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Kierownik: prof. dr Włodzimierz Żuk

Longin GŁADYSZEWSKI, Abdallah A. YOUSSEF*

Ionization Potentials of Di- and Triethylamine by the Surface Ionization Method

Pomiar potencjałów jonizacji dwu- i trójetyloaminy metodą jonizacji powierzchniowej

Измерение ионизационных потенциалов ди- и триэтиламина методом поверхностной ионизации

ABSTRACT

The ionization potentials of di- and triethylamine have been measured by using the surface ionization method. One-filament ion-source was used in the mass spectrometer. The measurements were performed on oxidized and clean tungsten surfaces in a temperature range from about 750 to 1600 K at a pressure of about 2×10^{-6} torrs. The obtained values of ionization potentials are compared with those of a previous work where a satisfactory agreement was observed.

INTRODUCTION

The method of surface ionization is of wide applicability since it is suitable for measuring isotopic abundance and in determining the ionization potentials for elements and appropriate compounds. The ion current produced from these types of ion sources is dependent on the ionization potential of the material and the work function of the ionizing

* Atomic Energy Establishment, Cairo, Egypt (ARE).

surface. However, for materials of high ionization potentials, a surface of high work function is needed for ionization. For tungsten filaments, it is well-known that the adsorption of oxygen considerably enhances the work function of tungsten. The maximum work function [1, 2, 3] of tungsten, coated with oxide, lies between 6.3 and 6.5 eV dropping to 4.5 eV for clean tungsten surface.

Watanabe et al. [4] measured the ionization potentials of several amines including di- and triethylamine by means of photoionization method. A one-meter monochromator having a resolution of 0.5 Å was used. Collin [5] reported a value of 8.44 V for the ionization potential of di-ethylamine. Zandberg et al. [6] measured the ionization potential of di-ethylamine by the surface ionization by means of a mass spectrometer with a three-filament ion source in a temperature range from 1100 to 1700 K at a pressure ranging from 5×10^{-7} to 10^{-6} torrs. The author did not observe the molecular mass M and reported a value of $5.9<V<6.7$ for the ionization potential of dissociation fragment M-1 (in volts).

The purpose of the present work is to measure the ionization potentials for di- and triethylamine by the surface ionization method with oxidized and clean surfaces of tungsten since an investigation of these materials by this method is rather scarce.

EXPERIMENTAL

The measurements in the present work were carried out by means of a mass-spectrometer of type MI 1201 equipped with a collector and D.C. electrometer. The high vacuum in the mass-spectrometer chamber was about 2×10^{-7} torrs. One filament ion-source was used with polycrystalline tungsten filament. In each experiment, the ionizing surface was oxidized by heating the filament at 900 K in a residual oxygen of pressure starting from 10^{-1} to 10^{-3} torrs for 20 min. The heating temperature was raised very slowly, by small steps, by a stabilized current measured, by a digital multimeter, with high accuracy. The temperature dependence of the ion current was measured in a temperature range from 800 to 1600 K for di- and triethylamine and their dissociation fragments.

THEORY

When an element of ionization potential V evaporates from a surface of work function $e\varphi$ at a temperature T, the ion current density is given by

$$I = a\, n\, e\, g^{+}/g^{0} \cdot \exp\left[\frac{e(\varphi - V)}{kT}\right] \tag{1}$$

where a is a coefficient depending on the geometry of the ion-source electrodes, n is the number of molecules coming in a unit time to the ionizing surface and g^{+}, g^{0} are the statistical weights of the ground states of the ions and the neutral molecules, respectively. The above equation can be written in the following form:

$$I = A \exp\left[\frac{11\,600}{T} \cdot (\varphi - V)\right] \tag{2}$$

where A is a constant at any temperature depending on the partition functions for ions and neutral molecules. From equation (2) it is seen that the ion current density increases if the temperature of the ionizing surface increases. For elements which have high ionization potentials, it is necessary to work with a surface with high work function $e\varphi$ to overcome the difference $(\varphi - V)$ at high temperatures. For this reason, the oxidized surface has to be used in these measurements.

Assuming the efficiency of the mass-spectrometer, flow of neutral particles n, and φ value to be constant, a logarithmic plot of the ion current density against $11\,600/T$ displays a straight line with slope of $\varphi - V$.

RESULTS AND DISCUSSION

The ion current produced by the surface ionization of di- and triethylamine and their dissociation fragments is measured as a function of temperature at a range from 800 to 1600 K. The results of measurements are presented in Fig. 1 and 2. One may see that the oxidized and clean surfaces are established in the temperature ranges from 800 to 1200 K and from 1400 to 1600 K, respectively. The results are in agreement with those reported by W e i e r s h a u s e n [2]. The data were subjected to a least square analysis where the slope of Langmuir line in these two ranges is obtained.

