



ABSTRACT

In this work, we examined the polarized Raman characteristics of C=O stretching modes of ethyl (EA), butyl (BA), and amyl acetates (AA), which are widely used as solvents in industry. The isotropic and anisotropic spectral bands of these liquids in their neat condition were recorded in the experiment. The concentration dependence of the Raman non-coincidence effect (NCE) of the C=O stretching bands of acetates is investigated in acetates/CCl<sub>4</sub> mixtures. The results in these binary mixtures were compared with the theoretical model of the Onsager-Fröhlich dielectric continuum model. In this work, we have provided the data necessary to understand the non-covalent interactions in EA, BA, and AA dimer clusters. Initially, the ABCluster code, which performs global optimization, was used to generate the global minima structures of acetates dimer clusters. In addition, intermolecular interactions in dimer clusters of these liquids were studied using various topological (NCI, RDG).

METHODS

Polarized Raman spectra of neat and at the various concentration solutions of ethyl, butyl, and amyl acetates were recorded at room temperature using a Renishaw inVia Raman spectrometer. The geometric structures of molecular complexes in solutions were optimized based on the set of DFT:B3LYP/6-311++G(d,p) functions in the Gaussian 09W program. Topological analyzes were carried out in Multiwfn and VMD software.

RESULTS

Figure 1. Polarized Raman spectra of C=O stretching modes of EA, BA, and AA

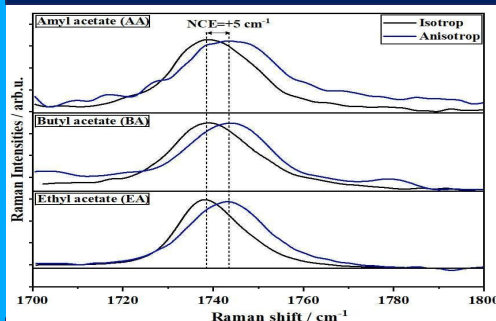


Figure 2. Computation polarized Raman spectra of C=O stretching modes of EA, BA, and AA

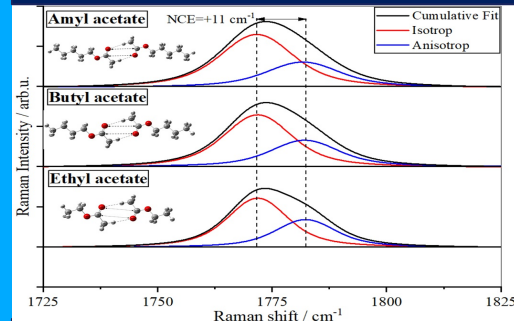


Figure 3. Dipole-dipole orientation of EA, BA, and AA dimer clusters

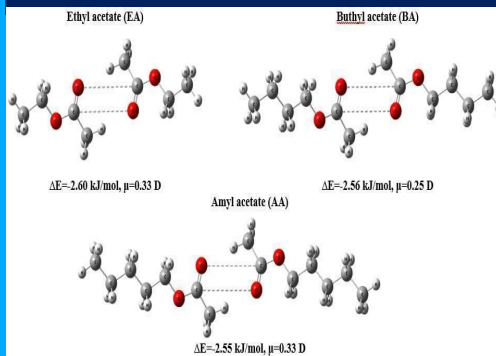


Figure 4. NCI and RDG maps of EA, BA, and AA

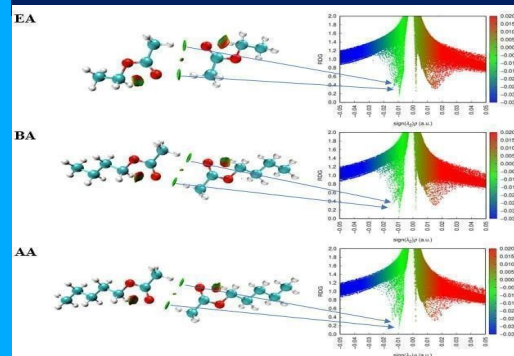


Figure 5. Polarized Raman spectra of C=O stretching modes of acetates/CCl<sub>4</sub> binary mixtures

