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Features of Component Interaction in Concentrated Solutions of Multicomponent Systems

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Abstract—Classical complex formation processes in the multicomponent systems $Cd(NO_3)_2$–MCl–H_2O (M = Li, Cs) occur at pre-eutectic concentrations of salts. At posteutectic concentrations of salts the formation of cadmium chloride complexes is of structurally enforced nature and depends on the type of the cybotactic group dominating in the solution. The example of the system $Cd(NO_3)_2$–LiCl–H_2O was used to show that the law of mass action does not apply to systems in which structurally enforced processes occur. Differences in the solubility of MCl (M = Li, Cs, Na) in concentrated solutions of cadmium nitrate are proposed to explain in terms of differences in interactions of cybotactic groups formed by cadmium nitrate and the corresponding chloride.

Our data for CdX_2–NaCl–H_2O (X = NO_3, ClO_4, Cl) systems were given in [1]. On their basis, a conclusion was drawn that, unlike the system $CdCl_2$–NaCl–H_2O, solutions of cadmium nitrate and perchlorate in the presence of NaCl are characterized by structural microheterogeneity, and a mechanism of formation of complexes of cadmium chloride in its concentrated solution was offered. Thus, the effect of the anion of the cadmium salt on acido complex-formation processes was revealed.

The aim of this work was to study the effect of the nature of the cation of a ligand-supplying salt on interactions between components at their pre- and post-eutectic concentrations. The objects of the study were $Cd(NO_3)_2$–MCl–H_2O (M = Li, Cs) systems at various salt ratios.

The Raman spectra were measured for 0.9 M (pre-eutectic area) and 4.1 M (posteutectic area) solutions of cadmium nitrate with lithium chloride added up to saturation (15 and 3 M, respectively). The general view of the spectrum of 0.9 M $Cd(NO_3)_2$–nLiCl–H_2O solutions in the frequency range 150–850 cm^{-1} is given in Fig. 1, and the difference spectra in the region of Cd–Cl stretching vibrations are shown in Fig. 2. As follows from Fig. 2, a broad band with a maximum 250 cm^{-1} is observed at 1 and 3 M concentrations of lithium chloride, which, according to [2], points to formation of all possible forms of cadmium chloride complexes and prevalence of the complex species $[CdCl_4(H_2O)_2]^{2-}$ ($[CdCl_2]$ 240, $[CdCl_3]^-$ 247, and $[CdCl_4(H_2O)_2]^{2-}$ 250 cm^{-1}).

As the LiCl concentration increases to 10 M, the band under discussion gets narrower and its maximum shifts to 270 cm^{-1}. We failed to assign this maximum to any complex species $[CdCl_n]$ on the basis of

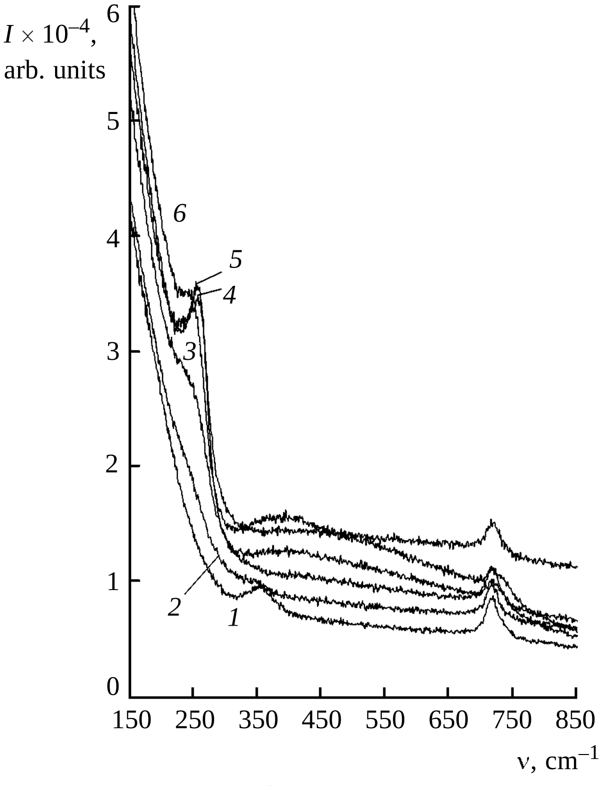

Fig. 1. Raman spectra of the system 0.9 M $Cd(NO_3)_2$–n M LiCl–H_2O in the frequency range 150–850 cm^{-1}. n: (*1*) 0, (*2*) 1, (*3*) 3, (*4*) 5, (*5*) 10, and (*6*) 15.

