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Comparative Analysis of the Solubility of Alkali Metal Chlorides in Cadmium and Zinc Nitrate Solutions at 25°C

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Abstract—Maximum solubilities of salts MCl (M = Li, Na, K, Cs) in cadmium and zinc nitrate solutions of various concentrations were measured. The effect of the structure of the solution on the mutual solubility was demonstrated.

Maximum solubilities of salts MCl (M = Li, Na, K, Cs) in cadmium and zinc nitrate solutions of various concentrations up to mutual saturation of the solutes were measured. The complexity of such multicomponent systems is associated with the fact that their microcomposition varies with salt concentrations. According to the model concepts [1, 2], the composition of cybotactic groups successively dominating in a solution as the salt concentration is increased corresponds to the composition of crystal hydrates that crystallize as the solution is cooled. In preeutectic solutions, the solvent is water. Concentrated solutions containing different cybotactic groups can be considered as a system of mixed solvents, and the role of a separate solvent component belongs to a set of equilibrium cybotactic groups of the same type. Thus, the solubility of alkali metal chlorides in cadmium and zinc nitrate solutions of various concentrations and formation of cadmium chloride and zinc chloride complexes will depend on their preferred interaction with one or another solvent (one or another cybotactic group).

Lithium chloride forms a number of different crystal hydrates, whereas sodium, potassium, and cesium chlorides crystallize water-free on saturation.

Figure 1a shows solubility curves for the systems $NaCl–Cd(NO_3)_2–H_2O$ and $NaCl–Zn(NO_3)_2–H_2O$. As seen, the solubility of NaCl in $Zn(NO_3)_2$ and $Cd(NO_3)_2$ solutions changes in a similar way. However, at low nitrate concentrations, the solubility of sodium nitrate in the $NaCl–Zn(NO_3)_2–H_2O$ system increases steeper than in $NaCl–Cd(NO_3)_2–H_2O$. At high concentrations, by contrast, the solubility of sodium chloride in cadmium nitrate solutions is higher. The increased solubility of sodium chloride in cadmium and zinc nitrate solutions of preeutectic concentrations can be explained by that dissolution of sodium chloride involves formation of $[CdCl_n(H_2O)_{6-n\,2-n}$ complexes and “liberation” of water molecules [reactions (1)–(4)].

$$Cl^-_{aq} + [Cd(H_2O)_6]^{2+} \rightleftarrows [CdCl(H_2O)_5]^+ + H_2O, \quad (1)$$

$$Cl^-_{aq} + [CdCl(H_2O)_5]^+ \rightleftarrows [CdCl_2(H_2O)_4] + H_2O, \quad (2)$$

$$Cl^-_{aq} + [CdCl_2(H_2O)_4] \rightleftarrows [CdCl_3(H_2O)_3]^- + H_2O, \quad (3)$$

$$Cl^-_{aq} + [CdCl_3(H_2O)_3]^- \rightleftarrows [CdCl_4(H_2O)_2]^{2-} + H_2O. \quad (4)$$

The complex formation in the $NaCl–Zn(NO_3)_2–H_2O$ system has the same mechanism and gives rise to a $[ZnCl_4]^{2-}$ complex species. Thus, on the one hand, dissolved chloride ions are bound into the complex and, on the other, “additional free” water molecules are formed. These two factors operate to enhance the solubility of sodium chloride compared with its solubility in straight water.

The maximum concentrations of sodium chloride in $Cd(NO_3)_2$ and $Zn(NO_3)_2$ solutions are 7.82 and 11.72 mol/kg H_2O, respectively. Analysis of crystallized bottom phases showed that the complex that crystallizes in the $NaCl–Cd(NO_3)_2–H_2O$ system has the composition $Na_2[CdCl_4] \cdot nH_2O$ (n varies from 1.5 to 3 depending on the concentration of cadmium nitrate) and the complex that crystallizes in the $NaCl–Zn(NO_3)_2–H_2O$ system has the composition $Na_2[ZnCl_4]$. It also follows from published data that cadmium ions form with chloride ions complexes containing water molecules, whereas zinc ions form water-free chloride complexes [3]. Thus, the formation of the latter complex liberates more water, which, too, favors enhanced solubility of sodium chloride. Moreover, as shown in [4], cadmium chloride complexes are more stable than zinc chloride ones.

