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New trends in capillary isotachophoresis

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Abstract. Modern ideas concerning electrical transport in electrolyte solutions and capillary isotachophoresis — one of the microanalytical methods based on the different mobilities of ions in electrolyte solutions — are briefly considered. The isotachophoretic methods are classified in terms of the positions of the solutions and the directions of motion of the boundaries. The application of the coulophoretic method to the analysis of solutions, the measurement of the amount of electricity passed through the system, and the measurement of the internal cross-section of the capillaries are described. A description is also given of the electromigration method for crystallisation in capillaries and the isotachophoretic method for the determination of the electrical transport of the solvent in electrolyte solutions. The bibliography includes 96 references.

I. Introduction

The phenomena associated with the motion of ions in electrolyte solutions were discovered in the middle of the XIXth century. It was then observed that species migrate in an electrolyte solution when a constant electric field is applied to the latter,[1–3] the cations and anions of the same electrolyte moving at different rates in the electric field in the solution.[4] The concepts of the mobility and transport numbers of ions in solution were therefore introduced. The formation of a boundary between two electrolyte solutions with a common ion was later observed in a constant electric field.[5] The boundary between solutions having a common anion migrates to the cathode while that between solutions having a common cation migrates to the anode. Kohlrausch and Whethem formulated the stability conditions in their classical studies.[6,7] They showed that a boundary between solutions which are stable in time may be formed only when the mobility of the non-common ion of the electrolyte, present ahead of the boundary in the direction of its motion under the influence of the electric field, is greater than the mobility of the non-common ion of the electrolyte to the rear of the boundary. Kohlrausch also established that the concentration of the solution to the rear of the boundary in the steady state is constant under the given conditions and is determined by the concentration of the solution ahead of the boundary. He derived theoretically the so-called regulating function, one of the forms of which was later given his name:

$$\frac{c_1 z_1}{c_2 z_2} = \frac{u_{c1}}{u_{c1} + u_{a2}} \frac{u_{c2} + u_{a2}}{u_{c2}} = \frac{t_{c1}}{t_{c2}} . \qquad (1)$$

Here c_1 and c_2 are the concentrations of two solutions with a common anion separated by a steady-state boundary, the subscripts 1 and 2 denote that the given quantity refers respectively to the front and rear solutions, u_c and u_a are the mobilities, i.e. the velocities in a unit electric field, of the cations and anions respectively, z_1 and z_2 are the charges on the cations, and t_c are the transport numbers of the cations. The Kohlrausch function (1) was formulated for a boundary between two solutions with different cations and a common anion.

The electrode solution (catholyte or anolyte) ahead of the boundary is called the leading solution (leader), while that to the rear of the boundary is called the terminating solution (terminator). The concentration of the terminating solution changes during the adaptation process (the attainment of the stationary state) in such a way that after a certain time, determined by the strength of the electric field and the difference between the mobilities $(u_{c1} - u_{c2})$, it becomes comparable to the quantity required by the regulating function. The adaptation constitutes an important property of such boundaries.

The formation of boundaries between two solutions is used to determine the transport numbers and mobilities of ions. The widths of the boundaries have been estimated theoretically.[8–10] Towards the end of the 1920s, the first attempts were made to use ionic boundaries for the separation of certain chemical elements.[11] Considerable interest in electromigration methods arose again in the 1960s in connection with the use of capillaries and the development of instrumental methods for the detection of boundaries in them. Such is a brief history of the development of *isotachophoresis* — the term applied to this phenomenon at the present time. This term implies the motion of non-common ions

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on either side of the boundary at the same rate (equal velocity motion).[12]

It is noteworthy that the study of the phenomenon of isotachophoresis involved mainly dilute solutions and certain fundamental problems of electrical transport in electrolyte solutions were not considered. Up to the 1960s, simplified ideas concerning the motion of species in electrolyte solutions predominated. It was assumed that, at least in strong electrolyte solutions, ions are rigidly bound to the nearest water molecules and migrate together with the latter under the influence of the field.[13] This led to the erroneous view that the water in the electrolyte solution is present in two states—'free' and 'bound'. The so-called free water was chosen as the reference system in the measurement of the mobilities and the corresponding transport numbers of ions. Hence appeared the widely used concepts of 'apparent' and 'true' transport numbers corresponding to the 'apparent' and 'true' mobilities, etc. The incorrect ideas about the kinetic phenomena in electrolyte solutions led to a whole series of errors, which entered into a familiar monograph on kinetic phenomena in electrolyte solutions[14] and electrochemical manuals.[15]

II. Modern ideas about electrical transport in electrolyte solutions

The initial concept in electrical transport phenomena is that of ionic mobility. The latter is considered, in particular, because it is assumed that the electrolyte under consideration dissociates in aqueous solution only into ions of known composition. According to modern ideas, this claim is valid only for a small number of strong electrolytes in an aqueous solution in the range of low and moderate concentrations. As regards the majority of ionogenic substances, one cannot assume that all the ions into which they dissociate in aqueous solutions are known over a wide range of concentrations. Therefore in the general case one introduces the concept of the mobility of an ionic component. This is the average mobility of all the ionic forms, which includes the ionic component under consideration.[16] For example, in a cadmium chloride solution, the ionic component (cadmium) forms part of the cations Cd^{2+} and $CdCl^{+}$ and the anions $CdCl_3^-$ and $CdCl_4^{2-}$, but at moderate concentrations it migrates to the cathode in an electric field. The experimentally measured quantity is in fact the transport number of the ionic component. It is equal to the number of equivalents of this component transported in the direction of the cathode (or anode) when one Farad (0.96×10^5 C) passes through the solution. Clearly, when the ion is identified with the ionic component, significant errors may arise in the interpretation of the experimental results for electrical transport.[16] Unfortunately, the necessary difference is not drawn between the ion and the ionic component in many monographs and textbooks.

The concept of mobility presupposes the existence of a reference system in the measurement of the rate of motion of the ionic component in a specified electric field. The reference systems may be various including stationary and mobile ones. The laboratory system linked to the measuring instrument is stationary. Mobile systems may be linked to any species migrating in the solution under the influence of the field, for example to solvent species. The reference system can move at a rate averaged over all the moving species constituting the solution (mass-average, molar-average, etc. rate).[17] Another characteristic of electrical transport is the transport numbers expressed in terms of the mobilities of the ionic components (J). According to IUPAC rules,[18] they should be referred to the ionic components and determined in the coordinate system in which the mobilities included in them have been measured. It is noteworthy that the majority of Russian textbooks on electrochemistry did not require, until very recently, the introduction of a reference system in the determination of mobilities and transport numbers (two textbooks are exceptions[19,20]). These problems have been considered in detail by the present authors.[21]

The question which transport numbers (and in what coordinate systems) are measured by the corresponding experimental methods is fundamental.

We shall begin its consideration with the isotopic boundary method,[22] since it made it possible to demonstrate experimentally the difference between the reference systems in the measurement of mobilities and transport numbers. The essential feature of the method is as follows. Conditions preventing the convective mixing of the solutions are established in the electrolytic cell. A boundary is formed in the cell between two solutions with the same electrolyte concentration but different concentrations of an isotope of one of the elements of the electrolyte and the solvent. The position of the isotopic boundary of the electrolyte and the solvent is fixed relative to the measuring tube. A definite amount of electricity is passed through the cell, after which a number of samples are taken and the isotopic concentrations of the ionic component and the solvent are measured in them. The positions of the isotopic boundaries of the solvent and the ionic component are found from these data after passing a current or, in other words, the migration of the ionic component in the solvent as a result of the passage of a definite amount of electricity is determined.

The isotopic boundary method can be applied using a specially developed apparatus.[23] In order to eliminate convective mixing, the working compartment is filled with finely dispersed quartz sand with a grain size of 20–40 μm. The introduction of a bypass tube with a tap precludes the possibility of hydrodynamic flow (and hence a displacement of the boundaries) by a process other than electromigration. The extent of electroosmotic flow (V_{osm}) and the displacement of the boundaries caused by it are calculated from preliminary measurements of the flow potential ΔV for a pressure drop ΔP from the thermodynamic relation

$$\frac{V_{osm}}{I} = \frac{\Delta V}{\Delta P},$$

where I is the electric current passed during the period of the experiment.

