

Sub- and supercritical equilibria in aqueous electrolyte solutions

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ABSTRACT - The phase behavior and molecular structure of aqueous electrolyte solutions at elevated temperatures and pressures are reviewed following a description of some peculiarities of these systems. Data for the construction of phase diagrams in sub- and supercritical regions are also discussed.

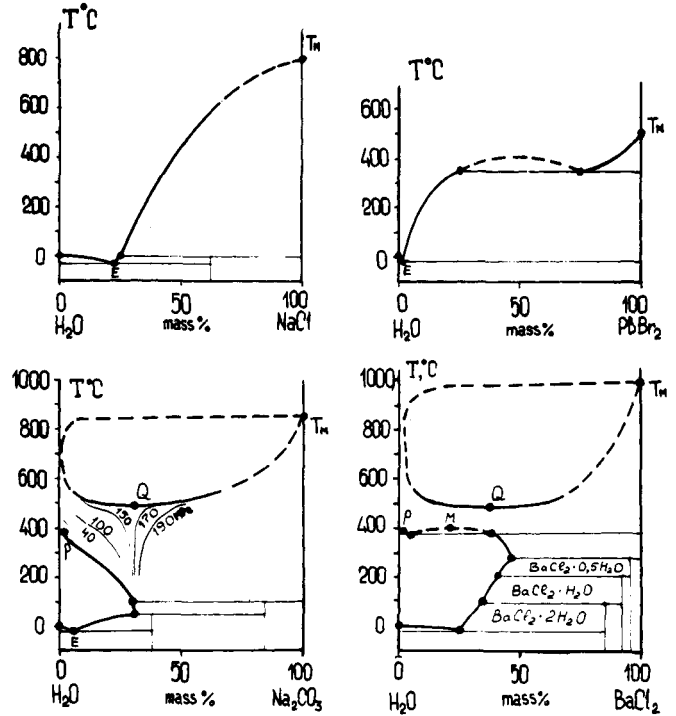
INTRODUCTION

Aqueous electrolyte solutions at elevated temperatures and pressures - in the subcritical as well as in the supercritical regions - behave in a way that is strikingly different, both in homogeneous and heterogeneous states, from the behavior of the same mixtures at normal temperatures. The new equilibria and considerable variations of fluid density and concentration, accompanied by changes in both the electrolytes dissociation and the solvent ability, arise in aqueous systems only at high parameters of state. All these properties of hydrothermal solutions play an important role in several geochemical and technological processes, e.g., the hydrothermal formation of ore deposits, corrosion and scaling in geothermal and water desalination systems as well as in boilers, power plants and cooling systems of nuclear reactors, hydrothermal crystal growth and materials synthesis, high-temperature hydrometallurgic and electrochemical processes (ref. 1). Besides that, water-salt systems at elevated and supercritical temperatures provide a unique field of study of extensive and continuous variations of physico-chemical properties with temperature, pressure and composition. At the same time, information available in this field is quite limited, due mainly to experimental problems. The purposes of the present review are to describe the progress that has been achieved in the recent years in the study of homogeneous and heterogeneous equilibria in sub- and supercritical regions, to state some regularities in the behavior of high-temperature electrolyte solutions, to determine the phase diagram construction, and to point out some problems for investigations to come.

HYDROTHERMAL EQUILIBRIA AND TRANSITION REGION

Analysis of experimental data on water-salt systems shows that high temperature phase equilibria are characterized by the absence of crystal hydrates and by the presence of various liquid-gas equilibria, including liquid-liquid immiscibility, critical phenomena and supercritical fluid equilibria. At temperatures not exceeding 200-250° C liquid-gas equilibria are very simple, because all of these phenomena are absent, but phase equilibria with solid phases can be complex, especially due to a wide distribution of crystal hydrates. These peculiarities of phase equilibria in various temperature ranges are illustrated in Fig. 1, where four phase diagrams of the water-salt systems are shown over a wide interval of temperatures. This observation has received fundamental support and interpretation from the structure and properties of pure water in the temperature range of 200-300° C. The latest X-Ray diffraction studies of water in a wide temperature range show that the second peak at 4 Å on the pair-correlation function of water, which provides strong evidence for tetrahedral ordering in water at low temperature, diminishes gradually and disappears in the range of 250-300° C at 100 MPa (ref. 2). These data demonstrate that the low-temperature structure of water gradually transforms itself during heating into a new one that does not correspond to the simple close-packing, but is characterized by weakened hydrogen bonds. Transformation of the low-temperature tetrahedral structure of water is completed at 250-300° C. A drastic molecular

