Structure of Clusters in Methanol-Water Binary Solutions Studied by Mass Spectrometry and X-ray Diffraction

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The structure of clusters in methanol-water solutions in its dependence on the methanol mole fraction x_M has been investigated by mass spectrometry on clusters isolated from submicron droplets by adiabatic expansion in vacuum and by X-ray diffraction on the bulk binary solutions. The mass spectra have shown that the average hydration number, $\langle n_m \rangle$, of m-mer methanol clusters decreases with increasing x_M, accompanied by two inflection points at $x_M = \sim 0.3$ and ~ 0.7. The X-ray diffraction data have revealed a similar change in the number of hydrogen bonds per water and/or methanol oxygen atom at ~ 2.8 Å. On the basis of both results, most likely models of clusters formed in the binary solutions are proposed: at $0 < x_M < 0.3$ the tetrahedral-like water cluster is the main species, at $0.3 < x_M < 0.7$ chain clusters of methanol molecules gradually evolve with increasing methanol content, and finally, at $x_M > 0.7$ chain clusters of methanol molecules become predominant. The present results are compared with clusters previously found in ethanol-water binary solutions and discussed in relation to anomalies of the heat of mixing of methanol-water binary solutions.

Key words: Methanol-water Binary Solutions; Mass Spectrometry; X-ray Diffraction; Clusters; Hydrogen Bonds.