ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 10, pp. 1899–1903. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © O.N. Pestova, A.G. David'yan, L.A. Myund, M.K. Khripun, A.Yu. Efimov, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 10, pp. 1618–1623.

Solubility Polytherms and Eutectic Concentrations of Scandium, Yttrium, and Lanthanum Perchlorate Solutions

O. N. Pestova, A. G. David'yan, L. A. Myund, M. K. Khripun, and A. Yu. Efimov

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: pestova_olga2004@mail.ru

Received June 23, 2014

Abstract—Freezing points of solutions $M(ClO_4)_3$–H_2O (M = Sc, Y, La) of different concentrations were determined. The solubility polytherms of the perchlorate systems studied, as well as aluminum, gallium, and indium perchlorates were compared with the concentration dependences of different properties of the corresponding solutions. Viscometry and IR spectroscopy allowed the special points on these dependences to be correlated with eutectic concentrations. Structural changes in the systems studied as a function of solute concentration were described.

Keywords: solubility polytherm, cybotactic group, eutectic concentration, inversion concentration, IR spectroscopy

DOI: 10.1134/S1070363214100053

The structural evolution of a water–salt system as the salt concentration increases up to saturation point is described in terms of the phenomenological structural model of aqueous electrolyte solutions [1–5]. According to the model [1], the key to understanding structural rearrangements in a solution is provided by the freezing point–solution composition phase diagram (solubility polytherm). Special points on it (eutectic, peritectic) divide the solution concentration field into fields where different structures are predominant. In the pre-eutectic solution, the predominant component is liquid water. As the temperature decreases, ice crystallization from such solution is observed. Once the eutectic point has been reached, further cooling leads to precipitation of the dissolved salt either as crystal hydrate or as the anhydrous form. The composition of the bottom phase changes in response to a change in the predominant solution structure. The structural unit of a solution, a cybotactic group, is a precursor of the solid phase that crystallizes when a solution of definite concentration is cooled or becomes saturated [6, 7]. Depending on the nature of the salt, either a single predominant structure of definite concentration (crystal hydrate, like in the lithium perchlorate–water system, or anhydrous salt, like in the potassium chloride–water system) or different structural dominants sequentially changing from one to another and present in dynamic equilibrium (lithium chloride–water) are possible in the posteutectic concentration range. In the latter case, several crystallization branches corresponding to crystal hydrates with different water fractions are observed in the solubility polytherm. The transition points between the crystallization branches are eutectics and periteutics. If one of the crystallization branches has a well-defined maximum (distectic), one can determine the composition of the congruently melting crystal hydrate. The generalized phenomenological structural model of electrolyte solutions can only be used if the phase diagram is known.

Recently [8] we obtained cryoscopy data for group III metal perchlorate solutions. Analogous data for group XIII metal perchlorates have never been published.

In the present work we obtained phase diagrams (soublity polytherms) for solutions of yttrium, scandium, and lanthanum perchlorates. The choice of perchlorate systems was motivated by weak complexing, proton-donor, and proton-acceptor abilities of the perchlorate anion, which makes it possible to trace the effect of the cation on the equtectic concentration and, as a consequence, on the concentration ranges of solutions with different predominant structures. By analogy with what was observed previously with solutions of aluminum, gallium, and indium perchlorates, in the present study we expected complications in the cryoscopic experiment, associated with strong hydration of cations, possible existence of multilayer hydration shells, and proton transfer from one shell to another. Glass formation after cooling and saturation, as well as a high sensitivity of the crystallizing compounds to moisture, were also expected. Therefore, cryoscopic measurements were performed in the range of the eutectic concentrations estimated from IR spectral data.

In solutions of salts crystallizing as crystal hydrates, there is a characteristic concentration at which the isotherms of relative values of certain properties[1] undergo inversion of mutual positions. This concentration is referred to as the inversion concentration [9]. Its values for the relative dynamic viscosity, relative proton magnetic relaxation, and relative chemical potential of water are fairly often quite close to the eutectic concentration. When water does not enter a new predominant structure, like with anhydrous salts, no isotherm inversion is observed.

