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ELECTRICALLY CONDUCTING NON-AQUEOUS SYSTEMS FORMED FROM NON-CONDUCTING COMPONENTS

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I. INTRODUCTION

The phenomenon of electrolytic dissociation in aqueous solution has been thoroughly studied, the number of papers on the electrical conductivity and the electrolytic dissociation of various electrolytes in aqueous solution having now reached several thousands. These papers are mainly concerned with extremely dilute solutions, the usual purpose of the work being to confirm the Debye–Hückel theory of electrolytic solutions. As a result, excessive attention has been paid to dilute aqueous solutions, whereas for a long time non-aqueous electrolyte solutions remained undeservedly outside the circle of interests of investigators. In this connection Lewis and Randall[1] correctly write: "Dilute solutions have played an extremely important part in the development of physical chemistry. Therefore exceptional, and perhaps even somewhat excessive, attention has been paid to very dilute solutions in both theoretical and experimental investigations".

Conant and Hall[2] in turn consider that "many chemical phenomena are obscured by our slavish devotion to water".

Thus comparatively little attention has been paid in the past to non-aqueous electrolyte solutions, although the study of electrolytic dissociation in non-aqueous media is not only of very great theoretical significance but also of great practical value in connection with the vigorous development of the electrochemical industry, especially the electrical synthesis of various substances from non-aqueous solvents.

It is sufficient to mention that in Brockman's monograph[3] alone, published as early as 1926, several hundreds of methods are described for preparing various organic compounds by anodic oxidation or cathodic reduction in organic solvents.

At the present time a vast literature has arisen on electrical synthesis in non-aqueous solvents[4-7].

As Antropov[5] correctly points out, however, in order that organic compounds can be obtained by electrical synthesis in non-aqueous solvents, the solutions employed must be good conductors; moreover, the mechanism of electrolytic dissociation of the substances forming the electrolyte in these non-aqueous solvents should be known. With most organic electrolytes, no data are available on their dissociation mechanism.

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Non-aqueous electrolyte solutions attracted the attention of individual workers a comparatively long time ago[8-20]. However, a more detailed study of such solutions was started only at the beginning of the present century.

In particular, Plotnikov concluded from an analysis of published data and his own results that the dielectric constant of the solvent is not the decisive factor in the dissociation of electrolytes. In support of this thesis he cited numerous data on the relation between electrical conductivity and the dielectric constant of the medium which contradict the Nernst–Thompson rule. Thus, for example, according to Plotnikov's results PBr_5 is non-conducting in water, but is a good conductor in bromine solution[21]. Cases are also known in which substances such as HCl and HI, which are strong electrolytes in water (D = 80), are not electrolytes in liquid HF, with the still higher dielectric constant of 84. On the other hand, many alcohols, carbohydrates, ketones, and other organic compounds, which are not electrolytes in water, behave as strong electrolytes in liquid HF.[22,23]

As a result of Plotnikov's work, it became generally recognised that in non-aqueous systems the dielectric constant of the medium is not the decisive factor (the "dissociating force") in the electrolytic dissociation of molecules.

Plotnikov's views were subsequently developed in numerous papers by Usanovich[24,25] who, following Konovalov[10], concluded, from an analysis of all the accumulated experimental results mainly on non-aqueous systems and from his own investigations, that the appearance of conduction in non-aqueous liquid systems produced from non-conducting components is due to the formation of electrically conducting complexes, not to the "dissociating power" of the solvent. This view was subsequently confirmed by other workers[26-28], and is now generally accepted, at least for systems formed from non-conducting components. The literature on this subject will be briefly surveyed below, the present Reviewer's researches on systems formed by organic isothiocyanates, thiocyanates, and various amines also being covered. More detailed attention will be paid to work on the mechanism of dissociation in the electrolytes formed. The present paper does not, of course, claim to cover fully the vast amount of experimental and theoretical work which has now been done on this problem.

II. ORGANIC ACID–AMINE SYSTEMS

Systems of this type were first studied by Konovalov[10]. On mixing pure acetic, propionic, and butyric acids with various amines (aniline, methylaniline, dimethylaniline, and *o*-toluidine) he obtained electrically conducting solutions, whose conductivity exceeded in individual cases 3×10^{-3} ohm^{-1} cm^{-1}. Separately, the components of these systems were practically non-conducting. Thus the conductivities of the acids and amines used did not exceed 10^{-6} ohm^{-1} cm^{-1}, so that the mixtures were better conductors than the components by a factor of 1000.

The conductivity isotherms of the binary systems formed from an acid and an amine passed through a maximum, which occurred at different ratios of the components in different systems (Fig. 1). Konovalov assumed that these maxima corresponded to a chemical compound formed when the components were mixed. A more detailed study of the acetic acid–aniline system, as well as the use of other methods of physicochemical analysis[29,30] has shown, however, that in the case of irrational systems† the maxima on the conductivity isotherms do not generally correspond in composition to the compounds which are formed in the system.

† The term "irrational system" is used in the Soviet literature apparently to denote a system in which chemical compounds are formed whose composition does not correspond to simple stoichiometric proportions of the components (Ed. of Translation).

Systems comprising an organic acid and an amine have formed the subject of many subsequent investigations [28-36], in all of which conductivity isotherms having a maximum have also been obtained. The absolute value of the conductivity is comparatively high, quite often exceeding that of 0.01 *N* potassium chloride solution at 18°. Such considerable conductivity in solutions formed from non-conducting components is undoubtedly due to the formation of a new compound which is an electrolyte.

In several cases conductance may not appear in the solutions when non-conducting components are mixed, as occurs very often with, for example, organic compounds (benzene and toluene, alcohols, etc.), but if the system does become conducting, an electrolyte must necessarily have been formed in it.

Apart from possible participation in the formation of chemical compounds, the role of non-conducting components consists mainly in the transfer of the compounds to the liquid state ("dissolution") if the latter are solid under the experimental conditions. This results in increased mobility of the ions.

Trifonov showed that, in the case of rational systems‡, the conductivity isotherm passes through a minimum at the composition of the compound which is formed [28,37], this minimum being caused by the high viscosity of the compound.

The view prevails in the literature that conductivity isotherms of rational systems formed from non-conducting components must necessarily have a minimum — if conducting compounds are formed — at the composition corresponding to such a compound. It appears to the Reviewer that this applies only to systems in which the viscosity of the compound is considerably greater than those of the components, as occurs, for example, in systems formed by mustard oil and piperidine [28]. When an electrolytic compound is formed in a system by interaction of the components, the conductivity isotherm should usually have one maximum, which does not always occur at the composition of the compound.

Investigation of Conducting Systems in a Third Component

Hölzl was the first to investigate the reaction of weak bases with organic acids in alcoholic solution [38].

Subsequently Izmailov demonstrated the advantage of investigating binary systems in a third, inert solvent [39,40]. He showed, in particular, that, when the components of a system are associated, physicochemical analysis of binary systems gives no positive indication of the presence or absence of interaction between them, whereas in a third component curves are obtained which may show not only interaction but also the composition of the compound which is formed. Any physical property (viscosity, refractive index, etc.) can be used for this purpose. More distinct maxima or inflections indicating compound formation appear on the conductivity isotherms for the ternary systems than on the diagrams of other properties, since in this case the conductivity is not appreciably affected by changes in the viscosity and the dielectric constant of the solutions.

The value of studying reaction between two components in a third, inert solvent has been shown also in a study [41] of the quinoline–acetic acid system. Although this system has been studied by various physicochemical methods, the number and the composition of the compounds formed between these components have not been finally established [42-44].

