



Classical problem of determination of limiting conductances of acetate anion revisited



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ARTICLE INFO

Article history:

Received 2 July 2017

Received in revised form 24 August 2017

Accepted 29 August 2017

Available online 20 September 2017

Keywords:

Acetic acid

Alkali metal acetates

Electrical conductance

Limiting conductance of acetate anion

Diffusion coefficients at infinite dilution

Stokes radius

ABSTRACT

Precise electrical conductivities of dilute aqueous solutions of acetic acid and its lithium, sodium, potassium and cesium salts were determined from 278.15 K to 313.15 K. Conductivities of alkali metal acetates from the literature and measured here were discussed in the framework of dissociation and hydrolysis model. This was performed by using the Quint-Viallard conductivity equations for 1:1 type electrolytes and the Debye-Hückel expression for activity coefficients. Excellent agreement between experimental and calculated conductances permitted to evaluate over the investigated temperature range, a consistent and reliable set of the limiting conductances of acetate anion, their diffusion coefficients at infinite dilution and the Stokes radius. Without using additional parameters, the classical problem of representation of acetic acid conductivities in dilute solutions was reexamined and solved, indicating internal consistency of applied molecular models.

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1. Introduction

Acetic acid is an extremely important chemical reagent in chemical and food industries. Its global demand is about 6–7 million tons per year, which is faraway from production of other organic acids. It is primarily used to produce cellulose and polyvinyl acetates which are employed in production of synthetic fibers, fabrics, photographic films and glues. Acetic acid serves as a food additive and acidity regulator and plays an exceptional role in metabolism of carbohydrates and fats. In physical chemistry, acetic acid always represented a typical case of weak 1:1 type electrolyte. Also its alkali metal salts, like sodium acetate and potassium acetate are produced in large quantities. They are used in textile and synthetic rubber industries, and they serve as catalysts in organic syntheses, as food additives, pickling and deicer agents, buffers in medicine. Lithium acetate by having relatively low electrical conductivity, is used as buffer for gel electrophoresis of DNA, RNA and proteins, and is also applied used to permeabilize the cell wall of yeast for use in DNA transformations.

Starting from late twenties up to seventies of the 20th century, to properties of weak electrolytes it had been paid a lot of attention in the literature. Evidently, considering their significant importance in many areas chemistry and biochemistry, aqueous solutions of acetic acid and alkali metal acetates were extensively investigated. These

studies were devoted to evaluation of two important parameters, the dissociation constant of acetic acid K and the limiting conductance of acetate anion $\lambda^0(\text{Ac}^-)$. This can be achieved by an analysis of electrical conductances in dilute solutions of acetic acid in two steps. Firstly, by using the Ostwald dilution law and corresponding expressions for activity coefficients to determine degrees of ionization $\alpha(c)$ of acetic acid. And in the second step, using electrical conductivities, by choosing accessible at that time conductivity equations, and the Kohlrausch law of independent ionic mobilities, to assess $\lambda^0(\text{Ac}^-)$ values. This was performed by extrapolating to infinite dilution conductances of four strong electrolytes in the form $\Lambda(\text{HAc}) = \Lambda(\text{HCl}) + \Lambda(\text{NaAc}) - \Lambda(\text{NaCl})$. This rather complex procedure to determine from conductance experiments consistent K and $\lambda^0(\text{Ac}^-)$ values is presented in a number of publications, part of them regarded as classical papers on this topic [1–22]. The indirect way to evaluate the limiting conductances of acetate anion is associated with an impossibility to measure accurately acetic acid conductivities in extremely dilute solutions (less than $c < 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, see Fig. 1). Besides, $\lambda(\text{H}^+)$ values are about eight times larger than $\lambda(\text{Ac}^-)$ values, so their contribution to determined conductivity are predominant, and this prevents to estimate correctly the part associated with acetate anion. Difficulties to obtain consistent results were in part experimental (e.g. calibration of electrodes, quality of used ultra-pure conductivity water, glass or silica cells, CO_2 in air and so on), and in part theoretical (e.g. used conductivity equations, form of activity coefficients, extrapolation procedures, corrections for impurities in water, hydrolysis and dissolved carbonic acid). Evidently, different experimental conditions and calculation procedures led to

