Spectroscopy of Ni(II) and Pt(II) complexes in carbamide and carbamide-halide melts

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In the present study, the composition and structure of Ni(II) and Pt(II) compounds have been investigated, using electronic absorption spectroscopy and IR spectroscopy, at chemical (C = 0.005 - 0.07 mol/l) and electrochemical (j = 5 - 50 mA/cm^2) dissolution of these metals in $CO(NH_2)_2$ and $CO(NH_2)_2$ - NH_4X (16 mol %), where X = Cl, Br, F.

In the case of chemical and electrochemical (anodic) dissolution of nickel in molten carbamide, electronic absorption spectra (EAS) exhibit bands at 25100 (25200), 15000 (15700) and 12900 (13000) cm^{-1} respectively, which are characteristic of octahedral chromophores $[NiL_6]$ and correspond to the transitions: $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^1E_g$.

In molten carbamide, Ni(II) ions form complexes $[Ni(CO(NH_2)_2)_6]^{2+}$ of O_h symmetry (10Dq = 9000 cm^{-1}, B = 820 cm^{-1}, β = 0.79). In the case of anodic dissolution of metallic nickel in a carbamide melt, isocyanate complexes $[Ni(NCO)_6]^{4-}$ of O_h symmetry (10Dq = 9900 cm^{-1}, B = 740 cm^{-1}, β = 0.71) are formed. The formation of isocyanate complexes has been confirmed by IR spectroscopic data (these are the vibration frequencies of NCO groups in a particular complex: ν_{as}(NCO) = 2200, ν_s(NCO) = 1360, δ = 630 cm^{-1}).

In the case of chemical (anodic) dissolution of nickel(II) in carbamide-halide melts, EAS's exhibit bands at 25000 (24900), 14900 (14900) and 13000 (13100) cm^{-1}. In carbamide-halide melts are formed octahedral carbamide complexes $[Ni(CO(NH_2)_2)_6]^{2+}$ of O_h symmetry with coordination of carbamide molecules through the nitrogen atom.

When $(NH_4)_2[PtCl_4]$ is dissolved in a carbamide melt and in carbamide-halide melts, square-planar complexes $[Pt(NH_3)_4]^{2+}$ of D_{4h} symmetry are formed. In EAS a band with the maximum at 35000 cm^{-1} has been found, which may be assigned to the transition $^1A_{1g} \rightarrow {}^1A_{2g}$. Ammonia complexes of Pt(II) are formed in a carbamide melt according to the scheme:
$(NH_4)_2[PtCl_4] + 4\ CO(NH_2)_2 = [Pt(NH_3)_4]Cl_2 + 2\ NH_4Cl + 4\ HCNO$.

In the case of anodic dissolution of platinum in a carbamide-fluoride melt, a band at 35000 cm^{-1} has also been revealed in EAS, which characterizes the formation of ammonia complexes $[Pt(NH_3)_4]^{2+}$ of D_{4h} symmetry.

In the case of anodic dissolution of platinum in carbamide-chloride (bromide) melts, the bands observed in EAS's characterise the formation of platinum complexes $[Pt(NH_3)X_3]^-$ of D_{2d} symmetry (where X = Cl, Br) and may be assigned to the transitions: 34000 (33000) cm^{-1} - $^1A_1 \rightarrow {}^1E$; 28700 (26900) cm^{-1} - $^1A_1 \rightarrow {}^1A_2$; 24000 (23000) cm^{-1} - $^1A_1 \rightarrow {}^3A_2$; 21000 (-) cm^{-1} - $^1A_1 \rightarrow {}^3B_1$; 19000 (19000) cm^{-1} - $^1A_1 \rightarrow {}^3E$. The spectroscopic parameters of the electronic structure for the complexes $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Br_3]^-$ formed are respectively: 10Dq = 31000 (29000) cm^{-1}, B = 500 (420) cm^{-1}, β = 0.83 (0.70). The incorporation of the NH_3 ligand into complex leads to a distortion of the square-planar configuration, which is characteristic of Pt(II) complexes, to D_{2d} symmetry. It is for such $[Pt(NH_3)X_3]^-$ complexes that three faint bands and two much more intense bands are observed, which relate to spin-forbidden and spin-allowed transitions respectively.

The regularities found of Ni(II) and Pt(II) complexes formation in ionic-organic molten electrolytes will make it possible to effectively control electrochemical processes in them.

References

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