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Pressure effects on resolution in ion mobility spectrometry

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Abstract

This paper explains the effect of pressure on separation factor, resolving power (defined based on a single peak), and resolution (defined based on two adjacent peaks) in ion mobility spectrometry. IMS spectra were recorded at various pressures ranging from 39 hPa (29 Torr) up to atmospheric pressure and various ion gates ranging from 50 to 225 μs. The results show that the IMS peaks shift perfectly linear with pressure so that separation factors remain unaffected by pressure. However, pressure has strong influence on resolving power and resolution. Reducing pressure at constant pulse width decreases the resolving power and resolution. On the other hand, the decrease in resolution can be compensated by shortening the ion pulse width since reducing pressure results in a higher ion current.

Keywords: Ion mobility spectrometry; Pressure; Separation factor; Resolution; Resolving power

1. Introduction

Ion mobility spectrometry (IMS) is a technique mostly used for detection and monitoring chemical warfare agents, explosives and drugs of abuse [1–3]. It is also used for the monitoring potential atmospheric pollutants as well as examining the conformation of peptides [4] and proteins [5] in the gas phase.

In IMS, ions are separated according to their individual velocities as they drift through an inert gas driven by an electric field [6–9]. As for any other separation technique, the ability of an IMS instrument to resolve two closely spaced peaks is of considerable interest. High-resolution IMS instruments can resolve structural isomers and provide an accurate measure of their average collision cross-section.

Resolution of IMS and its dependency on various experimental parameters such as temperature, the applied voltage and the pulse duration has been the subject of a number of studies. A theory was developed by Spangler and Collins to describe the shape of ion peak in IMS [10]. Considering the initial pulse width and diffusion of ions, Hill and co-workers [11] derived an equation for the dependence of IMS resolution on various instrumental parameters. Their results show that IMS resolution is directly proportional to the square root of the potential across the drift region and inversely proportional to the square root of the drift gas temperature. Siems et al. [12] in their study on IMS resolution illustrated that peak widths are wider than contributions from initial pulse width and diffusion predict. They suggested that the discrepancy between experimental and calculations is due mainly to electric field inhomogeneity and Coulombic repulsion. Dugourd et al. [13] described a high-resolution IMS to resolve and study the isomers with similar compact structures. They employed a special ion gate and reported a resolving power, which was an order of magnitude higher than that achieved using conventional injected ion drift tube techniques.

The temperature dependency of IMS peaks has also been investigated [12,14]. It has been experimentally and theoretically shown that the resolving power is inversely proportional to the square root of the drift gas temperature [11]. However, it was shown in our previous work that the peak-to-peak resolution may increase with temperature in some cases [14]. The increase or decrease in resolution at elevated temperatures has been attributed to different hydration and clustering tendency of ions.

In addition, the use of different drift gases to alter separation factors in ion mobility spectrometry has been demonstrated [15,16]. Separation factors were shown to be influenced by the drift gas polarizability. Therefore, two closely peaks may be resolved using an appropriate drift gas. Finally, an expanded

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theory for the resolving power of a linear ion mobility spectrometer was derived by Spangler [17].

Although the effect of drift voltage, gate pulse width and the shape and, temperature, drift time, and the effect of instrument dimensions as well as the drift gas on resolving power of IMS peaks have been studied, the effect of pressure has not been experimentally investigated. In this paper the effect of drift gas pressure on separation factors, resolving power and resolution of IMS peaks will be discussed.

