LOW TEMPERATURE SECONDARY ION MASS SPECTROMETRIC STUDY OF MIXTURES OF PRIMARY ALCOHOLS

M.V. Kosevich[1], V.S. Shelkovsky[1], O.A. Boryak[1], V.V. Orlov[1], A. Gömöry[2], K. Vekey [2]

[1] B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47, Nauky Ave., 61103, Kharkiv, Ukraine, e-mail: kosevich@igmail.com

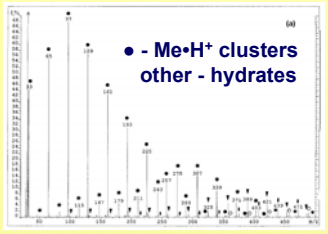
[2] Institute of Organic Chemistry of HUN-REN Research Centre for Natural Sciences, Budapest, H-1117, Hungary

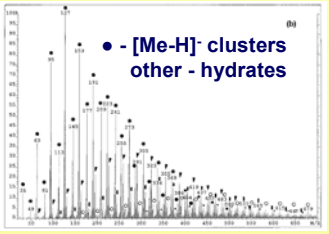
Background: Cooling of volatile primary alcohols permits to keep them in the liquid state under vacuum conditions. Due to this, sputtering of the liquid phase of alcohols becomes possible under Low Temperature (LT) fast atom bombardment (FAB) and secondary ion mass spectrometry (SIMS). Earlier we applied LT FAB/SIMS to individual alcohols methanol (Me) and ethanol (Et) [1, 2], as well as propanol (Pr) and butanol.

AIM: to investigate temperature dependences of the LT SIMS mass spectra of mixtures of primary alcohols methanol : ethanol : propanol

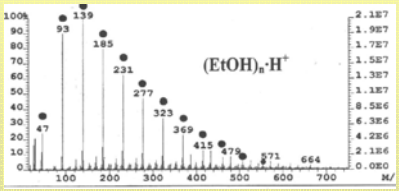
Spoiler: fractioning of alcohols on the heating of the liquid mixture

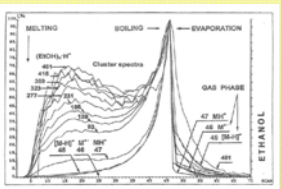
Previous results: Sputtering of sets of clusters both in the positive and negative ion modes, such as $Me_n \bullet H^+$, $Et_n \bullet H^+$, $[Me_n\text{-}H]^-$, $[Et_n\text{-}H]^-$ (n up to 30), was observed.





[1] M.V. Kosevich, G. Czira, O.A. Boryak, V.S. Shelkovsky, K. Vekey, Comparison of positive and negative ion clusters of methanol and ethanol observed by low temperature secondary ion mass spectrometry // *Rapid Commun. Mass Spectrom.*, **1997**, 11, pp. 1411-1416.





[2] M.V. Kosevich, G. Czira, O.A. Boryak, V.S. Shelkovsky, K. Vekey, Temperature dependences of ion currents of alcohol clusters under low-temperature secondary mass spectrometric conditions // *J. Mass Spectrom.*, **1998**, 33, pp. 843-849.

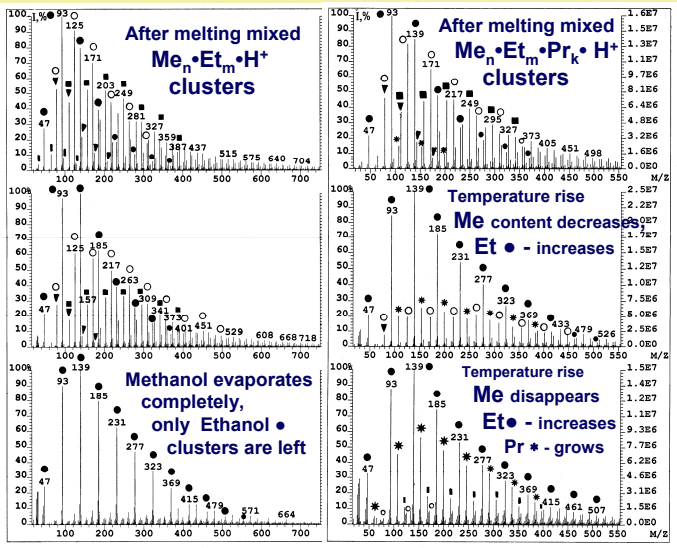
Temperature dependences of ion currents were obtained in the temperature range of the liquid phase existence from melting of the solid to completion of liquid evaporation.

Experimental details: a drop of alcohols mixture of about 5 μL was frozen down to liquid nitrogen temperature on steel sample holder and subjected to spontaneous thawing in the ion source. Secondary ions were produced due to sample sputtering by Cs^+ ions of 15 keV energy. The spectra were recorded in the 10-1000 Da mass range at a rate of 5 seconds per scan. SIMS measurements were performed on ZAB-SEQ mass spectrometer (Micromass, Manchester, UK).

SIMS of ALCOHOL MIXTURES

Reference data show that the volatility of primary alcohols decreases in the row Me>Et>Pr, which permits observation of fractioning of alcohols on the heating of the liquid mixture.

Methanol : Ethanol **Methanol : Ethanol : Propanol**



LT SIMS mass spectra are recorded on spontaneous warming of the liquid samples.

$(E_n \bullet M_m \bullet P_k \bullet H^+)$ are marked as: $E_n \bullet H^+$ (●), $E \bullet M_m \bullet H^+$ (▼), $E_n \bullet M \bullet H^+$ (○), $E_n \bullet M_2 \bullet H^+$ (■), $E_n \bullet P \bullet H^+$ (✱), $E_n \bullet P_2 \bullet H^+$ (▮).

Indeed, on gradual increase of the temperature of the liquid mixtures (starting from 135 K) the related changes in mass spectral pattern were observed. Mixed clusters incorporating molecules of all alcohols present in a sample are recorded right after the melting of initially solid frozen samples. In the case of binary methanol: ethanol mixture a variety of mixed clusters $Me_n \bullet Et_m \bullet H^+$ was gradually substituted by the ethanol-dominated clusters (m>n) in the course of methanol evaporation, finishing with pure ethanol $Et_n \bullet H^+$ cluster set. In the case of triple methanol:ethanol:propanol mixture, sets of $Me_n \bullet Et_m \bullet Pr_k \bullet H^+$ clusters with varied n:m:k ratios were recorded at the stage of appearance of the liquid phase. However, the most abundant sets contained mainly methanol and ethanol components: $Me \bullet Et_n \bullet H^+$, $Me_2 \bullet Et_n \bullet H^+$. Evaporation of methanol on temperature increase led to redistribution of abundances in favour of $Et_n \bullet H^+$ clusters and suppression of methanol-containing clusters. On further temperature increase evaporation of ethanol led to liquid enrichment by less volatile propanol, reflected in the growth of $Et_m \bullet Pr \bullet H^+$, $Et_m \bullet Pr_2 \bullet H^+$ sets. Thus, it is possible to monitor fractionation of alcohol mixtures under low temperature and low pressure conditions by means of LT SIMS.

The data obtained may be useful for model studies of space-related systems. In particular, a possibility of formation of liquid organic on space dust is to be accounted.

XXVIth Galyna Puchkovska International School Seminar "Spectroscopy of Molecules and Crystals" (ISSSMC-2024) September 22-25, 2024, Wojanow, Poland