The above work and the present Reviewer's researches [41] show that two compounds, 1 : 1 and 2 : 1, are formed together in this system. Both are well revealed on the conductivity isotherms (20°, Fig. 2) obtained at equal concentrations of this system in a third component (methanol). These results again confirm the advantage of physicochemical investigation of the interaction of substances in a third component.

A study of solutions of amine–acetic acid binary systems in water [45] clarified the mechanism of the electrolytic dissociation of the resulting compounds and explained the origin of the high conductivity of some mixtures in these ternary systems. For example, results on electrolysis

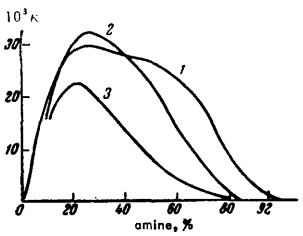


Fig. 1. Conductivity of binary systems formed by acetic acid with: 1) aniline; 2) methylaniline; 3) *o*-toluidine.

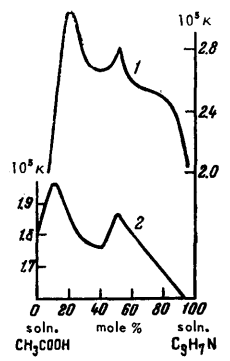


Fig. 2. Conductivity isotherms for the quinoline–acetic acid system in methanol: 1) 0.1 M solutions; 2) 0.01 M solutions.

‡ A "rational system" appears to be one in which a chemical compound of simple stoichiometric composition is formed (Ed. of Translation).

have suggested the following scheme for the dissociation of the complex compounds formed between acetic acid and aniline

$$C_6H_5NH_2 \cdot 2CH_3COOH \rightleftarrows C_6H_5NH_3^+ + CH_3COOHCH_3COO^-,$$

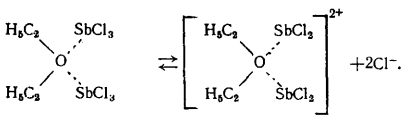
$$C_6H_5NH_2 \cdot CH_3COOH \rightleftarrows C_6H_5NH_3^+ + CH_3COO^-.$$

III. METAL HALIDE–ORGANIC COMPOUND SYSTEMS

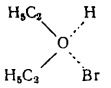
Systems formed from metal halides and organic compounds attracted the attention of investigators a long while ago. Thus as early as 1902, for example, Plotnikov[13] studied the conductivity of solutions of aluminium bromide in ethyl bromide, and concluded that the components interact to form a conducting complex.

The conductivity of the solutions exceeds many times those of the pure components at the same temperature. Subsequently Plotnikov and his pupils studied a series of systems formed by phosphorus and antimony halides in bromine and other non-aqueous media[46–50]. Complex formation was invariably observed, which, as is now known, is the reason for the high conductance of the solutions consisting of practically non-conducting components.

Systems formed from metal halides and organic compounds, principally ethers, have been studied in special detail by Usanovich and his coworkers[51–53]. Thus among others they studied[54] the antimony trichloride–diethyl ether system. From results on the conductivity and electrolysis of one such solution they conclude that the electrolyte here is a complex compound formed by interaction of the components



This compound resembles the oxonium compounds formed by the hydrogen halides with ether, discovered by Kablukov[55],



In aqueous medium it gives $[(C_2H_5)_2OH]^+$ ions, analogous to H_3O^+ ions.

Formation of such a compound in this system is confirmed by physicochemical data. In particular, the viscosity isotherm obtained by Kurnakov[56] has a maximum at 67 mole % of antimony trichloride. Usanovich and his coworkers have similarly studied other systems[57–60].

In the opinion of Usanovich[58] ethereal solutions are very convenient materials for study, since many substances are completely soluble in ethers with the formation of conducting solutions. This allows the examination of conductivity to be extended beyond a narrow concentration range, so that the system can be investigated as a whole with all possible proportions of the components.

Many workers have subsequently investigated systems formed by metal halides with esters. In 1936, for example, Kurnakov and Shternin studied the $SnBr_4$–$CH_3COOC_2H_5$ and $SnCl_4$–$CH_3COOC_2H_5$ systems by measuring the conductivity as well as the viscosity and melting point[61]. According to their results, compounds $SnX_4.2CH_3COOC_2H_5$ are formed in these systems. The conductivity isotherm passes through two maxima and one minimum which occurs at the composition of the compound (67 mole % of the ester). This minimum is caused by the high viscosity of the compound. Hence if the effect of viscosity is eliminated, the solution containing 67 mole % of the ester will possess the maximum conductivity. This indicates that the compound is an electrolyte.

Several papers have been published on the mechanism of the electrolytic dissociation of this and other similar compounds. Thus the Reviewer was the first to try to elucidate the mechanism of electrolytic dissociation of the compound formed in the tin(IV) chloride–ethyl acetate system[62]. For this purpose the two solutions of maximum conductivity (containing 20 and 60 mole % of stannic chloride) were electrolysed in a vessel having separate cathode and anode compartments. On the basis of analyses of catholyte and anolyte, together with measurements of several of their physical properties, the following scheme was suggested for the dissociation of the compound formed

$$(SnCl_4 \cdot 2CH_3COOC_2H_5)_2 \rightleftarrows Sn(CH_3COOC_2H_5)_4Cl_2^{2+} + SnCl_6^{2-}. \quad (1)$$

Cryoscopic measurements of the molecular weight of the compound by Vol'nov[63] confirmed that its composition corresponds to the doubled formula $(SnCl_4.2CH_3COOC_2H_5)_2$.

Subsequently Usanovich and his coworkers also studied the structure of several complexes, including $SnCl_4.2CH_3COOC_2H_5$, formed by metal halides with esters and other organic compounds[64]. Mainly on the basis of the results of electrolysis, it is considered[64] that the only electrolytes in this and similar systems are the compounds $SnCl_4.3RCOOR'$ and $SnCl_4.4RCOOR'$, where R' is a proton or an aliphatic radical. The mechanism of the electrolytic dissociation of these compounds must be represented as follows

$$SnCl_4.2RCOOR' + RCOOR \rightleftarrows [SnCl_4(RCOO)_2]R'^- + RCOOR'^+_2, \quad (2)$$

$$SnCl_4.2RCOOR' + 2RCOOR' \rightleftarrows [SnCl_4(RCOO)_2]^{2-} + 2RCOOR'^+_2. \quad (3)$$

It is seen from this scheme that stannic chloride occurs only in the anion, while the organic molecules occur both in the anion and in the cation. In the Reviewer's scheme the organic molecules are present only in the cation.

The experimental results obtained by Usanovich and his coworkers[64] on the electrolysis of these complex compounds of stannic chloride and ethyl acetate agree in the main with the Reviewer's results[62], but, as is evident from a comparison of Eqns. (2) and (3) with (1), their scheme of electrolytic dissociation differs fundamentally from the latter's.

The weak point in the Usanovich scheme of dissociation seems to be, as these workers themselves point out[64], that no data have been published indicating the existence of 1 : 3 and 1 : 4 compounds of stannic chloride and ethyl acetate. Furthermore, the explanation of the formation of metallic tin and of tin(II) chloride at the cathode lacks adequate experimental basis, and is therefore unconvincing.

Recently Vol'nov has repeated the electrolysis of the series of complex compounds formed by $SnCl_4$, $SnBr_4$, and SnI_4 with various alcohols, organic acids, and esters, including ethyl acetate, and reached the conclusion that the

experimental results cannot be explained by the Usanovich scheme. He considers that the Reviewer's scheme involving electrolytic dissociation of the compound $SnCl_4 . 2CH_3COOC_2H_5$ is the most probable [63].