Fig. 1 Projections of phase diagrams on coordinated "temperature - composition" plane for systems NaCl-H₂O, PbBr₂-H₂O, Na₂CO₃-H₂O and BaCl₂-H₂O.



transformation in the vicinity of 200° C can be seen from the analysis of temperature dependence of water properties. Fig. 2 shows the variation of spectral, thermodynamic and transport characteristics of pure water in that temperature range. In the subcritical region, values of isochoric heat capacity, viscosity, thermal conductivity and other properties of water and its behavior (see Fig. 2) became more and more similar to those of simple molecular liquids (ref. 1,3).

Dilute aqueous solutions and pure water are characterized by similar temperature and pressure variations of most properties, reflecting structure

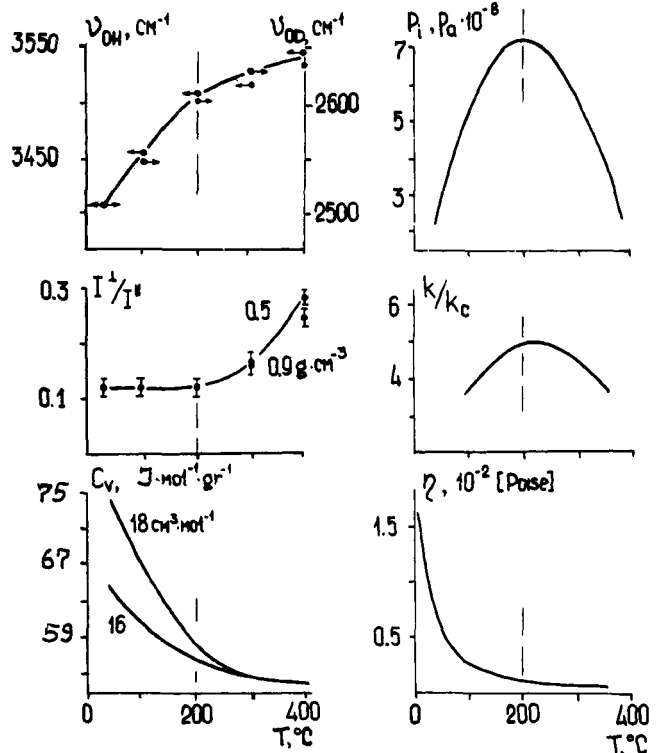


Fig. 2 Properties of water in temperature range 0-400 C

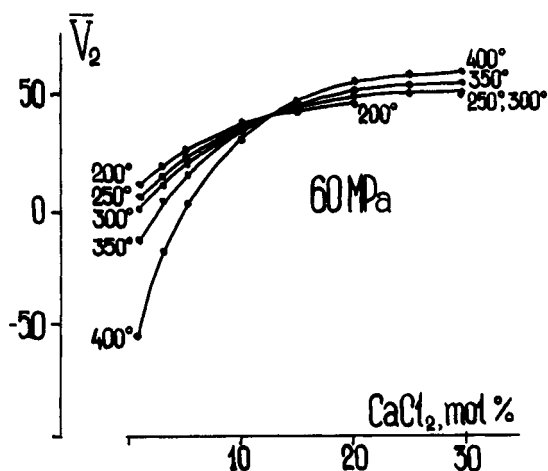
- ν - band maximum of OD or OH stretching mode
- I₁ / I₂ - depolarization ratio
- C_v - isochoric heat capacity
- P_i - internal pressure
- k/k_c - reduced thermal conductivity (k_c - const)
- η - viscosity

transformations and other peculiarities of the solute. The spectral measurements (ref. 4-6) and the data on partial molar entropy of water (ref. 7,8) show a uniform "structure-making" influence of various ions on water in dilute solutions at temperatures exceeding 200°C. At low temperatures different ions demonstrate both "structure-making" and "structure-breaking" effects. In addition dilute electrolyte solutions at hydrothermal conditions are distinguished by high negative values and uniformity of temperature and concentration dependencies of thermodynamic functions of solution (ref. 8,9), by a negative temperature coefficient of salt solubility (t.c.s) (ref. 10), by decreasing of electroconductivity (ref. 11) and by partial molar volume of electrolytes (ref. 12) at heating.

