RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

June 1976

Translated from *Uspekhi Khimii*, **45**, 961 - 997 (1976)

U.D.C. 541.49

The Solvation of Inorganic Substances and Complex Formation in Non-aqueous Solutions

A.M.Golub

Various views on the nature of the dissolution process are examined and the latter is explained as a consequence of the solvation of the solute. Methods for the determination of solvation numbers and solvating capacities of solvents are analysed and an attempt is made to explain solvation and the influence of the nature of the solvent on complex formation reactions taking into account modern ideas about chemical bonding. The fundamental characteristics of complex formation and inorganic synthesis in non-aqueous and mixed solutions are described.
The bibliography includes 358 references.

CONTENTS

I.	Introduction	479
II.	The solvent power of solvents and the properties of electrolyte solutions	480
III.	The solvation of inorganic substances	481
IV.	The quantum-chemical aspect of solvation	482
V.	Determination of solvate ion numbers	484
VI.	The donor activity of solvents	487
VII.	Complex-formation reactions in non-aqueous and mixed solutions	489
VIII.	The influence of supporting electrolyte ions and "stepwise" complex formation	490
IX.	Non-aqueous solutions in preparative inorganic chemistry	492
X.	Conclusion	493

I. INTRODUCTION

The study of the nature of solutions and of the influence of solvents on the reactivity of substances, particularly inorganic substances, has attracted the attention of chemists for a long time. This problem has become particularly urgent, since the majority of chemical engineering processes are carried out in solution and in view of the likely use of lanthanide complexes in non-aqueous solutions[1-3] as lasers. It is very remarkable that the quantum yield for $NdCl_3$ dissolved in a mixture of $SeOCl_2$ with $SnCl_4$ or $SbCl_5$ is ten times higher than for aqueous solutions of neodymium salts[4].

It is well known that the solvent has a significant influence on the state and properties of the solute; however, there is as yet no well-constructed theory on the basis of which one could predict the suitability of a particular solvent for given reactions or for the dissolution of various substances. Nor are there any fairly well-established views concerning solvation phenomena in solutions[5].

According to Mishchenko and Poltoratskii[6], "the nature of ionic solvation forces remains unexplained". On the other hand, there have been numerous studies on the structure of solutions and on complex-formation reactions in non-aqueous systems[7]. It is therefore necessary to analyse the data which have accumulated in order to discover the relation between solvation and complex formation, on the one hand, and to what extent the use of non-aqueous solutions promotes the development of inorganic synthesis, on the other.

II. THE SOLVENT POWER OF SOLVENTS AND THE PROPERTIES OF ELECTROLYTE SOLUTIONS

The old rule "like dissolves in like" is far from being universal, although attempts are sometimes made to revive it even now. Thus, after studying the dependence of the solubility of substances on the properties of the solvent, Semenchenko and then Shakhparonov[8-11] concluded that the relative polarities of the substances involved play a significant role. According to these investigations[8-11], solubility should be highest in those cases where the generalised moments, i.e. the ratios of the dipole moments and the molecular volumes, of the solute and the solvent are similar. Hildebrand and Scott maintain that substances having the same density of interaction energy are miscible[12]. According to Pearson, the so called hard acids or bases dissolve in hard solvents (which themselves behave as hard bases and acids respectively) and soft acids or bases are soluble in soft solvents[13]. However, Pearson's soft acids ($GaCl_3$, I_2, etc.) dissolve readily in alcohols, amines, and hydrazine, which are hard bases. The above rule is to some extent justified in relation to the miscibilities of organic compounds. The Lavoisier rule, developed by Shreder[14], is applicable to many solid non-electrolytes: other conditions being equal, the solubility of solids increases with decrease of their melting point. The rule is usually expressed by the Schroeder–Le Chatelier equation:

$$\lg s = -\frac{\Delta H_m}{RT} + \frac{\Delta H_m}{RT_m}, \qquad (1)$$

where s is the solubility, ΔH_m the heat of fusion, T the experimental temperature, and T_m the melting point.

In the case of electrolytes, the solvent power of solvents is usually estimated taking into account their dielectric constants[15,16]. After considering the solubilities of salts in water and some other solvent, Izmailov and coworkers[15,16] established the following relation:

$$\lg \frac{s_{H_2O}}{s_{Solv}} = L\left(\frac{1}{\varepsilon_{Solv}} - \frac{1}{\varepsilon_{H_2O}}\right) + P\left(\frac{1}{\varepsilon_{H_2O}} - \frac{1}{\varepsilon_{Solv}}\right), \qquad (2)$$

where L and P are constants and ϵ is the dielectric constant. When a number of assumptions are made, Eqn. (2) can be transformed into

$$\lg s_{Solv} = F + w\varepsilon, \qquad (3)$$

where F and w are constants.

The above view was originated by Born[17], who explained dissolution and solvation as a consequence of the ion–dipole interaction[18-24]. According to Born[17], when an ion is transferred from a vacuum into a medium with a dielectric constant ϵ, the solvation energy, equal to the difference between the field energies *in vacuo* and in the given medium, is evolved,

$$E = \frac{z^2e^2}{2r} - \frac{z^2e^2}{2\varepsilon r} = \frac{z^2e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right). \qquad (4)$$

Consequently, the solubility of salts should decrease with decrease of the dielectric constants of the corresponding liquids[25,26].

The limitations of the electrostatic concept become evident already in relation to propane-1,2-diyl carbonate, which has a high dielectric constant ($\epsilon = 69$) but dissolves many compounds much less effectively than dimethylformamide ($\epsilon = 36.1$) or dimethyl sulphoxide ($\epsilon = 48.9$). In highly polar nitromethane (dipole moment 3.54 D) the solubility of alkali metal halides is low; transition metal halides are also sparingly soluble in this solvent[27]. On the other hand, acetonitrile, which has almost the same dipole moment (3.2 D) and dielectric constant (38.8), readily dissolves compounds of different classes and even silver nitrate[28], which is sparingly soluble in water.

One cannot explain from this standpoint the low solubilities in water of salts of the type $Cs_2[PtCl_6]$, $[Co(NH_3)_6].[P(Mo_3O_{10})_4]$, and $BaSO_4$, which consist of large cations and anions, the decrease of the corrosion of lead–antimony alloys on passing from water to water–dioxan mixtures[29], the failure of zinc electrode potentials in $ZnCl_2$ solutions in acetonitrile to obey the Nernst equation[30], and the non-uniform variation of the conductivity of aluminium chloride with concentration in butyl ether[31].

In the vast majority of cases, electrolytes behave in non-aqueous solutions differently than in water. For example, thorium nitrate in acetonitrile has a low conductivity; $CuCl_2$ in acetone has a dark-yellow colour[32]; aluminium bromide dissolves in acetone with evolution of heat[33] and the solutions formed darken after a time and their conductivity increases.

The above and also many other data concerning the solubilities of certain salts in alcohols[34-36], dimethylformamide[37,38], acetone[35,39], pyridine[40-42], sulphur dioxide[43], etc.[44,45] show that the dissolution process is determined by the chemical nature of the solvent and the solute rather than by their physical properties. This is why Izmailov[15,16,46] concluded that the dependence of salt solubilities on the dielectric constant corresponding to Eqn. (3) is characteristic only of a series of solvents of the same chemical type, such as, for example, alcohols.

Numerous experimental data have shown that the dielectric constant is not a characteristic which determines solvent power. Thus CuH is insoluble in water but forms a red solution in pyridine (Py), for which $\epsilon = 12.3$, i.e. is lower than for water[47]. Copper iodide also dissolves in this solvent and, when the latter is distilled off, crystallises in the form of $[CuPy_2]I$.[48] The solubilities of many metal halides in pyridine decrease on passing from iodides to chlorides[44].

Hydrazine ($\epsilon = 51.7$) dissolves many salts at 25°C more effectively than does water ($\epsilon = 81$) and liquid HCN ($\epsilon = 123$ at 15.6°C). For example, HgI_2 dissolves in hydrazine more readily than $HgCl_2$ and $Cu(NO_3)_2$ is only sparingly soluble in this solvent[49]. It is difficult to account for the insolubility of CuCN, AgCl, $Ba(NO_3)_2$, $CuSO_4$, HgI_2, and $Ca(NO_3)_2$ and for the low solubilities of AgCN, CdI_2, $CoCl_2$, $HgCl_2$ and $HgBr_2$ in liquid HCN.

The above data show that the formation of the solution and its properties depends mainly on the chemical nature of the corresponding solvents, including stereochemical factors[51]. The rate of dissolution of the solid is higher the lower the activation energy for the transfer of surface species to the solution, which, apart from depending on temperature, is also a function of the strength of bonding between these species and solvent molecules.

Other conditions being equal, substances with a molecular lattice should exhibit the highest solubility and should

be followed in this respect by ionic compounds, since, in order to overcome dispersion forces or to dissociate an ionic linkage, it is necessary to expend less energy than for the disruption of atomic or metallic lattices. In particular, it has been noted that the activation energy for the dissolution process is less than 10 kcal mole^{-1} for compounds with ionic bonding[52], while for molecular crystals it is even lower. The dissolution of substances with a molecular lattice is probably preceded by dispersion interaction between molecules of different kinds, which is possible also in the so called indifferent solvents (CCl_4, C_6H_6, etc.).

The first stage in the dissolution of ionic crystals is apparently ion–dipole attraction. The solubilities of salts are therefore usually higher in polar solvents than in non-polar solvents. Substances with a molecular lattice, such as, for example $ThOx_4$, where Ox is the 8-hydroxyquinoline residue, dissolve, while ionic crystals, such as ThF_4, do not dissolve in solvents of the carbon tetrachloride type[53]. Compared with the ionic compound NaNCO, the covalent compound $Hg(OCN)_2$ dissolves more readily not only in alcohols, ethers, and ketones, but also in cyclohexane[54]. For this reason, neutral molecules should be more effectively extracted by solvents immiscible with water, which is in fact observed experimentally[35–57]. It is easier to replace one dispersion interaction by another than to dissociate an ionic linkage or polar molecules into ions.

However, despite its importance when the phases first come into contact, the ion–dipole interaction is not of decisive significance in the general assessment of solvent powers. This is seen from a comparison of the solubilities in water of calcium and cadmium sulphates, the ionic charges and radii of which are the same, and of sodium and copper(I) chlorides in liquid ammonia. Although the radii of the Na^+ (0.95 Å) and Cu^+ (0.95 Å) ions are the same, the solubilities of their salts are by no means identical. Only 3 g of NaCl dissolves in 100 g of ammonia at −35°C,[44,58] while the solubility of CuCl is much higher. In water, alcohols, acetone, etc. the solubilities of these compounds vary in the opposite sense, which cannot be explained by taking into account electrostatic concepts alone.

Sodium perchlorate dissolves readily in ethylenediamine (ϵ = 12.9 at 25°C) and forms with the latter the solvate $NaClO_4.3C_2H_4(NH_2)_2$.[59] On the other hand, this salt dissolves less readily in liquid sulphur dioxide (ϵ = 12.35 at 22°C); the corresponding solvate has not been obtained either[60]. Niobium and tantalum pentachlorides are very sparingly soluble in benzene, carbon tetrachloride, and chloroform[61] and are somewhat more soluble in ethers, ketones (acetone), tributyl phosphate[62], and acetonitrile[63]. For example, it has been shown that, when acetonitrile dissolves niobium pentachloride, it decomposes its polymeric molecules and forms the solvato-complex $[Cl_5NbNCCH_3]$.[63] Zirconium and hafnium tetrachlorides dissolve in many solvents with high solvating capacities[64,65], for example in alcohols and acetonitrile, with which they form the compounds $ECl_4.2Solv.$[64–66] The formation of E–Solv bonds has been confirmed by infrared spectroscopic[67] and thermochemical[68] data. The compounds ECl_4 do not dissolve in liquid hydrocarbons and carbon tetrachlorides, since they do not form adducts with these solvents[70,71]. Aluminium chloride forms more stable solvates and is therefore more effectively dissolved by acetone than by pyridine[58].

III. THE SOLVATION OF INORGANIC SUBSTANCES

It is seen from the above data that the main condition for dissolution is solvation of the species to be dissolved. Solvents with high solvent power in relation to inorganic substances can be divided into two groups: donor and acceptor. The former effectively solvate ions or molecules of the acceptor type and the latter those of the donor type.

Numerous reviews have been devoted to ion solvation[46,72–76], but they are almost exclusively concerned with aqueous systems. In these communications there is unfortunately no indication of the role of the chemical nature of the solvent in the formation of the solvation shells of ions.

Conway and Bockris[74] and also Samoilov[76] developed for aqueous salt solutions interesting ideas concerning primary and secondary ion hydration, suggesting the existence of different types of bonds in solvates. It is quite reasonable that in primary solvation the solute may undergo a significant change in its electrolytic properties. Thus iodine forms with pyridine conducting solutions, from which it is possible to isolate the compound $Py.2I_2$,[77] or more precisely $[IPy][I.I_2]$.

Owing to solvation, the covalent compound $TiCl_4$ dissociates in acetonitrile[78]:

$$2\,TiCl_4 + 4CH_3CN \rightleftarrows [TiCl_3(CH_3CN)_3]^+ + [TiCl_5(CH_3CN)]^-.$$

When $TiCl_4$ dissolves in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO), the molecules of the latter are attached to the titanium atom, expelling chloride ions to the outer sphere. This process takes place even more readily with $ZrCl_4$ and $HfCl_4$, which form with DMSO the compounds $ECl_4.9DMSO$.[79] Since the conductivities of dimethyl sulphoxide solutions of ECl_4 are high, they presumably contain the solvato-complexes $[E(DMSO)_8]^{4+}$ or $[E(DMSO)_6]^{4+}$. On being dissolved in tetramethylene sulphone (TMS), cobalt(II) perchlorate forms red conducting solutions, from which it is possible to isolate the compound $Co(ClO_4)_2.3TMS$, whose electronic spectrum resembles that of $[Co(H_2O)_6]^{2+}$.[80]

In contrast to primary solvation, secondary solvation arises as a result of the electrostatic attraction of dipoles or via hydrogen bonding. On the other hand, the formation of the first solvation layer around the solute species apparently plays a dominant role in the dissolution process, since the decrease of enthalpy on dissolution is in fact associated with this factor[82–84].

Since solvation processes in non-aqueous solutions have been studied much less thoroughly than in water, the problem of the relative stabilities of cations and anions in relation to solvation has not yet been solved unambiguously. Gutman[51] suggests that "... the solvation of anions by acceptor solvents usually takes place to a lesser extent than the solvation of cations by donor solvents", and, according to other workers[85–88], anions have higher hydration energies than cations of the same size. The latter is true of potassium, ammonium, rubidium, and caesium fluorides, which dissolve in water with evolution of heat. The same investigators[85–88] nevertheless stipulate that in aprotic solvents, which do not form hydrogen bonds with anions, the latter are less solvated than cations. It is difficult to agree with this view, firstly because in solvents with a high solvent power solvent molecules form the most compact structure around cations[89,90]. Secondly, the energy of the hydrogen bond is low compared with the energy manifested in real solvates, which are in most cases typical complexes.

Comparison of the radii of cations and anions found on the basis of the Stokes law with their crystal-chemical values led Prue and Sherrington [87] to the conclusion that in dimethylformamide and dimethyl sulphoxide cations have a larger solvation shell than anions. The same workers noted that in water and methanol anions have the same conductivities as cations with similar crystal-chemical radii. It has likewise been established that in many other solvents cations are much more solvated than anions [91-95]. On the other hand, for weakly solvated cations, salt solubilities increase in the following sequence of anions:

$$Cl^- < NO_3^- < Br^- < ClO_4^- < I^-,$$

The higher solubilities of potassium and certain other metal iodides compared with their chlorides in hydrazine, liquid sulphur dioxide, acetonitrile, and pyridine are due to the more effective solvation of the iodide ion. The dissolution of KCl in iodine monochloride can be hardly accounted for otherwise than by the solvation of the anion:

$$KCl + ICl = K[ICl_2].$$

This is in fact responsible for the higher conductivity of the solution compared with the pure solvent. When $[(C_2H_5)_4N]Cl$ dissolves in $POCl_3$, a similar interaction takes place [96].

Taking into account the solvation of both the cation and anion, it has been concluded [22] that a total solvation limit exists at which the number of moles of the solvent per mole of the salt is equal to the sum of the coordination numbers of the ions. Since the actual salt solubilities are in many solvents higher than the total solvation limits, an insufficiency of the solvent leads to competition between the ions for the solvating molecules with advantage going to the more active acceptors. According to Mishchenko and Sukhotin [22], the energy of hydration of bivalent cations exceeds by a factor of 5–7 the energy of hydration of anions. A higher degree of solvation is also indicated by many other data [97].

It is clear from the foregoing that the effect of the interionic interaction and structural packing density play an extremely significant role in the solubility of electrolytes in addition to ion solvation. In particular, this leads to the sparing solubility of salts consisting of small cations and small anions. The increase of the solubilities of alkali, alkaline earth, and many transition metal halides in the series from chlorides, to bromides, and to iodides can be accounted for by the decrease of the cation–anion interaction energy.

Even the solubilities of salts comprising the anions SO_4^{2-} and ClO_4^-, which have the same structures, are different. For readily solvated cations, the solubility of perchlorate is appreciably higher than that of sulphates. At 25°C the [saturated?] $NiSO_4.6H_2O$ solution contains 29.36% of the salt and the [saturated?] $Ni(ClO_4)_2.6H_2O$ solution 52.87%; [45] this is due to the different strengths of binding of coordinated water to their anions [98].

Thus the solubility of salts depends also on the mutual substitution of anions and solvent molecules in the first and second solvation layers of the cations owing to the different abilities of the anions to form covalent linkages with the cations and different strengths of the hydrogen bonds between a solvent molecule in the solvato-complex and a free solvent molecule, on the one hand, and between a coordinated solvent molecule and an anion, on the other. If the latter predominates over the former, then, when the contribution of the covalent component to the interionic interaction is appreciable, the salt will dissolve less effectively.