Reference must also be made to a series of interesting papers by Sumarokova and her coworkers on the reaction between stannic chloride and esters [65].

Other investigators have studied the interaction between metal halides and various classes of organic compounds. Gorenbein and his coworkers [66-68] have studied the conducting systems formed by $AlBr_3$, $AlCl_3$, and other metal halides in nitrobenzene, ethyl bromide, and other organic substances. They have shown in particular that aluminium bromide in nitrobenzene forms, according to conductivity data, three compounds, which are arranged in the following sequence of decreasing electrical conductivity [67]

$$(AlBr_3)_2 \cdot C_6H_5NO_2 > AlBr_3 \cdot 2C_6H_5NO_2 > AlBr_3 \cdot C_6H_5NO_2.$$

Usanovich and Sumarokova have studied systems formed by $SnBr_4$, $SnCl_4$, $SbCl_3$, and $AsCl_3$ with acetic acid and its chlorinated derivatives [70-73] and also with other acids [74-76]. These systems have attracted attention because $SnCl_4$ on Lewis and Randall's views, and $SbCl_3$ and $AsCl_3$ on the views of Usanovich, are aprotic acids. On the other hand, the acetic and chlorinated acetic acids which they used should act as oxonium bases towards these aprotic acids, and react with them by a kind of acid–base interaction. The isotherms for viscosity, conductivity, and other properties obtained by these workers support this hypothesis.

These investigators also studied several other electrically conducting systems formed by halides of metals in Groups IV and V of the Periodic System with various classes of organic compounds. For example, Usanovich [52] studied the conductivity of the systems formed by arsenic trichloride with nitrobenzene and with pyridine. The aim of this work was to prove that arsenic trichloride behaves towards nitrobenzene and pyridine as a substituted hydrochloric acid, somewhat as it behaves towards esters as an acid [52].

Interesting work has been done by Osipov and his coworkers on systems formed by the halides of titanium, zirconium, and germanium with esters and organic acids. They have made a detailed study, for example, of the conducting systems formed by the non-conducting components titanium tetrachloride with ethyl acetate [77], n-propyl acetate, and n-butyl acetate [78].

On the basis of physicochemical data (from diagrams of viscosity, heats of mixing, electrical conductivity, and other properties) they established that with esters titanium tetrachloride forms conducting complexes $TiCl_4.E$ and $TiCl_4.2E$, where E represents a molecule of an ester of a monobasic acid. Electrolysis showed that these complex compounds dissociate according to the scheme [78]

$$(TiCl_4.E)_2 \rightleftarrows [TiCl_2.2E].TiCl_6 \rightleftarrows [TiCl_2.2E]^{2+} + TiCl_6^{2-},$$
$$(TiCl_4.2E)_2 \rightleftarrows [TiCl_2.4E].TiCl_6 \rightleftarrows [TiCl_2.4E]^{2+} + TiCl_6^{2-}.$$

As the authors [79] themselves remark, this is analogous to the Reviewer's scheme of electrolytic dissociation for the complex compound $SnCl_4.2CH_3COOC_2H_5$. [62] Osipov and his coworkers have published many other papers on the reaction of zirconium halides with various organic compounds [80,81].

Recently Kudra and Ternovaya have studied the conducting systems formed by aluminium chloride with n-butyl ethyl ether and di-n-butyl ether [82].

IV. OTHER ELECTRICALLY CONDUCTING NON-AQUEOUS SYSTEMS FORMED FROM NON-CONDUCTING COMPONENTS

Among other electrically conducting non-aqueous systems, mention must first be made of those formed by the halogen compounds of iodine with various classes of organic compounds. Walden was one of the first to study the electrical conductivity of solutions of iodine monochloride, monobromide, and trichloride in liquid sulphur dioxide, sulphuryl chloride, and arsenic trichloride [83]. According to his results these solutions are comparatively weak electrolytes.

Later Bruns [84] and Bruner [85] measured the conductivity of iodine monochloride and trichloride in acetic acid and in nitrobenzene.

Further investigation of systems formed by iodine halides with organic substances showed the comparatively high conductivity of their solutions to be due to the formation of conducting complexes of the iodine halides with the solvent. For example, the complex compound formed in the highly conducting pyridine–iodine bromide system dissociates according to the scheme [86]

$$C_5H_5N.IBr \rightleftarrows [C_5H_5NI]Br \rightleftarrows [C_5H_5NI]^+ + Br^-,$$
$$C_5H_5NI_2 \rightleftarrows [C_5H_5NI]I \rightleftarrows [C_5H_5NI]^+ + I^-$$ [87].

Systems consisting of iodine halides and acid amides also form highly conducting solutions [86]. The conductivity of the systems formed by iodine monochloride with acetamide and benzamide in nitrobenzene has also been studied [86].

Among conducting systems formed from non-conducting components, reference must be made to those formed by phosphorus pentachloride and pentabromide with the iodine halides, which have been well studied by Fialkov and his coworkers. It is interesting that, as Fialkov and Kuz'menko have shown [88], phosphorus trihalides do not yield compounds and do not form electrolytic systems with iodine. But PCl_5 and PBr_5 behave differently, oxidising iodine to its monochloride and monobromide, and thereby being reduced to PCl_3 and PBr_3 respectively. The iodine halides combine with still unchanged PX_5 molecules to form the complexes PCl_6I and PBr_6I, which are strong electrolytes, the maximum conductivity in these systems reaching 0.04 $ohm^{-1}\ cm^{-1}$.

The nature of the ions was established by studying their transport in nitrobenzene solutions of PCl_6I and PBr_6I. On the basis of the results, the following scheme of electrolytic dissociation is suggested

$$PCl_6I \rightleftarrows [PCl_4]^+ + ICl_2^-; \quad PBr_6I \rightleftarrows [PBr_4]^+ + IBr_2^-.$$

Like the phosphorus trihalides, those of antimony also interact neither with bromine nor with iodine, whereas antimony pentachloride reacts readily with iodine to form the electrically conducting complexes $SbCl_5.2ICl$ and $SbCl_5.3ICl$. [89]

At 45° systems formed by different aluminium halides with iodine halides arrange themselves in the following sequence according to their conductivity in the region of the maximum

$$ICl - AlCl_3 > ICl - AlBr_3 > IBr - AlBr_3$$ [90].

The acetic acid–acetyl chloride system, which was also investigated by Usanovich [91], forms conducting solutions. Its conductivity is due to the formation of the complex compound $(CH_3CO)_2OH.Cl$. Acid–base interaction

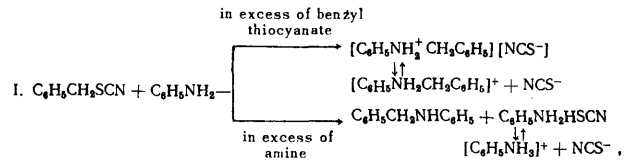
is assumed to take place, CH_3COCl being the acid, and CH_3COOH the base. From the results of electrolysis, the following scheme is suggested for dissociation of the conducting complex

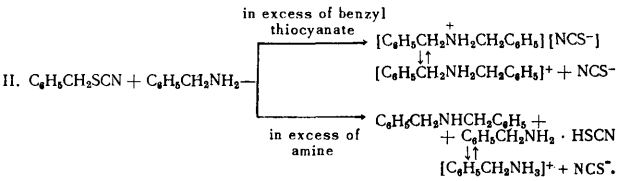
$$(CH_3CO)_2OH \cdot Cl \rightleftarrows (CH_3CO)_2OH^+ + Cl^-.$$

Finally, reference must be made to systems formed by organic thiocyanates and amines, which have recently been studied by Konovalova and Ust'-Kachkintsev[92]. They investigated the systems formed by ethyl thiocyanate with piperidine, aniline, dimethylaniline, and pyridine. In all these systems the solutions were good conductors, and the conductance increased on prolonged storage.