As the electrolyte concentration in aqueous solutions is increased not only the values, but the behaviour of the properties are changed and approach those of anhydrous melts. Sometimes the form and sign of temperature or pressure dependencies of water (or very dilute aqueous solutions) properties and those of anhydrous melts are different. In this case a change of the sign or form of dependencies can be used to determine the concentration of the transition region, where water-like structure and properties of diluted solutions are transformed into melt-like ones of the concentrated solutions (ref. 13). The sign change of temperature dependencies, shown in Fig. 3, is demonstrated for the example of partial molar volume of CaCl_2 in hydrothermal solutions, measured in our laboratory (ref. 6).

Similar behaviour of partial molar volumes of electrolytes is observed in hydrothermal solutions of NaOH and KOH, where the P-V-T measurements have been made to very high concentrations (ref. 14, 15).

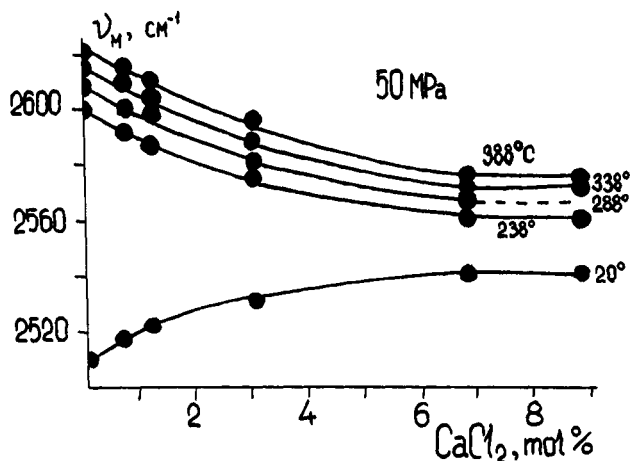
Fig. 3 Concentration dependence of partial molar volume of CaCl_2 in aqueous solutions at 60 MPa for 200, 250, 300, 350 and 400°C.



The most direct evidence of structure transformations taking place in the transition region is obtained by studies of the intermolecular stretching vibration of water by IR and Raman spectroscopy (ref. 4-6). Fig. 4 illustrates the influence of electrolyte concentration on the position of band maximum of OD stretching mode in aqueous CaCl_2 solutions. The spectral data show that the state of water molecules changes little at concentrations exceeding 5-6 mol % CaCl_2 . This is related to the destruction of the system of hydrogen bonds between water molecules and to the distribution of water among the ions forming the melt-like system of ionic bonds at the concentrations of transition region. These results completely coincide with those of the Italian scientists (ref. 16), who have used different experimental methods (Raman spectroscopy, inelastic and small angle neutron scattering, EXAFS, ultrasonic attenuation and other) in their studies of molecular structures of NiCl_2 , ZnCl_2 , CdCl_2 , CuCl_2 and other 2 - 1 electrolyte solutions to high concentrations at normal temperatures. They have found that the water-like structure of aqueous solutions is observed up to 3-6 mol.% of 2 - 1 electrolytes. At higher concentrations the solvated cations and complex anions interact to form a quasilattice local structure which extends over several interionic distances.

The transition region is represented by an interval of concentrations at which the most drastic transformations of the solution structure take place. Different properties fix different stages of the process and thus concentration values of the transition region, estimated on the basis of the different characteristics of a system, should not coincide. So