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published data. However, by examining the M–Hlg vibration frequencies for $[MHlg_4]^{2-}$ species (M = Zn, C, Si, Ti, Sn; Hlg = Cl, Br, I), we assigned it to the complex $[CdCl_4]^{2-}$. According to the law of mass action, we might further increase in the intensity of the band and preservation of its maximum at 270 cm^{-1}. However, at the lithium chloride concentration of 15 M the band again becomes broader and its maximum shifts to 250 cm^{-1}.

In our opinion, this fact is associated with special structural features of lithium chloride solutions. It is known that the solubility polytherm of lithium chloride involves several crystal hydrates of various composition [3]. According to our model [4], in this case the dominating structures corresponding to $LiCl \cdot 5H_2O$, $LiCl \cdot 3H_2O$, $LiCl \cdot 2H_2O$, and $LiCl–H_2O$ cybotactic groups change each other. Classical acido complex formation occurs in the solution containing 0.9 M $Cd(NO_3)_2$ at pre-eutectic concentrations of a ligand-supplying salt. On transition to posteutectic concentrations of lithium chloride, structurally enforced effects are superimposed on this process. The same processes also take place in the system under study, where the composition of forming cadmium chloride complexes will be determined by the dominating structure of the lithium chloride solution, which will constrain these complexes to exist in such a form that will allow them to form a common system of bonds with it: $[CdCl_4]^{2-}–LiCl \cdot 3H_2O$ (10 M LiCl, dominating structure $LiCl \cdot 3H_2O$, absorption maximum 270 cm^{-1}) and $[CdCl_4(H_2O)_2]^{2-}–LiCl \cdot H_2O$ (15 M LiCl, dominating structure $LiCl \cdot H_2O$, maximum 250 cm^{-1}). In the latter case, two water molecules liberated due to the natural process of changing the dominating cybotactic group $LiCl \cdot 3H_2O \rightarrow LiCl \cdot H_2O + 2\ H_2O$, appear to come under the influence of the complex species $[CdCl_4]^{2-}$. The concentration of Cd^{2+} ions is too low for them to form their own cybotactic groups. Therefore, the corresponding cybotactic group of lithium chloride controls the system behavior. In the region of dominating lithium chloride trihydrate (10 M), $[CdCl_4]^{2-}$ tetrahedra are formed, whereas in the region of dominating $LiCl \cdot H_2O$ cybotactic group (15 M), cadmium chloride complexes are forced to rearrange into new species, the dominating being $[CdCl_4(H_2O)_2]^{2-}$.

The system $LiCl–CdCl_2–H_2O$ has been studied in [5]. The following compounds were detected in its solubility isotherm: $4LiCl \cdot 3CdCl_2 \cdot 12H_2O$ on the side of a LiCl saturated solution and $LiCl–2\ CdCl_2 \cdot 5H_2O$ on the side of a $CdCl_2$ saturated solution. Their formulas points to the absence of complex compounds with a strictly defined composition. These compounds result from cooperative interactions of the crystal hydrate structures of lithium and cadmium chloride, formed by structure-enforced conjugation of the salts through common water molecules.