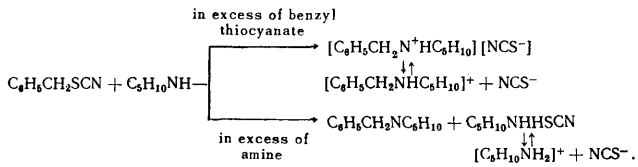
The Reviewer has also studied a series of systems[93] formed by benzyl thiocyanate with various amines (aniline, benzylamine, piperidine, and pyridine), which also are all good conductors. A high concentration of NCS^- ions can be detected in them by the usual qualitative tests. If this concentration is determined quantitatively (calorimetrically) as a function of composition, the resulting curve passes through a maximum at 50 mole %, which coincides with the maximum on the conductivity curve corrected for viscosity. Hence interaction of the components has yielded an electrolytic compound in which the anion is NCS^-. A detailed examination of these systems by various physicochemical methods and elementary analysis of the reaction products showed that two electrolytic compounds are formed from benzyl thiocyanate with primary and secondary amines depending on the proportions of the components.

It has been established[93] that the following reactions may occur on treatment of benzyl thiocyanate with aniline and with benzylamine





Benzyl thiocyanate reacts with piperidine according to the following scheme



Tertiary amines react with benzyl thiocyanate according to the same general scheme. In particular, pyridine forms one electrolytic compound, independently of the proportions of the components

$$C_6H_5CH_2SCN + C_5H_5N \rightleftarrows [C_6H_5\overset{+}{C}H_2NC_5H_5]\,[NCS^-] \rightleftarrows [C_6H_5CH_4NC_5H_5]^+ + NCS^-.$$

The saltlike compounds which are formed are responsible for the high electrical conductivity of the mixtures.

V. MUSTARD OIL–AMINE SYSTEMS

Zinin showed long ago[94] that, when mustard oil reacts with an amine, the corresponding substituted thiourea is obtained. Subsequently the interaction of mustard oils and various amines was more fully studied by Hofmann[95], Baxter[96], and other workers, who also found that substituted thioureas are formed. Kurnakov and his coworkers, who used various physicochemical methods to study a series of systems formed by mustard oils and amines, also confirmed that chemical reaction takes place with the formation of substituted thioureas in most cases of the mixing of mustard oils with primary and secondary amines[97].

Fig. 3 shows summary diagrams of the properties of the mustard oil–piperidine system taken from a paper by Trifonov[37]. These diagrams concern the formation of a thermally undissociated compound having the composition $C_5H_{10}NH.C_3H_5NCS$ *N*-allyl-*N'*-pentamethylenethiourea.

A considerable number of analogous systems formed by mustard oil and amines have been studied, among them being those formed by methylaniline[97,98], ethylaniline[28], etc.

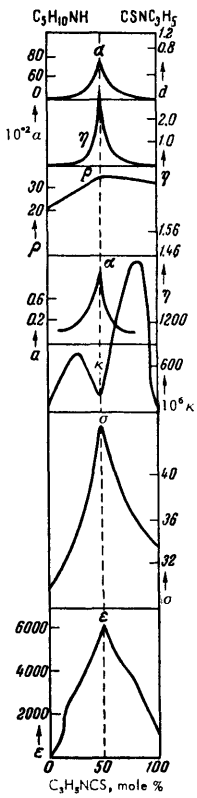


Fig. 3. Summary diagram of properties of mustard oil–piperidine system: η) viscosity; α) temperature coefficient of viscosity; P) polarisation; κ) conductivity; a) conductivity coefficient; σ) surface tension; ϵ) dielectric constant.

The conductivity isotherms of systems comprising a mustard oil and an amine show that the solutions possess considerable conductivity, which may sometimes exceed those of the components by factors of the order of 10^4.

Trifonov and Voskresenskaya studied the conductivity of many systems formed by mustard oil with various amines such as aniline, methylaniline, ethylaniline, *o*-toluidine, etc.[99]

Fig. 4 shows conductivity isotherms for systems comprising mustard oil and various primary and secondary amines. They all have two maxima and a minimum which occurs at 50 mole %, *i.e.* at the composition of the compound which is formed. As Trifonov[28] first established, such conductivity curves are characteristic of rational systems. If the effect of viscosity is eliminated, *i.e.* if the conductivity is corrected for viscosity and the result plotted against composition, a maximum is obtained in the place of the minimum. This indicates that in such systems the compound which is formed is actually the electrolyte.

If, however, it is supposed that a substituted thiourea alone is formed in the reaction of mustard oil with piperidine or other amine, in the present case *N*-allyl-*N'*-pentamethylenethiourea, it is difficult to imagine that this substance would be an electrolyte and decompose into ions. It is still less likely that either the mustard oil or the piperidine itself is an electrolyte. Trifonov calculated the equivalent conductance for piperidine in mustard oil as electrolyte, and for mustard oil in piperidine, and showed that in both cases the variation of equivalent conductance with dilution is anomalous[28]. In the opinion of Rabinovich[27] this indicates that the substances are not electrolytes.

We shall assume that in these systems the electrolyte is not the main product (substituted thiourea) formed by interaction of the components but a product of some side-reaction.

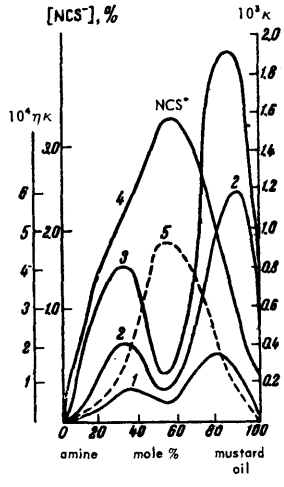


Fig. 4. Conductivity and corrected conductivity isotherms for systems formed by mustard oil with amines: 1) aniline; 2) anisidine; 3) piperidine; 4) [NCS⁻] in aniline system; 5) reduced conductivity in anisidine system.

A preliminary search for the ions into which this byproduct decomposes showed that the NCS^- ion can be detected in solution by qualitative tests on many systems formed by a mustard oil and an amine. This gave grounds for assuming that formation of the substituted thiourea was accompanied by that of a second compound, containing NCS^- as anion.

Further work by the Reviewer completely supported this hypothesis. It was therefore of interest to study in detail a series of such systems in order to establish the chemical nature of the compounds responsible for the comparatively high conductivity of these systems, and also to study the mechanism of electrolytic dissociation and measure the dissociation constants of the compounds in various solvents.

Systems formed by mustard oil with tertiary amines (pyridine, quinoline, dimethylaniline, etc.) are of especial interest. According to published data, tertiary amines do not interact with mustard oil. However, Voskresenskaya established that the conductance isotherm has a well-defined maximum, the conductivity of individual solutions exceeding those of the components by factors of the order of 10^4.

