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Structural Microheterogeneites in Strontium Perchlorate Solutions of Posteutectic Concentrations

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Abstract—Aqueous solutions of strontium perchlorate were studied in a wide range of concentrations at room temperature by X-ray diffraction, thermogravimetry, and calorimetry. The features of the solubility polytherm of strontium perchlorate, that distinguish it from those of other Group II metal perchlorates, were explained in terms of two coexisting interconverting crystal hydrates.

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Cryoscopic studies on aqueous solutions of Group II metal perchlorates [1, 2] showed that their solubility polytherms consist of two branches, each corresponding to the crystallization of a certain dominating structure: water (from dilute solution up to an eutectic, $0 < m < m_e$, where m is solution molality, mol kg^{-1} water) and crystal hydrate of a certain composition (after the eutectic concentration, $m > m_e$). The position of the eutectic concentration on the solubility polytherm depends on the salt nature [3]. Systematization and generalization of experimental data showed that m_e is also dependent on the number of water molecules entering into the composition of the crystal hydrate precipitated in the bottom phase after the eutectic (n) [4]. Trying to characterize the eutectic state of a system, we found that the activity of water in an eutectic solution at 25°C is close to the mole fraction of free water (water which does not enter into the composition of the crystal hydrate) $\nu_w \sim a_w(298$ [4]. It was found that the mole fraction of free water, related to the eutectic composition N_w (mole fractions) for all solutions of Group II cation perchlorates falls in the range 0.9 ± 0.02 [1, 2, 4]. For solutions of other salts the N_w range is extended due to additional effects, such as strong interaction with water or complex formation. Thus, in the perchlorate solutions under study the N_w value of 0.9 defines the eutectic state.

The system strontium perchlorate–water represents a special case. Three crystallization branches were found on its solubility polytherm [1]. The eutectic concentration is 3.99 m, and the peritectic concentration is 5.75 m. The difference in the freezing points of the eutectic and peritectic solutions ΔT was found to be 3°C±1°C, i.e., as the concentration increases from 3.99 to 5.75 m, the freezing point varies only slightly. This fact was correlated with measured relative dynamic viscosities: The inversion of the η(m) curves at 25 and 50°C represented not a point but a certain range from 4 up to 5.7 m, i.e. the curves coincided with each other between the eutectic and peritectic [1]. After the peritectic point (5.75–6.25 m), vitrification area was observed (5.75–6.25 m) and then, after the concentration of 6.25 m, strontium perchlorate tetrahydrate precipitated in the bottom phase [5]. There is an opinion in the literature [3] that strontium perchlorate solutions saturated with respect to the tetrahydrate contain only little water other than coordinated, and even this water is hardly free: It more likely acts as a bridge between the $Sr(H_2O)_n^{2+}$ and ClO_4^- ions to form an integral viscous system responsible for the tendency of the solutions for high supersaturation. Evidence for the special state of $Sr(ClO_4)_2$ solutions was provided by James and Culter [6] in the research on their Raman and ^{17}O and ^{35}Cl NQR. The resulting data allowed three concentration ranges with predominance of different structures to be recognized: Free perchlorate ions are present in the solution up to a 2 M concentration, perchlorate ions associated with aquated strontium ions appear starting from 2 M, and contact cation–anion ion pairs, starting from 4.5 M. In view of the different opinions of Latysheva [3] and

James and Culter [6] as to the forms of existence of strontium perchlorate in solution, we considered it interesting to study strontium perchlorate solutions in more detail by other methods in a wide range of concentrations.

Considering the structure of the solutions we relied on the model based on the shape of the the solubility polytherm of a salt [7–12]. According to this model, special points on the solubility polytherm divide the entire concentration range into zones where different structures, cybotactic groups (CG[1]), are dominating [13]. The dominating structure of a solution is analogous to the structure of a solid phase that crystallizes from the solution as the temperature is lowered. When a salt forms several crystal hydrates, structural microheterogeneity is realized in a posteutectic solution, and one sibotactic groups are gradually replaced by others, according to the change of the crystallization branches. It is necessary to note that the existence of CG in solutions of posteutectic concentrations has been confirmed experimentally [4, 14].

