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Electric field dependence of the ion mobility

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ABSTRACT

The dependence of mobility on electric field (the alpha function in differential mobility spectrometry, DMS) is a unique ion property used for separation and characterization of gas-phase ions in DMS. This study was conducted to determine the origin of this field dependence. Several models are suggested to rationalize the field mobility dependence and explain the alpha function behavior under typical experimental conditions. Alpha function properties, calculated in the framework of each model, are compared with experimental data. Qualitative and quantitative correlations between theory and experiment are analyzed as a proof of the validity of each model. Our examination reveals that clustering with dopant and drift gas molecules is the most relevant hypothesis explaining the observed phenomena. A clustering model can serve as a basis for further investigations aimed at significantly increasing DMS resolution by drift gas modification.

1. Introduction

The method of differential mobility spectrometry (DMS) proposed in Refs. [1–3] has been recognized as a powerful tool for the separation and characterization of gas-phase ions. Developed and refined over the past decade [4,5], DMS is also known as field ion spectrometry (FIS) [6] and field-asymmetric waveform ion mobility spectrometry (FAIMS) [7]. Several configurations of DMS analyzers have shown response at ambient pressure, often in air, to trace amounts of chemical species [8], including explosives [9], chemical warfare agent simulants [10] and a variety of other organic [11] and inorganic [12] substances. Hybrid DMS techniques [13] such as GC-DMS [14], DMS-MS [15] and DMS-IMS [16] can provide detection and identification of biological materials [17].

Differential mobility spectrometry expands the capabilities of ion mobility spectrometry (IMS) by extending ion characterizations over a broad range of electric field strengths. In conventional IMS ions are distinguished and identified due to the difference of their mobility values at low electric field strengths. In DMS ions are distinguished due to the difference in their mobility dependence on the applied field strength. This field dependence is characterized by the alpha function, a characteristic ion property [18] similar to the ion mobility in IMS or m/z in mass spectrometry. As an ion characteristic the alpha function can be used for ion separation and identification. The phenomenological aspect of alpha function as an ion property is well explored, but what is the physical nature of the field mobility dependence (the alpha function)?

Field mobility dependence arises because the interaction energy increases with the electric field strength. Based upon modern understanding of ion mobility several models can be suggested to explain field mobility dependence (alpha function) [19]. Accumulated experimental data contribute material for the testing of these models. To examine the models it is important to see how they correlate with experiment, not only qualitatively but also quantitatively.

The main goal of this article is to rationalize the alpha function. We begin with the general notion of the DMS, then we summarize known experimental facts about the alpha function, the basis of DMS, and finally we consider various phenomena presumably responsible for the alpha function and compare them with the experimental data. Qualitative and quantitative correlations between theory and experiment will be analyzed as a proof of validity of each particular model.

2. Differential mobility spectrometry

The notion of the alpha function was introduced in [3] to characterize an electric field dependence of ion mobility. An electric field of strength E causes ions to move through a gas of density N with a velocity related to the electric field strength through the coefficient of mobility, K. If the energy the ion gains from the electric field is small enough in comparison with the thermal energy, K is a constant independent of E/N. The natural unit for E/N is the Townsend, 1 Td = 10^{-17} V cm^2. Under standard conditions ($N_0 = 2.687\ 10^{19}$ cm^{-3}) 1 Td corresponds to 268.7 V/cm. In this article the electric fields are normalized to the gas density and are quoted in Td units. At high electric fields the mobility coefficient changes and the normalized field mobility dependence is defined

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as the alpha function,

$$\alpha(E) = \frac{K(E)}{K(0)} - 1 \tag{1}$$

where $K(0)$ is the mobility coefficient under low field conditions and E is the electric field. The alpha function has been shown to be a unique feature of ions that is utilized for their separation in DMS.

The method of differential mobility spectrometry is implemented by passing a gas stream containing ions through a gap between two electrodes (called the "filter gap"). A high amplitude, high frequency, asymmetric electric field (called the separation field, S) affects the ions. The ions undergo fast oscillations in response to this separation field. The displacements during the positive and negative half-period of the separation field differ slightly because of unequal mobility values at high and low field. As a result, ions drift perpendicularly to the gas flow, toward one of the electrodes. An ion's drift velocity and direction depend on the separation field amplitude, the waveform, and its alpha function. Drifting ions eventually reach one of the electrodes and are neutralized. Particular ion species may be restored to the center of the gap (i.e., compensated, with no net drift) by applying a low constant electric field (called the compensation field, C). The compensation field produces an offsetting drift, allowing ions to remain in equilibrium inside the gap. Compensated ions pass through the filter gap with gas flow and can be detected electrometrically. To obtain a full DMS spectrum of an ion mixture the compensation field is scanned at constant separation field. Every ion species is characterized by a compensation field value that depends on the separation field and the ion's alpha function.

An array of DMS spectra at different amplitudes of the separation field provides the dependence of the compensation field on the separation field, $C(S)$, for the ion species. The $C(S)$ dependence (also called the dispersion plot) is an extended DMS characterization of the ion species. The $C(S)$ dependence is closely related to the alpha function and can be derived from the known alpha function and separation field [3]

$$C = -\frac{S\left\langle \alpha f \right\rangle}{1 + \langle \alpha \rangle + S\left\langle \alpha' f \right\rangle}, \tag{2}$$

where C is the compensation field; S is the amplitude of the separation field; f is a normalized waveform; α is the alpha function; α' is the derivative of the alpha function; triangular brackets denote the average over the period of the separation field. The inverse problem also can be solved: knowing the experimental $C(S)$ dependence and separation field waveform one can calculate the alpha function, $\alpha(E)$.

