Low-frequency Raman Spectroscopy of Aqueous Solutions of Aliphatic Alcohols

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Low-frequency Raman spectra have been measured at room temperature as functions of the alcohol mole fraction in aqueous solutions of methanol, ethanol, 1-propanol, 2-propanol, and *tert*-butylalcohol (TBA). Intrinsic Raman spectra $R(\bar{\nu})$ were obtained from depolarized Rayleigh wing spectra. Isosbestic points have been observed in $R(\bar{\nu})$ of the aqueous solutions of ethanol, 1-propanol, and 2-propanol, suggesting that the structure of the solutions is characterized by individual alcohol aggregates and water clusters without a significant amount of alcohol-water mixed aggregates. The $R(\bar{\nu})$ spectra have been expressed as $R(\bar{\nu}, x) = wR(\bar{\nu}, 0) + aR(\bar{\nu}, 1)$, where $R(\bar{\nu}, 0)$ and $R(\bar{\nu}, 1)$ are those for pure water and pure alcohols, respectively, and x is the mole fraction of alcohols. The coefficients w and a show the inflection points at characteristic alcohol mole fractions, where microhetrogeneity and structural transition of the solvent clusters take place, as previously shown by X-ray diffraction. In the aqueous solutions of methanol, where no microhetrogeneity takes place, no clear isosbestic point in $R(\bar{\nu})$ has been observed. For aqueous solutions of TBA, an isosbestic point in $R(\bar{\nu})$ has appeared when $x_{\mathrm{TBA}} > 0.05$. Two inflections points in the coefficients have been observed at $x_{\mathrm{TBA}} \approx 0.1$ and 0.35; the former composition corresponds to the transition composition from the TBA-TBA intermolecular contact to the TBA-water molecular association, as previously reported by neutron diffraction.

Key words: Low Frequency Raman Spectroscopy; Liquid Structure; Alcohol-water Mixture.