2. Experimental

The corona discharge ion mobility spectrometer used in this work was constructed in our laboratory at Isfahan University of Technology. A detailed description of the instrument can be found in reference [18]. The IMS cell was specially designed to allow reducing pressure inside the drift tube. The cell was made of glass tube, 27 cm long and 36 mm inner diameter, with interchangeable ST conical joins on both ends. The sealing was achieved by the use of precisely machined caps on both ends. The guard rings were mounted outside the glass tube, where they always were exposed to atmospheric pressure. This configuration prevents sparking between the guard rings when the pressure inside the glass tube is reduced. The cell was evacuated using a rotary vacuum pump via a glass–Teflon tap. Two needle valves were employed to control the flow of the drift gas (nitrogen) and the sample. Desired pressure could be obtained by adjusting the inlet and outlet valves. Pressure could be adjusted between ambient pressure and 20 hPa (15 Torr) and was measured by a digital barometer (Afzar Azma JMB-30R). The drift tube was operating at ambient temperature (∼25 °C) and the electric field was about 270 V/cm. The pulse generator was able to apply sharp and short pulses from 20 to 300 μs for opening the shutter grid. A fast analog to digital converter (ADC-212 Picotech) was employed to record spectra. Ionization was achieved by corona discharge with a point-to-ring geometry.

3. Results and discussion

In the present work, the effect of reducing pressure on the separation factor, the resolving power, and resolution was evaluated and will be presented in the following sections.

3.1. Separation factors

The separation factor, α, is defined for two adjacent peaks as the ratio of the their corresponding drift times.

$$\alpha = \frac{t_{d2}}{t_{d1}} \tag{1}$$

Separation factor plays a major role in determining resolution. Separation of two peaks is proportional to the value of $1-\alpha$. Separation factor was proved to be affected by temperature[14] and drift gas [15]. However, separation factor was observed to be independent of pressure. In Fig. 1, IMS spectra for methyl iso-buthyl ketone (MIBK) in various pressures have been presented. The first peak is the reactant ion peak (RIP) and the second and the third are thought to be the protonated monomer and dimer, respectively. This figure shows that as pressure reduces, the peaks get closer to each other so that the drift times as well as their separations shorten by the same ratio. This means that the separation factor remains unchanged when pressure varies, as it is clear from Fig. 2 in which the spectra were reduced to a reference peak by dividing the drift times to the drift time of the reactant ion peak (RIP, $H(H_2O)_n^+$). All spectra superimpose on each other, i.e. the relative separations remain unchanged upon changing pressure. This is consistent with Mason–Shamp theory in which the drift time is linearly proportional to number density (pressure), hence the relative drift times are predicted to be invariant with pressure. However, this is different from what was observed for the case of temperature [14]. Such a different behavior has been attributed to the different effects of temperature and pressure on declustering and dehydration of ions, which was fully discussed in reference [19].

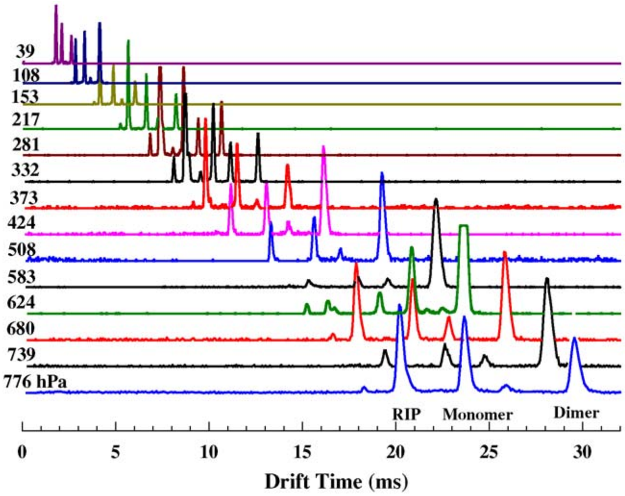

Fig. 1. Ion mobility spectra of methyl-iso-butyl ketone at different pressures.

