STRUCTURAL TRANSITION
TO ELECTROLYTE–WATER SOLVENT AND
CHANGES IN THE MOLECULAR DYNAMICS
OF WATER AND PROPERTIES OF SOLUTIONS

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A model of concentration transition “ions and complexes in a water structure → ionic and ionic-aqueous clusters → polymer structures of salt and crystal hydrate melts” is suggested. The appearance of cluster nanostructures outside the first zone of a water-like structure is regarded as a general characteristic of solutions. The characteristics of solutions, phase equilibria, and salts of complex composition are interpreted based on this model. Investigation of the complex dielectric constant of electrolytic solutions in the SHF and EHF bands (7-119 GHz) at high concentrations showed that there are two dispersion regions in which the relaxation times differ by a factor of 5-10. Relaxation processes are separated, the numbers of molecules in hydration shells are calculated, and relaxation times are determined for bulky tetrahedral water with hydration shells of ions, for clusters, and for ionic-aqueous polymer chains. It is shown that the two structure subsystems of water molecules in concentrated solutions may be described using the limited rotator/generalized diffusion molecular model.

In studies of aqueous electrolytic solutions in a wide range of concentrations (including highly concentrated and saturated solutions), the following questions arise: 1. What are the schemes of structural transitions to highly concentrated solutions or aqueous melts of salts and crystal hydrates when different interactions take place between the components with clear-cut differences in self-order of particles? 2. Which component determines the bond system in solution, leading to a uniform or nonuniform distribution of particles in different concentration zones?

In aqueous solutions of electrolytes, the water structure is present in the initial range of concentrations. The structure of salt and crystal hydrate melts is also typical and expressed by the radial distribution function (RDF) obtained from X-ray data. However, typical concentration structural changes are difficult to reveal by analyzing particle distributions in solution at a level of D-structure in RDF or the list of particle coordinates in an “instant” I-structure. The particle distributions in subsystems are considerably “smeared” even if the structural transition is localized in a narrow concentration zone. The moments of appearance or disappearance of new individual configurations and their singularities are hard to detect and may differ in concentration between properties and solutions. The system-forming factors and the concentration zones may be treated more consistently at a level of the local structures of deep minima on the potential surface of systems, which are often identified with V-structures of solutions. These structures are associated with long-lived configurations. The available schemes of concentration transition, showing singular points on the concentration scale, primarily refer to V-structural changes (although not all of the schemes refer to particular structures).

Concentration changes were treated using various models based on the micro- and macroscopic physicochemical data of solutions [1-7, etc.]. These models are closely related to the initial models of structure formation in electrolytic solutions during hydration of ions. In the general case pertaining to both low-hydrated ions with positive or negative hydration and hydration or ionic complexes, a model of structure formation in electrolytic solutions based on the water structure was developed [3, 6]. The boundary of the first concentration zone in the structure of solutions was established


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for more than 50 binary and ternary systems [3-6]. In the model suggested here, the structural transition has no destructured transition layer (as opposed, e.g., to Franck-Wen’s hydration model) and does not imply coexistence of the water and crystal hydrate structures in a wide concentration region without infinite dilution (as opposed to Samoilov’s scheme [1]). The physical sense of the boundary of the first structural zone of solutions also differs slightly from Mishchenko’s boundary of complete hydration [2]. In our case, the singular point (narrow zone) is not determined by the distribution of water molecules in the coordination spheres of ions; rather, it is determined by the disappearance of the tetrahedral bulky water and hence by the appearance of conditions eliminating the system-forming effect of the initial net of water H-bonds. With identical coordination numbers of low-hydrated ions, the concentration boundary in question corresponds to Mishchenko’s boundary of complete hydration. For high-hydrated ions forming hydrated complexes, this boundary is established at lower concentrations corresponding to the first coordination sphere of complexes. It is noteworthy that in concentrated solutions of salts ionic forms do not necessarily correspond to the structure of the “electrolyte” component, contrary to the assumption in [7].

We propose a general concept of a concentration structural transition from dilute solutions of electrolytes containing the water structure to highly concentrated solutions and aqueous melts of salts and crystal hydrates. The scheme of the transition involves formation of ionic or ionic-aqueous clusters in solution.

\[ \text{Ions and complexes in the initial water net} \quad \varepsilon_s \approx 60-80 \]
\[ \text{Ionic or ionic-aqueous clusters and fragments of the hydration spheres of ions} \quad \varepsilon_s \approx 40-20 \]
\[ \text{Polymeric aqueous melts of crystalline hydrates, salts, hydroxides, or acids} \quad \varepsilon_s \approx 20-5 \]

In several specific cases, other schemes of transition to polymeric structures of electrolytic melts are possible: for example, polymerization in solutions of Bi salts with relatively low concentrations or a continuous transition to HCl-H2O and NH4F-H2O structures based on tetrahedral water configurations, etc. (this variant is indicated by the dashed line in the scheme). The general scheme provides for the possibility of nonuniform distribution of particles in solution with medium-range order outside the first concentration structural zone. On the other hand, the relatively large electrostatic hydration contributions in the first zone (\(\varepsilon_s \approx 70-80\)) provide a uniform distribution of particles (complexes or associates are regarded as individual particles). When bulky tetrahedral water vanishes, the static dielectric constant \(\varepsilon_s\) of electrolytic solutions changes sharply. This follows from the data obtained by microwave dielectric studies of solutions over a wide range of concentrations [8-13]. Figure 1 shows an example of concentration changes in \(\varepsilon_s\) for LiCl solutions (literature and our data [8-12]). Similar changes are observed for other systems as well. On the other hand, the dielectric relaxation times \(\tau_d\) in Fig. 1 show that the water molecules in the first sphere of ions in the case of concentrated solutions are not completely “frozen out” and participate in polarization.

Thus formation of complex ionic or ionic-aqueous groups on/beyond the boundary of the water-like structural zone in a limiting electrostatic scheme is primarily explained by the lowered dielectric constant in the new solvent. The specific chemical components of interactions may affect this process and determine the diversity of further concentration transformations (in particular, formation of crystal hydrate structures). Investigating these components is the major goal of the coordination chemistry of solutions, since the effects of the water structure and large electrostatic contributions to hydration are eliminated at these concentrations. H2O molecules act as ligands along with other particles of solutions. The presence or absence of structured water determines (via changes in \(\varepsilon_s\) and other properties) the general specifics of the structural transformation occurring in a narrow concentration zone. In principle, the concentrations of solutions corresponding to unification of ions into new configurations and the boundary of the initial water structure are not bound to coincide. The similarity of these concentrations indicates that the new complex groups are unstable in the presence of bulky tetrahedral water with high \(\varepsilon_s\). Regrettfully, the data on \(\varepsilon_s\) and polarization involving ionic forms in solutions are very scarce. According to the dielectric spectra, \(\varepsilon_s\) increases in the presence of dipole ionic