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Isotachophoretic crystallization of ionogenic substances in electrolyte solutions

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Abstract

Grounds are given for the use of isotachophoresis for the crystallization of ionogenic substances from electrolyte solutions. Regulating function is the basis of this new isotachophoresis trend. A device for isotachophoretic crystallization in capillaries, based on a capillary isotachophoresis instrument is described. The process of sodium chloride crystallization from aqueous solution is described in detail. The applicability of the general rules formulated is confirmed by crystallization of potassium and sodium chlorides, cesium nitrate and potassium perchlorate in cationic isotachophoresis, and potassium bichromate in anionic isotachophoresis.

Keywords: Isotachophoresis; Crystallization; Electrolyte systems; Inorganic ions

1. Introduction

This report opens a new trend in isotachophoresis: isotachophoretic crystallization. Crystallization is a process widely used in research. The creation of supersaturation is the basis of crystallization methods. It is achieved by evaporation of the solvent, by alteration of external conditions and by conduction of the chemical precipitation reaction. The supersaturation of the ionogenic substance in an electrolyte solution may be created by means of using the isotachophoretic adjustment of the concentration of the investigated solution to the leader under the passage of the electric current. The adjustment process is a fundamental peculiarity of isotachophoresis.

2. Theoretical aspects

Mobility and transference number of the ionic component are the essential physical quantities in studies of electrotransference phenomena in electrolyte solutions. The ionic component transference number is the number of gram-equivalents of this component, transferred in cathode or anode direction through the column cross section under the passage of one Faraday of electricity [1]. The experimentally measured quantity is the transference number of the ionic component rather than that of a concrete type

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of ions, as the real type of ions transferring electricity even in strong electrolyte solutions is not known. The ionic component transference number is expressed through the mobilities (i.e. velocities in unit electric field) of cationic and anionic components. The mobilities are not invariant quantities and depend on the coordinate systems used. There are several coordinate systems. The laboratory system, related with measuring apparatus, and the system related with solvent, are more generally used. When an electric current is passed through an electrolyte solution a solvent flow arises in it towards cathode or anode. This solvent flow is caused by the interaction of moving ions with solvent molecules. Experimentally the existence of such solvent flow has been demonstrated recently by the isotopic boundary method by one of authors [2]. The difference between the considered coordinate systems is zero in infinitely dilute solutions and exceeds 10% in some concentrated solutions. The electrotransference of water is absent in aqueous solutions of potassium chloride in the whole concentration range from the dilute to the saturated one. As a consequence, the difference between the laboratory coordinate system and "the solvent" system is nonexistent in these aqueous solutions. Modern experimental methods measure the transference numbers in electrolyte solutions only in the coordinate system related to the solvent throughout the concentration range. All the aforesaid has been considered in detail in the recent survey publication of the authors [3]. It was demonstrated [4] that the regulating function of isotachophoresis has two different but equally valid forms:

$$C_1 z_1 / C_2 z_2 = t_1 / t_2 \quad \text{Kohlraush form} \tag{1}$$

$$C_1^0 z_1 / C_2^0 z_2 = t_1^0 / t_2^0 \quad \text{Hartley form} \tag{2}$$

where C_1 and C_2 are the concentrations of the leader and the adjusted to it solution under study, respectively, in mol/l (M); z_1 and z_2 are the valences of uncommon ionic components of these solutions; C_1^0 and C_2^0 are the concentrations of the same leader and test solutions but in mol/kg of water; t_1 and t_2 are the uncommon ionic component transference numbers of the leader solution (concentration C_1) and the solution under study (concentration C_2) in the laboratory coordinate system (in the absence of flow of solutions); t_1^0 and t_2^0 are transference numbers of the same ionic components of the same solutions, but relative to the solvent of "its own" solution. Eqs. (1,2) are equally employable for both cationic and the anionic isotachophoresis.

