

Temperature Dependences of Ion Currents of Alcohol Clusters Under Low-temperature Secondary Ion Mass Spectrometric Conditions

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The dependences of ion currents on temperature (ion thermograms) obtained by monitoring the abundance of different types of ions during the thawing of frozen samples of methanol and ethanol in low-temperature secondary ion mass spectrometry revealed special features in the temperature behaviour of the samples. Correlations between the changes in ion production and phase transitions (melting, boiling, evaporation) in the sample with temperature increase were revealed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: secondary ion mass spectrometry; low temperature; methanol; ethanol; clusters

INTRODUCTION

In a number of previous studies on low-temperature (LT) fast atom bombardment (FAB) and secondary ion mass spectrometry (SIMS) of organic solvents (such as methanol,^{1,2} ethanol,^{2–4} propanol,³ glycerol^{5,6} and ethylene glycol⁵) and aqueous solutions,^{6,7} a strong dependence of the spectra on the temperature of the sample was revealed. In contrast to ambient temperature FAB/SIMS, under which samples usually exist in the same physical state (solid or liquid) in the course of the whole experiment, phase transitions in the sample can be monitored over almost a 200 °C temperature range utilizing liquid nitrogen as a cooling agent. Under fixed ambient conditions the main changes in the spectra with time, if any, are connected with chemical (spontaneous or beam-induced) reactions, whereas the spectral transformations in the LT experiments are caused mainly by the changes in the physical state of the sample.

One of the main features of the LT FAB/SIMS technique is the production of relatively large sets of cluster ions (in a definite temperature range, characteristic for each particular sample). Comparison of the temperature behaviour of different types of clusters may give information on the nature of the physical processes in the sample. To provide a quantitative evaluation of the

spectra, a new approach to monitoring the temperature dependence of ion currents (so-called ion thermograms) of different types of ions present in the LT FAB/SIMS spectra is suggested. As an example, methanol and ethanol samples with a slight admixture of water (due to the hygroscopicity of the alcohols) were studied and conclusions concerning phase transitions in the samples during the process of thawing and also mechanisms of ion formation under LT SIMS were made. This method allowed us to reveal fine features of the quantitative changes in the cluster distribution of the two alcohols with temperature, which were unattainable in earlier studies.

EXPERIMENTAL

The LT SIMS experiments were performed on a VG-ZAB-SEQ mass spectrometer (Micromass, Manchester, UK) with a commercial SIMS (FAB) ion source. The intensity of the bombarding Cs⁺ beam energy was 15 keV. The procedure for obtaining LT SIMS spectra was the same as described earlier.² A droplet of alcohol was frozen on a stainless-steel probe tip in the vapor of liquid nitrogen and rapidly inserted into the mass spectrometer. Thawing of the samples occurred due to thermal leakage through the sample holder. During this process, mass spectra were continuously recorded in the mass range 10–1000 Da at a rate of 5 s per scan. Data processing allowed the reconstruction of ion thermograms of any ion in the spectra, that is, the dependence of the relative ion current (normalized to the maximum intensity value, recorded

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for this particular ion) on scan number (directly proportional to time passed from the start of the monitoring). The time-scale can roughly be converted to a temperature scale. As a direct temperature measurement was not available with the above set-up, complementary data, derived from the earlier measurements⁴ on an MI-1201E magnetic mass spectrometer (Electron Works, Sumy, Ukraine), equipped with an LT FAB ion source with temperature control, described elsewhere,⁸ were used. The temperature range for the existence of cluster-type LT FAB mass spectra of ethanol was determined to be from -130 to -110 °C;⁴ the spectra with the same pattern were recorded on the VG-ZAB instrument in 45–50 scans (5 s each), which suggested a 20 °C temperature rise in ~ 4 min. On this basis, the rate of thawing can roughly be estimated as 5 °C min^{-1} or 0.4 °C per scan. The general pattern of the ion thermograms obtained was qualitatively the same in a number of independent measurements.