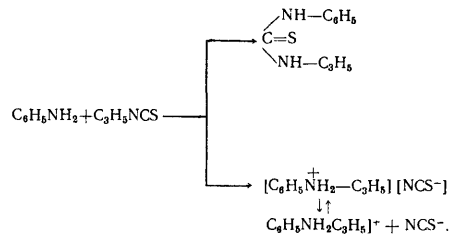
If no chemical reaction takes place between the components, the question arises as to what is the electrolyte in the system. It is quite improbable that the components of the mixtures would conduct the current[100]. In searching for the ions responsible for conduction in such solutions, the Reviewer also has detected the NCS^- ion. As will be shown below, in these systems, too, reaction of mustard oil with tertiary amines yields a saltlike compound having NCS^- as anion.

1. Mustard Oil–Primary Amine Systems

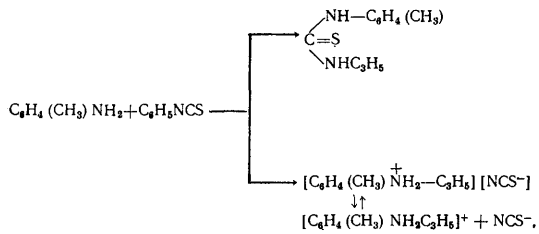
The mustard oil–aniline system has been studied by many workers[28,97]. The conductivity isotherms for 100° and 125° have two maxima and one minimum, which occurs at the composition of the compound (see Fig. 4). This is not because mixtures close to 1 : 1 in composition contain a lower concentration of electrolyte, but because these solutions are very viscous[97]. Indeed, if the effect of viscosity is eliminated — by measuring the conductivity in a third component (ethanol) or calculating the conductivity corrected for viscosity — the minimum is replaced by a maximum (see broken curve in Fig. 4). The conductivity of individual solutions in the system reaches 0.0043 $ohm^{-1} \times cm^{-1}$. The occurrence of such a high conductivity cannot be explained on the assumption that allylphenylthiourea is the sole product of interaction of the mustard oil with the aniline, since it is difficult to accept that this substance would undergo electrolytic dissociation. It therefore appears to the Reviewer that, in this and analogous systems, the electrolyte is not the substituted thiourea but a compound formed by some side-reaction. The NCS^- ion has been detected in all solutions in this system by the usual analytical methods (reaction with $FeCl_3$, etc.)[100]. It was therefore decided to measure the NCS^- concentration (by a colorimetric method) as a function of composition. The resulting curve (Fig. 4, curve *4*) runs roughly parallel to the curve for the corrected conductivity of this system. This indicates that the electrolyte is a compound having NCS^- as anion.

The Reviewer has been able by extraction with aqueous ammonia to isolate crystalline NH_4SCN from this system, which provides incontrovertible proof of the presence of NCS^- ions. From these and several other results it has

been shown that the aniline–mustard oil system contains, together with the substituted thiourea (a non-electrolyte) allylanilinium thiocyanate, which is the electrolyte responsible for the high conductance of the solutions:

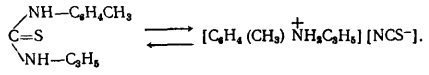


Reaction of *o*-toluidine with mustard oil also yields a substituted thiourea[94], which, according to the results of the Reviewer[100], is practically non-conducting ($\kappa_{100°} = 2 \times \times 10^{-6}$ ohm^{-1} cm^{-1}). However, as Trifonov[28] showed long ago, solutions of this system possess considerable conductivity ($\kappa_{max} = 10^{-3}$ ohm^{-1} cm^{-1}). The Reviewer has established that, in this system too, the comparatively high conductivity is caused by the formation, together with the main reaction product (allyl-*o*-tolylthiourea) when the components are mixed, the electrolyte allyl-*o*-toluidinium thiocyanate



The Reviewer has also proved that this electrolytic compound is formed in this and similar systems by studying ionic transport in a special apparatus[100]. As a result of electrolysis, NCS^- ions accumulate in the anode compartment, and $[C_6H_4(CH_3)NH_2C_3H_5]^+$ ions (in the form of the hydroxide) in the cathode compartment.

The concentration of this electrolytic compound in the system increases both on prolonged storage and especially on heating, as the Reviewer's experiments have shown. It was found that part of the substituted thiourea was converted, on being heated, into the allylammonium thiocyanate according to the equation[100]



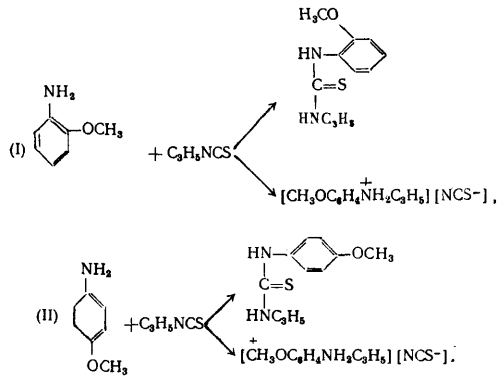
This agrees well with published information on the possibility of such changes[101,102].

Systems formed by mustard oil with other primary amines are not found in the literature, if we do not count the mustard oil–ethylenediamine system studied by Dianov and Trifonov[103], the conductivity of which has not been investigated, obviously because the system is not electrically conducting. With the aim of finding new conducting systems formed by mustard oil with other primary amines, the Reviewer has studied the reaction of the former with *o*- and *p*-anisidines, benzylamine, and also several aliphatic primary amines (methylamine, ethylamine, and isopropylamine).

Investigation of the systems containing *o*- and *p*-anisidines by physicochemical methods, including conductance[104], showed that mixtures of these systems are also good conductors ($\kappa^{60°}_{max} = 0.0012$ ohm^{-1} cm^{-1}) and contain the NCS^- ion.

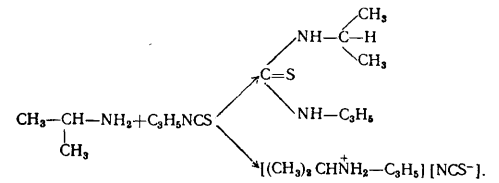
The conductivity isotherms also have two maxima and one minimum, which occurs at equimolecular proportions of the components, *i.e.* at the composition of the compound which is formed in the system (Fig. 4). Curves representing variation of the corrected conductivity and the NCS^- concentration with composition have well-defined maxima at 50 mole % of the components, which indicates that the compound formed in the system is the electrolyte.

On the basis of the property diagrams and several other results the Reviewer has shown that, in these systems too, two simultaneous reactions take place, with formation of a non-electrolytic compound (a substituted thiourea) and an electrolytic compound, according to the schemes



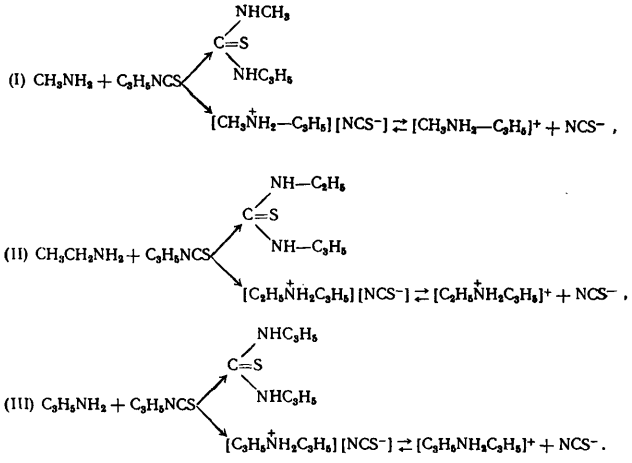
In several cases the Reviewer has been able to isolate this electrolytic compound and subject it to electrolysis. Analysis of catholyte and anolyte showed that NCS^- migrates to the anode, and the complex ion $[R'NH_2R]^+$ to the cathode. This confirms the above scheme of electrolytic dissociation of the compounds.