Special measures are taken in order to obtain results stable in relation to the flow potential. The isotopic solvent (water) boundary is established by adding deuterium-enriched water to the second solution. The concentration of deuterium does not then exceed several atomic per cent, which makes it possible to refer the measured characteristics of the electrical transport to aqueous solutions with the usual isotopic composition. The deuterium content in the water is determined by the highly sensitive temperature-flotation method from the temperature of the indifferent equilibrium of a quartz microfloat.[24] The isotopic analysis of the added components is carried out mass spectrometrically. The water and lithium isotopic boundaries in the lithium chloride solution under conditions where a 50 mA current is passed through the system for 5 h migrate in the tube towards the cathode without change in their initial form. The water isotopic boundary lags behind the lithium isotopic boundary. It should be noted specially that the migration of the boundary due to the electroosmotic flow of the entire solution is similar in terms of magnitude to the electromigration displacement even at the fairly high solution concentration of 2 M. Failure to take into account electroosmosis was apparently the principal cause of the considerable scatter in the experimental results in previous studies of electromigration in solutions.[25]

Thus it has been confirmed experimentally that water in the lithium chloride test solution migrates towards the cathode when the current is passed and the difference between the laboratory coordinate system and the 'solvent as a whole' system in the measurement of the mobilities and transport numbers was clearly demonstrated. This result agrees qualitatively with the idea that the frequency of exchange of the water molecules close to the surface of the strong electrolyte ion and the remaining water is close to the exchange frequency of the water molecules in water.[26] One may conclude that at the same time there are no grounds for

subdividing the solvent molecules into those which are bound and not bound to the electrolyte ion and for the selection of the free solvent as the reference system in measurements of mobilities and transport numbers. Naturally, all the above effects are manifested appreciably only at moderate and high concentrations of electrolyte solutions. When the solution concentration tends to zero, the differences between the reference systems disappear.

We shall consider, from the standpoint of modern ideas, the coordinate systems in which mobilities and transport numbers are measured by classical methods.

The *Hittorf method*–the first known method for the measurement of transport numbers—consists of the following steps. The change in the number of equivalents of the ionogenic substance is measured (the transport numbers of the ionic components are determined for this purpose) in the electrode compartment of the electrolytic cell after passing a definite amount of electricity. For this purpose, the cell is fitted with a tap, which makes it possible to remove part of the solution from the electrode compartment after electrolysis and to determine the concentration of the test substance in it. On the basis of the erroneous ideas concerning the water bound to ions, most workers assumed that the Hittorf method yields apparent transport numbers. This was explained by the presence of an unaccounted for amount of water transported into the electrode compartment, where the difference between the concentrations before and after electrolysis is determined.[13,15] However, the Hittorf method has one experimental feature which has not been noted by many investigators. The point is that the amount of solution in the section separated for analysis changes during electrolysis. Therefore one determines in this section not only the amount of the test substance but also that of the solvent. Since the volume of the corresponding section of the apparatus is known, the amount of the solvent in it before the start of the electrolysis is likewise known. The most important element of the calculation by the Hittorf method is the adjustment of the amount of the test substance after electrolysis to the amount of water which was present in the separated volume before the passage of current. Without such adjustment, the error in the interpretation of the results is negligible only for dilute solutions. It has been shown[27] that this computational procedure makes it possible to obtain transport numbers in a coordinate system linked to the solvent as a whole without determining the rate of migration of the solvent itself. The above study was carried out in a general form without resorting to any model ideas about electrical transport in electrolyte solutions.

There exist methods for the determination of transport numbers from measurements of the e.m.f.'s of concentration and galvanic cells in an external gravitational field. The accuracy of the determination of transport numbers by these methods is appreciably lower than that of the determination by other classical methods.[28]

The *isotachophoretic method* is based on the direct measurement of the rate of motion of ionic components (in the simplest case ions). In the past, this method was known under different names: ion migration, analysis based on ionic mobilities, and the moving boundary method. In its application, a steady-state boundary is created between two electrolyte solutions with a common ion. The theory of the method has been described most fully by Milios and Newman.[29] On the basis of the general postulates of the thermodynamics of irreversible processes, the authors showed that the isotachophoretic method makes it possible to obtain transport numbers rigorously in a 'solvent as a whole' coordinate system. A cell in the closed compartment around one of the electrodes, at which the electrode process is known exactly, is used for this purpose. This permits the calculation of all the changes in the volumes of the substances segregating and dissolving. A correction is also introduced for the volume change during diffusional mixing at the boundary between the saturated solution at the electrode and the working solution in the main volume. The hydrodynamic processes in the region of the isotachophoretic boundary have been considered in a theoretical study.[30] A general expression was obtained for the fluxes of all the components of the solutions on either side of the boundary:

$$\rho_i(v_i - w) = \text{const}\,,$$

where ρ_i is the concentration of the ith component (g cm^{-3}) and v_i and w are respectively the velocities of the component and the boundary in the laboratory coordinate system (cm s^{-1}). This equation was quoted without derivation by Milios and Newman.[29] We recall that the ith component can be characterised by the subscript 1 or 2 depending on whether the given species belongs to the leading or terminating solutions respectively. For the solvent (water), we have

$$\rho_{01} = \rho_{01}(v_{01} - w) = \rho_{02}(v_{02} - w)\,.$$

Hence it follows directly that, when a direct electric current is passed through the leading and terminating electrolyte solutions, component transfer of the solvent by electromigration should take place since the water concentrations in the two solutions are in general not equal ($\rho_{01} \neq \rho_{02}$). The occurrence of water transfer by electromigration in each of the solutions 1 and 2 considered separately for the electric fields which exist in them when they form an isotachophoretic boundary also follows from this relation. The attempts to measure the electromigration transport of the solvent were made a fairly long time ago, but the scatter of the experimental data was so great[25] that these studies can be regarded only as evidence for the occurrence of the effect itself. The modern method for the measurement of the electromigration transport of the solvent in electrolyte solutions, based on the isotachophoretic regulating function, will be considered below adducing some results obtained by the isotopic boundary method.

One of the versions of the isotachophoretic method is the *method involving the joint observation* of the motion of the ions and the solution.[31] It does not require the exact knowledge of the electrochemical process at the electrode and therefore expands the possibilities of the usual isotachophoretic method. Under certain conditions, the joint observation method also permits the determination of the transport number relative to the solvent.[32] This is confirmed by the agreement between the results of the measurements of the transport numbers by this method and by the Hittorf method.[28]

The regulating function (1) constitutes the basis of all the ideas about isotachophoresis. In principle, the boundary between two electrolyte solutions with a common ion can be created at any concentrations of these solutions, but, when a direct electric current is passed through this boundary, it will be stable as a function of time only when the concentrations of the solutions satisfy the regulating function. Otherwise the concentration of the terminating solution will vary continuously and spontaneously until it reaches the value determined by the regulating function. The regulating function can be written in the following forms:[33]

$$\frac{c_1 z_1}{c_2 z_2} = \frac{t_1}{t_2} \qquad \text{(Kohlrausch form)}\,, \qquad (2)$$

$$\frac{c_1^0 z_1}{c_2^0 z_2} = \frac{t_1^0}{t_2^0} \qquad \text{(Hartley form)}\,, \qquad (3)$$

where c_1 and c_2 are the molar concentrations of the solutions and c_1^0 and c_2^0 are the corresponding molal concentrations (mol/kg of water).

The transport numbers in Eqns (2) and (3) differ fundamentally from one another, since they are measured in different coordinate systems: in the first case, measurements are made in the laboratory coordinate system in the absence of the flow of the solutions as a single whole, i.e. in a coordinate system common to both solutions, while in the second case measurements are made relative to the solvent of each solution, i.e. in coordinate systems which are different for the two solutions, since the flow rates of the solvent in the leading and terminating solutions are different.

The discrepancy between the right-hand sides of Eqns (1) and (2) and the identity of the left-hand sides should be noted. The point is that in Kohlrausch's time it was assumed that the Hittorf method (the only one known at the time) yields transport numbers in the laboratory coordinate system which are suitable for the regulating function. It is now clear that only a small error was then introduced, since the experiments were carried out with fairly dilute solutions. The expression relating both forms of the regulating function was obtained for the first time by Gorshkov:[33]

$$\frac{t_1^0}{t_2^0} = \frac{\rho_{02} t_1}{\rho_{01} t_2} \quad (4)$$

We may note that the differences between the two forms of the regulating function vanish, like the differences between the reference systems for the measurement of transport numbers, when the concentrations of the solutions tend to zero. Eqns (2) – (4) have been used in the development of a method for the determination of the electromigration transport of the solvent (water) in electrolyte solutions over a wide concentration range.