Analytical-grade methanol and ethanol (Reanal, Budapest, Hungary) were used without additional purification. The latter means that $\sim 5\%$ of water is present in the samples.^{2–4} The results of all previous LT FAB studies on alcohols show that it is impossible in practice to avoid the incorporation of water molecules in alcohol samples at various stages of the experiment. However, no noticeable dependence of the cluster pattern on water content (either large or small) in the initial sample was observed, the reasons for which were elucidated previously.⁹

RESULTS AND DISCUSSION

The three main stages of the transformation of the spectra during the thawing of frozen samples of alcohols are the absence of a meaningful spectrum (i.e. virtually noise) at the lowest temperature, followed by the appearance of good-quality spectra consisting of protonated clusters in the intermediate temperature range and disappearance of the protonated cluster ions with a further rise in temperature. The results of previous LT FAB and SIMS studies on methanol^{1,2} and ethanol^{2–4} showed that in the temperature range of cluster-type spectra the main positive-ion sets correspond to protonated neat alcohol ($M_n \cdot H^+$), hydrate ($M_n \cdot (H_2O)_m \cdot H^+$) (due to the presence of water⁴) and 'fragment' clusters.

Ion thermograms of selected ions which are representative of the temperature behaviour of LT SIMS mass spectra of ethanol and methanol obtained in this work are presented in Figs 1–3. Two main features similar for all types of ions are that all of them appear at the same threshold temperature and reach a maximum abundance at about the same point (the maxima in the plots). These two features reflect the changes in the physical state of the samples. In the lowest temperature range (prior to the threshold) the samples are in the solid state. It is impossible to obtain meaningful spectra from such a state, which is likely to be connected with the well known difficulties of ion sputtering from organic solids under SIMS conditions.¹⁰ The temperature threshold for the emergence of a cluster-type mass spectral pattern was proved to be caused by the

melting of the sample.⁹ It should be noted that in the case of a two-component water–alcohol system the appearance of the liquid phase in the sample occurs at the eutectic temperature (which usually is lower than the melting points of the individual components of the mixture).⁹ The observation of the same temperature threshold for production of all types of cluster ions [neat, hydrate, fragment, present in Figs 1(a) and 2(a)] suggests that all of them originate from the same phase, i.e. the liquid. The alternative situation, in which different ions showed different temperature thresholds and ranges of existence, was observed earlier in the case of some heterogeneous frozen samples.^{6,7}

To our knowledge, reference data on boiling temperatures of water–alcohol mixtures at very low pressures characteristic of mass spectrometry are not available. It is suggested, that the boiling point of our samples is close to the sharp increase in the abundance of the ions in the LT SIMS spectra [Figs 1(a) and (b), 2(b) and 3(a)]. Reference to ion thermograms permitted the selection of the mass spectrum produced exactly at the point of the maximum recorded abundance [scan No. 46 in the case of ethanol, Fig. 1(a)]. After this point the cluster ion series, which were observed before, terminate abruptly. Note that maintaining the temperature of the sample in the range between the threshold and the maximum (which was available with the MI-1201E-based LT FAB set-up^{4,8}) allows the cluster-type spectra to be recorded for a long time (not less than 30 min). The estimate of the saturated vapor pressure of the alcohols at the relevant temperatures shows that it is about two orders of magnitude lower for ethanol than methanol, which provides a longer lifetime of the liquid phase in the case of ethanol [compare the range of cluster ion production in Figs 1(a) and (b) and 2(b)].

The marked difference in the ion thermograms of the two alcohols relates to the behavior of the clusters containing water. In the case of ethanol all types of clusters reach their maximum abundance at the same temperature [scan No. 46, Fig. 1(b) and (c)], whereas in the case of methanol the peak for di- and trihydrated cluster is shifted to slightly higher temperatures [scan No. 36, Fig. 3(b)] in comparison with that of neat methanol clusters [scan No. 35, Fig. 3(a) and (b)]. This suggests that the ratio of hydrated to non-hydrated methanol clusters increases with increase in temperature. The latter is supported by Fig. 3(c), showing the result of subtracting spectrum No. 35 and No. 36. The differential spectrum consists mainly of hydrated clusters.

