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ORIGINAL RESEARCH

Electric field dependence of ion mobilities of aromatic compounds with different ionic mass and different functional groups

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Abstract Ion mobility spectrometry with high electric fields complements the information from the spectra obtained using conventional time-of-flight ion mobility spectrometry by providing the field dependence of ion mobility. The formation and dissociation of ion clusters depending on the differences between high and low field strength is one process which has a considerable influence on the peak position in the resulting spectra. This process can be affected by the properties of substances. Therefore, one objective of our study was to determine possible influences of the nature and position of functional groups on the field dependence of ion mobilities. For this purpose, we investigated sets of compounds with different functional groups including chlorobenzenes, toluenes, anilines and phenols. Furthermore, it is known that ionic mass is an important parameter influencing the field dependence of ion mobility. Therefore, we also investigated unsubstituted aromatic hydrocarbons with different ionic masses. Although an influence of functional groups on the field dependence of ion mobilities was found, the ionic mass has a more significant influence. However, some isomers can be separated by applying high field amplitudes. Furthermore, the influence of ionic mass on the peak position is also more significant using high field amplitudes.

Keywords Ion mobility spectrometry · Differential mobility spectrometry · Functional groups · Photoionization

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Introduction

Although conventional ion mobility spectrometry (IMS) is successfully used in a number of different applications, the demands of modern field screening techniques have recently prompted the examination of its further miniaturization. The miniaturization of conventional drift tubes in IMS with corresponding reduction in the length and width of the drift region has reduced the sensitivity and resolution of ion mobility spectrometers. For this reason, novel methods of ion separation using high electric fields with radio-frequency (RF) asymmetric waveforms were introduced. These have been realized in differential mobility spectrometers (DMS) or field asymmetric waveform ion mobility spectrometers (FAIMS) [1–4].

In DMS, ions are entrained in a carrier gas flow between parallel plate electrodes. An asymmetric RF field between the electrodes causes an oscillating motion of ions along the drift channel. The ions are drawn towards one electrode or the other in each period of RF voltage depending on the polarity and the difference between high field and low field ion mobilities. The ions can therefore only reach the detector if their displacement is less than the drift channel height. The other ions collide with the electrodes and are neutralized. Selected ions can be maintained in the drift gas flow using low DC voltages. This weak DC field is superimposed on the RF field. Depending on the strength of DC voltage (compensation voltage), selected ions can pass the electrodes and are transported to the detector. The displacement of selected ions can be compensated. The compensation voltages (DC voltages) detected are characteristic for different ion species. The detailed operational principles were extensively described in previous articles [5–7].

In contrast to traditional IMS with weak electric fields <1,000 V cm^{-1}, DMS works with typical peak amplitudes between 10,000 and 30,000 V cm^{-1} and a frequency of 0.7–1.5 MHz.

DMS permits the simultaneous detection of positive and negative ions formed. Furthermore, information from the DMS spectrum complements conventional IMS by providing the field dependence of ion mobility which can be understand as relationship between the compensation voltage detected and the electric field strength (field amplitude). Alpha-functions can be derived from this relationship and describe the variation of ion mobility with varying electric field strength. The ion mobility of ions considering the electric field can be described as

$$K(E) = K_0[1 + \alpha(E)] \tag{1}$$

where K(E) is the ion mobility for any field, K_0 the ion mobility at low field and α a specific coefficient which describes the correlation between K(E) and E [8].

Using low electric fields, the motion of ions is affected by diffusion processes, the electric field, the gas density and ion-neutral interactions. Using high electric fields, additional processes can be expected in the drift channel of the DMS. The formation and dissociation of ion clusters can become a repeatable process at high frequency in field dependent methods. Furthermore, deformation and variation in cross-section in high electric fields are described in the literature. The differences in mobility at high and low field therefore also arise from the dynamics of clustering and/or folding [9–12].