Isotachophoretic crystallization principles are qualitatively as follows [5,6]. If the concentration of the solution under investigation differs from the stationary concentration, it changes under the action of electric current and attains this stationary value in the course of time. If the concentration of the leader solution is so great that the ionogenic substance concentration in the adjusted zone at stationary state must be higher than its saturated solution concentration, crystallization will occur in the zone. Part of the supersaturated substance will precipitate. The regulating function makes it possible to calculate stationary concentrations of the investigated solution and the terminator solution on the basis of the leader concentration and the transference numbers of uncommon ionic components of leader, investigated and terminator solutions. The regulating function can be used to construct the curves which are necessary to select crystallization conditions. The basis for construction of the characteristic curves of isotachophoretic crystallization is a regulating function in Hartley form (Eq. (2)), as it contains experimentally measured transference numbers.

Considering the construction of characteristic curves taking cationic isotachophoresis in chloride solutions as an example. Hydrochloric acid is the leader for all chloride solutions due to the anomalously large mobility of the hydrogen cationic component. Let us construct the dependence

$$\log(t^0 / C^0 z) = f(Cz) \tag{3}$$

for hydrochloric acid and for some salt, for instance, for potassium chloride in a concentration range from 1 M to saturated solutions. It will be recalled that C is the solution concentration in mol/l (M), but C^0 is the concentration of the same solution in mol/kg of water. The concentration dependencies of cationic component transference numbers [7] and the dependence of densities on solution concentration and solubility of substances in water at temperatures of transference numbers measurement [8,9] are the initial data. These two dependencies are shown in

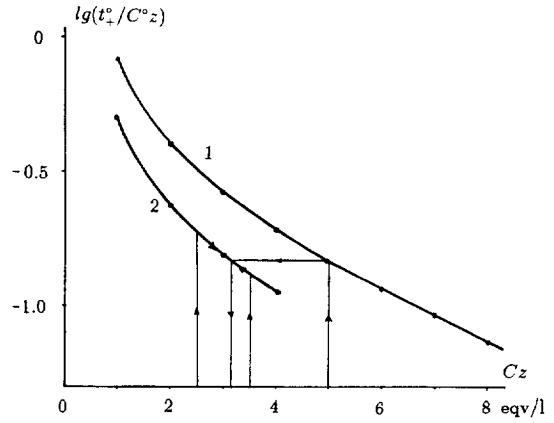

Fig. 1. Isotachophoretic characteristic curves of leader solution HCl and investigated solution KCl. Small black circles signify points, at which the dependence in Eq. (3) was constructed for HCl (curve 1) and for KCl (curve 2). Initial data are taken from the literature [7–9].

Fig. 1 (the logarithm is taken for convenience in the graph). Based on them, it can be predicted how the process of adjustment of isotachophoretic zones will occur. Suppose the concentration of a leader solution of hydrochloric acid is 5 *M*. The characteristic function corresponding to this concentration has the value −0.830. Regulating function (Eq. (2)) suggests that the potassium chloride solution adjusted to the leader solution will have the same characteristic function value. In other words, we draw a horizontal line from the intercept point of the 5 *M* ordinate and the hydrochloric acid curve up to its intersection with the potassium chloride characteristic curve. This intersection point corresponds to 3.15 *M* KCl solution. Just this concentration is the stationary concentration of KCl solution with the 5 *M* HCl solution as a leader. Now it is easy to understand what will happen with a potassium chloride zone of initial concentration 2.5 *M* under the current, if the leader, as before, is the 5 *M* hydrochloric acid solution: it will be concentrating up to 3.15 *M*. The initial 3.5 *M* potassium chloride zone will be, on the contrary, diluted under the same conditions and also become 3.15 *M*. Now suppose that the hydrochloric acid leader solution has an 8 *M* concentration and the initial potassium chloride investigated solution, a 3.5 *M* concentration. As follows from the aforesaid, the point describing the KCl solution state will move down along the characteristic curve when the current is passed through. It will come to the end of this curve, i.e. to saturated solution concentration, at 20°C, at which temperature the corresponding transference number was measured. In principle, a somewhat higher concentration must initiate the crystallization of potassium chloride in the zone. This crystallization will continue until precipitation of all that quantity of substance, which has created the supersaturation in the zone.

