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THERMODYNAMICS OF DISSOLUTION OF NON-ELECTROLYTES AND ELECTROLYTES IN NON-AQUEOUS SOLVENTS

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Experimental results on the ΔH_{soln} of noble gases, polar non-electrolyte molecules, porphyrins, their metallocomplexes and organic electrolytes in individual and mixed solvents are discussed. Xe was shown to indicate changes in solvent mixtures and also to exert a noticeable influence on the character of intermolecular interactions in solutions. The thermodynamic characteristics of the solvation of a series of non-polar and polar molecules are given and their dependence on the solvent nature, composition, isotopy and temperature is shown. For the first time the thermodynamic characteristics of porphyrins and metalloporphyrins in different non-aqueous solvents have been found by direct calorimetry. The possibility of axial coordination of porphyrin metallocomplexes is treated and a method is proposed for estimation of the influence of the functional substituents and the metal atom on the electronic effects in them. Compared to simple inorganic electrolyte solutions, the dependence of ΔH_{soln} on various factors reveals a specific character.

The problem of the solubility of substances of different natures in liquid media is still far from being solved. This is connected with the vast variety of interparticle interactions in dissolution processes, the paucity of investigations into the reasons for the dissolving power of solvents relative to various classes of substances, the lack of broad generalizations in this field due to the non-availability of experimental data on solubility, the influence of various factors on it, etc. The thermodynamic approach is one of the most general approaches to the solution of this problem [1–3].

Experimental result obtained by the author and his colleagues on noble gas solutions, non-electrolyte polar molecules, synthetic and natural porphyrins, their metallocomplexes and organic electrolytes (dyes) in individual and mixed solvents are discussed in this paper.

Noble gas solutions

The peculiarities of the thermodynamics of noble gas dissolution in individual and mixed solvents are considered on the example of Xe. For this purpose, precise data on the thermal effects of dissolution of Xe in water/methanol etc. individual (1,2-ethanediol and 1,2-propanediol) and mixed (water/methanol, water/1-propanol, water/1,2 ethanediol, water/1,2 propanediol and water/glycerine at 298.15 K, and water/ethanol at 278–318 K) solvents, and aqueous and methanol solutions of uni-univalent electrolytes (NaI, CsI and $(CH_3)_4NI$ at 278–318 K were obtained by means of a direct calorimetric method. Data on the ΔH_{soln} of Xe in water, methanol, ethanol and 1-propanol at 278–318 K are verified [4–5].

The data obtained allowed the conclusion the Xe was not only an indicator of changes, but also exerted a noticeable influence on the character of intermolecular interactions in the particular system. This clearly follows from a comparative analysis of the characteristics of the excess thermodynamic data of dissolution and the mixing enthalpies of the solvent components. We found that the thermal effects of the dissolution of Xe in alcohols depend on the temperature and on the electrolyte concentration in alcohol electrolytic solutions. For aqueous solutions, the thermal effects of Xe dissolution depend both on the temperature and on the electrolyte concentration. As these increase, the exothermicity of the $\Delta H^{o}_{\text{soln}}$ of Xe decreases. The thermal effect of Xe dissolution remains constant beyond certain temperature and concentration values.

The dependence of the dissolution enthalpy of Xe on the composition in water-alcohol solvents is of a non-linear character; it is manifested more strongly at lower temperatures, with longer alkyl radical length, and for higher numbers of OH groups in the alcohol molecules. The influence of the temperature on the ΔH_{soln} of Xe in aqueous ethanol solutions up to $X_{C_2H_5OH} \leqslant 0.35$ is the same as for aqueous solutions; at $X_{C_2H_5OH} > 0.35$, it is analogous to that for alcohol solutions.

A correct thermodynamic description of the vapour-liquid equilibrium has to take into account the composition of the vapour phase above the solution and to use a vapour phase of constant composition as standard. One then obtains comparable standard thermodynamic functions of gas transfer into solution for liquids of different natures. This gives the possibility of accounting for anomalous temperature-dependences of the dissolution of gases in liquids with regard to changes in the phase composition over the solution. Then, the $-\ln K = f(T)$ dependences are linear, and plots of $-\ln K_2 = f(T)$ for He and Ne in water are of an extremal character.

Solutions of polar non-electrolyte molecules

Thermochemical data on the ΔH^o_{soln} of both non-polar and polar non-electrolyte molecules in various solvents, and values related to them, are widely used to characterize their solvation.

