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Hydration of negative ions of trichloroacetic acid in aqueous solutions

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ABSTRACT

Mass spectrum of negative ions of trichloroacetic acid (TCA) in aqueous solution was obtained by mass spectrographic method of electrolyte solution electrospray in vacuum (ESESv). The TCA reactivity was neutralized by potassium hydroxide. The mass spectrum of TCA consists of the acid residue ions, $(CCl_3COO)^-$, hydrated by different number of water molecules. The $(CCl_3COO)^-$ ion hydrated by two water molecules has the maximum intensity. The ESESv method can be helpful for determination of the composition electrolyte solutions in ecological studies.

1. Introduction

Trichloroacetic acid (TCA) belongs to a wide class of chlorinated organic compounds frequently founded in the surrounding nature. It is a very active chemical compound having a negative impact on the environment and living organisms. TCA is practically uniformly distributed over the whole globe, because the sources of TCA are located both in the soil and in the atmosphere. The wind can carry TCA from the places of its formation over long distances, where the acid falls back to earth as precipitates. The study of ice cores of the 14th century [1] showed that natural sources of TCA existed even in the pre-industrial era. The important present-day natural source of TCA is the activity of microorganisms in the hyper saline lakes of the Caspian region and South Africa [2], leading to the formation of volatile halogenated hydrocarbons (chloroform, trichloroethylene, tetrachlorethylene, methyl chloroform). For example, Kara-Bogaz-Gol is a bay of the Caspian Sea containing one of the most saline water on the planet [3]. A total emission of volatile halocarbons from its surface is about 116 thousand tons per year. In the atmosphere, these compounds can be transformed into TCA as a result of photochemical homogeneous and heterogeneous processes. It should be emphasized that the total emissions of chlorine compounds from the hyper-saline lakes can exceed that by the all world industry. Other natural sources of TCA could be chemical processes with the participation of atomic chlorine. It is known [4] that the average global concentration of the chlorine atoms in the atmosphere is 3.7×10^4 molecule cm^{-3}. They can react with organic substances on the surface of the particles present in the atmosphere, producing TCA.

There are also anthropogenic sources of TCA. A few decades ago TCA was used in agriculture as herbicide, which led to the accumulation in the environment of TCA as well as of the products of its decay. Only in Germany about 30000 tons of TCA were produced over the past 50 years [5]. Another powerful anthropogenic source of TCA is the atmospheric degradation of vinyl chloride, which is a basic compound for the production of polyvinylchloride widely used in various areas of industry [6]. TCA is also one of the major by-products in disinfection of drinking water by chlorine employed in several countries. TCA can be also produced in the processes of biogeocoenose [7], in forest fires, during the burning of chlorine compounds and waste incineration. The detected TCA concentrations are in the range of 0.04–380 μg/kg in the soil and of 100–200 ng/l in rain water [8]. TCA can degrade in the process of deposition on the soil and percolate through it. However, the mechanism of degradation of halogenated acids in the environment is still poorly understood [9].

In a recent paper [10], the thermal degradation of chloroacetic acids in water was investigated at 15 C. The TCA life time of 46 years has been experimentally determined using extrapolation. The degradation products were found to be CO_2 and trichloromethane $CHCl_3$. The acid exerts a negative effect on the environment and living organisms. If rain water contains a significant amount of the acid, it causes damage to forests and crops. TCA can easily penetrate through the skin into the blood of humans and warm-blooded animals, where it becomes partly absorbed by the plasma protein or binds with plasma salts. The TCA behavior in aqueous solutions is one of the important environmental problems. The information about physical and chemical processes with TCA aqueous solutions is extremely limited.

Hydration shells of ions and their mass distribution must be taken into account in some of the calculations. For example, the calculation of the ion mobility in water requires knowledge of their hydrate shell. Thus, the study of TCA aqueous solutions is important both from theoretical and practical points of view.

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2. Experimental section

In aqueous solution, dissociation of trichloroacetic acid occurs according to scheme:

$$CCl_3COOH \rightleftarrows CCl_3COO^- + H^+$$

It is followed by a process of CCl_3COO^- ion hydration:

$$CCl_3COO^- + nH_2O \rightarrow (CCl_3COO)^-(H_2O)_n (n = 1, 2, 3, 4, \ldots).$$

Mass spectrographic method of electrolyte solutions electrospray in vacuum (ESESv) [11,12] was used to study the aqueous solution of TCA. In this method, the electrolyte solution is continuously sampled directly into the high vacuum chamber of a mass spectrograph through a capillary maintained under high electric potential of several kilovolts. At a certain flow rate of the solution (about 10^{-4}–10^{-5} g s^{-1}), its electrospraying at the output end of the capillary located in the high vacuum takes place and ions are emitted from the solution into the gas phase. A sign of the charge of the emitted ions coincides with the sign of the capillary potential. Both negative and positive ions can be emitted from the solution depending on a polarity of the capillary potential. Further, the emitted ions undergo a routine mass spectrographic analysis. An integrated registration method of mass spectra on a photographic film or plate was used, since ESESv emission has a pulse character.