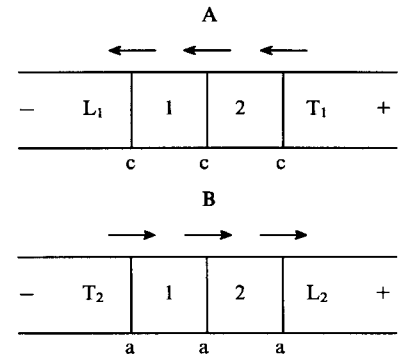
III. Modifications of the isotachophoretic method

Hitherto, in speaking of isotachophoresis, we considered only two solutions with a common ion. These solutions, placed in a electrolytic cell where their mixing is hindered, form after a time a moving steady-state isotachophoretic boundary when a current is passed. It is found that, when certain conditions are maintained in the electrolytic cell, several and not one boundary may exist. Depending on the type of these boundaries, on the direction of their motion in the electrolytic field, and on the disposition of the solutions in the column (electrolytic cell), it is possible to distinguish different varieties of isotachophoresis.[34]

1. Classical isotachophoresis

Classical isotachophoresis can be naturally subdivided into cationic and anionic. In the cationic version, the two electrolytes have a common anion and the boundary between the solutions with different cations accordingly migrates to the cathode. In anionic isotachophoresis, the electrolytes have a common cation and the boundary moves towards the anode in the electric field. The steady-state concentrations of the leading and terminating solutions are described by the regulating function. However, the terminating solution in the above pair can itself be the leading solution for a third solution if the mobility of the non-common ionic component of this third solution is lower than the mobility of the non-common ionic component of the given terminating solution. For the third solution, the former terminating solution becomes the leading solution. The concentration of the third solution is also determined by the regulating function, which includes the transport numbers of the non-common ionic components of the second and third solutions. Thus in cationic isotachophoresis it is possible to obtain a whole series of zones in the electrolytic cell, the boundaries between which correspond to the steady state. When the regulating function holds, they move to the cathode at the same rate. Similarly in anionic isotachophoresis it is likewise possible to obtain a series of zones of pure solutions, but this time with a common cation, which move at their constant rate towards the anode in the electric field. The disposition of the solutions in the direction of the movement of the boundaries in cationic (A) and anionic (B) isotachophoresis is illustrated in Scheme 1, which represents an electrolytic cell with solutions. The plus and minus signs in the scheme indicate the polarity of the applied potential, the numerals 1 and 2 denote the zones of the pure solutions, and L and T denote the leading and terminating solutions. The vertical lines indicate the boundaries of the solutions and the arrows show the direction of motion of the boundaries. The letters 'c' and 'a' denote the cationic and anionic boundaries.

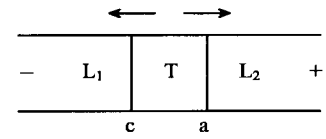
Scheme 1



2. Electrosynthesis at the ionic boundaries

The possibilities of isotachophoresis are greatly expanded when cationic and anionic boundaries are used simultaneously in the electrolytic cell. Electrosynthesis is the term given to the simultaneous formation and movement under the influence of the electric field of two diverging (cationic and anionic) isotachophoretic boundaries. The disposition of the solutions and the direction of the motion of the boundaries under the influence of the electric field are presented in Scheme 2.

Scheme 2

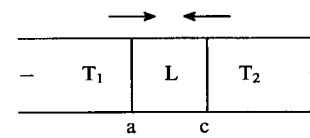


It is striking that one less electrically conducting solution can be synthesised from two more conducting solutions. During electrosynthesis, a third solution is formed from the leading solutions L_1 and L_2. It has a common cation with one leading solution and a common anion with the other. The amount of terminating solution synthesised increases continuously. The phenomenon of electrosynthesis frequently occurs in analytical capillary isotachophoresis and coulophoresis (see below). Electrosynthesis was first predicted by Kohlrausch.[6] Electrosynthesis at the ionic boundaries has nothing in common with the familiar synthesis of substances at electrodes. It makes it possible to obtain various electrolytic solutions — both inorganic and organic. Unfortunately, the method has not received a technological formulation and is not used in preparative let alone industrial practice.

3. Coulometric titration at ionic boundaries (coulophoretic method, coulophoresis)

In contrast to electrosynthesis, in coulophoresis the cationic and anionic isotachophoretic boundaries move towards one another under the influence of the electric field, as shown in Scheme 3.

Scheme 3



In this case, the leading solution is located between two terminating solutions and has a common cation with one of the terminating solutions and a common anion with the other. During electrolysis, the amount of the leading solution continuously diminishes up to its complete disappearance.

The coulophoretic method was proposed in 1974 as a new microanalytical method in capillaries based on the Faraday law.[35,36] The modifications of isotachophoresis (other than electrosynthesis) are considered below in the version performed

in capillaries, i.e. in the form of capillary isotachophoresis which is most widely used in practice.

IV. Classical capillary isotachophoresis

In order to carry out isotachophoretic processes, it is essential to ensure conditions under which convective stirring of the solutions in the column would be eliminated and instrumental methods for the detection of the boundaries must be available. The boundaries between coloured and colourless solutions can be detected visually at certain concentrations, but the region of applicability of isotachophoresis is then negligible. The conditions under which convective mixing is excluded in the electrolytic column have been examined.[37] The structure of the boundary between two solutions is influenced by the heat change. Heat is evolved in the column uniformly throughout its volume and is removed via the surface, as a result of which a temperature drop between the centre and the surface arises in the column cross-section. Since the mobility of ions depends on temperature, a convective mixing stream is superimposed on the rate of their translational motion. A second factor inducing the spreading of the boundary is the hydrodynamic and electroosmotic flow of the solutions in the column. All these factors can be described as purely diffusional mixing by introducing a quantity equivalent to the diffusion coefficient (D_{eq}). There exists an expression which makes it possible to estimate this quantity in columns with a circular cross-section.[37] Even for an electric field strength of 20–50 V cm^{-1}, the quantity D_{eq} differs little from the molecular diffusion coefficient provided that the column consists of a cylindrical capillary with an internal diameter of 0.2–0.5 mm. Even under the conditions of a hydrodynamic countercurrent the width of the majority of boundaries is then about 0.2 mm and the temperature drop between the centre and the periphery is about 1 °C. The countercurrent represents the hydrodynamic flow of both solutions against the motion of the boundary. If the velocity of the countercurrent is equal to the rate of mixing of the boundary in the electric field, then the boundary is stationary relative to the walls of the separating column.

The use of capillary columns makes it possible to eliminate the need for the maintenance of gravitional stability of the boundary. This means that in an electrolytic cell the boundary remains stable regardless of whether the denser solution is below it or above it. When columns with a large diameter are used, the mixing of the solutions due to the hydrodynamic flow, the operation of gravitational forces, and heating as a result of the evolution of heat are excluded by filling the column with an agar gel or finely disperse particles (sand, glass wool). The use of a gel is possible only in some cases, since it does not set at high concentrations of the solutions, decomposes in solutions of acids and alkalis, is sensitive to heating, and does not allow the use of a hydrodynamic countercurrent.

The choice of the geometrical parameters of the column and its operating conditions (the electric current, temperature, and the countercurrent) is made taking into account the proposed method for the detection of ionic boundaries. The optimum procedures for the detection of the boundaries are those which employ the common properties of the solutions. They include the thermometric method, the observation of the diffraction pattern when the capillary is illuminated with a narrow light beam, the measurement of the electrical conductivity of the solutions, and the measurement of the electric field in the solutions. These and other specific methods for the detection of boundaries in isotachophoresis have been briefly reviewed.[38] Yet another universal method for the detection of boundaries, based on detection with the aid of a thermoviewer of the IR radiation emitted from the surface of the column, was proposed in the same communication. For capillary columns with an internal diameter of 0.1–0.8 mm, it is most convenient to employ, depending on the tasks to be performed, the thermometric method and the methods involving the measurement of the electrical conductivity and the electric field, on the one hand, and the methods involving the observation of the diffraction pattern and the thermovisual observation, on the other. Such combination of a capillary electrolytic cell with instrumental methods for the detection of boundaries between the electrolyte solutions in them actually constitutes *capillary isotachophoresis*. It was proposed in 1962 in our country.[39,40] Studies on capillary isotachophoresis were subsequently published also abroad.[41]