The dissolution enthalpies of hexamethylphosphortriamide, nitromethane, 1,4-dioxane and formamide in mixtures of water and heavy water with C_1-C_3 alcohols of different isotopic compositions, with 1,2-ethanediol and with 1,2,3-propanetriol at 298.15 K, and of pyridine, acetonitrile, propylenecarbonate, deuterated methanol, ethanol, *n*- and iso-propanol, dimethylformamide, dimethylsulphoxide and 1,4-dioxane in heavy water 278.15 and 298.15 K have been measured for this purpose [7–10].

Standard dissolution and solvation enthalpies of non-electrolytes, and isotopic effects on the values noted, have been calculated on the basis of experimental and literature data. Here it is found that lengthening of the hydrocarbon radical of alcohol molecules weakens the electron-acceptor and electron-donor abilities of the solvents. With increase in the number of OH – groups in the molecules (transition from mono- to multi-functional alcohols), the electron-acceptor and electron-donor properties of the solvents also increase. The exchange of protium by deuterium in the OH groups leads to a strengthening of the electron-acceptor properties and weakening of the electron-donor properties. Deuterosubstitution in alkyl radicals of molecules acts in the opposite way.

The solvation enthalpies depend on the composition of mixed solvent in different manners for non-electrolytes with electron-donor and electron-acceptor properties.

Solutions of synthetic and natural porphyrins and their metallocomplexes

The importance porphyrines and metalloporphyrins primarily connected with the fact that such natural biologically active compounds as chlorophyll, blood haeme and other compounds of tetrapyrrole type belong in this class.

The development of the thermochemical approach to the investigation of various properties of porphyrin molecules (the influence of the metal and the various functional substituents on the ability of metalloporphyrins to coordinate additional molecular ligands, the electronic effects of coordination and functional substituents, the geometry of the conjugated system, etc.) is of great practical and theoretical interest.

Synthetic porphyrines

The dissolution enthalpies of tetraphenylporphin and its derivatives in aprotic, proton-acceptor and proton-donor solvents have been determined [11–13]. The transfer enthalpies of the investigated porphyrins from a standard solvent (benzene) into the studied one have been calculated. It has been established that the enthalpy of porphyrin dissolution is independent of its concentration in solution in the interval 10^{-3}–10^{-4} mole$\cdot$kg^{-1}. It has been found that the energetics of the porphyrin-solvent interaction is determined by the porphyrin-ligand electrondonicity and the solvent electrophilicity. The introduction of functional substituents into different positions of the tetraphenylporphin molecule does not change the porphyrin-ligand solvation. The macrocyclic effect of porphyrin-ligand solvation has been revealed, this consists in the fact that the conjugated system of macroring π-bonds blocks the solvation of the porphyrin reaction centre by electron-donor solvent molecules.

Natural porphyrins

The dissolution enthalpies of porphyrin ligands of the protoporphyrin and chlorophyll groups in different classes of solvents have been measured [14–16]. Similarly as in the previous case, $\Delta H^{m}_{\text{soln}}$ is independent of the concentration of the porphyrin in the solution over the entire range of concentrations studied. In the protoporphyrin series, the exothermicity of transfer enthalpies for aprotic, proton-donor and proton-acceptor solvents decreases in the sequence meso-, proto-, deutero- and haematoporphyrin. This allowed the assumption of a decrease in the electrondonicity (basicity) of porphyrin ligands in the same sequence. Porphyrin ligands in the chlorophyll group dissolve in organic solvents with an endoeffect. The presence of the large phytyl group ($-C_{20}H_{39}$) opposes dissolution. Compounds without the phytyl group dissolve in all solvents with an energy consumption 8–15 kJ·mole^{-1} lower than for phytyl-containing ones. On the whole, the character of the solvation and the type of the chlorophyll ligand-solvent interactions are close to those established for deutero- and haematoporphyrins. The cyclopentanone ring of chlorophyll does not exert an essential influence on the dissolution and solvation processes of porphyrins. The difference in solvation of the *a* and *b* series of chlorophyll ligands, differing only by CH_3 and CHO groups in position 3, is reported by Fischer to be practically inperceptible.

Porphyrin metallocomplexes

In parallel with the synthetic and natural porphyrins of the above classes, the ΔH_{soln} data for their metallocomplexes have been studied [13, 16]. The enthalpies of transfer and enthalpies of axial coordination of solvent molecules by porphyrin complexes have been calculated on the basis of the data obtained. Quantitative effects of functional substituents in porphyrin complexes have been determined via the thermochemical method.

The energetic parameters of solvation have been determined via the electronic effects of metal cation coordination with the porphyrin ligand, e.g. for synthetic porphyrin complexes with Ni(II), Cu(II) and Zn(II). The presence of various functional substituents in synthetic porphyrin complexes essentially influences their ability to achieve axial coordination with electron-donor solvent molecules. A method has been proposed for estimation of the influence of the functional substituents and the metal on the electronic effects in porphyrin complexes. An interrelation exists between the electronic effects of the substituents and their complex-forming properties.