Comparing data on proton relaxation rates and viscosities one can see that the isotherm inversion points correspond to different concentrations of the same salt. For example, the inversion concentration for the calcium chloride solution estimated from data on proton relaxation rates is 3.4 mol/kg water, whereas that estimated from the data on relative viscosities is 4 mol/kg water; the respective concentrations for lithium chloride are 6.7 and 7.2 mol/kg water. This difference can be understood taking into account that the transition from structure to a qualitatively new one takes place in a certain concentration range. Eutectic is an invariant point, where joint crystallization from a solution of a binary system of two solid phases with a negative, the lowest possible melting point, takes place. According to the ideas first advanced by Samoilov [10], the transition from one structure predominant in a solution to another occurs in a concentration range that gets wider the farther it is from the eutectic point. Therewith, the competition between possible structures results in excessive disorder. Different methods have their own specific features and, therefore, can detect the change in the predominant structure at different concentrations of the solution, which is indeed observed experimentally.

Since solubility polytherms are available not for all systems, we suggest that the eutectic concentration range can be estimated from the data obtained by the above-mentioned structure-sensitive methods. The validity of this approach to solving the inverse problem is confirmed by the experimental results obtained in the present work, as well as comparisons for perchlorate systems.

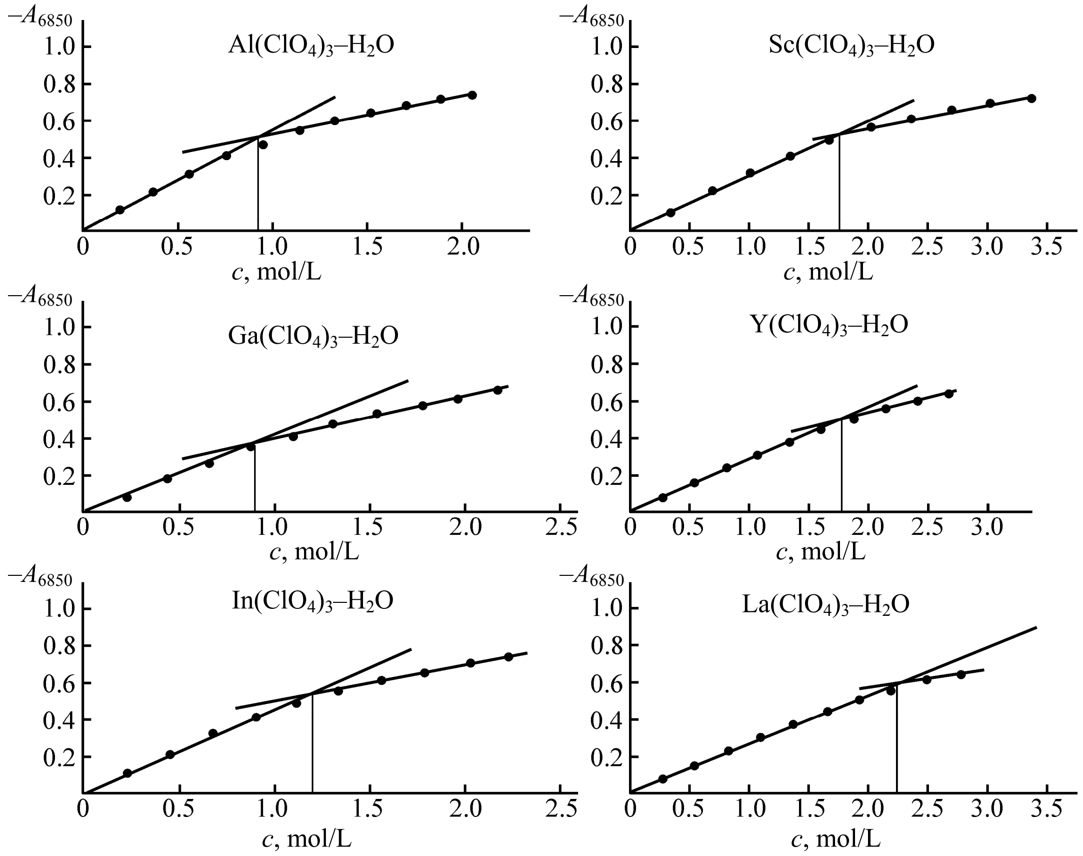
The vibration spectra of aqueous solutions of perchlorates in the first overtone region of water are sensitive to structural transitions in such systems [11, 12]. We expected that the concentration dependences of a number of vibration spectral parameters would allow the identification of the transition region corresponding to the eutectic concentration. The absorption maximum of liquid water is at 6850 cm^{-1}. When a salt is dissolved in water, the structure of the solvent is destroyed, and the absorption intensity at this frequency (A_{6850}) decreases. Water coordinates with salt ions depending on their ability to be hydrated. Therefore, changes in intensity at the absorption maximum of pure water can serve as a measure of the state of water molecules in different structures (cybotactic groups). The information on the concentration behavior of a system (specifically, structural transitions) can be obtained from the dependence of the optical density at the above frequency on the composition of the solution [11, 12]. The results obtained for group III metal perchlorate solutions are presented in the figure. The dependences of optical density on salt concentration (M) show a bend at a concentration almost coinciding with the eutectic concentration (Table 1), which, in our opinion, reflects a change of the predominant solution structure.