For the majority of chlorides, the strength with which water, dimethylformamide, dimethyl sulphoxide, and even alcohol molecules are bound to metal cations is greater than that for the chloride ion. For this reason, the molecules of these solvents displace chloride ions from the coordination spheres of many complexes [99]. Dimethyl sulphoxide is capable of substituting even covalently bound iodide ions; SbI_3, BiI_3 and PbI_2 form conducting solutions in this solvent [100].

The different capacities of salts for dissociation in different solvents are well known; they have in fact led to the concept of differentiating solvents [101]. Later, Parker [85], who gave preference to electrostatic interaction and hydrogen bonding, considered only two groups of solvents in his assessment of their different behaviour with respect to electrolytes: protic and dipolar aprotic solvents. However, although this approach has been successful in a few instances, it is too narrow and Miller and Parker therefore attempted to reconcile the differentiating action of solvents with solvation effects [86]. They put forward the following hypothesis: the degree of solvation of anions by protic solvents decreases with increase of their radii:

$$OH^-, F^- > Cl^- > Br^- > N_3^- > I^- > NCS^- > ClO_4^-,$$

while the degree of solvation by aprotic solvents decreases in the opposite sequence. In the former case, the strong solvation can be accounted for by the enhanced ability of the anions to form hydrogen bonds with small anions and in the latter by the polarising action of the aprotic dipoles on the large anions. Consequently, the greater the polarity of the solvent the stronger its interaction with anions (particularly large anions). Nevertheless, this hypothesis conflicts with many factors. In fact, the lower solubilities of many salts in nitromethane compared with acetonitrile (see Section II) are due to the greater ease of formation of salt solvates in acetonitrile and not to the difference between the polarities of their molecules [102]. In conflict with Miller and Parker's hypothesis [86], in acetone the silver ion combines more strongly with the iodide ion than with the chloride ion [103] and the solubility of metal halides in ammonia (a protic solvent) increases on passing from fluorides to iodides [51]. Furthermore, among the hydrates $NaHal.2H_2O$, $NaI.2H_2O$ is the most stable, while KI does not form stable hydrates at all. Consequently the effect of salt solvation depends more on the nature of the cation than on that of the anion. Miller and Parker's explanation of solvation processes and solubility is based on an electrostatic concept, which, however, cannot be adopted without significant improvements. From the point of view under consideration, anions of the F^- type should interact vigorously with aprotic solvents, since they have comparatively high field strengths; for this reason, LiF should be more soluble than KF even in water, which is not the case.

IV. THE QUANTUM-CHEMICAL ASPECT OF SOLVATION

The majority of known instances of high solubilities of inorganic substances in various solvents [57,67,77-80] cannot be explained without taking into account the donor–acceptor interaction of solvent molecules with both ions and neutral molecules of the solute. An intense absorption band at 3000 Å, indicating the occurrence of interaction between the system components, has been observed even for a solution of iodine in benzene [104]. The formation of a solvato-complex in this solution is also indicated by the increased dipole moment (1.8 D) [105] caused by charge transfer from benzene to iodine [105,106].

If it is assumed that this complex exists in two mesomeric forms, i.e.

$$C_6H_6 \cdot I_2 \leftrightarrow C_6H_6^+ - I_2^-,$$

then the system in the ground state can be described by a wave function of the following type:

$$\psi_N = a\psi_0(C_6H_6 \cdot I_2) + b\psi_1(C_6H_6^+ - I_2^-). \quad (5)$$

Since the C_6H_6–I_2 bond is weak, the relation between the coefficients a and b is given by the inequality

$$a^2 \gg b^2. \quad (5a)$$

For the excited state, in which the ionic form of the complex should predominate, the expression defining the wave function ψ_E is similar to Eqn. (5), but the coefficients a' and b' are different and the second term $b'\psi_1(C_6H_6^- - I_2^+)$ has a minus sign. The following relations hold between the coefficients a and b and between a' and b':

$$\begin{aligned} a^2 + b^2 + 2abS_{01} &= 1; \\ a'^2 + b'^2 - 2a'b'S_{01} &= 1, \end{aligned} \quad (5b)$$

where S_{01} is the overlap integral for the wave functions ψ_0 and ψ_1, which is proportional to the interaction integral between the orbital of the solvent molecule and the orbital of the solute species.

Using the Schroedinger equation, the ground state of the solvato-complex can be represented by the relation

$$H(a\psi_0 + b\psi_1) = E(a\psi_0 + b\psi_1), \quad (6)$$

where H is the Hamiltonian and E the energy. The following equations can be obtained by the variational method:

$$\begin{aligned} a(E_0 - E) + b(H_{01} - ES_{01}) &= 0; \\ a(H_{01} - ES_{01}) + b(E_1 - E) &= 0, \end{aligned} \quad (7)$$

where $E_0 = \int\psi_0 H\psi_0 d\tau$, $H_{01} = \int\psi_0 H\psi_1 d\tau$, and $E_1 = \int\psi_1 H\psi_1 d\tau$.

The expressions

$$E = E_0 - \frac{(H_{01} - ES_{01})^2}{E_1 - E}; \quad (7a)$$

$$\frac{b}{a} = \frac{H_{01} - ES_{01}}{E_1 - E}, \quad (7b)$$

can be found from Eqn. (7). To facilitate the calculation, it is assumed that the degree of charge transfer in the ground state of the solvato-complex defined by the wave function ψ_N is low. E can then be replaced by E_0 in Eqns. (7a) and (7b):

$$E_N = E_0 - \frac{(H_{01} - E_0S_{01})^2}{E_1 - E_0}; \quad (7c)$$

$$\frac{b}{a} = -\frac{H_{01} - E_0S_{01}}{E_1 - E_0}. \quad (7d)$$

The energy of the solvato-complex E_N in the ground state is equal to the heat of its formation from the components; E_0 is the energy of the electrostatic interaction between the solvent and solute molecules. The second term in Eqn. (7c) defines the covalent component of the A–Solv linkage. For the complex $I_2.C_6H_6$, both terms in Eqn. (7c) are comparable in magnitude. For more stable solvato-complexes, E_0 is very low and may be neglected. The heat of formation of the complex is then given by the expression

$$\Delta H = -\frac{(H_{01} - E_0S_{01})^2}{E_1 - E_0}, \quad (8)$$

or, after substituting Eqn. (7d),

$$\Delta H = -(E_1 - E_0)\frac{b^2}{a^2}. \quad (8a)$$

The transition from the ground to the excited state, to which corresponds the characteristic absorption band of the complex $I_2.C_6H_6$, is accompanied by electron transfer from the benzene molecule to the iodine molecule:

$$h\nu = E_E - E_N, \quad (9)$$

which transforms into the following expression when account is taken of Eqn. (7c) and the analogous expression for the energy of the excited state E_E:

$$h\nu = (E_1 - E)\left[1 + \left(\frac{b'}{a'}\right)^2 + \left(\frac{b}{a}\right)^2\right]. \quad (9a)$$

The expression for the energy $h\nu$ of the charge-transfer band of the solvato-complex can also be formulated in a different way:

$$h\nu = I_{C_6H_6} - F_{I_2} + J, \quad (9b)$$

where $I_{C_6H_6}$ is the ionisation potential of the benzene molecule, E_{I_2} the electron affinity of the I_2 molecule, and J a constant.

The energy $h\nu$ is related to the stability of the solvato-complex. For a given solute, for example, iodine, there is a linear relation between $h\nu$ for solvates formed with different solvents and their ionisation potentials.

As stated above, the nature of the interaction between the solute and the solvent can be inferred also from the change in the dipole moment of the solution. Thus, in a benzene solution of iodine, the admixture of $C_6H_6^+ - I_2^-$ to the ground state explains the polarity of the complex[107].

The dipole moment of the solvato-complex in the ground state is defined by the relation

$$\mu = e\int\psi_N\sum r_i d\tau, \quad (10)$$

where e is the electronic charge and r_i the vector-distance of the ith electron. Taking into account Eqns. (5) and (5b), Eqn. (10) can be written in the following form:

$$\mu_N = a^2\mu_0 + b^2\mu_1 + 2ab\mu_{01}, \quad (10a)$$

where μ_0 and μ_1 correspond to Eqn. (10) and $\mu_{01} = e\int\psi_0\Sigma r_i\psi_1 d\tau = 1/2S_{01}(\mu_0 + \mu_1)$. Ultimately one obtains

$$\mu_N = a^2\mu_0 + b^2\mu_1 + abS_{01}(\mu_0 + \mu_1). \quad (10b)$$

Taking into account Eqn. (5b) and the known dipole moment of the solvato-complex (μ_N), the overlap integral S_{01}, the induced dipole moment (μ_0), and the dipole moment of the $Solv^+ - A^-$ state of the solvato-complex (μ_1), it is possible to calculate from Eqn. (10b) the wave function coefficients a and b. For complexes of the type $I_2.C_6H_6$, the dipole moments of the components are assumed to be zero ($\mu_0 = 0$) and $\mu_1 = er$. Having adopted $r = 3$ Å, calculation yields $\mu_1 \simeq 15$ D. If the overlap integral $S_{01} = 0.1$, μ_N for the solvato-complex is equal to the dipole moment of the A – Solv linkage or

$$\frac{\mu_{A-Solv}}{er} = b^2 + abS_{01}. \quad (10c)$$

Eqn. (10c) expresses the degree of charge transfer in $Solv^+ - A^-$. It has in fact been shown in this way that the increase of the dipole moment in complexes of the type $I_2.C_6H_6$ is caused by charge transfer.

When the coefficients a, b, a', and b' and the overlap integral S_{01} have been calculated with the aid of Eqns. (5b), (8a), and (9a), then, using the experimental values of ΔH and $h\nu$ (for different values of $E_1 - E_0$), it is possible to estimate the dipole moment of the solvato-complex. For example, it has been found that $\mu_N = 2.1$ D for $I_2.O(C_2H_5)_2$ when $E_1 - E_0 = 4.2$ eV and $r = 3.0$ Å, which agrees well with

experiment (1.9 D).[108] Thus, quantum-chemical calculations have shown that the solvation process is accompanied by a redistribution of electrons characteristic of chemical interaction.

Bernal and Fowler[23] already noted that the solvation energy of a given cation approaches the overall ionisation potential of the corresponding atom. Although the authors adhered to the electrostatic point of view, they nevertheless explained this fact correctly by the return of the missing electrons to the ion (via none other than a donor–acceptor interaction). The validity of this conclusion also becomes evident when the solvation effects for ions bearing the same charges and having similar radii are compared. For example, the solvation energies of Cd^{2+} (0.92 Å) and Ca^{2+} (0.94 Å) are respectively 532 and 346 kcal g-ion^{-1} in ammonia, 430 and 367 kcal g-ion^{-1} in water, and 412 and 309 kcal g-ion^{-1} in formic acid[46]. A similar difference between solvation energies has been observed for Na^+ and Ag^+.[109]

The high solvation energies of cadmium, zinc, and silver ions in ammonia, water, and other electron-donating solvents can be more correctly attributed to the formation of coordinate bonds[81,92,109] rather than to a simple ion–dipole interaction. This is particularly evident from the fact that high solvation effects are observed for cations which usually behave as active complex-forming agents. A similar view has been defended also by other investigators[13,110], who identify solvation with interaction between Lewis acids and bases. However, according to Pearson[13] the bonds formed by Al^{3+}, La^{3+}, Ti^{4+}, Cr^{3+} and other so called hard acids with water, alcohols, and amines are electrostatic, which conflicts with experimental findings.

Solvents with a high donor capacity usually form stable solvato-complexes with cations, as a result of which conducting systems are produced[77–80]. For example, many compounds and even metals[111] which are insoluble in water dissolve in liquid ammonia; on the other hand, calcium chloride is almost insoluble in this solvent[112].

Since the ionic component of the bond does not exceed 50% even in compounds of the MgO type[113], in the solvato-complexes $[Zr(DMSO)_6]^{4+}$, $[Ag(CH_3CN)_2]^+$, etc. its contribution is even smaller. According to some data[114–116], the solvation energy cannot be reliably calculated on the basis of the electrostatic model. The interaction of solute species with solvent molecules can be regarded as ordinary complex formation. Solvation and the properties of solvato-complexes can then be reliably accounted for by the molecular orbital method. In fact, the ion solvates formed in solution can be described by a set of wave functions of the central ion (sp^3d^i) with certain hybrid functions of the solvent molecules:

$$\psi = a\psi_c + b\Phi, \tag{11}$$

where ψ_c are the wave functions of the atomic orbitals of the central atom involved in the formation of bonds and Φ is an average wave function of the solvent molecules attached to the central atom. The solvates of the simplest ions are usually more susceptible to a quantum-chemical interpretation. For example, calculations on the aquo-complexes of lithium and sodium by the LCAO-MO method have been carried out in a number of studies[117–121] and some investigators[119,120] examined only the simplest systems $Li...OH_2^+$, $Na...OH_2^+$, and $H_2O...Li...OH_2^+$.

Calculations have been made[122] by Hoffmann and Lipscomb's method[123] for different internuclear distances and it has been found that the equilibrium distances for Li^+ and Na^+ are appreciably lower than the sum of the crystal-chemical radii of the M^+ ions and water molecules for all values of m in $M(H_2O)_m^+$, which indicates an appreciable contribution of the covalent bond character in these aquo-complexes. The internuclear distances for the potassium aquo-ion are closer to the sum of the crystal-chemical radii. However, it appears somewhat strange that the hydration shells of lithium consisting of six molecules and those of sodium and potassium consisting of eight molecules are more favourable than the tetrahydrate and hexahydrate shells respectively.

Unfortunately, at the present time quantum-chemical calculations on solvation have not gone beyond the limits of aqueous systems. In contrast to water, certain non-aqueous solvents can form π bonds in addition to σ bonds with solute ions or molecules. In this case, the atomic orbitals of solute molecules should be used to calculate yet another molecular wave function Φ', which may combine with the atomic functions of the central ion ψ_c on formation of a π bond. Evidently solvents of the second type, such as, for example, DMSO, should possess an enhanced solvent power.

Chatt[124] took a view similar to the concepts just described; he believes that the enhanced solubilities of certain transition and d^{10} metal salts in π-acceptor solvents can be accounted for by the presence of the weakly held external di electrons of the cation. Using these ideas, it is possible to explain many instances of different types of behaviour of salts in different solvents[125–127], for example, the behaviour of $CaCl_2$ and $ZnCl_2$ in $POCl_3$.[127]

The solvent power and the dissociating capacity of the solvent should depend on the relative energy levels of the electrons of solvent molecules and the corresponding ion making the greatest contribution to the bonds formed.

V. DETERMINATION OF SOLVATE-ION NUMBERS

The study of mixed solutions is extremely fruitful in the determination of the composition of solvates. It is then possible not only to establish the composition of the solvent but also to estimate the relative capacities for solvation of a particular pair of solvents and to show which of them interacts with the solute in the presence of the other. The method of solubility has also proved useful in such cases[128–130].

In a mixture of two solvents, one of which hardly dissolves the given substance A and the other readily dissolves it, equilibrium is established following saturation:

$$A + m\,\mathrm{Solv} \rightleftarrows A \cdot m\,\mathrm{Solv}.$$

The constant

$$K = \frac{[A \cdot m\,\mathrm{Solv}]}{[\mathrm{Solv}]^m} \tag{12}$$

is a quantitative characteristic of the capacity of the substance for solvation by the given solvent in the presence of the other. By taking logarithms in Eqn. (12), we obtain the relation

$$\lg [A \cdot m\,\mathrm{Solv}] = m \lg [\mathrm{Solv}] + \lg K, \tag{12a}$$

which represents a straight line with a conventional slope m. Assuming that $[\mathrm{Solv}] = lc_{\mathrm{solv}}$, where l is a proportionality coefficient and c_{solv} the overall concentration of the solvent, it is possible to determine the solvation number via a combined graphical and analytical method and then also the equilibrium constant

$$K = \frac{[A \cdot m\,\mathrm{Solv}]}{\{c_{\mathrm{solv}} - m[A \cdot m\,\mathrm{Solv}]\}^m} \tag{12b}$$

itself.

By studying the solubility of $CuCl_2$ in dioxan–solvent (alcohols, dimethylformamide, water) mixtures, it was found that $m = 2$. Table 1 presents the solvation numbers found by the solubility method for a series of other salts. In most instances these numbers agree with the usual coordination numbers of the cations. The lower values of the solvate-ion numbers suggest that salt anions and in some cases also molecules of the second solvent enter into the coordination sphere.

Table 1. The solvation numbers of salts based on their solubilities in dioxan–solvent systems.

