MANIPULATION OF THE POPULATION OF NON-COVALENTLY BOUND SPECIES FORMED IN THE ELECTROSPRAY INTERFACE OF LC-MS

Amitha K. Hewavitharana and P. Nicholas Shaw
School of Pharmacy, University of Queensland, Brisbane, Qld 4072, Australia

Electrospray ionization (ESI) is recognised as a "soft" ionisation method, this being responsible for the promotion of intact molecular ions in the mass spectrum. This feature differentiates LC-MS from GC-MS, giving the former a competitive advantage in qualitative analysis. The desolvation process that occurs in electrospray is believed to be responsible for reducing the energy of the ions produced therefore generating low internal energy ions which are then introduced into the mass spectrometer (Gaskell, 1997). Several theories were proposed to describe the ESI mechanism. On the one hand, electrospray is thought to be a mere transfer process that carries already ionized molecules (in solution) from solution phase to the gas phase for MS analysis (Gaskell, 1997). However, another mechanism suggests that the electrospray capillary tip is similar to an electrolytic cell in which part of the charge transfer occurs in the gas phase (Kebarle and Tang, 1993). It is therefore suggested that electrochemical oxidation can produce radical cations from neutral molecules in solution, therefore indicating that electrospray is a true ionization method.

As Meng and Fenn (1991) have predicted, the understanding of solution conditions leading to the formation of dimer and other cluster species may ultimately help clarify details of the ESI mechanism. Although this phenomenon has been studied to a significant extent for larger molecules such as peptides, little has been published for small organic molecules. In the context of the development of an analytical method for the quantitation of BAY 11- 7082 ((E)-3-[4-methylphenylsulfonyl]-2-propenenitrile), we have investigated the effects of declustering potential, nebulizer gas flow, temperature, percentage organic solvent in sample and the sample pH on the formation/dissociation of non-covalently bound species. In this study we monitored the relative intensities of the following ions: MH^+, MNa^+, MH_2O, and $2MNa^+$. These were the identifiable species of the BAY compound observed in the electrospray spectra. The spectra were obtained using a flow injection analysis method of sample introduction.

All the above parameters affected the relative distribution of the ions, although the declustering potential and solution pH had the greatest influence on the formation/dissociation of the non-covalently bound species. We believe that the results of this study provide some details on the ESI mechanism for small molecules.

Gaskell S.J., J. Mass Spectrom. 32 (1997) 677.
Kebarle P, and Tang L., Anal. Chem. 65 (1993) 972A.
Meng C.K., and Fenn J.B., Org. Mass Spectrom. 26 (1991) 542.