Such spectroscopic criterion for estimating the eutectic concentration is not rigorous and accurate enough, because it is not based on proper deconvolution of the complex spectrum into individual bands. However, this method is simple and provides a satisfactory estimate for the eutectic concentration. The dynamic viscosities of group III metal perchlorate solutions could be found in the literature [13–15]. The inversion concentrations of aluminum, gallium, and indium perchlorates are also shown in Table 1. Obviously, these values, too, well correlate with the eutectic concentrations.

The found correlations led us to suggest that, having analogous data for scandium, yttrium, and lanthanum perchlorate solutions, we would be able to estimate the eutectic concentrations for these systems, too. From the inversion concentrations and the positions of bends

---

[1] By relative are meant the values for a solution, reduced to the value for a pure solvent (water, in our case).



Dependence of the optical density of perchlorate solutions at 6850 cm^{-1} (A_{6850}) on their molal concentration.

on the dependences of optical density (A_{6850}) on solution composition the eutectic concentrations of the scandium, yttrium, and lanthanum perchlorate solutions were estimated at 1.5–1.9, 1.8–2.3, and 2.2–3.1 mol/kg, respectively. We determined the freezing points of the solutions in these ranges and, indeed, observed the expected eutectics (Table 1).

Table 2 presents the cryoscopy results for the systems in study. The polytherms all have two branches: pre-eutectic (solution–ice equilibrium) and post-eutectic (solution–crystal hydrate equilibrium). The eutectic concentrations for the scandium, yttrium, and lanthanum solutions are 1.83, 2.26, and 3.02 mol/kg water, respectively. The solubility polytherm for the yttrium perchlorate–water solution has a maximum (distectic) at the concentration 2.8 mol/kg water similar to those in the polytherms for aluminum, gallium, and indium perchlorates [8]. The composition of the crystal hydrate corresponds to the formula $Y(ClO_4)_3 \cdot 20H_2O \pm H_2O$. It can be noted that the eutectic molal concentrations of the main group metal perchlorate solutions are lower compared to those of the complementary subgroup metal perchlorate solutions: from 0.92 to 1.27 and from 1.83 to 3.02 mol/kg, respectively. The dependence of the inversion concentration (m_{inv}) on the radius of the cation (increase of

Table 1. Experimental molal (mol/kg water) and molar concentrations at the eutectic points by different methods[a]

Salt	m_{inv}(visc)	m_{eut}(cryosc)	M_{eut}(cryosc)	M_{eut}(opt)
$Al(ClO_4)_3$	1.08	1.09	0.97	0.92
$Ga(ClO_4)_3$	1.2	0.92	0.87	0.89
$In(ClO_4)_3$	1.38	1.30	1.12	1.19
$Sc(ClO_4)_3$	1.57	1.83	1.56	1.75
$Y(ClO_4)_3$	1.86	2.26	1.81	1.78
$La(ClO_4)_3$	3.09	3.02	2.17	2.24

[a] {m_{inv}(visc)} Inversion molal concentration by viscometry data (mol/kg water); {m_{eut}(cryosc), M_{eut}(cryosc)} eutectic molal and molar concentration by cryoscopy data, respectively; {M_{eut}(opt)} molar concentration at the intersection point of the straight lines on the $A_{6850} = f(M)$ dependences for the corresponding metal perchlorates (eutectic concentration by optical data).