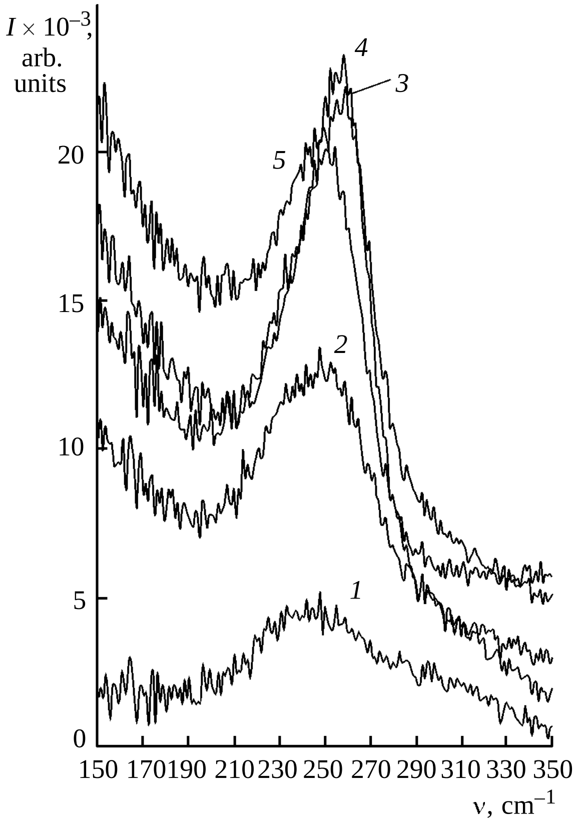

Fig. 2. Difference Raman spectra of the system 0.9 M $Cd(NO_3)_2$–*n* M $LiCl–H_2O$ in the region of Cd–Cl stretching vibrations. *n*: (*1*) 1, (*2*) 3, (*3*) 5, (*4*) 10, and (*5*) 15.

Complex formation in solutions of the system studied gives cadmium hydrate. On the assumption that cadmium completely enters into the composition of chloride complexes, the concentration of lithium nitrate is 1.8 M. In aqueous solution of lithium nitrate of the same concentration, the ν_4 vibration band of nitrate ions with a maximum at 720 cm^{-1} is fully symmetric, and only at $LiNO_3$ concentrations greater than 9 mol/1000 g H_2O it acquires a high-frequency shoulder at 740 cm^{-1} [6]. In the multicomponent system in hand at high concentrations of lithium chloride (10 and 15 M), the ν_4 band is split (Fig. 1). We suppose that this splitting is produced structurally enforced effects. Apparently, the structural incompatibility of lithium nitrate with dominating $LiCl \cdot nH_2O$ cybotactic groups results in local concentration of the latter, i.e. to origination of structural microheterogeneity in the solution. As known [6], lithium nitrate forms the crystal hydrate $LiNO_3 \cdot 3H_2O$ on

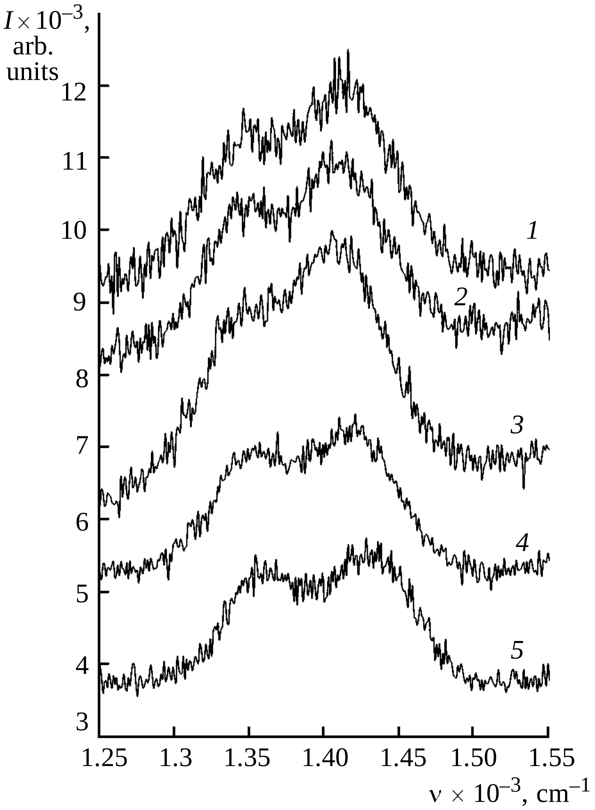

Fig. 3. Raman spectrum in the region of ν_3 frequencies of the NO_3^- ion in the system 0.9 M $Cd(NO_3)_2$–*n* M LiCl–H_2O. *n*: (*1*) 1, (*2*) 3, (*3*) 5, (*4*) 10, and (*5*) 15.

