

## On the Shift in Transference Numbers and Ionic Mobilities on Addition of Sucrose to Aqueous Electrolyte Solutions

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Transference numbers and ionic mobilities of potassium chloride, potassium propionate, potassium caproate, and tetraethylammonium iodide in aqueous sucrose solutions have been determined at 0°C by means of the moving boundary method.

The transference numbers have been found to depend on the sucrose concentration; the higher transference number of anyone of the electrolytes studied increases with increasing sucrose concentration. The transference number shifts are a consequence of different ions being retarded differently by a given concentration of sucrose. The magnitudes of the shifts show a fair degree of correlation with the relative sizes (allowing for probable hydration) of the ions of a given electrolyte except for tetraethylammonium iodide. The anomalous behaviour of the latter electrolyte is probably due to a certain degree of association between the iodide ions and the non-electrolyte. The results also indicate a considerable degree of ion-pair formation in aqueous 0.1 M tetraethylammonium iodide solution.

In work on separation of negatively charged proteins by means of zonal electrophoresis in a density gradient of sucrose solution, Sorof *et al.*<sup>1</sup> found that an increasing band of intense convection always occurred at the position of the "density shelf" supporting the initial zone if the current was sent downwards through the gradient, that is, if ascending electrophoresis was used. The electrical resistance was considerably higher in this band than in the rest of the column. Experiments with descending electrophoresis, on the other hand, could be done without complications.

This phenomenon was also observed by Svensson *et al.*<sup>2</sup> in similar experiments with the same type of buffer (sodium barbital). Moreover, by light absorption measurements at 284 nm on the content of the column after the separation, they found a deep minimum at the density shelf. The absorption values at this minimum were always much lower than those in the reference solution (light buffer solution). The deep minimum was also obtained in a run with barbital buffer without protein. These results showed that an appreciable rarefaction of salt took place at the density shelf. Svensson *et al.*

assumed this to be due to a shift in the transference numbers of the buffer salts under the influence of the large concentration change of sucrose at the density shelf. However, they had no experimental proof of this assumption.

Later, Stokes and his coworkers<sup>3,4</sup> have measured the limiting conductances for a number of simple electrolytes at 25°C in, *inter alia*, aqueous sucrose solutions. For one of the electrolytes (KBr) the limiting transference numbers were also determined. This made possible the evaluation of the separate ionic mobilities of all the electrolytes by the Kohlrausch principle. The transference numbers that may be calculated from these mobilities show a shift with the sucrose concentration in accordance with the suggestion of Svensson *et al.*

The mobilities reported by Stokes *et al.*<sup>4</sup> refer to sucrose concentrations of 10 and 20 % by weight. In the present investigation, transference number and mobility measurements have been carried out according to the moving boundary method over a larger interval of sucrose concentration, *viz.* 0–500 g/l in 100 g/l steps. To demonstrate the effect of the relative ionic sizes of a given electrolyte on the magnitude of the transference number shift, three of the electrolytes studied had a common cation (potassium) that was combined with one somewhat smaller anion (chloride) and two larger anions (propionate and caproate), respectively. Further, an electrolyte with a large cation and a small anion (tetraethylammonium iodide) has been investigated.

## EXPERIMENTAL

*Electrophoresis runs.* The moving boundary experiments were carried out at 0.5°C in a Tiselius-Svensson electrophoresis apparatus (type 3021), manufactured by LKB Produkter AB, Stockholm. The cell was a standard Tiselius cell of 3 × 25 mm<sup>2</sup> cross section. A modified top section<sup>5</sup> with attached small electrode vessels was used. The electrodes were 0.5 mm platinum wires, dipping down about 5 mm into the solutions. Gassing electrodes were chosen since they are much easier to handle than reversible ones, and since highest possible precision was not necessary in this investigation. The H<sup>+</sup> and OH<sup>-</sup> ions generated at the electrodes were prevented from reaching the moving boundaries by a proper design of the moving boundary systems<sup>6</sup> (*cf.* Table 1 and p. 1997).

