

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

Toshiyuki Takamuku, Toshio Yamaguchi<sup>a</sup>, Masaki Asato<sup>b</sup>, Masaki Matsumoto<sup>b</sup>, and Nobuyuki Nishi<sup>c</sup>

Department of Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi, Saga 840-8502, Japan

<sup>a</sup> Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan

<sup>b</sup> Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

<sup>c</sup> Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Reprint requests to Prof. T. Y.; Fax: +81-92-865-6030;

E-mail: yamaguch@sunsp1.sc.fukuoka-u.ac.jp

Z. Naturforsch. **55 a**, 513–525 (2000); received February 11, 2000

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  $\sim 0.7$ . The X-ray diffraction data have revealed a similar change in the number of hydrogen bonds per water and/or methanol oxygen atom at  $\sim 2.8 \text{ \AA}$ . 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.