In the next section we summarize known experimental facts about the alpha function for further comparison with theoretical models.

3. Experimental facts

It is important to emphasize that alpha is not a number like ion mobility or ion mass but a function. As a function, alpha should be considered over a wide range of the variable (electric field). The alpha functions for seven different ions shown in Fig. 1 are different despite of the fact that they are coincide at some points. It means that two ions cannot be resolved by DMS only if their alpha functions coincide at all values of the electric field.

Alpha is stable and device independent. This means that under the same experimental conditions the same alpha function will be obtained by any DMS instrument, even though instrumental parameters such as compensation and separation voltage and waveform can be different [18]. Moreover the alpha function changes predictably with the variations of drift gas pressure [20], temperature [21] and moisture [10].

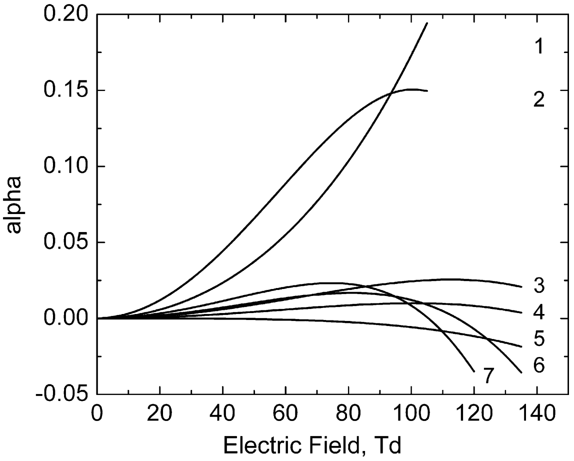

Fig. 1. Alpha vs. electric field, $\alpha(E)$, in dry clean air for positive and negative ions under conditions near standard: 1—positive reactant ions in purified air identified as the protonated water cluster $H^+(H_2O)_n$; 2—chloride ions, Cl^- (35 amu); 3—protonated methyl salicylate, H^+(MSa) (153 amu); 4—protonated diethyl ethylphosphonate, H^+(DEEP) (167 amu); 5—the proton bound dimer of diethyl ethylphosphonate, $H^+(DEEP)_2$ (333 amu); 6—deprotonated 2,4,6-trinitrotoluene ions $(TNT\text{-}H)^-$ (226 amu); 7—deprotonated 2,4-dinitrotoluene ions $(DNT\text{-}H)^-$ (181 amu).

By definition (see Eq. (1)) alpha passes through zero, $\alpha(0) = 0$, and is an even function of the electric field, $\alpha(-E) = \alpha(E)$, because of ion mobility isotropy. Alpha functions are smooth and continuous. Any break or discontinuity of the alpha function is evidence of ion transformation [20], i.e., chemical reaction. The typical pattern for alpha is to increase with the field, attain a maximum value and then decrease (see Fig. 1), but monotonic increases or decreases are possible. The values of the alpha functions in a clean dry drift gas are generally in the range −0.05 to 0.15.

The alpha function depends on dopant concentration, a dopant being a small amount (up to a few percent) of some volatile chemical in the drift gas. Usually water serves as a dopant, but other chemicals are used [9]. Alpha increases with the dopant concentration at constant field strength beginning from the level of 10 to 50 ppm$_v$. Alpha values at 80 Td for protonated monomers of organophosphorus compounds [10] are plotted against water concentration in Fig. 2a (alpha-dopant dependences). A dopant does not change the field dependence pattern of the alpha function (see Fig. 2b for the alpha-field dependence with dopant as a parameter) but increases its absolute value. Values of the alpha functions in a doped drift gas are generally in the range −0.05 to 0.3. The dopant effect may be of considerable practical importance because it increases the resolving power of the DMS instrument.

The alpha functions for ions of homologous series are proportional to the inverse ion mass [22,10]. The alpha-mass dependences, $\alpha(1/m)$, in dry clean air for the homologous series of protonated monomer and dimer ions of ketones and ions of organophosphorus compounds are presented in Fig. 3.

Below we consider processes of the ion–neutral interaction under conditions near standard (the current version of IUPAC's standard is a temperature of 0 °C and an absolute pressure of 100 kPa [23]) that might be responsible for the above behavior of the alpha function. Predicted in a framework of each model alpha properties will be compared with the experiment.

4. Ion mobility theory

Ion mobility and related phenomena have been discussed in detail in Refs. [24–26] and we provide here a brief overview of the basics involved in our analysis.