Thus, the isotachophoresis characteristic curves, constructed on the basis of the concentration dependence of ionic component transference numbers, enable us to predict whether the crystallization of a given ionogenic substance is possible or impossible in principle.

We write the relation which will be useful in future:

$$V = I(t_1 - t_2)/SF(C_2 - C_1)z + It_1/SFC_1z \qquad (4)$$

V (dm/s) is the velocity of the concentration boundary in the leader relative to the cationic boundary of the leader with the investigated solution. In Eq. (4) the first expression is the concentration boundary speed in an immovable leader solution [10,11], the second one is the speed of the cationic boundary between the leader and investigated solutions also in the absence of solution movement [4]. Sign "+" corresponds to boundaries moving in opposite directions to meet each other. Here I is the electric current, flowing through the column (A), S is the area of capillary canal (dm^2), F is the Faraday constant (C/equiv.), t_1 and t_2 are transference numbers of the leader solution cationic component at concentrations C_1 and C_2 respectively in the laboratory coordinate system, z is the component valency. In the described case a concentration boundary is the front of transition from a high leader concentration to a low one. There is a significant peculiarity here. A concentration boundary may come to a stationary state (collecting forces are balanced by diffusion) under the action of passing electric current in accordance with isotachophoresis laws. It is the result of a certain condition which is formulated primarily in Ref. [10], verified in Ref. [12] and inferred strictly in Ref. [11]. Its essence is that the concentration dependence of the cationic component transference number of a leader in the laboratory coordinate system must have a prominence.

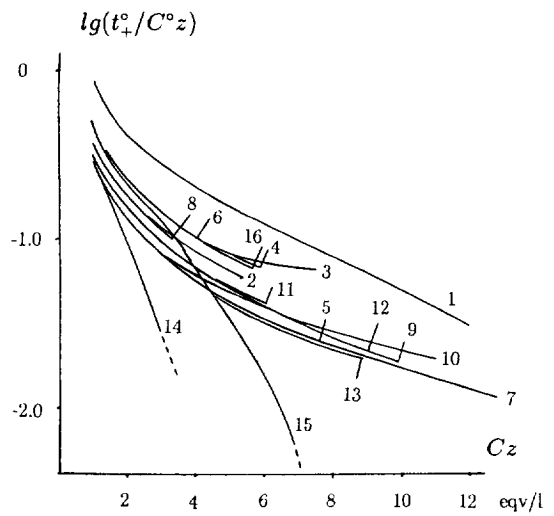

Fig. 2. The family of characteristic curves for cationic isotachophoresis in chloride solutions. 1 = HCl, 2 = NaCl, 3 = CsCl, 4 = RbCl, 5 = $CoCl_2$, 6 = KCl, 7 = LiCl, 8 = $BaCl_2$, 9 = $MgCl_2$, 10 = $CaCl_2$, 11 = $SrCl_2$, 12 = $CuCl_2$, 13 = $NiCl_2$, 14 = $ZnCl_2$, 15 = $CdCl_2$, 16 = NH_4Cl. The indicatory line drawn from the index to the curve terminates at the point corresponding to the saturated solution. Dotted lines at curves 14 and 15 correspond to the beginning of region of negative cation transference numbers in solutions. These data cannot be used for realization of isotachophoretic crystallization without supplemental study.

Fig. 2 shows the characteristic curves based on data from Refs. [7–9] for a great number of chlorides of alkaline and alkali-earth metals (except francium, beryllium and radium), zinc, cobalt and nickel, as well as for ammonium and hydrochloric acid. It will be recalled that the maximum concentration of the characteristic curve of each substance corresponds to its saturated solution at the temperature, at which the transference number is measured. Concentrated solutions of hydrochloric acid may be used in principle as a leader for isotachophoretic crystallization of the chlorides of potassium, sodium, rubidium, cesium, ammonium, barium and strontium. Crystallization of chlorides of cobalt, nickel, copper may be achieved if a saturated solution of calcium chloride is used as a leader. Lithium chloride cannot be isotachophoretically crystallized in chloride solutions. It does not mean, however, that the isotachophoretic crystallization of lithium chloride is impossible. It is necessary to build a family of characteristic curves for anionic isotachophoresis in solutions of lithium salts. A highly concentrated lithium hydroxide solution will serve as a leader solution. The possibility for crystallization of lithium chloride in the anionic isotachophoresis may be elucidated by similar examination of these characteristic curves.

