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STATE AND ROLE OF WATER IN SOLUTIONS OF ELECTROLYTES IN A WIDE RANGE OF SOLUTE CONCENTRATIONS

By

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Abstract

It is proposed an ice-like model of the structure of aqueous solutions of electrolytes over a wide range of concentrations of the solute. According to the model, ions, hydrate and ionic complexes are located in the ice-like framework of water with the formation of substitutional and interstitial structures. Geometrical models of inclusion more than 60 ions into water are constructed. The analysis also gives coordination numbers of ions and the forms of surrounding of ions by water molecules.

Volume properties of solutions of electrolytes can be calculated from the ice-like model of solutions. Theoretical dependences are in a good quantitative agreement with those obtained from density measurements. Apparent molar volumes of ions are calculated.

On the basis of the model we analyse the temperature dependence of solubility of electrolytes, molecular mechanisms of dissolution of non-polar gases in water and aqueous solutions of electrolytes and salting-out of gases. It is proposed the molecular model of the hydrophobic hydration of non-polar molecules and non-polar groups of molecules.

Anomalous behaviour of water as against other liquids is well-known at present. It has been recently demonstrated in the course of studies of solutions of electrolytes that physico-chemical properties of aqueous solutions also possess a number of specific features not peculiar to most of other systems (this refers not only to diluted solutions but also to more concentrated solutions in a wide range of concentrations of solute). We can note temperature variation in hydration of ions,[1,2] specific hydrophobic hydration of tetraalkyl ammonium salts,[3~5] change in dissolution heats of electrolytes with concentration and temperature,[5,6] the existence of stabilization of water structure in solutions of electrolytes,[7~9] the presence of maxima and minima on the curves of temperature dependence of solubilities of electrolytes,[10,11] minima on the curves of temperature dependence of solubilities of gases in

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solutions of electrolytes,[12] a different behaviour of viscosity of these solutions as against non-aqueous systems,[13] changes in dielectric relaxation time at higher concentrations of electrolyte opposite to those observed in non-structured liquids (*e.g.*, dimethylformamide),[14] *etc.*

The specific properties of water are known to result from its structure described in the best way in the model of SAMOILOV.[15] On the other hand, the properties of aqueous solutions of electrolytes in a wide range of concentrations have been until recently described in most of works on a different basis without any allowance for the role of water structure in the solutions of "real" concentrations.

The structure of aqueous solutions of electrolytes

The process of hydration and formation of structure of a solution in accordance with different models is shown schematically in Fig. 1. Originally, hydration was understood as the formation of multilayer hydrate shells around ions. This process is illustrated by Scheme 1 which is still being used in textbooks. According to the Scheme, ions bring about the ordering of water consisting of free dipoles not combined with each other. This means that the system of bonds in the solution is determined by ions, the solvent serving only as a supplier of polar molecules of water.

The change of concepts in the science of aqueous solutions is due to two major reasons. Firstly, direct experiments have shown that liquids (water to the greatest degree) are structured system. However, since the

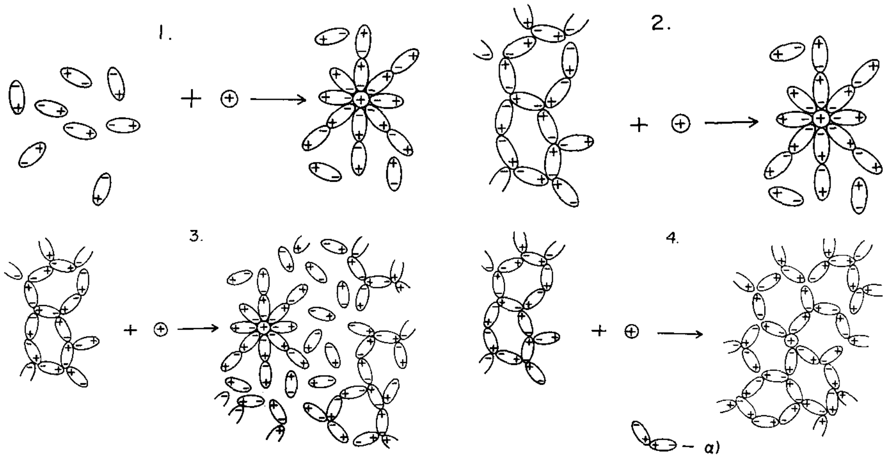


Fig. 1. Four schemes of hydration of ions and of formation of a system of bonds in a solution: α-orientation defects.

energy of bonds in water is relatively small compared to the energy of ion—water bonds, so in the case of usual comparison of total interaction energies the picture of hydration and formation of a bounds system in the solution did not undergo any essential change although later it took into account the contribution of the energy of breakdown of the structure of the initial solvent in the course of formation of a solution (Scheme 2, Fig. 1). A three-layer model of FRANK and WEN[16] which can be easily represented by Scheme 3 can be regarded as an improved modification of the previous picture. In passing from diluted solutions to solutions of medium concentrations, this model is inevitably reduced to the model of the system of hydrate spheres (*i. e.* to Scheme 2) since the solution does not have enough water molecules for the formation of three-layer shells around ions. Along with this, IR spectra of aqueous solutions of electrolytes did not reveal any water molecules free of hydrogen bonds.[17,18] (These molecules would have corresponded to the intermediate layer). A sharp division into hydrate water strongly bound by the ion and free water is a necessary requirement of the FRANK and WEN model as well because otherwise it loses sense. A direct experimental confirmation of negative hydration[19] shows that this idea is erroneous. Negative hydration, as it follows mainly from the works of SAMOILOV,[1,15] is related to the second circumstance changing considerably our concepts of solutions, *viz.* the state of particles in solutions is determined not by total energies of ion—water and water—water interactions but primarily by local gradients of these energies at distances of the order of the diameter of particles. With this approach, interactions between water molecules turn out to be equivalent to ion-dipole interactions. Therefore, the answer to the question which particles form a system of bonds in a solution, ions or water molecules, is ambiguous.

A model different from those described by Schemes 1∼3 is represented by Scheme 4 in Fig. 1. We propose[20,21] an ice-like model of structure of solutions common for solutions of electrolytes in a wide range of concentrations. According to the model, ions, hydrate and ionic complexes are located in the ice-like network of water with the formation of substitutional and interstitial structures. In the case of weak hydration, ions can substitute water molecules in points and cavities of water structure, *i. e.*, a determinative influence on water surrounding an ion is exerted by the structure of water. In the case of strong hydraton, we may speak of the most important role of the ion itself in the development of its immediate structural encirclement. Here the formation of substitutional and interstitial solutions involves the arrangement of hydrated complexes (formed by ions) on water matrix instead of the arrangement of individual ions. This model of structure of solutions takes into account to a great extent the properties of ions and water molecules in the surrounding ice-like water network.

Let us consider two principal problems determining the existence of this model:

1) the possibility of arrangement of ions and complexes in tetrahedral configurations of water structure without significant steric distortions;

2) the effect of the field of ions on the areas of free water, *i. e.*, the effect of electrostriction beyond the limits of the first sphere of an ion; an analysis of this factor can be made in the course of detailed examination of bulk properties of solutions.

In order to elucidate the first problem and construct the schemes of short-range order around any particular ion, geometric models can be used. It can be shown with the help of these models that ions or complexes of different geometric configurations made, in particular, of particles near in size to water molecules are located in the water structure practically without steric distortions. Ions of almost the same size as water molecules (such as K^+, Rb^+, Ba^{2+}, F^-, OH^- *etc.*) can be located in points or cavities of water network (the cavities are accessible to particles with radius smaller than 1.56 A). Fig. 2 represents a model of arrangement of tetrahedral oxygen-containing ions such as SO_4^{2-}, ClO_4^-, *etc.* This arrangement may take place given that two oxygen atoms of this tetrahedral ion substitute two water

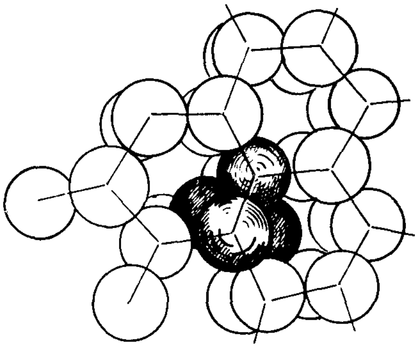


Fig. 2. A model of arrangement of tetrahedral oxygen complexes SO_4^{2-}, ClO_4^- type and a hydrate $Be(H_2O)_4^{2+}$ complex in the ice-like structure of an aqueous solution ($a=2$ $b=2$).