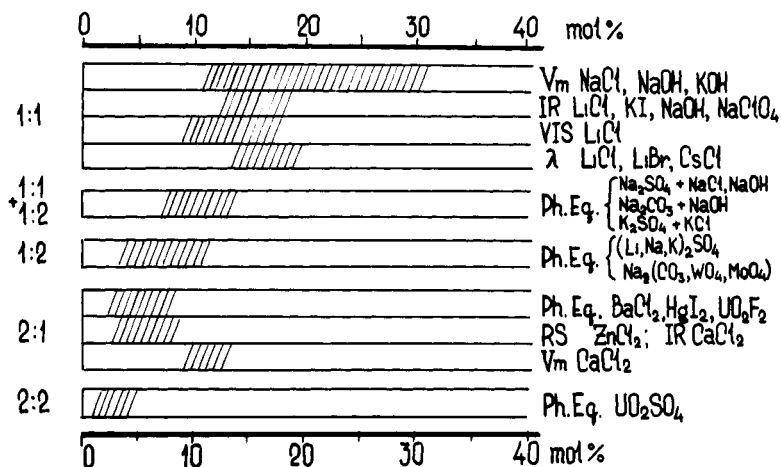
Fig.4 Concentration dependence of the O-D band maximum in aqueous CaCl_2 solutions at 50 MPa for 20, 238, 288, 338 and 388°C.



the spectral and diffraction data for 2 - 1 electrolyte solutions show the melt-like behaviour at concentrations exceeding 6 mol.% (see Fig. 4), but an intersection of isotherms of partial molar volume of CaCl_2 takes place only at 10-12 mol.% (see Fig. 3). A similar situation is observed in the case of aqueous solutions of 1 - 1 electrolytes, where the sign of the temperature coefficient of partial molar volume of NaOH and KOH (ref. 14, 15) changes at 25-30 mol.%. At the same time the other properties of 1 - 1 electrolyte solutions show melt-like behaviour as low as 15-20 mol.% (see Fig. 5). Fig. 5 sums up the data on concentration values of the transition region for hydrothermal solutions of 1 - 1, 1 - 2, 2 - 1 and 2 - 2 electrolytes. It clearly shows decreasing transition concentrations with an increase of ionic charge in solutions.

Fig. 5 Concentrations of transition region obtained using different physico chemical properties of systems.

V_m - volumetric data
 IR - IR spectroscopy
 VIS - spectrophotometric data
 RS - Raman spectroscopy
 PhEq - phase equilibria
 λ - electro conductivity



We include the results obtained from the analysis of the experimental data on phase equilibria in the summary illustrated by Fig. 5. As already mentioned, a negative the t.c.s. is a notable property of dilute hydrothermal solutions. If the concentration of such saturated solutions is increased (by increasing the pressure, adding a supported electrolyte or an immiscible strong electrolyte solution) to the transition region, the sign of t.c.s. is changed to positive (ref. 13). Another peculiarity of the transition region is the origin of liquid immiscibility in hydrothermal electrolyte solutions. The critical phenomena of solution take place at the concentrations of the transition regions in all studied water-salt systems with regions of liquid-liquid immiscibility. This confirms the idea of an increase in density fluctuations in the transition region where the molecular structure of solutions is transformed.

SUB- AND SUPERCRITICAL PHASE BEHAVIOUR

So far we have considered the results of an experimental study of hydrothermal systems to discuss the sub- and supercritical equilibria in aqueous electrolyte solutions. But water-electrolyte mixtures belong to a large class of systems consisting of components with different volatility. Water-salt systems, as well as water-organic, organic and other systems with different volatility components are characterized by similar topological types of phase diagrams. Therefore the volume of information on new heterogeneous equilibria and sequence of their realization, obtained for any system of this class, can be applied to water-salt mixtures too. From that point of view a theoretical approach to predicting phase behaviour on the basis of either the equations of state or molecular models of fluid mixture with different intermolecular potentials are of special interest. In some cases such approaches lead to satisfactory results even on the quantitative level (ref. 17, 18), but not in the case of real water-salt systems. Here we confine discussion to consideration of the topological types of fluid phase diagrams.

