Theoretical modeling of sensitivity factors of Bayard-Alpert ionization gauges

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ARTICLE INFO

ABSTRACT

Measuring the relative sensitivity factors (S_r) in Bayard-Alpert ion gauge is technically demanding and time-consuming. Moreover, the accuracy deterioration in the low pressure range (high vacuum) becomes problematic. Experimental S_r values are reported for 91 molecules of diverse molecular structures. A three-descriptor QSPR model based on experimental data is established. The model obtained, which explains more than 93% of the data variance, has a good statistical validity and stability. The three selected molecular descriptors, Kier & Hall index, charge difference on the molecular surface, and count of H donor sites appropriately describe the physicochemical background of the relative sensitivity factors. The model developed in this work is freely accessible through the web: http://www.ut.ee/qsar.

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1. Introduction

Gas-phase measurements of ion/molecule equilibriums have generated vast amount of different affinity (acidity and basicity) scales, which have been widely used for the studies of the reaction energetics and their utilization in different fields [1–5].

Equilibrium measurements in trapping devices such as ion cyclotron resonance (ICR) mass spectrometer [6] have been extensively used for the determination of Gibbs free energies of ligand exchange (relative basicities) as illustrated by reaction (1) for a cation M^+:

$$[L^1M]^+ + L^2 \leftrightarrows [L^2M]^+ + L^1 \tag{1}$$

Adduct ions are trapped in presence of known pressures of neutral ligands. When the trapping time is long enough to allow for a sufficient number of ion/molecule collisions, a steady state is observed, and the equilibrium constant K can be calculated from the ratios of pressures P and of ion intensities I:

$$K = \frac{I_{L^2M} \cdot P_{L^1}}{I_{L^1M} \cdot P_{L^2}} \tag{2}$$

The difference between the cation basicity of L^1 and L^2 is given by the standard thermodynamic relation $\Delta_r G = -RT \ln(K)$. The ions intensities are measured from mass spectra at adequate reaction times and the pressures are usually obtained from a Bayard-Alpert

(hot-cathode) ionization gauge. The choice of the Bayard-Alpert gauge is dictated by operating range (mostly high vacuum, especially for ICR) and their ease of operation. Nevertheless, the pressure reading of these gauges depends on the gas whose pressure is to be measured [7,8].

The true gas pressure (P_{true}) and the gas pressure measured by a Bayard-Alpert ion gauge (P_{BA}) are related through the following equation:

$$P_{BA} = S_A \cdot P_{true} \tag{3}$$

where S_A is defined as the absolute ionization gauge constant or sensitivity factor of an ion gauge [9]. The ion gauge sensitivity depends on several factors such as the grid potential [10,11], the ion gauge geometry [12,13], sorption phenomena and temperature effects [14,15] and finally the gas species. In other words, there are several operating conditions, as well as the nature of the gas, which are involved in the variation of the sensitivity factor. For a specific ion gauge operated under known conditions, a relative sensitivity factor S_r for a given gas was formulated by Dushman and Lafferty [16]. It is defined as the ratio of the absolute sensitivity relative to the sensitivity factor of a standard gas (usually N_2) (Eq. (4)).

$$S_r = \frac{S_A}{S_{N_2}} \tag{4}$$

Dushman and Lafferty [16] postulated that the relative sensitivity is a constant for a given gas, irrespective the external experimental conditions and the ion gauge used. This hypothesis has been tested by Summers [17] with 104 measurements obtained for different type of ion gauges and for 14 gas species.

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In addition, the molecular structure effects on the relative sensitivity have been studied in order to estimate these constants. Several quantitative relationships between the relative sensitivity and molecular parameters (calculated or measured) were established. The most commonly used relationship is the one with the polarizability, first established by Summers [17] and later extended by Bartmess and Georgiadis [18]. The relationship obtained for organic species (excluding hydrocarbons) is given by Eq. (5).

$$S_r = 0.36\alpha_V + 0.30 \qquad (5)$$

where α_V is the polarizability volume in (10^{-30} m^3) and is defined by Eq. (6).

$$\alpha_V = \frac{10^6}{4\pi\varepsilon_0}\alpha \qquad (6)$$

where α is the polarizability in C m^2 V^{-1} and ε_0 is the vacuum permittivity.

It should be noted that alkanes and alkenes (as well as rare gases) do not match this equation [18]. Relative sensitivity values calculated by Eq. (5) can be applied with reasonable confidence when comparing two gas pressures, in particular the pressure ratio in Eq. (2) is expected to be satisfactory for similar gases, but the general method accuracy is difficult to estimate. From the scatter of the plot S_r vs. α in the Bartmess and Georgiadis study [18], the experimental S_r deviates from the regression line by up to 10%. In a more general appreciation of the indirect estimation of gauge sensitivity for different gases from ionization cross section [19], Jousten estimated a level of accuracy of only 10–20%. Furthermore, it should be noted that in the previous model proposed by Bartmess and Georgiadis [18], the data set contained only a few carbonyl groups (one aldehyde and three ketones), or nitrogen containing functions (ammonia and three nitriles).