The current through the cell was kept constant by a current regulator (type LKB 3209) and read on a calibrated precision milliampere meter. Currents between 5 and 15 mA were used. Leakage current could be read on a separate meter. In most experiments, the leakage did not exceed 2 μA. The filled cell was thermostatted for 20 min before the current was switched on.

The boundary velocities were determined with the aid of a schlieren optical system<sup>7</sup> and a recording microdensitometer (type MK III C from Joyce, Loebel & Co., Ltd., Gateshead-on-Tyne, Great Britain). The schlieren peaks were photographed on 24 × 36 mm<sup>2</sup> film (Ilford HP3). The first exposure was taken about 20 min after the current had been switched on. The schlieren patterns were then photographed at 10 or 20 min intervals during the experiment, the shorter intervals being used with the highest current. In all 6–10 exposures were taken in a run.

*Evaluation of the boundary velocity.* The position of the moving boundary at the time for each exposure was determined by means of the microdensitometer. The most precise way of aligning the exposures on the specimen table of the microdensitometer was to cut the developed film into pieces of three exposures and orient each piece of film in a direction perpendicular to the recording direction. The three consecutive exposures could be successively brought into the measuring beam by moving the specimen table perpendicular to the recording direction. The optical density of each exposure was recorded along lines A–B and C–D (see Fig. 1). When recording from A to B, passage

Table 1. Results of moving boundary experiments at 0.5°C and conductivity and viscosity measurements at 0°C.

Experi- ment	Leading solution				Indicator solution		Sucrose conc. (g/l)	Transference number		Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	
	Salt	Conc. (M)	$\kappa \times 10^3$ (ohm <sup>-1</sup> cm <sup>-1</sup> ) at 0°C	$\eta$ (milli-poise) at 0°C	Salt	Conc. (M)		$T_+$	$T_-$	$u_+ \times 10^5$	$ u_-  \times 10^5$
1A		0.1001	7.121	17.82		0.05	0	0.4987	0.5013	36.81	37.00
1B			—	—			0	0.4994	0.5006	—	—
1C			—	—			0	0.4972	0.5028	—	—
2	KCl		5.684	24.88	NaOOC		100	0.4953	0.5047	29.15	29.70
3			4.380	35.39			200	0.4937	0.5063	22.39	22.96
4			3.238	55.37			300	0.4933	0.5067	16.54	16.99
5			2.273	94.04			400	0.4897	0.5103	11.52	12.01
6			1.497	179.7			500	0.4843	0.5157	7.51	7.99
7		0.1001	4.872	18.52		0.05	0	0.7088	0.2912	35.75	14.69
8			3.852	25.55			100	0.7143	0.2857	28.49	11.39
9	KProp.		2.931	37.41	NaProp.		200	0.7216	0.2784	21.90	8.45
10			2.122	58.62			300	0.7297	0.2703	16.03	5.94
11			1.461	100.8			400	0.7374	0.2626	11.15	3.97
12			0.943	191.8			500	0.7464	0.2536	7.29	2.48
13		0.1001	4.479	19.16		0.05	0	0.7698	0.2302	35.70	10.67
14			3.498	26.44			100	0.7795	0.2205	28.23	7.99
15			2.644	38.88			200	0.7863	0.2137	21.52	5.85
16	KCapr.		1.911	61.56	NaCapr.		300	0.7930	0.2070	15.69	4.10
17			1.306	106.4			400	0.8056	0.1944	10.89	2.63
18			0.834	203.5			500	0.8166	0.1834	7.05	1.58
19		0.1001	4.222	18.58		0.015	0	0.2631	0.7369	11.50	32.21
20			3.257	25.64			100	0.2605	0.7395	8.78	24.94
21	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NI		2.415	37.60	NH <sub>4</sub> OOC		200	0.2567	0.7433	6.42	18.58
22			1.708	58.90			300	0.2538	0.7462	4.49	13.19
23			1.139	102.1			400	0.2484	0.7516	2.93	8.86
24			0.703	195.6		0.05	500	0.2394	0.7606	1.74	5.54

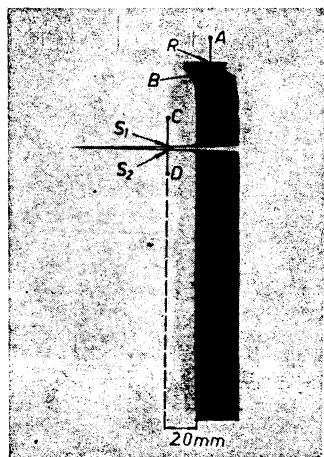


Fig. 1. Magnified reproduction of a schlieren photograph. For further explanations, see text.