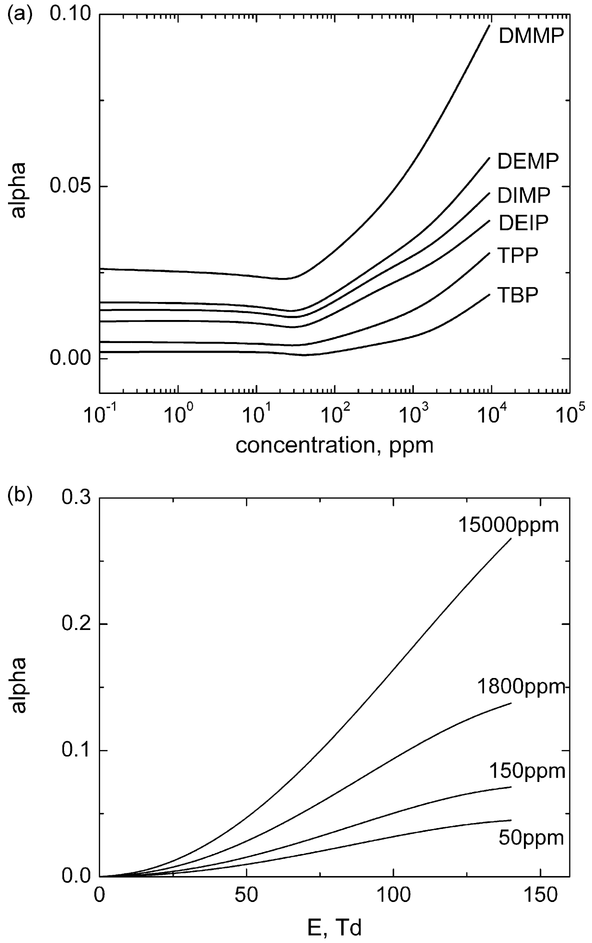

Fig. 2. (a) Alpha vs. dopant (water) concentration, $\alpha(C)$, for protonated organophosphorus compounds at 80 Td; (b) alpha vs. electric field, $\alpha(E)$, for protonated dimethyl methylphosphonate, H$^+$(DMMP), at various dopant (water) concentrations.

The ion–neutral interaction averaged over a number of collisions determines the ion mobility. Since the ion–neutral interaction depends on the interaction potential and the collision energy, the ion mobility depends on them as well. If the energy the ion gains from the electric field is negligibly small in comparison with the thermal energy, ion mobility is independent of the field; the average interaction energy is equal to the thermal energy and mobility coefficient is constant. At higher electric fields ion mobility becomes field dependent because the ions acquire substantial energy from the field and the nature of the ion–neutral interaction changes.

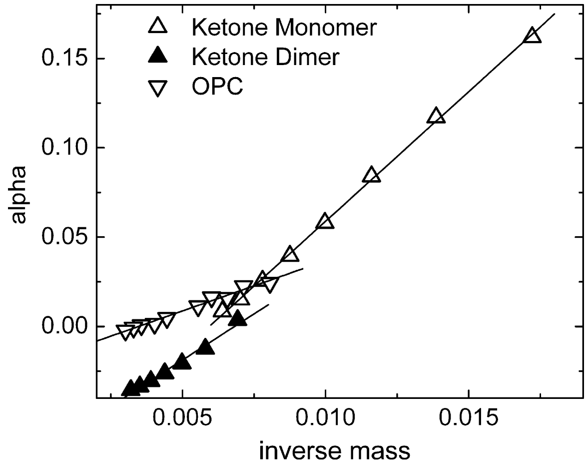

Fig. 3. Alpha vs. inverse ion mass, $\alpha(1/m)$, in dry clean air for a homologous series (protonated monomer and dimer ions of ketones and protonated organophosphorus compounds).

In terms of the kinetic theory, the velocity distribution function of the ions is different from the distribution function of the neutral gas particles if the electric field strength is not vanishingly small. In the two-temperature ion mobility theory [27], this ion velocity distribution is modeled as a Maxwellian but the ions are assigned an ion temperature that is higher than the neutral gas temperature. We use the results of that theory because it allows a simple physical interpretation and is accurate enough to make some estimation.

Two basic concepts of the two-temperature ion mobility theory are the effective ion temperature and the diffusion cross-section. The effective ion temperature, T_{ef}, is defined by the average energy of the ion–neutral interaction. The diffusion cross-section, σ, is an integral characteristic of the interaction potential and in general, diffusion cross-section depends on the energy of the ion–neutral interaction as well. The main equations of the two-temperature ion mobility theory are [28]

$$K = \frac{3q}{16N}\sqrt{\frac{2\pi(m+M)}{mMkT_{\mathrm{ef}}}}\frac{1}{\sigma(T_{\mathrm{ef}})} \tag{3a}$$

$$T_{\mathrm{ef}} = T + \frac{MK_0^2E^2}{3k} \tag{3b}$$

where K_0 is the reduced ion mobility; m is the ion mass; M is the drift gas molecular mass; N is the drift gas density; T_{ef}, is the ion effective temperature; T is the drift gas temperature; $\sigma(T_{\mathrm{ef}})$ is the diffusion cross-section; k is the Boltzmann's constant; q is the ion charge; and E is electric field strength in Td units.

Substituting Eq. (3a) into Eq. (1) yields alpha in dependence on the effective temperature

$$\alpha(T_{\mathrm{ef}}) = \frac{\sigma(T)}{\sigma(T_{\mathrm{ef}})}\sqrt{\frac{T}{T_{\mathrm{ef}}}} - 1 \tag{4}$$

Ion individuality through the ion–neutral interaction potential defines the diffusion cross-section and consequently the alpha function. The electric field defines the ion energy (effective temperature) and consequently the alpha-field dependence. Field, temperature and effective temperature relations in application to DMS are discussed in Ref. [21].