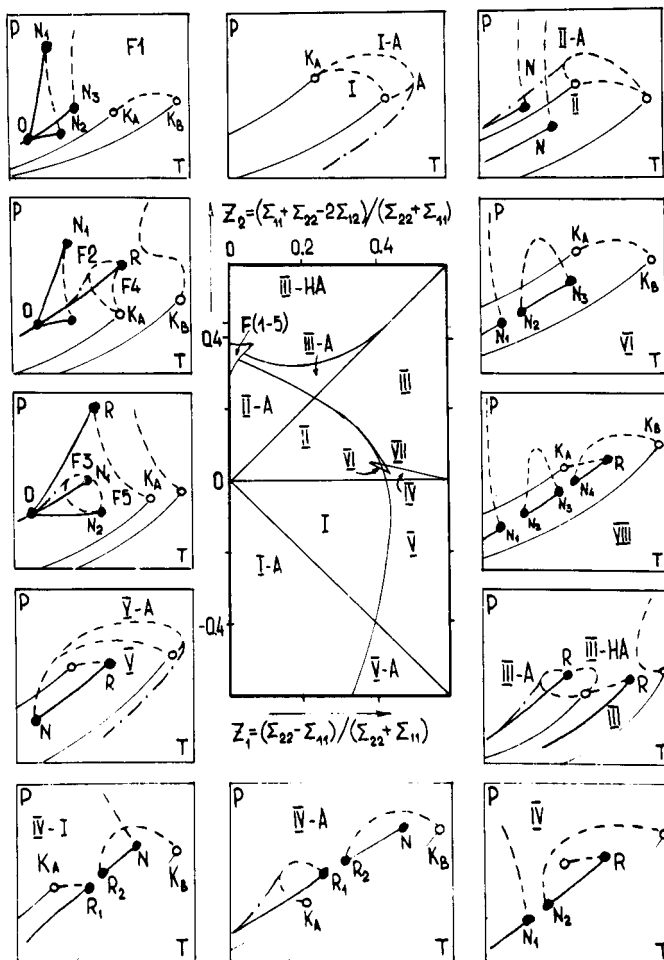


Fig. 6 Global diagram for binary mixtures of equal size Lennard-Jones molecules (in the middle) and different types of fluid phase diagrams (P-T projections) (ref. 19).

K - critical points of components A and B;
 N, O, R - nonvariant points of binary systems ($L_1 = L_2$
 - G; $L_1 - L_2 - L_3 - G$;
 $L_1 = G - L_2$)

A one-fluid model of the equation of state for binary a mixture of Lennard-Jones molecules (ref. 19) has been carefully studied and a global diagram of this artificial molecular system was produced. The global diagram, shown in the central part of Fig.6, describes the regions of energetic parameters of the model corresponding to different types of fluid phase diagrams. Some of the types (III-A, IV-A, V-A, VI, VII, F-types) have no experimental examples and among real systems there exist some phase diagrams absent in this global diagram. The general property of phase diagrams, shown in Fig. 7, is a presence of liquid-liquid immiscibility regions with the critical curves $L_1 = L_2$, possessing maximum and/or

minimum. These are the hypercritical solution points. The first three versions of the phase diagram (Fig. 7 a,b,c) have experimental examples and are usually included in general classifications, although none has been obtained by investigation of the equations of state or molecular models (ref. 17-22). Only Boshkov (ref. 19) has deduced a liquid-liquid immiscibility region with a hypercritical solution point (types VI and VII in Fig.6). The last version (Fig. 7d) has no experimental examples, but sometimes can be met in the classification (ref. 20) as a logical result of the existence of hypercritical points. It is evident that some of the discussed fluid phase diagrams are not realized in water-salt systems, especially the types with azeotropes, because the last phenomenon is unknown in aqueous electrolyte solutions. Nevertheless, information about the possible types of heterogeneous fluid equilibria is very important, especially for the hydrothermal systems where liquid immiscibility, critical phenomena and fluid equilibria are distributed.

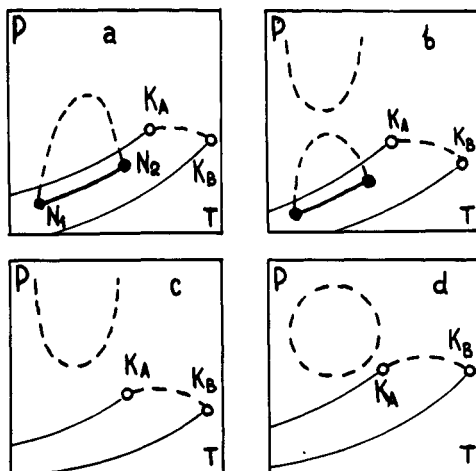


Fig. 7 Fluid phase diagrams (P-T projections) for binary systems liquid-liquid immiscibility and hypercritical solution points.