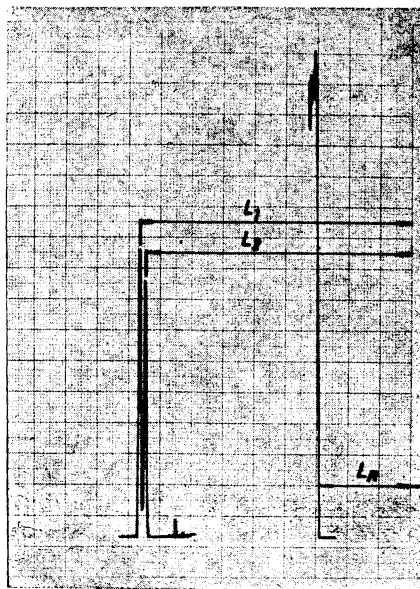


Fig. 2. Microdensitometer record of the schlieren photograph in Fig. 1. For further explanations, see text.

of the point R gave rise to an almost vertical line on the recording paper (Fig. 2). As the position of R was the same on all exposures, this vertical line could be used as a reference when determining boundary positions.

The double-peak in Fig. 2 results from recording along the line C—D, 2.0 mm from the left-hand edge of the base line. Each peak in the double-peak is due to passing of one limb of the schlieren peak (that is point S<sub>1</sub> resp. S<sub>2</sub> in Fig. 1). If the schlieren peak is symmetrical, its apex will correspond to a position (S) halfway between S<sub>1</sub> and S<sub>2</sub>. For unsymmetrical peaks the point S can still be used as the position of the schlieren peak (and the moving boundary) when determining boundary velocity, provided that the shape of the peak is constant in time. In a few runs, the peaks observed were not quite symmetrical. However, the breadth of the boundary was found to be constant within the measuring accuracy from one exposure to another, thus indicating constant peak shape in time.

The relative position of the moving boundary on the recording paper was determined for each exposure as follows. The distances L<sub>1</sub> and L<sub>2</sub> (see Fig. 2) from the double-peak to the right-hand end of the recording paper were measured, and their mean value L<sub>MY</sub> ( $= (L_1 + L_2) / 2$ ) was calculated. Then the distance L<sub>R</sub> from the reference line to the right-hand end of the recording paper was measured at a certain level (indicated by the arrow to the right in the figure). This level had to be the same for all exposures. Subtraction of L<sub>R</sub> from L<sub>MY</sub> finally gave the distance L as a measure of the boundary position with respect to the reference point R. The distances L<sub>1</sub>, L<sub>2</sub>, and L<sub>R</sub> could be measured by means of a ruler with an accuracy of  $\pm 0.1$  mm.

The distance L was plotted in a diagram *vs.* time. The resulting points falling on a straight line indicated constant boundary velocity during the run. The slope of the line, calculated according to the method of least squares, gave the velocity of the schlieren peak on the recording paper. Division by the total vertical magnification factor, *i.e.* the vertical magnification factor of the cell times the magnification factor of the microdensitometer, gave the velocity of the moving boundary in the cell.

*Total vertical magnification factor.* A metal plate with two rectangular holes of accurately known dimensions was placed in the cell stand in the plane of the middle of the cell with the shorter sides of the holes strictly horizontal. An exposure was taken, and its optical density was recorded with the microdensitometer in a direction corresponding to a vertical direction in the cell plane. The record showed four almost vertical lines due to the horizontal sides of the holes in the metal plate. By comparing distances between these lines to corresponding distances on the metal plate, the total vertical magnification factor was found to be  $2.867 \pm 0.005$ .