For Ni(II) and Cu(II) complexes with natural porphyrinc the thermochemical data reveal a noticeable axial coordination of solvent molecules only for solvents with high electron-donor properties. The solvation of chlorophyll and of haemine is determined by their strong inclination to axial coordination. Some other peculiarities of the behaviour of the complexes in solution have been considered.

Organic electrolyte (dye) solutions

The dissolution enthalpies of the dyes acid orange, active violet 4K and bright-red 5CX in water and dimethylformamide, and of active violet 4K in water-dimethylsulphoxide mixtures at various temperatures have been determined. Water-alcohol solutions of methyl yellow [17–23] have been studied by the EMF chain method without transfer.

The dissolution of acid orange in water is accompanied by an endothermic effect at all concentrations and temperatures, while for active violet 4K and bright-red 5CX an exothermic effect of dissolution is observed. In dilute dye solutions, in contrast with simple inorganic electrolyte solutions, there is no decrease in $\Delta H^m_{\mathrm{soln}}$ with increase of the dye concentration, the most noticeable increase in $\Delta H^m_{\mathrm{soln}}$ being observed for dilute solutions.

Unexpected results were obtained when the thermal effects of dissolution of violet 4K and bright-red 5CX were determined in dimethylformamide at 298–348 K. If the $\Delta H^m_{\mathrm{soln}}$ curves for these dyes in aquous solutions are of unitypical character, with a continuous increase in exothermicity with increasing dye concentration, their behaviours in dimethylformamide differ sharply not only from that in aqueous solution, but also between each other.

In mixed solvents, the dissolution enthalpies depend specifically on the concentrations of the components, due to their structural peculiarities and the specificity of the organic ion.

In conclusion, it should be noted that the thermodynamic characteristics of the considered non-electrolytes and electrolytes in non-aqueous and mixed solvents are not typical in many cases, and point to the complexity of the processes. The thermodynamic method itself appears fruitful for revealing the regularities and permitting an explanation of the behaviour of the studied systems.

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Zuzammenfassung — Experimentelle Daten zur Lösungswärme ΔH_{soln} von Edelgasen, polaren Nichtelektrolyten, Porphyrinen und ihren Metallkomplexen und organischen Eletrolyten in einfachen und gemischten Lösungsmitteln werden diskutiert.

Es wird gezeigt, dass Xe nicht nur auf Veränderungen in der Zusammensetzung von Lösungsmittelmischungen anspricht, sondern selbst einen merklichen Einfluss auf den Charakter der intermolekularen Wechselwirkungen ausübt. Thermodynamische Charakteristika der Solvatation einer Reihe unpolarer und polarer Moleküle werden aufgeführt und die Abhängigkeit von der Natur, Zusammensetzung (auch isotopisch) und Temperatur des Lösungsmittels wird gezeigt. Erstmalig werden die thermodynamischen Charakteristika von Porphyrinen und Metallporphyrinen in verschiedenen Lösungsmitteln direkt kalorimetrisch bestimmt. Die Möglichkeit einer axialen Koordination an Metall-Porphyrin-Komplexen wird gezeigt und eine Methode zum Abschätzen des dabei wirkenden Einflusses der funktionellen Substituenten und des Metallatoms auf die elektronischen Effekte vorgeschlagen. Verglichen mit einfachen anorganischen Elektrolyt-Lösungen ist die Abhängigkeit von ΔH_{soln} von verschiedenen Faktoren sehr substanzspezifisch.

РЕЗЮМЕ — Обсужден экспериментальный материал по $\Delta H_{\text{раств.}}$ благородных газов, полярных неэлектролитов, порфиринов, их металлокомплексов и органических электролитов в отдельных и смешанных растворителях. Установлено, что ксенон показывает изменения в смешанных растворителях и оказывает заметное влияние на характер межмолекулярных взаимодействий в растворах. Приведены термодинамические характеристики сольватации ряда полярных и неполярных молекул и показана их зависимость от природы растворителя, изотопного состава и температуры. Впервые методом прямой калориметрии определены термодинамические характеристики для порфиринов и металлопорфиринов в неводных растворителях. Определена возможность осевой координации в металлокомплексах порфирина и предложен метод определения электронного влияния заместителей и атома металла в таких комплексах. По сравнению с простыми неорганическими электролитными растворами, зависимость $\Delta H_{\text{раств.}}$ в изученных системах от различных факторов показывает специфический характер.