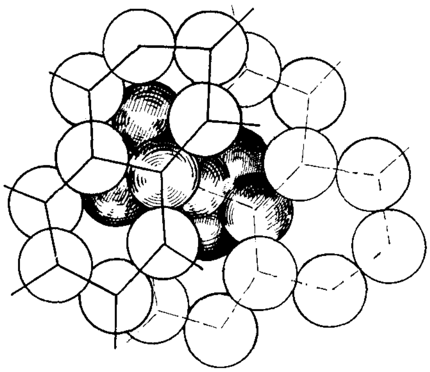


Fig. 3. A model of arrangement of complexes of the $S_2O_7^{2-}$, $Cr_2O_7^{2-}$ type in the ice-like structure of an aqueous solution ($a=3$ $b=4$).

molecules of equivalent size in points and two other oxygen atoms are located in two adjacent cavities. The same shape and similar sizes are peculiar to a hydrate complex $Be(H_2O)_4^{2+}$ and some other complex ions. All these ions are characterised by a similar arrangement. Complexes of the $S_2O_7^{2-}$, $Cr_2O_7^{2-}$ type occupy four cavities and three points of the ice-like network (Fig. 3). Arrangements of a number of ions are discussed in more detail in other works.[20~23]

The arrangement of 50 ions in the water structure found on the basis of geometric models is shown in Table 1 where *a* is the number of points of the ice-like network occupied by an entered ion or a complex, *b* is the number of occupied cavities. For some of the ions two arrangements equivalent from geometric considerations are possible. Hydrate complexes are regarded as independent structure units.

TABLE 1 Arrangement of Ions and Complexes in the Solution Structure

Ions and complexes	Arrangement
K^+, NH_4^+, Rb^+, Ba^{2+}, Tl^+, Na^+, F^-, OH^-	$a=1$ $b=0$ or $a=0$ $b=1$
H^+	$a=0$ $b=0$
Cs^+, Cl^-	$a=1$ $b=0$
Be^{2+}***)	$a=-2$ $b=2$*)
$Be(H_2O)_4^{2+}$	$a=2$ $b=2$
Mg^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+} Ni^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+}	$a=-3$ $b=3$*)
$Mg(H_2O)_6^{2+}$, $Zn(HO)_6^{2+}$, $Fe(H_2O)_6^{3+}$, etc.	$a=3$ $b=3$
Fe^{2+}, Cd^{2+}, Mn^{2+} (diluted solution)	$a=-3$ $b=3$*)
Ca^{2+}, Sr^{2+}, La^{3+}	$a=-2$ $b=2$*)
$Ca(H_2O)_8^{2+}$, $Sr(H_2O)_8^{2+}$	$a=6$ $b=2$
UO_2^{2+}	$a=0$ $b=2$
SO_4^{2-}, HSO_4^-, SeO_4^{2-}, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, ClO_4^-, MnO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, SiO_4^{4-}, GeO_4^{4-}, AsO_4^{3-}, BF_4^-	$a=2$ $b=2$
$Cr_2O_7^{2-}$, $S_2O_7^{2-}$	$a=3$ $b=4$
NO_3^-, BO_3^{3-}, CO_3^{2-}, HCO_3^-	$a=1$ $b=2$ or $a=2$ $b=1$
H_3BO_3	$a=1$ $b=2$**) or $a=2$ $b=1$
KOH	$a=1$ $b=1$ or $a=2$ $b=0$**)
$(UO_2NO_3)^-$ (bidentate complex)	$a=2$ $b=3$**)

*) Hydrate complexes of water molecules of the solution without allowance for their dissociation.

**) Associations and complexes.

***) Due to hydrolysis, the nearest surroundings of some of ions and complexes include OH^- groups but this does not lead to structural changes since H_2O, OH^-, and O^{2-} are almost of the same size.

If they are built of molecules of solution water, Table 1 gives *a* and *b* values corresponding to the summary redistribution of the number of points since for the formation of complexes water molecules from the ice-like network of water are taken.

Thus, the geometric analysis shows that the packing of particles (ions, complexes, and molecular groupings) in a solution can be sterically materialised in the form of the same structural configurations as those existing in liquid water.

Turning from the models made of wooden spheres to liquid systems, we must specify which structures in a liquid are covered by our analysis. First, we deal with elements of the surroundings of particles at a distance of 5～10 A, *i. e.*, with short-range orderliness existing in liquid state. Second, we consider configurations in a solution where the "lifetime" of particles is generally comparable to the "lifetime" of water molecules in water configurations.

Third, we consider the most probable configurations. In the proposed model of the structure of electrolyte solutions we identify them with ice-like configurations, that may be described by geometric models. Thus, at first approximation, we do not consider the distribution of configurations around their average values.

In this context, it seems to be expedient (as it is done for solids[17)]) to single out so called structure-insensitive properties of solutions (volume, radial distribution curve (RDC) from X-ray data, dielectric constant, heat conductivity, IR spectrum in the region of frequencies of stretching vibrations of water molecules, *etc.*) primarily related to the existence of a network of hydrogen bonds in a solution and structure-sensitive properties (electrical conductivity, relaxation, diffusion, characteristics of chemical equilibrium, *etc.*) related to the degree of perfection or the defects of the network. Although in liquid state this division is not so distinct as in solids and the transition region should be more and more smeared with temperature, it can be done quite well. Indeed, in accordance with the ice-like model of solutions, the properties of a system which are a function of the presence of a structure do not differ strongly, within a rather broad range of concentrations, from the properties of pure water or an infinitely dilute solution. Thus, it can be seen from X-ray studies conducted by BRADY[28,29)] that RDC of concentrated KOH solutions is close to RDC of water. According to FALK,[18)] in the region of frequencies of stretching vibrations of water molecule, IR spectrum changes insignificantly in going from HDO to a 1.7 M NaCl solution in HDO and the spectrum of a 2.7 M solution in HDO still can be regarded as a distorted spectrum of water. It is known that the large value of dielectric constant of water is due to the existence of a structured network of hydrogen bonds. Comparing the values of dielectric constant of water and 1~1.5 M solutions of electrolytes obtained by means of high frequency dielectric measurements, one can see that they are not very much far apart from each other. Thus, at 25°C $\varepsilon=78$ for water, $\varepsilon\approx70$ for 1 M solutions of NaCl and NH_4Cl (see refs. 25, 26), and $\varepsilon\approx64$ for 1 M solutions of LiCl,[27] $BeSO_4$[27], Et_4NCl,[26] and Me_4NCl.[26] For 2 M solutions of LiCl and Me_4NCl ε equals 52 and 65, respectively, for a 2.3 M NH_4Cl solution $\varepsilon=67$ (see ref. 26). This means that even for 2 M solutions ε values are much closer to that of water than to ε values for weakly structured solvents.

Let us discuss in more detail bulk properties of solutions of electrolytes. Average molar volume (V_M) of a solution can be expressed as follows:

$$V_M=(1-N)\,V_0+NV_1 \tag{1}$$

where V_0 is molar volume of solvent, V_1 is apparent molar volume of solute, N is molar fraction of solute. If a structured system consists only of molecules in points of the network, then $V_0=V_f$ where V_f is molar volume of the framework when it is composed of solvent particles and $V_1=aV_f'$ where a is the number of sites in the positions of the structure occupied by the intruding molecule, V_f' is volume per molecule or its part occupying a structural position of a solvent molecule. In water some molecules are located in cavities;[15] therefore,

$$V_0=V_f(1-x) \tag{2}$$

where x is molar fraction of molecules in cavities. The degree of filling of cavities, γ, equals $2x/(1-x)$. In the case of interstitial solutions, the particles of solute entering the cavities displace from these cavities the portion of water molecules which corresponds to the occupied cavities number (if b is the number of cavities occupied by the intruding molecule, the number of displaced water molecules is $b\gamma N$). If the distribution of water molecules (displaced into „free water" from points and cavities) between the two states and the distribution in the structure of "free water" are the same as in water, then V_1 can be found[20,21,30] from the relationship:

$$V_1=(a+b\gamma)\frac{2}{2+\gamma}\,V_f'. \tag{3}$$

However, this equality cannot be accepted beforehand for the solutions of electrolytes since it does not take into account the effect of long-range interactions between water molecules and ions (these interactions can lead to the shift of equilibrium between water molecules in cavities and in the frame work or to a bulk change in the solution). In the general case, the values γ' and x' (substituting γ and x for water) varying at different concentrations, will reflect all additional changes in the volume of the solution. If a geometric entity (a molecule or its part) substituting a water molecule in the framework is almost of the same size (as it has been demonstrated for a large number of ions with the help of geometric models), then $V_f \approx V_f'$ and relationships (1)~(3) make it possible to show that, as a first approximation, $\gamma \approx \gamma'$ in a certain temperature range. Calculations show that at 0°C a large variety of solutions of electrolytes have $\gamma \approx \gamma'$ (see refs. 20, 21). Thus, long-range forces in solutions at low temperatures do not lead to substantial changes of water structure beyond the limits of the first sphere, *i.e.*, as a first approximation, no electrostriction occurs in "free water" of solutions. The equality of γ values of water and solutions at 0°C makes it quite possible to suggest that, as a first approximation, $\gamma \approx \gamma'$ within a certain temperature range where the initial structure has not undergone strong changes. The values of γ of different electrolytes at the same temperatures fall close together and have a common temperature dependence.[20)] Here γ values are used for the calculations of bulk properties of solutions of electrolytes. At a fixed temperature, V_0=const. and the bulk properties of solutions of electrolytes (V_I and V_M) undergo changes as a function of a and b, *i.e.*, can be calculated on the basis of a correct choice of structure units and their arrangement from geometric models using the relationships: $V_M = (1-N) V_0 + (a+b\gamma) V_0 N$, $V_I = (a+b\gamma) V_0$.

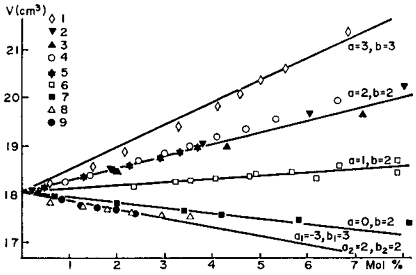
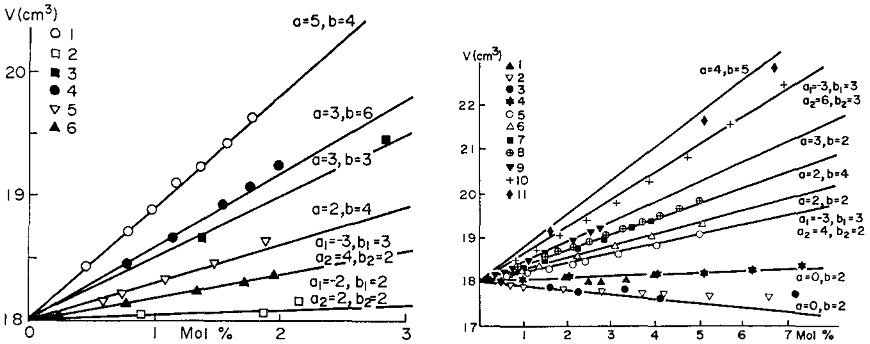


Fig. 4. Molar volumes of solutions of some electrolytes at 0°C: 1-$(NH_4)_2SO_4$; 2-H_3PO_4; 3-$HClO_4$; 4-NH_4NO_3; 5-$RbNO_3$; 6-HNO_3; 7-KOH; 8-$ZnSO_4$; 9-$MgSO_4$.
Straight lines represent theoretical dependences.

Calculated V_I values of ions are given in Table 2 together with experimental values at infinite dilution.[31)] Both sets of data are in a good agreement. Theoretical dependences of V_M on electrolyte concentration were calculated for 100 electrolytes[20~23)] on the basis of the proposed models of structural ordering of solutions and are given in Table 3. As it can be seen from Figs. 4, 5 and the Figures in the works referred to,[20~23)] theoretical V_M values are in a good quantitative agreement with those obtained experimentally from density measurements.[32,33)] For about 30 electrolytes, the model of



(a) (b)

Fig. 5. Molar volumes of solutions of some electrolytes at different temperatures:

a) 1-$(NH_4)_2Cr_2O_7$ (12°), 2-$BeSO_4$ (25°), 3-$(NH_4)_2CrO_4$ (13°), 4-$K_2S_2O_7$ (15°), 5-Rb_2SO_4 (0°), 6-$Mg(NO_3)_2$ (0°).

Straight lines represent theoretical dependences.

b) 1-Tl(OH), (15°); 2-Rb(OH), (18°); 3-KF, (15.2°); 4-NH_4F, (18°); 5-$Ni(NO_3)_2$, (18°); 6-H_2SeO_4, (20°); 7-K_2CrO_4, (18°); 8-$Be(NO_3)_2$, (18°); 9-NH_4ClO_4, (15°); 10-$Fe(NO_3)_3$, (17.5°); 11-$Ba(ClO_4)_2$, (25°).

Straight lines represent theoretical dependences.

TABLE 2. Apparent Molar Volumes of Ions and Complexes in Solution

Ions and complexes	V_1 (theoretical)	V_1 cm³ (ref. 31)	Temperature (°C)
H^+	0	0.1	35
NH_4^+	18	18.1	35
Rb^+ in framework	18	14.3	35
in cavities	~5		
Cs^+	18 or >18	21.1	25
Tl^+ in framework	18	9.4	25
in cavities	4.9		
Mg^{2+}	−39.4*)	−21.4	25
$Mg(H_2O)_6^{2+}$	68.5*)	—	25
Ca^{2+}	−26.3*)	−19	25
Fe^{3+}	−39.4*)	−30	25
Al^{3+}	−39.4*)	−42.9	25
UO_2^{2+}	9.8	—	25
$(UO_2NO_3)^-$ (bidentate complex)	50.6	—	25
$UO_2(NO_3)_2^0$ (bidentate complex)	91.4	—	25
F^- in cavities	4.9	− 1.8	25
Cl^-	18	18.1	35
Br^-	>18	25.3	35

Ions and complexes	V_1 (theoretical)	V_1 cm^3 (ref. 31)	Temperature (°C)
I^-	>18	37.2	35
ClO_4^-	46.1	45.6	35
HCO_3^-	27.7	22.3	25
MnO_4^-	45.7	42	25
$Cr_2O_7^{2-}$	73.4	73.4	25
SO_4^{2-}	45.7	15.4	25
NO_3^-	27	25	20

* Without allowance for dissociation of hydrate complexes.

TABLE 3. Electrolytes Whose Aqueous Solutions Have Been Described by Means of Models of Structural Orderliness

$CsCl$, $RbCl$, NH_4Cl, KCl, $NaCl$, $TlCl$, HCl, HBr, HF, KF, NH_4F, RbF, TlF, $NaOH$, KOH, $RbOH$, $TlOH$, $HClO_4$, HBF_4, $HMnO_4$, H_2SeO_4, H_2WO_4, H_3PO_4, H_3AsO_4, NH_4ClO_4, NH_4MnO_4, NH_4BF_4, $NH_4H_2AsO_4$, NH_4HSO_4, $KClO_4$, $KMnO_4$, $NH_4H_2PO_4$, KH_2AsO_4, $KHSO_4$, KH_2PO_4, Cs_2SO_4, Cs_2SeO_4, $(NH_4)_2SO_4$, $(NH_4)_2CrO_4$, $(NH_4)_2HPO_4$, Rb_2SeO_4, Rb_2SO_4, Tl_2SO_4, K_2SO_4, K_2CrO_4, K_2SeO_4, K_2HPO_4, K_2WO_4, K_2MoO_4, K_2HAsO_4, $BeSO_4$, $BeSO_4 \cdot 4H_2O$, $MgSO_4$, $MgSO_4 \cdot 6H_2O$, $ZnSO_4$, $NiSO_4$, $CuSO_4$, $CoSO_4$, $CdSO_4$, $FeSO_4$, $MnSO_4$, $MgCrO_4$, $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$, $Cr(ClO_4)_3$, $CaSO_4$, $CaCrO_4$, $Ba(ClO_4)_2$, $Ca(OH)_2$, $Ba(OH)_2$, $(NH_4)_2Cr_2O_7$, $K_2Cr_2O_7$, $K_2S_2O_7$, $(NH_4)_3AsO_4$, $(NH_4)_3PO_4$, HNO_3, H_3BO_3, NH_4NO_3, $CsNO_3$, $RbNO_3$, $TlNO_3$, KNO_3, $KHCO_3$, $Be(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Mg(NO_3)_2$, $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Co(NO_3)_2$, $Ni(No_3)_2$, $Mn(NO_3)_2$, $Cd(NO_3)_2$, $Fe(NO_3)_2$, $Fe(NO_3)_3$, $Cr(NO_3)_3$, $Al(NO_3)_3$, $La(NO_3)_3$.

arrangement of both ions is ascertained unequivocally from geometric models. The agreement between V_M^{theor} and V_M^{exp} in this case is the evidence of the correctness of the general approach and the individual models of the surroundings of ions. In cases when ions may have different locations in the ice-like structure (Table 1), the real arrangement is determined by the correspondence of V_M^{exp} with one of two theoretical dependences. In particular, a comparison of different models of the nearest surroundings of Li^+ ion in $LiCl$, $NiNO_3$ $LiClO_4$, and $LiOH$ solutions and of experimental V_M and V_1 values shows that Li^+ ions do not form octahedral hydrate complexes in structures of these aqueous solutions (to 5～7 mol%).