Especially, the cluster processes should be affected by the properties of substances investigated. Depending on the functional groups and their different interaction forces, differences in field dependence are possible. In addition to the electronic factors influencing the ion-neutral interaction forces, ionic mass has a considerable influence on ion mobility. It is known from literature that ionic mass determines the field dependence in high field ion mobility [13, 14].

For this reason, we investigated sets of compounds with different functional groups and unsubstituted hydrocarbons with different ionic mass. Photoionization with a krypton lamp was used as ion source. As known from literature, the formation of M^+ product ions can be expected due the most probable ionization pathway [15]. The unsubstituted hydrocarbons investigated include benzene (molecular weight: 78), naphthalene (128), fluorene (166) and fluoranthene (202). Furthermore, mono-substituted benzenes (78) with different functional groups (aniline (93), chlorobenzene (112), toluene (92) and phenol (94)) were measured. In addition to these substances, we determined the field dependence for chlorobenzenes, chlorinated anilines and chlorinated phenols with a different number of chlorine atoms in different positions within the molecules.

The objective of our study was to determine possible influences of the nature of functional groups on the field dependence using DMS. Therefore, these compounds were investigated with different RF field amplitudes. Furthermore, these compounds include also isomeric substances. It was the question whether different positions of the substituents can cause different field dependences. In addition to the influence of functional groups, the unsubstituted hydrocarbons were measured in order to classify the influence of ionic mass on the field dependence.

Experimental

The DMS measurements were undertaken using a SIONEX SDP-1 spectrometer (Sionex Corporation, Bedford, USA). The compounds were ionized by a miniature krypton discharge lamp with MgF2 window (CPI, Santa Rosa, USA) providing photons with energies of 10 eV (80%) and 10.6 eV (20%). The DMS spectra display the compensation voltage versus the intensity of ion current and were obtained at different RF fields: (600 V=12 kV cm^{-1}=44.7 Td, 800 V=16 kV cm^{-1}=59.6 Td, 1000 V=20 kV cm^{-1}=74.4 Td, 1200 V=24 kV cm^{-1}=89.3 Td, 1350 V=27 kV cm^{-1}=100.5 Td, 1500 V=30 kV cm^{-1}=111.7 Td). Townsend (Td) is the natural unit for E/N where E is the electrical field strength and N the neutral gas density. The electric field of the drift channel was provided with an asymmetric square waveform with a frequency of approximately 1.3 MHz. The distance between the plate electrodes is 0.05 cm. The following operational parameters were used to obtain the differential mobility spectra: steps of average: 2; scans to average: 1; scan duration: 1 s; number of steps/scan: 150; start compensation voltage: −45; stop comp. voltage: 12; ion gain: high.

It is necessary to transfer the solid and liquid samples into the gas phase. The spectrometer was therefore coupled with a gas chromatograph (GC HP 5890, Agilent, Palo Alto). The GC was equipped with a 30 m SE-54 capillary column (0.32 mm inner diameter, 0.25 μm film thickness). The initial temperature was 35°C (2 min). Subsequently, the temperature was increased at 25°C min^{-1} to 260°C. The final temperature was held for 6 min. Between 100 and 500 ng of each substance were injected (split/splitless injector, 220°C, split ratio 1:6). The carrier gas flow from the GC (about 5 mL min^{-1} nitrogen) was additionally rarefied with 230 mL min^{-1} of nitrogen: therefore maximum concentrations of 300 ng were transferred to DMS. Nitrogen with moisture of approximately 3 ppm_V was used as carrier gas for GC and DMS.

All chemicals used were analytical standards (>99%) and were obtained from Merck (Darmstadt, Germany). For the stock solutions 25 mg (average) of compounds were dissolved in a 25 mL-flask with methanol. For the different concentrations, the stock solutions were diluted with methanol in 1 mL vials. All solutions were kept in the dark at 4°C.