Calculation of diffusion cross-sections is a key problem in ion mobility studies. As of yet, there is no integrated model with either interpretative or predictive capabilities for a broad range of molecular ion sizes, structures, or functional groups. We therefore analyze simplified models to find ones correlating with experimental data.

5. Ion–neutral interaction

The non-linear field mobility dependence results from field-induced changes in the interaction energy and diffusion cross-section. That dependence may be understood as arising through several mechanisms.

The presence of ions in a gas polarizes the gas molecules. Induced dipoles interact with the ion. The attractive *polarization* potential of the ion-induced dipole interaction, $V(r){\sim}r^{-4}$, was found [29] to be dominant under low temperature and low field conditions in common drift gases (air, nitrogen). The diffusion cross-section for the polarization potential has been shown [30] to be inversely proportional to the square root of the effective temperature, $\sigma{\sim}(T_{\mathrm{ef}})^{-1/2}$. This accurate result is based on dimensional arguments alone. Substituting it into Eq. (4), zeroes the alpha function, i.e., $\alpha(T_{\mathrm{ef}}) = 0$. Thus the pure polarization potential of the ion–neutral interaction gives no field-mobility dependence, $\alpha(E) = 0$.

At higher interaction energy the short-range repulsive potential becomes important. A rigid sphere scattering model is a reasonable assumption for this case. Diffusion cross-section for the model does not depend on the interaction energy, $\sigma = \text{const}$. Substituting it into Eq. (4) yields a decreasing alpha function

$$\alpha = \sqrt{\frac{T}{T_{\text{ef}}}} - 1 \tag{5}$$

Notice that most of known molecular ions in light gases like air or nitrogen have falling branch of the alpha function at high enough electric field.

The presence of molecules with a permanent dipole moment in the drift gas is a typical situation (moisture). The long-range attractive ion–dipole potential, $V(r) \sim r^{-2}$, must be considered in that case. The diffusion cross-section of the ion–dipole potential is inversely proportional to the effective temperature [30], $\sigma \sim (T_{\text{ef}})^{-1}$. Substitution in Eq. (4) yields an increasing alpha function for the pure dipole drift gas

$$\alpha = \sqrt{\frac{T_{\text{ef}}}{T}} - 1 \tag{6}$$

Most ions are known to have a rising alpha function at low enough gas temperature.

Ion clustering with neutral molecules inevitably takes place in gases at moderate pressure. A cluster ion is a bound state of an atomic or molecular ion with a neutral atom or molecule. Clustering affects both the mass and the diffusion cross-section (and hence mobility) of an ion. The degree of clustering decreases with increasing effective temperature, so we may expect an increasing alpha function, $\alpha(E) > 0$.

The last three models may provide a set of principles to rationalize empirical trends. The best test of any model is its ability to reproduce experimentally observed phenomena both qualitatively and quantitatively. We will estimate the alpha function based on these models and compare predicted and observed its behavior. The field dependence, mass correlation and dopant effect will be investigated in a framework of the rigid scattering, ion–dipole and clustering models for conditions similar to those in typical experiments. The drift gas is clean air or nitrogen under conditions near standard. Small amount of dopant (10–10,000 ppm_v) may present in the drift gas. The electric field is limited by the breakdown value (120–150 Td). The core ions are assumed to be stable.

6. Comparison

Rigid sphere scatterings model. The diffusion cross-section for the rigid sphere scattering model does not depend on the effective temperature. Alpha is inversely proportional to the square root of the effective temperature. Substituting the effective temperature from Eq. (3b) into Eq. (5) yields the alpha function dependence on the electric field strength (alpha-field) for the rigid scattering model

$$\alpha_{rs}(E) = \frac{1}{\sqrt{1 + (MK_0^2E^2/3kT)}} - 1 \tag{7}$$

where K_0 is the reduced ion mobility; M is the drift gas molecule mass; T is the drift gas temperature; k is Boltzmann's constant; E is the electric field strength in Td.

We compare experimental alpha-field data for the proton bound dimers of DMMP, DEEP, TPP, TBP [10] (Fig. 4a, solid lines) and corresponding estimates from Eq. (7) for ions of the same mass 249, 333, 449, 533 amu respectively (Fig. 4a, dotted lines). The theoretical alpha-field dependences are qualitatively similar to those observed experimentally, but they differ quantitatively.

