

Cluster Ions in the Field Desorption Mass Spectrum of Sodium Benzene Sulphonate

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Summary The field desorption mass spectrum of sodium benzenesulphonate exhibits a range of intense cluster ions of general formula $(nM + Na)^+$, where M represents the sulphonate molecule and $n = 1-5$; the cluster ion corresponding to $n = 5$ is particularly stable.

ION clusters, such as HM_n^+ and M_n^+ , where M is a neutral molecule, are a not uncommon feature of both field ionisation (FI) and field desorption (FD) mass spectra.¹ Such ion clusters can be produced by the reaction of neutral molecules on the surface of the activated FI-FD emitter, the reactant molecules being adsorbed from the gas phase in the case of FI and from solution in the case of FD.

Although cluster ions have an obvious relationship with the solvation of ions in solution and FD mass spectra may be obtained for alkali metal salts,²⁻⁴ there have been no reported observations of cluster ions in which a metallic cation is associated with more than one neutral molecule. Ions corresponding to $(M + Na)^+$ or $(M + K)^+$, however, are very intense in the FD mass spectra of both sodium acetate² and potassium guaiacolsulphonate,⁴ and also in the

FD mass spectrum of guanine adsorbed from aqueous alkaline solution.² A closely related cluster ion of mass corresponding to the addition of two cations and one anion has been detected in the FD mass spectra of quaternary ammonium salts.⁵

TABLE

Field desorption mass spectra^a of sodium benzenesulphonate^b at various anode heating currents.^c

Cluster Ion	Anode heating current		
	18 mA	20 mA	22 mA
$(M + Na)^+$	53.7	9.3	100.0
$(2M + Na)^+$	25.8	32.3	0
$(3M + Na)^+$	2.8	26.3	0
$(4M + Na)^+$	0.9	2.4	0
$(5M + Na)^+$	0	19.7	0

^a Measured at a resolution of 1000 (10% valley) and an ion source temperature of 100 °C using a Varian MAT 731 spectrometer and a pre-conditioned 10 μm tungsten wire emitter.

^b Adsorbed on the emitter from aqueous solution (concentration 2 mg/cm⁻³). ^c Intensities expressed as % Σ_{60} inclusive of all isotopic contributions.

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In the work reported here sodium benzenesulphonate, under carefully controlled FD conditions, is shown to produce a range of intense cluster ions of general formula $(nM + Na)^+$, where M represents the sodium benzene sulphonate molecule and $n = 1-5$ (Table). The FD mass spectrum observed depended markedly upon the temperature of the emitter.† At the lowest field anode heating current necessary to produce a detectable ion current (18 mA), cluster ions corresponding to $n = 1-4$ were detected with intensity decreasing with increasing n . An increase of only 2 mA in the heating current had the dramatic effect of introducing into the spectrum two additional very intense ions, namely Na^+ and the cluster ion corresponding to $n = 5$. At 22 mA heating current only $(M + Na)^+$ was observed.

A reasonable interpretation of the above results is that the observed cluster ions correspond to solvated sodium ions, in which the bonding is primarily of the electrostatic, ion-dipole type. Each cluster ion has an optimum anode temperature for field desorption, but too high a temperature results in the thermal decomposition of the higher complexes. Thus, at 22 mA, only $(M + Na)^+$ is observed.

Although Bone^{6,7} has suggested that some clustered ions observed under photoionisation conditions have a hydrogen bonded chain-like structure, in the present context it would seem more likely that the sodium benzenesulphonate clusters, which cannot involve hydrogen bonding, have a more conventional solvation sphere structure. The high intensity of $(5M + Na)^+$ in the 20 mA FD spectrum

† The absolute emitter temperatures are not known with certainty, but are probably in the range 100–200 °C.³ On a relative basis, however, the temperature produced *in vacuo* by a current of 22 mA is probably not more than 50 °C higher than that produced by 18 mA.

relative to $(4M + Na)^+$ and the non-observation of $(6M + Na)^+$ would then suggest that the cluster ion corresponding to $n = 5$ has a particularly stable structure, possibly a trigonal bipyramid of sulphonate molecules around a central Na^+ ion. The high stability of $(5M + Na)^+$ is surprising since Na^+ in solution has a primary solvation sphere of four water or ammonia molecules. This is the first report of an ion cluster not involving water or ammonia which contains more neutral molecules than would be expected in the first solvation sphere.⁷

An additional interesting feature of the FD mass spectra of sodium benzenesulphonate is the appearance in the 18 mA spectrum of a relatively intense ($\% \Sigma_{60} = 3.3$), doubly charged, cluster ion corresponding to $(3M - 2H + 2Na)^{2+}$.

Attempts to observe a corresponding range of cluster ions in the FD mass spectra of other sulphonates were unsuccessful. Substituted sodium benzenesulphonates ($C_9H_{10}C_6H_4SO_3Na - C_{14}H_{20}C_6H_4SO_3Na$ inclusive) showed only ions corresponding to M^+ and $(M + Na)^+$, while sodium alkyl sulphonates ($C_{11}H_{23}SO_3Na - C_{18}H_{37}SO_3Na$ inclusive) showed only $(M + Na)^+$. In these cases it is possible that the higher clusters are sterically destabilised.

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³ H.-R. Schulten, H. D. Beckey, E. M. Bessell, A. B. Foster, M. Jarman, and J. H. Westwood, *J.C.S. Chem. Comm.*, 1973, 416.

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⁵ D. A. Brent, D. J. Rouse, M. C. Sammons, and M. M. Bursey, *Tetrahedron Letters*, 1973, **42**, 4127.

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⁷ L. I. Bone, *Adv. Mass Spectrometry*, 1974, **6**, 753.