Results and discussion

Figure 1 shows the field dependence of compensation voltages for unsubstituted aromatic hydrocarbons. Benzene with a molecular weight of 78, naphthalene (128), fluorene (166) and fluoranthene (202) were investigated. As discussed above, the formation of M^+ product ion peaks can be expected for these aromatic substances using photoionization. Therefore, no changes in ionic mass were expected in comparison to the molecular weight. While the compounds with a molecular weight above 100 show comparable values of compensation voltage at low RF fields, increasing differences in these values can be obtained with increasing RF field strength. A different behavior was observed for substances with low molecular weight, in this case benzene. A distinct shift to more negative values of compensation voltage can be observed with increasing RF field strength. For the other substances with molecular weights above 100, the changes in detected compensation voltages are not as distinct as observed for benzene. Substances with higher molecular weights show more positive compensation voltages with increasing RF field strength. It can be concluded from these data that a differentiation between hydrocarbons with different molecular weights can be only realized by applying high RF amplitudes. Using these conditions, DMS permit the clear differentiation of hydrocarbons depending on their ionic mass.

In addition to ionic mass, the possible influence of the nature and the position of functional groups was investigated. For initial investigation, we detected the compensation voltages for substituted benzenes with one functional group. Figure 2 shows the data for chlorobenzene, aniline, phenol and toluene. As known from textbooks of organic chemistry, these functional groups can cause different properties of the molecules due to the different distribution of electrons. The ionic mass of these compounds is comparable for the most substances and vary between 92 (toluene) and 94 (phenol) while the ionic mass of chlorobenzenes is 112. The ionic mass of aniline is 93 and close to those of toluene and phenol. The data of benzene are shown as reference values. As can be seen from Fig. 2 the compounds with a comparable ionic mass (phenol, aniline and toluene) show similar compensation voltages independent on the applied RF field strength. Although the mass difference between these substances and chlorobenzenes is ∼18, the compensation voltages detected for chlorobenzenes are nearly identical with those of the other substituted compounds. The mass difference between toluene and benzene is 14 and the compensation voltages detected for benzene permit a clear differentiation. Benzene shows a more distinct change of values to more negative compensation voltages depending on the RF field strength in comparison to the other substances. DMS does not permit the differentiation between the substituted benzenes investigated here. The influence of $-OH$, $-CH_3$ and $-NH_2$ groups on the field dependence of compensation voltages seems to be of minor importance. Although chlorobenzenes has a higher ionic mass, this substance provides similar values and an influence of chlorine on the compensation voltages detected can be supposed. Although the mass difference between chlorobenzene and benzene to the other substances is similar, only benzene provides deviating measuring values.

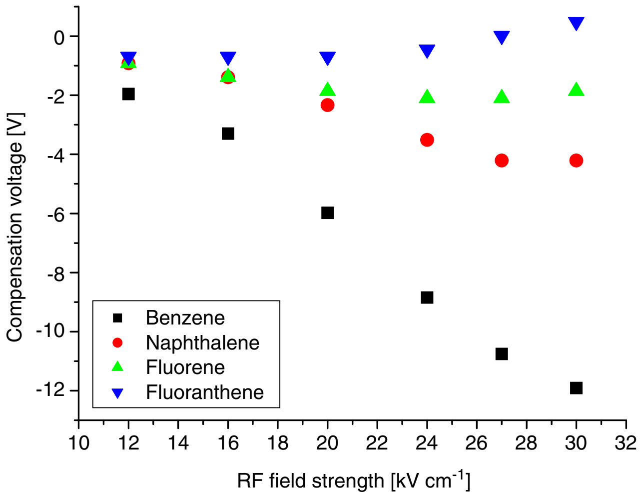

Fig. 1 Dependence of compensation voltages detected on the RF field for aromatic hydrocarbons with different ionic masses

