Modern aspects of thermodynamics and structure of nonaqueous solutions*

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Abstract - A set of general questions about the thermodynamics of ionic
processes in non-aqueous solutions and their dependence on composition and
external conditions is discussed; thermodynamic approaches for ascertaining
the role of a solvent, thermodynamic characteristics of solvation, methods
of definition of standard thermodynamic characteristics, properties of non-
aqueous solutions at lowered temperatures, and influence of microadmixtures.

Thermodynamic methods of investigating solutions are considered. The
fruitfulness and universitality of ascertaining the solvent role in chemical
reactions, their effectiveness for studying structural changes of solvents
and solutions with change of external factors (temperature, pressure),
nature of additions, composition and others is presented. The advantage
over many other solution investigation methods is that they characterize
structural changes of solutions, taking into account both energetic and
entropy factors.

Studies take into account the double function of a solvent, i.e. as medium
and as chemical reagent.

The absence of thermodynamic data for individual ions in solution is
marked. To ignore the different types of ion-molecular interactions for
cations and anions, and the thermodynamics of coordination and solvation
of individual ions is a major disadvantage.

Different methods of obtaining the standard thermodynamic characteristics
based both on extrapolation and non-extrapolation approaches are discussed.
The problems of creation of a physico-chemical 'passport system' of non-
aqueous solutions, data banks and others is considered. The properties of
non-aqueous solutions at lowered temperatures, the influence of added water
and the constituent gases in air are of specific interest.

Attention is paid to the need of the correct analysis of composition-
property diagrams and their rationalization, pointing to choices of
composition and property indices at which a linear dependence between them
in an ideal system is observed.

The influence of the solvent on solubility, physico-chemical properties
and state of species in solutions are considered with other issues.

Numerous examples illustrating the investigation are given.

INTRODUCTION

The scientific and practical importance of the chemistry of non-aqueous solutions is clear
from the existence of many chemical reactions, including industrial processes, which cannot
proceed in the presence of water. By participating directly in a chemical process the
solvent is a determining factor of that process. Thus new methods of inorganic and organic
synthesis, using multicomponent mixtures and diversification of technological procedures can
develop.

The solvent has a double role - both as the medium and as a reagent. While chemical
properties of the solvent influence the reactant's solvation processes remain of primary
importance.

Solvation of the particles in solution involves ion-molecular, ion-ion, and intermolecular interactions of a chemical nature (ref. 1). Thus it is important to study solvation properties. These are related to the properties of the reagents (atomic, molecular and ionic species), the various solvent properties, external conditions, solution composition, and any added species (such as air, gases, and small quantities of other components remaining even after the best purification). The general lack of information on solvation properties results from a gap which exists between the known information on solution properties and its generalised interpretation taking into account interactions in solution.

The range of problems is wide. The most important of them to be discussed are : solutions as chemical systems; elaboration of a theoretical base; method of rational parameters in physico chemical analysis; association of equilibria with physico-chemical properties; specificity of solvation of the most important macrocyclic compounds.

SOLUTIONS AS CHEMICAL SYSTEMS

A solution is a complex equilibrium system involving a solvent, a solute and products of their interaction. Investigation of solutions as chemical systems on a quantitative basis is one of the main directions in the development of solution theory.

Systems are characterised by their different interparticle interactions (specific and universal). Ascertaining the form of existence and mutual influence of the atomic-molecular particles in solutions over a wide range of compositions, component nature, and external conditions is of essential importance. The problem of describing 'solvent-solute' inter-actions by means of iodine-containing systems is arguable. One cannot do this without using approximate methods.

The interrelation of electrolyte solubility across various solvents highlights the complex nature of interparticle interactions in solution (ref. 2). Using the supposition (ref. 3) that their activity coefficients are equal in saturated solutions a linear correlation between the logarithms of solubility and dielectric penetrability should occur in the cases of slightly soluble and poorly associated electrolytes. Figure 1 shows the plotted $AgCl$, KCl, $CsClO_4$, $KClO_4$, data for AgCI, KCI, $CsClO_4$, $KClO_4$ against $\ln C_{sat}$ and $f(\ln \varepsilon)$.

It can be seen from Fig. 1 that two straight lines with various linear correlation constants for protonic and aprotic solvents are characteristic of AgCl. This indicates different stabilization mechanisms for ionic species in the various solutions. Deviation from linearity for hmpa and dmso can be explained by complex formation.

A linear correlation is not observed for KCl in dipolar aprotic solvents. One should note that the KCl solubility differs by some orders for the solvents which have nearly the same values of dielectric penetrability (AN, DMF, FFL = furfural, DMA).

$1-C_4H_8O; 2- i-C_5H_{11}OH; 3-CH_3COC_3H_7; 4-C_4H_9OH; 5- i-C_4H_9OH$
$6-C_6H_5COCH_3; 7- i-C_3H_7OH; 8-C_4H_8O; 9-C_3H_9OH; 10-(CH_3)_2CO$
$11-C_2H_5OH; 12-C_2H_2F_3OH; 13-HMPTA; 14-CH_3OH; 15-CH_3CN$
$16-DMFA; 17-DMAA; 18-C_5H_4O_2; 19-DMSO; 20-CHCOOH$
$21-PC; 22-H_2O; 23-FA; 24-MFA$
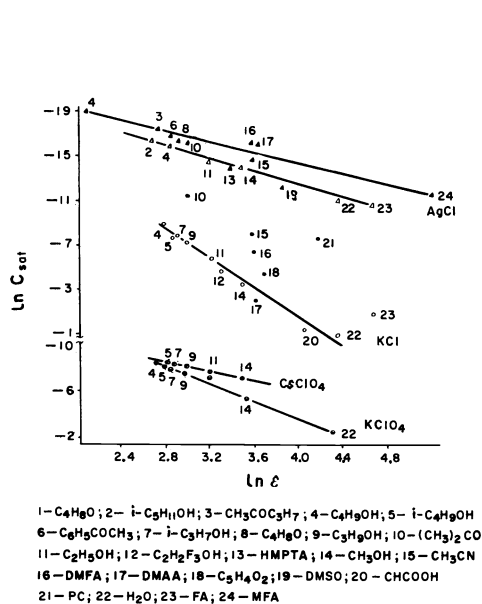
Fig. 1 $\ln C_{sat}$. vs. $f(\ln \varepsilon)$ for a number of electrolytes in various solutions at 298.15 K.