Capillary isotachophoresis makes it possible to solve all analytical problems using microamounts of test substances and microvolumes of the solutions. At the present time, there are two versions of the instrumental formulation of the capillary isotachophoretic method. The first version, mainly developed abroad, presupposes the use of capillaries with an internal diameter up to 0.8 mm and the detection of the boundaries by means of a point detector on the basis of the temperature, the electrical conductivity, and the electric field strength frequently combined with additional detection based on the absorption of UV light. Such a detector makes it possible to determine the positions of all the boundaries only consecutively. One usually detects under these conditions boundaries moving past a stationary detector, although sometimes the detector is also moved (for example, a thermometric detector) relative to the capillary. In the second version, use is made of long detectors capable of detecting all the boundaries simultaneously. Such detectors are based on the observation of a diffraction pattern from a slit with sharp edges obtained when the capillary is illuminated with a narrow light beam. The capillary then acts as a cylindrical lens and the zones of solutions with various refractive indices appear on the screen as rectangles of different widths within which there are interference bands approaching one another towards the centre† (Fig. 1). The sensitivity of the method ensures the detection of boundaries for a difference between the refractive indices of the solutions forming them of 0.001–0.002.[42] A long detector based on measurements of the electrical conductivity of the solutions,[43] which consists of a horizontal section of a 9 cm long column with a rectangular cross-section (1 × 0.4 mm) on which 256 electrodes have been deposited at distances of 340 μm, has been described. A long detector in which the absorption of UV light is employed has also been proposed.[44] The detector in which the boundaries are detected with the aid of a thermoviewer also belongs to the class of long detectors.[38]

We shall now compare qualitatively the types of long detectors described. The diffraction detector makes it possible to detect relatively readily all the boundaries in a cylindrical transparent capillary over a section of any reasonable length. There are instruments in which the length of such a section reaches 240 mm.[45] This method of detection does not alter the natural width of the boundary. The detector has been used[43] in a column with a large cross-sectional area where the width of the boundary

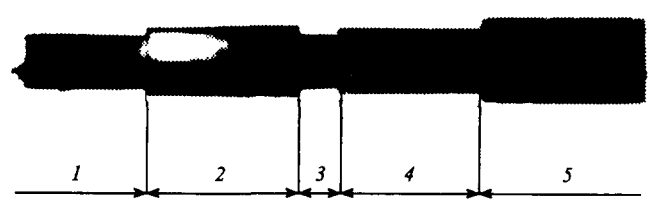


Figure 1. Photograph of the diffraction pattern obtained from a capillary after the separation of a mixture containing KCNS, K_2CO_3, and K_2TeO_3 solutions (a 0.5 mA current was passed for 2 h): *1*, terminating solution (4 M KCl solution); *2*, zone of KCNS solution; *3*, zone of K_2CO_3 solution; *4*, zone of K_2TeO_3 solution; *5*, leading solution (0.07 M KOH solution).

† These bands are visible only in the original and are lost on being rephotographed.

was therefore about 3 mm. The diffraction method is best used for highly concentrated solutions, although in the case of high-molecular-mass compounds the sensitivity indicated above (a difference between the refractive indices of 0.001–0.002) is attained at a concentration of about 0.01 M. A long thermal conductivity detector operates best in dilute solutions. Thus solutions with a concentration of about 0.01 M have been used.[43] The thermovisual method naturally has a higher sensitivity in the region of more dilute solutions. Industrial instruments in which this type of detection is employed have not so far been developed.

Evidently universal long detectors, effective over a wide concentration range (approximately from 0.001 M to saturated solutions) are most promising. Such detectors significantly facilitate the experiment, since they make it possible to observe the very process in which mixtures are separated into zones of pure solutions and one can make sure directly that it has reached completion when the lengths of the zones cease to change with time. The latter cannot be achieved when the zones move past a point detector and the completion of the separation process must be inferred in this case solely from indirect data.

Capillary isotachophoresis using the above methods for the detection of zone boundaries is a modern ultramicromethod for the qualitative and quantitative analysis of ionogenic substances in electrolyte solutions. The instruments used in capillary isotachophoresis in our country include the following: the single-channel AIP-1 apparatus,[37] the six-channel AIP-2 apparatus,[46] the four-channel IS-5501 apparatus,[45] and the single-channel ITFK-2-001 apparatus.[47] The electrolytic column and the optical part of the single-channel IS-5501 apparatus are illustrated schematically in Fig. 2.

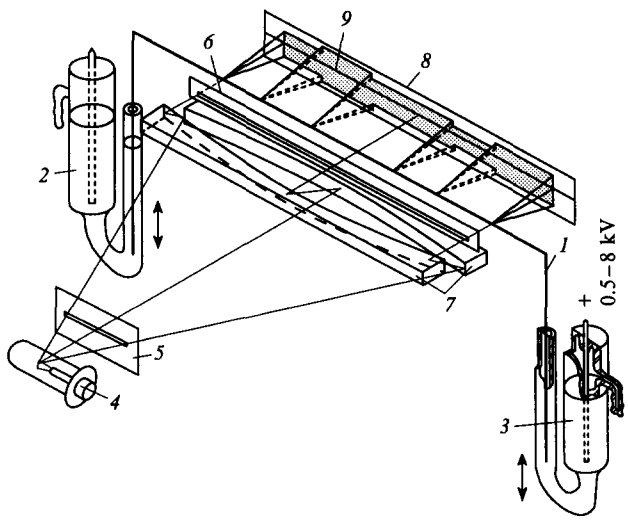


Figure 2. Schematic illustration of the optical component of one channel of the IS-5501 apparatus for capillary isotachophoresis: *1*, capillary with electrolyte solutions separated into zones; *2*, and *3*, electrode vessels with the leading and terminating solutions (the vessels can be lowered and raised in order to generate a hydrodynamic countercurrent); *4*, source of illumination; *5*, inlet diaphragm; *6*, outlet diaphragm; *7*, mirrors; *8*, screen; *9*, image of the capillary with the separated solutions.

1. Qualitative analysis

A method for qualitative analysis with the aid of capillary isotachophoresis, called the method of additives to standard mixtures, has been proposed recently.[48] Its essential feature is as follows. A preliminary study is carried out initially where the order in which the ionic components move to the electrode is investigated. For this purpose, one selects a series of compounds soluble in water (or another ionogenic solvent) with a common anion and another series with a common cation. The solutions are separated into zones with a single common anion by means of cationic capillary isotachophoresis and the sequence in which the zones move to the cathode is studied. This procedure includes the addition to the initial pure solution of a second solution with a common cation, the separation of the mixture into zones, the attainment of a steady state, and photography of the diffraction pattern. After this, the mixture is again separated changing the content of one of the components.

By comparing the photographs obtained, one can establish readily the order in which the two zones with a common anion follow one another. Next, a third pure solution is added with the same common anion, the mixture is again separated into zones and so on. It is thus possible to establish the order in which any number of zones with a common anion follow one another. For example, in solutions of formates the ammonium zone is followed by the sodium, barium, calcium, lithium, magnesium, cobalt, zinc, cadmium, and acetic acid zones.[49] At the same time conditions are selected under which the order in which the above zones follow one another is retained, i.e. the current, the concentration of the leading solution, and the concentration and pH of the terminating solution are selected.

The order in which the zones follow one another in solutions with other common anions and common cations are studied similarly. Examples of the separation of multicomponent solutions containing the cationic and anionic components of inorganic, organic, and amphoteric compounds have been published.[50–54] We may note that mixtures containing lanthanide ions and amino-acids, which are difficult to separate by the usual methods, were separated in the above investigations. The number of components in the mixtures separated sometimes reached 20. As already stated, the detection of the zone boundaries from the diffraction pattern is possible when the difference between the refractive indices of the solutions in the zones is not less than 0.001. For low-molecular-mass compounds, this difference is maintained when a solution with a concentration of about 0.5 M is used as the leading solution. For high-molecular-mass compounds, the lower limit of the concentration of the leading solution may be reduced by one or sometimes even two orders of magnitude.

The qualitative analysis of the mixture consists of the following steps. A standard solution with a known set of ionic components at approximately identical concentrations is separated under the chosen conditions with the aid of capillary isotachophoresis into zones of pure solutions. The zones obtained are then photographed. After this, part of the leading or terminating solution is removed from the capillary and the same volume of the test solution is introduced. An electric current is again passed through the column. Separation is carried out until the attainment of a steady state and the zones are photographed. The components of the test solution are then incorporated into the corresponding zones and increase their length [adaptation (Translator)]. The increase in the length of any one zone compared with the initial zone indicates the presence of the corresponding component in the test specimen.

The sensitivity of the qualitative analytical method described is determined by the width of the boundaries between the zones. The width is about 0.2 mm. The length of the zone for a specified amount of the substance in it is determined by the concentration and cross-sectional area of the column. If the initial length of the column of the test mixture placed in the capillary is 50 cm for a concentration of the leading solution of 0.5 M, then, in order that the length of the zone after adaptation should reach 0.2 mm (the width of the boundary), the concentration of the component in the solution should be not less than 10^{-4} M. There is in principle no upper limit to the concentration.

The analysis is carried out most readily when the concentrations of the components in the test solution differ by not more than two orders of magnitude for a length of the column

of solution of about 10 cm. In other cases, certain special procedures must be carried out in a preliminary step, which makes it possible to remove from the capillary the excess of the component present in an overwhelming amount. We may note that the qualitative analytical method considered requires the application of a universal long detector which detects simultaneously all the boundaries, for example a diffraction detector or a thermoviewer.