Salt	Solvent					References
	H_2O	CH_3OH	C_2H_5OH	DMF	CH_3COCH_3	
$Pb(NO_3)_2$	4; 6	—	—	—	—	129
$MgSO_4$	6	—	—	—	—	131
$CaSO_4$	4; 6	—	—	—	—	131
$MgCl_2$	—	4; 6	4; 6	4; 6	—	12
$CaCl_2$	—	4	3	4	—	128
$NiSO_4$	6	—	—	—	—	131
$CuSO_4$	4; 6	—	—	—	—	131
$NiCl_2$	—	2; 4	2	2; 4	—	132
$CoCl_2$	—	2; 4	—	2; 4	—	128
$MnCl_2$	—	2; 4	—	—	—	131
$ZnSO_4$	6	—	—	—	—	131
$CdSO_4$	4; 6	—	—	—	—	131
$ZnCl_2$	—	2	2	2	—	131
$CdCl_2$	2; 4	—	2	2	—	130
$AlCl_3$	—	—	—	1	1	133

The solvation numbers of undissociated molecules or salts with weakly solvated anions can be most effectively determined by this method. On the other hand, when the salt solvation proceeds in accordance with equilibrium

$$AB_l + n\,Solv \rightleftarrows A \cdot m\,Solv^{+l} + l\,B\,i\,Solv^{-},$$

Eqn. (12a) becomes

$$\lg [A \cdot m\,Solv^{+l}] = \frac{n}{l+1} \lg [Solv] + D, \qquad (13)$$

where D is a constant. In this case the plot based on Eqn. (13) yields the slope

$$\frac{n}{l+1} = \text{slope}, \qquad (14)$$

and hence gives only an approximate idea about the solvation of the salt. In order to determine the solvation number of the cation, it is necessary to have additional data concerning the number of molecules i of the solvating solvent attached to the anion. Then,

$$m = \text{slope}\,(l+1) - i. \qquad (14a)$$

To determine the solvation number in mixed solvents, one can sometimes use successfully also the spectrophotometric method[132] in conjunction with the Bjerrum procedure[135] or by plotting the simpler relation

$$\lg \frac{D_x}{D_{max} - D_r} = m \lg [Solv] + \lg K, \qquad (15)$$

where D_X and D_{max} are the optical densities of solutions with partial and complete solvation of the solute and

$$K = \frac{[A \cdot m\,Solv]}{[A][Solv]^m}. \qquad (16)$$

The compositions and formation constants of the dimethylformamide solvates of $CoCl_2$, $NiCl_2$, and $CuCl_2$ in methanol and ethanol were determined by this method[136,137]. It was found that $m = 4$ (moderate DMF concentrations) and $m = 6$ (high concentrations of the solvating solvent) for the first two salts. Under analogous conditions, $m = 2$ and 4 for $CuCl_2$.

In a spectrophotometric study of UO_2Cl_2 solutions in a carbon tetrachloride–tributyl phosphate (TBP) mixture, plots based on Eqn. (15) established the existence of the solvato-complexes $[UO_2Cl_2.3TBP]$ and $[UO_2Cl_2.2TBP]$.[138] The addition of two molecules of pyridine to $CoCl_2$ was established by the same method in the presence of acetone[139,140]. The solvation numbers have been determined spectrophotometrically in a number of investigations[141–145]. Those of neodymium, amounting to 6–8[144] and 4[145], have been found for aqueous alcoholic solutions of $NdCl_3$. The latter number must be regarded as too low, since the solvation shell of neodymium probably incorporates alcohol molecules as well as those of water[140,147]. Other literature values of the solvation numbers of neodymium are 6[148] and 8–9.[149–151]

In order to determine the composition of solvato-complexes by the Bjerrum method, the average solvation number $\bar{n}$ can be calculated for two series of solutions with constant but different salt concentrations and uniformly increasing contents of the solvating solvent:

$$\bar{n} = \frac{c''_{Solv} - c'_{Solv}}{c''_A - c'_A}, \qquad (17)$$

where c''_A and c'_A, on the one hand, and c''_{Solv} and c'_{Solv}, on the other, are the overall concentrations of the components in two solutions belonging to two different series. In order to evaluate the formation constants, one calculates initially the equilibrium concentration of the solvating solvent:

$$[Solv] = \frac{c''_A c'_{Solv} - c'_A c''_{Solv}}{c''_A - c'_A}, \qquad (18)$$

and then one plots the relation

$$m = f(\lg [Solv]). \qquad (18a)$$

By studying the electronic spectra, one can follow the formation of complexes with different solvation numbers (up to the maximum value) and one can observe also the variation of the actual geometry of the solvato-complex. The vibrational spectra (infrared and Raman spectra) can be used to investigate solvation, like the electronic spectra. Compared with the pure solvent, the infrared spectra of solvato-complexes show new bands corresponding to the stretching and deformation vibrations of the bonds and reveal shifts of the vibrational wavenumbers and changes in the intensities of certain absorption bands of the solvating solvent. Since solvates dissociate in solution, the measured vibrational spectra show absorption bands referring both to the complex itself and to free solvent molecules. With increase of solvate concentration, the intensity of the former increases and that of the latter falls. In order to determine the composition of solvates, the vibrational spectroscopic results can therefore be treated similarly to electronic spectra. For example, the addition of one ethyl oxalate and one ethyl malonate molecule to $SnCl_4$ was demonstrated by the change in intensity of the stretching vibration band of the bound and free C=O groups in a benzene solution[152].

In a study of the infrared spectra of acetone solutions of MI and $MClO_4$ (M = Li or Na), it was noted that the C=O stretching vibration band shifts towards lower wavenumbers by 3 cm^{-1} for Na^+ and by 8 cm^{-1} for Li^+.[191] Since this shift is independent of the nature of the anion, it was

natural to conclude that the cations are solvated much more intensely than the anions[192] and that the capacity for solvation increases from Na^+ to Li^+.

Conductimetric[153] and cryoscopic[154-163] measurements are sometimes used in the study of salt solvates. Thus the solvation of Al_2Br_6 by acetone and nitrobenzene leads to the formation of two compounds: $AlBr_3$.Solv and $AlBr_3$. .2Solv.[164] The decrease of the conductivity of an ethereal solution of $AlCl_3$ with increase of the chloride concentration[31] can be accounted for by the conversion of the more complicated partly dissociated solvato-complex into the less complicated compound $[Cl_3Al.O(C_2H_5)_2]$, which agrees with the literature[165,166].

When cryoscopic measurements are used, it is first necessary to determine the association factor of the solvating solvent:

$$F_c = \frac{\Delta t}{\Delta t'}, \tag{19}$$

where $\Delta t'$ and Δt are the freezing point depressions of the solutions found experimentally and calculated theoretically. It is convenient to use dioxan, in which many solvents are not associated, as the inert solvent[131]. The variation of the freezing point depressions of solutions of the solvating solvent and the test substance in dioxan yields

$$\Delta t_1 = qc_1; \tag{20}$$

$$\Delta t_2 = qc_2, \tag{20a}$$

where c_1 and c_2 are the molar concentrations of the solvating solvent and the solute respectively. When solvato-complexes involving the addition of m solvent molecules are formed, the overall freezing point depression is

$$\Delta t = q(c_1 - mc_2 + c_2), \tag{21}$$

whence

$$m = \frac{qc_1 + qc_2 - \Delta t}{qc_2}. \tag{22}$$

The addition of one $POCl_3$ molecule to $FeCl_3$ and $AlCl_3$ in nitrobenzene[167] has been demonstrated cryoscopically.

A frequently used method for the determination of solvation numbers is that of Stokes. By following the movement of the solvated ion in an external electric field, it is possible to calculate the radius of the solvato-complex as follows:

$$r = \frac{0.82z}{\eta\lambda}, \tag{23}$$

where z is the absolute charge of the ion, λ the limiting equivalent conductance of the solution, η the viscosity of the solvent.

In order to find a more accurate value of the radius of the solvated ion, the following equation has been proposed[168]:

$$r' = \frac{0.82z}{\eta\lambda} \cdot \frac{r_{cr}}{r}, \tag{24}$$

where r' is the exact radius of the solvato-complex and r_{cr} the crystal-chemical radius of the ion investigated.

Table 2 shows that the radii of the solvated ions calculated by Eqn. (24) are higher than the Stokes values. Furthermore, according to Della Monica and Senatore[169], the solvation of cations should take place more vigorously than that of anions, since the radii of the solvato-complexes of the latter are smaller.

The volume of the solvation shell can be found from the radii of the solvated ions by means of the equation

$$V_{Solv} = \frac{4}{3}\pi(r^3 - r_{cr}^3), \tag{25}$$

and then the solvation number can be obtained:

$$m = \frac{V_{Solv}}{V}, \tag{26}$$

where V is the volume of one solvent molecule. Calculation based on Eqns. (24)–(26) led to the determination of the solvation numbers of Li^+: 4.6 (in water); 5 (in acetone); 6 (in acetonitrile); 11 (in ethanol). We believe these values to be too high.

Table 2. The radii r and r' (Å) of certain solvated ions in a number of solvents calculated by Eqns. (23) and (24).[169]

Ion	Methanol		Acetonitrile		DMF		Sulpholane		Nitrobenzene		Formamide	
	r	r'	r	r'	r	r'	r	r'	r	r'	r	r'
Li^+	3.77	4.74	2.98	4.13	4.12	5.10	1.92	3.74	—	—	2.92	4.36
Na^+	3.32	4.46	3.10	4.24	3.45	4.46	2.30	4.23	2.78	3.99	2.46	3.99
Cs^+	2.40	3.88	2.44	3.68	2.99	4.04	1.95	3.78	—	—	1.84	3.48
Cl^-	2.86	4.16	2.54	3.76	1.87	3.00	0.89	1.98	2.04	3.32	1.45	3.14
I^-	2.39	3.88	2.38	3.56	1.97	3.09	1.15	2.47	2.22	3.49	1.45	3.21
NO_3^-	2.80	4.14	2.24	3.48	1.80	2.92	—	—	2.00	3.30	1.44	3.14

In order to investigate ion solvation, a potentiometric method was proposed in 1958[92,93,95] whereby it is possible to deduce the existence of both homogeneous and mixed solvato-complexes. As in the usual complex-forming systems[170-172], the inert solvent should possess some ionising capacity and the metal corresponding to the salt should form an effective electrode of the first kind. If the solvating solvent binds metal ions into solvates more effectively than the inert solvent, its introduction into the system leads to a decrease of the electrode potential. Knowing the overall concentration of metal ions c_M and having determined its equilibrium value [M] potentiometrically, it is possible to calculate the solvation number of the ion:

$$m = \frac{d\lg\frac{c_M - [M]}{[M]}}{d\lg[Solv]}, \tag{27}$$

where [Solv] is the concentration of the solvating solvent. The formation constant of the solvato-complex can be calculated from Eqn. (16), having assumed that $[A.mSolv] = c_M - [M]$ and having replaced [A] by [M].

A combined graphical and analytical treatment of the potentiometric data[95,172] established that the hydration of lead and silver ions changes by 3–4 coordination sites as high concentrations of dioxan and acetone are reduced in the presence of water[93,170]. This is due to the formation of mixed solvates. Homogeneous hydrates of lead ions $[Pb(H_2O)_6]^{2+}$ are detected at high water concentrations in the $Pb(ClO_4)_2$–CH_3OH–H_2O system[173] and the solvates $[M(DMF)_6]$ are detected[174] in the $M(ClO_4)_n$–DMF–H_2O systems, where M = Cd, In, or Sn.

The formation of solvato-complexes can be observed also in a direct study of the properties of solvent molecules. This is achieved best with the aid of the NMR method[175-177] using the chemical shift δ. When the experiments are performed at a fixed frequency $\nu_{av} \simeq \nu_0$,

the distance between the signals of the test and standard solutions being determined, the chemical shifts can be estimated as follows:

$$\delta_i = \frac{\nu_i - \nu_{av}}{\nu_{av}} = \frac{\nu_i - \nu_{i\,av}}{\nu_0}. \quad (28)$$

If the solvent molecules with resonating nuclei are attached to a solute molecule or ion, the chemical shift of the nuclei is displaced relative to that of the free solvent molecules. In the absence of exchange between the solvato-complex and free molecules or when its rate is low, the NMR spectrum shows lines due to the resonance of the nuclei of the coordinated and free solvent molecules. By measuring the integral signal intensities, it is possible to determine the concentrations of the bound and free solvent and to calculate from the known concentration of the solute the solvation number and the equilibrium constant for the formation of the solvato-complex[175-188]. In particular, the solvation number can be calculated[184,185] with the aid of the equation

$$m = i\frac{S_c}{S_c + S_f}, \quad (29)$$

where i is the total number of moles of the solvent per mole of the solute and S_c and S_f are the areas under the signals due to the bound and free solvent. Using Eqn. (29), Yatsimirskii et al.[186] found that five water molecules are retained by Lu^{3+} in an acetone solution of $Lu(NO_3)_3.6H_2O$. However, the overall coordination number of lutetium reaches at least 8, since the conductivity of the test solution at a concentration of 0.01 M is extremely low.

On the other hand, when there is an appreciable exchange between the free and bound components of the solvato-complex, the NMR spectrum reveals a single signal:

$$\delta = \delta_1\frac{c_1}{c} + m\frac{c_m}{c}\delta_m, \quad (30)$$

where δ is the average chemical shift of the solvent molecules, δ_1 and δ_m are the chemical shifts of the atoms in the free solvent and the solvent bound in the complex, m is the solvation number, and c_1, c_m, and c are the concentrations of the free solvent, the bound solvent, and the entire active solvent in the system. In particular, the presence of the complexes $[Gd(H_2O)_9]^{3+}$,[182] $[ThCl_4.2DMF]$,[94] and $[Al(DMF)_6]^{3+}$ [188] has been established using Eqn. (30). The solvation numbers found for Mg^{2+} are 5 in liquid ammonia[183] and 5 with respect to methanol and 5.7 (with respect to water) in water–methanol mixtures. The authors explained the deviation of the overall solvation number of magnesium from 6 by the partial incorporation of perchlorate ions in the coordination sphere[184]. The more vigorous solvation of Li^+ was established in a study of the NMR spectra of solutions of lithium and sodium salts in DMSO.[187]

In the course of solvation, it is possible to determine the chemical shift of the solvent also in the presence of paramagnetic ions, which influence the NMR spectra as a result of the exciting effect of the unpaired electron on the electronic structure of the solvent molecule. The chemical shift can then be defined as follows:

$$\delta = \frac{8\pi|\psi(0)|^2}{3p}c_{Solv}, \quad (31)$$

where $|\psi(0)|$ is the probability that the unpaired electrons are located near the solvent protons, c_{Solv} the concentration of the solvating solvent in solution, and p a quantity which includes the solvation number of the metal ion. The hexasolvates of nickel and cobalt(II) in acetonitrile have been detected with the aid of Eqn. (31).[189,190]

The X-ray diffraction method is promising for the detection of solvato-complexes. It has been stated[193-196] that there is an analogy between the structures of solids and the corresponding liquid systems. In particular, an octahedral environment has been demonstrated for copper, cobalt, and nickel cations in aqueous solutions[194]. The intensities of X-ray scattering by the solvent and the solution are usually determined by this method and data for the structure of the liquid are obtained by analysing the areas under the maximum of the atomic-electronic density distribution function. The position of the maximum on the distribution curve yields the average distance between the coordinated species. Having measured the area under the maximum on the experimental distribution curve, it is possible to determine the coordination number of the species. Although X-ray diffraction analysis does not always lead to an accurate determination of the bond lengths and valence angles, nevertheless, it has shown that hexasolvate cations are formed in 2–2.5 M $CuCl_2$ and $CoCl_2$ solutions in methanol, ethanol, and dimethylformamide. The chloride ions are then distributed in the secondary solvation shell[136,137].

In order to confirm the conclusions concerning the possible solvates in solution, their preparative study is extremely useful[128,197,198]. As in the physicochemical study of solutions, the synthesis of solvates from different solvents does not by any means always yield the same solvation numbers. This is due to the nature of the solvating solvent and the specific conditions governing the applicability of the research technique.

VI. THE DONOR ACTIVITY OF SOLVENTS

Data concerning the displacement of molecules of one solvent by another in solvato-complexes[92,200-202] can serve as a basis for the estimation of their donor activity. In this respect, valuable information is provided by infrared spectroscopy. For example, the decrease of the solvating capacity of alcohols with respect to Co^{2+} in the following sequence has been demonstrated on the basis of the shift of the absorption band due to the stretching vibrations of the OH group[203]:

$$\text{R} \quad CH_3CH((OH)CH_3 > (CH_3)_3COH > C_2H_5OH > CH_3(CH_2)_2OH \simeq CH_3(CH_2)_3OH > > CH_3CH(OH)C_2H_5 > CH_3(CH_2)_4OH.$$

The solvating capacity of solvents is sometimes estimated from their basicity:

$$H^+ + Solv \rightleftarrows HSolv^+.$$

The higher the constant K_a for the above equilibrium the higher the donor activity of the solvent. Thus the pK_a values for acetone (7.2) and acetonitrile (10.13), which in most cases behave as weakly solvating solvents, are appreciably lower [higher?] than that for dimethyl sulphoxide (0.00).[204]

The sequence of solvent basicities indicated above is consistent with the sequence of solvating capacities determined by other methods. Thus the following sequence in the variation of the donor activities of solvents has been established by NMR from the concentration variation of the chemical shift δ[Eqns. (30) and (31)] of the water protons in water–non-aqueous solvent mixtures in the presence of $AlCl_3$, $TiCl_4$, or $CoCl_2$:[205]

$$DMSO > CH_3OH > C_2H_5OH > [(CH_3)_2N]_2CO \simeq THF > (CH_3)_2CO \simeq CH_3CN \simeq C_4H_8O_2.$$

As was to be expected, the values of δ for the solvating solvent protons are not correlated with their dipole moments and the dielectric constant ϵ.

To compare the abilities of various ions to combine with the same solvent, Izmailov[206] determined their solvation energies assuming them to be similar for isoelectronic ions and assuming that they decrease with increase of the square of the principal quantum number (n^2) of the vacant orbitals. The determination of the solvation energy of the ion reduces to the extrapolation of the almost linear function

$$\Phi = \frac{1}{2}[Q_{ion} + (Q_{Hal} - Q_{M^+})]. \quad (32)$$

The calculations are performed for $n = 3$, 4, 5, or 6 and Eqn. (32) is then extrapolated to $1/n^2 = 0$. In this case, M^+ is the alkali metal ion. The corresponding sums and differences are determined from the e.m.f.'s of cells with and without transport:

$$\lim \Phi = Q_{ion} \text{ when } \frac{1}{n^2} \to 0.$$

The values of Q for M^+ and Hal^- in water, ammonia, methanol, and ethanol were calculated from the experimental data. The results of the calculation for the same metal ion lead to the conclusion that the donor activities of the solvents vary.