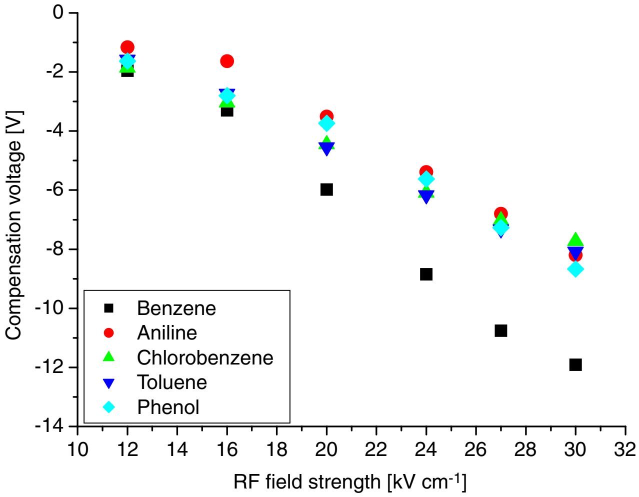

Fig. 2 Dependence of compensation voltages detected on the RF field for aromatic hydrocarbons with different substituents

The measurements of chlorobenzenes are summarized in Fig. 3. We investigated compounds with one, two and three chlorine atoms. Different positions of chlorine atoms were additionally considered for dichlorobenzenes. 1,2- and 1,4-

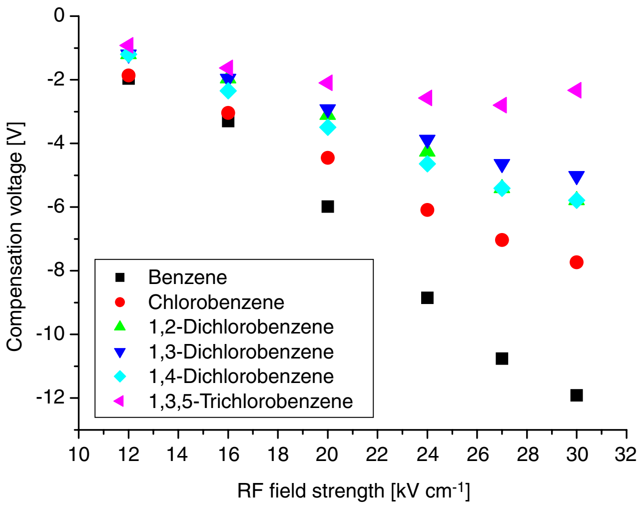

Fig. 3 Dependence of compensation voltages detected on the RF field for chlorinated aromatic compounds

dichlorobenzene provide nearly identical values of compensation voltage over the whole range of RF field strength while slight differences can be observed for 1,3-dichlorobenzene. However, the general behavior of these compounds is the same as described above. All chlorinated benzenes provide similar measuring values at low RF field strength. Increasing RF field strength lead to a distinct change in compensation voltages depending on the number of chlorine atoms and subsequently on the ionic mass.

A similar behavior was observed for chlorinated anilines as shown in Fig. 4. The increasing differences in compensation voltages with increasing RF field strength can be reproduced. In contrast to dichlorobenzenes with a similar behavior of 1,2- and 1,4-dichlorobenzene, the isomers of 2-chloroaniline and 4-chloroaniline can be differentiated. Both compounds provide different compensation voltages over the whole range of RF field strength. However, it must be generally noted that the compensation voltages detected are considerably influenced by the experimental conditions. For example, small changes in moisture of the carrier gas can cause differences in peak position. Furthermore, the carrier gas flow rate and the temperature can affect the resulting compensation voltage. Therefore, further investigations are necessary in order to reproduce the capability of DMS for separating isomers. In contrast to the disubstituted isomers, the compensation voltages of different dichloroanilines are nearly identical. Therefore, DMS does not permit the differentiation between these isomers.