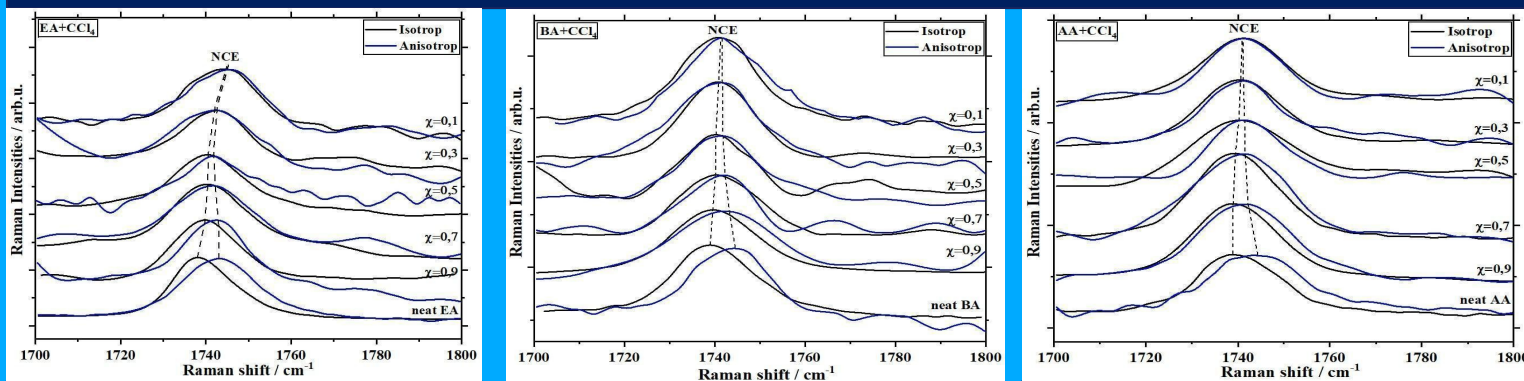


Figure 6. Variation of the quantity F as a function of solute concentration in solvent

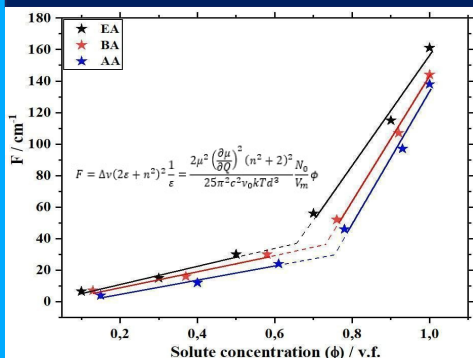


Table 7. Variation of the quantity F as a function of solute concentration in solvent

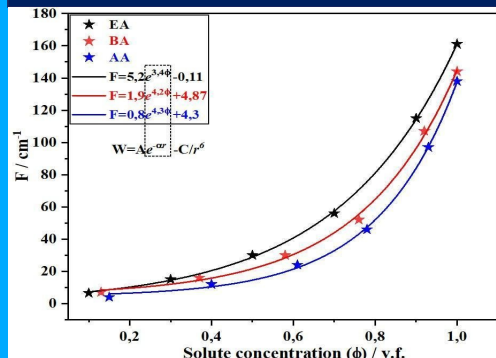
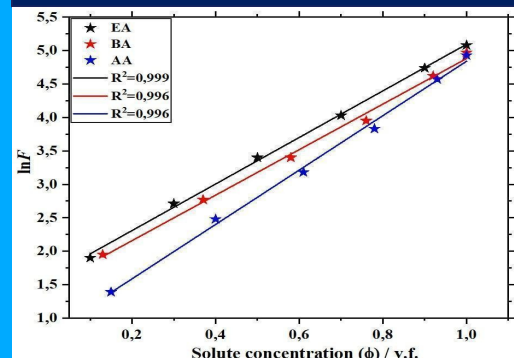


Figure 8. Variation of lnF as a function of solute concentration in solvent



CONCLUSIONS

The C=O stretching modes of EA, BA, and AA were found to have the same +5 cm<sup>-1</sup> Raman NCE. From this result, it can be predicted that EA, BA, and AA have almost similar molecular orientation, and as a result, they form the same dipole-dipole resonance couples. DFT analysis confirmed this conclusion. The concentration dependence of the Raman NCE of the C=O stretching modes is investigated in acetates/CCl<sub>4</sub> mixtures. It was observed that the value of NCE decreases as the fraction of solvent in the solution increases. The results in these binary mixtures were compared with the theoretical model of the Onsager-Fröhlich dielectric continuum model. A break from linearity was observed in the interval [0.5;0.7] in the dependence graph of F on φ. The dependence function of F on φ has an exponential character. This model showed that repulsive forces play an important role in acetates/CCl<sub>4</sub> mixtures.