On the basis of the analysed scheme a general classification of bulk properties of solutions of electrolytes is being developed. An accordance between theoretical and experimental dependences for V_M of solutions is observed in a number of case at electrolyte concentrations up to 7～10 mol%;

for some other salts experimental curves exhibit deviations at these concentrations. It is quite understandable since the solutions enter a transitional region on the way to aqueous melts where we cannot speak of the determinative influence of water structure on the properties of solutions. V_M of about ten electrolytes is quantitatively described by theoretical dependences only at concentrations less than $1 \sim 2$ mol%. For four electrolytes ($FeCl_3$, $CoCl_2$, $MgCl_2$, $CaCl_2$) there has been found no quantitative agreement even at lower concentrations. It can be shown[23,24] that the observed deviations may be related to the emergence of new structural groupings in solution[35,36] and the dissociation of hydrate complexes.

There can be made an analysis of geometrically possible structures in aqueous solutions of concrete electrolytes, the formation of the structures allowing bulk properties of solutions to be calculated. The analysis gives coordination numbers (c. n.) of ions and makes it possible to consider the character of the nearest water surroundings (Table 4). The most probable aqueous polyhedra of ions are shown in Fig. 6. A good agreement between obtained values of coordination numbers and c. n. values of strongly hydrated ions (Be^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}) determined quite unequivocally by physical methods[36~41] should be pointed out. On the basis of our data a conclusion can be drawn that if there exist several geometrically possible ways of arrangement of ions in the ice-like structure, c. n. values of these ions may vary with temperature and electrolyte concentration and also with composition of a solution. The existing ambiguity in determination of c. n. values of weakly hydrated ions by experimental methods may be due, at least partially, to this feature. It should be noted that the presence of ions in cavities of the ice-like structure of solutions and the possibility of their distribution between points and cavities are confirmed by X-ray data for KF,[42] NH_4F,[43] KOH,[28,29] NaOH and NaCl.[43]

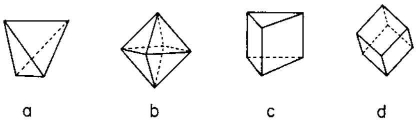


Fig. 6. Idealised aqueous polyhedra of ions in the ice-like structure of a solution:

a-tetrahedron; b-octahedron; c-trihedral prism; d-rhombohedron.

The possibility of application of a general model of structure of solutions assuming the formation of substitutional and interstitial structures on the basis of the initial structure of water at various concentrations of electrolyte makes feasible the expansion of the principle of least variation of water structure during the formation of a solution (formulated by SAMOILOV for diluted solutions[15]) to a wide range of concentrations of solutions since just

TABLE 4. Coordination Numbers of Ions in Aqueous Solutions

Ion	c. n.	Ion	c. n.	Ion	c. n.
Be_2^+	4	Li^+	*ca.* 4	SO_4^{2-}, HSO_4^-	6+2 water molecules
Mg^{2+}	6	Na^+	4 and 6	PO_4^{3-}, HPO_4^{2-}	at a longer distance
Ca^{2+}	8	K^+	6 and 4	$H_2PO_4^-$, ClO_4^-	
Sr^{2+}	8	Rb^+	4 and 6	MnO_4^-, SeO_4^{2-}	
Ba^{2+}	6	Cs^+	4	CrO_4^{2-}, WO_4^{2-}	
Zn^{2+}	6	NH_4^+	4 (sometimes 6)	MoO_4^{2-}, BF_4^-	
Co^{2+}	6	Tl^+	4 and 6	AsO_4^{3-}, $H_2AsO_4^-$	
Ni^{2+}	6	F^-	4 and 6	GeO_4^{4-}, SiO_4^{4-}	
Cu^{2+}	6	OH^-	4 and 6	$Cr_2O_7^{2-}$	*ca.* 10
Fe^{3+}	6	Cl^-	4	$S_2O_7^{2-}$	*ca.* 10
Al^{3+}	6	Fe^{2+}	6*)	NO_3^-	4+2 at a longer
Cr^{3+}	6	Mn^{2+}	6*)	BO_3^{3-}	distance, or 6+1
UO_2^{2+}	6	Cd^{2+}	6*)	CO_3^{2-}	

* In case of diluted solutions.

at the arrangements under discussion the structure of water changes to the smallest degree. It can be asserted on the basis of the above analysis that it is the distorted structure of water which serves as a matrix where interactions in aqueous solutions of electrolytes occur within a wide range of concentrations.

We shall analyse the consequences of application of this concept to the description of properties of water-electrolyte systems by examining the effect of water structure in a solution: (1) on the characteristics of heterogeneous equilibrium electrolyte-solution in a broad temperature range and (2) on the characteristics of equilibrium non-polar gas-aqueous solution of electrolyte. Thus, we shall dwell upon two major problems, *viz.* temperature dependence of solubility of electrolytes and of salting-out of gases.

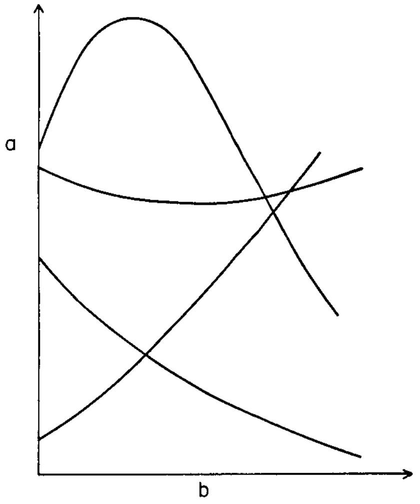


Fig. 7. Four types of solubility polyterms of electrolytes in aqueous solutions:
a–concentration of salt;
b–temperature.

Temperature dependence of solulility of electrolytes

It has been already noted that the temperature variation of solubility of electrolytes points out that heterogeneous equilibria in systems water-electrolyte are more complex than those in melts and organic mixtures. The changes in solubility of electrolytes with temperature can be represented by solubility polyterms of four types shown in Fig. 7. The shape of these polyterms can be explained on the basis of studies of the relation between energetic characteristics of dissolution figuring in thermodynamic equations determining temperature coefficient of solubility (t. c. s.) and interactions in a system. It is known that

$$\left(\frac{\partial N_i}{\partial T}\right)_{p,\mathrm{sat.}} = \frac{\overline{\Delta H}}{T\left(\frac{\partial \bar{g}_i}{\partial N_i}\right)_{p,T}} \tag{4}$$

where N_i and $\bar{g}_i$ are respectively the solubility and the partial free energy of the component i in a saturated solution. If $\overline{\Delta H}>0$, then $\partial N_i/\partial T>0$ and if $\overline{\Delta H}<0$, then $\partial N_i/\partial T<0$ since $\partial \bar{g}_i/\partial N>0$. Thus, the sign of t. c. s. is determined by the sign of $\overline{\Delta H}$ and the slope of solubility polyterms in various solutions should generally correspond to $\overline{\Delta H}$ value. Assuming partial dissolution heat, $\overline{\Delta H}$, as a sum

$$\overline{\Delta H} = \lambda_{\mathrm{m}}^{T} + \overline{\Delta H}_{\mathrm{mx}} \tag{5}$$

where λ_{m}^{T} is hypothetical heat of melting at temperature T and $\overline{\Delta H}_{\mathrm{mx}}$ is heat of mixture of one mole of electrolyte and a large amount of a solution near saturation. We can see that in the ideal solution where the interactions between dissimilar particles do not differ from those between similar particles $\overline{\Delta H}_{\mathrm{mx}} \approx 0$. The specific features of polyterms of water-electrolyte systems are associated with $\overline{\Delta H}_{\mathrm{mx}}$, *i. e.*, with similarity or difference in molecular interactions in equilibrium phases. $\overline{\Delta H}_{\mathrm{mx}}$ determines the behaviour of $\overline{\Delta H}$ since λ_{m}^{T} is small and positive and its temperature variations are rather insignificant. $\overline{\Delta H}$ and $\overline{\Delta H}_{\mathrm{mx}}$, as partial values, refer to electrolyte but it is evident that they reflect the whole set of changes in solution caused by dissolution of electrolyte. $\overline{\Delta H}_{\mathrm{mx}}$ is equal to the sum of ehthalpies of the "products" of dissolution process less the sum of enthalpies of the "initial substances":

$$\overline{\Delta H}_{\mathrm{mx}} = \sum \overline{\Delta H}_{\mathrm{fin}} - \sum \overline{\Delta H}_{\mathrm{init}}\,. \tag{6}$$