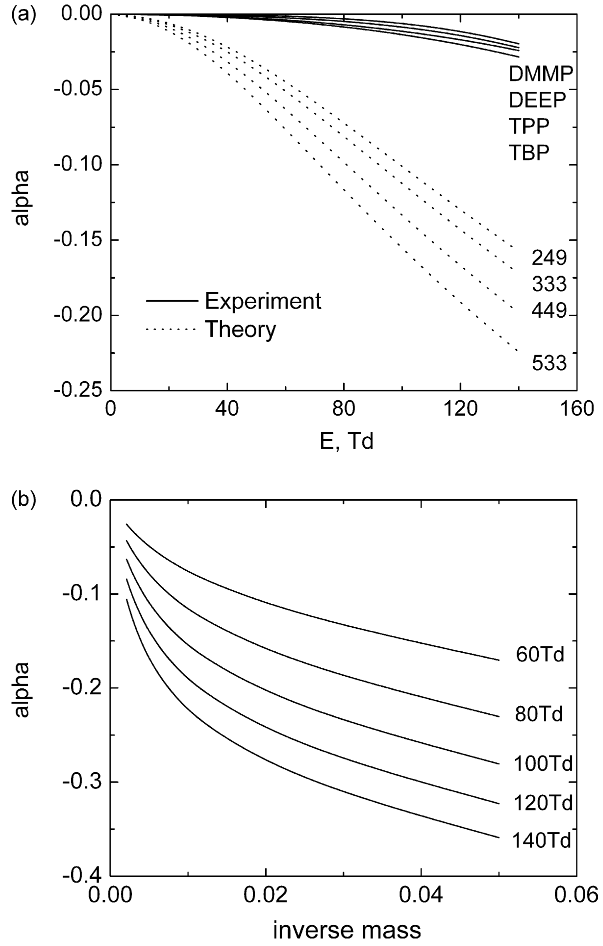

Fig. 4. Rigid scatterings model: (a) alpha-field dependence, $\alpha(E)$, experimental data for dimers of DMMP, DEEP, TPP, TBP (solid lines) and corresponding (249, 333, 449, 533 amu) estimations in a framework of the rigid scattering model (dotted lines); (b) alpha-mass dependence, $\alpha(1/m)$.

Alpha in the rigid scattering model depends on the ion mass only through the reduced mobility (K_0). The dependence of the reduced ion mobility on the ion mass is given by the empirical relation [31]

$$K_0 = A - B\ \ln(m), \tag{8}$$

where $A = 4.8\ \text{cm}^2/\text{V s}$; $B = 0.65\ \text{cm}^2/\text{V s}$ and m is the ion mass in amu. The accuracy of Eq. (8) is about ±20% for structurally unrelated ions and about ±2% for homologous series (with corresponding constants). The dependence of the alpha function on the ion mass (alpha-mass) in Fig. 4b differs from the experimental one in Fig. 3.

Obviously, the alpha function is independent of the dopant concentration in a framework of the rigid scattering model.

Ion–dipole interaction. The diffusion cross-section for the ion–dipole potential is inversely proportional to the effective temperature so the alpha is proportional to the square root of the effective temperature. Substituting the effective temperature from Eq. (3b) into Eq. (6) yields the alpha-field dependence for the ion–dipole interaction

$$\alpha_{id}(E) = \sqrt{1 + \frac{MK_0^2E^2}{3kT}} - 1. \tag{9}$$

The ion–dipole interaction is expected to be dominant in a dipolar drift gas. Eq. (9) is in a fair agreement with experiment studies of alkali ions in pure water vapors [32].

Neither oxygen nor nitrogen, the most used drift gases in DMS, has a permanent dipole moment so only the dopant molecules (e.g., water molecules) may be involved in ion–dipole interactions. Let us estimate the alpha function in a typical experimental condition of a two component gas media: drift gas and dopant. The drift gas molecules are considered as induced dipoles (polarization potential of interaction, alpha is zero) and the dopant molecules as dipoles (dipole potential of interaction, alpha is positive).

Blanc's law for a dopant present in low concentration yields an estimate of ion mobility in the mixture

$$\frac{1}{K} \approx \frac{1}{K_1} + \frac{C}{K_2}, \tag{10}$$

where $C \ll 1$ is the dopant concentration; K_1 is the ion mobility in pure drift gas; K_2 is the ion mobility in pure dopant gas.

The alpha function for the mixture is

$$\alpha = \frac{\alpha_1}{1+x} + \frac{\alpha_2}{1+\alpha_2} \cdot \frac{x}{1+x}, \tag{11}$$

where $x \equiv C(K_1/K_2)$ and $\alpha_1, \alpha_2, \alpha$, are, respectively, the alpha functions in the drift gas, the pure dopant gas and the mixture.

Assuming $\alpha_1 = 0$ and $x \ll 1$, Eq. (9) and Eq. (11) allow estimation of the alpha function dependence on the electric field strength (alpha-field), dopant concentration (alpha-dopant) and ion mass (alpha-mass). Results of the calculations for air as a drift gas and water as a dopant are presented in Fig. 5.

Calculated and experimental alpha-field, alpha-mass and alpha-dopant dependencies are qualitatively similar, however quantitatively the calculated dependencies are much smaller than the experimentally observed ones (compare Figs. 1–3 and Fig. 5). Because of such a serious disagreement with experiment we conclude that the ion–dipole model does not adequately describe ion–neutral interaction in a DMS analyzer.

Clustering. A cluster ion is a bound state of an ion with neutral molecules, which may be dopant molecules, drift gas molecules or its own neutral molecules. The cluster bond energy is relatively low (0.1–1 eV) and the cluster ion mobility is expected to depend strongly on the electric field strength [33]. An increase of cluster ion mobility at high field strength arises from a decreasing effective ion cross-section that is governed by the degree of clustering. The degree of clustering is strongly dependent on the electric field strength because of the low bond energy. At high fields, the more weakly held neutrals are removed as the effective temperature of the cluster ion increases while at low field clustering increases as the effective temperature is lowered.