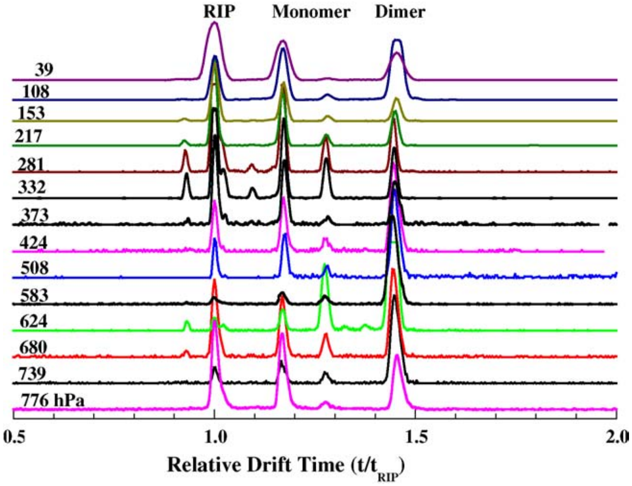

Fig. 2. Normalized ion mobility spectra of methyl-*iso*-butyl ketone at different pressures. The drift times were normalized to the drift time of the reactant ion.

3.2. Resolving power

The generally accepted resolving power, R_p, for IMS is based on single-peak [12], which is defined as

$$R_p = \frac{t_d}{W_{1/2}} \tag{2}$$

where t_d is the ion drift time and $W_{1/2}$ the ion pulse duration at the detector measured at half of the maximal intensity. The drift time of an ion is related to the drift length, L, electric field in which the ion is drifting, E, and the mobility of the ion, K as following [7]

$$t_d = \frac{L}{KE} \tag{3}$$

The peak width of an IMS peak can be attributed to different broadening mechanism: initial pulse width, diffusion, charge repulsion, ion–molecule reaction, and inhomogeneity in the electric field. The two first mechanisms are the major factors determining the shape and the width of the IMS peaks. So that

$$W_{1/2}^2 = W_0^2 + W_d^2 \tag{4}$$

where W_0 is the width of initial pulse gated into the drift at half-height and W_d the width at half-height of the Gaussian peak that would be produced by diffusional broadening of an infinitely narrow initial pulse. W_d can be derived from the temporal duration of an IMS peak as following [12],

$$W_d = \left(\frac{16 \ln 2kT}{qEL}\right)^{1/2} t_d \tag{5}$$

Combining Eqs. (2), (4) and (5) yields

$$R_p = \frac{1}{\left((W_0^2/t_d^2) + (16 \ln 2kT/qEL)\right)^{1/2}} \tag{6}$$

The theoretical influence of pressure on resolving power can be realized from Eq. (6). In this equation, only t_d is pressure dependent. As shown before [19], t_d is linearly proportional to the pressure. Thus, the effect of pressure on resolving power is expected to be similar to the drift time effect that has been investigated by Hill and co-workers [11]. If t_d in Eq. (6) is substituted with βP where, β is an appropriate coefficient, then the resolving power can be expressed as;

$$R_p = \frac{1}{\left((W_0^2/(\beta P)^2) + (16 \ln 2kT/qEL)\right)^{1/2}} \tag{7}$$

This equation shows that at constant temperature and electric field, resolving power generally increases with pressure. However, the rate of increase depends on the initial pulse width and the pressure range. For wide pulses, the term ($16 \ln 2kT/qEL$) can be neglected. Then the resolving power gently increases with pressure. Conversely, for short pulses, the term $W_0/\beta P$ is important only at low pressures. Consequently, at low pressures, the resolving power increases rapidly but at high pressures, it approaches an asymptotic value of $qEL/16 \ln 2kT$. This value is usually referred to the diffusion limited resolving power [11], R_d.

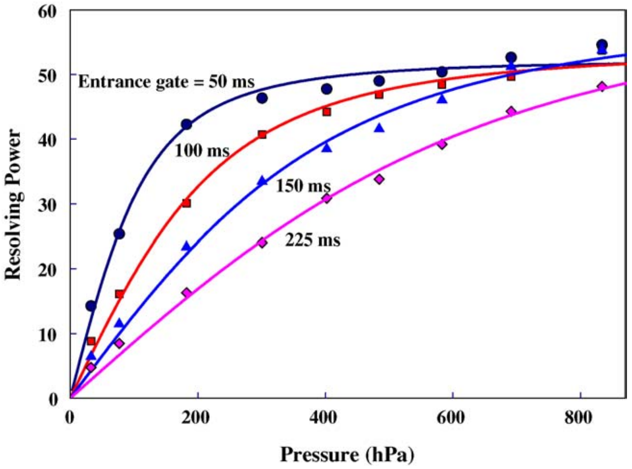

Fig. 3. Predicted and measured resolving power with different gate widths at various pressures. Eq. (7) was used for calculation of theoretical resolving power.

