows that the position of the extremal value is determined by the relationship

$$\delta_{dilt}^{extr} = \frac{V_{EC}\delta_{EC} - nV_E\delta_E}{V_{EC} - nV_E}. \qquad (12)$$

In the systems examined by Vdovenko and his coworkers[204] this extremal value was a maximum. It follows from

Eqn. (11) that the second derivative of $\lg \alpha$ with respect to δ_{dilt} is proportional to $nV_E - V_{EC}$, so that the extremal value may be a maximum when the molar volume of the compound being extracted is greater than the sum of the molar volumes of the molecules of extractant in the compound. In these instances, with diluents of low polarity and the lowest values of δ, increase in δ for the diluent should lead to an increase in the extractive power of the amine salt solution. In most extraction systems, however, such a relationship is not realised, and only a decrease in the extractive power of the salts takes place with increase in the value of δ for the diluent. It follows from Eqns. (11) and (12) that this may also be observed when $nV_E > V_{EC}$, i.e. when the dependence of $\lg \alpha$ on δ_{dilt} passes through a minimum. Such a relationship has been described for the extraction of metal salts by tri-(2,2,4-trimethylpentyl)ammonium chloride[206], for which the partition coefficients decrease with increase in the value of δ for the diluent (in the order—hexane > toluene > benzene) and for extraction by tri-n-octylammonium chloride[51,200-210] (decane > mesitylene > xylene > toluene > benzene) and tridodecylammonium nitrate (cyclohexane > xylene > benzene)[211]. An unambiguous prediction of the nature of the dependence of $\lg \alpha$ on δ_{dilt} obviously requires an estimate of the ratio of the values of V_{EC} and nV_E.

It follows from the foregoing that, when there is no significant specific solvation, the influence of a diluent on the extractive power of amine salts, like its influence on their solubility, can be estimated approximately on the basis of the theory of regular solutions, from the known values of δ for a wide range of solvents. A knowledge of the values of δ_E and δ_{EC} for a larger number of amine salts and extractable compounds is required for the most extensive verification and application of this approach to estimating the influence of solvents.

Another approach has recently been proposed, which makes it possible to predict quantitatively the influence of various diluents on extraction. It is based on the observed[207] linear relationships shown by the free energies of many extraction systems with different diluents. The existence of these relationships has made it possible to develop a scale of DE-values (diluent effects) by means of which extraction constants K can be calculated for extraction systems with different diluents, if the corresponding constants K_0 for systems with a standard diluent are known[207]. The calculation is carried out using the formula $\lg K = \lg K_0 + \rho DE$, where ρ is a coefficient which is constant for a series of extraction systems of constant composition with different diluents, and DE is a constant which depends only on the nature of the diluent. The results of the calculation show good agreement with the experimental data for a large number of systems.

VI. THE INFLUENCE OF SPECIFIC SOLVATION ON THE EXTRACTION PROPERTIES OF AMINE SALTS

All solvation interactions of a solvent or of added reagents with a substance to be dissolved, leading to solubilisation of the latter, produce a decrease in the activity of this substance in the solution§. For example, solvation of the anions of amine salts by alcohols, leading to an increase in the solubility of these salts, simultaneously produces a decrease in the effective concentration of the free amine salt in the extractant, i.e. a decrease in its thermodynamic activity. As noted in the preceding Section, the change in extractive power produced by a diluent depends on the ratio of the changes in the activity coefficients of the extractant and the compound being extracted. Thus a decrease in the distribution constant for an element when an alcohol or other solubilising agent is added to the extraction system will take place if the extractant—the amine salt—is more extensively solvated than the compound being extracted.

In the extraction of metal salts by amine salts, the volume of the anions of the compounds being extracted is usually much greater than the volume of the anions of the simple salts used as extractants. This leads to greater delocalisation of the negative charges on the anions of the compounds being extracted, diminishes their electron-donating power, and hence decreases their solvation by electron-acceptor molecules relative to the solvation of the anions of the extractant. Thus the addition of alcohols usually leads to a marked decrease in the extractive power of amine salts. The extraction of uranium(VI) and zinc by tri-n-octylamine from hydrochloric-acid solutions[51,160] is decreased considerably when octanol is added to the extractant. The extraction of nitric acid[213-215] and a number of quadrivalent actinide elements by amine nitrates from nitric-acid solutions[164,216], the extraction of many elements by amine chlorides from hydrochloric-acid solutions[163,217-220], and the extraction of uranium(IV) sulphate by amine sulphates from sulphuric-acid solutions[221] also decrease when alcohols and chloroform are added. A similar effect should be observed on the addition of other solubilising agents which are electron acceptors capable of solvating anions—organic acids, halogenated hydrocarbons, etc.

It should be noted that, in the extraction of metal salts, this action of solubilising agents is observed only when the metal concentrations are low compared with the concentration in the non-polar diluent of the dissolved amine salt used as extractant. If the concentration of metal salt in the organic phase is high, the partition coefficient may even be greater in the presence of solubilising agents than in their absence. This phenomenon is due to the fact that, when a diluent of low polarity does not contain a solubilising agent, a considerable proportion of the amine salt is used up not only in the formation but also in the solvation of the compound being extracted, as a result of which, with increase in the concentration of the latter, the concentration of the extractant decreases rapidly with a corresponding rapid decrease in the partition coefficient[182]. In the presence of an excess of solubilising agent, the molecules of the compound being extracted are solvated not by the extractant but by molecules of this solubilising agent, and this leads to a decrease in the consumption of extractant and to a slower decrease in the distribution constant with increase in the concentration of the compound being extracted. As a result, at high concentrations of the compound being extracted, the value of the distribution constant in the presence of the solubilising agent may be greater than that in the absence of the solubilising agent.