1—AN; 2—Ac; 3—PC; 4—DMAA
5—DMFA; 6—THF; 7—HMPTA; 8—DMSO
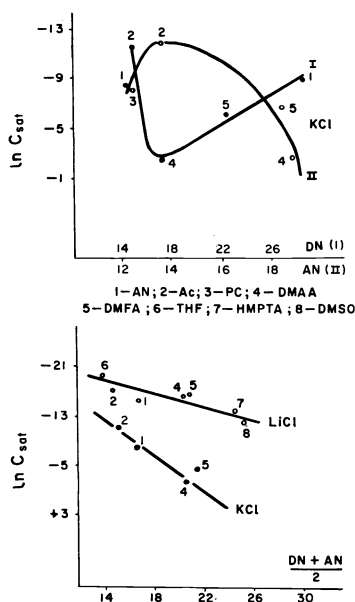
Fig. 2. Dependence of $\ln C_{sat}$. vs. $f(DN$ or $AN)$ for KCl, and $\ln C_{sat}$. vs. $f\{(DN + AN)/2\}$ for KCl and AgCl

This appears to be connected with specific interaction of electrolyte ions with the given solvents which act both as electron pair donors and as acceptors. Donor and acceptor values used separately allow a description of the changes of relative solubility in aprotic solvents. In this respect the average of donor and acceptor values is more successful (ref. 2). (Figure 2).

Solutions can be regarded as a statistical ordering of interacting atomic-molecular particles This view considerably changes our traditional concepts of liquid and solution models. These concepts are changed by their generalized description through the series of characteristic peculiarities of structure which constitute the base of the generalized model concepts.

It should be noted that none of the existing methods of investigation yields complete information about the solvent and solution structure. Taking into account what has been said above, this problem can be solved only by the combination of results obtained from several types of investigation. Arbitrary interpretation of results is as great a disadvantage as the limited number of the methods. Thus, on the one hand, there is a need for purposeful choice of experimental method for which at least specificity, sensibility and the applicability of conditions are known. On the other hand, it is necessary to compare the properties of chemical systems which consist of the same number of particles. The use of the unitary concentration scales, mole (rational) parameters, etc. meets these requirements. Only in this case is a quantitative interrelation between macro-macro and macro-micro-properties possible.

ELABORATION OF THE THEORETICAL BASE

The theoretical basis of non-aqueous solution chemistry requires new approaches and methods because for many decades the physical chemistry of solutions was based on aqueous solutions.

Work in this direction is aimed at creation of a theory of non-aqueous solutions which connects structural and thermodynamic properties with the characteristics of the molecules and ions forming the solution. This should explain individual singularities of chemical interactions in non-aqueous media and allow purposeful choice of solvent for chemico-technological processes, and should yield possibilities of *a priori* calculation of the properties of complex systems.

Phenomenological and statistical thermodynamics, the method of comparison and generalisation of vast amounts of experimental information, methods of physico-chemical analysis, and others are the theoretical foundation of these approaches.

Active work in this area is carried out in many countries (USSR, USA, UK, France, GDR, Japan, Canada etc.). Here it is impossible in a short time to consider even the main of them briefly, and I present here just the least known results of our investigations carried out since 1962. These constitute the basis of a structural-thermodynamic theory of electrolyte and nonelectrolyte solutions. A quantitative approach of the description of ion and molecule solvation processes reveals the contributions related to the energetic and structural solvent changes as thermodynamic solvation functions.

Contributions to ionic systems are evaluated by considering cavity formation within a solvent (dependent on ionic size), the transfer of a neutral particle isoelectronic with the ion into the cavity) and the redistribution of the electron cloud between the ion and the solvent molecules (the contribution of other interactions depend on the ionic charge). The entropic contribution (depending on the ionic size and redistribution of the electron cloud) is the most important quantitative characteristic of solvatability of ions and structural solvent changes.

On the basis of developed theoretical hypotheses and the vast amount experimental information we have obtained, the thermodynamic functions of dissolution and solvation, and their structural components for a large number of ions in different solvents have been defined. More than a hundred salts in different organic and inorganic solvents and a large number of their mixtures have been investigated. Gas solubility data for a wide series of solvents has also been obtained. Conclusions about structural solvent changes, made on the basis of the thermodynamic characteristics, were confirmed by studies using other physical methods (NMR, EPR, radiation, etc.).

Changes in solvatability of species and the dependence on the ion and solvent nature have been established; the phenomenon of negative solvation of ions in mixed solvents has been established and the conditions under which this phenomenon is possible has been defined; the dependence of solvation on temperature has been established and the phenomenon of the local solvation of ions at lowered temperatures discovered; the influence of hydrophilic molecule fragments on the solvent structure has been defined for solutions of organic substances and solvophobic effects in non-aqueous solutions discovered. These are discussed fully in our monograph (ref. 1).

It was found in the investigations that a temperature increase leads to increase of positive, and decrease of negative, solvation of ions in individual solvents. Nonelectrolytes added to water can both increase and diminish positive and negative solvation effects depending on their nature, concentration and temperature.

An anomalous behaviour of heat of dissolution in non-aqueous solvents, manifested by increase of exothermicity with temperature decrease (below 273 K), has been discovered for a series of electrolytes. From these data a conclusion emerged concerning the existence of the of local solvation. The NMR method showed this to be related to the temperature decrease and the corresponding formation of hydrogen bonds versus the action of ions and their disruption. A new effect similar to the hydrophobic effect was discovered by ascertaining the role of the energetic and structural factors for systems with a spatial hydrogen bond net. The hydrophobic effect was observed on large complex ions not containing hydrophobic groups.

New standard states and measuring levels allowing thermodynamic functions to be obtained for coordinated ions and atoms, in the gaseous state and in solution, are proposed. They are based on taking into account the real distribution of particles and use the coordinated values of the thermodynamic characteristics of the proton. Calculation methods are elaborated and the thermodynamic properties of a large number of ions, rare-earth and actinide elements are included over a wide interval of temperatures.