A comparative assessment of the solvating capacities of the solvents can be made also by comparing the equilibrium constants for the dissolution of substances in mixed solvents evaluated by Eqn. (12). Thus it has been shown for dioxan–solvent mixtures[128,190] that the solvating capacity varies in the following sequence: ethanol < methanol < dimethylformamide.

Table 3 shows that the negative logarithms of the constants for the equilibrium

$$CuCl_2 + 2Solv \rightleftarrows CuCl_2 \cdot 2Solv$$

in dioxan solution increase from dimethylformamide to ethanol. According to the pK value, water follows ethanol in this sequence, which appears to show that its solvating activity is weak. This can be accounted for by the ability of dioxan[207] to form strong hydrogen bonds with water. Bearing this in mind, the method under consideration cannot be regarded as universal for the estimation of the donor activities of solvents. The method based on the comparison of the formation constants of solvates calculated by Eqn. (16) and other methods involving the use of an inert solvent suffer from the same disadvantage.

Table 3. The negative logarithms of the formation constants of the solvates $MCl_5 \cdot 2Solv$ in dioxan solutions.

Solvent	ε	pK		
		$CuCl_2$	$CdCl_2$	$NiCl_2$
Methanol	32.6	2.30	3.67	2.62
Ethanol	24.3	2.36	3.75	2.72
Dimethylformamide	36.1	1.44	3.58	2.51
Water	81	2.89	4,36	—

Depending on the donor activity of the solvent, the heat of the solvation reaction

$$A + mSolv = A \cdot mSolv + \Delta H$$

will be different. Makarova and Pominov demonstrated in this way the different solvating capacities of alcohols, acetone, and acetonitrile in relation to $CoCl_2$.[208] However, here too one cannot estimate the absolute solvent activities. For this reason, Lindquist and Zackrisson[209] suggested that the donor capacity be determined relative to a standard acceptor ($SbCl_5$ or $SnCl_4$) with which the given donor is combined in 1 : 1 proportions (this should entail the same entropy change). The authors established calorimetrically the following series of solvents based on their decreasing donor capacities:

$$(CH_3O)_3PO > (CH_3)_2SO > (CH_3)_2CO > POCl_3 > SOCl_2.$$

Gutmann and Wychera used the same considerations and introduced the concept of the donor number, which is understood as the numerical value of the enthalpy of addition of a solvent molecule to a molecule of antimony pentachloride in dichloroethane[210]:

$$DN_{SbCl_5} = -\Delta H_{Solv \cdot SbCl_5}. \quad (33)$$

Table 4 shows that the dielectric constant and the donor number of the solvent do not vary in parallel. This shows that the covalent interaction predominates over the electrostatic interaction in solvation processes.

Table 4. The donor numbers and the dielectric constants of certain solvents[51].

Solvent	ε	DN_{SbCl_5}	Solvent	ε	DN_{SbCl_5}
1,2-Dichloroethane	10.1	—	Ethyl ether	4.3	19.2
Nitromethane	35.9	2.7	Tetrahydrofuran	7.6	20.0
Acetonitrile	38.0	14.1	Tributyl phosphate	6.8	23.6
Tetramethylene sulphone (sulpholane)	42.0	14.8	Dimethylformamide	36.1	26.6
Acetone	20.7	17.0	Dimethyl sulphoxide	45.0	29.8
Ethyl acetate	6.0	17.1	Pyridine	12.3	33.1
Water	81	18	Hexamethylphosphoramide	30.0	38.8

A calorimetric study of the solvation of ECl_4, where E = Zr or Hf, in nitromethane established[211] the following series based on the donor activities of solvents:

$$(CH_3)_2SO > (CH_3)_2NCOH > CH_3CN > CH_3NO_2,$$

It agrees with the data in Table 4.

Nevertheless, the same solvent can manifest different solvating capacities with respect to different solutes. Because of this, the solvating capacities of solvents cannot be treated as non-relative quantities and Gutmann's donor numbers cannot be treated as absolute solvent characteristics. For example, acetonitrile does not possess a high capacity for the formation of compounds with Na^+, Pb^{2+}, and Ca^{2+} ions, but it forms solvato-complexes with $AlCl_3$, $GaBr_3$, BF_3, $SnCl_4$, and $TiBr_4$ (without substituting halide ions).[87]

In contrast to the available donor numbers of acetone, ethyl ether, and other ethers (Table 4), the energy of solvation of $NbCl_5$ by acetonitrile (−37.8 kcal) is much higher than the energy of solvation by ethyl and butyl ethers (−21.0 kcal), dioxan, and esters[212]. These findings suggest that the donor activities of solvents are determined not only by their individual properties but also by the specific features of their interaction with the solute.

For a more objective determination of the donor activities of solvents, one can isolate the solvates and determine thermochemically the solvation energies[128,130]. Such a calculation can be performed in connection with the determination of the integral heats of solution of the solvate (ΔH_3), the substance in the absence of the solvating

solvent (ΔH_2), and the corresponding solvents (ΔH_1) in water or another liquid in which all the substances enumerated dissolve. The solvation energy can be calculated from the equation

$$\Delta H = \Delta H_1 + m\Delta H_2 - \Delta H_3. \quad (34)$$

Table 5 shows that the solvating capacity of dimethylformamide is highest, water occupying the second place as regards donor activity. The value of the hydration energy obtained for $CuCl_2 \cdot 2Solv$ is somewhat difficult to understand[130].

Table 5. The solvation energies (kcal) of certain metal chlorides.

Solvent	$CuCl_2 \cdot 2Solv$	$CaCl_2 \cdot 2Solv$	$ZnCl_2 \cdot 2Solv$	$NiCl_2 \cdot 2Solv$
Methanol	7.41	4.16	8.20	5.68
Ethanol	7.32	4.49	—	5.62
Dimethylformamide	10.32	7.14	13.13	9.78
Water	7.20	6.10	—	8.47

VII. COMPLEX FORMATION REACTIONS IN NON-AQUEOUS AND MIXED SOLUTIONS

In contrast to aqueous solutions, in the interaction of ions in non-aqueous solutions a multiplicity of anomalies are observed. In the presence of water, the stability of the halides of $s^2p^6d^{10}$ and $s^2p^6d^{10}s^2$ cations decreases in the sequence $I^- > Br^- > Cl^-$. On the other hand, according to a number of workers[213-215], the variation of the conductivities of halides in pyridine solutions follows the opposite sequence. However, if one employs a series of salts with the same anion, then their conductivities in pyridine decrease in the sequence

$$Ag^+ > Li^+ > K^+ > Na^+,$$

i.e. in conformity with the ability of the cations to form pyridine complexes. Only the position of potassium in this series is somewhat incomprehensible, since K^+ is usually less solvated than Na^+. Since potassium ions form relatively unstable solvato-complexes with pyridine, the interaction of $AgNO_3$ with KSCN and even with K_2HgI_4 in this solvent takes place only in consequence of the precipitation of KNO_3.[40,41]

The role of non-aqueous solutions in complex-formation processes involving readily hydrolysed ions is especially great. In particular, the study of the majority of metal selenocyanates involves considerable difficulties. The C⋯Se bond in the selenocyanate ion $N \overline{\overline{\cdots}} C \overline{\overline{\cdots}} Se^-$ is weak and the ion therefore decomposes with elimination of selenium both under the influence of light and in an acid medium. It is quite reasonable that $NCSe^-$ should be stabilised when the electron density of selenium is increased, i.e. when the selenocyanate ligand is bound to a central atom with an enhanced π-donor capacity. Mainly $s^2p^6d^{10}$ ions in the Fifth and Sixth Periods of the Periodic System possess this property. This is why it is possible to detect in aqueous solutions the selenocyanate complexes of silver, mercury, cadmium, gold and one or two more metals with electronic structures similar to that indicated above. On the other hand, La^{3+}, Cr^{3+}, V^{3+}, Mn^{2+}, Zr^{4+}, etc. exhibit only a weak capacity for the formation of dative bonds and, in contrast to the metals listed above, form only unstable E–NCSe linkages, which cannot compete with the $E-OH_2$ or E–OH linkages arising in consequence of hydrolysis. A decrease of pH results in the decomposition of the selenocyanate ligand in such systems and the efficiency of the formation of transition metal selenocyanates can therefore be increased only in non-aqueous solutions[216,217]. Similar effects occur in the study of complex-formation reactions between polyvalent cations and nitrite ions and other weak acid anions[218].

Interesting data have been obtained for the influence of solvents on the complex-formation reaction[61] when silver halides are dissolved in the presence of $AgNO_3$ and $AgClO_4$.[103] The Ag_3I^{2+} dissociation constant varies as a function of the nature of the solvent in the following way:

$(CH_3)_2CO$	H_2O	$(CH_3)_2SO$	CH_3CN
10^{-19}	$10^{-14,1}$	$10^{-10,8}$	10^{-10}

It is seen from these results that dimethyl sulphoxide, in its role as an active solvating agent (with a donor number of 29.8), promotes to a greater extent than water the dissociation of the complex, while acetone tends to stabilise it, although the donor number of acetone is close to that of water (Table 4). On the other hand, acetonitrile has a much lower donor capacity (a donor number of 14.1) and the stability of the complex Ag_3I^{2+} in this solvent is lower than in other solvents. Similar facts have been quoted by Surpina et al.,[219] who noted that in acetonitrile the interaction of $NbCl_5$ with azoles and Schiff bases proceeds with greater difficulty than in esters. This demonstrates yet again that Gutmann's donor numbers are relative[51].

Like dissolution, complex formation depends wholly on the solvation of the central ion and the ligands. The greater the strength of their bonds with solvent molecules, the more difficult it is to make them come together. On the other hand, if the solvent molecules can be removed from the solvato-complexes by binding them to another solvent, then an interionic linkage is formed more readily. This is why it has been possible to detect in aqueous dioxan solution the complex $[Cd(SCN)_6]^{4-}$, which is not formed in water, other conditions being equal[95]. The study of complex-forming systems in mixed and purely non-aqueous solutions permits the formulation of the rule governing the composition of the complexes: the addition to an aqueous solution of a donor-active solvent at moderate and high concentrations of the latter permits the formation of complicated complexes, but, following the attainment of a concentration of 90—100%, the number of acido-ligands in the coordination sphere falls again[95,173,220]. This rule operates in the study of not unduly stable complexes and can be explained by the fact that, at moderate concentrations of the non-aqueous solvent, the latter binds water and facilitates the incorporation of acido-ligands in the coordination sphere in place of water. When its concentration is higher, the non-aqueous solvent itself combines with the central atom and prevents the addition of other ligands.

As a result of the formation of stable dioxan–water compounds[205,220], the activity of water falls and lead–antimony alloys cease to be corroded in the mixed solvent[89]. An increased solvation effect prevents the formation of nickel and cobalt hexaselenocyanate and even tetraselenocyanate complexes in pure dimethylform amide[221], of anionic copper(II) complexes in dimethyl sulphoxide[222],

and of molybdenum(V) complexes in hexamethylphosphoramide[223]. Tin forms only $[Sn(NCS)_3]^-$ in dimethylformamide, while the complex in methanol and acetonitrile is $[Sn(NCS)_4]^{2-}$.[174,224] On the other hand, cadmium combines with four thiocyanate ligand species in methanol and dimethylformamide and with six such species in acetonitrile. The stability of cadmium, indium, and tin thiocyanate complexes increases on passing from dimethylformamide to acetonitrile via methanol[225,226].

The examples examined above show that, contrary to the conclusion reached in the literature[227,228], the chemical nature of the solvent has a greater influence on complex formation than the dielectric constant. In solvents which form stable solvates with metal ions, the combination of these ions with other ligands proceeds with greater difficulty. In acetonitrile, $ZnCl_2$ behaves as a stable complex because Zn^{2+} is only weakly solvated by the molecules of this solvent. As a result, the variation of the zinc electrode potential with the concentration of such a solution is anomalous[30]. In acetonitrile, zinc forms anionic chlorocomplexes more readily than highly solvated mercury(II). $HgCl_2$, which forms stable solvato-complexes is converted into $[HgCl_4]^{2-}$ in acetonitrile with greater difficulty than in water[229], although the donor number of water is higher[51].

Depending on the nature of the solvent, the sequence of ligands in the series based on the stability of the given metal complexes can also change. For example, the stability of cadmium and lead halide complexes in alcohols and water increases from the chlorides to the iodides, while in dimethylformamide the variation is in the opposite sequence[230-233]. The inversion of the stability sequence of lead halides can be readily accounted for by the enhancement of the solvation of the anions by dimethylformamide and by the increase of their radii. That this is indeed so can be seen from the fact that NaI dissolves more readily in dimethylformamide (and formamide) than NaCl. Furthermore, the enthalpies of solution of metal halides in DMSO vary in the sequence[234]

$$Cl^- > Br^- > I^-.$$

The study of mercury(II) halides in DMF[235], DMSO[236], and dimethylacetamide (DMA)[237], which have very similar donor numbers, has revealed an appreciable variation of the stabilities of these complexes in the following sequence of solvents:

$$DMSO < DMF < DMA < H_2O.$$

The explanation of the dependence of the complex formation reaction on the nature of the solvent taking into account solvation has been confirmed in numerous experiments[220-226,238-244]. The electronic absorption spectrum of the $Co(ClO_4)_2$–NaNCSe–DMF solution with a monomolecular or bimolecular proportion of selenocyanate has a band at 525 nm, i.e. in the region corresponding to the absorption by the octahedral complexes $[Co(NCSe)(DMF)_5]^+$ formed (only the optical density increases). On the other hand, in the presence of a large excess of $NCSe^-$, a new band appears at 625 nm,[243] which is due to the tetrahedral complex $[Co(NCSe)_4]^{2-}$.

In choosing a solvent promoting complex formation, one must take into account both its solvent power with respect to the reactants and the nature of its interaction with the complex formed. The most marked effect of complex formation can be achieved when the donor activity of the solvent is low. For example, in acetone mercury(II) nitrate behaves as a stable complex[242]. Whereas, in acetone, acetonitrile, and other similar solvents Pb^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and In^{3+} ions form readily hexa- and tetra-halogeno- and hexa- and tetrathiocyanato-complexes, in dimethylformamide and dimethyl sulphoxide complexes with low coordination numbers are formed even in the presence of an excess of acido-ligand[221,224,244]. In DMSO, even the proton is very strongly bound[245].

The study of the Raman laser spectra and the freezing points of the solutions showed that, depending on the concentration, phosphorus pentachloride forms the following complexes in acetonitrile, nitromethane and nitrobenzene:

$$2PCl_5 \rightleftarrows [PCl_4]^+ + [PCl_6]^- \qquad (>0.03 \text{ M})$$

or

$$PCl_5 \rightleftarrows [PCl_4]^+ + Cl^-. \qquad (<0.03 \text{ M}).$$

On the other hand, in solvents such as benzene and carbon tetrachloride, it behaves as the neutral complex $[PCl_5]$.[246]

By selecting solvents in accordance with the above relations, it is possible to detect in non-aqueous solutions numerous complexes which are not formed in aqueous solutions.

VIII. THE INFLUENCE OF SUPPORTING ELECTROLYTE IONS AND "STEPWISE" COMPLEX FORMATION

In many non-aqueous solutions, the initial electrolytes exist as ion pairs, but it is nevertheless possible to demonstrate in such solutions the formation of complexes with substances capable of forming strong bonds with the ions of the given electrolyte. The composition of the complexes in such systems can be readily determined by physicochemical methods and it is even possible to calculate conventional equilibrium constants for the complex-formation reactions. However, depending on the nature of the initial salt of the given metal, the equilibrium constants are not the same in the particular solvent. Thus, the formation of the complex $[Co(NCSe)_4]^{2-}$ with a conventional equilibrium constant of 7.0×10^{-14} was established in the $Co(ClO_4)_2$–NaNCSe–$(CH_3)_2CO$ system[240], while in the presence of cobalt nitrate the equilibrium constant for the same complex proved to be higher.

On the other hand, if the initial salt includes anions which can be bound strongly to the given cation, then the determination of the composition of the complexes yields a low number of ligand species incorporated. This can be explained by the formation of mixed complexes. In particular, a study of the $MoOCl_3$–NaNCSe–$(CH_3)_2CO$ system established the existence of the complex $[MoOCl_3(NCSe)]^{2-}$, which is then converted into $[MoOCl_2(NCSe)_3]^{2-}$ and $[MoOCl(NCSe)_4]^{2-}$.[247]

The formation of a large number of mixed complexes in both aqueous[248] and non-aqueous[245-253] solutions has now been demonstrated. In many instances, mixed complexes are formed more readily than homogeneous complexes. This is apparently due to an energy gain in consequence of the formation of an asymmetric structure, as happens in platinum complexes in accordance with the *trans*-influence principle[254]. When mixed complexes are formed, both the mutual influence of the ligands and the nature of the solvent play an extremely significant role. It is appropriate to note here that the $O(C_2H_5)_2$ molecule combines with BF_3 more readily than the fluoride ion[256,257] in consequence of "chemical symbiosis".[255]

Attempts are sometimes made to explain why mixed complexes are favoured by thermodynamic factors on the basis of the concept of hard and soft acids and bases[13]. In terms of Pearson's rule, the bonds formed by Be^{2+} and

Al^{3+} with acetate ions as well as those formed by the proton with OH^- and F^- should be regarded as ionic, the hydride ion should readily combine with Hg^{2+}, and the Cl^- ion in complexes should behave like the fluoride ion.

In reality this is not so. The formation of hydrides is not characteristic of silver, gold, and mercury. The chloride ion behaves similarly to bromide, iodide, and even thiocyanate. This is why there is a possibility of their mutual substitution with formation of mixed complexes [248,258,259].

For example, the formation of mixed complexes of the type $[E(NCS)_2Cl_2(Solv)_2]$ by zirconium and hafnium can be demonstrated by conductimetric study of the ECl_4–NaNCS–CH_3CN system [260] and $[E(OH)_2(NCS)_2(Solv)_2]$ can be detected when $E(OH)_2Cl_2.7H_2O$ is ground with NH_4NCS in the presence of tributyl phosphate or cyclohexanone [261]. The fact that these are coordination compounds is confirmed by infrared spectra.

