

Infrared Spectroscopy of Liquid Water-*N,N*-dimethylformamide Mixtures

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The imaginary molar polarisability spectra, $\alpha_m''(\tilde{\nu})$, of mixtures of water with *N,N*-dimethylformamide (DMF) over the entire composition range ($0 \leq x_{DMF} \leq 1$) at 25 °C were obtained between 4000 and 700 cm^{-1} by use of calibrated multiple reflection attenuated total reflection (ATR) technique [1]. The composition dependent molar fractions of water bonded and DMF bonded OH groups, together with water bonded and free carbonyl groups, were determined from the integral intensities C_{OH} , C_{CO} , C_{NCO} , the areas under the $\nu(OH)$, $\nu(CO)$ and $\delta(NCO)$ bands, respectively, in the $\tilde{\nu}\alpha_m''(\tilde{\nu})$ spectra. The obtained results are compared with thermodynamic properties of the system [2], and with results of molecular dynamics simulations [3, 4].

Behaviour of molar fraction of OH species indicates presence of stable aggregates of H₂O molecules over the large composition interval, $0.2 < x_{DMF} < 0.9$. Aggregates of DMF, in which methyl groups are placed apart from surrounding water, are established in the interval $x_{DMF} < 0.2$. For higher x_{DMF} , DMF molecules orient in random orientation, giving rise to dipole-dipole pairs. Only in the interval $x_{DMF} > 0.9$ water is dispersed into small clusters of water surrounded by DMF molecules.

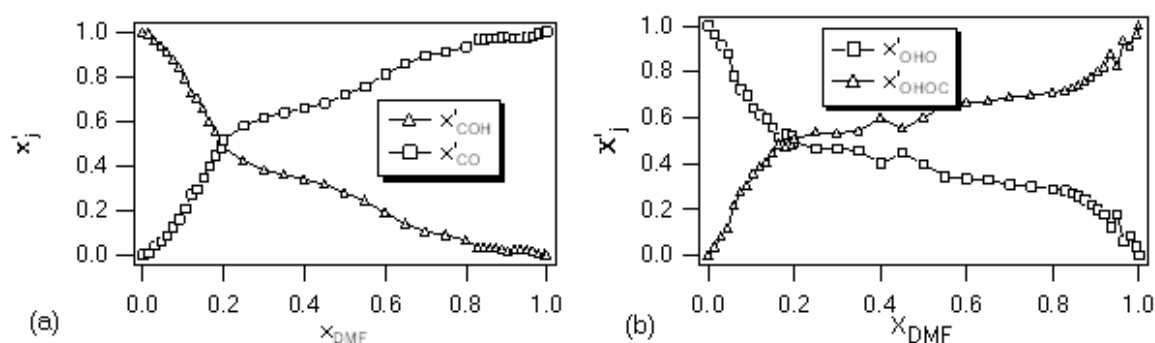


Fig. 1: (a) Fraction of DMF CO oscillators which are free, x'_{CO} , and hydrogen bonded with water molecule, x'_{COH} , against molar fraction of DMF, x_{DMF} . (b) Fraction of water OH oscillators which are hydrogen bonded with another water molecule, x'_{OHO} , and with DMF, x'_{OHOC} , against molar fraction of DMF, x_{DMF} .

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