Another notable feature of hydrothermal phase behaviour is connected with high melting temperatures of inorganic compounds which may exist as a solid phase in sub- and supercritical equilibria. Such phenomena complicate the construction of fluid phase diagrams leading to complete phase diagrams. A complete phase diagram describes all the equilibria that are possible in the system with gas (G), liquid (L) and/or solid (S) phases participating throughout the entire range of parameters at which the noncrystalline phases remain heterogeneous.

TOPOLOGICAL TRANSFORMATION OF COMPLETE PHASE DIAGRAMS

BINARY SYSTEMS. Analytical methods of theoretical derivation of fluid phase diagrams show continuous transformation of one diagram to another when the model parameters are changed. Special boundary versions of phase diagrams arise in the process of transformation. The curves in the global diagram, shown in Fig. 6, divide the diagram field into regions of different phase behaviour and correspond to the boundary versions of phase diagram. Such boundary versions have properties of both types but cannot be realized since they, in violation of the Gibbs Rule, contain equilibria which are possible only in more complicated systems.

We have applied his approach, considering all the diagrams as stages of a continuous process of topological transformation, to complete phase diagrams and have obtained the systematization, including both the known types of complete phase diagrams and the new ones, filling the empty places in the chain of continuous transformation (ref. 6, 23). Systematization of the main types of complete phase diagrams, shown in Fig. 8, is complete within the framework of the following limitations:

1. Solid-phase transformations: polymorphism, formation of solid solutions and compounds from the components as well as azeotropes in liquid-gas equilibria are absent.
2. Only one region of liquid immiscibility, limited by the critical curve $L_1 = L_2$ from the high pressure side, can exist in a system.
3. All geometrical elements of phase diagrams, their reactions and shapes (but not the combination of these elements) have to be confirmed by experimental examples.

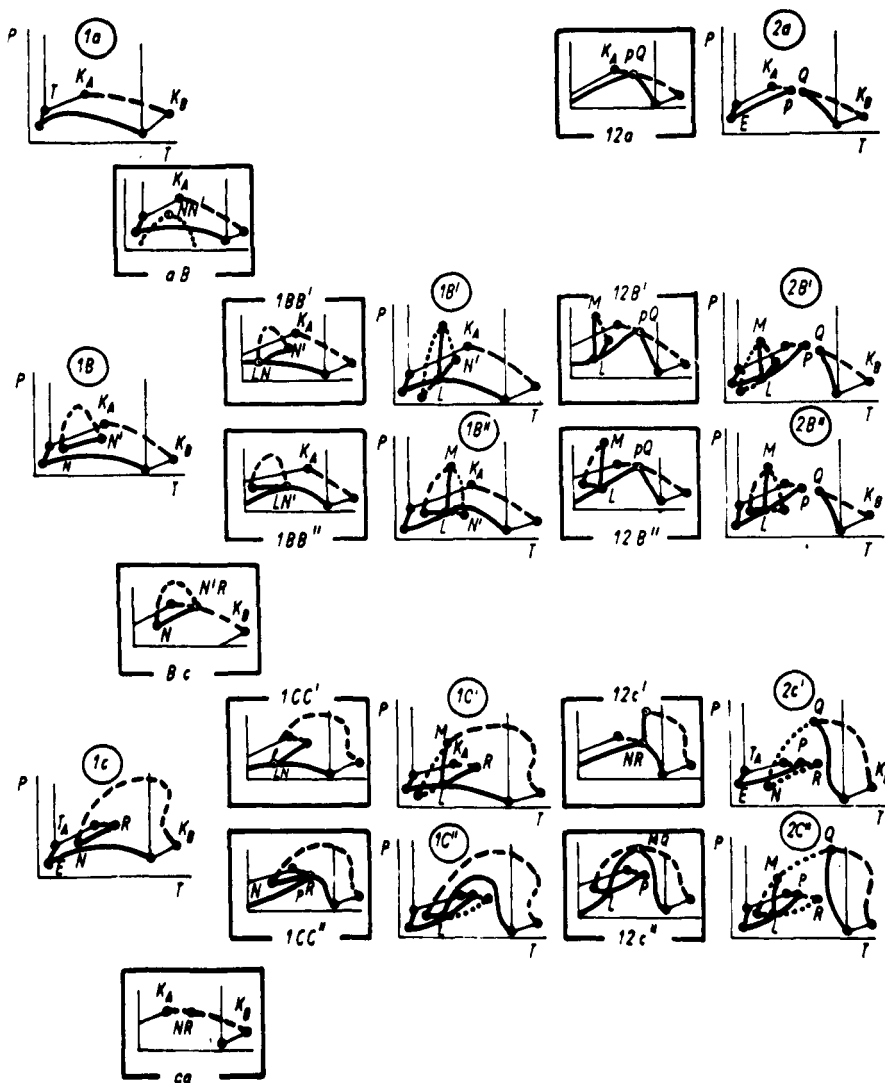


Fig. 8 Systematization of the main types of complete phase diagrams (P-T projections) of binary systems.