The field dependence of phenols is shown in Fig. 5. Figure 5a shows the comparison of phenol with a molecular weight of 94, 2-chlorophenol (128) and 2-nitrophenol (139). It can be seen from Fig. 5a that a correlation between ionic mass and detected compensation voltage can be only observed for low RF field strength. Comparable compensation voltages can be detected for phenol and 2-

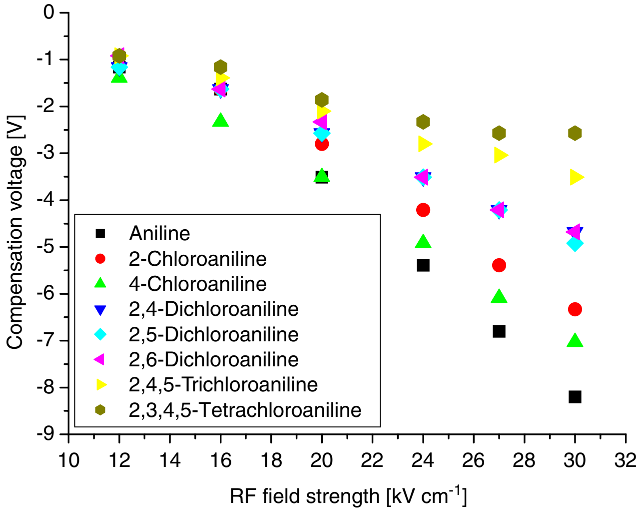

Fig. 4 Dependence of compensation voltages detected on the RF field for chlorinated anilines

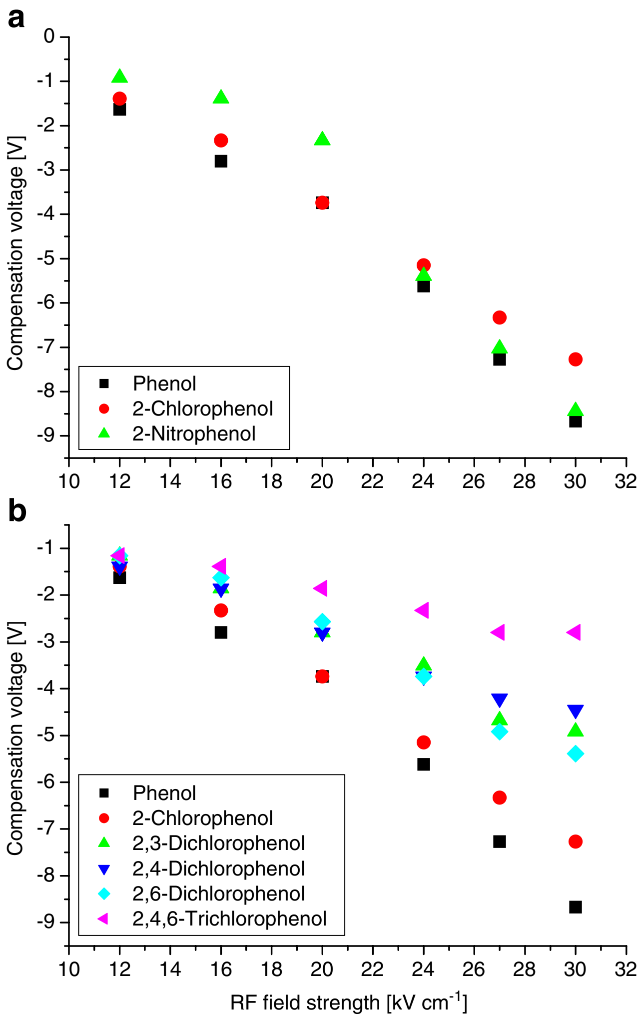

Fig. 5 Dependence of compensation voltages detected on the RF field for phenol and substituted phenols (**a**) and chlorinated phenols (**b**)