To explain the difference in the temperature behavior of hydrates of methanol and ethanol we have to consider the properties of the liquid two-component water–alcohol systems. In the case of the water–methanol solution, methanol is the lower boiling component, and therefore starts to evaporate first. The removal of methanol enriches the remaining liquid in water, which leads to an increase in the abundances of water-containing clusters in the spectrum. It can be said that we are observing a process of distillation at the low temperatures and reduced pressure. Ethanol, on the other hand, forms an azeotropic mixture with water.¹¹ As the liquid and gas phase are in azeotropic equilibrium, there is no change in the composition of the liquid and,

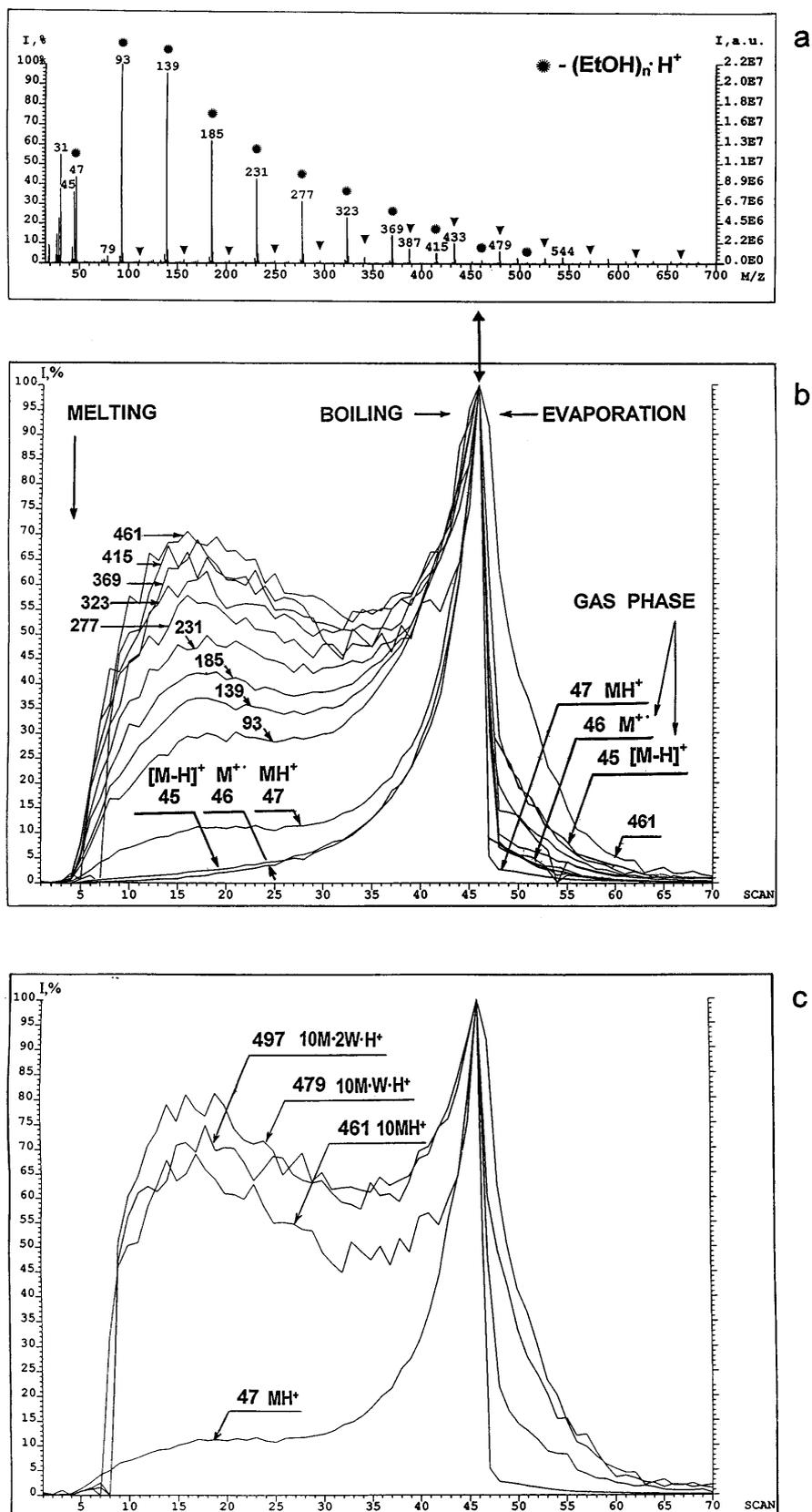


Figure 1. Ion thermograms of selected ions in the LT SIMS spectra (a) of ethanol; (b) represents neat $M_n \cdot \text{H}^+$ ethanol clusters with $n = 1-10$ and monomer-related $[\text{M}-\text{H}]^+$, M^{++} ions, while (c) provides a comparison of neat ($m = 0$) and hydrate ($m \geq 1$) $M_n \cdot W_m \cdot \text{H}^+$ clusters ($M = \text{ethanol}$; $W = \text{water components of the clusters}$). Scan numbers on the abscissa are directly proportional to time and temperature increase during thawing of the sample (see Experimental for details).