Study of the reaction of mustard oil with aliphatic amines was of considerable interest, since they are more strongly basic than are aromatic amines. No information on systems comprising mustard oil and aliphatic amines were found in the literature, and the Reviewer has therefore made a detailed physicochemical examination (by determining crystallisation temperature, density, viscosity, electrical conductivity) of the mustard oil–isopropylamine system[105]. The curves for all these properties have singular points at the composition of the 1 : 1 compound, a crystalline substance being formed. Elementary analysis showed it to be a substituted thiourea, *i.e.* allylisopropylthiourea. However, the high conductivity of this system ($\kappa^{50°}_{max} = 0.0016$ ohm^{-1} $\times$ $\times$ cm^{-1}), as well as the considerable concentration of NCS^- ions in these mixtures, indicates the simultaneous formation of allylisopropylammonium thiocyanate, according to the scheme



When this system is heated, both the conductance and the NCS^- concentration increase rapidly, owing to partial conversion of the substituted thiourea into the thiocyanate at the high temperature.

The Reviewer has also studied the interaction of mustard oil with methylamine, ethylamine, and allylamine[106]. Here, too, simultaneous reactions take place, with formation of a substituted thiourea (non-electrolyte) and of an allylammonium thiocyanate according to the scheme

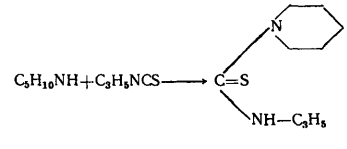


Summarising the reactions between mustard oil and primary amines, we can conclude that they form mainly non-conducting crystalline substances — substituted thioureas — but that a simultaneous side-reaction results in the formation of an allylammonium thiocyanate, which is an electrolyte and responsible for the high electrical conductivity of these systems. In individual cases the content of this electrolytic compound is 3% (in the mustard oil–isopropylamine system), increasing after heating to 24%.

Thus the Reviewer has succeeded in showing that conduction in these systems is not due to the principal reaction product (a substituted thiourea), as had previously been assumed[28,29], but to an electrolytic compound formed by a side-reaction.

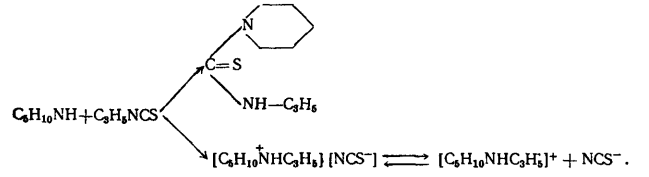
2. Mustard Oil–Secondary Amine Systems

Among systems formed with secondary amines, the mustard oil–piperidine system has been very thoroughly studied. It was assumed on the basis of viscosity, density, refractive index, and other measurements (see Fig. 3) that the compounds interact completely to form allylpentamethylenethiourea



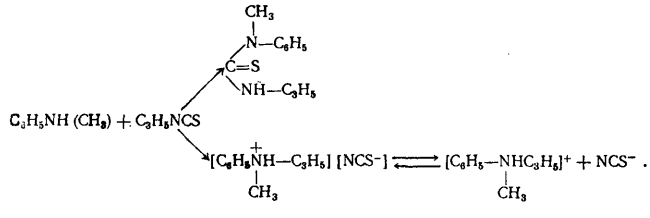
However, as measurements by Trifonov and his coworkers[28,107] showed, mixtures in this system possess comparatively high conductivity ($\kappa_{max}^{25°} = 0.0014$ ohm^{-1} cm^{-1}), and its conductivity isotherm has the form typical of rational systems, *i.e.* with one minimum and two maxima, the minimum occurring at the composition of the compound. Trifonov showed that neither component is an electrolyte[28]. He therefore assumed that allylpentamethylenethiourea was the electrolyte. It seems to the Reviewer highly improbable that a substituted thiourea would break down into ions, especially as Trifonov gave no experimental evidence.

As early as 1953 the Reviewer was able to show, on the basis of experimental results[108], that here, too, a parallel reaction takes place, with simultaneous formation of a substituted thiourea and allylpiperidinium thiocyanate, the latter of which is the electrolyte and is responsible for the high conductivity of the system



Later the Reviewer again studied this system, by electrolysing the electrolytic compound and also measuring the e.m.f. of the voltaic cell comprising glass and calomel electrodes[109]. The resulting e.m.f.–composition curve for the system resembles a potentiometric titration curve for a strong acid with a strong base, indicating the acid–base character of the interaction between the components with formation of a salt-like compound. This is consistent with the above scheme of interaction between the components with formation of allylpiperidinium thiocyanate.

The system formed by mustard oil and methylaniline has also been well studied by many physicochemical methods[28,97,98]. The isotherms of all properties are singular in character, and indicate the formation of a substituted thiourea, allylmethylphenylthiourea. Thus Voskresenskaya found[99] that the system possesses considerable conductivity. The Reviewer's investigations of this system[110] showed that here, too, the main reaction product (allylmethylphenylthiourea) is accompanied by allylmethylanilinium thiocyanate, dissociation of the latter being responsible for the conductivity of mixtures in the system



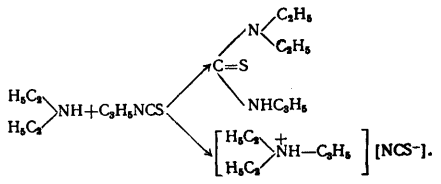
The curve obtained by the Reviewer for variation of the concentration of NCS^- ions with the composition of the mixtures show a parallel variation to the corrected conductivity isotherm, which indicates that the electrolyte is in fact allylmethylanilinium thiocyanate.

The viscosity, density[111], and surface tension[28] of the mustard oil–ethylaniline system have been studied. The diagrams of these properties have a singular maximum and indicate the formation of allylethylphenylthiourea. Trifonov and Cherbov[34], as well as Voskresenskaya[99], measured the conductivity of this system, and also obtained a "double-humped" isotherm, the maximum conductivity of individual solutions reaching 0.0013 ohm^{-1} cm^{-1}. The high conductivity was attributed to the reaction product, allylethylphenylthiourea. The Reviewer's investigations of this system

showed that the electrically conducting compound is not the substituted thiourea but allylethylanilinium thiocyanate $[C_6H_5\overset{+}{N}H(C_2H_5)C_3H_5][NCS^-]$, which is formed in considerable quantities (up to 25%), especially on heating.

It was of interest to investigate the nature of the reaction of mustard oil with aliphatic secondary amines, since the latter are stronger bases than the corresponding aromatic amines. No data on such systems were found in the literature, and therefore the Reviewer[112] has studied the melting point, viscosity, and density of the mustard oil–diethylamine system. The diagrams of all the properties indicate formation of a 1 : 1 compound, confirmed by the precipitation of crystals. The measurements showed that this system, too, is a good conductor ($\kappa^{40^\circ}_{max} = 0.0015$ ohm^{-1} × × cm^{-1}).

All solutions in this system give an intense reaction for NCS^-, the concentration of which varies with composition in the same sense as the isotherm for the reduced conductivity (corrected for viscosity). From these and other experimental results the Reviewer has shown that simultaneous reactions take place in this system, too, with the formation of a substituted thiourea and of allyldiethylammonium thiocyanate (an electrolyte)



3. Mustard Oil–Tertiary Amine Systems

As already stated above, there are indications that tertiary amines do not react with mustard oil. Thus Kurnakov studied viscosity and density in the mustard oil–pyridine system[97], and obtained smooth isotherms for the former, slightly concave to the concentration axis. Such curves are known to be obtained in the absence of interaction between the components of a system. A similar conclusion was reached by Fialkov and Muzyka[113] from a cryoscopic study of this system, and also by Sheka and Karlysheva[114], who investigated dielectric constant and polarisation.