Assuming that the work functions of the oxidized and clean tungsten surfaces are 6.3 and 4.5 eV, respectively, the ionization potentials of di- and triethylamine and their fragments $(M-1)$ and $(M+1)$ are calculated.

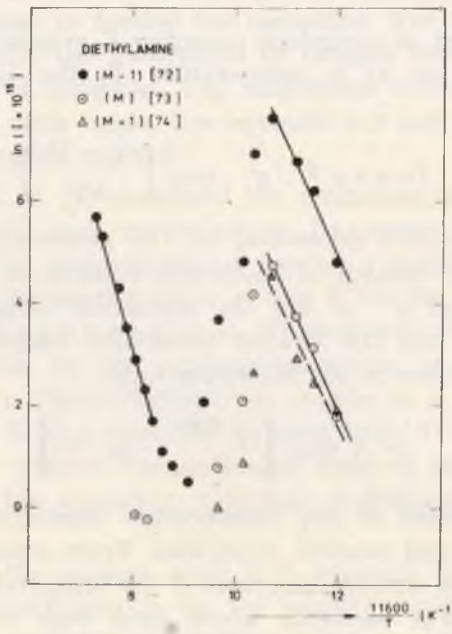

Fig. 1. Temperature dependence of the ion current for diethylamine

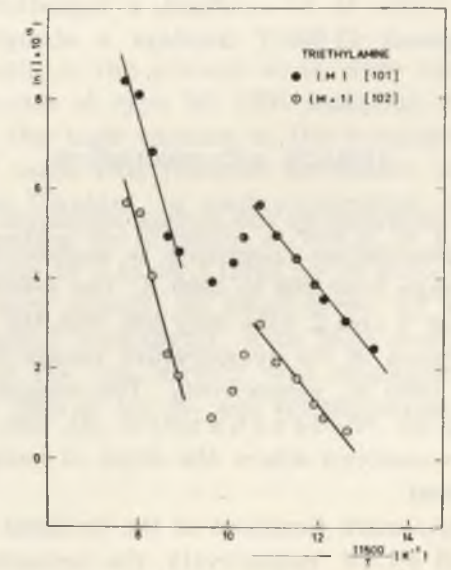

Fig. 2. Variation of the ion current with temperature for triethylamine

The obtained values are summarized in the Table in addition to the previous data. Our data for di-ethylamine are in good agreement with the value reported by Collin [5] and in poor agreement with that obtained by Watanabe et al. [4] for the two amines. The values of ionization potentials obtained by Watanabe et al. were somewhat uncertain because: 1) the amines showed very low photoionization cross-section near the ionization threshold as in the case of NH_3 and 2) each sample of amine apparently contained other amines.

It is also seen from Fig. 1 for di-ethylamine that the ion currents for the masses M and $M+1$ are relatively weak for the clean surface, and the ionization potentials are not calculated. As shown in Tab. 1,

Tab. 1. Values of the ionization potentials of di- and tri-ethylamine

Amine	M/e	V (present work)		V (previous work)	
		oxidized surface	clean surface	Watanabe [4]	Collin [5]
Di-ethylamine					
C_2H_5	72	8.33 ±0.07	8.22 ±0.07		
N—H	73	8.59 ±0.10	—	8.01	8.44 ±0.01
C_2H_5	74	8.41 ±0.27	—		
Tri-ethylamine					
C_2H_5	101	7.52 ±0.02	8.01 ±0.30		—
C_2H_5—N					
C_2H_5	102	7.45 ±0.04	8.00 ±0.33	7.82	—

the ionization potential of the fragment $(M-1)$ for di-ethylamine is nearly the same for the oxidized and clean surfaces. Moreover, the obtained value for di-ethylamine is in good agreement with that reported by Collin [5]. On the other hand, the ionization potentials for tri-ethylamine (M) and the mass $(M+1)$ observed by the oxidized surface are somewhat lower than those obtained for the clean surface. As a general feature, the ionization potentials for the mass $(M+1)$ in the two amines are nearly the same as those for mass (M) within the experimental error.

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STRESZCZENIE

Za pomocą metody jonizacji powierzchniowej zmierzono potencjały jonizacji dwu- i trójetyloaminy. Pomiary przeprowadzono dla utlenionej i czystej powierzchni wolframu, osiągając dobrą zgodność wartości potencjałów jonizacji z danymi uzyskanymi przez innych autorów na drodze fotojonizacji.

Opracowana metoda może okazać się przydatna w chemii analitycznej molekuł o wysokich potencjałach jonizacji.

РЕЗЮМЕ

Методом поверхностной ионизации измерены потенциалы ионизации диэтиламина и триэтиламина. Измерения производились на окисленных и чистых поверхностях вольфрама. Результаты измерений имеют хорошое согласие с результатами полученными другими авторами методом фотоионизации.

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