Earlier [11], it has been experimentally shown that the ions are emitted from the solutions without distortion of their composition and quantitative relation. This was demonstrated by the experimental observation of the linear dependence of the logarithm of the ratio of the intensities of two hydrated ions against a reverse temperature of the solution (Van't Hoff law).

The main problem when dealing with TCA was its chemical activity. This problem could not be solved by using solutions with low TCA concentration, because the evaporation of the solvent (water) at the output end of capillary resulted in a significant increase of TCA concentration. Acidic activity of TCA solution was neutralized by adding potassium hydroxide in amount required to obtain pH = 7.

Figure 1 shows the scheme of the experimental set-up. The aqueous TCA solution was fed from the test-tube into the vacuum chamber through the copper capillary (internal diameter 0.3 mm, external diameter 1 mm) under the adjustable pressure of atmosphere air. The potential of −10 kV was applied to the capillary. Pressure of $\sim 10^{-5}$ Torr in the high vacuum chamber was maintained by cryogenic pumping out of water and TCA vapors at the liquid nitrogen temperature. Experimental parameters: the pressure in the vacuum chamber and the inlet orifice diameter (10 mm) were fixed. The temperature of the copper capillary of 298 K was maintained during the experiment. But the solution was cooled by evaporation in a vacuum on the end of the capillary, so that it was not possible to determine the temperature in the emission zone. The concentration of neutralized TCA was 0.01 M. The TCA used was Sigma–Aldrich commercial product of 99% purity.

The experiments were carried out using a double focusing mass spectrograph EMAL-2 ('Electron', Sumy, Ukraine) which was modified for direct sampling electrolyte solutions into the high vacuum camera. The EMAL-2 energy analyzer was tuned to transmit only the ions with the kinetic energy of 10 keV. The mass range of registered ions was $10 \div 300$. The dynamic range of registered ion intensities was about 30. Pulsed ion current was detected using photo film UV-4. The intensities of ions were determined from the photo film blackening of corresponding mass spectral lines with the help of a MD-100 microphotometer. Eight measurements of the mass spectra were carried out. The rate of feed of the solution through the capillary varied from 2×10^{-5} to 9×10^{-5} g s^{-1}. Under these conditions, the results were reproduced with an accuracy of ~15%.

3. Results and discussion

Figure 2 shows the mass spectrum of negative singly charged ions of the TCA aqueous solution neutralized by KOH. It consists of single ions and hydrated ions forming a $A^-(H_2O)_n$ ($n = 0, 1, 2, \ldots$) series. Each series begins with a head, non-hydrated ion,

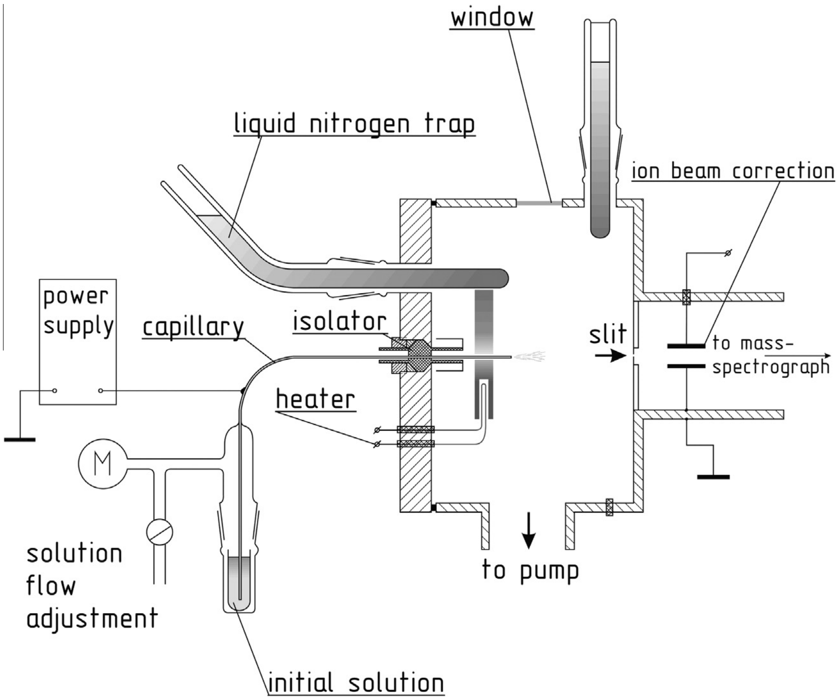

Figure 1. Scheme of the experimental set-up.