On the basis of the discussed structural model of solutions there can be introduced a thermodynamic model reflecting the separation of contributions of $\overline{\Delta H}_{\mathrm{mx}}$ in solutions of electrolytes within a wide range of concentrations*:

$$\overline{\Delta H}_{\mathrm{mx}} = \overline{\Delta H}_{\mathrm{ion\text{-}ion}} + \overline{\Delta H}_{\mathrm{water\text{-}water}} - \overline{\Delta H}_{\mathrm{hydr}}\,. \qquad (7)$$

where $\overline{\Delta H}_{\mathrm{ion\text{-}ion}}$ corresponds to the endothermic effect of breakdown of bonds between ions of liquid electrolyte, $\overline{\Delta H}_{\mathrm{water\text{-}water}}$ corresponds to the effect of breakdown of bonds between water molecules in solution, $\overline{\Delta H}_{\mathrm{hydr.}}$ makes allowance for the formation of a new system of bonds in solution. The

TABLE 5. Electrolytes with Different Types of Temperature Coefficient of Solubility**

Negative t.c.s. (strong hydration of ions)	t.c.s. sign change from (+) into (−) with temperature	t.c.s. sign change from (−) into (+) with temperature	Positive t.c.s. (weak hydration of ions and complexes)
	LiF, NaF, CaF_2,		KF, RbF, TlF,
	BaF_2		NH_4F, $CsF \cdot H_2O$
$Mg(OH)_2$,		LiOH	NaOH, KOH, RbOH,
$Ca(OH_2)$			CsOH, $LiOH \cdot H_2O$
Li_2SO_4,	K_2SO_4, Ag_2SO_4	Na_2SO_4 (rhombic)	$(NH_4)_2SO_4$,
Na_2SO_4 (monoclinic)		$Li_2SO_4 \cdot H_2O$	Cs_2SO_4, Tl_2SO_4,
$MgSO_4$, $CaSO_4$,	$SrSO_4$, $BaSO_4$		$MgSO_4 \cdot 6H_2O$
$ZnSO_4$, $MnSO_4$			$MnSO_4 \cdot 7H_2O$
$CdSO_4$, $FeSO_4$,	$CaSO_4 \cdot 2H_2O$		$FeSO_4 \cdot 7H_2O$
$CoSO_4$, $NiSO_4$			$FeSO_4 \cdot 4H_2O$
$BeSO_4 \cdot H_2O$,			$BeSO_4 \cdot 4H_2O$
$FeSO_4 \cdot H_2O$			
$ZnSeO_4$	$CaSeO_4 \cdot 2H_2O$	Na_2SeO_4	
$MgMoO \cdot 2H_2O$	$CaMoO_4$		Na_2MoO_4, K_2MoO_4
			$Na_2MoO_4 \cdot 2H_2O$
			$MgMoO_4 \cdot 5H_2O$
$CaWO_4$		Na_2WO_4	$Na_2WO_4 \cdot 2H_2O$,
			$Na_2WO_4 \cdot 10H_2O$
Li_2CO_3, Na_2CO_3,			K_2CO_3,
$Na_2CO_3 \cdot H_2O$			$Na_2CO_3 \cdot 10H_2O$
$MgCO_3$, $CaCO_3$			
Na_3PO_4,			Ka_3PO_4, $(NH_4)_2HPO_4$,
$Na_3PO_4 \cdot H_2O$			$Na_3PO_4 \cdot 8H_2O$

** The Table lists compounds for which data obtained at low and elevated temperatures and small pressures under the conditions of triphase equilibrium are available.

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* It should be noted that a similar allowance for the contribution of the breakdown of water-water bonds with the formation of ion-water bonds in solutions of electrolytes within a wide range of concentrations seems to be needed also in analysing the components of other partial thermodynamic values.

following conclusions result from relationships (4)~(7):

1. If the exothermic contribution of heat of mixture is large, then $\overline{\Delta H}<0$ and t. c. s. of electrolytes is negative. As it can be seen from relationship (7), the negative sign of t. c. s. results from a strong hydration of ions in solution which is due, in particular, to a large value of dielectric constant in solutions because of structure of free water (negative t. c. s. of electrolytes can be found not only for diluted solutions). In the absence of structured water when the same electrolytes can be dissolved in aqueous melts of other strongly soluble electrolytes, their t. c. s. should be positive. This is the case in experiment; thus, t. c. s. of Na_2SO_4 in concentrated NaCl solutions,[45] t. c. s. of $Ca(OH)_2$ in $NaNO_3$ solutions, t. c. s. of Na_3PO_4 in NaOH solutions,[47] *etc.* is positive.

2. Since the energy of ion-dipole or similar to it ion-water interaction in solutions is more strongly dependent on distance (and accordingly, on the size of ions) than the energy of ion-ion interaction in electrolyte, the exothermic component of heat of mixture, $\overline{\Delta H}_{\mathrm{hydr}}$, should undergo a greater variation in passing from one ion to another (in the case of essentially ionic compounds with large anions) than the endothermic contribution, $\overline{\Delta H}_{\mathrm{ion\text{-}ion}}$, in electrolyte. Thus, the differences in $\overline{\Delta H}$ and t. c. s. values between the series of electrolytes result from specific features of interactions in solution rather than in solid body. In general no expected correlation is observed between t. c. s. of electrolytes and energetic characteristics of solid phase (such as heat of melting, lattice energy or melting temperature). Temperature coefficient of solubility should been growing with the increase in lattice energy in series of electrolytes. However, in practice t. c. s. falls, as it can be seen from Tables 5~8.

3. It follows from relationship (7) that the higher the degree of hydration of ions in solution and the smaller the variation in structure of solvent during the intrusion of ions (or the smaller the fraction of structure in sol-

TABLE 6. Electrolytes with Different Values of Temperature Coefficient of Solubility

Negative t.c.s.	Positive t.c.s.	Temperature, °C
$CaCrO_4$, $SrCrO_4$	$BaCrO_4$, K_2CrO_4	25- 40
Li_2SeO_3, Na_2SeO_3	K_2SeO_3	30-100
Na_2SeO_4, $SrSeO_4$	$(NH_4)_2SeO_4$, Tl_2SeO_4	<100
$LiHCO_3$	$NaHCO_3$, $KHCO_3$, $CsHCO_3$	<100
$SrSeO_4$, $SrCrO_4$	$Sr(ClO_3)_2$, $Sr(NO_3)_2$	25 -75

←increase of hydration of ions in solution

TABLE 7. Temperature Coefficient of Solubility of Electrolytes in Water, $\frac{\text{g.-mol of salt/1000 g } H_2O}{\text{degree}}$

Temperature, °C	t. c. s. of electrolyte NaCl	KCl	RbCl	CsCl
10— 20	0.003	0.042	0.056	0.071
20— 30	0.006	0.039	0.053	0.063
80—100	0.011	0.033	0.047	0.061
100—120	0.010	0.031		0.060
	NaI	KBr	KI	CsI
10— 20		0.048*) 0.051	0.053	0.069
20— 30		0.049 0.048	0.047	0.072 0.065
80—100	0.019	0.036 0.040	0.045	0.082 (88-102°)
100—120	0.027	0.042 0.040	0.045	0.089 (100-110°)

* Data of various authors.