The energy of solvation of the anions of an amine salt by alcohols and other acidic substances depends on the

§ Some authors[212] therefore suggest that the term solubilisation should be taken to mean not only the solvent action of additives, but also any decrease in the activity of a dissolved substance in a homogeneous binary solution when a third component is added.

electron-donating power of these anions[5,61,222,223]. With decrease in the electron-donating power and the associated decrease in the solvation of the anions, the influence of solvating solvents is reduced[149,154,224]. Thus the influence of the addition of alcohols and chloroform on the extractive power of amine sulphates is less than its influence on that of the corresponding nitrates, and its influence is less on the properties of the salts of secondary amines than on those of the salts of tertiary amines[225,226].

In the extraction of acids by an anion-exchange mechanism, a solvating solvent may not influence the extraction equilibrium if the free energy of solvation of the anions of the compound being extracted differs from the hydration energy of these anions in the aqueous phase by an amount close to the corresponding difference for the anions of the amine salt used as extractant. Thus addition of the solvating solvent chloroform to the extractant does not decrease the distribution constants in the extraction of TcO_4^- by amine sulphates[227]. In the extraction of TcO_4^- by an amine nitrate, the addition of solvents which solvate the anions decreases the distribution constant of technetium[228], since the amine nitrate is solvated by the solvent molecules to a greater extent than is the sulphate[224,229,230].

As noted above, the solvation of anions is an acid–base interaction. On this basis, it has been suggested[51] that this solvation is also important for diluents which have extremely weak acidic properties, e.g. aromatic hydrocarbons. Study of the extraction of zinc by tri-n-octylammonium chloride from hydrochloric-acid solutions[51] has in fact shown that, when a series of aromatic diluents is used, the partition coefficients of zinc decrease to a greater extent the stronger the acidic (electrophilic) properties of the diluent.

When the solubilising agent solvates the cations of the amine salt, the result may be not only a decrease in the distribution constant of the metal salt, but also in some instances an increase in the distribution constant[5,51]. Decrease in the distribution constant for extraction by tertiary amines takes place for reasons which are the same as those for solvation of the anion. Solvation of both cations and anions of amine salts leads to a decrease in the association of their molecules. Change in the degree of association of the normal salts of tertiary amines[182] does not lead to a significant change in their extractive power. In contrast to this, with the salts of primary amines and to some extent secondary amines, and also with the acid salts of tertiary amines, change in the degree of association leads to a significant change in extractive power, since the association of these salts is due to the formation of intermolecular hydrogen bonds involving their anions, and this decreases considerably their extractive power. As noted in Section III, the presence of solubilising agents which solvate the cations leads to depolymerisation of the salts and also an increase in their polarity[5], and hence to a marked increase in their extractive power[51]. Nemodruk[231] observed a marked increase in the extractive power of a salt of the primary amine aniline in the presence of a ketone. An increase in the extractive power of dioctylamine was also observed[51] when 4-methylpentan-2-one was added to the diluent; this phenomenon was not observed when the ketone was added to the salts of tertiary amines. From these data it follows that a necessary condition for an understanding of the general features of the influence of solvating diluents on extraction is an investigation to determine which part of the molecule of the amine salt is solvated by molecules of the diluent.

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THE ELECTRONIC STRUCTURE AND PROPERTIES OF THE σ-BONDS IN THE MOLECULES OF ORGANIC COMPOUNDS

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1. INTRODUCTION

The importance of σ-bonds in organic chemistry lies not only in the fact that most organic compounds do not contain other types of bond but also in the fact that σ-bonds form the framework of all molecules in general. Approximately 80% of the energy of formation of aromatic molecules corresponds to σ-bonds, their elastic properties are determined to a considerable extent by σ-electrons, most chemical reactions are accompanied by the rupture and formation of σ-bonds, in many instances the sign of the dipole moments is determined by the σ-electrons, etc.

It is often assumed that the σ-bonds in polyatomic molecules are localised and that their interaction can be neglected. This view is refuted by a large number of experimental facts, for example the dependence of the ionisation potential of alkanes on the length of the chain of σ-bonds, the dependence of the position of the electronic absorption bands in the optical spectra on the length of this chain, the non-additivity of the dipole moments of halogenated alkanes, the hyperfine structure of their nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.) spectra, and many others.

From the viewpoint of quantum mechanics, strictly speaking, it cannot be assumed that the electronic wave functions in a molecule are localised on individual bonds or groups of bonds. Since the molecule is a single unit, the electronic wave functions should characterise the molecule as a whole. When the LCAO-MO† method is used, this means that the one-electron wave functions of the molecule ψ_i should be made up of linear combinations of the atomic orbitals φ_k of *all* the atoms in the molecule:

$$\psi_i = \sum_k c_{ik} \varphi_k. \qquad (1)$$

According to this formula generally speaking in the stationary state each electron has a finite probability of being found close to each atom in the molecule. The need to represent the molecular orbital in form (1) for molecules with saturated bonds was demonstrated by Walsh[1] in his interpretation of the electronic spectra of a number of simple molecules AB_2, ABC, AB_3, HAAH, H_2AB, etc. Starting from the delocalised molecular-orbital model, Walsh developed a method by which it was possible not only to interpret the spectrum but also to predict the geometry of the molecule in the ground and excited states and also the vibrational structure of the spectrum, to determine the selection rules and polarisation of the bands, etc. The need to use delocalised molecular orbitals of type (1) can be seen particularly clearly for symmetrical molecules.

† LCAO-MO = molecular orbital approximated by a linear combination of atomic orbitals.