The equilibrium constants were separated into the enthalpy, entropy and structural components. The role of the solvent in oxidation-reduction, acid-base, complex-formation, precipitation, and exchange reactions, in concentrated solutions was characterised using the structural components. The analytical results obtained showed that, in many cases, changes in the thermodynamics of processes in solutions are determined by change of solvent.

Other thermodynamic approaches are used to ascertain the solvent role in chemical reactions. Thermodynamic functions for reactions in the solution and the gaseous phases (for two different solvents – one taken as the standard) are used and solvatothermodynamic and donor-acceptor characteristics are introduced. An approach revealing the role of the solvent in complex formation and based on the use of the thermodynamic characteristics of the solvation (transfer) of each of the reaction reagents, is elaborated. The approach is based on a large experimental database of the thermodynamics of complex formation reactions in non-aqueous and mixed solvents.

The influence of small concentrations of component admixtures (gases, water etc.) on the thermodynamic functions of dissolution into non-aqueous media is very important and new results are presented; this required a critical literature survey. Numerous difficulties relating to the necessity of taking into account specific solvent properties and the degree of purity, the modernization and creation of experimental equipment, and the treatment and interpretation of the results obtained, were overcome. Precision calorimeters and apparatus for determining gas solubilities, and many other physico-chemical properties of solutions under a wide variety of conditions were used.

METHOD OF RATIONAL PARAMETERS IN PHYSICOCHEMICAL ANALYSIS

Analysis of the condition-property diagrams remains an effective means of studying thermo-dynamic and transport properties of solutions. It offers the means of establishing relationships between the deviation of a parameter from additivity and a property of an interacting component. In the case of the formation of a compound in a binary system, or an interaction governed by the law of mass action, the ideal corresponds to stoichiometric quantities. A change of equilibrium constant due to temperature or pressure causes only a change in the absolute value of deviation, without influencing the limiting position relative to the composition axis.

When several compounds are formed, the character of the isotherm of the deviation of the mole parameter from additivity is defined by the correlation of all the equilibria of a system. Here the extreme of the deviation from additivity can depend on T and P. To establish a more substantiated correspondence between the elements of the composition-property diagram and the chemical processes in a system a new method of approach – the method of rational parameters – should be used. This is based on a transformation of the property such that it will always characterise the same number of initial particles in a mixture. This transformation is called rationalization and the parameters obtained – rational (ref. 2). Rationalization of the composition-property diagrams supposes a choice between the property and the composition indices at which a linear dependence between them is observed in an ideal system. When the composition coordinates are expressed in mole fractions, mole parameters are rational. Only those parameters depending on the substance quantity (Δc_p, ΔH, etc.) can be easily trans-formed into mole parameters. The majority of experimentally determined parameters are independent of the substance quantity (ε – dielectric permeability, n^D – refraction index, η – viscosity, V_{sound} – sound velocity, D – dipole moment, etc.). Numerous attempts at finding their dependencies on composition in ideal systems (based on models,and empirically) were unsuccessful.

Under these conditions another approach seems a reasonable alternative. Essentially this is the finding of new parameters determined by the observed values on the one hand, and which also depend on the substance quantity on the other. Consequently, it is possible to pass from the above parameters to their rational analogues : molar viscosity, molar dielectric permeability, molar velocities of ultra-sound and electromagnetic vibration spreading (ref. 2) In contrast to hydrodynamic viscosity, electrostatic dielectric permeability and others, molar indices are the true physico-properties in the medium.

It sould be noted that on passing from specific and relative parameters to molecular ones not only the absolute values but the sets of properties also change. It is worth noting that the dynamic viscosity of methanol is nearly twice as much as that of acetone (this gave some authors grounds to draw conclusions about structural differences between solvents), but their molar viscosity values are practically the same.

The use of rational parameters allows the exclusion of noncoordinated conclusion when the same systems are investigated by different experimental methods.

Some authors (refs. 3,4,5) have noted the complicated and heterogeneous nature of the dependence of the series of properties (ε, n^D, η, V, C_p, ΔH, etc.) on composition, when studying the H_2O-DMF system (fig. 3).

Figure 3 shows the property dependence on the composition in conventional units ($Y_{c.u.}$). These are related linearly to the real properties by

$$Y = Y_o + kY_{c.u.} \tag{1}$$

Numerical values of Y and k for a series of properties of H_2O-DMF system at 293 K are given in Table 1.

It did not allow them to prefer any of the possible stoichiometric component interaction mechanisms. The use of this approach shows that the extreme of the deviation of all the rational parameters of the properties mentioned refer to the same mixture composition, namely $x \approx 0.33$ mole fraction of DMF (fig. 3).
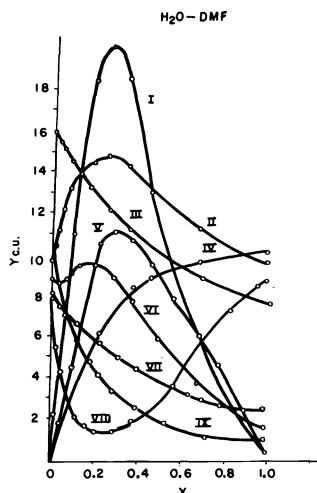

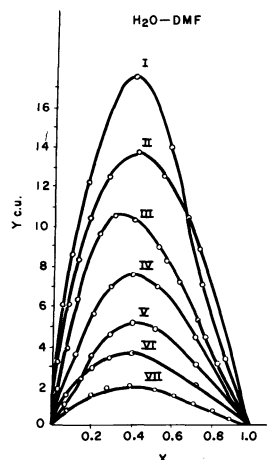Fig. 3. Dependence of physico-chemical parameters on the DMF-H_2O mixture at 293 K.

Fig. 4. Concentration dependence of H_2O-DMF solutions of the deviation of molar properties from additivity at 293 K.