To study special features of strontium perchlorate solutions we applied the structure-sensitive X-ray diffraction method. Earlier we modified this method to applied it to studying the structure of solutions of Group I, II, and III metal salts [14–16] with the aim to obtain evidence for the existence of cybotactic groups in concentrated solutions. Thus we could estimate the size of CG dominating in solutions and to trace the influence of electrolytes on water structure. Figure 1 shows the X-ray diffraction pattern of pure water, namely the dependence of scattering angle θ (4°– 24°) on scattering intensity *I* (arb. units). Narrow lines in the region of large θ angles relate to the cell window material (aluminum). A broad strong peak (halo) at 3.14 Å and a weaker peak at 2.32 Å are seen in Fig. 1. Their positions coincide with those of the maxima in the X-ray diffraction pattern of ice of tetragonal symmetry, i.e. the X-ray diffraction pattern of water consists of broad lines of ice, implying lack of a long-range and presence of a short-range order in the structure of liquid water.

The X-ray diffraction patterns of the system strontium perchlorate–water are presented in Fig. 2. As the electrolyte concentration is increases, the intensity of the water halo decreases, that points to gradual

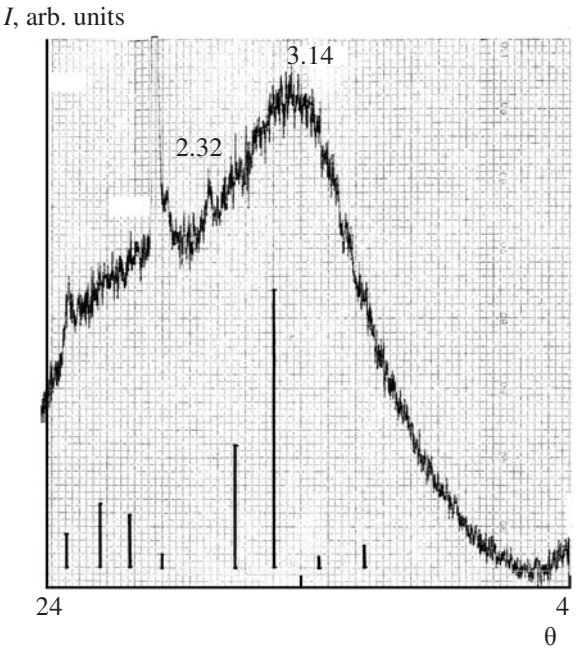

Fig. 1. X-ray diffraction pattern of pure water and prime diagram of tetragonal ice.

destruction of the intrinsic water structure. The halo decreases up to the eutectic concentration, and after that a new halo appears with a maximum not coinciding in its position with the water halo, i.e. a new dominating structure appears. Starting from the concentration of 4.0 m (eutectic for this system) one halo appears (at 19.3 θ), and, as the concentration increases further, an additional halo with a maximum at 28.3 θ appears. It is seen from the figure that the intensity of the additional halo increases with concentration (5.5–6 m), then it becomes as intense as the first halo (6.5 m), and, finally, starts to predominate (7.2 m). The appearance of the second halo points to the presence of two crystal hydrates of strontium perchlorate, i.e. to gradual replacement of one dominating cybotactic group by the other.

The cryoscopic and X-ray diffraction data led us to suggest that the system contains two crystal hydrate forms of strontium perchlorate: hexahydrate and tetrahydrate. Thus, in the concentration range of 4–5.75 m, the water-enriched form, strontium perchlorate hexahydrate, stable only at low temperatures, precipitates in the bottom phase. As to the solution structure in the vitrification region (above 5.75 m), our opinion does not coincide with the opinion of the authors of [3, 6]. We explain vitrification by interconversion of the two crystal

[1] CG is a certain space mode of mutual ordering of particles, a structural type of associates formed in concentrated solutions.