*Moving boundary systems.* Four different moving boundary systems were used to determine the transference numbers and mobilities reported. Compositions of the solutions used are given in Table 1. Fig. 3 is a schematic representation of the systems after passage of current. Added sucrose is regarded as part of the solvent and therefore omitted in the figure.

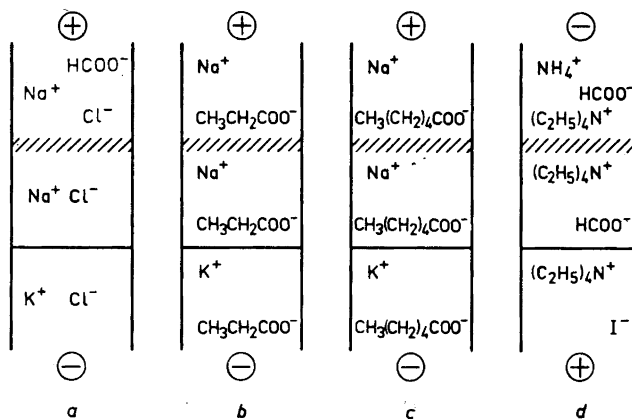


Fig. 3. Schematic representation of the moving boundary systems after passage of current. Horizontal line indicates descending boundary,  $////$  indicates concentration boundary near the initial boundary position.

To test the reproducibility and accuracy of the moving boundary experiments, three runs were carried out with the first system (Fig. 3a) at zero sucrose concentration.

In the fourth system (Fig. 3d), it was found necessary to prevent the tetraethylammonium ions from reaching the anode. Otherwise a brown precipitate was formed. On the surface of this precipitate, gas bubbles of oxygen, produced at the anode, were adsorbed, thereby displacing the whole system towards the cathode. In addition, the hydrogen ions, liberated at the anode, had to be hindered from reaching the iodide-formate boundary. Both these disturbing effects were eliminated if the upper half of the anode vessel was filled with 0.05 M sodium formate solution (no sucrose added!) instead of tetraethylammonium iodide solution.

*Preparation of solutions.* The leading solutions used were prepared in a calibrated volumetric flask at a temperature equal to the cooling bath temperature during the electrophoresis run. 500 cm<sup>3</sup> proved to be a suitable volume. About half this volume was consumed in the electrophoresis run; conductivity, viscosity, and density measurements could be made with the remaining amount of solution. If the solution in question was to contain sucrose, the desired quantity was weighed out directly in the volumetric flask on a top-loading balance before adding the electrolyte.

All but two of the salts investigated were commercial products of *pro analysi* grade; they were used without further purification. The *sucrose* was of Mallinckrodt's analytical reagent grade. The *potassium propionate* and *caproate* were not commercially available.

They had to be prepared in the laboratory by titration of a potassium hydroxide solution with propionic acid and caproic acid, respectively. 25.0 ml of a 2.00 M potassium hydroxide solution was diluted to 100 ml with conductivity water. The diluted potassium hydroxide solution was stirred with a magnetic stirrer while the actual acid was added slowly from a 5 ml syringe through a very narrow cannula. The pH of the solution was continuously measured with a Radiometer (Copenhagen) pH-meter, model TTT1c, and a glass electrode, Radiometer type GK 2021 C. As endpoint for the titration, the pH previously measured in an equally concentrated solution of the corresponding sodium salt was chosen. The titrated solutions were treated as described above.

*Conductivity measurements.* The conductivity of the leading solution was measured at 0°C with an LKB Conductivity Bridge, type 3216 B. The conductivity cell used was of the conventional type (LKB 3225 J-3). The filled cell was thermostatted in a Dewar vessel containing a mixture of crushed ice and water. The cell constant was determined as suggested by Alberty<sup>8</sup>. All resistances measured were above 1250 ohm, thus giving an accuracy better than  $\pm 1/1250$  or  $\pm 0.08\%$ .