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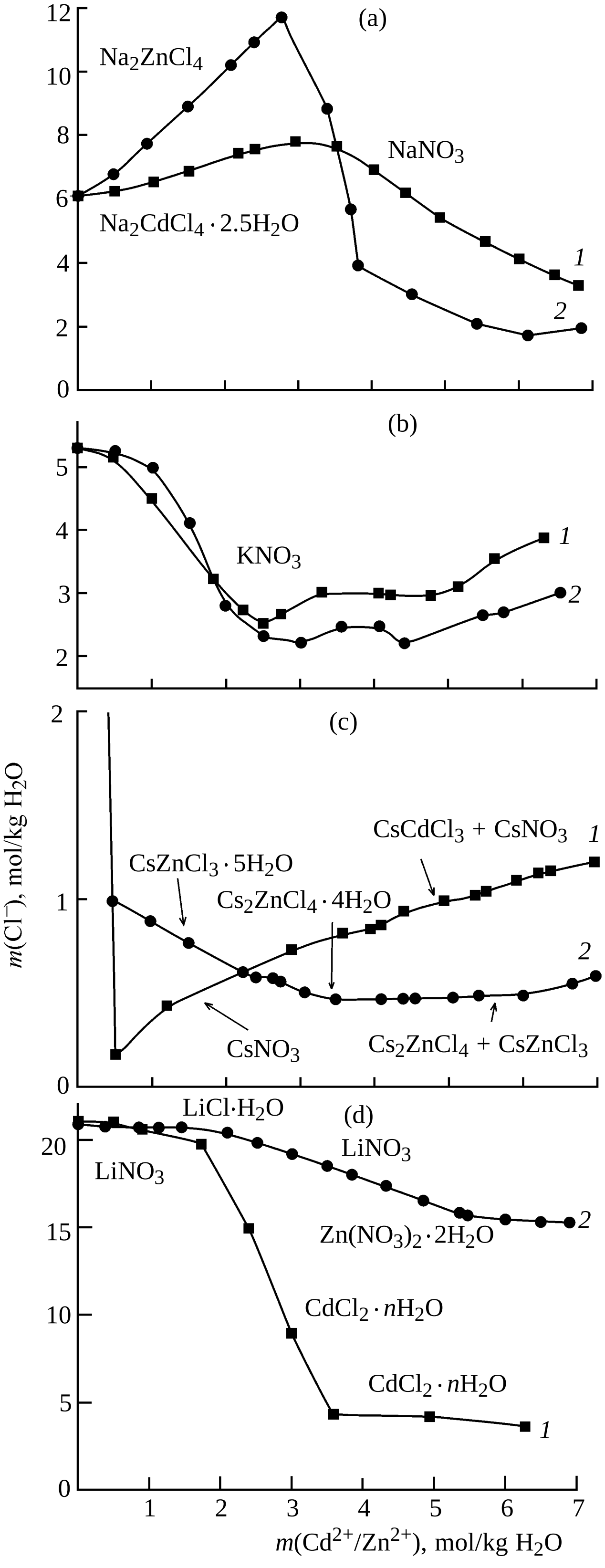

Solubilities in (*1*) $Cd(NO_3)_2$ and (*2*) $Zn(NO_3)_2$ solutions at 25°C of (a) NaCl, (b) KCl, (c) CsCl, and (d) LiCl.

Therefore, for all zinc ions to enter into the $[ZnCl_4]^{2-}$ complex requires a higher concentration of chloride ions.

As the nitrate concentrations are increased further, the solubility of sodium chloride decreases to 1.7 mol/kg H_2O in $NaCl–Zn(NO_3)_2–H_2O$ and 3 mol/kg H_2O in $NaCl–Cd(NO_3)_2–H_2O$. At eutectic and posteutectic nitrate concentrations, various-composition cybotactic groups begin to form on the basis of zinc and cadmium crystal hydrates. The qualitative change in the structure of the solution, associated with the formation in posteutectic solutions of cybotactic groups like $Cd(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, attenuates complex formation. In our opinion, sodium chloride dissolves due to interaction with residual “free” activated cadmium and zinc ions whose quantities decrease with increasing nitrate concentration and thus adversely affect the solubility of NaCl. Cybotactic groups on the basis of zinc nitrate have a more rigid structure and include more water molecules compared with cybotactic groups on the basis of cadmium nitrate. Therefore, at the same concentrations of cadmium and zinc nitrates, the concentration of “free” activated complex-forming ions and the number of water molecules not incorporated into cybotactic groups and capable of dissolving NaCl in the $NaCl–Zn(NO_3)_2–H_2O$ system should be smaller than in $NaCl–Cd(NO_3)_2–H_2O$. This reasoning explains the steeper decrease in the solubility of NaCl in zinc nitrate compared with cadmium nitrate solutions.