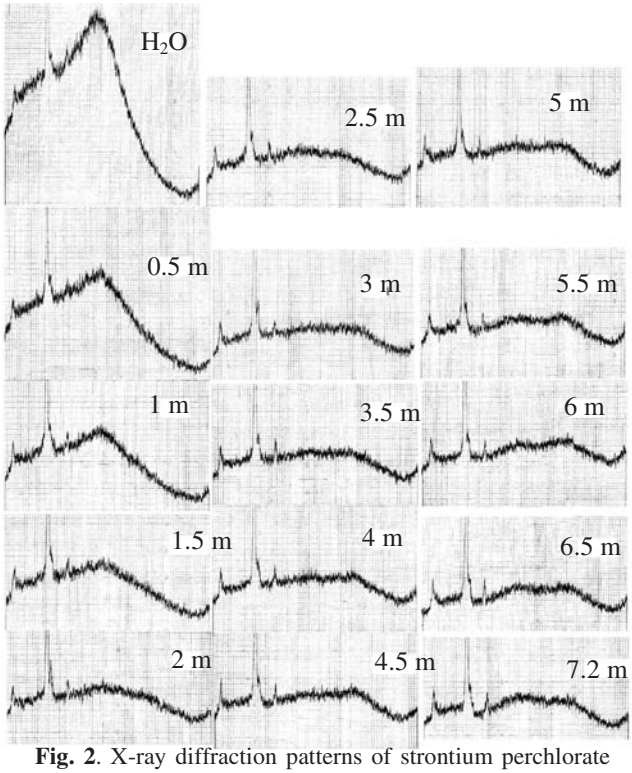

Fig. 2. X-ray diffraction patterns of strontium perchlorate solutions.

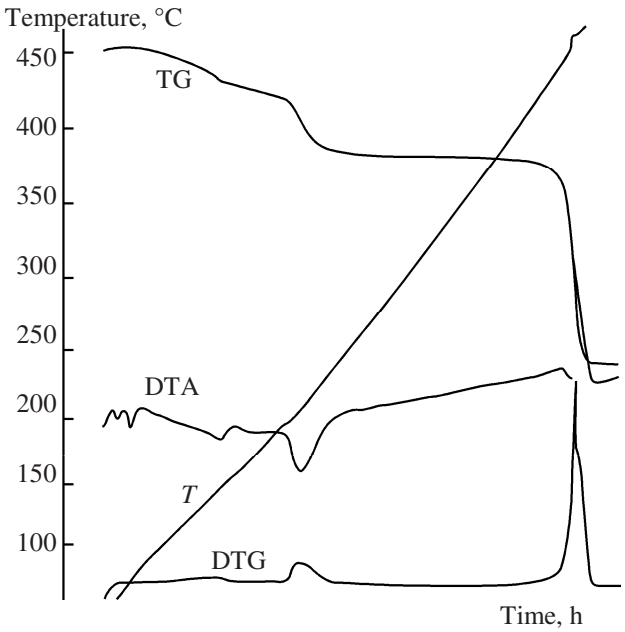

Fig. 3. Thermoanalytical curves of a 5 m solution of strontium perchlorate in water.

hydrate forms. The solution is still insufficiently concentrated to form strontium perchlorate tetrahydrate as the dominating structure (like with barium perchlorate), but there is already insufficient free water to form a stable predominating structure based on strontium perchlorate hexahydrate (as with calcium perchlorate). These two structures (hexa- and tetrahydrate) inconvert in the solution with the participation of two water molecules: $Sr(ClO_4)_2 \cdot 6H_2O \leftrightarrow Sr(ClO_4)_2 \cdot 4H_2O + 2H_2O$. Thus, there is dynamic equilibrium between the two strontium perchlorate crystal hydrates in the vitrification region, and, consequently, two water molecules in strontium perchlorate hexahydrate should have a different energy than the other four. This is proved by thermogravimetric analysis (TGA).