If no account is taken of the formation of mixed complexes, then the result of physicochemical study of the corresponding system might lead to the conclusion that the simplest complexes are produced. In reality coordination saturation always takes place in solution owing to the formation of mixed complexes.

The view that complex formation takes place in steps has been firmly established in the literature [135,262-266]. The appearance of each new complex is attributed solely to the kinetic factor, i.e. to the displacement of the equilibrium caused by the increase of ligand concentration. However, this approach is valid only for relatively unstable complexes and provided that account is taken of the incorporation of solvent molecules in the coordination sphere when the E–L and E–Solv bond energies are similar. On the other hand, if $Q(E\text{-}L) \gg Q(E\text{-}Solv)$, then homogeneous complexes EL_n with $n \gg 1$ may be formed even at low ligand concentrations. Under these conditions, only complexes corresponding to the greatest decrease of Gibbs free energy are as a rule produced. Consequently, the thermodynamic and not the kinetic factor is more significant in the formation of stable complexes. Thus when Cu^{2+} interacts with ammonia, the first four NH_3 molecules are bound to the central atom equally strongly, while the fifth molecule combines less effectively [135]. This fact is satisfactorily accounted for by the Jahn–Teller theorem.

Bearing in mind that the incorporation of new ligand species in the complex results in its rearrangement, strengthening some and weakening other bonds, the breakdown of a rigorous sequence based on the increase in the number of species in the complexes with increasing concentration of the corresponding ligand, is quite reasonable. This is why Bjerrum's method has frequently proved unsuitable in the study of non-aqueous solutions [135]. In its general form, this method appears to give a positive result and the relation defined by Eqn. (18a), in which [Solv] has been replaced by the concentration of the acido-ligand, is smooth with distinct horizontal plateaux indicating a high probability of individual complexes. For example, only complexes with $m = 2$, 4, or 6 have been clearly detected in the $E(ClO_4)_2$–NaNCSe–CH_3OH systems, where E = Co or Ni.

It is very remarkable that in methanol, where the stability of nickel selenocyanate complexes is low, the formation function varies more uniformly than in acetone [243]. The formation curve for the cobalt complex reveals the presence of steps also in methanol for $NCSe^- : Co^{2+} = 2$, 4, and 6. [240] More distinct inflections occur in the curve for the acetone solutions, where the stability of the complex is higher.

In contrast to the dimethylformamide solution, an intense band at 400 nm and a weak band at 630 nm appear in the spectrum of the acetonitrile solution already for $Co^{2+} : NCSe^- = 1 : 1$. [243] Bjerrum's formation curve clearly reveals only two steps with $\bar{n} = 1$ and $\bar{n} = 4$. Palladium coordination numbers of 4 and 2 are most clearly manifested in the $PdCl_2$–NaNCSe–DMF system. The latter corresponds to the mixed complex $[PdCl_2(SeCN)_2]^{2-}$. [267]

The formation of only HgI_2 and $[HgI_4]^{2-}$, which are thermodynamically more stable than HgI^+ and HgI_3^-, can be demonstrated in the $Hg(ClO_4)_2$–NaI–solvent systems, where the solvent is an alcohol, acetonitrile, etc.

In dimethyl sulphoxide, Fe^{3+} ions react with CN^- to form only $Fe(CN)_2^+$, $Fe(CN)_3$, and $Fe(CN)_4^-$, or, more precisely, mixed complexes, while the reaction with the fluoride ion yields $[FeF_4(DMSO)_2]^-$. [268] It is of interest that in such cases there are no complexes with six acido-ligands. On the other hand, cobalt chloride forms two complexes in dimethylacetamide: $[CoCl(DMA)_5]^+$ and $[CoCl_3(DMA)_3]^-$. [269]

A series of complexes up to $[E(NCS)_8]^{4-}$ were detected in a study of ECl_4–KNCS systems in acetonitrile and dimethylformamide by Bjerrum's method [260], but they are not all equally probable. This is why the presence of $E(NCS)_4$ is established in experiments involving isomolar series of solutions in dimethylformamide, while $[E(NCS)_6]^{2-}$ is found in acetonitrile. The higher solvating capacity of dimethylformamide under the same conditions leads to the formation of complexes with a smaller number of NCS ligand species than in acetonitrile. It would appear that $E(NCS)_4$ are simple complexes with a coordination number of 4. However, this is not the case, because the complexes $E(NCS)_4.4DMF$, where according to infrared spectra the NCS groups and solvent molecules are coordinated to the metal atom, are isolated from solution [260].

The study of non-aqueous solutions demonstrated the possibility of the coordination of ions which do not usually form complexes in aqueous solutions. In particular, the nitrate ion hardly behaves as a ligand in consequence of its hydration in dilute aqueous solutions. Only at high concentrations of NO_3^- does the potential of the lead electrode decrease [270]. In acetone and even in alcohols, which combine with the nitrate ion less effectively than water, the nitrate ion ceases to be indifferent [44,60]. The coordination compound $[K_2Pb(NO_2)_3(NO_3)]$, in which the nitrate ions behave as a ligand, can be obtained from methanol [271].

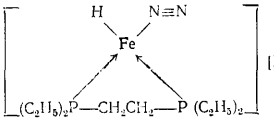
Bearing in mind that in many non-aqueous solutions the so called indifferent anions are only slightly dissociated from the corresponding complex-forming agent, in the determination of the compositions of the most involved anionic complexes, one must employ series of solutions with a constant concentration of the initial salt. The study of isomolar series in many instances leads to the determination of the simplest complexes, which are in reality mixed complexes [267,272,273]. The complex $[Pd(SeCN)_4]^{2-}$ has been detected spectrophotometrically in the $PdCl_2$–NaNCSe–DMF system at a constant palladium concentration and variable NaNCSe concentrations, while in the isomolar series of solutions only $[PdCl_2(SeCN)_2]^{2-}$ was detected [267]. Similar results have been obtained also for thorium thiocyanate [273].

Valuable information can be obtained by studying complex formation using the solubility method. In contrast to other methods, the application of which requires a constant concentration of the central atom, in this case both the concentration of the ligand and of the central atom is varied from mixture to mixture. This is why in systems where the ligand and the central atom

are capable of forming strong bonds, the solubility method leads to the detection of complexes with a lower component ratio than other methods. This rule[220,274,275] has been confirmed in a large number of experiments[274-283]. While the anionic complexes $[Pb(XCN)_6]^{4-}$ have been detected potentiometrically in methanol[274,282], only the complexes $[Pb(XCN)_4]^{2-}$, where X = S or Se, have been detected by the solubility method and in acetone only the complexes $[Pb(XCN)_3]^-$ have been found[277,283]. In aqueous acetone solution with an acetone concentration of 7 M, the complex $[Ag(SCN)_4]^{3-}$ has been detected potentiometrically at a constant silver concentration, while, according to the results obtained by the solubility method, the complex $[Ag(SCN)_2]^-$ predominates in acetone[277]. Copper[279] silver[280], palladium[267], mercury(II),[281] and lead[282-284] iodides and selenocyanates behave similarly.

IX. NON-AQUEOUS SOLUTIONS IN PREPARATIVE INORGANIC CHEMISTRY

The use of non-aqueous solutions has greatly extended the scope of inorganic synthesis in the field of organometallic compounds[285-287], metal polycarbonyls and their derivatives[288], metal and semimetal hydrides[289-291], salt-like inorganic compounds which are extremely sensitive to water and atmospheric oxygen[292,293], boron compounds with organic ligands[294], and coordination compounds of transition metals with molecular nitrogen[295-297] and carbon dioxide[298]. For example, the iron compound[294]



has been obtained in acetone.

The reaction of cyclopentadiene with metallic potassium in benzene was discovered as early as the beginning of the present century[285]. On the other hand, NaC_5H_5 was not obtained until 50 years later in DMF, THF and 1,2-dimethoxyethane. The so called sandwich compounds of transition metals were synthesised by exchange reactions between NaC_5H_5 and metal halides in tetrahydrofuran or other similar solvents[300] and then also mixed compounds, for example $C_5H_5Fe(CO)_3$.[301] The reactions of metal polycarbonyls with halides[302], isonitriles[291,300], amines, and cyanides[303,304] made it possible to obtain many mixed coordination compounds.

Since several reviews have been devoted to the problem of the synthesis of the above and other compounds, one need consider only the general characteristics of the preparation and crystallisation of coordination compounds from non-aqueous media taking into account solvation effects. In particular, diborane reacts with LiH to form $LiBH_4$ only because the lithium ion can be solvated by ethyl ether, but there is no interaction between diborane and NaH.[305]

Interesting data have been obtained for the synthesis of coordination compounds from boranes[306-308]. Thus diborane reacts with sodium amalgam in ether to form the triboranide NaB_3H_8 (together with sodium tetrahydroborate), while tetraborane reacts with ammonia to give $[(NH_3)_2BH_2][B_3H_8]$ and $[H_3NB_3H_7]$,[306] and with $(C_6H_5)_3P$ to give $[(C_6H_5)_3PB_3H_7]$. Solvents with a higher donor activity than ether decompose the triborane skeleton[308,309].

Another no less important factor concerns the structure of the solvents in which the synthesis is carried out. While the dissolution of salts in water reduces initially to the formation of the hydrates of cations and anions within the limits of the water structure, the majority of even dilute non-aqueous systems consist of combinations of mixed solvato-complexes, where the immediate environment of the cation consists not only of solvent molecules, but also of salt anions behaving as ligands.

At a high concentration of the non-aqueous solution, its structure approaches increasingly that of the corresponding solvate or the pure solute, depending on the solvating properties of the solvent. If in the given solution solvent molecules are not bound very strongly to salt ions, the introduction of another solvent having the same solvating capacity but forming hydrogen or dipolar bonds with the first solvent can lead to the formation of salt crystals without solvent molecules. This is very important for the synthesis of anhydrous salts such as nitrates, perchlorates and others, the hydrates of which undergo hydrolytic decomposition on heating.

When salt solutions in solvents with a high donor activity (DMSO, DMF, etc.) are concentrated, the formation of crystalline structures is preceded by the appearance of comparatively weak forces in the interaction between anions and the molecules of the solvate environment or by electrostatic attraction to the solvated cation. Solvates with a comparatively large (in the case of weakly coordinated anions) or small (if the anions give rise to fairly stable coordinate bonds) content of solvent molecules should be formed from such a solution. For example, copper, cobalt, zinc, aluminium, gallium, indium and many other metal nitrates and perchlorates crystallise in the form of the complexes $MB_n.6Solv$, e.g. $Al(ClO_4)_3.6DMF$,[188] while the halides, thiocyanates, and selenocyanates of these metals form crystals of $MB_2.4Solv$[221,224] and $ML_3.3Solv$ and $CuCl_2.2Solv$.[222] Solvates of this type are produced from a solvent with a lower donor activity also by nitrates and even perchlorates: $Zn(NO_3)_2.2CH_3CN$, $Sn(ClO_4)_2.2CH_3CN$, $Ni(NO_3)_2.2CH_3CN$,[311] and $Ni(ClO_4)_2.2CH_3CN$.[312]

In contrast to the perchlorates, an increase of the concentration of the solution leads in the case of halides, thiocyanates, and selenocyanates to a more appreciable substitution of solvent molecules in the solvation shell of the cation by the anions. Such mutual ordering of the ions and solvent molecules with increase of concentration is completed by the separation from the solution of solvates with a reduced content of the solvent, for example: $CdCl_2.2(CH_3)_2CO$,[313] $InBr_3.3N_2H_4$,[314] $ZnPy_2(NCSe)_2$,[315] $Co(NCS)_2.3N_2H_4$,[316] and $Sn(NCO)_2.2C_4H_8O_2$.[316] If a solvent with a high σ-donor activity hinders crystallisation, then active acido-ligands readily enter into the inner sphere and therefore give rise to crystals with a low content of the solvent: $SbCl_3.CH_3COOH$,[317] $SnBr_4.CH_3COOH$,[318] $In(NCS)_3.0.5CH_3CN$,[225] $Sn(NCS)_2.OP(C_6H_5)_3$,[319] $Ga(NCO)_3.THF$,[316] and $MoOCl_3.2THF$.[310]

When the anion is strongly bound to the cation, the solvent molecules may be completely displaced by the anions. The crystallisation structure then involves short-range order with participation of desolvated ions, which is observed in the formation of the solid phase in an ethereal solution of HgI_2 or $Hg(OCN)_2$[99] and in a formamide solution of $PbCl_2$.[320] Potassium chloride crystallises from dimethylformamide in the unsolvated form and $MgCl_2$ with four solvent molecules[131]. Consequently, the influence of the solvent, hindering crystallisation, is regulated both by the strength of the bonding between its molecules

and ions and by interionic forces. As a rule, by selecting the right solvent, it is easy to synthesise many simple and coordination compounds unstable in the presence of water, for example, selenocyanates[216,217,321-326], cyanates[327-330], and mixed coordination compounds each containing two or more different ligands[327-336].

Since the introduction of a non-aqueous solvent miscible with water weakens hydrolysis, the stability of readily decomposed compounds of certain metals can be appreciably increased even in mixed solutions. The influence of the non-aqueous solvent is more appreciable when the E–L bonding is weaker and hydration of the central ion competes appreciably with it. This is why transition metal and aluminium, gallium, bismuth, etc. isothiocyanates, cyanates, and particularly selenocyanates, which are unstable in water, can be isolated from non-aqueous or even aqueous–non-aqueous systems. The use of non-aqueous solvents in the case of lanthanides makes it possible to prevent the decomposition of the selenocyanate ion. However, the solvation of cations is not then prevented. In order to weaken the influence of the latter and to accelerate the separation of the corresponding compounds, it is useful to employ the chelation effect. In particular the following reactions

$$3\,KNCSe + RCl_3 = 3\,KCl + R(NCSe)_3,$$

where R = Sc, Y or lanthanides, can be achieved in a series of solvents. However, after the separation of KCl, $R(NCSe)_3$ is virtually impossible to crystallise in view of the high stability of the complex species $[R(Solv)_n]^{3+}$. If 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) and diantipyrinylmethane (dant) are introduced into such a solution, compounds of the type $[R(NCSe)_3(bipy)_2]$, $[R(NCSe)(dant)_4](NCSe)_2$, and $[R(NCSe)_3(phen)_3]$ are formed immediately[325-327].

The synthesis of zirconium and hafnium selenocyanates $[E(NCSe)_4(bipy)_2]$ from acetonitrile solutions[321], the thiocyanates $R(NCS)_2Ox.6CH_3OH$ from methanol solutions[334], and the complexes MB_2Ox,[335,336] where $B = NO_2^-$, NO_3^-, Cl^-, NCS^-, or ClO_4^-, R = lanthanide, Al, or Ga, and Ox is the 8-hydroxyquinoline residue, is based on the same principle.

With cations which form less stable solvato-complexes than lanthanides, it is possible to obtain many selenocyanates and mixed coordination compounds $Cat_n[E(NCX)_mB_l]$, where X = O, S, or Se, B = Br, I or Py, and Cat are univalent cations, even from acetone[326-331], methanol, acetone–dioxan, and aqueous methanol[332] solutions.

When the double decomposition reaction between ECl_n and AgNCO is carried out in methanol and AgCl is separated, then, using the chelation effect, it is possible to obtain $[In(NCO)_3phen]$, $[In(NCO)_3bipy]$, $[In(phen)_3](NCO)_3$,[329] $[E(NCO)_2(phen)_2]$, and $[E(NCO)_2(bipy)_2]$,[332,333] where E = Mn, Co, Ni, Zn, or Cu. When a solution containing large outer-sphere cations is added to a methanol solution of $In(NCO)_3$, the compound $Cat[In(NCO)_4]$ is formed[324]. $K_n[Pb(NCO)_{n+2}]$ and $K_2[Pb(NCO)_2(NCS)_2]$,[337] where n = 1, 2 or 3, can be obtained from dimethylformamide.

When $(C_5H_5)_2ZrCl_2$ was allowed to react with AgNCO, the compound $[(C_5H_5)_2Zr(NCO)_2]_2O$ was obtained from acetone solution, and, when gaseous HNCO was passed into the above solution of dicyclopentadienylzirconium chloride, the compound $[(C_5H_5)_2Zr(NCO)_2]$ was formed[338]. The latter as well as $[(C_5H_5)_2Zr(NCS)_2]$ can be obtained also by double decomposition reactions of $(C_5H_5)_2ZrCl_2$ with AgNCO or AgSCN, but in this case in dichloroethane solution[339]. In the latter case the stabilisation of zirconium cyanates is achieved by sandwich-type chelation. It is remarkable that in acetone HOx reacts with $ThCl_4$ to give only the adducts $ThCl_4.mHOx$, where m = 1, 2, 4 or 6, with different coordination numbers. Infrared spectra failed to reveal the presence of free HOx in these compounds; its addition takes place via the nitrogen atom. On the other hand, when a solution of $Th(NCS)_4$ is prepared in the same solvent and an acetone solution of HOx is added, a compound having a different composition is produced: $[Th(NCS)_n(Ox)_{4-n}].nHOx$.[340]

Depending on the nature of the solvent, the same starting materials interact differently. For example, the reaction of $Ni(NCS)_2$ with $[(C_6H_5)_4P]N(CN)_2$ or $[(C_6H_5)_4As]N(CN)_2$, taken in proportions of 1 : 2, results in the formation of $(Cat)_2\{Ni[N(CN)_2]_2(NCS)_2\}$ in methanol and $(Cat)\{Ni[N(CN)_2]_3\}$ and $(Cat)_2[Ni(NCS)_4]$ in acetone[341].

On the other hand, when $Co[N(CN)_2]_2$ interacts with $[(C_6H_5)_4P]NCS$, $(Cat)_2\{Co[N(CN)_2]_2(NCS)_2\}$ is formed in acetone and $(Cat)_2\{Co[N(CN)_2](NCS)_3$ and tetrathiocyanatocobaltate(II) in methanol[342]. [This should be Ref. 341 (Ed. of Translation.]