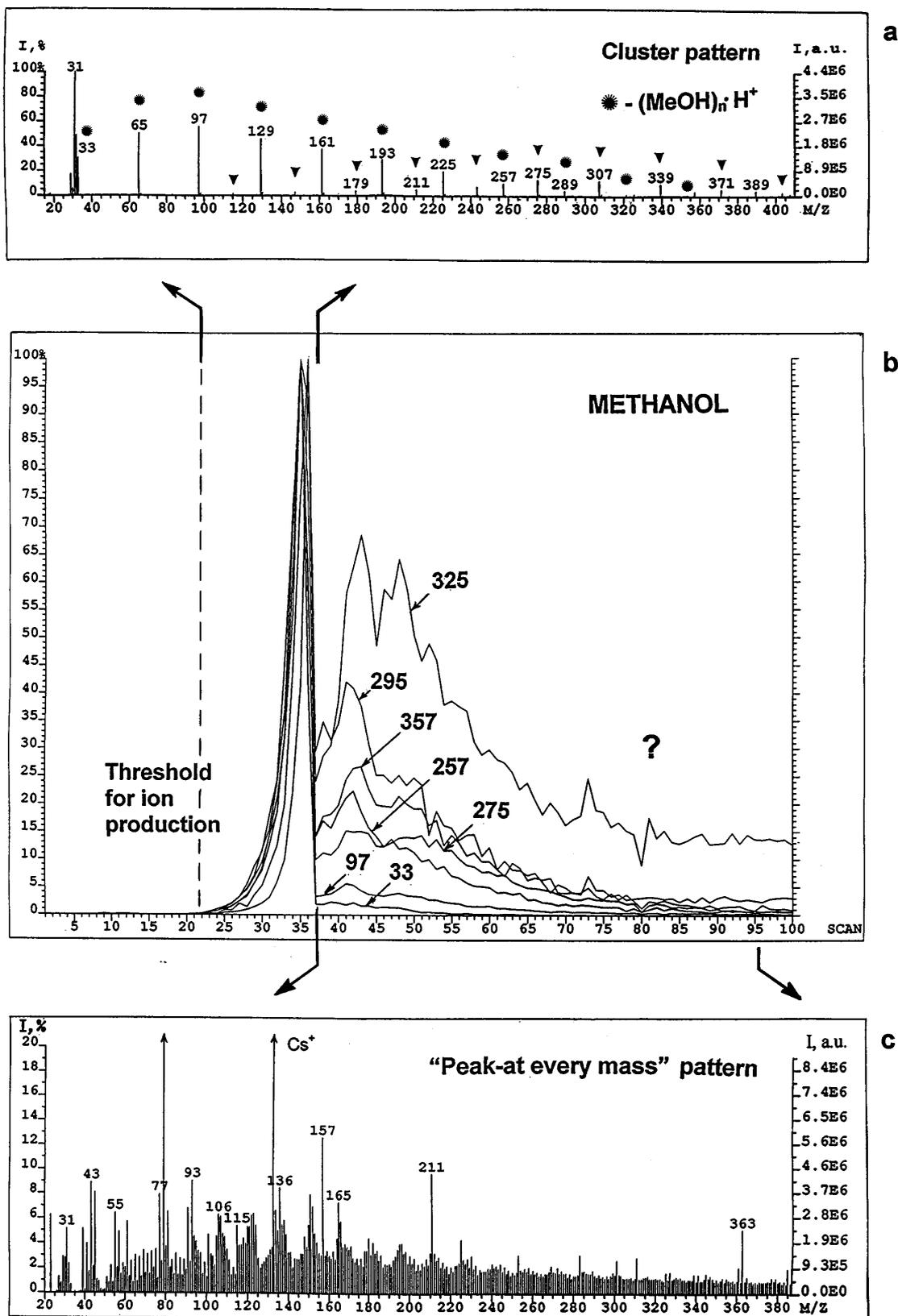


Figure 2. Ion thermogram (b) of selected ions in the LT SIMS spectra (a), (c) of methanol. Cluster-type spectra (a) are observed up to scan No. 37, after which only 'peak-at-every-mass' spectra (c) are recorded (peaks at m/z 79, 157 and 211 in (c) (scan No. 41) relate to reproducible background, m/z 133 - Cs^+).

consequently, hydrated and non-hydrated clusters show a similar time dependence.

Between the threshold and the maximum in the ion thermograms there is an interval of nearly steady ion

production. The spectra show a cluster-type pattern [Figs 1(a) and 2(a)], as described in several previous studies.¹⁻⁴ In these studies with lower 'temperature resolution' no change in the cluster pattern was noted