2. Quantitative analysis

Quantitative analysis with the aid of capillary isotachophoresis is based [40] on the regulating function. This is why so much attention was devoted above to the examination of its different forms. The quantitative analytical method may be absolute if the transport numbers of the ionic components of the leading and terminating solutions are known beforehand with the necessary accuracy (or, which is equivalent to the above, the concentration of the terminating electrolyte incorporated in the leading solution) over a wide range of concentrations of the solutions. Unfortunately, there are very few experimental data of this kind [28, 55–57] and the method is therefore used as a relative procedure requiring comparison with a standard. For this purpose, the length of the zone of the component to be determined (or the rate of movement of the zone past the detector, which is proportional to the above quantity) is measured in the standard and text mixtures under identical conditions. The methods for the quantitative analysis of dilute and concentrated solutions have been described in detail in numerous original communications and monographs [58–69] and we shall not be concerned with them here. We may note only that industrial products from different industries, natural waters and brines, aminoacids, as well as certain natural products were analysed.

Interesting features of the isotachophoretic separation of a two-component mixture have been noted.[70] It was found that the separation after adaptation is not accompanied by a change in the total volume of the solution. Therefore, by measuring during the separation process the lengths of the zones of the pure electrolyte solutions and the unseparated mixture, it is possible to determine, without waiting for the end of the separation process, the time required for the total separation and the contents of the components.

Thus the suitability of capillary isotachophoresis for both qualitative and quantitative analysis makes it an independent instrument in the laboratory identification and determination of ionogenic substances in electrolyte solutions.

3. Preparative possibilities of capillary isotachophoresis

A characteristic feature of capillary isotachophoresis is the use of ultrasmall amounts of substances and a virtually 100% separation of mixtures into pure solution zones, which leads to the possibility of its application as a preparative method. This concerns the isolation of a solution of the required substance from a mixture of electrolyte solutions and its separation in space for use in the solution of specific problems where pure substances in small amounts are required. Capillary isotachophoresis has been used, for example, for the separation of lithium salts from sodium salts.[71] The pure lithium chloride solution zone was cut off together with part of the capillary for subsequent isotopic analysis with the aid of a mass spectrometer.

The preparative possibilities of the method include also the concentration and dilution of solutions by adaptation with respect to the regulating function. A special case of such concentration is crystallisation with the aid of isotachophoresis.

Capillary isotachophoresis makes it possible to enrich a mixture of components present at low concentrations. The enrichment takes place as a result of the prolonged withdrawal of an element from a large volume into the capillary column. This preparative procedure has been used to determine small amounts of potassium chloride in an aqueous lithium chloride solution.[72]

The transfer of an ionic substance from one solvent to another can also be regarded as a preparative application of capillary isotachophoresis.[73] This procedure is based on the ability of the isotachophoretic boundary to transmit only the common ion and the solvent.

Thus capillary isotachophoresis may be used for preparative purposes. However, the use of large diameter columns will apparently become most promising in preparative isotachophoresis.

V. The coulophoretic method

1. Theoretical principles

Isotachophoresis was classified above in terms of the positions of the leading and terminating solutions in the column. One of its varieties is the coulophoretic method (coulometric analysis of the electrolyte solutions using ionic boundaries). A characteristic feature of the method is the presence in the electrolytic cell of cationic and anionic isotachophoretic boundaries moving towards one another (see Scheme 3). The formula for the rate of movement of a steady-state boundary between two solutions with a common anionic component is used in the theory of isotachophoresis.[29, 74, 75] It can include the characteristics of both the leading and terminating solutions. Thus the rate of movement of the cationic boundary v_c of the leading solution L_1 is

$$v_c = \frac{It_c}{zc_qS}.$$

where (in addition to the previous notation) I is the electric current (A), S the internal cross-sectional area of the electrolytic cell (dm^2), and c_q the concentration of the charges of the same sign per unit volume of the leading solution (C litre^{-1}). We recall that t_c is the transport number of the non-common cationic component in the laboratory coordinate system. A similar relation describes also the rate of movement of the second, anionic boundary between the above leading solution and the second terminating solution T_2:

$$v_a = \frac{It_a}{zc_qS}.$$

It includes the transport number of the anionic component of the leading solution in the same laboratory coordinate system. We transform the linear rates of movement of the boundaries into volume rates (v_cS and v_aS) and add together the last two expressions:

$$S(v_c + v_a) = \frac{I(t_c + t_a)}{zc_q},$$

where $S(v_c + v_a)$ is the volume traversed by the two (cationic and anionic) boundaries per unit time. We introduce yet another quantity – the time from the start of electrolysis until the instant t when the boundaries meet, and multiply both sides of the last equation by this time. Since $S(v_c + v_a)t = V$ is the volume of the leading solution before the start of electrolysis (as already mentioned, during the passage of current this volume continuously diminishes and becomes zero at the instant when the boundaries meet) and $t_c + t_a = 1$, it follows that

$$Vc_qz = VFcz = It, \qquad (5)$$

where F is the Faraday constant.

Eqn (5) constitutes the basis of the coulometric analysis of solutions using ionic boundaries. We shall consider it in greater detail. It relates the concentration of the leading solution investigated to the amount of electricity passed through the system and to the volume of the solution taken for analysis. Eqn (5) can be used to determine one of the three quantities mentioned above when the other two are known. The greatest interest attaches to the determination of the concentration of the solution from the amount of electricity passed through it and the volume traversed by the two boundaries. We have called this procedure the coulophoretic method of analysis of the solution or

coulometric analysis using ionic isotachophoretic boundaries. This analytical method will be examined in greater detail below. The second possibility presented by Eqn (5) consists in the determination of the amount of electricity passed in the circuit from the concentration of the solution and its volume. Such determination constitutes the basis of the new method, proposed by the authors, for the measurement of the amount of electricity by observing the motion of boundaries (see below). The determination of the volume traversed by the boundaries when the concentration of the solution and the amount of electricity passed through it are known constitutes the basis of the method for the determination of the internal cross-sectional area of the capillary and for the monitoring its constancy along the length.

The following characteristic features of the coulophoretic method may be noted. It is based on the Faraday law. However, the method differs fundamentally from the method of analysis of substances from their amounts produced at the electrode and the coulometric titration method, which is also associated with the reaction at the electrode. In the coulophoretic method, one compares the direct motion of the ions with the amount of electricity passed through the system, while the boundaries between the leading test solution and the two terminating solutions are actually set up in order to be able to follow the motion of the ions. Each boundary operates in a certain sense as an electrode with a 100% current yield;[76] only the common ionic component and the solvent pass through it. The rate of movement of the non-common ionic component constitutes the rate of movement of the boundary itself. The coulophoretic method is independent of the nature of the electrodes employed, the nature of the electrode reactions, and their current yield. This constitutes the fundamental difference between the electrodeposition and coulometric titration methods.

2. Analysis of electrolyte solutions

The theoretical aspects of the coulophoretic method were examined above. We shall now proceed to the description of its analytical application. The method may be used to solve three different problems: the determination of the concentration of the pure electrolyte solution; the analysis of a mixture of electrolyte solutions after its preliminary separation by capillary isotachophoresis into zones of pure solutions; the analysis of a two-component mixture without its complete separation into pure solutions.

Analysis of the pure solution. In order to determine the concentration of the test solution in conformity with Eqn (5), one should know the volume of the solution taken for analysis. For this purpose, a mercury column 20 – 30 cm long is introduced into a π-shaped capillary filament and narrow markers, 0.1 mm wide, are deposited on its ends with coloured sealing wax. The terminating electrolyte solutions are selected for the electrolyte test solution in accordance with the rules of isotachophoresis — one solution in terms of the cations and the other in terms of the anions; their chosen concentrations are close to that of the test solution. The exact concentration is unimportant, since the concentrations of the terminating solutions in the region of the boundaries automatically adapt to the concentration of the test solution in conformity with the regulating function when a current is passed. It is desirable that the concentrations of the terminating solutions should be below the equilibrium values, whereupon their adaptation is faster. In practice all these concentrations should not differ from the equilibrium concentrations by a factor greater than 10.

The capillary is filled with solutions with the aid of a water pump in the following way. Initially the entire capillary is filled with distilled water and then a tiny bubble (about 1 mm long) is formed at its end and beyond it one of the terminating solutions is introduced — up to the first marker. The bubble serves as an indicator of the movement of the solutions. The end of the capillary is then lowered into the test solution and the latter is introduced into the capillary until the indicator bubble moves to the second marker. Next, the end of the capillary is lowered into the second terminating solution and is filled until the bubble emerges from the capillary. As a result, the test solution is present in the middle part of the capillary between the markers and the terminating solutions are on either side of it. The ends of the capillary are lowered into approximately 5 cm^3 electrolytic vessels filled respectively with the solutions present at the two ends of the capillary. At the same time, the passage through the cell of a stabilised direct current is begun and a stopwatch, reckoning the time from the start of electrolysis to the instant when the boundaries meet, is started.

