Water-Ethanol Clusters at the Liquid Surface under Atmospheric Pressure Observed by Liquid Ionization Mass Spectrometry

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By controlling the flow rate of a sample solution, information about clusters existing at the liquid surface were obtained by liquid ionization (LI) mass spectrometry. The relative abundances of binary cluster ions, $(C_2H_5OH)_m(H_2O)_nH^+$, with large m and n increased with the flow rate, while the abundances of ethanol cluster ions, $(C_2H_5OH)_mH^+$, increased by decreasing the flow rate. Molar ratios of water to ethanol observed were much higher than those observed by other methods.

Studies of hydrogen bonded clusters are important for understanding differences in properties of compounds between the gas and liquid phases. [1,2] Water-ethanol clusters are one of the most interesting clusters, because of existing in various kinds of alcoholic liquors and having a sterilizing power. Water-ethanol clusters have been studied by mass spectrometry with several techniques, such as supersonic beam techniques[3] and adiabatic expansion of liquid jet. [4,5] In those mass spectra, however, the molar ratios of water to ethanol observed were too small, compared with those calculated from their concentrations, probably because the measurements have been carried out in a vacuum.

Liquid ionization (LI) mass spectrometry, [6-8] in which a liquid sample is ionized by collision with excited argon atoms under atmospheric pressure, was applied to investigate clusters in water-ethanol mixture and various kinds of alcoholic liquors. The instrument used was a quadrupole mass spectrometer (Extrel EXM 2000) equipped with the LI ion source. A syringe pump[8] was used to supply a sample solution constantly onto the sample holder (needle tip). The size distribution of cluster ions observed is dependent on several experimental conditions. The conditions for soft ionization were found to be adequate for measuring clusters, i.e., needle voltage (V_E): 1.35 kV, pinhole voltage: 25 V, and voltage of skimmer-1: 10 V. Temperature of samples in this paper were ambient (ca. 25 °C). It was found that the flow rate of the sample solution was very important parameter. By varying the flow rate from 0.2 to 2.0 μl/min, information about liquid surface was obtained. Each mass spectrum between m/z 10 and 600 or 800 was scanned in 2 s and recorded repeatedly about 20 times using a personal computer (NEC 9801BX) as a data system.

All cluster ions observed in LI mass spectra were represented as $(C_2H_5OH)_m(H_2O)_nH^+$ (referred to as m-n) as shown in Figures 1 and 2 for a 38% (by volume) ethanol aqueous solution, obtained with different sample flow rates. Each mass spectrum is an average of 20 mass spectra successively recorded. Pure ethanol cluster ions (n=0) were observed with m less than 6 and varied their abundances according to the flow rate. Figure 3 shows the influence of the sample flow rate on the abundances of main cluster ions, although a value "p/scan" was used in stead of the flow rate. The p/scan means the base peak intensity averaged for each scan. By decreasing the flow rate, the p/scan values and the abundances of ethanol cluster ions (2-0 ~ 5-0) increased. In contrast, the relative abundances of binary cluster ions (e.g., 6-8 and 7-14) increased with the flow rate (=decreased with the p/scan). Mass spectra with the p/scan values of 200~300 resembled each other.

The voltage applied to the needle (V_E) has three important functions. [6,8] One of them is to remove electrons. Since the recombination of a positive ion and an electron produced by

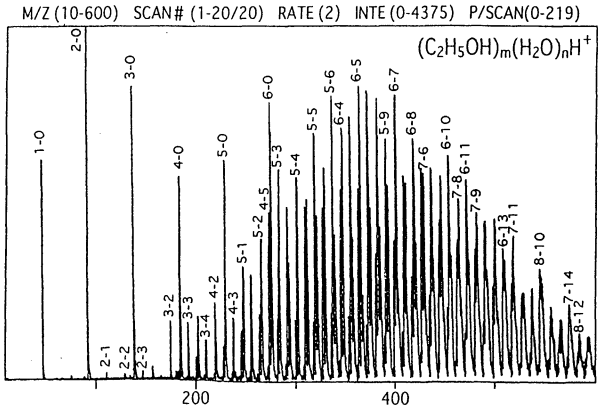

Figure 1. Liquid ionization (LI) mass spectrum of 38% (v/v) ethanol aqueous solution measured at the sample flow rate of 1.3 μl/min.