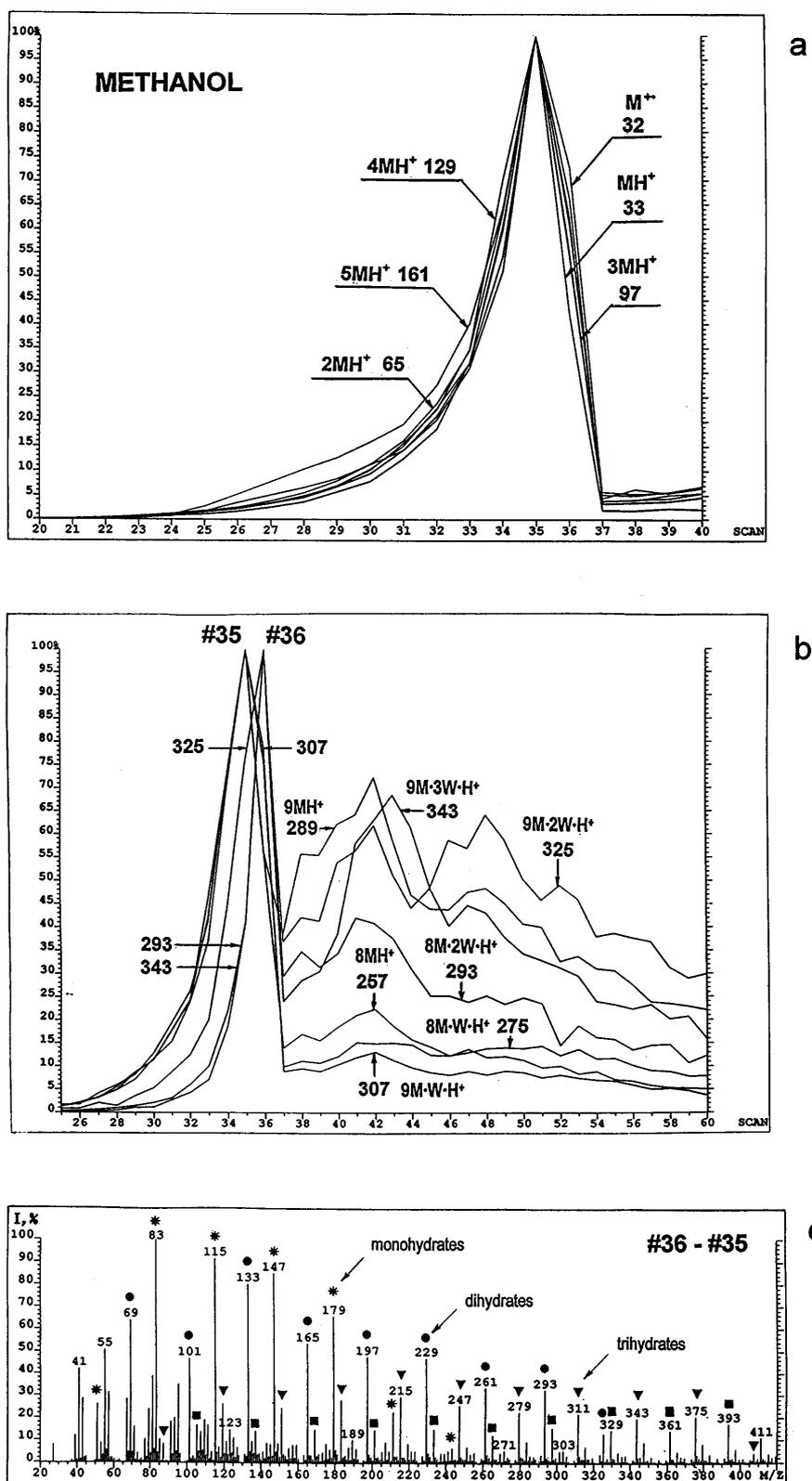


Figure 3. Ion thermograms of small neat $M_n \cdot H^+$ (a) and hydrate $M_n \cdot W_m \cdot H^+$ (b) clusters of methanol. (c) Represents results of subtracting of two spectra recorded at scans corresponding to maximum abundances of hydrates (scan No. 36) and neat methanol clusters (scan No. 35). Hydrate cluster sets of the $M_n \cdot (H_2O)_m \cdot H^+$ type are marked in accord with m value as *, ●, ▼ and ■ for $m = 1, 2, 3$ and 4, respectively. Note that in the 'tails' after scan No. 37, all marked ions are no longer represented by distinguished peaks, but are on the general level of the 'peak-at-every-mass' spectral pattern [see Fig. 2 (c)].

over the whole temperature range of cluster production. Analysis of ion chromatograms in the present work revealed differences in the behavior of different types of ions. In the case of ethanol, in general, the relative effi-

ciency of production of small clusters is smaller at lower temperatures, but it shows a noticeable and monotonic increase as the temperature of the sample approaches the boiling point. Larger clusters are abundant at lower

temperatures, but show a decrease of 15–20% prior to the spike [Fig. 1(b)]. The behavior of the mixed ethanol–water clusters is similar to that of the neat ethanol clusters [Fig. 1(c)]. Methanol, in contrast to ethanol, does not exhibit such a peculiarity. Ions of all sizes show a monotonic increase with temperature up to the maximum [Fig. 3(a) and (b)].