The cationic and anionic boundaries, moving towards one another, are formed between the test solution and the terminating solutions. The boundaries are observed with the aid of, for example, diffraction. At the instant when the boundaries meet, the stopwatch is arrested and the time from the start of electrolysis to the instant of the disappearance of the test solution is determined. The concentration of the test solution is calculated by Eqn (5). A universal long detector, for example a thermoviewer, is also suitable for the detection of the boundaries between the solutions. In certain cases the instant when the boundaries meet can be simply recorded visually.

The coulophoretic method has been used to determine the concentrations of solutions of various electrolytes: acids, alkalis, simple salts, and complexes with a low instability constant. The concentrations of an acid and alkali can be determined by this method with the aid of only one terminating solution, forming both the cationic and anionic boundaries, and salts can also be determined with the aid of another salt.[36]

Analysis of mixtures of electrolyte solutions. Mixtures are analysed after their preliminary separation into zones of pure solutions by isotachophoresis. The analytical method is as follows: as in the previous case, the volume of the marked section of the capillary is determined with the aid of mercury. Next, using the rules of isotachophoresis, the leading and terminating solutions are selected. The capillary column is filled with solutions in such a way that the test mixture is located in the capillary between the leading and terminating solutions. After this, the mixture is separated into pure solutions under the conditions of a hydrodynamic countercurrent. The separation is terminated when the number of zones becomes equal to the number of components to be determined and the lengths of the zones no longer vary with time. The leading solution is then replaced by a new solution (the second terminating solution prepared beforehand) in order to form a boundary moving through the solutions in opposition to the zones.

If the initial mixture was separated in terms of the cations, then the leading solution is the catholyte and is replaced by another solution, which serves as the terminating solution for the common anion of all the zones. Conversely, if the separation was carried out in terms of the anions, the leading solution is the anolyte and is replaced by another solution — the terminating solution for the common cation of the zones. In order to replace the leading solution by the second terminating solution, an electric current is switched on, the electrode vessel with the leading solution is lowered and is replaced by an electrode vessel with the new terminating solution prepared beforehand. This procedure should be carried out as fast as possible (about 3 s) in order to avoid the leakage of the solution, mixing, etc. After this, the current is switched on again and a boundary, moving through the leading solution in opposition to the zones, is formed at the end face of the capillary.

When this boundary meets the boundary of the first zone, the first stop-watch is started and the time up to the meeting of the given boundary with the boundary of the second zone is measured. At this instant, the first stopwatch is arrested and the second is started. The time reckoned by the first stopwatch is the initial quantity for the determination of the concentration of the

solution in the first zone. The time for the traversal of the second zone by the boundary is measured similarly, the stopwatch being stopped when this additional boundary encounters the beginning of the third zone. The first stopwatch, used for the preliminary reckoning of the time taken by the additional boundary to traverse the first zone, is started simultaneously. Thus one determines the time taken to traverse all the zones and hence also the concentrations of the solutions in these zones.[77] If a solid is analysed and all the components are determined by the coulophoretic method, it is not necessary to know the volume of the solution taken up into the capillary.

Analysis under conditions of incomplete separation of the mixture. In practice, one may encounter situations where a two-component mixture cannot be separated into zones of pure solutions by isotachophoresis. This happens, for example, if the mixture analysed includes a leading solution for which it is impossible to select a second leading solution with a greater mobility of the non-common ionic component. However it is found that the concentrations of the components of such a mixture can also be determined coulometrically by means of ionic boundaries, but this requires the use of standard specimens and a partial preliminary separation of the mixture analysed.[78]

We shall now estimate the error of the above coulophoretic method for the determination of the concentrations of solutions. It includes the contribution by the error of the determination of the volume of the capillary between the markers, the error of the measurement of the volume of the solution filling the capillary, the error of the determination of the time of traversal of the test solution by the boundaries, the error of the measurement of the current, and the errors of the stopwatches. The main contribution to the error of the method comes from that in the measurement of the volume of the section of the capillary between the markers ($\sim 0.5\%$) and also the error of the measurement of the volume of the solution taken up into the capillary (also $\sim 0.5\%$). The relative error of the measurement of the time of traversal of the zone by the additional boundary is equal to the ratio of the width of the boundary to the initial length of the zone. For a zone approximately 10 cm long and a width of the boundary of 0.2 mm, the error reaches 0.2%. Thus the overall error of the coulophoretic method for a zone length of 10 cm is not more than 1%.

The sensitivity of the method is determined by the potential of the chosen procedure for the detection of the boundaries. Thus when the diffraction pattern is used, the concentrations of the solutions should be not less than 0.1 M and for lower concentrations preliminary enrichment is necessary.

The following chemical compounds have been analysed hitherto by the coulophoretic method: HCl, KCl, NaCl, LiCl, NH_4Cl, $BaCl_2$, $CaCl_2$, $MgCl_2$, $CoCl_2$, $SmCl_3$, $NaNO_3$, NH_4NO_3, Na_2SO_4, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, KCNS, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$. Many of these were part of the composition of industrial products (fluxes, alloys, brines, melts, electrolytes), natural waters, and minerals.[36, 77, 79]

We may note the characteristic features of the coulometric analysis of solutions with the aid of ionic boundaries. The method is suitable for any ionogenic solutions of inorganic and organic substances and permits the analytical determination of the cationic and anionic components of electrolyte solutions. It is an ultramicromethod, which is fairly accurate, sensitive, and rapid. The method is absolute and does not require the use of standard specimens (with the exception of cases where a mixture with incomplete separation or with incomplete dissociation of ionogenic substances is analysed). In the analysis of a multi-component mixture where all the components are determined by the coulophoretic method, there is no necessity to know the weight of the initial mixture.[77] In practice, this method can be applied fairly simply: one can use commercial apparatus for capillary isotachophoresis with the detection of boundaries from the diffraction pattern; the capillary columns can be prepared under laboratory conditions; the capillaries need not necessarily have a constant internal cross section along the length; repeated use of the same capillary column is possible. Finally, a characteristic feature of all isotachophoretic methods, due to the adaptation of the terminating solution concentration, is the possibility of using terminating solutions at concentrations which have been determined only approximately.

The coulophoretic method has certain unique possibilities. It permits the analysis of a given solution with the aid of any terminating solution from the enormous set of those which are possible and conversely one can analyse many solutions using only one terminating electrolyte solution.[80] Terminating solutions containing mixed solvents can also be employed. Inert additives to a terminating solution do not affect the analyses. The coulophoretic method is perhaps the only one which makes it possible to determine the concentration of pure acids, alkalis, and salts with the aid of a solution of only one salt.[80] The method also permits the transfer of the ionogenic substance from one solvent to another simultaneously via two boundaries.[73]

However, the method described, which has important advantages, has not unfortunately found a sufficiently wide application consistent with its possibilities. This is probably associated with the rare use of the method of detection of the boundaries from the diffraction pattern.

3. Determination of the amount of electricity

The amount of electricity passed through the circuit is one of the fundamental quantities used in electrochemical studies. Therefore the new method for its measurement, proposed by Ansorg,[81] merits attention. The method is based on a familiar phenomenon — the transport of electricity by ions in the bulk of the electrolyte solution. The motion of the ions is followed by creating isotachophoretic boundaries between the solutions which can be readily detected experimentally. We recall that Eqn (5) relates the amount of electricity passed through the system to the number of charges of the same sign per unit volume of the solution and to the volume traversed by both boundaries (cationic and anionic) when a given amount of electricity is passed through the capillary.

The method of measurement of the amount of electricity depends on the electrolyte selected.

1. Suppose that a strong electrolyte solution, for which c_q is known and the degree of dissociation is unity, has been chosen. Then $c_q = czF$, where c is the molar concentration of the solution. In this case, the method of determining the amount of electricity passed through the circuit by Eqn (5) is absolute.

