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A Mathematical Model for Magnesium Chloride-Fatty Acid Adducts in Electrospray Ionization Mass Spectrometry

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The formation of adducts among analyte species is a well known phenomenon in electrospray ionization mass spectrometry (ESI-MS). The presence of salts usually promotes the formation of adducts by electrostatic and van de waalse bonds among various ions present in solution. In this study, we describe a simple mathematical model to explain the patterns for mass distribution and peak intensity for adducts formed by magnesium chloride and various fatty acid anions.

Negative-ion mass spectra were collected using a Finnigan MAT LCQ quadropole ion trap mass spectrometer, scanned from 50-1000 m/z. Samples were directly infused into the mass spectrometer by a built-in syringe pump at a flow rate of 8 µl/min. Figure 1 shows the mass spectrum of a mixture of 0.5 mM of each of propionic, butyric, pentanoic, hexanoic, and heptanoic acids mixed with 1.0 mM of magnesium chloride. The inset shows spectrum of the same fatty acids but without magnesium chloride. As expected, the deprotonated fatty acid anion peaks were observed without magnesium chloride. In contrast, numerous adduct peaks were observed roughly from m/z 300 to 1000 in the mass spectrum of fatty acid mixture containing magnesium chloride. The distribution of the peaks broadly followed five groups with each following a normal (Gaussian) distribution pattern. The adjacent peaks in a group showed a mass difference of 14 reflecting the increase in carbon chain length due to $-CH_2-$ in the series of fatty acids used. Each group of peaks can be represented by a general formula (the m/z values below refer to the monoisotopic peaks in the clusters): groups I (m/z 337-505), II (m/z 375-599), III (m/z 413-693), IV (m/z 507-787) and V (m/z 583-975) corresponding to the formulas $Mg_2Cl_2L_3^-$, $Mg_2ClL_4^-$, $Mg_2L_5^-$, $Mg_3Cl_2L_5^-$ and $Mg_3L_7^-$, respectively, where L represents any one of the five deprotonated fatty acids. We verified these formulas by comparing the experimental data with theoretical calculations for mass and isotopic distribution for the various peaks.

Table 1 gives the possible combinations of three fatty acids for adducts in group 1 with the general formula $Mg_2Cl_2L_3^-$, and indicates that several different combinations can give rise to ions with the same ionic mass. Thus, for any peak, the intensity should reflect the sum of contributions from all the related isomers:

$$I_x = \sum_{i=1}^{n} I_i \qquad 1$$

where I_x is the intensity of adduct(s) with m/z equal to X, I_i is the intensity contributed from the ith isomer, and n is the number of isomers. Figure 2a gives relative intensity vs. m/z calculated using equation 1 with the assumption that the intensities contributed by different isomers are the same. However, according to statistical theory, the probabilities for different adduct formations are different, depending on how many fatty acids are identical in the adduct:

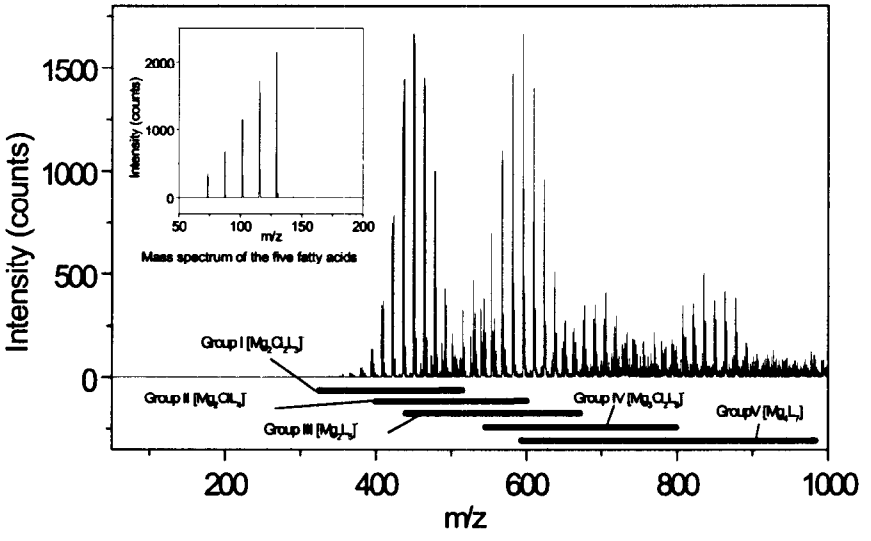

Figure 1. Negative-ion mass spectra of a mixture of five fatty acids (0.5 mM each) with 1.0 mM $MgCl_2$ and a mixture of the five fatty acids only (inserted figure).