The general tendency for the increase in the absolute abundances of ions can be explained by the decrease in the viscosity of liquids with increasing temperature, which is known to enhance the ion production in FAB and liquid SIMS.¹² The differences in behavior of methanol and ethanol clusters with temperature increase may point to differences in the structure of the H-bonded networks in these two compounds. Not single molecules, but H-bonded chains or clusters, may be transferred to the gas phase in the case of alcohols and then participate in the subsequent steps of cluster formation. The lower the temperature of the sample, the larger are the 'primary' clusters that can be preserved, while close to the boiling point the H-bonded network in the liquid disintegrates substantially and monomers and smaller clusters are produced more easily.

In the spectrum of ethanol in Fig. 1(a), recorded at the maximum at scan No. 46, the distribution of ions with $m/z < 47$ is similar to that of its electron ionization mass spectra. It should be noted that the fragment ions at m/z 14–31 were not recorded at lower temperatures (as reported elsewhere^{2,4}). The origin of these ions in gas-phase SIMS ionization at relatively high temperatures seems likely based on certain features of ion chromatograms. Among ions related to the monomer ethanol, $[M - H]^+$, $M^{+\cdot}$ and MH^+ [Fig. 1(b)], the abundance of the protonated species is higher than that of $M^{+\cdot}$ at the beginning, while the behaviours of $M^{+\cdot}$ and $[M - H]^+$ are identical. After the evaporation spike, the peak of MH^+ vanishes rapidly, whereas $M^{+\cdot}$ and $[M - H]^+$ ions persist longer. It may be suggested that at scans higher than 48, the $M^{+\cdot}$ radical ion is formed due to gas-phase SIMS ionization^{6,13} of the

single molecules in the vapor of ethanol, $[M - H]^+$ being a characteristic fragment of $M^{+\cdot}$.⁴

The ion thermograms reveal one more feature of the sample after the evaporation maximum, which was missed in the previous studies. Whereas small clusters show a sharp decrease after the boiling of the sample, the peaks corresponding to higher masses are still registered in the spectrum; in the case of methanol these ions are more abundant and more long-lasting than in the case of ethanol [Figs 1(b) and 2(b)]. The cluster pattern is no longer observed in the spectra [after scan No. 47 in Fig. 1(b) and scan No. 36 in Fig. 2(b)], but the spectrum of the residual film is still different from that of the bare sample holder. A typical pattern of the mass spectrum of the methanol sample in this range is presented in Fig. 2(c). It is characterized by an abundant 'peak-at-every-mass' set, but there are also well distinguished, resolved and comparatively intense peaks. A chemical suggestion could be made that the residue left after boiling is probably comprised of radiation damage products of alcohols, having low volatility. However, following the initial statement in the Introduction, the occurrence of a physical phenomenon should not be neglected: rapid evaporation of liquid leads to a substantial decrease in the temperature of the sample surface, which may result in, if not re-freezing, then an increase in viscosity leading to a reduction of efficiency of cluster ion production and an increase in the degradation products.

The results show that ion thermograms of different types of ions, obtained during thawing of frozen samples of ethanol and methanol, exhibit correlations with physical state and phase transitions in the sample. Different mechanisms of ion formation are involved at different stages of the transformation of alcohol samples, and their reflection in the characteristic features of ion thermograms is summarized in the Table 1.

It should be noted that earlier analysis² of the results of a number of studies on LT FABMS of alcohols revealed the absence of noticeable dependence of the

Table 1 Different mechanisms of ion formation, observed during thawing of the frozen alcohol samples, and their reflection in ion thermogram features