TABLE 1. Coefficients of equation (1)

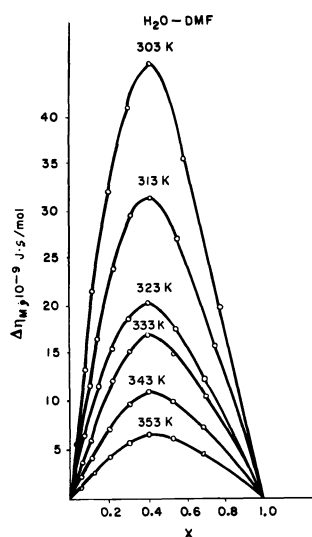|	I	II	III	IV	V	VI	VII	VIII	IX
Y	$\eta \cdot 10^5$	V_{sound}	ε	n^D	ΔH_{mix}	ρ	c_p^{sp}	$\beta_y \cdot 10^5$	σ
	$g.cm^{-1}.s^{-1}$	$m.s^{-1}$	298 K		303 K $J.mol^{-1}$	$g.cm^{-3}$	298 K $J.g^{-1}.K$	atm^{-1}	$J.cm^{-1}$
Y_o	800	1000	0	1.33	0	0.94	1	30	35
k	100	50	5	0.01	209	0.0067	0.4	2	3.33

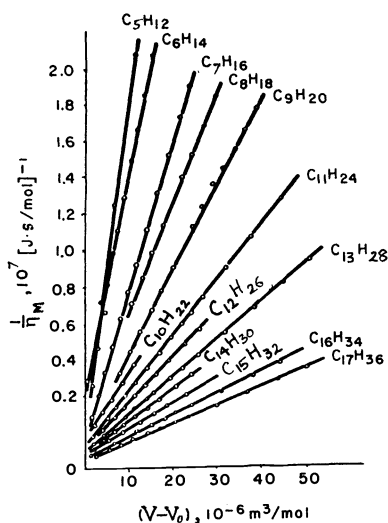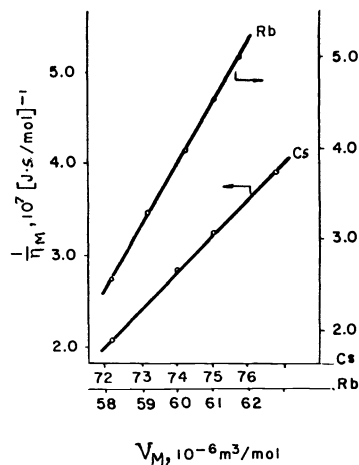Fig. 5. Dependence of surplus molar viscosity on the concentration of H_2O-DMF at different temperatures.

Fig. 6. Dependence of reciprocal molar viscosity $(1/\eta_M)$ of liquid metals (Cs, Rb) on molar volume (V_M).

In fig. 4 real properties (Y) are related to the properties in conventional units $(Y_{c.u.})$ by

$$Y = kY_{c.u.} \tag{2}$$

Numerical values of k are given in Table 2.   The extreme position on the composition axis is independent of temperature (Fig. 5). This points to the formation of labile molecular complexes of 2:1 composition in H_2O-DMF systems.

The use of the rational parameters allowed a series between the relative change of molar fluidity and mole or free mole volume of a large number of solvents including alkanes, unsaturated and aromatic hydrocarbons, halogenic and cyclic compounds, alcohols, ketones, organic acids and even liquid metals (Fig. 6).

It was found also that the effect of the 'negative' viscosity, determined by the decrease in the dynamic viscosity of a solution on addition of an electrolyte (e.g., KI to water), when compared with the solvent viscosity, is absent.

From this view point, the changes in the thermodynamic functions of complex formation, ionic association and solvation processes on the change of the solvent composition is of interest. The existing system of the use of experimental thermodynamic parameters results in erroneous conclusions, because practical thermodynamic parameters standardized, according to molality and molarity scales, depend on the number of solvent moles in unit mass or volume and, consequently, on solvent composition.

Experimentally determined thermodynamic functions of processes in solutions are, thus, complex values containing two contributions. One yields information about the process in the form of a rational part $(\Delta G_N^{\,o}, \Delta S_N^{\,o})$, and the other takes into account the number of moles of a solvent in a unit of its mass or volume, i.e.,

$$\Delta G_{m(c)}^{\,o} = \Delta G_N^{\,o} + \nu RT \ln \frac{10^3}{M} (\rho)_c \tag{3}$$

$$\Delta S_{m(c)}^{\,o} = \Delta S_N^{\,o} - \nu R \ln \frac{10^3}{M} (\rho)_c \tag{4}$$

TABLE 2. Coefficients of equation (2)

	I	II	III	IV	V	VI	VII
	$\Delta\eta.10^{-5}$	$-\Delta\tau_M$	$-\Delta H_{mix}$	$-\Delta\tau_{sound}.10^{-2}$	$-\Delta V_M.10^{-6}$	$-\Delta c_M.10^{-12}$	Δc_p^{mol}
	$J.s.mol^{-1}$	$s.mol^{-1}$	303 K $J.mol^{-1}$	$s.mol^{-1}$	$m^3.mol^{-1}$	$\phi.mol^{-1}$	298 K $J.mol.K^{-1}$
k	4	0.084	209.2	0.05	0.2	0.375	4

TABLE 3. Rational and experimental stability constants (mol/l) of cobalt monoammines in aqueous methanol solutions at 298.15 K.

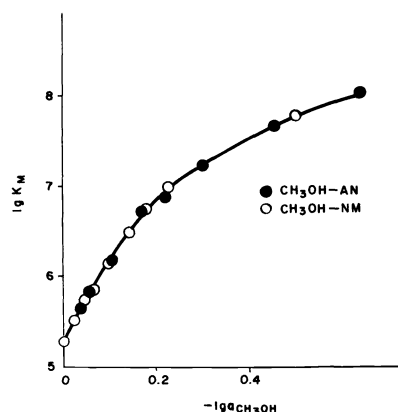| X_{CH_3OH}	0.00	0.05	0.11	0.16	0.21	0.32	0.43	0.55
$\lg K_C$ $\pm$ 0.01	1.98	2.01	2.03	2.04	2.05	2.09	2.18	2.19
$\lg K_N$ $\pm$ 0.01	3.73	3.74	3.73	3.72	3.72	3.70	3.74	3.71

Fig. 7. Dependence of the rational stability constants of triiodide complexes on methanol activity in mixed solvents.