*Viscosity measurements.* The viscosity of the leading solution at 0°C was determined in an Ubbelohde-viscometer,<sup>9</sup> a glass capillary-viscometer manufactured by Jenaer Glaswerk, Schott & Gen., Mainz, Germany. The viscometer was surrounded by a cooling mantle of glass, through which water from the cooling bath of the electrophoresis apparatus was circulated. Lowering the bath temperature to  $-0.1^\circ\text{C}$  was found to be suitable to maintain a mean temperature in the viscometer of  $0 \pm 0.05^\circ\text{C}$ . The filled viscometer was thermostatted for half an hour before starting the measurement.

The quantity primarily measured with an Ubbelohde viscometer is the time required for the meniscus of the actual liquid to move between two marks on the viscometer. According to the theory of Hagen-Poiseuille, this "running time", when corrected for the change in kinetic energy when the liquid enters and leaves the capillary (the Hagenbach-Couette correction<sup>9</sup>), is directly proportional to the kinematic viscosity of a Newtonian liquid. The proportionality constant has been determined by Schott & Genossen before delivery of the Ubbelohde-viscometer. It refers, however, to 20°C, and therefore recalibration was made in this laboratory at 0°C. The recalibration was carried out with two sucrose solutions, each holding exactly 40 % by weight. The viscosity of such a solution is given in the literature.<sup>10</sup> The values of the resulting viscometer constants agreed within 0.06 %.

In order to transfer kinematic viscosity to absolute viscosity, the viscosity measurements had to be accompanied by density measurements.

*Density measurements.* The normally used pycnometer was replaced by a volumetric flask (volume 50 ml) for the following reason. As the pycnometer had to be filled at 0°C and weighed at room temperature, a portion of the liquid flowed out through the capillary due to thermal expansion. In a volumetric flask, there is space for such expansion. Of course, densities cannot be determined with the same high accuracy in volumetric flasks as in pycnometers. However, triple measurements on a sucrose solution showed the reproducibility to be  $\pm 0.035\%$ , a satisfactory figure in this connection. The volumetric flask was calibrated at 0°C, using distilled water as liquid and density value from the literature.<sup>11</sup>

## EVALUATION OF TRANSFERENCE NUMBERS AND MOBILITIES FROM BOUNDARY VELOCITIES

For an arbitrary ion  $j$ , present only in the solution ahead of a moving boundary (the leading solution), the moving boundary equation<sup>12,13</sup> can be expressed as follows:

$$T_j = c_j z_j F v / i \quad (1)$$

where  $T$  denotes transference number,  $c$  molar concentration and  $z$  valence of the  $j$  ion,  $F$  denotes the Faraday constant,  $v$  boundary velocity, and  $i$  current density. Valence  $z$  and boundary velocity  $v$  are signed quantities, the latter being positive for boundaries migrating in the direction of the

current. All other quantities are positive (unless  $z$  and  $v$  have opposite signs, which does not occur in this investigation).

The transference number  $T_j$  as obtained from eqn. (1) can be used for calculation of the mobility of the  $j$  ion,  $u_j$ , provided that the conductivity  $\kappa$  of the leading solution is measured. This is evident from the general equation

$$T_j \kappa = F c_j z_j u_j \quad (2)$$

which follows directly from the well-known relations:

$$\kappa = F \sum_j c_j z_j u_j \quad (3)$$

$$\sum_j T_j = 1 \quad (4)$$

The mobility is positive for cathodically, negative for anodically migrating ions.

In the present work, the leading solution contained only two species of ions (except those due to the ionization of water). For one of them, the transference number was determined by means of eqn. (1). Eqn. (4) then gave the transference number of the other ion species. The transference numbers thus obtained were inserted into eqn. (2) together with the corresponding concentrations and the conductivity of the solution as measured at 0°C. The resulting mobilities could be regarded as valid at 0°C (*cf.* Tiselius<sup>14</sup> and Alberty<sup>8</sup>). No correction was carried out on the boundary velocity for the volume changes at the electrodes; thus the reported transference numbers and mobilities refer to the apparatus as the plane of reference.

## RESULTS AND DISCUSSION

The transference numbers and mobilities obtained are collected in Table 1 together with, *inter alia*, conductivity and viscosity values of the leading solutions used.