2. Suppose that an electrolyte solution for which c_q is not known beforehand, has been adopted. Then the proposed method is relative and requires preliminary calibration, i.e. the determination of c_q in the chosen solution at the concentration adopted by measuring, using some other procedure, the amount of electricity Q and the pathway traversed by both boundaries (cationic and anionic) ($l_c + l_a$) during the measurement. Clearly, such calibration constitutes simultaneously an independent method of determining the degree of dissociation of the electrolyte under the chosen conditions. These data could be of interest for the study of electrolyte solutions, particularly in the light of the attempts undertaken recently to consider certain strong electrolytes in solution as incompletely dissociated.[82]

The experimental formulation of the method for the measurement of the amount of electricity considered is in the main the same as that of the coulophoretic method for the determination of the concentration of a one-component solution, which was described above. The difference consists in the fact that in the given instance it is essential to have a capillary column with a constant cross-sectional area along its length. This makes it possible to determine the amount of electricity passed through the circuit during any time interval. The quantity measured directly as $l_c + l_a$. The maximum amount of electricity measured in an individual experiment is determined by the length

of the zone of the leading solution taken up into the capillary. The dependence of the amount of electricity passed on the path traversed by the cationic and anionic boundaries is linear, as can be seen from Eqn (5), which must be included among the advantages of the method. The range in which the amount of electricity can be measured depends on the concentration of the chosen solution, the cross-sectional area of the capillary, and the length of the column of the solution placed in the capillary. It can be readily varied. The optimum range is 0.15–3 C, the absolute sensitivity is 4 μC, and the accuracy of the determination for a column length of 200 mm is 0.1%. We may note that the method considered requires the use of high-voltage sources (1–10 kV).

4. Determination of the internal cross-sectional area of the capillary and the monitoring of its constancy along the length

Capillaries have been used widely in recent times in physicochemical practice—in capillary isotachophoresis, in high-pressure capillary chromatography, in ionic chromatography, and in capillary electrophoresis.[37,83–85] It is frequently necessary to measure the internal cross-sectional areas of transparent glass or quartz capillaries and to monitor their constancy along the length. The mercury method has been used traditionally for this purpose, but it suffers from evident disadvantages: it is laborious, it is difficult to automate, and it requires definite safety measures. The coulophoretic analytical method examined above can serve as a basis also for a novel method of measurement of the internal cross-sectional areas of transparent capillaries and for the monitoring of their constancy along the length.[86] In the horizontal part of the capillary the cross-sectional area of which is to be determined, one selects a column of the leading solution of a definite length between the two terminating solutions. By passing a stabilised direct current, one of the boundaries is made stationary relative to the walls of the capillary by means of a countercurrent. One then measures the distance Δl over which the secondary boundary moves during a time Δt. The average cross-sectional area of the capillary along the section Δl is found from the formula

$$S_{av} = \frac{I\Delta t}{Fcz\Delta l},$$

where z is the charge of the non-common ion of the leading solution forming the moving boundary. If the quantity $I\Delta t/F$, i.e. the amount of electricity passed through the column, is plotted against $cz\Delta l$, then the slope of the curve at a given point yields the internal cross-sectional area of the column at this point. The linearity of the relation indicates the constancy of the internal cross-sectional area of the capillary along its length. It has been suggested that a fully dissociated strong electrolyte solution be used as the leading solution. The accuracy of the determination of the internal cross-sectional area by this method for a width of the boundary of 0.2 mm is 2% along a section 1 cm long.

The method is suitable also for the determination of the free cross-sectional area of a column consisting of a transparent tube up to 10 mm in diameter with a filler (particle size 20–50 μm). The leading solution should then be coloured and the terminating solutions should be colourless or conversely. The positions of the boundaries at different times can be observed visually in this instance. Owing to the considerable width of the boundary, the accuracy of the determination of the free cross-sectional area of the tube with the filler is about 5% along a section 10 cm long.

The electrochemical procedure considered permits the measurement and the monitoring of the constancy of the internal cross-sectional areas of transparent capillaries with diameters of 0.05 to 0.8 mm without breaking them. This range is determined by the possibility of observing steady-state isotachophoretic boundaries in capillaries regardless of the ratio of the densities of the solutions employed. The method also permits the determination of free cross-sectional areas of columns with a diameter up to 10 mm and containing a finely dispersed filler.

VI. Steady-state concentration boundaries in isotachophoresis

The concentration boundaries are special types of boundaries in isotachophoresis. As a result of the passage of a direct current through the cell containing two electrolyte solutions with different concentrations of the same substance, it is possible to achieve a distribution of the concentrations of this substance in the intervening region which is stable as a function of time. The boundary between the solutions migrates to one of the electrodes at a constant rate. The conditions for the attainment of a steady distribution of concentrations or, in other words, the formation of a steady-state concentration boundary have been formulated by Stefanovskii:[87] (1) a stable boundary can exist only in solutions of electrolytes characterised by a non-linear dependence of the transport numbers of the ionic components on the concentration; (2) if the boundary is formed in such a way that $\partial c/\partial x > 0$ (the direction of the x axis coincides with the direction of motion of the cationic component in the electric field), then it will be stable for solutions of electrolytes where $\partial^2 t/\partial c^2 < 0$; (3) if the boundary is formed in such a way that $\partial c/\partial x < 0$, then it will be stable provided that $\partial^2 t/\partial c^2 > 0$ (here t is the transport number and c the concentration of the electrolyte solution). It has been shown in a study[88] where this process was examined most rigorously that the above conditions for the stability of concentration boundaries are valid only when the quantities t are understood as the transport numbers of non-common ionic components in the laboratory coordinate system and not relative to the solvent, as was implied in Stefanovskii's study.[87]

The criteria of the stability of concentration boundaries formulated above have been used to test the validity of the relations obtained by different workers between the transport numbers and the concentration of the electrolyte solution and for the prediction of the form of such relations if they have not yet been derived. For this purpose, the capillary column was filled with two solutions at different concentrations and a direct current was passed through it under the conditions of a hydrodynamic countercurrent. The migration of the concentration boundary was followed from the diffraction pattern. If the concentration boundary corresponding to the chosen direction of the current became stable after a time, the experiment was terminated. If the boundary remained unstable, the experiment was repeated having reversed the electric current. The direction of the current for which the concentration boundary is stable with time was found in this way.

The nature of the required relation was established from the results obtained, on the basis of conditions (1)–(3), i.e. it was found if this relation is convex or concave relative to the concentration axis in the chosen range. The instability of the boundary for any direction of the current implied that the concentration dependence of the transport number is linear in the selected range. The nature of the dependences of the transport numbers of the cationic and anionic components on the concentration in aqueous HCl, H_2SO_4, LiCl, NaCl, KCl, NH_4Cl, $BaCl_2$, $CuCl_2$, $NiCl_2$, Li_2SO_4, $LiNO_3$, $NaNO_3$, NaAc, KAc, $K_2Cr_2O_7$, $Na_2Cr_2O_7$, LiOH, NaOH, and KOH solutions was established by the method described.[89,90] The validity of the determination of the form of the relations (convex, concave) was confirmed by classical methods. At the same time, the conclusions concerning the form of the relations found by the method based on incorrect theoretical ideas concerning the motion of ions in electrolyte solutions were partly disproved. Certain concentration ranges were found in solutions of potassium and ammonium chlorides in which concentration boundaries are not formed whatever the direction of the current, which indicates a linear concentration dependence of the transport numbers.

Thus the apparatus for capillary isotachophoresis with detection of the boundaries from the diffraction pattern without any partitions can be used in experiments with concentration boundaries. Specially complex concentration boundaries,

considered, for example, by Stefanovskii,[91] require a comprehensive and systematic study.

VII. Electrocrystallisation with the aid of isotachophoresis

One of the most important features of isotachophoresis, namely the possibility of adaptation, i.e. a change in the concentrations of all the solutions following the leading solution when they differ from the steady-state concentrations, was examined in detail above. It was found that this feature can be used as a basis of a new electrochemical method for the crystallisation of ionogenic substances in a capillary.[92] The essential feature of the method is as follows. The transport numbers of any one ionic component of a saturated solution at room temperature are found directly from the literature or by extrapolating literature data. The leading solution having an ion in common with the solution to be crystallised, in which the mobility of the non-common ionic component is greater than that of the non-common ionic component of the solution crystallised, is selected on the basis of the accumulated data. The concentration of the leading solution, which as a result of adaptation determines the concentration of the saturated solution and the solution to be crystallised which follows it, is found from the regulating function (3). Next, the concentration of the leading solution calculated in this way is increased by 20% – 30% depending on the nature and properties of the solution to be crystallised. This is necessary for a number of reasons, including the possible inaccuracy of reference data, the tendency of the solution to be crystallised to become supersaturated in view of the small number of crystallisation centres, and the presence of a long latent period in which the onset of crystallisation is delayed when the degree of supersaturation is low. The crystallisation is carried out in a capillary employing the usual device for capillary isotachophoresis. The adaptation of the solution to be crystallised is followed from the diffraction pattern. The passage of current leads to the precipitation of crystals, which is manifested by a darkening of the diffraction pattern. The crystallisation of an aqueous potassium chloride solution with an initial concentration of 1 M using a hydrochloric acid solution at a concentration of 10 M as the leading solution and a cobalt chloride solution at a concentration of 1.5 M as the terminating solution has been described.[92] As a result of the passage of a direct current of 3 mA for 3 h, fine (approximately 0.1 mm) crystals were formed in the potassium chloride zone. As the potassium chloride solution zone migrated to the cathode under the influence of the electric field, the crystals migrated in the same direction.