We carried out a thermogravimatric analysis of a posteutectic strontium perchlorate solution (5 m). The water-enriched crystal hydrate form is present in the solution of this composition. The corresponding TGA curve is presented in Fig. 3. As seen, water is lost nonuniformly: free (uncoordinated) water leaves first at temperatures of up to 100°C. Then the water of crystallization is lost; the weight loss corresponds to six molecules. Therewith, the water of crystallization can be divided into two nonequivalent parts: the first two water molecules are lost more readily (T 145°C, weak exo effect), and the remaining four leave (T 210°C, well-defined exo effect). These results provide further evidence showing that strontium perchlorate has two crystal hydrate forms.

To understand what happens in the eutectic and peritectic from the energy viewpoint, we have measured the heat of dilution of aqueous strontium perchlorate. The results of this experiment are presented in Fig. 4 as the plot of *dH*/*dm* against concentration. As seen, the concentration dependence of *dH*/*dm* is divided into two regions with slopes with opposite signs, i.e. with two qualitatively different structures changing each other in the region of the eutectic concentration. In the posteutectic region, two portions with different slopes are observed. The slope changes at the concentration of 5.75 m which corresponds to the peritectic in the solubility polytherm. Thus, we have a minimum *dH/dm* in the eutectic region, and starting from 5.75 m the growth of *dH/dm* slows down. Such a correspondence of the character of the concentration dependence of dH/dm and the shape of the $Sr(ClO_4)_2$ solubility polytherm gives one more evidence for the existence of two qualitatively

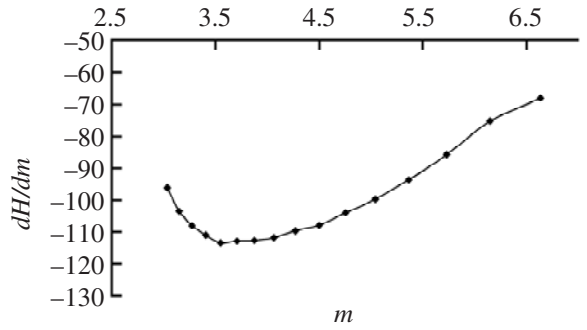

Fig. 4. Dependence *dH/dm* on concentration (*m*, mol kg^{-1} water).

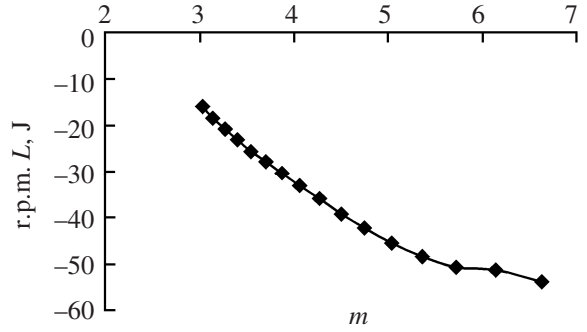

Fig. 5. Dependence of r.p.m. $L(H_2O)$ on concentration (*m*, mol kg^{-1} water).

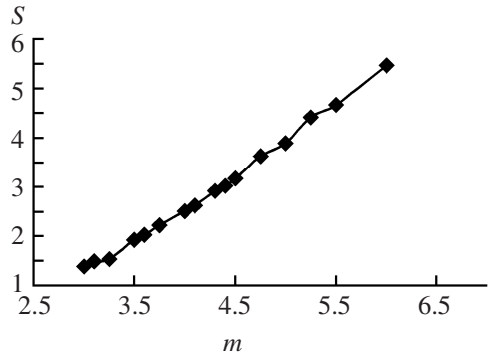

Fig. 6. Dependence of excess r.p.m. $S(H_2O)$ on concentration (*m*, mol kg^{-1} water).

different structures in strontium perchlorate solutions in the posteutectic concentration region.