Below we make quantitative estimations [19] of these phenomena and compare them with experimental data. To formalize the calculation task we consider a drift gas containing ions and cluster prone neutrals at a much higher concentration than the ions. The probability of the ions being clustered with n neutrals is denoted W_n. By definition

$$\sum_{n=0}^{\infty} W_n = 1. \tag{12}$$

The number of the neutrals in the cluster is determined by the competitive processes of association and dissociation. The dynamical equilibrium may be characterized by the averaged number of the neutrals clustered with the ion, which depends on the external conditions and the cluster bond energy. Notice that the average number of the neutrals clustered with the ion is not an integer.

$$n_{av} = \sum_{n=0}^{\infty} n W_n. \tag{13}$$

Since the clustering is a dynamic process the cluster mobility should be considered as an average value. At each moment the ion mobility is determined by the actual number of the neutrals clustered with the ion. But only the average cluster mobility, K, is measured experimentally

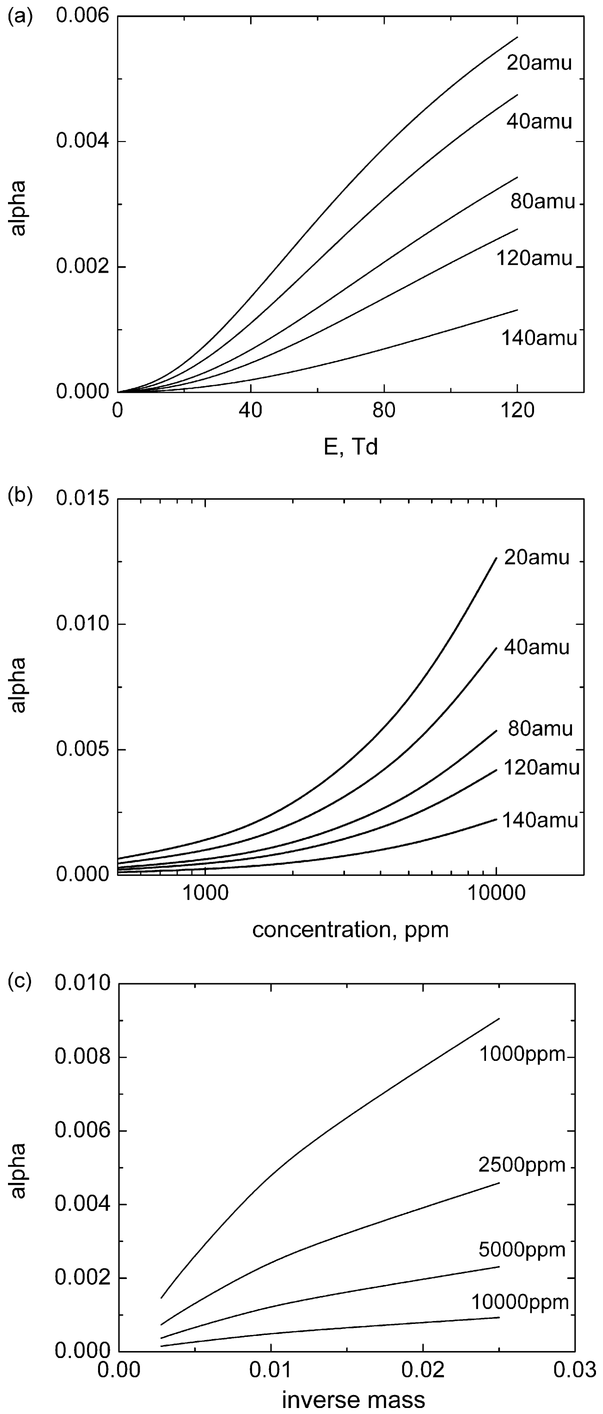

Fig. 5. Ion–dipole interaction: (a) alpha-field dependence, $\alpha(E)$, for ions of various masses at 5000 ppm$_v$ of water; (b) alpha-dopant dependence, $\alpha(C)$, for ions of various mass at 80 Td; (c) alpha-inverse mass dependence, $\alpha(1/m)$, for various dopant concentrations at 80 Td.

$$K = \sum_{n=0}^{\infty} W_n K(n), \tag{14}$$

where $K(n)$ is mobility of the ion clustered with n neutrals.

An accurate calculation of $K(n)$ is beyond the scope of this paper. For estimation we assume that clustering affects the mobility only through the mass of clustered ion. The effects of shape, softness and field conformation are ignored. This aspect has received attention in Ref. [34] that is devoted to the dipole alignment of heavy organic ions in strong electric fields in application to DMS.

Despite that simplification, our assumption is quite accurate for a limited variation of the effective temperature due to the electric field. Under that assumption the average cluster mobility is

$$K = K(n_{av}) = K(m + n_{av}M), \tag{15}$$

where m is the ion mass, M is the neutral mass. Any mass mobility correlation may be used for the estimation, e.g., the popular notation given by Eq. (6). Thus in the framework of our model, cluster mobility estimation is reduced to the calculation of the average number of neutrals clustered with the ion, n_{av}, given by Eq. (13).