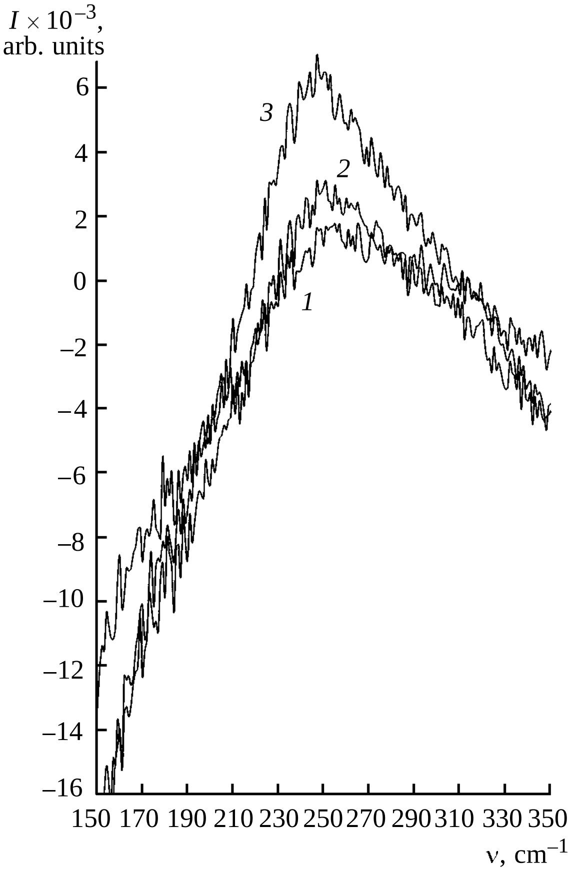

Fig. 4. Difference Raman spectra in the region of Cd–Cl stretching vibrations in the system 4 M $Cd(NO_3)_2$–*n* M LiCl–H_2O. *n*: (*1*) 1, (*2*) 3, and (*3*) 3.

saturation, which passes to the anhydrous state at 30°C. We earlier found [7] that the solubility isotherm of the system $Ca(NO_3)_2$–$LiNO_3$–H_2O consists of three crystallization branches: $Ca(NO_3)_2 \cdot 4H_2O$, $LiNO_3 \cdot 3H_2O$, and $LiNO_3$, and in presence of $Ca(NO_3)_2$ crystal hydrate, lithium nitrate is dehydrated at high concentrations and exists in this system as ionic melt.

It is most likely that the same tendency for lithium nitrate to convert to the state of ionic melt at high concentrations is also observed in our case. It is confirmed by the Raman spectra in the region of the ν_3 vibration of nitrate ions (Fig. 3). The maxima of the split band tend to shift on concentration to the region of vibration frequencies characteristic of $LiNO_3$ melt (1386 and 1468 cm^{-1}). Changes in the ν(Cd–O) band of aquated cadmium ions (maximum at 350 cm^{-1} [6]) seem rather interesting. At first, on transition from low concentrations of LiCl to high concentrations, this band completely disappears owing to complex formation. In the region where LiCl di- and trihydrate structures prevail, a broad band appears in the range 280–650 cm^{-1}. It is known that the range 280–550 cm^{-1} may correspond to Li–O vibrations (data for solid crystal hydrate) [6] and to libration vibrations of water [8]. In our opinion, these changes are also associated with cooperative interactions, and none of the above-mentioned assumptions can be ruled out.

The difference spectra of Cd–Cl stretching vibrations for 4 M $Cd(NO_3)_2$–*n* M LiCl–H_2O solutions are shown in Fig. 4. We should note at once that the solubility of lithium chloride in a concentrated $Cd(NO_3)_2$ solution is insignificant.

Cybotactic groups like $Cd(NO_3)_2 \cdot 4H_2O$ are dominating in a 4 M solution of cadmium nitrate, where the cybotactic group $Cd(NO_3)_2$–$9H_2O$ is also present in small amounts. This solution can be presented as a composite solvent for LiCl, where the mole fraction of cadmium tetrahydrate is much greater than the fraction of cadmium nonahydrate. The solubility of sodium chloride in a similar solution of cadmium nitrate is higher than in water [1]. Therefore, considering the 4 M solution of cadmium nitrate as a composite solvent, one can consider as preferential interactions both of sodium chloride with a $Cd(NO_3)_2 \cdot 4\,H_2O$ solvent (in excess in the system) and of lithium chloride with a solvent like $Cd(NO_3)_2 \cdot 9H_2O$ (in deficit in the system, which explains the poor solubility of LiCl).