Calorimetric data were used to calculat the relative partial molal (r.p.m.) enthalpies of water [$L(H_2O)$] and r.p.m. entropies of water [$S(H_2O)$]. The r.p.m. $L(H_2O)$ were calculated using own data by the formulas described in [17]. The r.p.m. $S(H_2O)$ were calculated with the chemical potentials which, in turn, were calculated using the water activities reported in [18].

Figure 5 shows the concentration dependence of r.p.m. $L(H_2O)$ and Fig. 6, the concentration dependence of excess r.p.m. $S(H_2O)$. As the concentration increases, the absolute value of r.p.m. $L(H_2O)$ monotonically increases. However, after the concentration of 5.2 m, a tendency of $L(H_2O)$ for lower absolute values is observed. It is interesting that this takes place in the concentration region where the solution vitrifies with lowering temperature.

Thus, the interconversion of the crystal hydrates is accompanied by a weak endo effect. On the other hand (Fig. 6), the excess partial molal entropy of water [$S^E(H_2O)$] in the entire concentration range increases monotonically. In the case of $Sr(ClO_4)_2$ solutions, such an increase in $S^E(H_2O)$ is caused by increasing diversity states of water molecules due to interconversions of crystal hydrate structures. A characteristic feature of the strontium perchlorate solution is that it contains a microheteroheneity concentration region, where two independent cybotactic groups corresponding to different crystal hydrates not only simply coexist, but also are in dynamic equilibrium and undergo continuous interconversions involving two water molecules, leading to formation of a supersaturation region.

We believe that the reason for the special behavior of the $Sr(ClO_4)_2$–H_2O system lies in the electronic structure of the strontium atom [19]. Strontium and rubidium are postkainosymmetrics, since the kainosymmetric 3*d* screen appears in their electronic structure for the first time. The presence of such a screen in Group IV elements (from gallium to bismuth) leads to a reduced stability of compounds of these elements in the highest oxidation state. Rubidium and strontium have a single oxidation state each, +1 and +2, respectively. Even though solutions of strontium salts do not substantially differ in properties from solutions of the corresponding calcium and barium salts, we cannot neglect the presence of an inner 3*d* screen which seems to be responsible for the special features described in this work.

EXPERIMENTAL

Preparation of solutions. Solutions of strontium perchlorate were prepared from strontium carbonate taken in excess and 57% perchloric acids (chemical grade). The solutions were twice recrystallized. Concentrated solutions were analyzed for the metal cation and ClO_4^- anion. The determination of ClO_4^- was

carried out by passing solutions through a KU-2 ion-exchange column followed by pH-metric titration of perchloric acid with a borax solution. The determination of Sr^{2+} was carried out by gravimetry (precipitation in the form of sulfate). The error in the concentrations did not exceed 0.5%. Solutions with lower salt concentrations were prepared by dilution of the initial concentrated solutions by weight.

X-ray scattering. The X-ray diffraction patterns were obtained on a DRON 2.0 diffractometer with Bragg–Brentano focusing and a vertical sample position, CuK_α radiation (λ 1.54 Å), Ni filter, and the following tube operation mode: U 18 kV and I 18 mA. The patterns were obtained in the θ range 4°–24° at room temperature, scanning rate 1 deg min^{-1}. The sample was placed in a 1-ml duralumin cell supplied with an aluminum foil window for radiation input and output. The sensitivity was 10 nm, and the error of the intensity measurements was 3%.

Thermogravimetric analysis. The experiment was carried out on a MOM derivatograph. Dry strontium perchlorate tetrahydrate (0.10875 g; heating rate 10 deg min^{-1}) and its aqueous solution (0.11320 g, concentration 5 m, heating rate 5 deg min^{-1}) were analyzed.

