^{13}C CP/MAS NMR Study of Motion and Local Structure of Phenethylammonium Ion in $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I)

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Ionic motion and local structure of phenethylammonium ion ($C_6H_5CH_2CH_2NH_3^+$) in a series of phenethylammonium lead(II) halides, $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I) were studied by means of ^{13}C cross polarization/magic angle sample spinning (CP/MAS) NMR technique. Among the three salts, remarkable differences in the spectra were observed in the signals corresponding to the phenyl carbons. The peaks from C2, C3, C5, and C6 in the phenyl group were split into three for the chloride and into two for the bromide, although in the iodide those were observed as a single peak. Coalescence of those peaks, as well as line broadening were observed on heating. This indicated that peak split brings about disorder of the orientation in the phenyl group around the C1-C4 axis, suggesting to have three and two orientations for the chloride and the bromide, respectively. Above room temperature the phenyl group undergoes chemical exchange among these orientations, and at higher temperature, reorientation with a large amplitude takes place around its axis. The apparent activation energies of the reorientation of the phenyl group for the chloride and bromide were estimated from the temperature dependence of the linewidth of the resonance peaks to be about 24 kJ mol^{-1}, 25 kJ mol^{-1}, respectively, which is similar to in the iodide (25.0 kJ mol^{-1}). Ab initio molecular orbital energy calculation was carried out to evaluate the potential barrier of the internal rotation of the phenyl group in a free phenethylammonium ion. The intramolecular interaction was evaluated to be 13.9 kJ mol^{-1} from the calculation, and the intermolecular interaction results to be 10 kJ mol^{-1}.

Key words: ^{13}C CP/MAS NMR; Layered compound; Disorder; Reorientation; Activation energy.

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