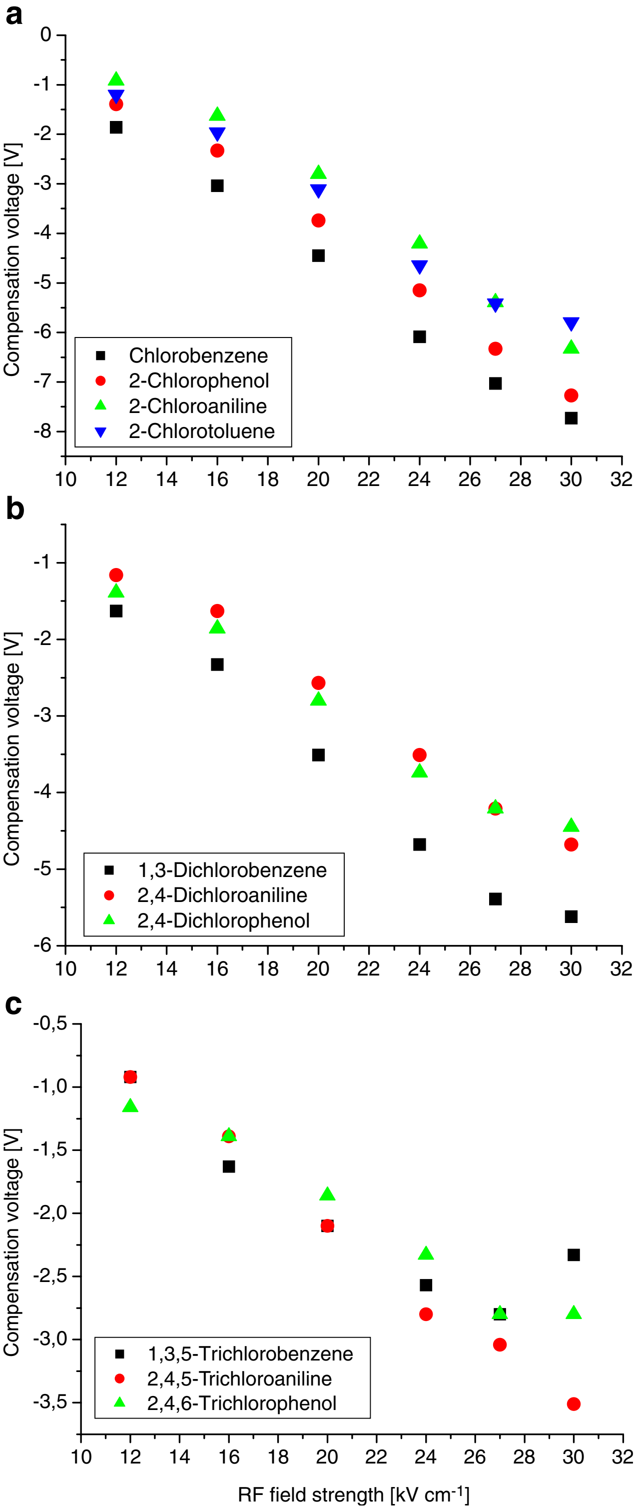

Fig. 6 Dependence of compensation voltages detected on the RF field for aromatic compounds with one (**a**), two (**b**) and tri (**c**) chlorine atoms

nitrophenol with increasing RF fields while 2-chlorophenol provides more positive compensation voltages. Although the influence of functional groups seems to be of minor importance a comparison of the compensation voltage detected for naphthalene (−4.21 V) with that of 2-chlorophenole (−7.27 V) shows the general influence of the cross section on the DMS spectra. Both substances have an identical molecular weight (128). Figure 5b shows field dependence of compensation voltages for chlorinated phenols. A similar behavior in comparison with chlorinated anilines and chlorobenzenes can be observed. While comparable values of compensation voltage were detected at low RF field strength a clear dependence of these values on the ionic mass can be observed with increasing RF field. Furthermore, the isomers of dichlorophenol provide slight differences in compensation voltages. The values detected (2,3-dichlorophenol: −4.92 V; 2,4-dichlorophenol: −4.45 V; 2,6-dichlorophenol: −5.39) permit a differentiation between these substances using high RF field strength.