So far the possibility of isotachophoretic crystallization has merely been considered in principle, i.e. in terms of the conditions necessary but perhaps not sufficient.

In reality the isotachophoretic crystallization of any substance is conditioned by a number of additional circumstances. Among these are a latent period of crystallization delay, the least requisite supersaturation and the presence of foreign particles as crystallization centers. Besides, for concentrated solutions in isotachophoresis there is no exact theory of the adjustment of zone concentrations to stationary state. Mistakes in transference numbers table data are also possible, particularly in the region near saturation where extrapolated data are used sometimes. These mistakes may reveal themselves in the region where the isotachophoretic characteristic curves of different substances are near each other. Here even a small mistake in measured transference numbers may result in an order of zone sequence other than it follows from characteristic curves. In this case a special investigation into the order of sequence of divided zones is required.

For the reasons outline here, an experimental study of isotachophoretic crystallization is imperative.

3. Experimental realization

So far the peculiarities of isotachophoretic crystallization have been discussed in general. In practice, its realization demands observation of some additional conditions. They are as follows:

1. Besides isotachophoresis conditions, formulated above, care should be taken that (a) there is a specially chosen terminator. Non-common ionic component mobility of the investigated solution should be greater than that of the terminator, (b) the electric polarity is such that boundaries move in the direction from the terminator to the leader (in the absence of a hydrodynamic contraflow).

2. Conditions should be set up for sufficiently low

convective mixing of solutions (the effective diffusion coefficient must not differ strongly from the molecular one).

3. The investigated solution boundaries with a leader and a terminator must be periodically checked.

4. Gravitational stability of solutions and crystals in solution must be maintained. It means that: (a) the difference in density of solutions forming the ionic boundary, does not affect their mixing in the boundary region, (b) localization of crystals in its own mother solution is ensured.

5. Temperature dependence of solubility of the ionogenic substance must be taken into consideration.

6. There must exist a possibility of observing the crystal appearance and growth.

7. Withdrawal of grown crystals should be possible.

The enumerated conditions may be combined most completely if transparent capillary columns without packing are used. Such capillaries together with the diffraction method of boundary registration were offered by one of the authors, when she elaborated analytical capillary isotachophoresis in 1963 [13]. The capillary columns make it possible to crystallize isotachophoretically the substances under study over the range of solution volumes from tens of picolitres to fractions of a microlitre.

4. Experimental apparatus

The device for the investigation of isotachophoretic crystallization is schematically shown in Fig. 3. A glass capillary has an inner diameter in the interval 0.15–0.5 mm and outer diameter in the interval 0.3–0.9 mm. The capillary has a II-form with an additional crook in the middle part. The capillary can be fixed immovably in special support cuts, so that its "DE" part is horizontal. The capillary ends "AB" and "GH" are immersed in electrode vessels of a U-form 12 cm in height. Inner diameter of one part was 12 mm and of the other part, 6 mm. The capillary part "CDEF" may be immersed, if needed, in a bath with cooling water of the required temperature. The electrode vessels are attached to special mechanisms provided with a