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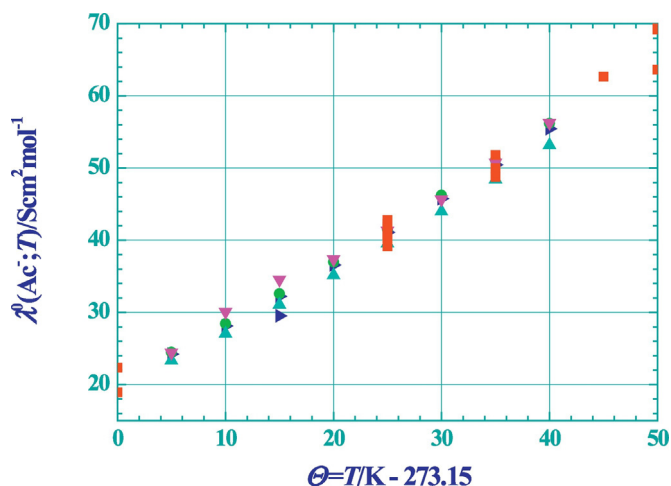


Fig. 1. The limiting conductance of acetate anion in water as a function of temperature as determined from the literature values for NaAc and KAc and in this work from LiAc; NaAc and KAc; CsAc. ■ - determined from the literature NaAc, KAc; this work: ▲ - LiAc; ● - NaAc; ▲ - KAc; ▼ - CsAc.

different values of dissociation constants and limiting conductances of acetate anions. For example, at 298.15 K, the literature values lie in the following intervals $1.5 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3} < K < 1.9 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ and $37.85 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} < \lambda^0(\text{Ac}^-) < 40.90 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ (hereafter in the text these units will be omitted). The reliability of determined dissociation constants in conductivity determinations was confirmed by an alternative experimental technique, the electromotive force measurements of cells without liquid junctions. Actually, tabulated in the literature K values for acetic acid are coming from these investigations [8–10]. With establishing experimental and calculation procedures, an applied treatment was later extended to other weak acids and bases in salt solutions or in organic solvents [23–31].

Electrical conductances of acetic acid, and of only few sodium acetate and potassium acetate solutions, started to be measured early. Determined conductivities, which are of rather historical value, are coming from Kohlrausch in 1876 at 291.15 K, Ostwald [32] in 1889 at 298.15 K and from the Jones group [33] in 1912, from 273.15 K to 338.15 K. Evidently, they are considerably less accurate than modern determinations and they were at that time analyzed by using only the Ostwald dilution law. With improved experimental accuracy (acetic acid conductivities in extremely dilute aqueous solutions up to 10^{-7} M , were measured by Hlasko and Salit [17]), determined results in all following investigations were treated by including a simultaneous examination of HCl, NaCl, HAc and NaAc conductivities, different forms of conductivity equations and the Debye–Hückel expressions for activity coefficients. In spite of the fact that hydrolysis of sodium acetate was reported early [34,35], usually it was assumed that sodium acetate (salt of weak acid) behaves as a strong electrolyte, and if hydrolysis exists it is too small to be taken into account. Only Jeffery and Vogel [6] corrected their conductances by taking into consideration the effect of hydrolysis of Ac^- anion and the effect of dissolved in water H_2CO_3 . The hydrolysis in solutions with acetate anions were investigated much later [36,37]. Contrary to expected, the performed experiments were limited to only few temperatures, and the Robinson and Stokes tabulation [38] gives only $\lambda^0(\text{Ac}^-; 273.15 \text{ K}) = 20.1$, $\lambda^0(\text{Ac}^-; 291.15 \text{ K}) = 35.0$ and $\lambda^0(\text{Ac}^-; 298.15 \text{ K}) = 40.9$ values.