The diagrams in frames are the boundary versions of phase diagrams with high-order non-variant points LN, RN, pR, pQ, MQ (empty point), corresponding to equilibria $L_1 = L_2 - G - S, L_1 = L_2 = G, L_1 - L_2 = G - S, L = G - S, L_1 \square L_2 - S$.

Filled points are non-variant equilibria of one-(points T and K) and two-component (points L, N, p, Q, R) systems.

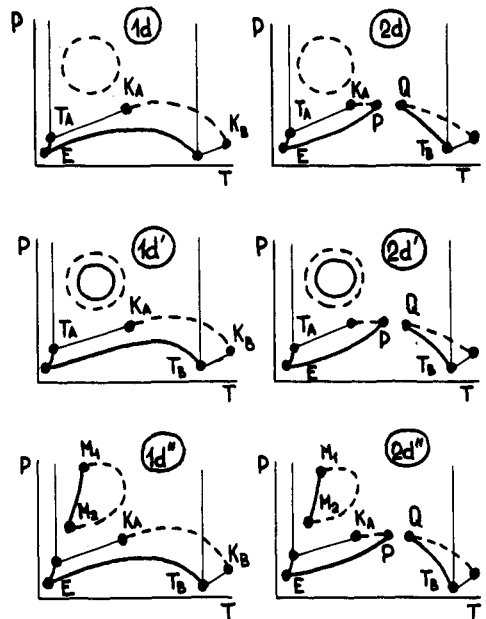
Thin lines are the monovariant curves of one-component systems. Thick lines are the monovariant curves of binary systems. Dashed lines are the monovariant critical curves of binary systems. Dotted lines are the metastable parts of monovariant curves, bounding the regions of immiscibility.

This classification (Fig. 8) has two general features resulting from the limitations listed above. The first limitation brings the topological schemes shown as close as possible to the description of phase equilibria in hydrothermal systems, which are known for an absence of azeotropes and a minimum number of solid phase transformations. The two other limitations, which decrease the general number of diagrams, lead to a closed topological transformation of phase diagrams only in one direction. Only the sequences of phase diagrams in the vertical columns demonstrate the closed process of

transformation, always bringing back to the starting type of the phase diagram (for example, 1a - ab - 1b - bc - 1c - ca - 1a). To close the topological transformation in the horizontal rows, a rejection of one of the limitations is necessary.

Using the method of continuous topological transformation and the main types of complete phase diagrams (Fig. 8) it is possible, by removing the mentioned limitations one after another, to deduce phase diagrams of any degree of complication. It is not a problem to remove the two first limitations, because the known phase equilibria were rejected. Rejection of the last limitation is much more complicated, because this limitation includes both geometrical elements of the known type that have no experimental examples (such as the closed critical curve $L_1 = L_2$ (see Fig. 7d), the nonvariant equilibria of three liquids with gas (point O in F-types in Fig. 6)) and unknown ones. For example, it is not known what kind of equilibria will result from the interaction of the lower hypercritical solution point or the lower critical solution end-point with the critical curve $L = G$ in the vicinity of the critical point of a volatile component. Fig. 9 shows some probable versions of the results of intersection of the two-phase region of liquid-liquid immiscibility, limited by the closed critical curve $L_1 = L_2$, with liquid-solid equilibria. It is interesting to

Fig. 9 Complete phase diagrams (P-T projections) for binary systems of the 1st and 2d (p-Q) types with a region of liquid-liquid immiscibility, limited by closed critical curve, and different forms of liquid-liquid-solid three-phase region.