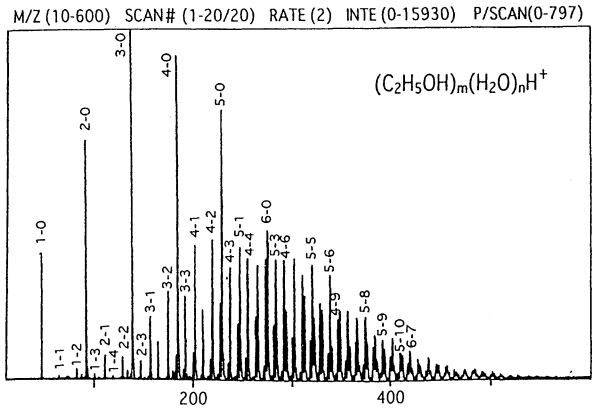

Figure 2. LI mass spectrum of 38% (v/v) ethanol aqueous solution measured at the sample flow rate of 0.5 μl/min.

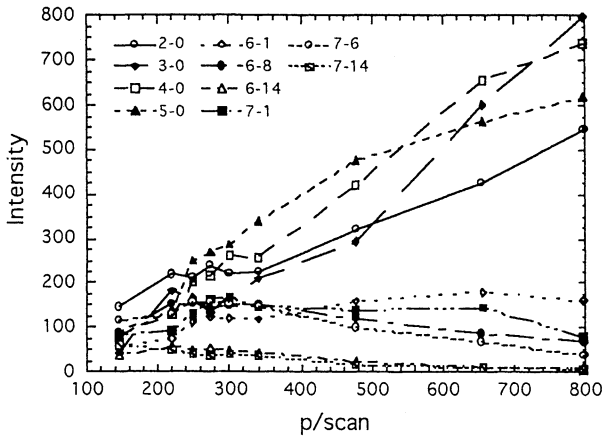

Figure 3. Influence of the sample flow rate (p/scan are used, in stead) on the abundances of main cluster ions.

Penning ionization is very rapid under atmospheric pressure, [9] no ions were observed without V_E. When the flow rate was high and the liquid layer on the needle tip became too thick, no ion was observed (p/scan = 0), because the effective electric field (V_{eff}), which is neccessary to capture electrons, could not reach to the liquid surface. By decreasing the flow rate, the liquid layer became thinner and the V_{eff} could reach above the liquid surface as shown in Figure 4, and then, cluster ions were observed.

Larger cluster ions (larger n and m) were observed with the smaller p/scan values, because the liquid layer was adequately thick to observe the cluster ions produced near to the liquid surface. Figure 1 was obtained with the flow rate of 1.3 μl/min. By decreasing the flow rate further, the thickness of the liquid layer became thinner and V_{eff} reached to the place far from the liquid surface. Then, the abundances of pure ethanol cluster ions (n=0) increased with p/scan values. Figure 2 was obtained when the flow rate was as low as 0.5 μl/min. As seen in Figure 3, the increases of ion abundances were observed mainly for pure ethanol cluster ions. Since vapor pressure of ethanol is higher than that of water, it is reasonable that pure ethanol cluster ions are more abundant at the place far from the liquid surface. It is interesting to note that the increase in abundance of cluster ions containing only one water molecule (e.g., 6-1) was much slower than those of pure ethanol cluster ions.