The dependencies of the experimentally determined thermodynamic properties of processes on the solvent composition and its macroscopic properties are often defined by the change of the number of moles of a solvent in the unit mass or volume but not by the effect of the physico-chemical interactions. Thus it results in an incorrect interpretation. We can give the example that the change of the experimental constants of the constancy of cobalt mono-amine complexes in water-methanol media with change of solvent composition is related to the change of the 'packing fraction' and not to solvation effects, as discussed earlier. Rational constants of the constancy do not depend on the solvation composition here (Table 3).

The change of the rational parameters between complexes containing mono- and polydentate ligands leads to the other important result. Proceeding from the analysis of the experimental thermodynamic parameters many investigators interpret the 'chelate effect' as entropically governed; due to substitution of two or more solvent molecules by a polydentate ligand. On passing to the rational thermodynamic parameters the chelate effect is seen to be determined in a number of cases by the enthalpy contribution.

It is essential that only the rational parameters are used to differentiate the role of a solvent as reagent and medium in complex formation in mixed solvents. It is possible not only to ascertain the role of the separate components of a binary solvent, but possibly also to establish the mechanism of solvation and resolvation of the reactants.

Thus it is possible to establish that the stability of triiodide complexes, in systems which incorporate methanol, corresponds in mixed solvents containing different corresponding proportions of the second component (Fig. 7).

ASSOCIATE EQUILIBRIA IN LIQUIDS AND THEIR PHYSICOCHEMICAL PROPERTIES

Quantitative prediction of the physico-chemical solution properties on the basis of data concerning the structure of molecules and intermolecular interactions is one of the central problems of solution chemistry. Nowadays a strictly liquid state theory, based on the formalism of distribution functions, yields practical results only for the simplest models (solid spheres with different diameters). The use of computer simulation methods (Monte-Carlo and molecular dynamics) leads us to ignore the entropy factor because of the limited number of particles. This is why there is interest in different variants of lattice theories, group models of ASOG, UNIFAC, and others. In spite of the possibility of calculating solution properties, the disadvantage of these models lies in the use of the adjusted parameters.

Equilibrium theory is being further developed. The existence of associates and complexes in a solution considerably influences its properties, the excess functions in particular. A method of calculation of the excess macroscopic solution properties from the associate parameters of its component is developed. The essence of the approach is in finding the functional dependence of any parameter chosen for calculating the physico-chemical properties and of any thermodynamic parameter of the system (ΔG, ΔH), which can be calculated from quantitative data on associated species and complexes.

Information about associates and complexes in solution, obtained by different methods, and often by the same method but by different authors, is far from being consistent. For example, association constant values differ considerably even within the same experimental method. There are no objective criteria for selection of one model rather than another.

Let us consider the example of the three physico-chemical properties of a system: heat capacity, viscosity and diffusion. The excess molar heat capacity of a binary solution of a non-electrolyte can be calculated

$$C_p^E = \frac{\partial H_{ass}}{\partial T} = \frac{\partial}{\partial T} (\sum_i X_i H_i) \tag{5}$$

where X_i is the concentration of different associates, and H_i is the enthalpy of formation of each. We have derived (ref. 6) a method of correlation for calculating C_p^E for various cases of association in solution. The applicability of these correlations was illustrated by a series of binary non-aqueous systems (ethanol-cyclohexane, chloroform-benzene, acetone-chloroform). In order to calculate viscosity, we used the activation of the viscous flow mechanism, according to which molecules overcome an energy barrier when they move relative to each other. The value of molar viscosity, ηV_M, depends on the height E of this barrier by

$$\eta_M = \eta V_M = A \exp(E/RT). \tag{6}$$

In the case of associated liquids and solutions the height of the barrier includes the energy necessary for the disruption of a bond caused by a molecule leaving an associate or complex. Rapid exchange between associated forms results in the height of the energy barrier for all the molecules being averaged (confirmed by the validity of equation (6)). Now

$$E = X_1 E_1 + X_2 E_2 + \Delta E_{ass} \tag{7}$$

where E_1 and E_2 are values of the 'physical' contributions to the activation energy for each of the components; X_1 and X_2 are the concentrations of the components of the binary system; ΔE_{ass} reflects the association process. Following from,

$$E = E_1 X_1^o + E_2 X_2^o + \sum_i X_1^i E_1^i + \sum_i X_2^j E_2^j \tag{8}$$

where X_1^o and X_2^o are the proportions of non-bonded molecules; E_1^i and E_2^j are the energies of bonding component molecules 1 and 2 in i and j associates (or complexes) respectively; X_1^i and X_2^j are the relative proportions of component molecules forming the associate (or complex), then

$$\Delta E_{ass} = \sum_i (E_1^i - E_1) X_1^i + \sum_j (E_2^j - E_2) X_2^j. \tag{9}$$

From (6) to (9) we obtain an expression for the molar viscosity logarithm as follows;

$$\ln(\eta V_M) = X_1 \ln(\eta V_M)_1 + X_2 \ln(\eta V_M)_2 + (\Delta E_{ass})^E, \tag{10}$$

where

$$(\Delta E_{ass})^E = \Delta E_{ass} - X_1 \Delta E_{1ass} - X_2 \Delta E_{2ass} \tag{11}$$

Equation (10) establishes a relationship between the viscosity of the associated non-electrolyte solutions and the parameters of the association equilibria. The applicability of equation (10) was examined using the examples of acetonitrile-carbon tetrachloride, acetonitrile-acetone, acetonitrile-ethanol systems (ref. 7). Satisfactory agreement of experiment with theory was obtained in all the cases.

The temperature dependence of self-diffusion coefficients of the solution component of non-electrolytes is also described by the following expression:

$$\frac{D_A}{V^{2/3}} = B \exp(-\frac{E_{dif}^A}{RT}) \tag{12}$$

where B = constant, E_{dif} is the activation energy of the self-diffusion processes for component A in solution. With the same reasoning as above for deriving the correlations for the solution viscosities, we obtain:

$$\ln \frac{D_A}{V^{2/3}} = X_A \ln \frac{D_A^A}{V_A^{2/3}} + X_B \frac{D_B^A}{V_B^{2/3}} - \sum_i (\alpha^i - X\alpha_B^i) E_{ass} \tag{13}$$

where D_A^A is the self-diffusion coefficient of A in a pure solvent A, D_B^A is the diffusion coefficient of A in an infinitely dilute solution of B, α^i is the degree of molecules of component A forming the associate (or complex) of type i,

$$\alpha_B^i = \lim_{X_A \to 0} \alpha^i.$$

It should be noted that none of the correlations presented contain empirical coefficients.