The influence of the solvent on the structure of the compounds formed merits special attention[218]. In particular, the same starting materials KNCO and AgNCO form $K[Ag(NCO)_2]$ following their interaction in DMF and potassium difulminatoargentate(I) $K[Ag(CNO)_2]$ after interaction in acetone, i.e. a compound having a different structure[343].

X. CONCLUSION

The present development of industry and the associated reduced amount of fresh water available per member of the population have stimulated attempts to place chemical industry on a non-aqueous basis[344]. The problem of solid-phase reactions, the use of fused salt systems, for example the synthesis of monosilane from $SiCl_4$ and LiH in the KCl–LiCl eutectic mixture[345], and of other solutions to carry out various chemical processes with subsequent regeneration of the solvent is already extremely urgent.

Compared with water, the nature of the chemical reaction[50] and the properties of the various substances[223,239] are radically different in many non-aqueous solvents. Thus the solubilities of silver halides in liquid ammonia, acetonitrile, DMSO, and pyridine are much higher than in water. Solubility determinations[346] have shown that the solvent power in relation to AgCl, AgBr, and AgI decreases in the sequence

$$CH_3CN > (CH_3)_2SO > (CN_3)_2CO > C_2H_3NO_2 > CH_3OH.$$

It is interesting that this sequence is inconsistent with the variation of the donor numbers of solvents (Table 4). This is very important both for the solution of preparative problems (for example, the synthesis of anhydrous salts[347]) and in connection with the use in homogeneous catalysis of certain compounds insoluble in water.

The donor (acceptor) activity of the solvent is the most important factor (compared with others) determining its influence on the corresponding processes. However, such activity may vary with the nature of the solute. The higher the activity, the greater the difficulty of the interaction of the complex-forming agent with other ligands and the greater the ease of formation of mixed solvato-complexes. In the presence of two different acido-ligands, mixed complexes involving them are usually formed more readily in solvents with a lower donor activity. Consequently, depending on the latter, the composition of the complexes of a given central atom with the same ligands should vary in different ways in different solvents.

The influence of the solvent on oxidation-reduction reactions merits attention. Thus, bromine reacts with hydrogen sulphide with liberation of sulphur in the presence of water and with formation of thiohypobromous acid in chloroform [348]:

$$H_2S+Br_2 \rightleftarrows HBr+HSBr.$$

This is associated with different degrees of solvation and hence dissociation of the corresponding compounds in different solutions (as well as the different behaviour of PCl_5 in acetonitrile, nitromethane, and nitrobenzene on the one hand and in benzene and carbon tetrachloride on the other [246]). The unusual influence of the medium has, in fact, made it possible to obtain many at first sight uncommon coordination compounds, including those with zero and negative degrees of oxidation of the central metal atom [349,350]. In the presence of aluminium chloride, fused bismuth chloride is reduced in accordance with the equation

$$BiCl_3+2Bi+3AlCl_3=3Bi[AlCl_4].$$

Bismuth tetrachloroaluminate has a melting point of 253°C. [351] Gallium(I) and cadmium(I) salts can be obtained similarly.

In view of the enhanced specificity of the reactions when water is replaced by other solvents, many [non-aqueous?] solutions are being increasingly used not only in syntheses but also in titrimetric analysis [352-354]. One is then usually dealing with complex-formation reactions.

The study of complex-formation reactions in non-aqueous solutions has greatly extended the range of these reactions [355-358] and permitted the formulation and to some extent also the solution of a number of new problems. It is therefore extremely important to seek an objective characteristic of the solvent which will make possible a more complete prediction than can be done at present of its solvent power in relation to various substances, its influence on complex-formation reactions, and the possibility of synthesising new compounds.

When account is taken of the σ-donor and π-acceptor activities of solvents and also of the ability of various ligands to be coordinated to the corresponding metal atoms, it is possible to predict the dissolution in a number of liquid multicomponent systems under the usual conditions of many substances, such as, for example, oxides, sulphides, selenides, and even metals, which are usually regarded as absolutely insoluble in water, alcohols, ketones, and similar liquids. This problem is of considerable interest from both theoretical and practical points of view.

REFERENCES

1. H. Samelson, A. Lempicki, V. A. Brophy, and C. Brecher, J. Chem. Phys., 40, 2547 (1964).
2. H. Samelson, A. Lempicki, and C. Brecher, J. chim. phys. phys.-chim. biol., 64, 173 (1967).
3. I. M. Batyaev, Uspekhi Khim., 40, 1930 (1971) [Russ. Chem. Rev., No. 11 (1971)].
4. A. Heller, J. Amer. Chem. Soc., 89, 167 (1967).
5. W. L. Jolly, J. Chem. Educ., 44, 304 (1967).
6. K. P. Mishchenko and G. M. Poltoratskii, "Voprosy Termodinamiki i Stroeniya Vodnykh i Nevodnykh Rastvorov Elektrolitov" (Problems of the Thermodynamics and Structure of Aqueous and Non-Aqueous Electrolyte Solutions), Izd. Khimiya, Leningrad, 1968, p. 55.
7. R. S. Drago and K. F. Purcell, Symposium, "Nevodnye Rastvoriteli" (Non-Aqueous Solvents), Izd. Khimiya, Moscow, 1971, p. 201.
8. V. K. Semenchenko, "Fizicheskaya Teoriya Rastvorov" (The Physical Theory of Solutions), Gostekhkhimizdat, Moscow–Leningrad, 1941.
9. V. K. Semenchenko and M. I. Shakhparonov, Zhur. Fiz. Khim., 22, 243 (1948).
10. V. K. Semenchenko and M. I. Shakhparonov, Zhur. Fiz. Khim., 22, 1256 (1948).
11. M. I. Shakhparonov, "Vvedenie v Molekulyarnuyu Teoriyu Rastvorov" (Introduction to the Molecular Theory of Solutions), Gosizdat, Tekh.-Teor. Lit., Moscow, 1956.
12. J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes", Dover Publications, Inc., New York, 1964.
13. R. G. Pearson, J. Chem. Educ., U5, 581, 643 (1968).
14. I. F. Shreder, Gornyi Zhur., 4, 272 (1890).
15. N. A. Izmailov, I. V. Krasovskii, V. V. Aleksandrov, and E. I. Vail', Dokl. Akad. Nauk SSSR, 74, 91 (1950).
16. N. A. Izmailov and V. N. Izmailova, Zhur. Fiz. Khim., 29, 1050 (1955).
17. M. Born, Z. Phys., 1, 45 (1920).
18. M. G. Evans, Trans. Faraday Soc., 34, 49 (1938).
19. W. Latimer, J. Chem. Phys., 39, 90 (1955).
20. K. J. Laidler and C. Pegis, Proc. Roy. Soc., A, 241, 80 (1957).
21. Ya. I. Tur'yan, Zhur. Neorg. Khim., 1, 2337 (1956).
22. K. P. Mishchenko and A. F. Sukhotin, Zhur. Fiz. Khim., 27, 26 (1953).
23. J. D. Bernal and R. H. Fowler, Uspekhi Fiz. Nauk, 14, 586 (1934).
24. A. F. Kapustinskii and K. B. Yatsimirskii, Zhur. Obshch. Khim., 36, 941 (1957).
25. F. Kleinberg, W. F. Argersinger, and E. Griswold, "Inorganic Chemistry", Heath, Boston, 1960.
26. M. C. Day and J. Selbin, "Theoretical Inorganic Chemistry" (Translated into Russian), Izd. Khimiya, Moscow, 1969, p. 360.
27. F. A. Cotton and R. H. Holm, J. Amer. Chem. Soc., 82, 2979 (1960).
28. A. M. Golub and T. P. Lishko, Zhur. Neorg. Khim., 19, 2366 (1974) [Russ. J. Inorg. Chem., No. 9 (1974)].
29. M. Karsulin and T. Markovic, Intern. Comm. Electrochem. Thermodyn. Kinetics, 282 (1957).
30. V. A. Pleskov, Zhur. Fiz. Khim., 22, 352 (1948).
31. O. K. Kudra and N. I. Ternonkaya, Ukrain. Khim. Zhur., 27, 613 (1961).
32. J. Gazo, Chem. Zvesti, 10, 612 (1956).
33. E. Wertiporoch, Ber., 64, 1369 (1931).
34. E. Lloyd, J. Chem. Soc., 644 (1928).
35. M. Etard, Ann. Chim. Phys., 2, 564 (1894).
36. Handbook, "Solevye Sistemy" (Salt Systems), Izd. Khimiya, Moscow, 1964, Vol. 4.
37. F. K. Andryushenko, K. G. Parfenov, and O. A. Skotin, Elektrokhimiya, 2, 741 (1966).
38. P. R. Chand, B. R. Sreenathan, and S. L. Chadha, J. Inorg. Nuclear Chem., 28, 1225 (1966).
39. R. P. Bell, J. Chem. Soc., 16, 186, 342 (1933).
40. A. Naumann, Ber., 37, 3600 (1904).
41. J. Schroeder, Z. anorg. Chem., 44, 1 (1905).
42. C. F. Nelson, J. Amer. Chem. Soc., 35, 658 (1913).
43. G. Jander, Naturwiss., 26, 779 (1938).

44. L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents" (Translated into Russian), Inostr. Lit., Moscow, 1955.
45. V. B. Kogan, V. M. Fridman, and V. V. Kafarov, "Spravochnik po Rastvorimosti" (Handbook of Solubility), Vol. I, Izd. Akad. Nauk SSSR, Leningrad, 1961–1963; Vol. III, Izd. Nauka, Leningrad, 1969–1970.
46. N. A. Izmailov, "Elektrokhimiya Rastvorov" (Electrochemistry of Solutions), Izd. Khar'kov, Univ., Kharkov, 1959.
47. H. Remy, "Lehrbuch der anorganischen Chemie" (Translated into Russian), Izd. Mir, Moscow, 1966, Vol. II, p. 410.
48. R. Varet, Compt. rend., 112, 390 (1891).
49. L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine" (Translated into Russian), Inostr. Lit., Moscow, 1954.
50. G. Jander, "Die Chemie in wasserähnliche Lösungsmitteln", Kap. V, Springer, Berlin, 1949.
51. V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions" (Translated into Russian), Izd. Mir, Moscow, 1971.
52. G. A. Kataev and B. A. Kulikov, Symposium, "Voprosy Khimicheskoi Kinetiki, Reaktsionnoi Sposobnosti Veshchestva" (Problems of Chemical Kinetics and Reactivity), Izd. Tomsk. Univ., Tomsk, 1962.
53. D. I. Ryabchikov and E. K. Gol'braikh, "Analiticheskaya Khimiya Teoriya" (Analytical Chemistry of Thorium), Akademizdat, Moscow, 1960.
54. E. Soderbäck, Acta Chem. Scand., 11, 1622 (1957).
55. A. M. Golub and Au Van Long, Zhur. Prikl. Khim., 45, 1776 (1972).
56. Yu. A. Zolotov, "Ekstraktsiya Vnutrikompleksnykh Soedinenii" (Extraction of Chelate Compounds), Izd. Nauka, Moscow, 1968.
57. N. A. Turova, N. S. Kedrova, K. N. Semenenko, and A. V. Novoselova, Zhur. Neorg. Khim., 9, 905 (1964) [Russ. J. Inorg. Chem., No. 4 (1964)].
58. C. C. Addison, G. Jander, and H. Spandau, "Chemistry in Non-Aqueous Ionizing Solvents", Braunschweig–New York–London, 1966, Vol. 1, Part 1.
59. H. S. Isbin and K. A. Kobe, J. Amer. Chem. Soc., 67, 464 (1945).
60. P. Walden and E. J. Birr, Z. phys. Chem., 144, 269 (1929).
61. F. Fairbrother, J. E. Nixon, and H. Prophet, J. Less Common Metals, 9, 434 (1965).
62. A. M. Golub and A. M. Sych, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 647 (1962).
63. D. Kepert and R. Nyholm, J. Chem. Soc., 2871 (1965).
64. I. A. Sheka and B. A. Voitovich, Zhur. Neorg. Khim., 2, 676 (1957).
65. R. C. Paul, R. Kumar, K. S. Dhindsa, S. P. Narula, and S. C. Ahluwalia, Indian J. Chem., 6, 641 (1968).
66. E. M. Larsen and L. V. E. Trevorrow, J. Inorg. Nuclear Chem., 2, 254 (1956).
67. G. S. Rao, Z. anorg. Chem., 304, 351 (1960).
68. W. M. Graven and R. V. Peterson, J. Inorg. Nuclear Chem., 31, 1743 (1969).
69. W. B. Blumenthal, "The Chemical Behaviour of Zirconium" (Translated into Russian), Inostr. Lit., Moscow, 1963.
70. D. C. Bradley and W. Wardlaw, J. Chem. Soc., 280 (1951).
71. C. R. Simmons and R. S. Hansen, J. Phys. Chem., 59, 1072 (1955).
72. J. F. Hinton and E. S. Amis, Chem. Rev., 71, 627 (1971).
73. N. A. Izgaryshev and S. V. Gorbachev, "Kurs Teoriticheskoi Elektrokhimii" (A Course of Theoretical Electrochemistry), Khimteoritizdat, Moscow, 1951.
74. B. E. Conway and J. O'M. Bockris, "Modern Aspects of Electrochemistry" (Translated into Russian), Inostr. Lit., Moscow, 1958.
75. V. I. Kondrat'ev and N. D. Sokolov, Zhur. Fiz. Khim., 29, 1265 (1955).
76. O. Ya. Samoilov, "Struktura Vodnykh Rastvorov Elektrolitov i Gidratatsiya Ionov" (The Structure of Aqueous Electrolyte Solutions and Ion Hydration), Izd. Akad. Nauk SSSR, Moscow, 1957.
77. O. Hassel and H. Kope, Acta Chem. Scand., 15, 407 (1961).
78. I. M. Kolthoff and F. G. Thomas, J. Electrochem. Soc., 111, 1065 (1964).
79. H. L. Schläfer and H. W. Wille, Z. anorg. Chem., 340, 40 (1965).
80. C. H. Langford and P. O. Langford, Inorg. Chem., 1, 184 (1962).
81. A. F. Golub, Naukovi Zap. Kiivsk. Univ., 16, No. 25, 13 (1957).
82. K. P. Mishchenko and M. L. Klyueva, Teor. Eksper. Khim., 1, 201 (1965).
83. K. P. Mishchenko, V. V. Subbotina, and S. Krumgal'z, Teor. Eksper. Khim., 5, 268 (1969).
84. E. P. Prosviryakova, K. P. Mishchenko, and G. M. Poltoratskii, Teor. Eksper. Khim., 5, 129 (1969).
85. A. J. Parker, Quart. Rev., 16, 163 (1962).
86. J. Miller and A. J. Parker, J. Amer. Chem. Soc., 83, 117 (1961).
87. J. E. Prue and P. J. Sherrington, Trans. Faraday Soc., 57, 1795 (1961).
88. A. D. Buckingham, Discuss. Faraday Soc., 24, 151 (1957).
89. S. N. Andreev and M. F. Smirnova, Zhur. Neorg. Khim., 11, 2226 (1966) [Russ. J. Inorg. Chem., No. 10 (1966)].
90. V. I. Golovorushkin, A. M. Golub, A. K. Dorosh, A. F. Skryshchevskii, and V. Ya. Proshko, "XI Vsesoyuznoe Soveshchanie po Khimii Kompleksnykh Soedinenii, Tezisy Dokladov, Alma-Ata, 1973" (The 11th All-Union Conference on the Chemistry of Complex Compounds, Abstracts of Reports, Alma-Ata, 1973), pp. 235, 236.
91. B. S. Krumgal'z, Teor. Eksper. Khim., 8, 817 (1972).
92. A. M. Golub and V. M. Samoilenko, Ukrain. Khim. Zhur., 29, 59 (1963).
93. A. M. Golub and A. A. Baran, Zhur. Strukt. Khim., 2, 671 (1961).
94. A. M. Golub, V. A. Kalibabchuk, and V. S. Kuts, Zhur. Neorg. Khim., 12, 2983 (1967) [Russ. J. Inorg. Chem., No. 11 (1967)].
95. A. M. Golub, Dokl. Akad. Nauk SSSR, 120, 1255 (1968).
96. M. Agermann, H. H. Andersson, J. Lindquist, and M. Zackrisson, Acta Chem. Scand., 12, 4777 (1958).
97. P. Kebarle, Canad. J. Chem., 20, 42 (1968).
98. A. V. Koryakin, A. V. Petrov, Yu. P. Gerlit, and M. E. Zubrilina, Teor. Eksper. Khim., 2, 494 (1966).
99. D. G. Holan and J. P. Fackler, Inorg. Chem., 4, 954 (1965).