Two events are responsible for a renew interest in strong and weak electrolytes. In late sixties of 20th century, under guidance of Professor J. Barthel from the Institute of Physical and Theoretical Chemistry of the Regensburg University, it was developed a modern equipment and new procedures were applied to determine outstandingly accurate conductances of electrolyte solutions. They included construction of new measuring cells and superior standardization of them, and the

exceptional temperature control over a wide temperature range [39–42]. Measuring procedures and similar superb equipment was later relocated to Chair of Physical Chemistry, Faculty of Chemistry and Chemical Technology of the Ljubljana University and later modified and upgraded [43]. The second event was in 1976, when Quint and Viallard [44–47] proposed a new conductivity equation to represent conductivities of electrolytes of any type. By using this equation, the need for the extrapolations from determined $\Lambda(\text{HAc}) = \Lambda(\text{HCl}) + \Lambda(\text{NaAc}) - \Lambda(\text{NaCl})$ conductivities is unnecessary and dissociation constants and limiting mobilities are evaluated simultaneously by proper computation procedure (for its explicit representation see also [48]).

The aim of this study is to present very accurate and systematic conductivities of lithium acetate, sodium acetate, potassium acetate, cesium acetate and acetic acid in the 278.15 K to 313.15 K temperature range, and to reexamine the literature conductances of acetates and acetic acid. Using the Quint and Viallard conductivity equation, the Debye–Hückel expression for activity coefficients, and taking into account hydrolysis reactions, the “best” reliable set of limiting conductances $\lambda^0(\text{Ac}^-)$ is proposed. A knowledge of these limiting conductances and $\lambda^0(\text{H}^+)$, K , and K_w values from the literature [10,38], permits to evaluate consistent conductivities of acetic acid without additional adjustable parameters. The validity of proposed molecular model is confirmed by observing a very good agreement between experimental and calculated conductivities.

2. Experimental

2.1. Materials

Lithium acetate (product no. 517992, 99.95%), sodium acetate (product no. 229873, 99.995%), potassium acetate (product no. 255785 99.98), cesium acetate (product no. 450154, 99.99%) and acetic acid (product no. 338826, glacial, 99.99%) were purchased from Sigma Aldrich. All salts were dried for 24 h at room temperature with a vacuum line ($p < 0.01 \text{ Pa}$) and stored in a desiccator over P_2O_5 before use.

Demineralized water was distilled two times in a quartz bidistillation apparatus (Destamat Bi 18E, Heraeus). The final product with specific conductance $< 6 \cdot 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ was distilled into a flask permitting storage and transfer of water into the measuring cell under an atmosphere of nitrogen. Stock solutions were prepared by mass and were stored under nitrogen.

2.2. Conductivity measurements

The conductivities of the solutions were determined using an equipment described in detail previously [43]. The three-electrode measuring cell was calibrated with dilute potassium chloride solutions [41,42]. The measuring procedure, including corrections and extrapolation of the sample conductivity, κ , to infinite frequency, has been described in [43]. The densities, d , of the stock solutions and the final solutions in the conductivity cell were determined at $298.15 \pm 0.01 \text{ K}$ by Anton Paar density meter DMA 5000 (Anton Paar, Graz, Austria) with a declared reproducibility $\sim 1 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$. A linear change of density at temperature T , $d(T) = d_0(T) + b \cdot m$, where $d_0(T)$ is the density of water at given temperature, and m the molality of the electrolyte. From these data the density gradients b for all the examined electrolytes were determined (b parameters are given in Tables S1–S5 in Supporting information). The corresponding molar concentration $c(T)$ were calculated by using the relation $c(T) = m \cdot d(T) / (1 + M_2 \cdot m)$, where M_2 is the molar mass of the solute and $d(T)$ is the density of the solution at temperature T . Considering the sources of error (calibration, measurements, impurities), the specific conductivities are estimated to be accurate within 0.3%.

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