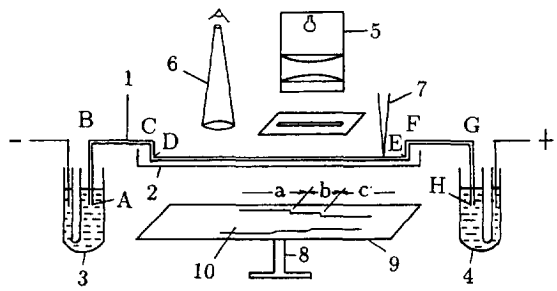

Fig. 3. Experimental device. 1 = Glass or quartz capillary of dimensions: AB = 65 mm, BC = 35 mm, CD = 15 mm, DE = 120 mm, EF = 15 mm, FG = 50 mm, GH = 65 mm. 2 = Bath for cooling water, 3 = cathode vessel filled with leader solution HCl, 4 = anode vessel filled with terminator solution $CoCl_2$, 5 = light source with the slit, 6 = microscope, 7 = thermocouple, 8 = table, 9 = screen, 10 = diffraction picture of the arranged solution before crystallization: a = leader, b = investigated solution, c = terminator.

worm and a cogged bar, which permits the vessels to be shifted vertically up to 4 cm in order to build up and regulate the required counterflow in the capillary. The counterflow makes it possible to keep the boundary in any part of the capillary immovable. Platinum electrodes are immersed in narrow parts of the electrode vessels. Power supply guarantees direct current 10 mA at 2 kV. A light source can be placed above the fixed capillary on a support with two guides, along which it can be moved. A parallel beam of white light from the source passes through a narrow rectilinear slit with sharp edges. A screen for observation of the diffraction picture is placed on a table under the capillary. The picture represents an array of rectangles of different width with the axis of symmetry coincident with the capillary axis. In most cases the transition zone between two adjusted solutions has an extent of about 0.2 mm and well visible on the screen if the difference in refraction indexes of solutions forming the boundary is not smaller than 0.001 [14]. The diffraction method is extremely convenient as it permits all boundaries to be observed in the capillary simultaneously. The method offers a means of controlling the concentration adjustment process and the separation of solutions in capillary itself. A plate-holder with photo-paper may be fixed on the table when it is necessary to photograph the diffraction picture. In this case the whole of the device should be screened from outside light by a dark cloth. The support with

the light source may be removed and replaced by a microscope MBS-1 with its own light source and camera attachment. It can be easily brought to the capillary by means of a simple mechanism with rotating vertical pivot. The microscope secures 70-fold maximum magnification. A copper-constantan thermocouple made from 0.1 mm diameter wire measures the capillary temperature at any point. The second thermocouple junction is immersed in a Dewar flask filled with water–ice mixture. The thermocouple e.m.f. is measured by a digital voltmeter "1516" on a 50 mV scale.

5. Experimental procedure

The capillary is filled with solutions through one of its ends. When the end of a dry capillary is immersed in solution, it begins to fill the capillary by the action of capillary forces. After the solution–air boundary has entered the middle part of the capillary, its filling with all the solutions may be easily done by inclining the capillary. An insufficiently dried capillary requires a water jet pump for its filling. Firstly, the solution which must fill the opposite capillary end is introduced. Secondly, the solution under investigation is introduced and finally the third solution, which must fill the capillary completely is introduced. Naturally, the described method of capillary filling results in some inevitable, although insignificant, intermixing of investigated solution with leader and terminator. Usually, capillaries with a constant inner cross-section are employed. Therefore it is convenient to control the column length of subsequently introduced solutions by observing the shift of the meniscus of the first introduced solution, or of a small air bubble specially introduced at the very beginning. Before crystallization the solution under study must be collected in the stationary isotachophoretic zone and at the same time cleaned of impurities and of leader and terminator admixtures. To this purpose, there must be a leader solution in the capillary which would ensure that in accordance with the characteristic isotachophoretic curves the concentration of investigated solution after adjustment is somewhat below the saturation point. Only after the clean zone of solution under investigation has been formed, the leader should be replaced by a more concentrated one which would guarantee crystallization. An original way has been found for the realization of this version. A leader solution of lower concentration is introduced in the capillary together with the investigated solution and the terminator solution as described above. The capillary end filled with that leader is immersed in an electrode vessel filled with the same leader but of higher concentration, permitting crystallization of the adjusted solution under study. The condition for the existence of stationary concentration boundary has been formulated above in the theoretical section. The concentration dependence of the transference number of the leader cationic component in the laboratory coordinate system must have a prominence. Precisely such is the character of the concentration dependence of the hydrogen cationic component in hydrochloric acid solutions within a range of 5–12 *M*. One can be readily convinced of it by constructing the concentration dependence of these transference numbers in the system "solvent" [7], as the transference numbers in these two systems usually differ from each other by 10–20%. Just the approach of the concentration front to the adjusted zone of the investigated solution points to the substitution of a more concentrated leader for that originally introduced in the capillary. It leads to crystallization of the adjusted zone of solution under study.