100. F. Gaizer and M. T. Beck, J. Inorg. Nuclear Chem., 29, 21 (1967).
101. P. Walden, "Elektrochemie nichtwässerigen Lösungen", Leipzig, 1924.
102. R. A. Walton, Quart. Rev., 19, 126 (1965).
103. D. C. Luehrs and K. Abate, J. Inorg. Nuclear Chem., 30, 551 (1968).
104. H. A. Benesi and J. H. Hildebrand, J. Amer. Chem. Soc., 71, 2703 (1949).
105. G. Kortüm and H. Walz, Z. Elektrochem., 57, 73 (1953).
106. H. Tsubomura and R. S. Mulliken, J. Amer. Chem. Soc., 82, 5966 (1960).
107. L. J. Oosterhoff, Symposium, "Sovremennaya Khimiya" (Modern Chemistry) (Translated into Russian), Izd. Mir, 1968, Part 1, p. 143.
108. M. Tamres and S. M. Brandon, J. Amer. Chem. Soc., 82, 2134 (1960).
109. A. M. Golub, "I Vsesoyuznaya Nauchnaya Konferentsiya po Issledovaniyu Neorganicheskikh Soedinenii v Nevodnykh Rastvorakh, Tezisy Dokladov" (The 1st All-Union Conference on Inorganic Compounds in Non-Aqueous Solutions. Abstracts of Reports), Izd. Kievsk. Univ., Kiev, 1970.
110. R. S. Drago and K. F. Purcell, Prog. Inorg. Chem., 6, 271 (1964).
111. M. Linhard and M. Stephan, Z. phys. Chem., A163, 185 (1933).
112. M. Linhard and M. Stephan, Z. phys. Chem., A167, 87 (1937).
113. A. A. Levin, Ya. K. Syrkin, and M. E. Dyatkina, Uspekhi Khim., 38, 217 (1969) [Russ. Chem. Rev., No. 2 (1969)].
114. N. A. Izmailov and Yu. A. Kruglyak, Dokl. Akad. Nauk. SSSR, 134, 1390 (1960).
115. N. A. Izmailov, Yu. A. Kruglyak, R. Gaspar, and I. Tamassy-Lentei, Acta phys. Acad. scient. hung., 13, 203 (1961); Ref. Zhur. Khim., 15B6(1962).
116. Yu. A. Kruglyak, Uch. Zap. Kharkov. Univ., 133, 179 (1963).
117. R. E. Burton and J. Daly, Trans. Faraday Soc., 66, 1281 (1970).
118. H. Lischka, T. Plesser, and P. Schuster, Chem. Phys. Letters, 6, 263 (1970).
119. G. H. F. Diercksen and W. P. Kraemer, Theor. Chim. Acta, 23, 393 (1972).
120. W. P. Kraemer and G. H. F. Dierksen, Theor. Chim. Acta, 23, 396 (1972).
121. R. E. Burton and J. Daly, Trans. Faraday Soc., 67, 1219 (1971).
122. D. A. Zhogolev, Yu. A. Kruglyak, B. Kh. Bunyatyan, and I. V. Matyash, Teor. Eksper. Khim., 8, 745 (1972).
123. R. Hoffmann and W. N. Lipscomb, J. Chem. Phys., 37, 2872 (1962).
124. J. Chatt, J. Inorg. Nuclear Chem., 8, 515 (1958).
125. J. E. Prue, "Ionic Equilibria", Pergamon Press, Oxford, 1965, p. 97.
126. R. S. Mulliken, J. Amer. Chem. Soc., 77, 884 (1955).
127. V. Gutmann, "Proceedings of the 17th International Congress on Theoretical and Applied Chemistry in Munich" (Translated into Russian), Inostr. Lit., Moscow, 1963.
128. A. M. Golub and V. I. Golovorushkin, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 10, 754 (1967).
129. A. M. Golub, V. I. Golovorushkin, and S. I. Mukha, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 13, 1441 (1970).
130. A. M. Golub and V. I. Golovorushkin, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 10, 754 (1967).
131. V. I. Golovorushkin, Candidate's Thesis, The University, Kiev, 1971.
132. A. M. Golub and V. I. Golovorushkin, Ukrain. Khim. Zhur., 34, 1207 (1968).
133. Fam Van Cha and V. M. Samoilenko, Ukrain. Khim. Zhur., 37, 626 (1971).
134. R. F. Pasternak and R. A. Plane, Inorg. Chem., 4, 1171 (1965).
135. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", Copenhagen, 1957.
136. A. M. Golub, V. I. Golovorushkin, A. F. Skryshchevskii, and A. K. Dorosh, "II Nauchnaya Konferentsiya po Sintezu i Issledovaniyu Neorganicheskikh Soedinenii v Nevodnykh Sredakh, Tezisy Dokladov, Moskva, 1971" (The 2nd Conference on the Synthesis and Investigation of Inorganic Compounds in Non-Aqueous Media. Abstracts of Reports, Moscow, 1971), p. 39.
137. A. M. Golub, V. I. Golovorushkin, A. K. Dorosh, A. F. Skryshchevskii, and V. Ya. Proshko, Zhur. Strukt. Khim., 15, 14 (1974).
138. V. M. Vdovenko, A. A. Lipovskii, and S. A. Nikitina, Radiokhimiya, 5, 139 (1963).
139. L. I. Katzin and E. Gebert, J. Amer. Chem. Soc., 72, 5455 (1950).
140. L. I. Katzin and E. Gebert, J. Amer. Chem. Soc., 72, 5464 (1950).
141. A. K. Babko and L. L. Shevchenko, Dokl. Akad. Nauk Ukrain. SSR, 9, 970 (1958).
142. N. S. Pominov, Zhur. Fiz. Khim., 31, 2184 (1957).
143. I. N. Antipova-Karataeva and E. A. Vainshtein, Zhur. Neorg. Khim., 6, 816 (1961) [Russ. J. Inorg. Chem., No. 4 (1961)].
144. A. Zaidel' and V. Rotshtein, Dokl. Akad. Nauk SSSR, 57, 587 (1947).
145. V. Rotshtein, Dokl. Akad. Nauk SSSR, 71, 335 (1950).
146. N. S. Pominov, Zhur. Fiz. Khim., 31, 1926 (1957).
147. N. K. Davidenko and L. N. Lugina, Zhur. Neorg. Khim., 13, 980 (1968) [Russ. J. Inorg. Chem., No. 4 (1968)].
148. J. Bjerrum and H. Jörgensen, Acta Chem. Scand., 7, 961 (1953).
149. L. O. Morgan and A. W. Nolle, J. Chem. Phys., 31, 365 (1959).
150. L. O. Morgan, J. Chem. Phys., 38, 2788 (1963).
151. K. Bukietunska, B. Jezowska-Trzebiatowska, B. Keller, and J. Legendziewiz, Roczniki Chem., 42, 421 (1968).
152. A. Kemula and R. Iwamoto, J. Phys. Chem., 72, 1335 (1968).
153. E. Ya. Gorenbein, Zhur. Obshch. Khim., 24, 1710 (1954).
154. E. Ya. Gorenbein and A. G. Ponomarenko, Zhur. Neorg. Khim., 6, 1928 (1961) [Russ. J. Inorg. Chem., No. 8 (1961)].
155. R. E. Van Dyke and T. S. Harrison, J. Amer. Chem. Soc., 73, 402 (1951).
156. R. E. Van Dyke and H. E. Crawford, J. Amer. Chem. Soc., 73, 2018 (1951).
157. V. V. Udovenko, Izv. Sektora Fiz.-Khim. Anal., 17, 101 (1949).

158. V. V. Udovenko and S. F. Babak, Zhur. Obshch. Khim., 17, 655 (1947).
159. Ya. A. Fialkov and I. D. Muzyka, Izv. Sektora Fiz.-Khim. Anal., 18, 802 (1948).
160. Ya. A. Fialkov and I. D. Muzyka, Izv. Sektora Fiz.-Khim. Anal., 19, 314 (1949).
161. N. A. Izmailov, Zhur. Obshch. Khim., 25, 1070 (1951).
162. N. A. Izmailov, Zhur. Obshch. Khim., 27, 807 (1953).
163. E. Ya. Gorenbein, Zhur. Neorg. Khim., 4, 1643 (1959) [Russ. J. Inorg. Chem., No. 7 (1959)].
164. E. Ross and R. E. Van Dyke, J. Amer. Chem. Soc., 73, 398 (1951).
165. A. M. Golub, Fam Van Cha, and V. M. Samoilenko, Zhur. Fiz. Khim., 44, 2779 (1970) [Russ. J. Phys. Chem., No. 11 (1970)].
166. R. L. Harris, R. E. Wood, and U. R. Ritter, J. Amer. Chem. Soc., 73, 3151 (1951).
167. B. A. Voitovich and A. S. Barabanova, Zhur. Neorg. Khim., 6, 2098 (1961) [Russ. J. Inorg. Chem., No. 9 (1961)].
168. E. R. Nightingale, J. Phys. Chem., 63, 1381 (1959).
169. M. Della Monica and L. Senatore, J. Phys. Chem., 74, 205 (1970).
170. A. M. Golub, "IV Ukrainskoe Soveshchanie po Neorganicheskoi Khimii, Tezisy Dokladov, Kiev, 1960" (The 4th Ukrainian Conference on Inorganic Chemistry, Abstracts of Reports, Kiev, 1960), p. 61.
171. A. M. Golub, Candidate's Thesis, The University, Kiev, 1951.
172. A. M. Golub, Ukrain. Khim. Zhur., 19, 205 (1953).
173. A. M. Golub, Doctoral Thesis, Institute of General and Inorganic Chemistry, Moscow, 1961.
174. A. M. Golub and V. M. Samoilenko, Zhur. Neorg. Khim., 10, 328 (1965) [Russ. J. Inorg. Chem., No. 2 (1965)].
175. A. I. Rivkind, Dokl. Akad. Nauk SSSR, 117, 448 (1958).
176. J. D. Roberts, "Nuclear Magnetic Resonance—Applications to Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1961.
177. P. A. Zagorets, V. I. Ermakov, and A. P. Grunau, Zhur. Fiz. Khim., 37, 2155 (1963) [Russ. J. Phys. Chem., No. 10 (1963)].
178. G. W. Brody, J. Chem. Phys., 33, 1079 (1960).
179. J. Rauben and D. Fiat, Israel. J. Chem., 4, 54 (1966).
180. J. F. Hinton and E. S. Amis, Chem. Rev., 67, 367 (1967).
181. M. Saunders and J. B. Hyne, J. Chem. Phys., 29, 253 (1958).
182. W. B. Lewis, J. A. Jackson, J. F. Lemons, and H. Taube, J. Chem. Phys., 36, 694 (1962).
183. T. J. Swift and H. H. Lo, J. Amer. Chem. Soc., 89, 3988 (1967).
184. J. H. Swinehart and H. Taube, J. Chem. Phys., 37, 1579 (1962).
185. S. Nakamura and S. Meiboom, J. Amer. Chem. Soc., 89, 1765 (1967).
186. K. B. Yatsimirskii, V. A. Bidzilya, and N. K. Davidenko, Dokl. Akad. Nauk SSSR, 202, 1379 (1972).
187. B. W. Maxey and A. I. Popov, J. Amer. Chem. Soc., 90, 4470 (1968).
188. W. G. Movius and N. A. Matwiyoff, Inorg. Chem., 6, 847 (1967).
189. N. Bloembergen and L. O. Morgan, J. Chem. Phys., 34, 842 (1961).
190. N. Matwiyoff and S. Hooker, Inorg. Chem., 6, 1127 (1967).
191. I. S. Perelygin, Ukrain. Fiz. Zhur., 9, 497 (1964).
192. B. W. Maxey and A. I. Popov, J. Amer. Chem. Soc., 89, 2230 (1967).
193. V. I. Danilov, "Struktura i Kristallizatsiya Zhidkostei" (The Structure and Crystallisation of Liquids), Izd. Akad. Nauk Ukrain. SSR, Kiev, 1956.
194. A. Z. Golik, A. K. Dorosh, A. F. Skryshchevskii, and P. P. Cholpan, Ukrain. Fiz. Zhur., 11, 79 (1966).
195. A. K. Dorosh and A. F. Skryshchevskii, Zhur. Strukt. Khim., 5, 911 (1964).
196. A. L. Skryshchevskii, "Rentgenografiya Zhidkostei" (X-Ray Diffraction of Liquids), Izd. Kiev. Univ., Kiev, 1966.
197. A. M. Golub and T. P. Lishko, "VII Ukrainskaya Konferentsiya po Neorganicheskoi Khimii, Tezisy Dokladov, Odessa, 1971" (The 7th Ukrainian Conference on Inorganic Chemistry. Abstracts of Reports, Odessa, 1971), p. 11.
198. G. V. Tsintsadze, Zhur. Neorg. Khim., 16, 1160 (1971) [Russ. J. Inorg. Chem., No. 4 (1971)].
199. I. I. Antipova-Karataeva and Yu. I. Kutsenko, Zhur. Neorg. Khim., 9, 615 (1964) [Russ. J. Inorg. Chem., No. 3 (1964)].
200. A. M. Golub and V. M. Samoilenko, Ukrain. Khim. Zhur., 29, 789 (1963).
201. P. K. Migal' and N. Kh. Grinberg, Zhur. Neorg. Khim., 7, 1309 (1962) [Russ. J. Inorg. Chem., No. 6 (1962)].
202. W. Gerrard, M. F. Lappert, and J. W. Wallis, J. Chem. Soc., 2178 (1960).
203. I. I. Antipova-Karataeva and N. N. Rzhevskaya, Zhur. Neorg. Khim., 17, 1650 (1972) [Russ. J. Inorg. Chem., No. 6 (1972)].
204. E. Segal and C. Vasile, Anal. Univers. Bucuresti, Ser. St. Nat. Chimie, 15, 17 (1966).
205. A. Fratiello, R. E. Lee, D. P. Miller, and V. M. Nishid, Mol. Phys., 13, 349 (1967).
206. N. A. Izmailov, Dokl. Akad. Nauk SSSR, 149, 884 (1963).
207. A. E. Makovetskii, Zhur. Russ. Khim. Obshch., 40, 752 (1908).
208. E. K. Makarova and I. S. Pominov, Ukrain. Fiz. Zhur., 12, 239 (1967).
209. J. Lindquist and M. Zackrisson, Acta Chem. Scand., 14, 453 (1960).
210. V. Gutmann and E. Wychera, Inorg. Nuclear Chem. Letters, 2, 257 (1966).
211. A. M. Golub and T. P. Lishko, "XV Mezhdunarodnaya Konferentsiya po Koordinatsionnoi Khimii, Tezisy Dokladov, Moskva, 1973" (The 15th International Conference on Coordination Chemistry. Abstracts of Reports, Moscow, 1973), p. 392.
212. L. V. Surpina, Yu. V. Kolodyazhnyi, and O. A. Osipov, Zhur. Neorg. Khim., 18, 2853 (1973) [Russ. J. Inorg. Chem., No. 10 (1973)].
213. P. Walden, L. F. Audrieth, and E. J. Birr, Z. phys. Chem., A160, 337 (1932).
214. W. F. Luder and C. A. Kraus, J. Amer. Chem. Soc., 69, 2491 (1947).
215. D. S. Burgess and C. A. Kraus, J. Amer. Chem. Soc., 70, 706 (1948).
216. A. M. Golub and V. V. Skopenko, Uspekhi Khim., 34, 2098 (1965) [Russ. Chem. Rev., No. 12 (1965)].
217. A. M. Golub and V. A. Kalibabchuk, Zhur. Neorg. Khim., 12, 2370 (1967) [Russ. J. Inorg. Chem., No. 9 (1967)].