The results of experiments 1A–1C indicate that the uncertainty in the transference numbers reported here (about 0.2 %) is somewhat greater than that in the transference numbers determined by Longworth<sup>12</sup> with a similar schlieren-photographic technique. Part of this greater uncertainty is probably due to the fact that gassing electrodes were used, meaning that both ends of the apparatus had to be open to the atmosphere during the experiment. Longworth's moving boundary runs were (as is usual) performed with non-gassing electrodes and with one side of the apparatus kept closed.

The mean value of the cation transference numbers obtained in experiments 1A–1C is 0.498. At the same temperature, 0.5°C, Longworth<sup>15</sup> determined a value of 0.496. The value 0.496 is also obtained on extrapolating the very precise data of Allgood, Le Roy, and Gordon<sup>16</sup> from 15 to 0°C, using an equation of Owen.<sup>17</sup> Thus in addition to the accidental error there seems to be a systematic deviation of about +0.5 % in the transference numbers determined with the first system, *i.e.* experiments 1–6. A possible cause of this is the fact that the transference number values 0.498 and 0.496 refer to different planes of reference, the apparatus and the solvent, respectively.

The transference numbers have been plotted *vs.* the absolute viscosity in Fig. 4. It is apparent from the figure that when the absolute viscosity in a water solution of either of the 1:1-electrolytes investigated is increased by the addition of sucrose, the higher transference number of the actual

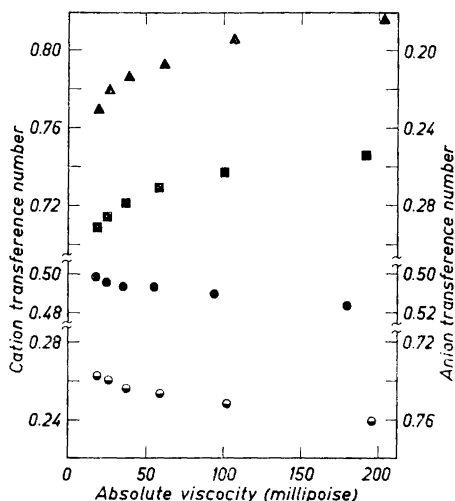


Fig. 4. Transference numbers at 0°C in 0.1 M aqueous sucrose solutions of potassium chloride (●), potassium propionate (■), potassium caproate (▲), and tetraethylammonium iodide (⊖) *vs.* absolute viscosity.

electrolyte increases, whereas the lower one decreases. For the three potassium salts, the effect of added sucrose is greater the more distant from 0.5 a transference number is in sucrose-free solution. These transference number shifts are easily understood by inspecting Tables 1 and 2 and by considering that transference numbers are measures of the relative mobilities of the ionic species constituting an electrolyte. As can be seen from Table 1, the mobilities of all the ions studied were reduced by the addition of sucrose. Different ions were affected to a different extent by the non-electrolyte. This is evident from Table 2, which shows the relative ion mobilities  $R$  in the solutions investigated. The quantity  $R$  is the ratio of the mobility in the mixed solvent to its value in water. Furthermore, for the electrolytes investigated the slower one of the ions of a given electrolyte is hindered more by the addition of sucrose than the faster one. Thus in 0.1 M potassium propionate, *e.g.*, the propionate ion gets an  $R$ -value of 0.168 when 500 g/l sucrose is added, whereas the corresponding  $R$ -value for the potassium ion is 0.204.

The shift of the transference numbers of 0.1 M tetraethylammonium iodide with the sucrose concentration is not as large as could be expected. Thus the iodide shows smaller transference number shifts than the propionate. Although its transference number values in sucrose-free solution are more distant from 0.5 than those of the propionate. A possible explanation of this anomaly is given on p. 2002.

It is generally accepted that the motion of an ion in solution under influence of a constant and not too strong electric field is limited by the viscous drag of



Table 2. Relative ion mobilities in aqueous sucrose solutions at 0°C.