Unlike lithium chloride, CsCl is poorly soluble in a 0.9 M solution of cadmium nitrate. The highest attainable concentration of cesium chloride in such a solution is 0.8 M. X-ray phase analysis showed that the bottom phase formed on addition of excess CsCl (more than 0.8 M) consists of the complex $CsCdCl_3$ and $CsNO_3$. Thus, at pre-eutectic concentrations of cadmium nitrate, where the intrinsic structure of water is dominating, the rather free interparticle exchange in solutions allows presence of all possible forms of cadmium chloride complexes, which finally (with excess cesium chloride) results in the transition of the least soluble complex (CsCdCl3) into the bottom phase.

On passing to posteutectic concentrations of cadmium nitrate (4 M), the solubility of cesium chloride doubles (the maximal solubility proved to be 1.5 M). As with lithium chloride, the poor solubility of CsCl in a 4 M $Cd(NO_3)_2$ solution results from the preferential interaction of $Cs^+–Cl^-$ associates (dissociation of CsCl in such solutions is suppressed) with the solvent $[Cd(NO_3)_2 \cdot 9H_2O]$ whose fraction in this solution is insignificant.

The NO_3^- ion is in the outer sphere of the hydrated cadmium cation in the structure of cadmium nitrate nonahydrate, which allows the cesium ion to form $Cs^+–NO_3^-$ associates and opens access for the Cl^- ion into the inner sphere of the cadmium ion. The enhanced, compared with a dilute $Cd(NO_3)_2$ solution, solubility of CsCl is explained by kinetic difficulties associated with formation of the poorly soluble $CsCdCl_3$ complexes in a concentrated solution. In a dilute solution, there are different forms of cadmium chloride complexes, including the anionic species $[CdCl_3]^-$ and $[CdCl_4 \cdot (H_2O)_2]^{2-}$ and free Cs^+ ions, which leads to the transition of the least soluble $CsCdCl_3$ into the bottom phase. In a concentrated solution of cadmium nitrate, $Cs^+–NO_3^-$ associates are formed. Their dissociation is suppressed, and, therefore, free Cs^+ ions required for formation of the poorly soluble $CsCdCl_3$ compound are unavailable in this solution. It seems that the CsCl solubility in a concentrated $Cd(NO_3)_2$ solution grows because of the competition of nitrate and $[CdCl_3]^-$ anions for association with Cs^+ ions.

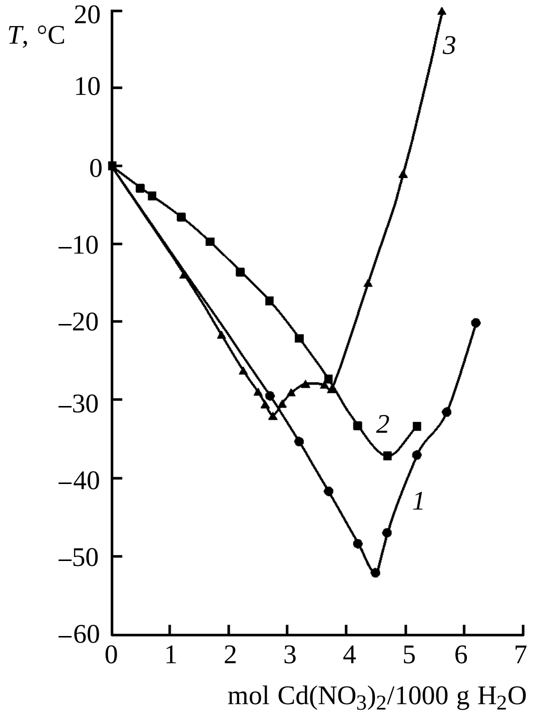

Fig. 5. Solubility polytherms. (*1*) $Cd(NO_3)_2$: LiCl = 1.7 : 1, (*2*) $Cd(NO_3)_2$: CsCl = 2.5 : 1, and (*3*) $Cd(NO_3)_2$: NaCl = 1 : 1.6.