The molar ratio of water to ethanol calculated from the mass spectrum of 43% ethanol aqueous solution observed by liquid jet technique [5] has been less than 0.4 / 1, which is less than one tenth of the value calculated from its concentration (molar ratio is 4.5 / 1). The molar ratios of water to ethanol calculated from LI mass spectra for the 38% ethanol solution shown in Figures 1 and 2 were 1.3 / 1 and 1 / 1, respectively (molar ratio in the solution is 5.3 / 1). The mass spectrum shown in Figure 1 is likely to represent the size distribution of clusters existing closer to the liquid surface compared with that shown in Figure 2.

The highest molar ratio observed so far was 2.8 / 1 with the p/scan of 65. LI mass spectra of these mixtures and alcoholic liquors indicated that a sample with higher ethanol concentration gave the cluster ions with larger m more abundantly, and one with lower ethanol concentration gave the binary cluster ions

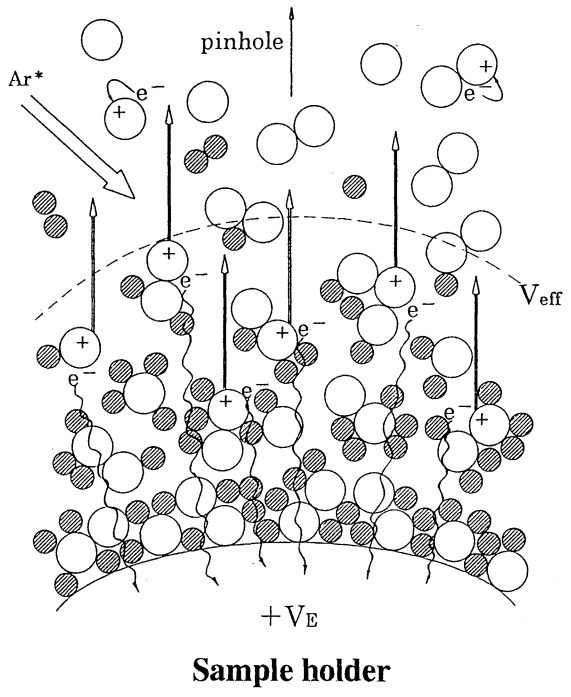

Figure 4. Schematic illustration for mechanisms of ionization, recombination and ion desorption. ⇧: Direction to which ions move. ○: ethanol molecule, ⊘ : water molecule.

with larger n more abundantly.

Although LI mass spectral patterns are dependent on experimental conditions, it is likely that the value "p/scan" can be used as an adequate index for indicating the place where the ionization of clusters take places. LI mass spectra with small p/scan values suggest the size distribution of neutral clusters existing at the liquid surface (nearer to the liquid, compared with other methods), although the distribution of cluster ions observed might be somewhat different from that of neutral clusters. Such difference, however, is thought to be small for large clusters.

References

1 A.W.Castleman and R.G.Keese,*Chem. Rev.*, **86**, 589 (1986).
2 J.F.Garvey, W.J.Herron, and G.Vaidyanathan, *Chem. Rev.*, **94**, 1999 (1994)
3 J.Q.Searcy and J.B.Fenn, *J. Chem. Phys.*, **61**, 5282 (1974).
4 N.Nishi, and K.Yamamoto, *J. Am. Chem. Soc.*, **109**, 7353 (1987).
5 N.Nishi, K.Koga, C.Ohshima, K.Yamamoto, U.Nagashima, and K.Nagami, *J. Am. Chem. Soc.*, **110**, 7353 (1988).
6 M.Tsuchiya and H.Kuwabara, *Anal Chem.*, **56**, 14 (1984).
7 M.Tsuchiya, S.Teshima, T.Kaneko, and T.Hirano, *Nihon Kagaku Kaishi*, **1993**, 687.
8 M.Tsuchiya, "Advances in Mass Spectrometry, Volume 13" ed by I.Cornides, Gy.Horvath, K.Vekey, John Wiley (1995) p. 333.
9 D.A.Armstrong, *Radiat. Phys. Chem.*, **20**, 75 (1982).