The expected behavior was practically examined by measuring IMS resolving power as a function of pressure at various entrance gate widths. The primary reactant ion was used to measure instrument resolution at selected pressures. The results are illustrated in Fig. 3. The data fit reasonably well in a function of $R_p = [(W_0/\beta P)^2 + \delta]^{-1/2}$ where β and δ are the fitting parameters. Eq. (7) reveals that, as pressure goes to zero, regardless of the initial pulse duration, the resolving power goes to zero too; this behavior is clear from Fig. 4. On the other hand, although resolving power increases with pressure, as Eq. (7) shows, it cannot exceed a certain value. This value, or the diffusion limited resolving power ($R_d = qEL/16 \ln 2kT$) is pressure independent. For the narrowest pulse width and at elevated pressures, the resolving power is almost independent of pressure.

3.3. Resolution

The separation efficiency of IMS may also be measured in terms of peak-to-peak resolution, $R_{p\text{–}p}$, defined on the basis of

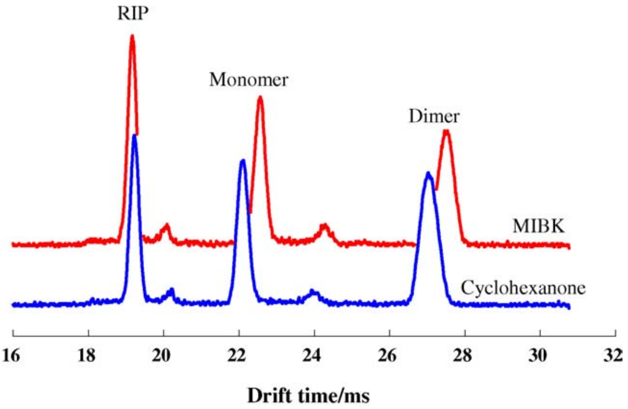

Fig. 4. Ion mobility spectra of cyclohexanone and MIBK at ambient pressure.

separation of pairs of adjacent peaks, as in chromatography [20],

$$R_{\text{p–p}} = \frac{2(t_{\text{d2}} - t_{\text{d1}})}{w_{\text{b1}} + w_{\text{b2}}} = \frac{\Delta t_{\text{d}}}{w_{\text{b avg}}} \tag{8}$$

where t_{d2} and t_{d1} are the drift times of the two adjacent peaks, and w_{b1} and w_{b2} their respective widths at the base. The two resolutions are connected together by

$$R_{\text{p–p}} = 0.589 R_{\text{p}} \frac{\alpha - 1}{\alpha} \tag{9}$$

where α is the separation factor [14]. It was shown that the separation factor is not affected by pressure. Thus, the behavior of the resolving power and peak-to-peak resolution would be the same upon changing pressure. Therefore, the resolution decreases with reducing pressure. This was practically examined by recording IMS spectra of cyclohexanone and MIBK with partially overlapping monomer peaks (Fig. 4) at various pressures.

The resolution gets worse by decreasing pressure. However, as Eq. (7) shows, reducing the gate width compensated the negative effect of reducing pressure on resolution. Similar result was observed for the case of ethyl-acetate and amyl-acetate, which have overlapping spectra at ambient pressure.

4. Conclusions

The changes in separation factor, resolving power, and resolution have been studied varying the pressure in IMS below the ambient pressure. Results show that unlike increasing temperature, reducing pressure has no effect on separation factors but decreases the resolving power and resolution. However, at reduced pressure the ion current is high enough to allow using narrower gate widths to partially compensate the negative effect of decreasing pressure on resolution.

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