Figure 1b shows solubility curves for the systems $KCl–Cd(NO_3)_2–H_2O$ and $KCl–Zn(NO_3)_2–H_2O$. In both systems, the solubility of KCl varies in a similar way but differently from what is observed with NaCl. The solubility of KCl first decreases up to $Cd(NO_3)_2$ and $Zn(NO_3)_2$ concentrations corresponding to the eutectics in the solubility polytherms of the $Cd(NO_3)_2–H_2O$ and $Zn(NO_3)_2–H_2O$ binary systems (2.5 and 3.3 mol/kg H_2O, respectively) and then smoothly increases with increasing nitrate concentration. Over the entire concentration range, water-free KNO_3 crystallizes from the solutions.

As in the above-considered $Cd(Zn)(NO_3)_2–NaCl–H_2O$ systems, at preeutectic concentrations of cadmium and zinc nitrates, a classical complex formation takes place. However, whereas the solubility of sodium nitrate is higher than those of the zinc and cadmium chloride complexes $Na_2[CdCl_4] \cdot nH_2O$ and $Na_2[ZnCl_4]$, that were found in the solid phases in the $Cd(Zn)(NO_3)_2–NaCl–H_2O$ systems, potassium nitrate formed by an exchange process is weaker soluble than the cadmium and zinc complexes. Therefore, in the $Cd(Zn)(NO_3)_2–KCl–H_2O$ systems, potassium nitrate is found in the bottom phase both in the pre- and posteutectic ranges. With increasing concentrations of cadmium and zinc nitrates, and, consequently, of nitrate ions, the solubility of potassium nitrate decreases (salting-out effect).

As in the systems with NaCl, the solubility of KCl at posteutectic nitrate concentrations is lower in zinc nitrate compared with cadmium nitrate solutions, which results from different “rigidities” of structural formations in the nitrate solutions. At higher nitrate concentrations [above 5 mol/kg H_2O of $Cd(NO_3)_2$ and above 4.3 mol/kg H_2O of $Zn(NO_3)_2$], cybotactic groups like $Cd(NO_3)_2 \cdot 4H_2O$ become to dominate in cadmium nitrate solutions and cybotactic groups like $Zn(NO_3)_2 \cdot 6H_2O$, in zinc nitrate solutions. Nitrate ions are incorporated into cybotactic groups, and $nH_2O \cdot (NO_3)Cd(Zn)–(NO_3)–K^+$ interaction effects binding or stabilization of potassium nitrate in the solution, and thus slightly enhances its solubility.

The solubility of CsCl in cadmium and zinc nitrate solutions is poor compared with its solubility in water (Fig. 1c). At preeutectic nitrate concentrations, a classical acido complex formation occurs, giving rise to various forms of chloride complexes ($CsMeCl_3$, Cs_2MeCl_4, Cs_3MeCl_5) that are poorly soluble and crystallize water-free [5, 6]. Apart from chloride complexes, cesium nitrate is also formed. It is also poorly soluble and can form the bottom phase. Obviously, at increased concentrations of cadmium and zinc nitrates, both the poorly soluble salts can stabilize in the corresponding solutions due to the equilibrium $CsCdCl_3 + NO_3 \rightleftarrows CsNO_3 + CdCl_3^-$. Increased concentration of nitrate ions favors further stabilization both of complexes and $CsNO_3$ by the above competitive process.

At posteutectic concentrations of cadmium and zinc nitrates, nitrate ions are incorporated into cybotactic groups and, like in the systems with NaCl, the $nH_2O \cdot (NO_3)Cd(Zn)–(NO_3)–Cs^+$ interaction produces further stabilization of cesium nitrate and, as a consequence, chloride complexes in the solution.

Thus, at preeutectic concentrations of cadmium and zinc nitrates, dissolution of sodium, potassium, and cesium chlorides is accompanied by a classical acido complex formation. The chlorides are better soluble in zinc nitrate solutions because of the lower thermodynamic stability of zinc chloride complexes. For all zinc ions to be bound in the $[ZnCl_4]^{2-}$ complex species a higher concentration of chloride ions is required. The different solubility patterns are explained by the different solubilities of cadmium and zinc chloride complexes and the corresponding alkali metal nitrates formed by an exchange process. The solubility of the nitrates decreases in the order $NaNO_3 > KNO_3 > CsNO_3$. The same solubility order is characteristic of the complexes.

At posteutectic concentrations of cadmium and zinc nitrates, the different solubilities of the chlorides are explained, on the one hand, by structural features of cadmium and zinc nitrate solutions. Because of the higher hydration ability of zinc ions compared with cadmium ions, cybotactic groups on the basis of zinc nitrate are more stable compared with those on the basis of cadmium nitrate. One more explanation consists in the ability of alkali metal cations to associate with anions; at high concentrations of cadmium and zinc chlorides, dissociation of chlorides is suppressed. The associative ability increases in the order CsCl > KCl > NaCl. The associative ability of alkali metal nitrates increases in the same order.