218. J. L. Burmeister, R. L. Hassel, and R. J. Phelan, Inorg. Chem., 10, 2032 (1971).
219. L. V. Surpina, Yu. V. Kolodyazhnyi, and O. A. Osipov, Zhur. Obshch. Khim., 41, 1420 (1971).
220. A. M. Golub, "Shorichnik Kiivs'k Universitetu za 1956 r." (The 1956 Kiev University Annual), Izd. Kiev. Univ., 1957, p. 578; Nauch. Dokl. Vys. Shkoly, Khim. i Khim. Tekhnol., 685 (1958).
221. V. V. Skopenko and A. I. Brusilovets, Ukrain. Khim. Zhur., 30, 24 (1964).
222. V. Gutmann, G. Hampel, and I. R. Masaguer, Monatsh., 94, 822 (1963).
223. A. M. Golub, V. V. Trachevskii, N. V. Ul'ko, and N. D. Samovskaya, Zhur. Neorg. Khim., 20, 2704 (1975) [Russ. J. Inorg. Chem., No. 10 (1975)].
224. A. M. Golub and V. M. Samoilenko, Ukrain. Khim. Zhur., 29, 590 (1963).
225. A. M. Golub and V. M. Samoilenko, Ukrain. Khim. Zhur., 29, 472 (1963).
226. A. M. Golub and V. M. Samoilenko, Ukrain. Khim. Zhur., 29, 789 (1963).
227. Ya. I. Tur'yan, Zhur. Neorg. Khim., 4, 813 (1959) [Russ. J. Inorg. Chem., No. 4 (1959)].
228. Ya. I. Tur'yan and N. G. Chebotar', Zhur. Neorg. Khim., 4, 599 (1959) [Russ. J. Inorg. Chem., No. 3 (1959)].
229. H. M. N. H. Irving, Chem. Soc. Spec. Publ. No. 13, 13 (1959).
230. K. Pool, J. Polarog. Soc., 13, 23 (1967).
231. V. M. Samoilenko, Zhur. Neorg. Khim., 13, 79 (1968) [Russ. J. Inorg. Chem., No. 1 (1968)].
232. V. M. Samoilenko and V. I. Lyashenko, Zhur. Neorg. Khim., 19, 2984 (1974) [Russ. J. Inorg. Chem., No. 11 (1974)].
233. V. M. Samoilenko and M. P. Zhukov, Ukrain. Khim. Zhur., 36, 765 (1970).
234. R. F. Roodewald, K. Mahendran, J. L. Bear, and R. Fuchs, J. Amer. Chem. Soc., 90, 6698 (1968).
235. M. Yoshihisa and D. Voshio, Bull. Chem. Soc. Japan, 43, 2052 (1970).
236. A. Foll, M. Le Demezet, and J. Courtot-Coupez, Bull. Soc. chim. France, 1207 (1972).
237. M. Breant, J. Georges, J. L. Imbert, and D. Schmitt, Ann. Chim. (France), 6, 245 (1971).
238. P. A. McCusker and S. M. Kennard, J. Amer. Chem. Soc., 81, 2976 (1959).
239. A. M. Golub and O. E. Andreichenko, Zhur. Neorg. Khim., 7, 549 (1962) [Russ. J. Inorg. Chem., No. 3 (1962)].
240. A. M. Golub and V. V. Skopenko, Zhur. Neorg. Khim., 7, 1012 (1962) [Russ. J. Inorg. Chem., No. 5 (1962)].
241. A. M. Golub and V. V. Skopenko, Zhur. Neorg. Khim., 7, 1266 (1962) [Russ. J. Inorg. Chem., No. 6 (1962)].
242. A. M. Golub and L. I. Romanenko, Zhur. Neorg. Khim., 5, 1086 (1960) [Russ. J. Inorg. Chem., No. 5 (1960)].
243. A. I. Brusilovets, Candidate's Thesis, The University, Kiev, 1970.
244. A. M. Golub and V. M. Samoilenko, Zhur. Neorg. Khim., 9, 70 (1964) [Russ. J. Inorg. Chem., No. 1 (1964)].
245. J. A. Olabe, M. C. Giordana, and A. I. Arvia, Electrochem. Acta, 12, 907 (1967).
246. R. W. Suter, H. C. Knachel, V. P. Petro, J. H. Howatson, and S. G. Shore, J. Amer. Chem. Soc., 95, 1474 (1973).
247. A. M. Golub, V. A. Grechikhina, V. V. Trachevskii, and N. V. Ul'ko, Zhur. Neorg. Khim., 18, 2119 (1973) [Russ. J. Inorg. Chem., No. 8 (1973)].
248. Ya. D. Fridman, "Ustoichivost' Smeshannykh Kompleksnykh Soedinenii" (The Stability of Mixed Complexes), Izd. Ilim., Frunze, 1971.
249. W. B. Lewis, J. A. Lackson, J. F. Lemons, and H. Taube, J. Chem. Phys., 36, 694 (1962).
250. A. M. Golub, V. V. Skopenko, and A. Zhumabaev, Zhur. Neorg. Khim., 14, 2995 (1969) [Russ. J. Inorg. Chem., No. 11 (1969)].
251. B. A. Buslaev, E. G. Il'in, S. A. Bainova, and M. N. Krutkina, Dokl. Akad. Nauk SSSR, 198, 374 (1971).
252. Yu. A. Buslaev, E. G. Il'in, and M. N. Krutkina, Dokl. Akad. Nauk SSSR, 200, 1345 (1971).
253. Yu. A. Buslaev, Yu. V. Konusov, V. A. Bochkareva, and E. M. Sustorovich, Zhur. Neorg. Khim., 17, 3184 (1972) [Russ. J. Inorg. Chem., No. 12 (1972)].
254. I. I. Chernyaev, Trudy. Inst., Platiny, 4, 213 (1926).
255. C. K. Jörgensen, Inorg. Chem., 3, 1201 (1964).
256. V. Gasselin, Ann. Chim. Phys., 3, [7], 5 (1894).
257. B. P. Susz and P. Chalondon, Helv. Chim. Acta, 41, 1332 (1958).
258. F. Gaizer, L. Muray, and M. T. Beck, Acta Chim. Acad. Sci. Hung., 67, 251 (1971).
259. A. D. Gel'man and L. N. Essen, Dokl. Akad. Nauk SSSR, 75, 693 (1950).
260. A. M. Golub and T. P. Lishko, Zhur. Neorg. Khim., 15, 1527 (1970) [Russ. J. Inorg. Chem., No. 6 (1970)].
261. A. M. Golub and V. N. Sergun'kin, Zhur. Prikl. Khim., 43, 1203 (1970).
262. J. Bjerrum, G. Schwarzenbach, and L. Sillén, "Stability Constants of Metal Ion Complexes", Chem. Soc., London, 1957, 1958.
263. A. K. Babko, "Fiziko-khimicheskii Analiz Kompleksnykh Soedinenii v Rastvore" (Physicochemical Analysis of Complexes in Solution), Akademizdat, Kiev, 1955.
264. V. P. Vasil'ev and K. B. Yatsimirskii, "Konstanty Nestoikosti Kompleksnykh Soedinenii" (Instability Constants of Complexes), Izd. Khim. Lit., Moscow, 1959.
265. G. L. Shlefer, "Kompleksoobrazovanie v Rastvorakh" (Complex Formation in Solutions), Izd. Khimiya, Moscow–Leningrad, 1964.
266. F. J. C. Rossotti and H. S. Rossotti, "Determination of Stability Constants and Other Equilibrium Constants in Solution) (Translated into Russian), Izd. Mir, Moscow, 1965.
267. A. M. Golub, G. B. Pomerants, and S. A. Ivanova, Zhur. Neorg. Khim., 14, 2826 (1969) [Russ. J. Inorg. Chem., No. 10 (1969)].
268. B. Csiszar, V. Gutmann, and E. Wychera, Monatsh., 98, 12 (1967).
269. S. Buffagny and T. M. J. Dunn, J. Chem. Soc., 5105 (1961).
270. A. M. Golub and L. I. Romanenko, Ukrain. Khim. Zhur., 26, 418 (1960).
271. A. M. Golub and R. Akmyradov, Ukrain. Khim. Zhur., 31, 136 (1965).
272. A. M. Golub and A. M. Sych, Zhur. Neorg. Khim., 9, 1085 (1964) [Russ. J. Inorg. Chem., No. 5 (1964)].
273. A. M. Golub and V. A. Kalibabchuk, Zhur. Neorg. Khim., 11, 590 (1966) [Russ. J. Inorg. Chem., No. 3 (1966)].
274. A. M. Golub, Zhur. Neorg. Khim., 4, 1577 (1959) [Russ. J. Inorg. Chem., No. 7 (1959)].

275. A. M. Golub, Zhur. Obshch. Khim., 26, 1845 (1956).
276. A. M. Golub, Zhur. Neorg. Khim., 1, 2523 (1956).
277. A. M. Golub, L. I. Romanenko, and V. M. Samoilenko, Ukrain. Khim. Zhur., 25, 50 (1959).
278. A. M. Golub and G. B. Pomerants, Zhur. Neorg. Khim., 9, 1924 (1964) [Russ. J. Inorg. Chem., No. 8 (1964)].
279. A. M. Golub, S. M. Sazhienko, and L. I. Romanenko, Ukrain. Khim. Zhur., 28, 562 (1962).
280. A. M. Golub and G. B. Pomerants, Zhur. Neorg. Khim., 4, 770 (1959) [Russ. J. Inorg. Chem., No. 4 (1959)].
281. V. A. Pyankov and I. G. Krasnousova, Zhur. Neorg. Khim., 16, 853 (1971) [Russ. J. Inorg. Chem., No. 3 (1971)].
282. A. M. Golub and Yu. E. Kosmatyi, Zhur. Neorg. Khim., 4, 1347 (1959) [Russ. J. Inorg. Chem., No. 6 (1959)].
283. A. M. Golub, Zhur. Neorg. Khim., 4, 1577 (1959) [Russ. J. Inorg. Chem., No. 7 (1959)].
284. V. V. Skopenko, G. V. Tsintsadze, and A. M. Truba, Visnik. Kiivsk. Univ., Ser. Khim., No. 11, 9 (1970).
285. A. N. Nesmeyanov and N. A. Nesmeyanov, "Nachala Organicheskoi Khimii" (Principles of Organic Chemistry), Izd. Khimiya, Moscow, 1970, Vol. 11, p. 380.
286. E. O. Fischer and H. Werner, "π-Complexes" (Translated into Russian), Izd. Mir, Moscow, 1968.
287. P. L. Pauson, "Organometallic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1970.
288. V. G. Syrkin, "Khimiya i Tekhnologiya Karbonil'nykh Metallov" (The Chemistry and Technology of Carbonyl Metals), Izd. Khimiya, Moscow, 1972.
289. V. I. Mikheeva, "Gidridy Perekhodnykh Metallov" (Transition Metal Hydrides), Izd. Akad. Nauk SSSR, Moscow, 1960.
290. D. T. Hurd, "Introduction to the Chemistry of the Hydrides" (Translated into Russian), Inostr. Lit., Moscow, 1956.
291. A. F. Zhigach and D. S. Stasinevich, "Khimiya Gidridov" (The Chemistry of Hydrides), Izd. Khimiya, Leningrad, 1969.
292. C. C. Addison, "Advances in Inorganic Chemistry and the Chemistry of Organic Derivatives of the Elements. Proceedings of the 17th International Congress of Pure and Applied Chemistry, Munich, 1959" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 233.
293. V. Ya. Rosolovskii and G. N. Shirokova, "XI Vsesoyuznoe Soveshchanie po Khimii Kompleksnykh Soedinenii, Tezisy Dokladov, Alma-Ata, 1973" (The 11th All-Union Conference on the Chemistry of Complex Compounds. Abstracts of Reports, Alma-Ata, 1973), p. 56.
294. V. A. Dorokhov, V. I. Seredenko, and B. M. Mikhailov, "XI Vsesoyuznoe Soveshchanie po Khimii Kompleksnykh Soedinenii, Tezisy Dokladov, Alma-Ata, 1973" (The 11th All-Union Conference on the Chemistry of Complex Compounds. Abstracts of Reports, Alma-Ata, 1973), p. 44.
295. A. D. Allen and C. V. Senoff, Chem. Comm., 621 (1965).
296. A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, J. Amer. Chem. Soc., 89, 5595 (1967).
297. Yu. G. Borod'ko and A. E. Shilov, Uspekhi Khim., 38, 761 (1969) [Russ. Chem. Rev., No. 5 (1969)].
298. I. S. Kolomnikov, T. S. Belopotatopova, and M. E. Vol'pin, "XV Mezhdunarodnaya Konferentsiya po Koordinatsionnoi Khimii, Tezisy Dokladov, Moskva, 1973" (The 15th International Conference on Coordination Chemistry. Abstracts of Reports, Moscow, 1973), p. 358.
299. J. M. Bancroft, M. J. Mays, and R. E. Prater, Chem. Comm., 1223 (1968).
300. P. L. Pauson, H. Zeiss, G. E. Coates, and F. Glockling, "Organometallic Chemistry" (Edited by H. Zeiss) (Translated into Russian), Izd. Mir, Moscow, 1964.
301. B. F. Hallam and P. L. Pauson, J. Chem. Soc., 642 (1958).
302. W. Hieber, Z. Naturwiss., 36, 312 (1949).
303. A. Burg and J. Dayton, J. Amer. Chem. Soc., 77, 3233 (1949).
304. W. Hieber and C. Bartenstein, Z. anorg. Chem., 276, 12 (1954).
305. H. I. Schlesinger, H. C. Brown, H. R. Hoekstra, and L. R. Rapp, J. Amer. Chem. Soc., 75, 199 (1953).
306. G. Codama, R. W. Parry, and J. C. Carter, J. Amer. Chem. Soc., 81, 3534 (1959).
307. B. W. Craybill and J. K. Ruff, J. Amer. Chem. Soc., 84, 1062 (1962).
308. C. W. Heitsch and J. G. Verkade, Inorg. Chem., 1, 863 (1962).
309. B. M. Mikhailov and M. E. Kuyamova, Uspekhi Khim., 35, 1349 (1966) [Russ. Chem. Rev., No. 8 (1966)].
310. A. M. Golub, V. V. Grachevskii, and N. V. Ul'ko, Koord. Khimiya, 2, 59 (1976).
311. H. Schmidt, Z. anorg. Chem., 271, 305 (1952).
312. A. E. Wickenden and R. A. Krause, Inorg. Chem., 4, 404 (1965).
313. T. Pavlopoulos and H. Strehlow, Z. phys. Chem., 2, 89 (1954).
314. G. J. Sutton, Austral. Chem. Inst. J. and Proc., 16, 115 (1949).
315. G. Spacu and R. Ripan, Bull. Soc. Stiinte Cluj, 4, 3 (1928).
316. Ts. L. Makhatadze, Candidate's Thesis, GPI, Tbilisi, 1973.
317. M. I. Usanovich, V. V. Klimov, and T. N. Sumarokova, Zhur. Obshch. Khim., 21, 987 (1951).
318. M. I. Usanovich, V. V. Klimov, and T. N. Sumarokova, Dokl. Akad. Nauk SSSR, 113, 364 (1957).
319. J. D. Donaldson and D. G. Nicholson, J. Chem. Soc. (A), 145 (1970).
320. G. Röhler, Z. Elektrochem., 16, 419 (1910).
321. A. M. Golub, T. P. Lishko, and V. V. Skopenko, Ukrain. Khim. Zhur., 37, 835 (1971).
322. A. M. Golub, M. V. Kopa, and G. V. Tsintsadze, Zhur. Obshch. Khim., 41, 15 (1971).
323. A. M. Golub, M. V. Kopa, V. V. Skopenko, and G. V. Tsintsadze, Ukrain. Khim. Zhur., 36, 851 (1970).
324. A. M. Golub, V. V. Skopenko, M. V. Kopa, and G. V. Tsintsadze, Z. anorg. Chem., 375, 302 (1970).
325. V. V. Skopenko and A. I. Brusolovets', Ukrain. Khim. Zhur., 34, 1210 (1968).
326. O. E. Andreichenko, Ukrain. Khim. Zhur., 30, 1255 (1964).
327. A. M. Golub, G. V. Tsintsadze, and A. M. Mamulashvili, Ukrain. Khim. Zhur., 36, 1207 (1970).
328. G. V. Tsintsadze, Yu. Ya. Kharitonov, A. Yu. Tsivadze A. M. Golub, and A. S. Managadze, Zhur. Neorg. Khim., 15, 2336 (1970) [Russ. J. Inorg. Chem., No. 9 (1970)].

329. A. M. Golub, G. V. Tsintsadze, and Ts. L. Makhatadze, Soobshch. Akad. Nauk Gruz. SSR, **61**, No. 1, 57 (1971).
330. G. V. Tsintsadze, A. S. Managadze, A. M. Golub, and E. A. Kvazereli, Trudy. Gruz. Politekh. Inst., No. 5 (153), 5 (1972).
331. G. V. Tsintsadze, A. M. Golub, and A. S. Managadze, Trudy. Gruz. Politekh. Inst., No. 1 (136), 52 (1970).
332. A. M. Golub, G. V. Tsintsadze, and A. M. Mamulashvili, Zhur. Neorg. Khim., **14**, 3013 (1969) [Russ. J. Inorg. Chem., No. 11 (1969)].
333. A. Yu. Tsivadze, G. V. Tsintsadze, Yu. Ya. Kharitonov, A. M. Golub, and A. M. Mamulashvili, Zhur. Neorg. Khim., **15**, 1818 (1970) [Russ. J. Inorg. Chem., No. 7 (1970)].
334. A. M. Golub and Au Van Long, Zhur. Neorg. Khim., **14**, 90 (1969) [Russ. J. Inorg. Chem., No. 1 (1969)].
335. A. M. Golub and Fam Van Cha, Ukrain. Khim. Zhur., **36**, 233 (1970).
336. A. M. Golub and Fam Van Cha, Zhur. Neorg. Khim., **15**, 2071 (1970) [Russ. J. Inorg. Chem., No. 8 (1970)].
337. G. V. Tsintsadze, A. M. Golub, Ts. L. Makhatadze, and A. Yu. Tsivadze, Trudy. Gruz. Politekh. Inst., No. 5 (153), 25 (1972).
338. R. S. P. Coutts and P. C. Wailes, Austral. J. Chem., 19, 2069 (1966).
339. J. Z. Burmeister, E. A. Deardorff, A. Jensen, and V. H. Christiansen, Inorg. Chem., 9, 58 (1970).
340. W. I. Wallace, A. M. Golub, and R. W. Dabeka, "Proceedings of the XVth ICCC", Nauka, Moscow, 1973, p. 292.
341. H. Köhler, T. P. Lischko, H. Hartung, and A. M. Golub., Z. anorg. Chem., **403**, 35 (1974).
342. H. Köhler, H. Hartung, and A. M. Golub, Z. anorg. Chem., **403**, 41 (1974).
343. G. V. Tsintsadze, A. Yu. Tsivadze, and Ts. L. Makhatadze, Soobshch. Akad. Nauk Gruz. SSR, **56**, 303 (1969).
344. H. Ginsberg, Aluminium (DRF), **32**, No. 3, 145 (1956).
345. W. Sundermeyer and O. Glemser, Angew. Chem., **70**, 625 (1958).
346. D. C. Luehrs, R. T. Iwamoto, and J. Kleinberg, Inorg. Chem., **5**, 201 (1966).
347. L. Audrieth, "Acids, Bases and Non-aqueous Systems", State College, Pa, 1949.
348. M. Schmidt and J. Löwe, Angew. Chem., **72**, 79 (1960).
349. S. Herzog and R. Taube, Angew. Chem., **70**, 469 (1958).
350. S. Herzog and R. Taube, Z. anorg. Chem., **306**, 159 (1956).
351. J. D. Corbert and R. K. McMullan, J. Amer. Chem. Soc., 78, 2906 (1956).
352. G. A. Harlow and D. H. Morman, Anal. Chem., **40**, 418 R (1968).
353. J. J. Lagowski, Anal. Chem., **U2**, 305R (1970).
354. A. P. Kreshkov, L. N. Bykova, and N. A. Kazaryan, "Kislotnoosnovnoe Titrovanie v Nevodnykh Rastvorakh" (Acid–Base Titration in Non-Aqueous Solutions), Izd. Khimiya, Moscow, 1967.
355. A. M. Golub and F. F. Grigorenko, Zhur. Neorg. Khim., **6**, 2344 (1961) [Russ. J. Inorg. Chem., No. 10 (1961)].
356. R. N. Sauder and I. I. Lauder, Electrochem. Techn., **4**, 179 (1966).
357. A. K. Pikaev, "Sol'vatirovannyi Elektron v Radiatsionnoi Khimii" (The Solvated Electron in Radiation Chemistry), Izd. Nauka, Moscow, 1969.
358. M. J. Blandamer, L. Shields, and M. C. R. Symons, J. Chem. Soc., 3759 (1965).

Department of Inorganic Chemistry,
Faculty of Chemistry, Shevchenko
Kiev State University