COORDINATION CHEMISTRY OF DI(2-ETHYLPHEXYL)PHOSPHORIC ACID SALTS IN EXTRACTION PROCESSES
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The wide use of di(2-ethylhexyl) phosphoric acid (D2EHPA, HX in formulas) determined the interest in the composition and structure of complexes formed in the extracts. Besides, some of these complexes may act as extracting agents which complicates the extraction picture.

The organic phase in the D2EHPA extraction contains, in the general case, a mixture of partially hydrated neutral and acid salts of D2EPA and to understand the entire picture of the extraction it is necessary to study separately the states of neutral salts in nonequorous organic solvents and their interaction with water and H₂X₂ molecules and also the hydration of acid salts. To achieve this we performed an IR, electron, and NMR⁵¹P spectroscopic study of the structure of neutral salts MX (M-alkali metals and NH₄⁺), MX₂ (M=Mg²⁺,Ca²⁺,Ba²⁺,Co²⁺,Ni²⁺,Cu²⁺, Zn²⁺,V₂O₇), and their hydration in CCl₄, C₆H₆, n-C₆H₁₄ as well of the composition, structure, hydration of acid di(2-ethylhexyl)phosphates of Co²⁺,Zn²⁺,Zr⁴⁺,Hf⁴⁺.

Neutral and, in some cases, acid salts formed by D2EHPA, both in nonequorous solvents and in the presence of water, tend to polymerize to form associates of a complex structure. The various features of these associates are a result of diversity of the modes in which the POO groups coordinate to the metal cations.

The following types of mono-, bi-, and tridentate coordination of the POO-groups to the cations M were found

In nonaqueous solutions of neutral alkali metal salts type I-III coordination takes place. LiX solutions give rise only to long-chain linear polymers (LiX)ₚ (type II). In the series of salts NaX, KX,RbX, CsX the amount of the linear polymers (MX)ₚ and the average degree of polymerization p drop (terminal type I POO-groups appear) while the fraction of the monomeric molecules with type III POO-groups sharply increases. In contrast to alkali metal carboxilates, there is no equalization of the multiplicity of the phosphorus-oxygen bonds of the POO-groups in the studied salts.

Transition metal salts MX₂ form in solutions linear polymers (in the case of CuX₂ only at high salt concentrations) in which the cation is in a distorted tetrahedral ligand field. (ZnX₂)ₚ and (CoX₂)ₚ molecules with p of about 4 contain non-equivalent chelate terminal POO-groups of the type III₁ and III₂ differing by the degree of equalization of the phosphorus-oxygen bonds multiplicities (index 1 denotes that the bonds are to a large extent equalized, index 2 shows that one bond
is largely of a double character while the other is mainly a simple bond. NiX₂ (in contrast to CoX₂) and also CuX₂ give rise, in diluted solutions, to cyclic tri- and tetramers with type IV POO-groups similar to those described in [17] for Cu(II)dioctylphosphinate. Due to this the coordination number (CN) of Ni²⁺ and Cu²⁺ increases to 6. Rearrangement of the linear polymers (CuX₂)ₚ to cyclic tri- and tetramers at C_{CuX₂} from ~0.3 to 0.05 mol/1 (in terms of the monomer) was studied in [27]. Beyond this concentration interval, linear cyclic (up to 5·10⁻³ mol/1) species prevail. The VOX₂ salt produces only dimers over the concentration range from 5·10⁻³ to 0.5 mol/1.

Hydration of neutral salts. In contrast to (CuX₂)ₚ and (NiX₂)ₚ, the linear polymers (ZnX₂)ₚ, (CoX₂)ₚ and the (VOX₂)₂ dimer do not coordinate water molecules due to coordination saturation of their Zn²⁺, Co²⁺, and VO²⁺ cations. Hydration of (CuX₂)ₚ molecules in CCl₄ was studied using differential IR spectroscopy. The spectra of CuX₂ solutions containing different amounts of water were measured relative to a nonaqueous solution, with the reference cell thickness chosen so as to compensate for the spectrum of non-hydrated (CuX₂)ₚ species. It was found that in 0.05 molar solutions of CuX₂ in CCl₄ with up to 0.03 mol/1 of water, the H₂O molecules enter into cyclic associates with the molar ratio CuX₂·H₂O=3:2. The structure of these associates is discussed. With further increase in C_{H₂O} a mixture of water-containing cyclic associates of different composition is formed and the amount of hydration increases. In solutions at equilibrium with water the average composition of the water-containing associates is close to (CuX₂·2H₂O)₄ but even under these conditions 10 to 30% of CuX₂, depending on the solvent, exist in the form of nonhydrated associates.

Hydration of cyclic molecules (NiX₂)ₚ (P= 3+4) in CCl₄ was studied at the molar ratios n=H₂O/NiX₂ from 1 to 11 (at equilibrium with water). With the increase in n from 0 to 2 the electronic spectra of the solutions show a systematic increase in the rates of 3_A₂g(F)→3_T₂g(F), 3_A₂g(F)→3_T₁g(F), and 3_A₂g(F)→3_T₁g(F) transitions corresponding to the Ni²⁺ cations in an octahedral ligand field while the molar absorption coefficient of the 3_A₂g(F)→3_T₁g(F) transition sharply decreases from 23 to 10 l·mol/cm. This implies that the H₂O molecules are coordinated directly to the cations displacing the POO oxygen atoms from the first coordination sphere. At n = 2+6 the first coordination sphere of Ni²⁺ is successively filled with water molecules while the POO-groups are all displaced into the second sphere, each POO group being connected to the H₂O molecules through hydrogen bonds (HB). At n=6+11 the number of water molecules in the outer sphere of Ni²⁺ gradually increases and they concentrate in the center of the micelle. Thus, the micelle structure consists of a core of H₂O molecules bonded to each other through HB's, which is surrounded by a shell of
rated molecules Ni(H$_2$O)$_6^{2+}$ and a next shell of POO-groups attached through HB's to the protons of the water molecules. Owing to such a structure, the micelle molecule is able to capture CoX$_2$ molecules when (II) is present in the aqueous phase of the extraction system. At NiX$_2$/CoX$_2$ molar ratios almost all of the cobalt enters the micelles where it acquires an octahedral environment whereas the absence of Ni$^{2+}$ the tetrahedral forms (CoX$_2$)$_p$ remain unhydrated.