Table 1. Theoretical calculation results of adducts in group I

m/z	N[a]	Possible combinations of three fatty acids[b]	I[c]	II[d]	III[e]
337	9	3,3,3(1).	1	1	0.12
351	10	3,3,4(3).	1	3	0.66
365	11	3,3,5(3); 3,4,4(3).	2	6	2.35
379	12	4,4,4(1); 3,4,5(6); 3,3,6(3).	3	10	6.63
393	13	4,4,5(3); 3,5,5(3); 3,4,6(6); 3,3,7(3).	4	15	15.8
407	14	4,4,6(3); 3,5,6(6); 4,5,5(3); 3,4,7(6).	4	18	31.0
421	15	4,4,7(3); 3,5,7(6); 4,5,6(6); 3,6,6(3); 5,5,5(1).	5	19	52.5
435	16	4,6,6(3); 4,5,7(6); 3,6,7(6); 5,5,6(3).	4	18	79.5
449	17	5,6,6(3); 4,6,7(6); 3,7,7(3); 5,5,7(3).	4	15	96.8
463	18	6,6,6(1); 5,6,7(6); 4,7,7(3).	3	10	100
477	19	6,6,7(3); 5,7,7(3).	2	6	87.8
491	20	6,7,7(3).	2	3	59.5
505	21	7,7,7(1).	1	1	24.5

[a] Sum of carbon atoms of the three fatty acids.
[b]Carbon atoms of the three fatty acids, respectively. In the parentheses is the relative probability of the isomer formation.
[c,d,e]Calculated relative intensities of peaks in group I based on equations 1, 3 and 4, respectively.

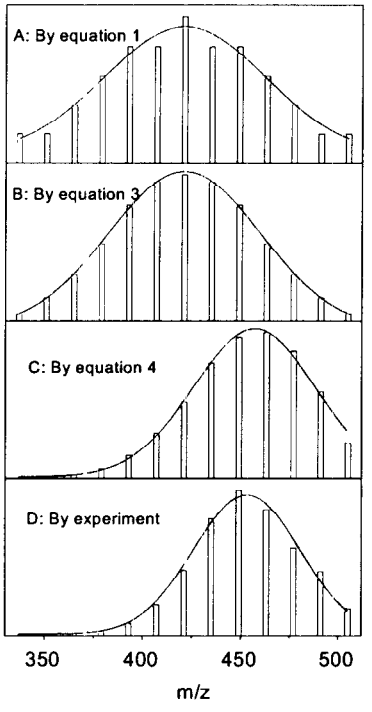

Figure 2. Profiles of group I by different treatments

$$P_i = M!/\prod_{K=1}^{r} Q_k! \qquad 2$$

where P_i is the relative formation probability of the ith isomer, M is the number of fatty acids in the adduct, and Q is the number of the same fatty acids. For group I with M=3, P_i value is 1 when all the three fatty acids are the same (P_i=3!/3!=1), 3 when two fatty acids are the same (P_i=3!/2!1!=3), or 6 when none of the fatty acids are the same (P_i=3!/1!1!1! =6); thus equation 1 can be modified as:

$$I_x = K\sum_{I=1}^{n} P_i = K\sum_{i=1}^{n} (M!/\prod_{K=1}^{r} Q_k!)_i \qquad 3$$

where K is a normalization constant. Figure 2b gives the plot based on equation 3, which shows a better fit to normal distribution of the variation of peak intensity with m/z.

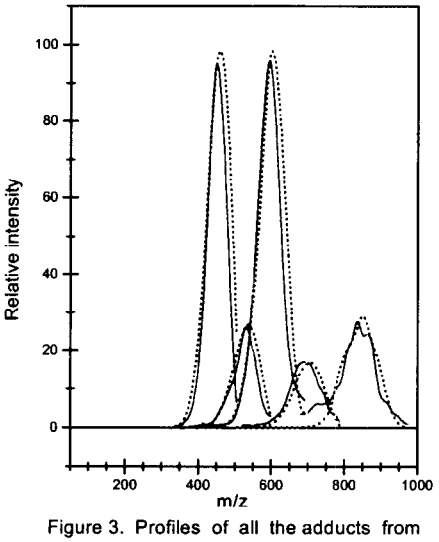

Figure 3. Profiles of all the adducts from experiment (solid line) and theoretical calculation (dash line) based on equation 4

The experimental data on relative intensity vs. m/z for group 1 peaks (Figure 2d) showed essentially a normal distribution but the maximum was shifted to a higher m/z value. This shift could be due to differences in sensitivities of the five fatty acids in ESI-MS (inserted in Figure 1). The relative ratio of the responses (peak intensities) of the five fatty acids are 0.17, 0.31, 0.54, 0.81 and 1.00, although the concentrations are the same. To compensate for this difference in response, the theoretical peak intensity due to each isomer was multiplied by the response ratio for each corresponding fatty acid. Thus, equation 3 can be modified as:

$$I_x = K\sum_{i=1}^{n} (M!/\prod_{K=1}^{r} Q_k!)_i \prod_{j=1}^{s} F_j \qquad 4$$

where F_j is the intensity ratio of the jth fatty acid in the isomer. Figure 2c gives the plot based on equation 4, showing a good agreement with the experimental data (Figure 2d).

Figure 3 shows the variation of peak intensity vs. m/z for all the adduct peaks in the five groups. The good agreement between the theoretical results based on equation 4 and experimental data indicates that equation 4 is a reasonable mathematical model for the magnesium chloride-fatty acids system.