The approach proposed allows the 'true' values of the association parameters in a system to be obtained. Obviously, if the same initial data of the association parameters allow calculation of different physico-chemical solution properties (thermodynamic Δc_p, transport η, D and others) precisely enough, this is a criterion for the value of the association parameter.

Acetone-chloroform was chosen as a test system to examine the correlations obtained. This system can be studied by both physico-chemical and spectroscopic methods. The structure of complexes formed by acetone and chloroform molecules with the association equilibrium constants used are as follows

$$
\begin{array}{ll}
H_3C & \\
\quad \diagdown & \text{Kass = 0.967} \\
\quad\quad C=O\ldots H-CCl_3 & \\
\quad \diagup & \\
H_3C & \Delta Hass = 10.5 \text{ kJ/mol}
\end{array}
\qquad
\begin{array}{ll}
H_3C & H-CCl_3 \quad \text{Kass = 1.117} \\
\quad \diagdown & \\
\quad\quad C=O & \\
\quad \diagup & \\
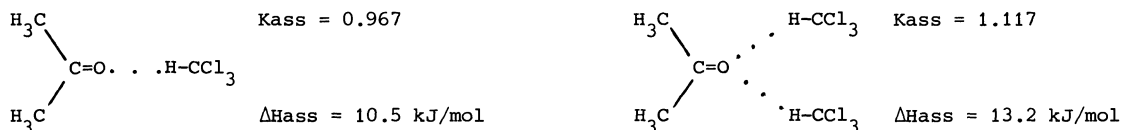H_3C & H-CCl_3 \quad \Delta Hass = 13.2 \text{ kJ/mol}
\end{array}
$$

Figure 8 shows the theoretical and experimental dependence of the molar viscosity in the chloroform-acetone system. The continuous lines show the calculated dependencies, and the circles the experimental ones; agreement is good. The dependencies of acetone in the same mixture are also given.

The dependencies of excess free energy, enthalpy of mixing, excess heat capacity and the deviations of the coefficient of CO_2 solubility from additivity in the chloroform-acetone mixtures were calculated using the approach outlined to examine the validity of the association scheme chosen.

In all the cases the equations obtained satisfactorily describe the experimental data.
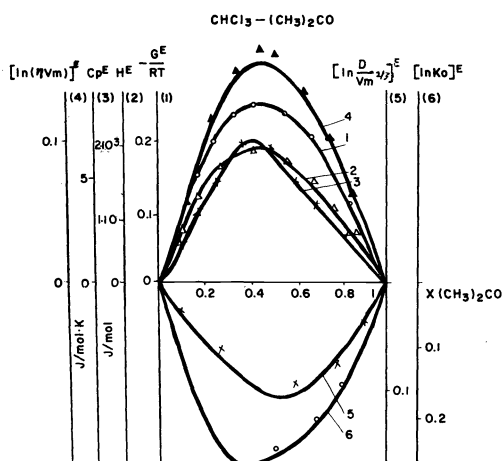
Fig. 8. Dependence of a series of physico-chemical properties on the composition of chloroform-acetone.
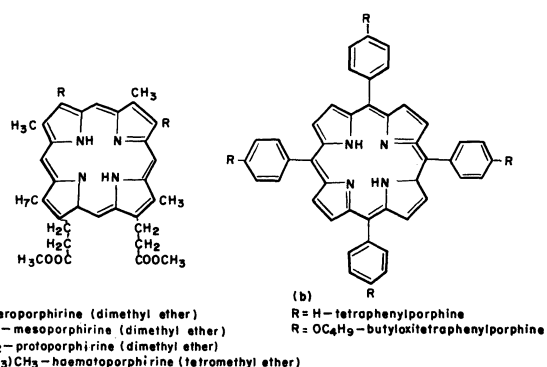
Fig. 9. The porphyrin molecule structure:
a) deutero-, meso-, proto- and haematoporphyrins;
b) tetraphenyl- and paraoxitetraphenylporphyrins.

SPECIFICITY OF SOLVATION IN IMPORTANT MACROCYCLIC COMPOUNDS

Thermodynamic and structural aspects of non-aqueous solutions of macroheterocyclic compounds of the porphyrin type (porphyrin ligands and their metallocomplexes) are of great interest. The energetic characteristics and solvation phenomena of these compounds are of great importance.

It must be pointed out that much current activity is devoted to investigating the properties of macroheterocycles. The interest derives from the fact that two natural biologically active substances - chlorophyll, blood haem and other fragments of the tetrapyrrole type contain the porphyrin group. Their synthetic analogues are also widely used technically as catalytically active substances. Investigation of the physico-chemical properties of porphyrins was mainly carried out in non-aqueous media. Analysis of the information concerning chemical reactions of porphyrin (and other groups) shows that knowledge of the solvation characteristics of each of the reagents is necessary to ascertain the solvent's role. In this connection it should be noted that the solvation data in the literature is unreliable. Consequently, the solvent influences porpyrins in solution, and the processes in which they participate. Systematic thermochemical investigations of these processes in a wide variety of solvents with macroheterocycles of different structure can answer some of the questions.

An investigation of the dissolution of more than forty natural and synthetic porphyrin ligands (and their metallocomplexes) in different solvents (aprotic, proton-donor and proton-acceptor) was carried by thermochemical methods (refs. 8,9).

Quantitative characteristics of dissolution, specificity of solvation and an interpretation of the results obtained, were considered using the example of porphyrins of the proto-porphyrin group: haematoporphyrin (H_2HP), deuteroporphyrin (H_2DP), protoporphyrin (H_2MP), and tetraphenylporphyrin (H_2TPP) and some of its substituted derivatives.

Porphyrin molecules are schematically presented in fig. 9.