Statistical physics provides a suitable apparatus for such tasks. An equilibrium system with possible transfers between states (assuming a Boltzmann energy distribution and Gibb's energy as the cluster bond energy) obeys the equation [35]

$$W_n = W_{n-1} C \exp\left(\frac{H_n}{T} - S_n\right) = C^n \exp\left(\sum_{i=1}^{n}\left(\frac{H_i}{T} - S_i\right)\right), \tag{16}$$

where C is the relative concentration of the clustering molecules; H_n is the enthalpy and S_n is the entropy of the transfer from the cluster state $n-1$ to the state n; T is the cluster temperature.

Substituting Eq. (16) into Eq. (13) yields the average cluster size

$$n_{av} = \sum_{n=1}^{\infty} nC^n \exp\left(\sum_{i=1}^{n}\left(\frac{H_i}{T} - S_i\right)\right), \tag{17}$$

In general, values of the enthalpy and the entropy depend on the cluster state n, but if we consider a limited range of conditions at high dopant concentration, constant enthalpy and entropy may be used for the estimation. If H_i and S_i are constants, Eq. (17) has following analytical solution

$$n_{av} = \frac{C\, \exp((H/T) - S)}{1 - C \exp((H/T) - S)} \tag{18}$$

Thus the cluster size (and hence the cluster mobility) is sensitive to the concentration of clustering particles, cluster temperature and bond energy. According to the concept of effective temperature an electric field influences the cluster in the same way as a temperature. An electric field increases the effective temperature of the cluster and hence reduces the averaged number of the neutrals bound to the ion. The cluster mobility increases with the electric field (alpha is positive) because the cluster mass decreases.

Assuming enthalpy and entropy values to be constants ($H = 5500$ K, $S = 14$) we derive the alpha-mass and alpha-dopant dependencies for the dopant concentration of 5000 ppm$_v$ (see Fig. 6). Despite some level of assumption Eq. (18) yields quite good agreement with the experimental data for the alpha-field, alpha-dopant and alpha-mass dependencies (compare Figs. 1–3 and Fig. 6).

Notice that the ion–dipole model and the clustering model give very similar alpha dependencies (compare Figs. 5 and 6). 10 times scaling makes them practically identical. This similarity is not accidental because the physical reality behind both models is a strong attractive potential. That potential is considered as a long-range in the ion–dipole model. The same potential results in the ion bound state accounted in the clustering model. Apparently cluster formation is more relevant than long-range interaction for ion mobility in general and particularly for DMS.

Clustering model accuracy can be improved by using the exact values of the enthalpy and entropy of clustering for certain ions (data can be found on the NIST web-site http://webbook.nist.gov/chemistry/). These data allow accurate comparison with experiment. The alpha-field dependence for the positive reactant ions $H^+(H_2O)_n$ was calculated by Eq. (17) for low water concentration (50 ppm$_v$). Theory and experiment are in a good quantitative agreement (see Fig. 7a).