TABLE 8. Temperature Solubility Coefficient of Electrolytes in Water, $\frac{\text{g.-mol/1000 g } H_2O}{\text{degree}}$

	Li^+	Na^+	K^+	Rb^+	Cs^+	Temperature, °C
F^-	0.002	0.013	0.248			60- 80
NO_3^-	0.129	0.130	0.272	0.410 (63-76°)	0.115 (65-79°)	60- 70
	0.113	0.160	0.311			70- 80
OH^-	(−t. s. c.)	0.375	0.986			100-125

vent), the lower $\overline{\Delta H}_{mx}$ (since the contributions of electrolyte do not affect the process) and the lower should be t. c. s. of electrolyte. This conclusion (as it will be also evident from the further analysis of experimental data) can be regarded with good reasons as a general rule. For various ions the difference caused by the change of solvent ($\overline{\Delta H}_{\text{water-water}}$) is small if a large number of structurally simple ions are intruding. Therefore, there should be seen a direct relationship between $\overline{\Delta H}_{mx}$ and thereby t. c. s. of electrolytes, on the one hand, and hydration of ions of electrolytes in solutions, on the other. This conclusion is confirmed by experimental values of t. c. s. given in Table 5. Table 5 contains compounds for which there are data available for temperatures from low to high (0～400°C) under the conditions of triphase equilibrium at small pressures.[10,11] Electrolytes whose ions are weakly hydrated are characterized by positive t. c. s. and those strongly hydrated are characterized by negative t. c. s. values. A transitional region can be isolated when $\overline{\Delta H}_{\mathrm{mx}}$ and its changes are comparable with λ_{m}^{r} (the second and third columns in Table 5). The change in t. c. s. sign for these compounds is due (as it will be demonstrated later) to the effect of temperature dependent degree of structure formation of solution. At 300°C, the boundary between compounds with positive and negative t. c. s. lies between the second and third columns of Table 5. Table 6 lists salts for which there are no experimental data within a wide temperature range.[10,11] It can be seen from Tables 7～8 that the growth of t. c. s. with radius of ions (and the decrease of their hydration in solution) can be followed for electrolytes with the same t. c. s. sign (temperatures taken for consideration are determined by the region where all salts do not form crystallohydrates).

The relationship between t. c. s. of electrolytes and hydration of ions is clearly confirmed in the series of crystallohydrates containing various amounts of water molecules. If number of water molecules in solid decrease, the hydration degree of electrolyte in solution grows and, t. c. s. should drop. This accounts for the specific shape of solubility diagrams for crystallohydrates with different numbers of water molecules (Fig. 8), the crystallohydrates belonging to a large number of systems with strongly hydratable ions.

Thus, the scheme discussed forms a basis for a general classification of solubility temperature variations in series of electrolytes under the conditions of triphase equilibrium at temperatures 0～400°C.

4. The relationships discussed show clearly that if "free water" is structured, then the perturbation of water structure in solution (at saturation concentration) leads to the decrease of t. c. s. and the strengthening of the structure gives rise to higher t. c. s. values (since in the first

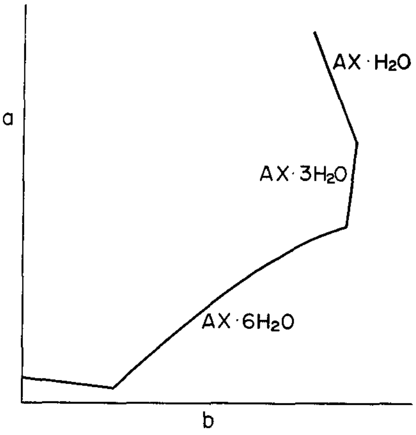

Fig. 8. Typical shape of solubility diagram of crystallohydrates: a-temperature; b-solubility of salt; c-ice.

case $\overline{\Delta H}_{\text{water-water}}$ falls and in the second case it grows). The perturbation of water structure leads also to a certain increase in the degree of short-range hydration[1,2] and, as a result, to a larger contribution of $\overline{\Delta H}_{\text{hydr}}$ into heat of mixture and hence to a more pronounced dependence. As it follows from refs. 1, 6, the portion of structure formed in water can be changed under the effect of temperature, pressure, stabilising and destructing additives. The effect of stabilisation on t. c. s. of electrolytes can be seen from experimental data.[7~9] The growth of pressure at low temperatures leads to the breakdown of bonds in water and if the influence of pressure on other bonds in solution is weaker (what is quite probable), the increase in pressure at low temperatures should bring about reduction of t. c. s. The growth of pressure at high temperatures favours the development of a more structured system and the influence of pressure on t. c. s. should have an opposite sign. Indeed, as it follows from works of RAVICH *et al.*,[48] the negative sign of t. c. s. at elevated temperatures changes into a positive one with pressure. Unfortunately, we have until now no information on the effect of pressure on t. c. s. at low temperatures because of lack of any experimental data.

The effect of structure of solvent on t. c. s. of solution manifests itself quite clearly when aqueous and non-aqueous systems are compared (in systems where solvent is more structured than in aqueous solution t. c. s. should be lower). Solutions in D_2O where the solvent is more structured than H_2O, other properties being similar, have larger t. c. s. values (Table 7, 9). Liquid ammonia is known to be a considerably less structured polar solvent as against water. Endothermic value, $\Delta H_{\text{solvent}}$, in relationship (7) should be essentially smaller in ammonia than in water. For this reason t. c. s. of alkali chorides in ammonia is negative[10] while in water these salts have positive t. c. s. values. Acetone is the least structured solvent in the series water —hydrazine— acetone and, accordingly, t. c. s. of CsI in acetone should have the smallest value. This prediction has been confirmed experimentally.[49] CsI has a positive t. c. s. in water, t. c. s. near to zero in hydrazine, and a negative t. c. s. in acetone as well as in ammonia. Thus, varying the state of solvent in a solution (or changing the solvent), we can purposely modify the solubility diagram which is important for practice.

Let us consider a complicated and interesting case of the change of shape of solubility polyterms of electrolytes with temperature. We shall analyse which parameters and in what directions undergo variation in electrolyte with temperature. First, energetic components of heat of dissolution change in diverse ways since they are determined by different types of in-

TABLE 9. Temperature Coefficient of Solubility of Electrolytes in D_2O, $\dfrac{\text{g.-mol of salt/55.51 mole } D_2O}{\text{degree}}$

Electrolyte	Temperature, °C				
	10–20	20–30	60–80	80–100	100–120
KCl	0.048	0.043	0.037	0.036	0.036
KBr	0.056	0.051	0.041	0.040	0.040
KI	0.061	0.055	0.049	0.049	0.048
NaCl	0.008	0.009	0.009	0.011	0.011
NaBr	crystallohydrates			0.0135	0.0165
NaI	of NaBr and NaI are formed			0.0195	0.025

teractions between particles. Average energy of water-water interaction decreases with temperature most rapidly, that of ion-water interaction decreases slower, and that of ion-ion interaction remains practically constant. Second, different variations in interactions give rise to specific temperature changes in equilibria in solution, the equilibria being related to "lifetimes" of particles in temporary equilibrium positions with respect to one another and to the number of contacts of certain types in the solution. Short-range hydration of ions in solution should grow with temperature or fall at a reduced rate because of a more rapid weakening of bonds between water molecules compared to ion-water bonds. It can be shown on the basis of molecular kinetic relationships determining short-range hydration that the degree of hydration of strongly hydrated ions should decrease with temperature and that the degree of hydration of weakly hydrated ions should increase. Short-range hydration of ions in diluted solutions is known to be defined[1,15] by the relationship $\tau_i/\tau_0 \approx \exp(\Delta E_i/RT)$ where τ_i is the average residence time of a water molecule in the nearest surroundings of an ion and τ_0 is the average residence time of a water molecule in the surroundings another water molecule. $\Delta E_i = E_i - E_0$ where E_i and E_0 are energies required for the escape of a water molecule from the first sphere of ion or that of another water molecule. In solutions of electrolytes within a wide range of concentrations, short-range hydration will be described by a similar expression where τ_0 will be substituted by τ_0', "lifetime" of water molecules in temporary equilibrium positions in "free water" of a solution of a given concentration. In the presence of structured free water in a solution of electrolyte, τ_0' should be sufficiently large (it is clear, however, that $\tau_0' < \tau_0$ since ions perturb the orientation of water molecules). The relationship discussed shows that the degree of short-range hydration of negatively hydrated ions should grow with temperature (since $\Delta E_i < 0$, the ratio τ_i/τ_0 grows with temperature) and the degree of hydration of positively hydrated ions in the nearest surroundings should drop (since $\Delta E_i > 0$). Due to the E_0 value, apparently, slightly decreasing with temperature[24,50] and E_i remaining relatively constant, the boundary line determining the sign of temperature variation of hydration will be shifted towards more strongly hydratable ions. Thus, the growth of the degree of hydration of ions in solution with temperature results entirely from the existence of water structure in solutions of electrolytes and should not be observed in the studies of solvation in unstructured solvents.