$C_S$ \ E	KCl		KOOCH <sub>2</sub> CH <sub>3</sub>		KOO(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>		(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NI	
	$R_+$	$R_-$	$R_+$	$R_-$	$R_+$	$R_-$	$R_+$	$R_-$
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
100	0.792	0.803	0.797	0.775	0.791	0.749	0.763	0.774
200	0.608	0.621	0.613	0.575	0.603	0.548	0.558	0.577
300	0.449	0.459	0.448	0.404	0.439	0.384	0.390	0.410
400	0.313	0.325	0.312	0.270	0.305	0.246	0.255	0.275
500	0.204	0.216	0.204	0.168	0.197	0.148	0.150	0.172
$\frac{\eta_0}{\eta_{500}}$	0.099		0.097		0.094		0.095	

E is the actual electrolyte.

$C_S$  is the concentration of sucrose in g/l.

$R$  is the ratio of the mobility in the mixed solvent to its value in water. + and - indicate cation and anion, respectively.

$\eta_0$  is the viscosity at the sucrose concentration 0 g/l,

$\eta_{500}$  is the viscosity at the sucrose concentration 500 g/l.

The ratio  $\eta_0/\eta_{500}$  is called the relative fluidity at the sucrose concentration 500 g/l.

the solvent. The viscous (frictional) force on the ion balances the force of the electric field. If the well-known law of G. G. Stokes<sup>18</sup> is applied to the motion of an ion, the radius of which is assumed independent of the medium, eqn. (5) results.\*

$$|u| \cdot \eta = \text{const.} \quad (5)$$

$u$  is the mobility of the ion,  $\eta$  the viscosity of the medium.

If the viscous effect on the ionic motion were of the simple kind demanded by eqn. (5) (or Stokes' law), the mobility of an ion should be inversely proportional to the absolute viscosity. This means that a plot of  $u$  vs.  $1/\eta$  should give a straight line through the origin. As may be seen from Fig. 5, none of the ions studied shows a linear variation of the mobility with the reciprocal viscosity. In no case is the mobility reduced to the extent that the increase in viscosity would demand, that is, the relative mobility,  $R$ , is always higher than the relative fluidity (cf. Table 2). However, there seems to be a fair correlation between the size of an ion (allowing for probable hydration) and the degree of validity of eqn. (5) for this ion. Thus eqn. (5) is more closely approached by the large caproate and tetraethylammonium ions than by the small chloride ion. Steel, Stokes, and Stokes<sup>4</sup> have given a qualitative justification for this in the following words: "Very large ions can be expected to move in accordance with Stokes' law, shouldering aside both water and added non-electrolyte molecules in their progress; small ones, on the other hand, will treat the non-electrolyte molecules as obstacles to be avoided, and will

\* In the special case of infinite dilution, eqn. (5) expresses the so-called Walden's rule.<sup>19</sup>

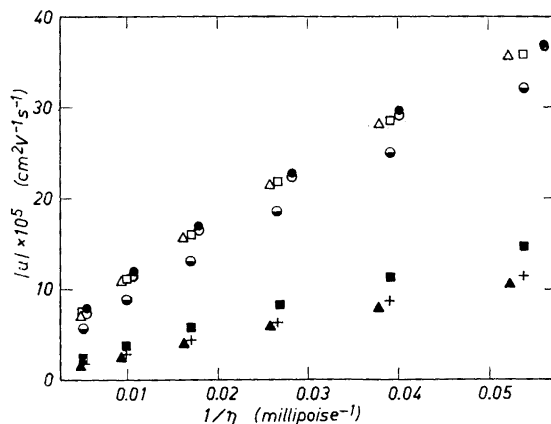


Fig. 5. Ionic mobilities at 0°C in 0.1 M aqueous sucrose solutions of potassium chloride ( $\circ$   $\text{K}^+$ ,  $\bullet$   $\text{Cl}^-$ ), potassium propionate ( $\square$   $\text{K}^+$ ,  $\blacksquare$   $\text{CH}_3\text{CH}_2\text{COO}^-$ ), potassium caproate ( $\triangle$   $\text{K}^+$ ,  $\blacktriangle$   $\text{CH}_3(\text{CH}_2)_4\text{COO}^-$ ), and tetraethylammonium iodide ( $+$   $(\text{C}_2\text{H}_5)_4\text{N}^+$ ,  $\ominus$   $\text{I}^-$ ) vs. reciprocal absolute viscosity.

move essentially through a medium of water molecules only." According to Steel, Stokes, and Stokes, the increased resistance which the latter ions experience is best regarded as due to "the increase in the length of their paths in avoiding the obstacles".