Table 2. Solubility polytherms for the systems studied

$Sc(ClO_4)_3$		$Y(ClO_4)_3$		$La(ClO_4)_3$	
m, mol/kg water	fp, °C	*m*, mol/kg water	fp, °C	*m*, mol/kg water	fp, °C
1.24	–19	1.65	–8.6	2.04	–10.8
1.63	–24.2	2.06	–10.3	2.5	–13
1.78	–28.1	2.14	–12.8	2.8	–14.6
1.82	–48.8	2.21	–15.7	2.97	–22
2.035	–41.2	2.29	–28	3.17	–28
2.27	–31	2.37	–23	3.27	–20
2.41	–26.1	2.46	–20.1	3.35	–14.9
		2.56	–18.7		
		2.67	–17.2		
		2.78	–15		
		2.88	–16.1		
		2.98	–17.5		

Table 3. Eutectic concentrations of group II and III metal perchlorate solutions and the hydration enthalpies and ionization potentials of the cations

Salt	ΔH_{hydr}, kJ/mol	M_{eut}, mol/kg water	*I*, eV
$Mg(ClO_4)_2$	1921	3.45	15.03
$Ca(ClO_4)_2$	1577	4.15	11.87
$Sr(ClO_4)_2$	1443	3.99	11.026
$Ba(ClO_4)_2$	1305	4.02	10
$Zn(ClO_4)_2$	2046	3.00	17.96
$Cd(ClO_4)_2$	1807	3.43	16.904
$Hg(ClO_4)_2$	1824	3.90	18.751
$Al(ClO_4)_3$	4665	1.09	28.44
$Ga(ClO_4)_3$	4700	0.92	30.7
$In(ClO_4)_3$	4112	1.30	28
$Sc(ClO_4)_3$	3897	1.83	24.75
$Y(ClO_4)_3$	3583	2.26	20.5
$La(ClO_4)_3$	3296	3.02	19.17
$Tl(ClO_4)_3$	4105	1.20[a]	29.8
Correlation coefficient	–0.968		–0.957

[a] Predicted from the correlation plot.

m_{inv} in going from Al^{3+} to In^{3+}), noted in [13–15], is also characteristic of the systems in study. In going from Sc^{3+} to La^{3+} the eutectic molal concentration shifts to higher values.

Table 3 lists the eutectic concentrations for group II [16] and III [7] metal perchlorate solutions and certain characteristics of the corresponding cations (hydration enthalpies [17] and ionization potentials [18]), obtained previously and in the present work. In the last line we present the calculated correlation coefficients. As seen from Table 3, there are strong correlations between m_{eut} and ΔH_{hydr} and m_{eut} and *I*. Taking this into account, we can predict the eutectic concentration for the system thallium perchlorate–water for which no published data are available. The eutectic concentration for this system, estimated from the published $\Delta H_{\text{hydr}}(Tl^{+3})$ and I_3 values for thallium, varies from 1.1 to 1.3 mol/kg water.

Comparing the experimental and published data, we can conclude that the eutectic concentrations estimated from the solubility polytherms, viscometry data, and concentration dependences of optical density (at 6850 cm^{-1}) correlate with each other, depend on the nature of the cation, and, according to the phenomenological model, point to a change of the predominant structural zones in the solution. The eutectic concentrations for the perchlorate solutions studied in the present work depend on the nature of the cation. The stronger interaction of the cation with the first hydration shell, the lower the eutectic concentration, and the narrower the range where the solvent is water, and the earlier a chemical compound, specifically a crystal polyhydrate, is formed.