We measured solubility polytherms for solutions with the compositions $Cd(NO_3)_2$: CsCl = 2.5 : 1 and $Cd(NO_3)_2$: LiCl = 1.7 : 1 [the maximal solubilities of the salts in a $Cd(NO_3)_2$ solution] (Fig. 5). The solubility polytherm of the $Cd(NO_3)_2$: NaCl = 1 : 1 solution is also given in Fig. 5 for comparison. For the sake of convenience in comparing with published solubility polytherms of binary mixtures, the polythermal measurements are presented as plots of the freezing point of a solution on the molal concentration (m) of Cd^{2+}. As seen from Fig. 5, the eutectic in the solubility polytherms of the systems under consideration is shifted to higher concentrations of cadmium nitrate (4.7 and 4.4 m, respectively), by contrast with the corresponding solution with sodium chloride (2.5 m). Apparently, this points to absence of the crystallization branch of $Cd(NO_3)_2 \cdot 9H_2O$ [the eutectic in the system $Cd(NO_3)_2–H_2O$ corresponds to the concentration of 2.5 m]. In the system with lithium chloride, the peritectic was found in the region of 5.7 m. The eutectic in the solubility polytherm of the system $Cd(NO_3)_2–LiCl–H_2O$ coincides to a high accuracy with the eutectic in the solubility polytherm of the binary mixture $CdCl_2–H_2O$, which allows the second crystallization branch to be assigned to of the crystal hydrate $CdCl_2 \cdot 4H_2O$. On the other hand, the peritectic in the solubility polytherm of the system corresponds to the peritectic in the solubility polytherm of cadmium nitrate. Thus, it is quite logical to assign the third crystallization branch to $Cd(NO_3)_2 \cdot 4H_2O$.

The positively hydrated Li^+ ion or its crystal hydrate cybotactic groups need water which they take from the solution, thus further retarding formation of cadmium nitrate nonahydrate.

Thus, systems $Cd(NO_3)_2$–MCl–H_2O (M = Na, Li, Cs) systems in the region of high component concentrations radically differ from each other. Namely, the mechanism of formation of cadmium complexes in the presence of NaCl results from structurally enforced insertion of Na^+–Cl^- associates into the internal sphere of cadmium in the cybotactic group $Cd(NO_3)_2 \cdot 4H_2O$ (which is dominating at these concentrations) with expulsion of nitrate ions. Probably, lithium and cesium chlorides, vice versa, are unable to interact with $Cd(NO_3)_2 \cdot 4H_2O$ cybotactic groups. The Cs^+–Cl^- associates are too bulky (steric factor), while lithium chloride which does not exist in the anhydrous state forms its own cybotactic groups ($LiCl \cdot nH_2O$), requiring water. Since, however, complexes do form, one can suggest that lithium and cesium chlorides interact only residual cybotactic groups $Cd(NO_3)_2 \cdot 9H_2O$.

Dissolution of CsCl in a concentrated cadmium nitrate solution destroys the weak $Cd(NO_3)_2 \cdot 9H_2O$ structure with subsequent formation of chloride complexes. Lithium chloride modifies $Cd(NO_3)_2 \cdot 9H_2O$ cybotactic groups, dehydrating them, and forms complexes with these modified cybotactic groups by the mechanism of structurally enforced conjugation. Apparently, in a saturated solution of cadmium nitrate, LiCl is not entirely involved in formation of such structurally enforced complexes and remains in part in solution as $LiCl \cdot nH_2O$ cybotactic groups. Thus, the complex formation is weakened as compared to a dilute solution of cadmium nitrate with the same concentration of lithium chloride (3 M LiCl).

Such a different behavior of the three salts in concentrated solutions of cadmium nitrate is connected to differences in their nature, their state at high concentrations, and also in the size of of their alkali metal cations.