At elevated temperatures when bonds between water molecules are weakened to a large degree or a considerable portion of the bonds is broken, "free water" exerts practically no influence on the hydration of ions. At these temperatures the degree of short-range hydration should decrease essentially with temperature in all cases. It is possible that it is the reduction of the degree of short-range hydration of ions that is related with the observed endothermicity of the process of association and a considerable growth of association in aqueous solutions of $1-1$ electrolytes at elevated temperatures.[51] Thus, for aqueous solutions of electrolytes (primarily, electrolytes formed by weakly hydratable ions) there can be isolated two temperature existence regions of solution differing in specific features of interaction of particles, *viz.* the zone of primary destruction of bonds between water molecules in solution and the zone of primary decomposition of hydrate complexes. According to the data available,[52,53] transition region for water exists at $250\sim300°\text{C}$ at pressures near to the saturation pressure of water and, probably, at higher temperatures under larger pressures.

The change of state of solutions with temperature leads to the variation of dissolution heats and, accordingly, of solubility polyterms of electrolytes. In relationships (5)$\sim$(7) determining $\overline{\Delta H}$, all contributions decrease with temperature. However, in the first temperature zone $\overline{\Delta H}_{\text{water-water}}$ drops faster than other components (λ_{m}^{T} and $\Delta H_{\text{ion-ion}}$, for a first approximation, are temperature-independent and the changes of water-water bonds are stronger than those of ion-water bonds). This results in the growth of exothermicity of dissolution. For weakly hydrated ions, a certain increase in short-range hydration with temperature should give rise to an enhancement of this dependence. In consequence, the negative t. c. s. of electrolytes should grow and the positive t. c. s. should fall. The difference in the extent of t. c. s. variation for different electrolytes should be determined by unlike changes in short-range hydration of ions with temperature (since $\Delta H_{\text{water-water}}$ and $\partial\Delta H_{\text{water-water}}/\partial T$ values for structurally simple ions fall close together). As it follows from the discussed molecular kinetic relationships determining short-range hydration, the growth of hydration degree is the highest for ions with the most intense negative hydration. For this reason, t. c. s. should undergo stronger variations in the case of electrolytes with this sort of ions*). Thus, in the series NaCl—CsCl the drop of t. c. s. should be the strongest for CsCl which is the case in experiment[10] at temperatures 10~40°C (Table 7). If exothermic and endothermic contributions into $\overline{\Delta H}$ have similar values and $\overline{\Delta H}>0$, then the growth of dissolution exothermicity with temperature will result in t. c. s. sign changing from plus into minus, *i. e.*, a maximum on the graph of electrolyte solubility *vs.* temperature may appear because of primary destruction of bonds of structured water in solution with temperature. This contribution can be "eliminated" in two ways:

1. By increase of temperature, *i. e.*, by transfer of a solution to temperatures where structural perturbations of solvent during the intrusion of ions can be left out of account (transfer to the second temperature zone).
2. By increase of solution concentration with the help of readily soluble electrolytes, *i. e.*, by transfer to the region of aqueous melts where no "free water" exists (also in both ways together for compounds with positive t. c. s.).

At elevated temperatures the contribution of $\overline{\Delta H}_{\text{water-water}}$ can be neglected; mostly a decrease of exothermic component of heat of dissolution occurs with temperature because ion-water bonds break down with temperature faster than ion-ion bonds. As a result, the endothermicity of dissolution and t. c. s. of electrolytes grow and a change of t. c. s. sign from negative into positive should be observed, t. c. s. being slightly negative in the second temperature zone. Table 10 describes the behaviour of experimentally studied systems (see refs. 10, 11, *etc.*). The change of sign of t. c. s. of electrolytes with "intermediate" hydration of ions from plus into minus is indeed observed in the first temperature zone; in all experimentally studied cases, corresponding temperatures are lower than 280°C, *i. e.*, belong to the region where structured solvent is contained in solution. In the second temperature zone the growth of t. c. s. is noted; for LiOH the change from negative into positive t. c. s. has been found at ca. 300°C. It is to be noted that the first temperature zone is smeared out for systems where the short-range hydration of ions is expressed sufficiently strongly (if hydration of ions decreases in the whole temperature range, the drop of $\overline{\Delta H}_{\text{ion-water}}$ superimposes over the variation of $\overline{\Delta H}_{\text{water-water}}$). If this process determines the variation of heat of mixture with temperature, t. c. s. grows in the whole temperature range

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* Some complications are introduced by the association of ions but it can be taken into account in the relationships under discussion.

TABLE 10.

First temperature zone	Second temperature zone	
change of t.c.s. from (+) into (−)	decrease of (−) t.c.s.	increase of (+) t.c.s.
LiF, NaF, K_2SO_4, $CaMoO_4$, CaF_2, BaF_2, Ag_2SO_4, $SrSO_4$, $BaSO_4$, $CaSO_4 \cdot 2H_2O$, $CaSeO_4 \cdot 2H_2O$	LiF, Na_2SO_3, Na_2SO_4, Li_2SO_4, Na_3PO_4, $SrSO_4$, LiOH (change of t.c.s. sign from (−) into (+)	LiCl, NaCl, KCl, KF, NaBr, $Ca(NO_3)_2$, $FeCl_3$

and the two temperature regions will not stand out clearly.

In the case when free water is "eliminated" by the increase of concentrations of other ions in solution, salts changing t. c. s. sign in water from plus into minus with temperature should not display such a change in strongly concentrated solutions of readily soluble electrolytes since there will be no preponderant decrease of endothermic component of heat of mixture with temperature (in the present case this is due to the absence of breaking water-water bonds and of the contribution of $\overline{\Delta H}_{\text{water-water}}$). Such systems have been studied experimentally[54~58] (Table 11).

TABLE 11.

Electrolytes changing t.c.s. sign in water from (+) into (−)	Systems where t.c.s. sign does not change in concentrated solutions
K_2SO_4	K_2SO_4-KCl-H_2O
$CaMoO_4$	$CaMoO_4$-NaCl, KCl-H_2O
NaF	NaF-NaCl, KCl-H_2O
$BaSO_4$	$BaSO_4$-NaCl-H_2O
CaF_2	CaF_2-LiCl-H_2O

Thus, the changes of shape of solubility polyterms of electrolytes in aqueous solutions with temperature are related to the features of temperature variations of ion-ion, ion-water, and primarily water-water interactions; this confirms a general concept about the presence of strongly structured water in solutions of a wide range of concentrations. Therefore, hydrophilic hydration represents an interaction of ions with a network of hydrogen bonds in a solution of a given concentration. Hydrophobic hydration which we shall discuss for a simple gas-water system is also an interaction of particles of solute with a system of bound water molecules; however, molecular mechanisms of interaction of particles in these two cases are different.

Characteristics of heterogeneous equilibrium nonpolar gas-aqueous solution

In order to describe the mechanism of dissolution of gases in water and solutions we shall use the ice-like model of water and solutions of electrolytes. We propose to consider the process of dissolution of gases on the basis of a scheme of interaction of inherent defects of the ice-like network (water molecules in interstices and vacancies in framework points) and impurity defects (gas molecules in interstices). As a quasi-chemical approximation, we shall consider a solution containing W_K water molecules in points of the ice-like network, C cavities, W_C water molecules in cavities, G_C gas molecules in cavities, v vacancies, and G_v gas molecules occupying vacancies. The solution is in equilibrium with vapour containing molecules of admixture G (partial pressure of gas is p_i). In this case the following reactions in the system and corresponding expressions for the law of mass action should be taken into account:

$$W_K \rightleftarrows v, \quad K_1 = \frac{[v]}{[W_K]}; \tag{8}$$

$$W_K + C \rightleftarrows W_C + v, \quad K_2 = \frac{[W_C]\,[v]}{[W_K]\,[C]}; \tag{9}$$

$$G + C \rightleftarrows G_C, \quad K_3 = \frac{[G_C]}{[G]\,[C]}; \tag{10}$$

$$G + W_C \rightleftarrows G_C W_K, \quad K_4' = \frac{[G_C W_K]}{[G]\,[W_C]}, \quad K_4 = \frac{[G_C W_K]}{p_i [C] \dfrac{K_2}{K_1}}; \tag{11}$$

$$G_C + W_C \rightleftarrows G_C W_K + C, \quad K_5' = \frac{[G_C W_K]\,[C]}{[G_C]\,[W_C]}, \quad K_5 = \frac{[G_C W_K]}{p_i [C] K_3 \dfrac{K_2}{K_1}} \tag{12}$$

$$G + v \rightleftarrows G_v, \quad K_6 = \frac{[G_v]}{[G]\,[v]}. \tag{13}$$

It can be shown that K_6 is very small and for this reason we do not take this particular process into account. Relationships (10)–(12) are not mutually independent and we can use any two equations of three. The total solubility of gas in water, c_{sol}, is

$$c_{sol} = [G_C] + [G_C W_K], \tag{14}$$

i. e. c_{sol} is small; $C \approx c_x$ where c_x is the total number of cavities in water, the cavities being free of water molecules. It follows from the previously discussed relationships that $c_x = \frac{1-x}{2} - x$.

$$c_{\text{sol}} = c_x p_i \left(K_3 + \frac{K_2}{K_1} K_4 \right). \tag{15}$$

K_2 and K_1 in relationship (15) correspond to the concentration of defects of the FRENKEL and SCHOTTKY types in water and can be evaluated on the basis of the model of water structure. K_3 can be found from the calculations of the energy of dispersion interaction of gas molecules with the fixed ice-like surroundings (in the case of gases located in the cavities of water structure) or with the dodecahedral surroundings for gas molecules of larger sizes. K_4 (or more directly K_5) reflects the effect of stabilisation of water structure by gas molecules in cavities. This effect can be evaluated from the data describing bulk properties of solutions of gases in water. The above scheme accounts for the anomalies of solutions of gases in water[62,64] as against solutions in other liquids (in particular, anomalous heats and entropies of dissolution of gases).