Another problem in experimentation with concentrated solutions in capillaries is the liberation of dissolved gas bubbles from solutions. The essence of the problem is as follows. The solubility of gases in electrolyte solutions decreases with increasing temperature. When a current is passed through the capillary, the solution temperature increases as a consequence of Joule heat release in the solution volume. This effect is greater in a terminator and smaller in a leader because of the specific resistance decreasing with transition from the terminator to the leader. If solutions are saturated with gases at 20°C, gas bubbles are formed with the increasing temperature. They gradually grow in volume, plug the capillary canal, interrupt the current and sometimes create an arc discharge on the bubble surface. This phenomenon is observed in the first place in terminator solutions. There are some methods to overcome this difficulty. The first is to prepare all the necessary solutions just before the experiment using

freshly boiled distilled water as a solvent. The boiling of water reduces the concentration of dissolved gases in it by nearly one half [9]. It is enough for isotachophoretic crystallization to be carried out in most cases if the solution temperature does not exceed 50–60°C. In another method, all the solutions must be degassed just before the experiment during 20 min in small glass vessels, using a water jet pump under heating to 50–60°C and intensive shaking. An inert liquid may be deposited on the electrolyte solutions exposed to air to protect them from dissolution of atmospheric gases.

6. Experiments and results

The main experiments on isotachophoretic crystallization were performed in aqueous solutions of chlorides. A glass capillary with inner diameter of 0.42 mm and outer diameter of 0.92 mm was used. Measurements were made on capillary butt ends by means of a microscope. The inner cross section constancy was controlled visually using a microscope, with a precision of 0.02 mm. We describe the crystallization of sodium chloride solution in detail. A solution zone of NaCl (1.2 *M*) 2 cm in length was placed in the horizontal part of a capillary between the solutions of HCl (7.0 *M*) and $CoCl_2$ (3.5 *M*). The capillary end filled with HCl was immersed in a cathode vessel filled with 10.0 *M* HCl. The second capillary end was immersed in an anode vessel filled with $CoCl_2$ solution (3.5 *M*). So the concentration boundary 10.0 *M* HCl/7.0 *M* HCl and two ionic boundaries 7.0 *M* HCl/1.2 *M* NaCl and 1.2 *M* NaCl/3.5 *M* $CoCl_2$ were formed in the capillary. A direct current of 2 mA was switched on and maintained during the experiment. The position of boundaries in the horizontal part of the capillary was controlled by observing the diffraction picture on the screen, when the light source was being switched on periodically for several seconds. The ionic boundary NaCl/$CoCl_2$ was kept in the horizontal part of the capillary close to the anode end by adapting the positions of the electrode vessels by height. The estimation of the rapprochement speed of the ionic and concentration boundaries by Eq. (4) gave the value 0.0168 mm/s. In this case the transference numbers in laboratory system were replaced by those measured relative to the solvent [7]. The time of the meeting of the concentration and ionic boundaries is 3.1 h from the beginning of the experiment. The first NaCl crystal appeared after the boundaries had met, followed in a few seconds by a chaotic accumulation of crystals of irregular shape at the extent of 0.3 mm. Crystals are seen as a dark strips perpendicular to the capillary axis in the diffraction picture or directly in the microscope. The next crystal group developed from several thread-like crystals which had grown from one center within a few seconds and thickened slowly during 3 min. This group was situated at a distance of 4 mm from sodium/cobalt boundary. The third, forth and fifth crystal groups appeared on the 8 mm section later. With time the number of crystal groups decreases, within 5 min they draw together and unite in a common zone 3.2 mm in length. The crystals occupy almost the whole of the capillary canal but rather freely. When an electric current is passed through the capillary in the absence of the counterflow the crystals are dissolving at the terminator zone side and growing at the leader one. Thus the crystal zone constantly shifts in the direction of the boundary movement under the action of electric current.