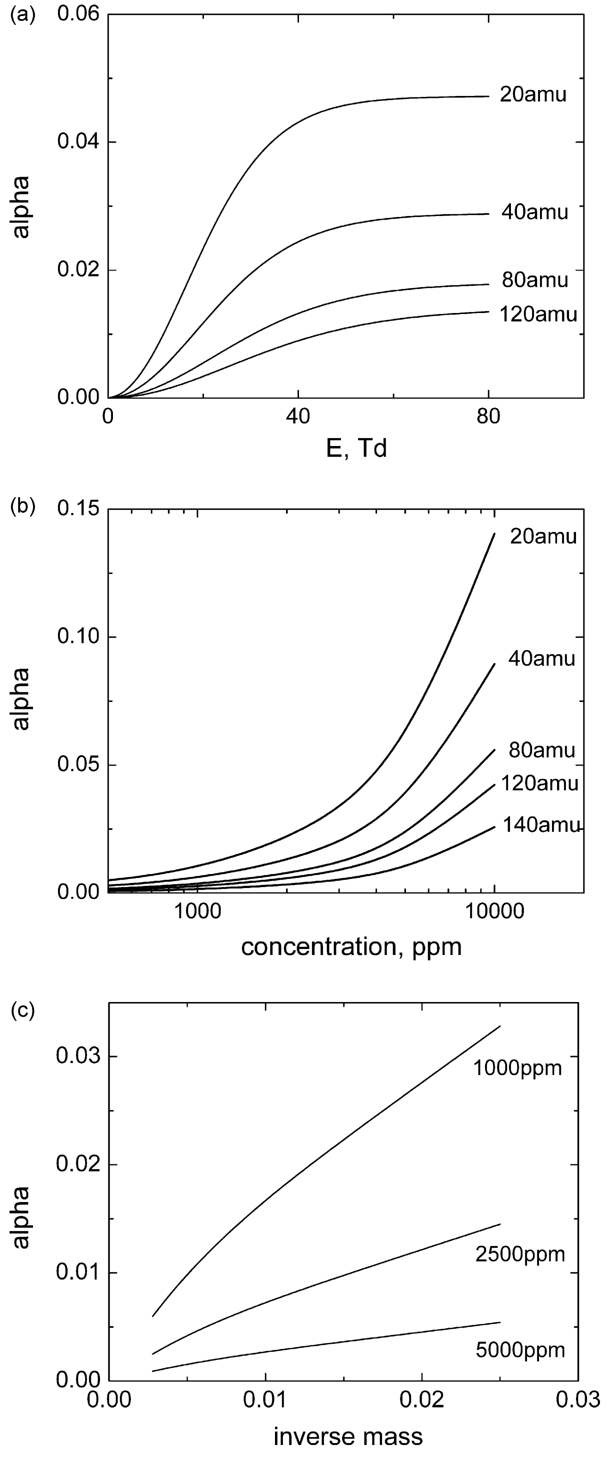

Fig. 6. Clustering model at high water concentrations: (a) alpha-field dependence, $\alpha(E)$, for ions of various mass clustered with water at 5000 ppm$_v$; (b) alpha-dopant dependence, $\alpha(C)$, for ion of various mass clustered with water at 80 Td; (c) alpha-mass dependence, $\alpha(1/m)$, for a hypothetical homologous series at 80 Td and various dopant concentrations.

The alpha-dopant dependence presented in Fig. 6b yields a zero alpha value at zero dopant concentration. But DMS separation at very low dopant concentration was experimentally observed (see Fig. 2a). It means that the alpha-field dependence exists even in the dry and clean drift gas. It can be explained in a framework of

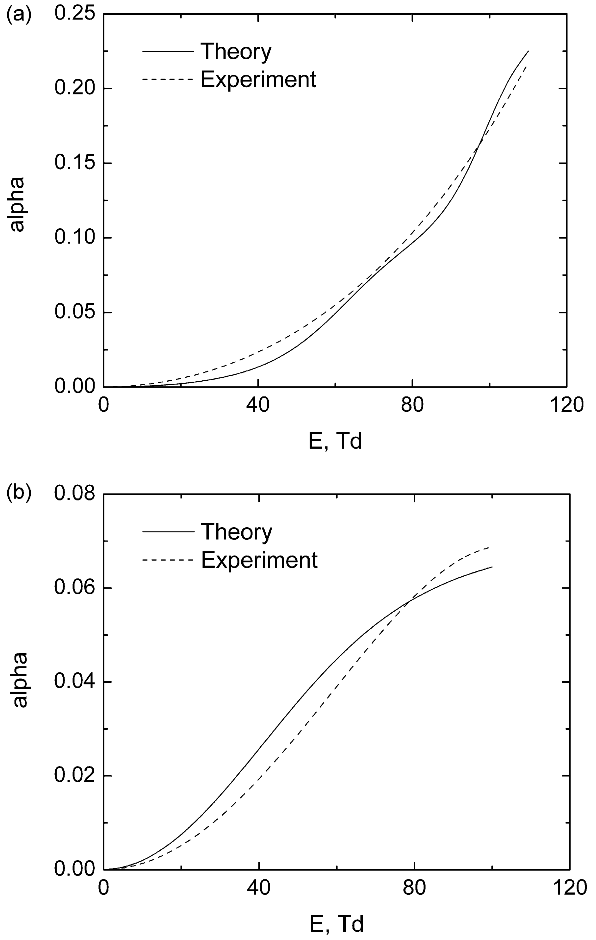

Fig. 7. Comparison of the clustering model results with experimental data: (a) water clustering, alpha-field dependence, $\alpha(E)$, for positive reactant ions $H^+(H_2O)_n$ at 50 ppm_v of water; (b) nitrogen clustering, alpha-field dependence, $\alpha(E)$, for NO^- in a very dry (water < 1 ppm_v) nitrogen.

the clustering model because the ions can cluster with the drift gas molecules, e.g., nitrogen. The bond energy for the nitrogen molecules is much lower than for the water molecules but the drift gas concentration is much higher than dopant concentration, so the combined effect is comparable. Data for the estimation of nitrogen clustering can also be found on NIST web-site. Calculated curve for the NO^- ion is in a good agreement with experimental data (see Fig. 7b).

7. Conclusion

To rationalize the alpha function (normalized field mobility dependence) we considered three models of the ion–neutral interaction at elevated electric field strength: the rigid sphere scattering, the long-range ion–dipole attraction and the clustering. In the framework of each model we evaluated three dependencies: the alpha-field, the alpha-dopant and the alpha-mass, and compared the predictions with experimental data.

Our examination reveals that ion clustering with the dopant molecules and/or the drift gas molecules is the most relevant hypothesis explaining the observed phenomena. Theory and experiment in a framework of this model are in good quantitative agreement.

Rigid sphere scattering is important at elevated interaction energy and should be taken into account for the heavy ions, high electric fields and high temperatures.

The long-range ion–dipole attraction makes a small contribution to the field mobility dependence. It provides a small correction term for the clustering model.

In general our models give a reasonable explanation of the observed phenomena and may serve as a basis for further investigations aimed at significantly increasing DMS resolution by the drift gas modification.

In this area of study much research remains to be done. First of all, effects considered separately superimpose, i.e., the modeled phenomena affect ion mobility simultaneously. Generally speaking dopant clustering, drift gas clustering and the rigid sphere scattering should be considered together for accurate prediction of the alpha function over a wide range of experimental conditions.

Also it would be of great interest to understand how the ion's shape, softness and field conformation affect the alpha function. These findings may be of considerable practical value for the DMS separation of heavy organic molecules in biological and medical applications.

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