The field dependence of chlorinated compounds is summarized in Fig. 6. The compounds with one chlorine atom are depicted in Fig. 6a. Generally, the toluenes, anilines and phenols have comparable ionic masses while the mass difference of chlorinated compounds without further functional groups is 14 or 15. As can be seen field strengths above 12 kV cm^{-1} permit a differentiation between these compounds. Chlorobenzene was detected at the most negative compensation voltages (−7.73 V at 30 kV cm^{-1}). Although the mass difference between the other substances is negligible, differences in compensation voltages were found. At a RF field of 30 kV cm^{-1} the signals appear at −5.79 V (2-chlorotoluene), −6.33 V (2-chloroaniline) and −7.27 V (2-chlorophenol). Therefore, an influence of functional groups on the peak position of product ions can be supposed. Dichlorobenzene with the lowest molecular weight of the substances with two chlorine atoms (Fig. 6b) appears also at the most negative compensation voltages. Slight differences between 2,4-dichloroaniline and 2,4-dichlorophenol can be established

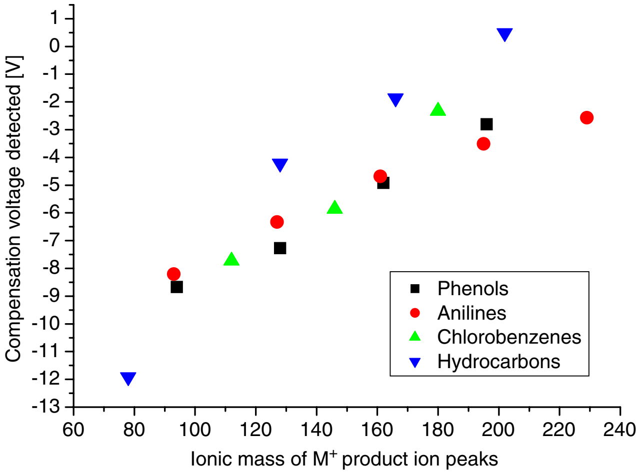

Fig. 7 Correlation between compensation voltages detected at RF amplitude of 30,000 V cm^{-1} and the ionic mass of M^{+} product ion peaks

at a RF field of 30 kV cm^{-1}. Compounds with three chlorine atoms can be differentiated at high RF field strength (Fig. 6c). In contrast to the compounds with one or two chlorine atoms, trichlorobenzene shows the most positive compensation voltage.

In order to classify the parameters influencing the field dependence of ion mobility, the detected compensation voltage for all substances were correlated with ionic mass. Figure 7 shows the compensation voltages (obtained at 30 kV cm^{-1}) for phenol and chlorinated phenols, aniline and chlorinated anilines, chlorobenzenes and unsubstituted hydrocarbon. Only one substance was considered for isomers. Although no strong linear correlation can be established, a clear dependence of peak position of product ions on their ionic mass was found. The variation of compensation voltages around the regression line indicates a possible influence of structural features. Furthermore, different slopes of correlation lines can be observed depending on the nature of functional groups. As can be seen from Fig. 7, the ionic mass has a distinct influence on the compensation voltages detected. An influence of structural features including physical size, shape and the electronic factors describing the ion-neutral interaction forces was also found. However, this influence seems to be less significant.

Conclusion

Improved separation efficiency can be observed with increasing RF field. The differences in compensation voltages detected for different compounds are more distinct using RF amplitudes higher than 1,000 V in comparison with data obtained with lower RF fields. The investigations have shown that the ionic mass is the main influencing parameter for compensation voltages detected for the substances investigated here. The nature and position of functional groups have also an influence on the peak position in DMS. However, this influencing parameter is of minor importance in comparison to ionic mass.

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