The salting-out of gases can be also considered on the basis of the ice-like model of solutions. In going from water to a solution of electrolyte, the ratio K_2/K_1 in relationship (15) is almost a constant value (since it has been demonstrated that $\gamma \approx \gamma'$), K_3 reflecting the relationship of a gas molecule with the surroundings of a cavity should not vary in the presence of electrolyte, and c_x and K_4 become variable. For gases whose molecules have room in the cavities of the ice-like structure, c_x can be found[59] from the formula:

$$c_x = \frac{1-x}{2} - x + \frac{N\left[a + b\gamma\,(1 - x - ax + x - 1\right]}{2} - (b + ax)N + N\left[x + b\gamma\,(1-x)\right]. \tag{16}$$

Relationship (16) makes it possible to determine c_x values for solutions of salts provides the model of arrangement of ions is known.

The variation of K_4 in solutions of electrolytes represents the changes in substitution of water molecules in cavities by gas molecules in the presence of the field of ions. With electrolyte present, water molecules and gas molecules substituting them are not equivalant any more. Due to the orientation of polar molecules of water in the field of ions in cavities, these water molecules are in an energetically more favourable state than in pure water. At the same time, the state of gas molecules in cavities does not change, as a first apporximation, in the presence of electrolyte. For this reason, $K_4^{el} < K_4^{H_2O}$ and equilibrium (4) in going from water to a solution shifts towards the initial substances, *i. e.*, the solubility of a gas in this case should decrease. Thus, the salting-out of gases is regarded as a wholly structural effect. In the present scheme (which is likely to hold true not only for gases but also for other molecules (with non-polar groups), salting-out can be explained by the influence of electrolyte on the stabilisation of water structure by nonpolar molecules or on the hydrophobic hydration of nonpolar molecules). A more detailed analysis of the process requires also a consideration of the change in the state of the displaced water molecules in the ice-like structure. The perturbations of the ice-like network in solutions should lead to a stronger manifestation of this relationship and the binding of the displaced water molecules by ions should result in a reverse change.

The salting-out effect of electrolytes is usually characterised by the coefficient S_{s-o} of the SECHENOV equation which can be represented as follows:

$$S_{s-o} = \frac{1}{m} \log \frac{c^0_{sol}}{c_{sol}} = \frac{1}{m} \left[\log \frac{c_{x\,H_2O}}{c_{x\,sol}} + \log \frac{1+AK_4^{H_2O}}{1+AK_4^{slo}} \right] \qquad (17)$$

where $A = \frac{K_2}{K_1 K_3}$, and m molality.

It follows from the scheme that:

1. The degree of salting-out a gas increases with the concentration of an electrolyte and the charge of ions in a solution; this has been indeed observed for the most of experimentally studied systems.

2. The solubility of a gas in various solutions of electrolytes should correspond with the number of unoccupied cavities in the structure of solutions (at similar effective charges of ions in a solution). This conclusion is confirmed by experimental values of solubility of neon in aqueous electrolytes[59,60] for which c_x figures can be found on the basis of the model of structure of solutions. Neon is a convenient subject of studies since its monoatomic molecule can find room in a void of the ice-like network of water.[59,61] The larger is c_x (for the solutions studied, $c_{x\,NH_4Cl} = c_{x\,RbCl} > c_{x\,KCl} > c_{xKF} > c_{x\,KOH} > c_{x\,MgSO_4}$) the smaller should be the salting-out of neon. The order of decrease of the degree of salting-out found in experimental studies of neon solubility is: $NH_4Cl < RbCl < KCl < KF < KOH < MgSO_4$. In another series $c_{x\,Mg(NO_3)_2} \approx c_{x\,Ca(NO_3)_2} \approx c_{x\,Ba(NO_3)_2} > c_{x\,MgSO_4}$. The degree of the salting-out of neon changes in the following way for these salts: $Mg(NO_3)_2 \approx Ca(NO_3)_2 \approx Ba(NO_3)_2 < < MgSO_4$.

3. If the proposed mechanism of dissolution of gases is correct, the

salting-out these gases should decrease with temperature since the effect of the field of ions on the orientation of water molecules in voids diminishes with temperature (accordingly, the variation of the constant K_4 in passing from water to a solution will be smaller at a higher temperature). The temperature dependence of the coefficient S_{s-o} in the SECHENOV equation was calculated for neon from experimental values of solubility of the gas in solutions of electrolytes.[12] As it can be seen from Fig. 9, the salting-out of neon drops with temperature for all electrolytes. A decrease in the salting-out other gases in solutions of electrolytes with temperature has been found in other studies.[62,63] Fig. 10 shows that the decrease of the salting-out of neon with temperature gives rise to an interesting phenomenon, *viz.* while in water and diluted solutions of electrolytes the solubility of neon drops with temperature (10~30°C), the solubility of the gas in electrolytes with concentrations increases with temperature. Minima of solubility are observed for solutions of intermediate concentrations.

4. For a first approximation, pressure should not affect the salting-out of gases, as it follows from the scheme discussed, since the influence of a water molecule and that of a gas molecule in cavities are almost similar

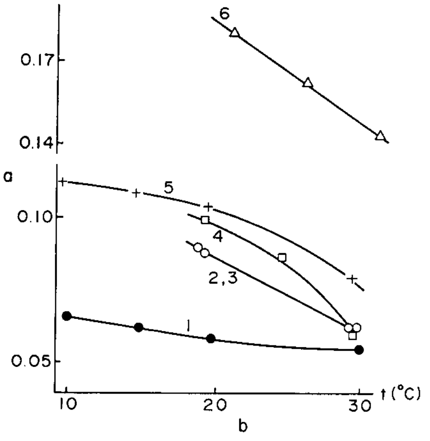

Fig. 9. Temperature dependence of salting-out coefficient of the SECHENOV equation for the solutions of gaseous neon:

1-NH_4Cl; 2-$CsNO_3$; 3-$LiNO_3$; 4-KNO_3 ; 5-KCl; 6-$Mg(NO_3)_2$.

a-S_{s-o}; b-temperature, °C.

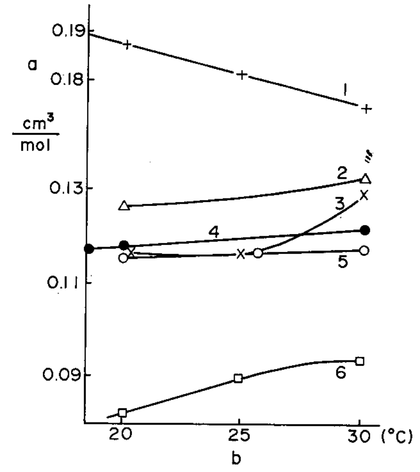

Fig. 10. Solubility of gaseous neon in water and 2 m solutions of electrolytes at different temperatures:

1-H_2O; 2-$LiNO_3$; 3-KNO_3; 4-KCl; 5-$NaNO_3$; 6-$Mg(NO_3)_2$.

a-solubility, cm³/mole; b-temperature, °C.

and $K_4 \approx$const. Indeed, experimental studies have demonstrated that, for a first approximation, the dependence of the SECHENOV salting-out coefficient on pressure can be left out of account.[62]

The above analysis emphasizes once again the important role played by the initial structure of water and its effect on the structure and properties of such a complex system as an aqueous solution within a wide range of electrolyte concentrations and allows the large and diverse amount of experimental data to be decribed on a unified basis.

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