It follows from fig. 9 that various possible modes of solvation (=N-H, =N-, π- system) exist. The hydrogen atoms of the amino-groups (=N-H) promotes solvation to the porphyrin nucleus by proton-donor or proton-acceptor solvents. The electron pairs of the tertiary nitrogen atoms (=N-) favour interaction of the porphyrin with proton-donor solvents. The conjugated π-system provides a favourable environment for the solvation of the porphyrin by different types of solvents.

Thus, solvation will be determined specifically by one, or by all the reaction centres depending on experimental conditions.

Figure 10 shows the concentration dependencies of the dissolution enthalpies of some porphyrin ligands in benzene.

The heat terms of dissolution do not depend on solute concentration characteristics of non-electrolyte solutions in dilute solution. This simplifies ΔH_{soln} standardisation. The average value of experimental ΔH_{soln}^{m} is taken as the standard ΔH_{soln}^{o}. The error of the measurements is 1-5%.

Table 4 yields the data of ΔH_{soln}^{o} and ΔH_{tr}^{o} of some porphyrin ligands. It follows from these that ΔH_{soln}^{o} for porphyrin ligands in the solvents investigated does not depend solely on the electron-donor properties of solvents (donor numbers).
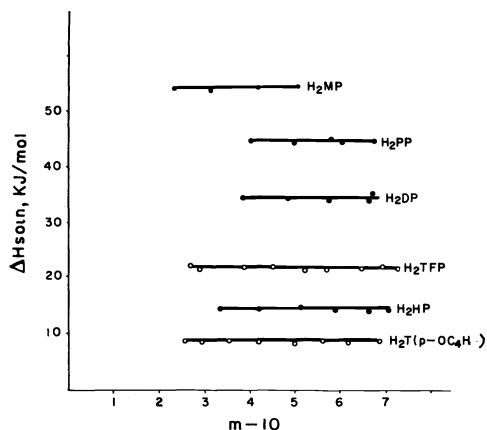

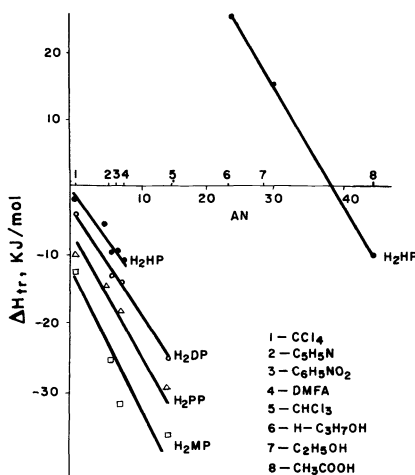Fig. 10. Dependence of ΔH_{soln}^{o} of porphyrin ligands on their concentration in benzene.

Fig. 11. Dependence of ΔH_{tr}^{o} of some porphyrin ligands on the electron- acceptor numbers of Gutmann and Meyer.

This testifies to the fact that electron-acceptor properties of a porphyrin ligand do not determine the solvation process.

Table 4 contains the data of ΔH_{tr}^{o} of porphyrin ligands, from benzene, taken as the standard, into another solvent. Comparison of ΔH_{tr}^{o} shows that, in spite of different solvent behaviour, they are close enough. This leads to the conclusion that the main contribution to solvation of porphyrin ligands is through the conjugate π-electron system of the macroring.

Equations of the type, $H_{solv} = A_o + \sum_{1}^{5} A_i.Y$, where Y is a solvent property, were used to evaluate the influence of the organic solvent properties on the solvation of tetraphenylporphyrin. Analysis of this equation showed that parameters such as polarizability density of the energy of cogezy, and basicity of a solvent, do not influence the energetics of solvation. ΔH_{solv}^{o} of H_2TPP, with the correlation coefficient of 0.958, is determined by the polarity and the electrophilic properties of a solvent.

Figure 11 shows the dependence of ΔH_{tr}^{o} of porphyrin ligands of the protoporphyrin group on the electron-acceptor characteristics of solvents according to Gutmann and Meyer.

TABLE 4. ΔH°_{soln} and ΔH°_{tr} of porphyrin ligands in organic solvents

Solvent / Ligand		C_6H_6	$C_6H_5CH_3$	CCl_4	$CHCl_3$	$C_6H_5NO_2$	DMFA	C_6H_5N	$C_5H_{10}NH$
H_2PP	H°_{soln}	13.6 ± (0.2)	11.5 ± (0.2)	10.8 ± 0.2	-18.8 ± 0.1	3.8 ± 0.1	4.0 ± 0.1	8.5 ± 0.2	23.1 ± 0.2
	H°_{tr}	0	-2.1	-2.8	-32.4	-9.8	-9.6	-5.1	-9.5
H_2PP	H°_{soln}	35.2 ± 0.1	-	34.2 ± 0.3	15.5 ± 0.4	21.5 ± 0.2	26.3 ± 0.6	30.6 ± 1.5	-
	H°_{tr}	0	-	-10.1	-28.8	-22.8	-18.0	-13.7	-
H_2TPP	H°_{soln}	20.7 ± 0.2	17.6 ± 0.3	16.8 ± 0.2	9.9 ± 0.2	13.7 ± 0.3	10.3 ± 0.2	19.2 ± 0.4	21.2 ± 0.2
	H°_{tr}	0	-3.1	-3.9	-10.8	-7.0	10.4	1.5	1.2
$H_2TnBuPP$	H°_{soln}	9.9 ± 0.1	-	12.6 ± 0.2	-1.9 ± 0.1	-	9.8 ± 0.1	11.1 ± 0.4	23.3 ± 0.1
	H°_{tr}	0	-	2.7	-11.8	-	-0.1	1.2	13.4

TABLE 5. Solvation enthalpies of H_2TPP and its complexes with Cu^{2+}, Ni^{2+} and Zn^{2+}

Solvent / Porphyrin and its complexes	C_6H_6	$C_6H_5CH_3$	CCl_4	$CHCl_3$	$C_6H_5NO_2$	DMFA	C_6H_5N	$C_5H_{10}NH$	CH_3COOH
H_2TPP	-125.7	-128.8	-129.6	-136.5	-132.7	-136.1	-127.2	-124.5	-179.2
CuTPP	-114.2	-119.8	-119.8	-127.2	-	-	-114.3	-	-
NiTPP	-89.7	-92.8	-95.1	-97.4	-	-	-	-	-
ZnTPP	-85.2	-88.4	-85.6	-97.8	-89.1	-129.8	-133.9	-161.2	-

TABLE 6. Transfer enthalpies of porphyrins and their complexes (kJ/mol).