According to Voskresenskaya[99], however, this system possesses high electrical conductivity, which increases on storage. The conductivity isotherm for the mustard oil–pyridine system after standing for a month (Fig. 5)[99] shows that the maximum conductivity reaches 0.0016 ohm^{-1} cm^{-1} at 50° and occurs at about 50 mole % of the components. This seems to the Reviewer to contradict the results of physicochemical analysis, since it is impossible to explain the occurrence of such a high conductivity if it is accepted that the components do not interact. There are no grounds for assuming that either of the components is an electrolyte. The Reviewer therefore assumed that in this case the mustard oil nevertheless reacts with pyridine to form a conducting complex. Obviously, the fact is merely that at room temperature this reaction takes place to such a slight extent that it cannot be detected by the viscosity method or other methods of physicochemical analysis owing to their relative insensitivity.

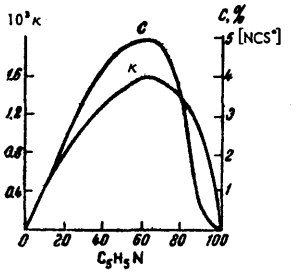


Fig.5. Conductivity (κ) and NCS^- concentration in the mustard oil–pyridine system.

Electrical conductivity is known to be one of the most sensitive properties, and therefore its isotherm shows a clearly defined maximum. Further investigations by the Reviewer on the mustard oil–pyridine system[115] showed also that mixtures contain the NCS^- ion (see NCS^- curve in Fig. 5), the concentration of these ions increasing very rapidly and exceeding 60% on heating, while the viscosity isotherm shows a sharp maximum. All these and other experimental results undoubtedly indicate that a Menshutkin type of reaction is taking place here between the components[116]

$$C_6H_5N+C_2H_5NCS = [C_6H_5\overset{+}{N}—C_3H_5][NCS^-] \rightleftharpoons [C_6H_5NC_3H_5]^+ + NCS^-.$$

The saltlike compound which is obtained is known to be a strong electrolyte and is responsible for the high conductance. This reaction is analogous to the well-known reaction between methyl iodide and pyridine

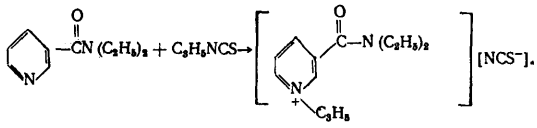
$$C_5H_5N + CH_3I = [C_5H_5\overset{+}{N}CH_3]I^-.$$

The Reviewer has shown[117] analogously that, in the mustard oil–quinoline system at room temperature, interaction between the components is too feeble to be detected on the viscosity and density diagrams. However, here, too, the conductivity isotherm passes through a maximum, approximately at 50 mole % of the components, which indicates that very weak interaction between the components is taking place at this temperature. On heating, this reaction becomes very vigorous, and then the viscosity and density isotherms show well-defined maxima at the same composition. All these and other results show that here, too, an electrically conducting saltlike compound is formed, as a result of interaction between mustard oil and quinoline

$$C_9H_7N+C_3H_5NCS = [C_9H_7\overset{+}{N}C_3H_5][NCS^-] \rightleftharpoons [C_9H_7NC_3H_5]^+ + NCS^-.$$

Subsequently the Reviewer also studied the mustard oil–diethylnicotinamide system, the second component in which is also a cyclic tertiary amine. The viscosity and density isotherms obtained curve smoothly from one component to the other without passing through any extremal points, which indicates that interaction is either absent or very weak. However, the mixtures conduct an electric current, although only slightly, and give a positive reaction for the NCS^- ion. After heating, the viscosity and density isotherms show well-defined maxima, while the conductivity and the NCS^-

concentration in the mixtures increase markedly. The Reviewer has shown that, in this system, too, an electrolytic complex compound is formed by the reaction [118]

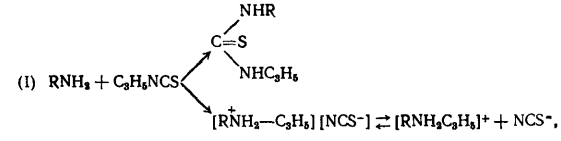


Finally, the Reviewer has also studied one system comprising mustard oil and triethylamine, which is an aliphatic tertiary amine. The viscosity and conductivity isotherms show that the components react feebly at room temperature (more strongly than in the case of cyclic tertiary amines), but the reaction becomes vigorous on heating, with formation of a conducting compound

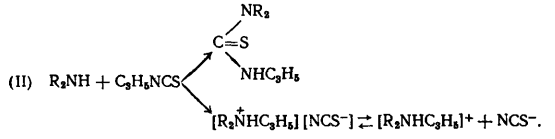
$$(C_2H_5)_3N + C_3H_5NCS = [(C_2H_5)_3\overset{+}{N}C_3H_5][NCS^-] \rightleftharpoons [(C_2H_5)_3NC_3H_5]^+ + NCS^-.$$

Thus the results of these investigations disprove the statement by several authors that tertiary amines do not react with mustard oil. According to these data, interaction takes place even at room temperature, with the formation of electrically conducting solutions.

Summarising, we can state that reaction of mustard oil with primary and secondary amines yields, together with substituted thioureas (non-electrolytes), allylammonium thiocyanates (electrolytes) according to the following general scheme



(I) $RNH_2 + C_3H_5NCS \rightarrow [\overset{+}{R}NH_2{-}C_3H_5][NCS^-] \rightleftarrows [RNH_2C_3H_5]^+ + NCS^-$,



(II) $R_2NH + C_3H_5NCS \rightarrow [R_2\overset{+}{N}HC_3H_5][NCS^-] \rightleftarrows [R_2NHC_3H_5]^+ + NCS^-$.

With tertiary amines only the one, electrolytic compound is formed, according to the general scheme

$$R_3N + C_3H_5NCS = [R_3\overset{+}{N}C_3H_5][NCS^-] \rightleftarrows [R_3NC_3H_5]^+ + NCS^-.$$

The Reviewer has confirmed this by a spectrophotometric method [119].

4. Dissociation Constants of the Electrolytic Compounds

Most of these saltlike compounds were isolated [120], and their electrolytic dissociation constants measured by the conductivity method in various solvents (water, methanol, and ethanol). The results are summarised in the accompanying Table, in which all the saltlike complex compounds obtained by the Reviewer are arranged in order of increasing basic dissociation constant of the amine (third column).

The dielectric constants of the solvents used differ considerably among themselves, which makes it possible to trace their effect on the dissociation constants of the electrolytes. From the data in the Table it is seen that:

1. The dissociation constants of the electrolytes in water decrease with decrease in the dissociation constant of the amine which they contain. This generalisation does not apply when the solvent is methanol or ethanol.
2. The dissociation constants of the salts increase with decrease in the dielectric constant of the medium, whereas the equivalent conductance at infinite dilution increases with increase in the dielectric constant.

These results are not consistent with the Nernst–Thompson rule, according to which the dissociation power of a solvent should increase with increase in the dielectric constant of the medium.

It seems that this is associated with hydrolysis of these substituted ammonium thiocyanates, resulting in the appearance of more mobile ions. At very high dilutions in aqueous

TABLE.