Experiments have been carried out for the crystallization of some other salts. Potassium chloride was crystallized isotachophoretically by means of smaller hydrochloric acid leader concentrations, 5.0 *M* and 7.0 *M* respectively.

Another experiment, a qualitative one, was conducted in chloride solutions. An attempt was made to crystallize a 3.5 *M* solution of cobalt chloride. The leader solution of calcium chloride (5.5 *M* concentration) and the terminator solution of lithium chloride (9.0 *M*) were used. The characteristic curves of these substances, shown in Fig. 2, testify that isotachophoretic crystallization in these conditions is possible in principle. In practice, however, the crystallization of cobalt chloride does not occur. This may be accounted for by two reasons. The first is inaccurate data on ionic component transference numbers of lithium and cobalt in concentration ranges 7–11 *M* for LiCl and 3.5–5.5 *M* for $CoCl_2$. It is likely that the cobalt component fails to create a single stationary zone and switches places with lithium component. The second reason is the fact that there is a great delay in crystallization of

substances which form crystallohydrates. This fact calls for additional investigation.

Besides, some preliminary experiments have been carried out on isotachophoretic crystallization in the absence of necessary data about ionic component transference numbers. So the fact of crystallization of cesium nitrate has been established, with nitric acid (8.0 *M*) as a leader and strontium nitrate (1.25 *M*) as a terminator. The crystallization takes place only if the capillary is cooled by water or the current is switched off upon the procedure, since the solubility of the substance is strongly temperature dependent. Potassium perchlorate was also crystallized using chloric acid (5.0 *M*) as a leader and cobalt perchlorate as a terminator. The fact of crystallization of potassium bichromate has been established in anionic isotachophoresis, with potassium chloride (4.0 *M*) as a leader and potassium nitrate (2.0 *M*) as a terminator.

It should be noted that the data on ionic component transference numbers in the range of concentrated solution are not available in the literature. However, they may be obtained with the described device by the method used in Ref. [15].

7. Discussion

So far isotachophoresis has been dealing with one-phase systems–liquid electrolyte solutions. However, it has been ascertained recently that the isotachophoresis potentialities are considerably wider. Isotachophoresis may operate with two-phase systems–electrolyte solutions and crystals derived from them.

The described experiments on isotachophoretic crystallization of chloride solutions demonstrate the correctness of general theoretical approach to the study and description of this so far unknown phenomenon. The proposed method of crystallization has some peculiarities which call for investigation. First of all it is the process of concentration adjustment of the studied solution to the chosen leader. Upon investigating the method itself in detail, it may be used to elucidate the peculiarities of generation and growth of crystals of some ionogenic substances. This is due to the fact that in the isotachophoretic crystallization method supersaturation is created by electric current and may be done in the conditions permitting a careful observation. Of interest is the possibility to produce perfect crystals by using leader concentrations which should be as close as possible to those required by the characteristic curves. Naturally, the work with isotachophoretic crystallization of weak organic and inorganic electrolytes opens up various new possibilities in organic and inorganic chemistry, biochemistry, physiology. Among the unique peculiarities of the discussed method noteworthy are the simultaneous isotachophoretic cleaning of crystallized substances from admixtures during the isotachophoretic adjustment and the possibility to produce crystals doped by some admixture by creating the through flow of the ionic component of interest. Another peculiarity is the applicability of the method for the crystallization of any (but naturally, only ionogenic) substances not only in aqueous solutions, but also by using non aqueous solvents. A more extensive application of the discussed method requires the development of special transparent, dismountable columns providing a sufficient working volume under the minimizing of convection and an intensive cooling. Wide use of the isotachophoretic crystallization method would stimulate research on measurement of the transference numbers of the ionic component in concentrated electrolyte solutions.

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