EXPERIMENTAL

Scandium, yttrium, and lanthanum perchlorates were prepared by treatment of the corresponding oxide (analytical grade) with 57% perchloric acid (chemical grade) followed by double recrystallization from distilled water. Concentrated solutions were analyzed for metal cations (back titration with a zinc salt) [19] and perchlorate anion (ion exchange on a KU-2 resin) [20]. Solutions with lower salt concentrations were prepared by diluting the stock solutions (by gravimetry or volumetry). The densities of the solutions (for recalculation of molar to molal concentrations) were determined by picnometry at 25°C.

The freezing points were determined by the visual polythermal method [16] as a mean of three measurements. The reaction vessel was cooled with liquid nitrogen. The rate of cooling was controlled by the immersion depth and varied from 0.3 to 1 deg/min. As a result, the dependence of the freezing point on the molal concentration was obtained. The eutectic point and concentration were determined by extrapolation. The freezing points were determined with an accuracy of ±1°C.

REFERENCES

1. Khripun, M.K., *Doctoral (Chem.) Dissertation*, St. Petersburg, 1993.
2. Khripun, M.K., Myund, L.A., Baranova, G.I., Smirnova, O.A., and Maslennikova, T.N., *Russ. J. Gen. Chem.*, 1998, vol. 68, no. 4, p. 515. DOI:
3. Khripun, M.K., Chervonenko, K.Yu., Kiselev, A.A., and Khripun, A.V., *Russ. J. Gen. Chem.*, 2001, vol. 71, no. 1, p. 23.
4. Khripun, M.K., Chervonenko, K.Yu., Kiselev, A.A., and Petranovskii, V.P., *Russ. J. Gen. Chem.*, 2002, vol. 72, no. 6, p. 870.
5. Kiselev, A.A., Zubtsov, M.K., and Khripun, M.K., *Vestn. Sankt-Peterb. Gos. Univ., Ser. 4: Fiz. Khim.*, 2002, no. 3, p. 51.
6. Stewart, G.H., *Indian J. Phys.*, 1932, vol. 7, p. 603.
7. Khripun, M.K., Lilich, L.S., and Efimov, A.Yu., *Probl. Sovr. Khim. Koord. Khim.*, 1983, no. 7, p. 58.
8. Pestova, O.N., David’yan, A.G., Myund, L.A., and Khripun, M.K., *Russ. J. Gen. Chem.*, 2011, vol. 81, no. 8, p. 1583.
9. Penkina, N.V., *Zh. Fiz. Khim.*, 1977, vol. 51, no. 3, p. 637.
10. Samoilov, O.Ya., *Struktura vodnykh rastvorov elektrolitov i gidratatsiya ionov* (Structure of Aqueous Solutions and Ion Hydration), Moscow: Akad. Nauk SSSR, 1957.
11. Davidian, A.G., Kudrev, A.G., Myund, L.A., and Khripun, M.K., *J. Near Infrared Spectrosc.*, 2014, vol. 22, no. 1, p. 27. DOI: 10.1255/jnirs.1090.
12. Davidian, A.G., Kudrev, A.G., Myund, L.A., and Khripun, M.K., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 3, p. 415.
13. Penkina, N.V. and Smaev, V.N., Available from VINITI, 1974, no. 2596-74.
14. Penkina, N.V. and Smaev, V.N., Available from VINITI, 1974, no. 2597-74.
15. Penkina, N.V. and Smaev, V.N., Available from VINITI, 1974, no. 598-74.
16. Pestova, O.N., Myund, L.A., Khripun, M.K., and Prigaro, A.V., *Russ. J. Appl. Chem.*, 2005, vol. 78, no. 3, p. 409. DOI: 10.1007/s11167-005-0306-z.
17. Latysheva, V.A., *Vestn. Sankt-Peterb. Gos. Univ., Ser. 4: Fiz. Khim.*, 1998, no. 4, no. 25, p. 99.
18. *Spravochnik khimika* (The Chemist’s Handbook), Nikol’skii, B.P., Ed., Leningrad: Khimiya, 1971, p. 325.
19. Samuelson, O., *Ion Exchange Separations in Analytical Chemistry*, New York: Wiley, 1963.
20. Charlot, G., *Les methodes de la Chemie analytique. Analyse quantitative Minerale*, Paris: Masson, 1961.