note the correlation between the sequence of phase diagrams, obtained as a result of topological transformation, and the values of thermodynamic characteristics of components. One can find examples of such correlations (refs. 20, 23) which discuss a series of binary systems with a constant component combined with the second one, being systematically altered, but belonging to the same chemical type of substances (such as homologues or inorganic salts of alkali metals with one anion). The sequences of phase diagrams of such related systems are the same as shown in Fig. 8. The decrease of mutual liquid miscibility in the systems, corresponding to the sequence of diagrams in the vertical columns (Fig. 8), is correlated with the increase of critical temperature of the second components. Transition from the 1st to the 2d (p-Q) type^a of the phase diagram (the series of diagrams along the

 Note a: In the designation of complete phase diagrams in Fig.8 we have used the traditional classification of phase behaviour in aqueous systems into two types (ref. 10, 13, 24, 25). Systems of the 1st type are characterized by the positive t.c.s. in three-phase equilibrium L - G - S and by absence of critical phenomena $L = G$ in solutions saturated by solid. Systems of the 2d (p-Q) type are distinguished by the negative t.c.s. in the subcritical L-G-S equilibria and by the critical phenomena in saturated solutions (critical end-points p and Q).

horizontal rows in Fig. 8) is realized for such systems if the melting temperature (or the heat of melting) of the second component is increased.

TERNARY SYSTEMS The scheme of classification of binary phase diagrams, given in Fig. 8, may be used to derive (within the same limitations) complete phase diagrams of ternary systems, if the phase diagrams of the boundary binary systems are known (ref. 6, 23). The task of constructing a topological scheme for the ternary systems consists in finding new non-variant equilibria, being a result of monovariant curves intersection, originating from nonvariant points of the boundary binary systems. While passing from one boundary system to another through the three-component region of composition a phase diagram of the boundary system must undergo continuous topological transformations. If the phase diagrams of the boundary systems are present in Fig 8, all the steps of topological transformation between the diagrams are shown in the same figure, including the nonvariant points of ternary systems, described by the boundary versions of binary phase diagrams.

CONCLUSION

Wide opportunities for theoretical derivation of topological schemes for phase diagrams of two- and three-component systems arise if we provide minimal information about the phase equilibria of the system. In other words, this approach enables one to direct experimentation efficiently by choosing the variable corresponding to the system in question. Information gained in this way should be especially important for a hydrothermal study, because it shows all the phase equilibria possible in aqueous systems at elevated parameters of state and points out ways to optimize experimental work. Regularities of sub- and supercritical equilibria that have been discussed above make possible an estimation of the range of temperature and concentrations at which liquid immiscibility or a change of the t.c.s. sign in hydrothermal electrolyte solutions will occur. Similar predictions of pressure coefficients for salt solubility in aqueous systems have been evaluated in (ref. 26).

Further progress in sub- and supercritical equilibria investigations is connected with an increase of experimental data on the physico-chemical properties of fluid systems and theoretical studies of homogeneous and heterogeneous equilibria in aqueous and nonaqueous systems. Deduction of various versions of fluid phase diagrams, including the studies of molecular models and thermodynamic conditions of different phase equilibria existence, in particular, the immiscibility region, limited by the closed critical curve, is still an important problem.

Quantitative correlations of composition and properties behaviour of electrolyte solutions in hydrothermal equilibria with molecular characteristics of components and mixtures are essential to the theoretical prediction of complete phase diagrams. At the present time such correlations are empirical and qualitative. Additional experimental results are also needed for some systems. For example, it has been shown that concentrations of transition regions play an important role in the behaviour of liquid-liquid and liquid-solid equilibria, but such concentrations have no influence on the liquid-gas equilibria. In most water-salt systems the concentration ranges of the change of the t.c.s. sign and of the critical phenomena of the solution coincide, but this is not the case for $\text{BaCl}_2 - \text{H}_2\text{O}$ system (ref. 27).

Aqueous electrolyte solutions have been studied in a rather limited interval of concentration values (up to 10-30 mol.%) even at hydrothermal conditions. Drastic property changes take place in the transition region of concentrations where the dominating types of intermolecular interactions are transformed. But behavior in a very wide concentration range from the transition region through hydrated melts to the unhydrous melts is presently poorly understood. Undoubtedly a careful study of this region would bring not only new information about the molecular construction of strong electrolyte solutions and transformations of the molecular structure, but give us a better understanding of the already known phenomena in concentrated solutions.

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