The method considered makes it possible to carry out crystallisation under mild conditions, varying smoothly the degree of supersaturation. This variation can be made even smoother by altering the concentration of the leading solution during the experiment. The method is universal and permits the crystallisation of any inorganic, organic, and bioorganic ionogenic substances. One may add to this the advantages of the capillary isotachophoresis itself, the possibility of the preliminary purification of the solution itself and of the crystallisation of several zones simultaneously, as well as the possibility of using microgramme amounts of the substances and microlitre volumes of the solutions.

All the foregoing considerations make the proposed method promising, particularly in the study of the crystallisation process itself and for the practical preparation of small amounts of crystals of especially rare and expensive ionogenic substances.

VIII. The isotachophoretic method for the determination of the electromigration transport of the solvent in electrolyte solutions

The two forms of the regulating function and Eqns (2) – (4) relating them have been used to develop a relative method for the measurement of the electromigration transport of the solvent in electrolyte solutions.[93,94]

Electromigration transport of the solvent, constituting the migration of the solvent as component (not hydrodynamic) migration to the cathode or anode associated with its interaction with the ions, may occur in electrolyte solutions. This process, which takes place when a direct current passes through electrolyte solutions, has been the object of study since the 1930s, but hitherto the scatter of the experimental results has been considerable. This made it necessary to consider these data as only qualitative, indicating merely the occurrence of the effect itself.

The proposed method makes it apparently possible to solve this problem. One selects an electrolyte which forms aqueous solutions over a wide concentration range. It is necessary that the transport numbers of the cationic (or ionic) components of these solutions relative to the solvent are known. Suppose that the concentration of this solution is c_1 and the transport number relative to the solvent at the given concentration is $t_1^0(c_1)$. Next, one selects another, test electrolyte in solutions of which it is necessary to determine the electromigration mobility of the solvent (water). We shall assume for the sake of specificity that the transport numbers of the cationic component are smaller in the electrolyte solution investigated, which is the terminating solution, and that a steady-state isotachophoretic boundary may be formed between this solution and the first solution. For solutions of the test electrolyte, the transport numbers $t_2^0(c)$ of the cationic components relative to the solvent must also be known over a certain concentration range or must be specially measured. The relation

$$\frac{t_2^0}{c_2^0 z_2} = f(\lg c) \,. \tag{6}$$

is derived from these data.

According to the regulating function (2), a steady-state isotachophoretic boundary arises between the first and second solutions with concentrations (mol/kg of water) c_1^0 and c_2^0 respectively. Therefore, having calculated the quantity $t_1^0/c_1^0 z_1$ for the chosen concentration c_1 of the leading solution, the concentration c_2 of the terminating solution, forming with the former a steady-state isotachophoretic boundary, is found from the plot of Eqn (6). Next, the transport number $t_2^0(c_2)$ of the cationic component relative to the solvent is found for this concentration from reference data. After this, the quantity

$$t_2(c_2) = t_1(c_1)\frac{t_2^0(c_2)\rho_2^0}{t_1^0(c_1)\rho_1^0} \,, \tag{7}$$

i.e. the transport number of the same cationic component of the test solution at the concentration c_2 but this time in the laboratory coordinate system for a stationary solution, is found from Eqn (4). The electromigration mobility of water u_0 (the rate in a unit electric field) is calculated from these data:

$$u_0 = \frac{10^3 K}{czF}(t_2 - t_2^0) \,,$$

where K is the specific conductance of the test solution at the concentration c_2.

Eqn (7) includes one unknown quantity — $t_1(c_1)$, i.e. the transport number of the cationic component in the first (leading) solution at the concentration c_1 in the laboratory coordinate system, which must be measured independently.

A procedure for the determination of the electromigration mobility of the solvent in the chosen solution at a concentration c_2 was described above. The second, third, fourth, etc. concentrations of the initial solution are selected similarly and the corresponding second, third, fourth, etc. concentrations of the test solution are obtained, i.e. the concentration dependence is found. For each concentration of the two solutions, the transport numbers of the cationic components relative to the solvent must

be known. The transport numbers in the first solution at the chosen concentrations in the laboratory coordinate systems are unknown, which implies that their concentration dependence over a certain range or, what amounts to the same thing, the quantitative characteristic of the electromigration transport of water at the same concentrations, is unknown. A similar computational procedure can be applied to all electrolyte solutions where it is necessary to determine the electromigration transport of water. Using initial aqueous potassium chloride solutions at concentrations of 1 and 3 M, the absence of electromigration transport of water was noted by the isotopic boundary method. This means that $t_1(c_1)/t_1^0(c_1) = 1$ in Eqn (7).

The proposed method permits the calculation of the electromigration mobility of water in solutions of any electrolytes over a wide concentration range. The transport numbers relative to the solvent and the fact that there is no transport of the solvent in potassium chloride solutions at all concentrations are used in the calculations. The characteristics of the electromigration transport of water in solutions of a number of alkali metal halides and alkaline earth metal, zinc, cobalt, copper, and cadmium chlorides as well as a series of water-containing substances such as hydrochloric acid, ammonium chloride, and potassium hydroxide over a wide concentration range have been published.[94] The internal consistency of the method considered was confirmed by the results of measurements by the isotopic boundary method of the characteristics of the electrical transport of water in aqueous lithium chloride solutions at concentrations of 1 and 2 M and in rubidium chloride solutions at concentrations of 1 and 3 M and by comparing the results of these measurements with calculated data.

The characteristic features of the above method for the determination of the electromigration mobility of the solvent (water) are as follows.

1. The regulating function of isotachophoresis, constituting the basis of the method, is itself based on the law of conservation of matter and is therefore applicable without limitations as regards the types and concentrations of the solutions.

2. In proving the validity of the method, no model ideas and no mechanisms of the motion of the species in solutions were resorted to.

3. The method can be applied equally successfully to the determination of the electromigration mobility of any non-aqueous solvent.

4. Using a small number of experimental data, the method can be used to obtain the characteristics of the electrochemical transport of the solvent in all aqueous solutions of electrolytes for which the transport numbers relative to the solvent have been measured by the usual experimental methods.

IX. Conclusion

Progress in the development of new aspects of capillary isotachophoresis is linked directly to the establishment of modern ideas concerning the kinetic phenomena in electrolyte solutions and processes occurring near the isotachophoretic boundary. The aspects considered include those which are of purely theoretical importance as well as applied aspects. Thus the method for the determination of the electromigration transport of the solvent is important for the establishment of the physical picture of the passage of electric current through electrolyte solutions. Analytical capillary isotachophoresis has already become fairly common and in the present instance has been supplemented only by qualitative analysis. The coulophoretic analytical method constitutes a separate analytical electrochemical field. Methods for the measurement of the amount of electricity passed through the system, for the determination of the internal cross-sectional area of the capillary, for the monitoring of the constancy of the cross-sectional area of the capillary along its length, and for the determination of the free cross-sectional area of a tube with a filler have been developed on its basis. A property fundamental for isotachophoresis — the adaptation of the concentrations of all the solutions following the leading solution — has been used as the basis of a novel method for the electrocrystallisation of an ionogenic substance on passage of an electric current. In contrast to electrocrystallisation which occurs when a substance is segregated at electrodes, in this case crystallisation takes place in solution when opposed fluxes of cations and anions meet. The electrosynthesis of electrolyte solutions with the aid of ionic boundaries, which is one of the modifications of isotachophoresis for which this principle had already been nidicated by Kohlrausch, has expanded significantly the possibilities of capillary isotachophoresis as a preparative method.

All the modifications of isotachophoresis examined are characterised by a high resolving capacity, adequate sensitivity and accuracy, applicability over a wide concentration range (from dilute to saturated solutions), and satisfactory time parameters. The methods described make it possible to use microgramme amounts of test substances and microlitre volumes of the solutions and to work with aqueous and non-aqueous electrolyte solutions.

All the features listed above are possible exclusively owing to the availability of the universal diffraction method for the detection of electrolyte boundaries in capillaries. The ecological purity of all the processes examined, to which much attention has been devoted recently, is especially attractive.[95] The foregoing permits the assumption that capillary isotachophoresis and its modifications constitute a promising set of analytical and preparative methods.[96]

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