Ionisation mechanism	State (type) of sample	Features of the LT SIMS spectrum	Related features of the ion thermograms
Solid SIMS ¹⁰	Frozen solid sample	Noisy, featureless spectrum of low abundance	Ion currents close to zero
Liquid SIMS ¹⁰	Liquid state formed by melting	Good-quality, abundant cluster-type spectrum	Increasing ion currents with increasing temperature; some dependences on cluster size and type
Gas-phase SIMS ¹⁴	Gas-phase monomers	Production of $M^{+\cdot}$ radical ions, electron ionization-like fragmentation (forming $[M - H]^+$)	$M^{+\cdot}$, $[M - H]^+$ ions with relatively high abundances
Uncertain process	Residual film, virtually solid	Abundant 'peak-at-every-mass' pattern	Relatively abundant 'tails' after the evaporation maximum

spectral pattern on the type and energy of the ionizing agents applied, type of the instrument used and method of sample preparation. This confirms that the temperature changes in the spectra are predetermined by the physical processes in the sample itself.

CONCLUSIONS

Analysis of continuous ion thermograms was shown to be efficient in obtaining information about the fine details of the temperature behavior of frozen alcohol samples, which does not follow directly from the analysis of the separate LT FAB/SIMS spectra. While the reflection in the ion thermograms of phase transitions in the samples such as melting and boiling could be expected, the conclusion about the different boiling characteristics of two water-alcohol mixtures, which is azeotropic in the case of ethanol and non-azeotropic in the case of methanol, becomes possible owing to the fine temperature 'resolution' of differences in neat and hydrate cluster production of methanol, provided by ion thermograms. Differences in the temperature behav-

ior of clusters of different size was observed in the case of ethanol, which points to the dependence of cluster production on the temperature of the liquid sample.

In addition to fundamental interest, several practical conclusions important for correct interpretation of the results of the LT FAB/SIMS experiments follow from the analysis of the ion thermograms. Although the existence of strong temperature dependences of the spectra are clearly understood, some of their features are not so obvious. In particular, in the studies of clusters, the possibility of a change in the ratio of the components of the mixture in the course of the experiment, demonstrated by methanol, should be taken into account. The presence of the residual sample after the evaporation maximum, which continues to produce ions coinciding in mass with the already extinct clusters, needs to be accounted for during selected ion monitoring studies.

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REFERENCES

1. R. N. Katz, T. Chaudhary and F. H. Field, *J. Am. Chem. Soc.* **108**, 3897 (1986).
2. M. V. Kosevich, G. Czira, O. A. Boryak, V. S. Shelkovsky and K. Vekey, *Rapid Commun. Mass Spectrom* **13**, 1411 (1997).
3. R. A. W. Johnstone and A. H. Wilby, *Int. J. Mass Spectrom. Ion Processes* **89**, 249 (1989).
4. O. A. Boryak, M. V. Kosevich and V. S. Shelkovsky, *Int. J. Mass Spectrom. Ion Processes* **163**, 177 (1997).
5. R. N. Katz, T. Chaudhary and F. H. Field, *Int. J. Mass Spectrom. Ion Processes* **78**, 85 (1987).
6. O. A. Boryak, M. V. Kosevich, V. S. Shelkovsky and Yu. P. Blagoy, *Rapid Commun. Mass Spectrom.* **9**, 978 (1995).
7. O. A. Boryak, I. O. Stepanov, M. V., Kosevich, V. S. Shelkovsky, V. V. Orlov and Yu. P. Blagoy, *Eur. Mass Spectrom.*, **2** (1996) 329.
8. O. A. Boryak, M. V. Kosevich and V. S. Shelkovskii, *Instruments and Experimental Techniques*, Vol. 6, p. 935. Plenum Press, New York (1993).
9. M. V. Kosevich, *Eur. Mass Spectrom.* **3**, 320 (1997).
10. A. Benninghoven, F. G. Rudenauer and H. W. Werner, *Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends*. Wiley, New York (1987).
11. *CRC Handbook on Chemistry and Physics*, CRC Press, Boca Raton, FL (1992-93).
12. J. T. Shiea and J. Sunner, *Int. J. Mass Spectrom. Ion Processes* **96**, 243 (1990).
13. M. Takayama, *Int. J. Mass Spectrom. Ion Processes* **152**, 1 (1996).