Sodium chloride does not form well-defined crystal hydrate cybotactic groups and associates. Furthermore, sodium ions have the same size as cadmium ions and they only slightly disturb dominating cybotactic groups based on cadmium crystal hydrates. The cesium ion is too large and tends to associate (Cs^+–Cl^- or Cs^+–NO_3^-), thus disturbing the weak $Cd(NO_3)_2 \cdot 9H_2O$ structure. The Li^+ ion, vice versa, is too small and has a high affinity to water and draws it again from the weak $Cd(NO_3)_2 \cdot 9H_2O$ structure.

These features of the ligand-supplying salts also affect the shape of their solubility polytherms. Sodium chloride does not hinder formation of $Cd(NO_3)_2 \cdot 9H_2O$ cybotactic groups (second crystallization branch) and forms complexes based on $Cd(NO_3)_2 \cdot 4H_2O$ cybotactic groups (third crystallization branch of $CdCl_2 \cdot 4H_2O$). In presence of cesium chloride, the concentration of chloride complexes is too low, and the structure of $Cd(NO_3)_2 \cdot 9H_2O$ is partially destroyed; as a result, we can see a lengthy branch of water in the solubility polytherm of this system. The poor solubility of lithium chloride in a concentrated solution of cadmium nitrate [small quantity of complexes and domination of $Cd(NO_3)_2 \cdot 4H_2O$ cybotactic groups] results, as the temperature decreases, first in crystallization of $Cd(NO_3)_2 \cdot 4H_2O$ (third branch) at then, with dilution and correspondingly increasing concentration of cadmium chloride complexes, crystallization of $CdCl_2 \cdot 4H_2O$ occurs. The crystallization branch of $Cd(NO_3)_2 \cdot 9H_2O$ is also absent.

Thus, the resulting data allow the following conclusions. In the composite systems $Cd(NO_3)_2$–Li/CsCl–H_2O studied, a classical acido complex formation takes place only at concentrations of the components, corresponding to pre-eutectic regions of the solubility polytherms of the binary systems. We apply the term “classical” only to those acido complexes whose kinetics of formation can formally be described by the law of mass action. Cadmium chloride complexes are also formed in the region of post-eutectic concentrations of at least one of the components, however, the law of mass action in its classical formulation is no longer applicable, and formation of any particular cadmium chloride complexes essentially depends on the mechanism of interaction between cybotactic groups of the components. The mechanism, in its turn, is determined by the nature of interacting components and their concentrations (by the type of the cybotactic group dominating in the solution). The term “nature of interacting components” should not be considered as a sort of “ring-buoy” in dealing with processes, the reason of which is yet to be explained. This “nature” underlies the solubility polytherms of systems, whose shape allows us to forecast the behavior of components in their interaction in composite systems. In this work we have considered a system containing the same complex-forming cation (Cd^{2+}) and various ligandsupplying salts. We suppose that the offered scheme of interaction of salts in multicomponent solutions is universal and will not principally change in the case when both components are varied (complex-forming cation and ligand-supplying salt). Formally, a concentrated multicomponent solution in which various cybotactic groups interact with each other can be considered as a system of mixed solvents, where a combination of similar cybotactic groups plays the role of a separate solvent component.

EXPERIMENTAL

The Raman spectra were measured on a PC-controlled DFS-52 spectrometer. The spectra were excited by a 488-nm line of an Ar^+ laser and recorded with an FEU79 photomultiplier in the photon-counting mode, step 1 cm^{-1}, time constant 1 s, spectral slit width 3 cm^{-1}. The wave numbers were accurate to within 0.5 cm^{-1}.

The difference spectra were obtained by subtracting the spectrum of a cadmium nitrate solution from the spectrum of the system $Cd(NO_3)_2$–MCl–H_2O system with the same concentration of cadmium nitrate [for example, from the spectrum of a 0.9 M $Cd(NO_3)_2$ solution was subtracted from the spectrum of a solution containing 5 M lithium chloride and 0.9 M cadmium nitrate].

The freezing points of solutions were determined by the visual polythermic method. The convergence of the data was within 0.5°C.

Chemically pure grade cadmium nitrate and lithium chloride were recrystallized two times. Special purity grade cesium chloride was used without additional purification. All working solutions were prepared with twice distilled water.

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