Eqn. (5) implies that there does not occur any specific interaction between the ion and the added non-electrolyte. The results reported here, however, and those of Hale and De Vries<sup>20</sup> as well, indicate a considerable interaction between iodide ion and added non-electrolyte, if the latter is sucrose, maltose, or ethyl acetate. As mentioned earlier (p. 2000), the transference numbers of 0.1 M tetraethylammonium iodide show an anomalous viscosity dependence. This can be a consequence of either an unexpectedly small retardation of the tetraethylammonium ion or an unexpectedly large retardation of the iodide ion. An inspection of the  $R$ -values (Table 2) and the mobility values at zero sucrose concentration (Table 1) indicates that the  $R$ -values of the tetraethylammonium ion are plausible with respect to its mobility in sucrose-free solution. The iodide ion, on the other hand, is retarded almost as much as the propionate ion, though their mobility values in sucrose-free solution are  $32.21 \times 10^{-5}$  and  $14.69 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. A reasonable explanation of the low  $R$ -values of the iodide ion is that this ion to a certain extent is associated with the non-electrolyte.

When the sucrose is exchanged for maltose, the association becomes so strong that it causes the transference number of the iodide ion in tetraethylammonium iodide solution to decrease with increasing viscosity. This is apparent from the results of Hale and De Vries.<sup>20</sup> A decrease is also found for the tetramethylammonium iodide. The effect is still more pronounced with ethyl acetate as the non-electrolyte. Tetrapropylammonium iodide solutions, on the other hand, show an increase in the transference number of the iodide ion when

maltose is added. Here the cation obviously is large enough to be retarded more than the iodide ion even if the latter is associated to a considerable extent with non-electrolyte molecules.

From the foregoing it seems reasonable to conclude that the magnitude of the viscosity effect on the transference numbers of a 1:1-electrolyte in the main depends on the dimensional ratio of its (hydrated) ions, provided that possible specific interaction between the viscosity-increasing solute and the ions can be neglected. This means that just as the viscosity dependence of the transference numbers is low for the two small ions of potassium chloride, it could be expected to be low for the two large ions of tetraethylammonium caproate. Because of experimental difficulties, no measurements have been done to prove this.

The mobility values obtained in the sucrose-free solutions are of course lower than the corresponding values at infinite dilution that are given in the literature. It is surprising, however, that the iodide ion, being about 1 % faster than the chloride ion at infinite dilution, is found to be about 13 % slower than this ion in the 0.1 M solution used here. Certainly a 0.1 M tetraethylammonium iodide solution has a higher viscosity than an equally concentrated potassium chloride solution, but the difference (~4 %) is too small to be responsible for the whole effect observed. One possibility is a so-called structure-enforced ion-pair formation<sup>21,22</sup> between a fraction of the iodide ions and the tetraethylammonium ions.

The results obtained explain the experimentally observed phenomena mentioned in the introduction. In sodium barbital buffers, the barbital anion is considerably larger than the sodium ion. Thus its mobility is the one most affected by the change in the sucrose concentration at the level of the density shelf. Consequently, the cationic transference number increases going downwards the shelf. This means, if the current is assumed to flow downwards (as in ascending electrophoresis of negative proteins), that the amount of sodium ions leaving the level of the shelf is larger than the amount arriving. The same is valid for the barbital anions, since they move upwards and their transference numbers increase in this direction. Thus the buffer concentration decreases at the level of the density shelf. This leads to excessive heating and convection in this part of the column.

It is easily perceived that a reversal of the current direction gives rise to an accumulation of salt at the density shelf. This explains why convection was not observed by Sorof *et al.*<sup>1</sup> in descending zonal density gradient electrophoresis.

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