One of the methods to measure the sensitivity factor of an ion gauge is a comparison between its pressure reading with that of an absolute gauge [8,20]. Although these types of measurements are relatively simple for permanent gases and volatile compounds for which a steady pressure is easily obtainable, complications arise in the case of compounds of low volatility. Indeed, these compounds are often polar and "sticky" (strong surface adsorption on the vacuum vessel), and lead to sorption phenomena that increase the time to reach a steady pressure. Consequently, the measurement of sensitivity factors for these type of compounds could be rather time consuming and prone to errors. The aim of the present work is to develop more comprehensive and more accurate predictive model for the relative sensitivity of Bayard-Alpert ionization gauges by means of quantitative structure–property relationships (QSPR). QSPR approaches are widely used for the prediction of diverse properties of chemical compounds and materials [21].

2. Methodology

2.1. Experimental background

All compounds presented in Table 1 were of commercial origin (Air Liquide-France for gases, Carlo Erba, Peypin, France, and Sigma–Aldrich-Fluka, Lyon, France for liquids) of the highest purity available. Gases and vapors were introduced through leak valves (Varian, Turin, Italy, or Meca 2000, Nanterre, France) in the ultrahigh vacuum chamber of a laboratory made FT-ICR spectrometer (electropolished and breakable stainless steel analyzer) and pumped by a 300 L s^{-1} diffusion pump (Alcatel Crystal 100, Annecy, France) or a 250 L s^{-1} turbomolecular pump (Leybold Turbovac, Villebon-sur-Yvette, France). The gases or vapors were used without further purification, except for removal of the non condensable gases by several freeze-pump-thaw cycles. System design

was fully described by Gal and coworkers [22]. In particular, the two gauges to be compared were located at the same position on the duct connected to the high-vacuum pump to ensure that they were submitted to the same pumping speed.

Before each experiment, the whole vacuum system was baked-out above 150 °C. The measurements were performed when the parts were stabilized at room temperature (air conditioning, 23 ± 0.5 °C). The Bayard-Alpert gauge (glass envelope, Alcatel BN 111) was degassed by electron bombardment during 15–30 min. The pumping speed of the vacuum chamber was reduced by partially closing the isolation valve of the analyzer. Just after the degassing period, the pressure was often above 10^{-7} mbar (1 mbar = 100 Pa), and decreased slowly. The background was read when the ion gauge (IG) reading became stable after about 15–30 min. The baseline pressure given by the Bayard-Alpert gauge was typically about 5×10^{-8} mbar. This pressure was subtracted from the pressure reading of the Bayard-Alpert ion gauge.

The spinning rotor gauge (SRG) [23,24] is an absolute gauge when the molecular mass of the gas is known. It allows the calibration of any other vacuum gauge by direct comparison in a wide pressure range. In the present work this range was approximately 10^{-6} to 10^{-4} mbar. The steel ball of the SRG, which is a kind of viscosity gauge, was then put in rotation. The SRG (Leybold Viscovac VM 210; located just in front of the IG) is sensitive to temperature. The SRG residual pressure (apparent background, called "offset") should be stable to obtain a constant value of the offset. In addition to the IG stabilization, a period of offset stabilization (15–30 min) was necessary, considering that each measurement with the SRG takes 2–3 min. The offset measurement of the SRG was recorded, for correcting the pressure reading. Afterward, the leak valve was slowly opened in order to obtain a steady pressure in the 10^{-6} to 10^{-5} mbar range (Bayard-Alpert gauge reading). The stability of pressure was observed by the means of a digital voltmeter and an analog pen recorder, both connected to the analog socket of the ion gauge controller.

The first step of the calibration process involved the determination of the absolute sensitivity of N_2 as reference gas. The compound under study was measured in a second step. We also checked in several instances that the N_2 sensitivity did not change significantly after the introduction of organic compounds in the system. When a steady pressure was reached, the pressure measurements were performed using simultaneously the SRG and the Bayard-Alpert gauge. Measurements were carried out at several pressures from the high 10^{-6} mbar to the low 10^{-4} mbar range (Bayard-Alpert reading). An example of the direct comparison between the pressure readings obtained with the two gauges is shown in Fig. 1. In all cases, the slope of the calibration line for N_2 was stable (0.95 ± 0.01), and close to the expected unit value for an ion gauge calibrated for N_2. For a given species the slope a of the line obtained from the least square regression analysis is equal to the absolute sensitivity factor of the ionization gauge. The ratio of absolute sensitivity factor of the species under study to that of the reference gas (N_2) gives the relative sensitivity factor S_r, Eq. (4). The relative sensitivity S_r for 2-methylpropane is therefore 4.207/0.942 = 4.466 in this case.

2.2. QSPR modeling of ion gauge sensitivity factors

Relative sensitivity factor (S_r) values for the most commonly used gases are presented in several sources [17,18,25,26]. In the present work, the experimental S_r values were taken from the work of Gal and coworkers [22] and are reported in Table 1.

Altogether, a total number of 93 organic species were used and respective experimental and predicted values are presented in Table 1.

Several free or commercial softwares or web-applications and tools are available for development of predictive models and