Unlike sodium, potassium, and cesium chlorides, lithium chloride exhibits a very high solubility in water. According to the solubility polytherm of $LiCl–H_2O$ [7], with increasing concentration of lithium chloride, cybotactic groups on the basis of different crystal hydrates $LiCl \cdot nH_2O$ will form. The formation of such cybotactic groups in the $M(NO_3)_2–LiCl–H_2O$ (M = Cd, Zn) systems strongly affects the mutual solubility of the components, as well as complex formation.

The solubility of lithium chloride decreases with increasing concentration of cadmium nitrate (Fig. 1d). The steepest decrease is observed at the eutectic composition of the $Cd(NO_3)_2$ solution (2.6 mol/kg H_2O). Once the concentration of $Cd(NO_3)_2$ has attained ca. 3.5 mol/kg H_2O, the solubility of lithium chloride begins to change slowly but proceeds to decrease.

At low concentrations of cadmium nitrate, according to the analysis of the solid phase, crystallization of lithium nitrate occurs. This salt is structurally incompatible with the dominating cybotactic groups $LiCl \cdot nH_2O$ and is present in the solution in a state similar to ionic melt. At cadmium nitrate concentrations higher than 3.5 mol/kg H_2O, the solubility of lithium chloride changes only slightly and is preserved at a level of about 4 mol/kg H_2O. The complex $CdCl_2 \cdot nH_2O$ (n varies from 1 to 2.5 depending on the concentration of cadmium nitrate) was found in the bottom phase. The sharp decrease in the solubility of LiCl at posteutectic concentrations of cadmium nitrate suggests structural incompatibility of cybotactic groups on the basis of cadmium nitrate, lithium chloride, and cadmium chloride complexes. Lithium chloride dissolves exactly to a point where saturation of “free” activated cadmium cations to the dichloride state can be attained.

The solubility of lithium chloride in the $Zn(NO_3)_2$–LiCl–H_2O system is high over the entire concentration range and varies only slightly (see Fig. 1d). The dissolution of lithium chloride is accompanied by formation of $LiCl \cdot yH_2O$ crystal hydrate cybotactic groups, which requires water molecules. Presumably, the dissolved lithium chloride forces cybotactic groups on the basis of zinc nitrate to modify into water-poorer forms. Evidence for this suggestion comes from the composition of the solid phase that crystallizes at high concentrations of zinc nitrate [$Zn(NO_3)_2 \cdot 2H_2O$; see Fig. 1d]. The modified cybotactic groups $Zn(NO_3)_2 \cdot 2H_2O$ undergo complex formation with $LiCl \cdot yH_2O$ by the structurally forced conjugation mechanism. Such structures can conjugate through water molecules and nitrate or chloride ions. The high solubility of lithium chloride suggests formation of a common bond system in the solution.

Thus, at low concentrations of cadmium and zinc nitrates, the state of Cd^{2+} and Zn^{2+} ions is determined by the dominating structure of the lithium chloride solution. In the posteutectic region, the mutual solubility of the salts depends on whether a common bond system can [$Zn(NO_3)_2$–LiCl–H_2O] or cannot [$Cd(NO_3)_2$–LiCl–H_2O] be formed on the basis of $LiCl \cdot yH_2O$ and $Zn(Cd)(NO_3)_2 \cdot nH_2O$ cybotactic groups and complexes formed.

EXPERIMENTAL

Solutions of cadmium and zinc nitrates were prepared by addition of excess solid crystal hydrates of analytical grade to twice distilled water and subsequent separation of undissolved residues. The concentrations of cadmium and zinc ions were determined by complexometric titration [titrant 0.1 N solution of Trilon B (the concentration of the Trilon B solution was determined to the fourth decimal point), indicator eriochrome black]. The concentration of chloride ions was determined by titration with mercury(II) nitrate (indicator diphenylcarbazone).

The composition of solid phases was determined by adding excess MCl to the above solutions, after which the mixtures were thermostated for 3 days, and the solid phases were separated and analyzed. The error in the solubility was formed by the errors in the concentrations of ions (±0.1 mol/kg H_2O for concentrations of cadmium, zinc, and chloride ions lower that 5 mol/kg H_2O and ±0.2 mol/kg H2O for concentrations of cadmium, zinc, and chloride ions higher than 5 mol/kg H_2O) and in the quantity of the precipitate formed (no higher than ±0.1 mol/kg H_2O).

The solubility of MCl was measured so as to determine the maximum quantity of the chloride capable of dissolving in a cadmium or zinc nitrate solution of certain concentration without solid-phase formation. To this end, anhydrous salt MCl was added to a continuously stirred solution of cadmium and zinc nitrate until crystallization began. The solution was then filtered, and the filtrate was analyzed. To determine the composition of the solid phase, excess MCl was added to the same solution, and the solid phase was analyzed.

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