Solvent / Complex	C_6H_6	$C_6H_5CH_3$	CCl_4	$CHCl_3$	$C_6H_5NO_2$	CH_3NO_2
H_2HP	0	-2.1	-2.8	-32.4	-9.8	4.8
CuHP	0	-	-	-30.2	-11.1	3.6
ZnHP	0	-0.2	-	-33.9	-7.6	-
H_2TPP	0	-3.1	-3.9	-10.8	-7.0	-
CuTPP	0	-5.6	-5.5	-13.0	-	-
ZnTPP	0	-4.2	-0.4	-12.6	-3.9	-

A good linear correlation is observed. For associated solvents (alcohols, acetic acid) the role of the structural factor increases. An increase of exothermicity of solvation occurs in the series: $H_2HP<H_2DP<H_2PP<H_2MP$, in the same direction as the donicity of the porphyrin ligands, i.e., their basicity.

Thus we conclude that the contribution to solvation by the conjugate π-system of the macrocycle is a determining factor, and the existence of such a system blocks solvation at the reaction centre by the electron-donor solvent.

The study of solvation of porphyrin metallacomplexes is important because porphyrins manifest their biological and catalytic functions through them. Solvation enthalpies of some porphyrin metallocomplexes are given in Table 5.

This shows that metallocomplexes are solvated to a lesser degree than the porphyrin ligand. A considerable decrease of the solvation enthalpy exists. It can be correlated with a decrease in aromaticity of the π-system of the porphyrin ligand, due to redistribution of the electron cloud, to an increase in its symmetry, and to a decrease of polarizability.

The contributions of a ligand, and complex former, were revealed by supposing that the influence of complex formation on the solvation of a ligand. Part of a complex is expressed as a constant value in a solvent relative to the free ligand. Data for noncoordinating solvents confirmed this supposition (Table 6).

TABLE 7.   Enthalpies of extracoordination of solvents by the porphyrin
           complexes (kJ/mol).

Solvent Complex	C_6H_6	$C_6H_5CH_3$	CCl_4	$CHCl_3$	$C_6H_5NO_2$	DMFA	C_6H_5N	$C_5H_{10}NH$
CuHP	0	–	2.6	–1.5	2.2	–23.0	–42.9	–51.8
ZnHP	0	–	–	2.1	–1.3	2.0	5.2	–12.3
CuTPP	0	–0.1	3.5	–1.8	3.1	–34.2	–47.2	–77.2
ZnTPP	0	–2.5	–1.7	–2.2	–	–	1.4	–

TABLE 8.   Comparison of literature and experimental data for $\Delta H_{e.c.}$ (kJ/mol)

Complex	Ligand	Extraligand number	Literature data	Our data
ZnHP	DMSO	2	29.3 ± 1.3	33.2 ± 0.3
ZnDP	DMSO	2	22.6 ± 1.3	24.1 ± 1.0
ZnPP	DMSO	2	18.8 ± 0.8	22.5*
ZnMP	DMSO	2	16.3 ± 1.3	16.0*
ZnTPP	C_5H_5N	2	42.3 ± 2.0	47.3 ± 1.5

* Obtained by interpolation.

This approach allowed evaluation of the energy parameters of formation of the molecular
complexes of metalloporphyrins with axially bonded ligands (the way in which solvent
molecules interact). Here

$$\Delta H_{e.c.} = \Delta H_{tr}^{K} - \Delta H_{tr}^{L} \qquad (14)$$

where ΔH_{tr}^{K} and ΔH_{tr}^{L} are the transfer enthalpies of complex and ligand respectively. Addition
of solvent molecules to an atom of the porphyrin metallocomplex was called extracoordination,
$\Delta H_{e.c.}$ Values calculated according to equation (14) are given in Table 7. This shows that
for all noncoordinating solvents $\Delta H_{e.c.}$ values are equal to zero. With coordinating solvents
(DMF, pyridine, piperidine) a contribution to solvation by a complex former appears.
Comparison of our data (ref. 9) with the literature (ref. 10) (spectrophotometric) shows
satisfactory agreement (Table 8).

The above confirms the conclusions concerning the absence of considerable solvation at an
(=N–N) group at the reaction centre of the free porphyrin by electron–donor solvents.

We have dealt with a relatively small part of a wide range of problems related to the
thermodynamics and structure of non-aqueous solutions. The role of non-specific and specific
interactions and their contributions to the energetics of interparticle forces, the influence
of the nature of the component, the external conditions and many other factors, remain a
major problem. New ideas and approaches, the use of modern methods of investigation,
international cooperation and unification of efforts are necessary. There is no doubt,
however, that we shall soon see the fruits of fundamental research in this branch of
solution science.

REFERENCES

1. G.A. Krestov, Thermodynamics of Ionic Processes in Solutions, in Chemistry, Leningrad
    Publishing House, Leningrad (1984).

2. V.A. Abakshin, G.A. Krestov, Dokl. AN USSR, in press (1987).

3. T. Davis, J. Ricci, J. Amer. Chem. Soc., 61, 3272 (1939).

4. V.N. Afanasev, G.A. Krestov, Dokl. AN USSR., 269, 620 (1983).

5. N.I. Larionov, N.A. Dmitrieva, G.V. Goryachko, In. collect. Ultra-acustic Application for
    Substances Study, (1958).

6. M.I. Shachparonov, B. Reiche, M.V. Lapshina, In collect. Physics and Physical Chemistry
    of Liquids, (1973).

7. K. Fumio, N. Hiroyasu, A. Makoto, M. Yutoka, Bull. Chem. Soc. Japan, 52, 3135 (1979).

8. M.Y. Nikiforov, G.A. Alper, G.A. Krestov, J. Phys. Chem., 59, 585.

9. G.A. Krestov, M.B. Berezin, A.I. Vjugin, Dokl. AN USSR, in press (1987).

10. A.I. Vjugin, V.I. Smirnov, G.A. Krestov, J. Phys. Chem., in press (1986).