Calorimetry. Calorimetric measurements were carried out on a modified Calvet microcalorimeter [20]. The calorimeter was calibrated under conditions of partial heat release. Aqueous KCl was used as reference. The calorimeter constant K_c was 5.92 W V^{-1}. The calibration of the pump necessary to determine the feed rate of water υ (ml h^{-1}) was carried out by gravimetry, υ 2.39 ml h^{-1}.

REFERENCES

1. Pestova, O.N., Myund, L.A., Khripun, M.K., and Prigaro, A.V., *Zh. Prikl. Khim.*, 2005, vol. 78, no. 3, p. 413.
2. Pestova, O.N., Myund, L.A., and Khripun, M.K., *Vestn. S.-Peterb. Gos. Univ.*, 2005, no. 4, p. 5.
3. Latysheva, V.A., *Vodno-solevye rastvory, sistemnyi pod khod* (Water–Salt Solutions. A Systemic Approach), St. Petersburg: S.-Peterb. Gos. Univ., 1998, p. 224.
4. Pestova, O.N., *Cand. Sci. (Chem.) Dissertation*, St. Petersburg, 2006.
5. Kirgintsev, A.N., Trushnikova, L.N., and Lavrent'eva, V.G., *Rastvorimost' neorganicheskikh veshchestv v vode. Spravochnik* (Solubility of Inorganic Substances in Water. Handbook), Leningrad: Khimiya, 1972.
6. James, D. and Culter, P., *J. Chem.*, 1986, vol. 39, p. 137.
7. Khripun, M.K., Myund, L.A., Baranova, G.I., Smirnova, O.A., and Maslennikov, T.N., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 4, p. 550.
8. Khripun, M.K., Chervonenko, K.J., Kiselev, A.A., and Khripun, A.V., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 1, p. 25.
9. Khripun, M.K., Chervonenko, K.J., Kiselev, A.A., and Petranovskii, V.P., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 6, p. 932.
10. Kiselev, A.A., Zubtsov, M.K., and Khripun, M.K., *Vestn. St. Peterb. Gos. Univ., Ser. 4*, 2002, no. 3, p. 51.
11. Khripun, M.K., Lilich, L.S., and Efimov, A.Yu., in *Problemy sovremennoi khimii koordinatsionnykh soedinenii* (Problems of Modern Chemistry of Coordination Compounds), Leningrad: Leningr. State Univ., 1983, no. 7, p. 58.
12. Khripun, M.K., in *Rastvory–elektrolitnye sistemy* (Solutions–Electrolyte Systems), Ivanovo: Inst. Nonaqueous Electrolyte Solutions, Akad. Nauk SSSR, 1988, p. 16.
13. Khripun, M.K., *Doctoral (Chem.) Dissertation,* Leningrad, 990.
14. Khripun, M.K., Kostikov, Yu.P., Kiselev, A.A., and Pestova, O.N., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 2, p. 190.
15. Pestova, O.N., Kostikov, Yu.P., and Khripun, M.K., *Zh. Prikl. Khim.*, 2004, vol. 77, no. 7, p. 1082.
16. Kiselev, A.A., *Cand. Sci. (Chem.) Dissertation*, St. Petersburg, 2003.
17. Mishchenko, K.P. and Poltoratskii, G.M., *Voprosy termodinamiki vodnykh i nevodnykh rastvorov elektrolitov* (Problems of the Thermodynamics of Aqueous and Nonaqueous Electrolyte Solutions), Leningrad: Khimiya, 1968, p. 184.
18. Robinson, R.A. and Stokes, R.H., *Electrolyte Solutions. The Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in Solutions of Simple Electrolytes*, London: Butterworths, 1959, 2nd ed.
19. Shchukarev, S.A., *Neorganicheskaya khimiya* (Inorganic Chemistry), Moscow: Vysshaya Shkola, 1974, vol. 2, p. 382.
20. Golubev, B.A., Kondrat'ev, Yu.V., and Sheitel'man, B.I., USSR Inventor's Certificate no. 1283553, 1985, *Byull. Izobret.*, 1986, no. 3937336.