Formula of thiocyanate	Name of cation	Dissociation constant of amine	Water, $D = 81$		Methanol, $D = 35$		Ethanol, $D = 25.4$	
			λ_∞	$10^4 K_{diss}$	λ_∞	$10^4 K_{diss}$	λ_∞	$10^4 K_{diss}$
$[C_5H_{10}\overset{+}{N}HC_3H_5][NCS^-]$	allylpiperidinium	1.6×10^{-3}	85	3.8	94	33.1	38	50.1
$[(CH_3)_3\overset{+}{N}C_3H_5][NCS^-]$	allyltriethylammonium	5.6×10^{-4}	225	2.0	180	11.0	65	20.0
$[C_5H_5\overset{+}{N}C_3H_5][NCS^-]$	allylpyridinium	1.7×10^{-9}	232	1.51	127	3.16	60	7.94
$[C_6H_5\overset{+}{N}(C_2H_5)HC_3H_5][NCS^-]$	allylethylanilinium	1.3×10^{-9}	220	1.3	110	5.62	52	10.4
$[C_9H_7\overset{+}{N}C_3H_5][NCS^-]$	allylquinolinium	6.3×10^{-10}	228	0.89	192	2.88	66	11.2
$[C_6H_5\overset{+}{N}(CH_3)HC_3H_5][NCS^-]$	allylmethylanilinium	5×10^{-10}	220	0.74	140	4.36	44.5	10.0
$[CH_3OC_6H_4\overset{+}{N}H_2C_3H_5][NCS^-]$	allyl-*o*-anisidinium	2.5×10^{-10}	245	0.39	130	7.08	48	13.5
$[(C_2H_5)_2NCOC_5H_4\overset{+}{N}C_3H_5][NCS^-]$	1-allyl-3-diethylcarbamoylpyridinium	–	255	0.31	184	1.90	58	13.8

medium it is possible that these salts are completely hydrolysed with the formation of hydrogen ions, which possess the highest mobility, according to the scheme

$$[R\overset{+}{N}H_3{-}C_3H_5][NCS^-] + H_2O \rightleftharpoons [R\overset{+}{N}H_2C_3H_5][OH^-] + HSCN$$
$$+H_2O \downarrow\uparrow$$
$$H_3^+O + NCS^-$$

This hypothesis is supported by the fact that the equivalent conductance of these salts at infinite dilution in aqueous solutions reaches values of 220–225 ohm^{-1} cm^2.

Similar phenomena were observed also by Burmistrova[121] in a study of the electrolytic dissociation of quaternary ammonium salts in methanol and ethanol. She found that on dilution the equivalent conductance of such salts at first increases steadily though not greatly, but when a concentration of about 10^{-4} M is reached, a rapid rise in equivalent conductance begins with most salts. She observed a similar phenomenon in aqueous solutions of quaternary ammonium salts too. She regards the great increase in equivalent conductance at high dilutions as being due to interaction between solvent and electrolyte, *i.e.* to solvolysis.

According to Burmistrova's results, solvolysis is greater in methanol than in ethanol. Values obtained by the Reviewer for the equivalent conductance at infinite dilution of the salts which he studied were also considerably greater in methanol than in ethanol. This indicates that these salts, too, undergo stronger solvolysis in the former solvent.

Burmistrova also assumes that a proton can be split off more readily from an allyl than from a benzyl group. The salts examined by the Reviewer contain an allyl group, which makes his explanation involving hydrolysis (solvolysis) of the salts probable.

Of all the salts studied by the Reviewer, only allylpiperidinium thiocyanate has a relatively low value of λ_∞ in all solvents, especially water. This is probably because, owing to its stability, this compound is hydrolysed less or not at all in water. This agrees with Burmistrova's experimental results[121], showing that λ_∞ for solutions of NaBr in ethanol does not increase so rapidly as for salts of quaternary ammonium bases even at very high dilutions.

It is possible that the presence of such a strong base as piperidine in a salt confers stability on the latter and protects it from hydrolysis (solvolysis).

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There is no doubt that study of the electrical conductivity of non-aqueous solutions will continue in the future to make a great contribution to the formulation of a single, generally applicable theory of electrically conducting solutions. Attempts have already been made to work out such a theory. An example is provided by Izmailov's theory of solutions[122-124], which takes into account the properties of non-aqueous conducting solutions.

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MODERN VIEWS ON THE PLASTICISING OF POLYMERS

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1. INTRODUCTION

There have been various fundamental changes in views on the structure of linear polymers and the nature of plasticising which have not found their way into the reviews on the subject (see *e.g.* Tager[1]). We thought it desirable to collect the main facts about the plasticising of polymers by low-molecular-weight plasticisers without considering the questions of chemical and mechanical plasticising and the plasticising of polymers by high-molecular substances.

Polymers without additives are comparatively rarely used in technology because of their considerable brittleness, their tendency to crack during storage and use, the difficulty of forming them into articles, and various other deficiencies; the polymers are therefore modified, *i.e.* their properties are changed (improved).

One of the most important methods of modifying the properties of linear polymers is to plasticise them with low-molecular-weight substances. This type of plasticising can be considered as the combination of the polymers with certain low-molecular-weight substances of a definite chemical structure to form, because of steric effects and the altered energy relationships, polymeric materials which are usually more plastic and more elastic. The substances producing this effect are known as plasticisers.

For a long period the problem of plasticising has been solved purely empirically. A theoretical founding of this effect became possible only after the basic kinetic features of the behaviour of polymers had become evident, and after the discovery of the relaxation mechanism of the deformation of polymeric materials and the introduction of the concepts of the macromolecular and then of the globular-packet structure of high-molecular-weight compounds.

It has been shown[2] that the extent of highly elastic deformation has a clearly expressed relaxation (retardation) character, *i.e.* it depends on the period over which deformational stresses act on the polymer. Brittleness appears in polymers when the increase in stress in specimens subjected to deforming forces is not accompanied by macromolecular rearrangements leading to stress-relaxation[3]. Hence it is concluded that the brittleness of polymers can be reduced by the introduction of plasticisers, since in their presence the rates of relaxation processes are increased and the growth of cracks is stopped or greatly reduced.

The mechanical properties of polymeric materials have been determined as a function of the period over which external forces act upon them[4]; the strength of polymers and similar materials depends greatly on the duration of deforming stresses on the specimen, and all polymeric materials have such a strength *vs.* time relationship[5-7].

X-Ray and electron diffraction of amorphous polymers[8-10] have clarified the structure of such substances and allowed the orientated state of the chains to be considered as an enforced and unstable state of the polymeric system. Similar conclusions were reached from an investigation of the differential heats of sorption of polymeric materials[11].

The change in views of the structure of polymers has enabled knowledge of their behaviour on deformation to be expanded. In linear polymers under certain conditions there is movement of the chains as a whole, causing the plastic properties (flow) of polymers, and movement of individual segments of the chains, producing flexibility and elasticity of the polymeric material[12]. The flexibility of the macromolecular chains is in its turn determined by the potential barrier, *i.e.* the energy required to pass from one conformation to another. The potential barrier depends on the chemical nature and structure of the chains producing the intramolecular and intermolecular interactions, and on the temperature and various other factors. Depending on the temperature, polymers can exist in three main physical states[13-15]: vitreous, highly elastic, and viscous liquid; the length and flexibility of the macromolecules play a significant part in these transformations. Further studies led[16] to a theory of the mechanical properties of amorphous linear polymers and to two mechanisms for