Hydration of alkali metal salts gives rise to inverse micelles similar to (NiX$_2$·11H$_2$O)$_p$. Hydration of alkaline metal salts decreases in a series: BaX$_2$ (inverse micelles) < CaX$_2$ < MgX$_2$ (no hydration).

Acid salts. When HX is added to solutions of ZnX$_2$ and CoX$_2$ its molecules first coordinate to the terminal III$_1$ and III$_2$ groups of the near (MX$_2$)$_p$ polymers producing non-equivalent acid groups V$_1$ and V$_2$.

\[
\begin{align*}
V_1: & \quad O=\vdash=O \\
V_2: & \quad O=\vdash=P=O \\
V_3: & \quad M=O=O=M
\end{align*}
\]

with the polymerization degree of the (MX$_2$)$_p$ oligomers remaining unchanged and only a large excess of HX results in HX coordination to a middle (bridging) POO-groups of the polymer, a process which leads, the end, to complete monomerization and formation of coordinatively unhydrated M(HX$_2$)$_2$ molecules with two V$_1$ groups which are incapable of coordinating water.

Acid salt polymers MX$_2$(HX$_2$)$_2$ (M= Zr, Hf) in decane contain, in the absence of an excess of HX, a large number of non-equivalent POO-cups of which types II, III$_1$, IV, V$_1$, V$_2$ were identified [4].

In the real extraction systems with D2EHPA all of the above processes occur simultaneously. The equations such as

\[
M^{2+} \text{(aq)} + 2HX_2 \text{(o)} \rightleftharpoons M(HX_2)_2 \text{(o)} + 2H^+ \text{(aq)}
\]

ten used to describe the ion exchange equilibria in such systems are certainly too simplified. In many cases the extraction selectivity is terminated by factors not included in these equations. For example, the increasing temperature the octahedral hydration environment of 2$^+$ becomes unstable preventing the cation from entering into the xed micelles which leads to a considerable improvement of the separation factor for Co/Ni.

**Extraction with D2EHPA salts.** Solutions of CuX$_2$ in CCl$_4$, C$_6$H$_5$, and C$_6$H$_{14}$ extract chlorides and bromides of alkali metals and NH$_4^+$ [5] and also BaCl$_2$ and CuX$_2$ from their aqueous solutions by an acceptor mechanism to form complexes MA (M = K, Rb, Cs, NH$_4^+$) and [M(H$_2$O)$_m$H$^+A^-$]$_n$ (M = Na, Ba, Cu) where A$^-$ is the complex anion [(CuX$_2$)$_4$Hal]$^-$, Hal = Cl, Br. Such a mechanism is possible due to the presence in the extracting solvent of the metal cation (Cu$^{2+}$) - an electron acceptor. The structure
of $A^-$ was established by IR and EXAFS spectroscopy. The halogenide-ion lies in the center of a tetrahedron of 4 copper atoms to which it is bonded by weak Cu-Hal bonds. In scheme A the curved lines represent bidentate bridging POO groups and each second acid residue is conventionally shown as a tridentate one since one of its two POO groups is coordinated to Cu$^{2+}$. Scheme B shows the coordination environment of Cu$^{2+}$.

The MA salts form in organic solvents contacting and solvate-separated ionic pairs whereas in the $M(H_2O)_mA^-$ salts the first coordination sphere of the $M^{n+}$ cations is completely filled with water molecules attached to the POO groups of $A^-$ through HB's.

The acid salts $M_{x2}(H_2X_2)(M = Zr,Hf)$ extract much better than $HX$ itself, $HNO_3$, Fe$^{3+}$, Eu$^{3+}$, and Sc$^{3+}$ from nitrate media /4/. The extraction of $HNO_3$ with the salts of Zr(IV) and Hf(IV) proceeds by the acceptor mechanism according to the equilibrium

$$M_{x2}(H_2X_2) + HNO_3 \rightleftharpoons M_{x2}(H_2X_2)HNO_3$$

and only at high $C_{HNO_3}$ values its extraction also takes the usual coordination path involving addition of $HNO_3$ through a proton to the P=O groups of the $M_{x2}(H_2X_2)$ salts.

$Hf_{x2}(H_2X_2)$ solutions extract Fe(III) from solutions with $C_{HNO_3} = 0.01-6$ mol/l in the form of complex cations $FeNO_3^{2+}$ and $Fe_2(NO_3)_4^{2+}$ (by cation exchange mechanism) and neutral dimer $Fe_2(NO_3)_6$. The extraction of Fe(III) with acid di(2-ethylhexyl)phosphate of Zr(IV) is somewhat different. The extracted species are $Fe(NO_3)_2^{2+}$ and $Fe_2(NO_3)_6^{2+}$.

The structure of these forms was established. The salts of Zr(IV) and Hf(IV) extract Eu(III) as $Eu(NO_3)_2^{2+}$ and $Eu(NO_3)_2^{2+}$.

Thus in the extraction with D2EHPA it should be taken into account that the cation exchange extraction products may themselves act further as extracting agents. There are reasons to believe that the coordination chemistry of systems with D2EHPA is in many respects similar to that of the systems with phosphinic and phosphonic acids.

References