

## DIFFUSION COEFFICIENT OF POTASSIUM CHLORATE IN WATER AT 25°C

Václav VACEK<sup>a</sup> and Vladislav HANČIL<sup>b</sup>

<sup>a</sup> *Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 160 00 Prague 6 and*

<sup>b</sup> *Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague 6*

Received April 27th, 1983

The concentration dependence of diffusion coefficient of potassium chlorate in water has been measured at 25°C using the Taylor technique. The results have been treated according to the extended Hartley-Crank interpretation of the concentration dependence of diffusion coefficient and compared with diffusivities published for lithium and sodium chlorates.

In interpreting many processes on a quantitative basis, diffusivities of the substances involved are the basic component of the starting information on the system under study. Although many techniques have been developed for measuring diffusion coefficients, very little accurate data on diffusivities are available (see, *e.g.*, reviews of the present state of knowledge on diffusion in electrolyte solutions in refs<sup>1-7</sup>). Potassium chlorate attracts interest in regard to diffusivity determination because, among other reasons, kinetic studies have been made on recrystallization of this salt from aqueous solution<sup>8,9</sup>, and diffusivities of lithium and sodium chlorates have been published<sup>10</sup>.

As a cooperative effort, measurements of the diffusion coefficient of potassium chlorate in water have been made by the diaphragm-cell method at the Department of Physical Chemistry, Institute of Chemical Technology, Prague<sup>11</sup>, and by the Taylor technique of trace injection dispersion in laminar flow of liquid in pipes using an apparatus developed by Hančil, Rod and Rosenbaum<sup>12</sup>. The latter method has been used by a number of investigators to measure the diffusion coefficient<sup>13-28</sup>. Experimentally, one follows a quantity  $z$  proportional to concentration or a suitable concentration difference, depending on the type of the analytical concentration sensor employed. For highly sensitive sensors, it has proved desirable<sup>12,19</sup> to correct the response to the initial pulse for a linear drift of the null signal of the sensor. The final theoretical form for the response to a concentration pulse is then

$$z(t) = B_4 t^{-1/2} \exp[-12B_1(t - B_2)^2/B_3t] + B_5 t + B_6, \quad (1)$$

where  $B_1 = D$ ,  $B_2 = L/V$ ,  $B_3 = d^2/4$  and  $B_4$  involves (in addition to quantities characterizing the amount and concentration of the sample injected into a stream of the carrier liquid) a constant characterizing the proportionality between the concentration and the final amplitude of the recorded response.

Assuming precise measurement of time, a constant variance of the quantity  $z(t)$ , uncorrelated errors and their normal distribution with zero mean, the method of maximum likelihood can be used to estimate the required parameter  $B_1$  from Eq. (1) on the basis of experimentally determined response  $z(t)$  (refs<sup>12,19</sup>). Alternatively, it is possible to evaluate the diffusivity by the method of moments which, in principle, may be equally accurate<sup>19</sup>.

### EXPERIMENTAL

The procedure and the apparatus have been described in detail elsewhere<sup>12</sup>. A new feature of the apparatus was a stainless steel capillary of length  $L = 2.80$  m and 1.5 mm inner diameter. About 5 mm<sup>3</sup> of sample was admitted to the stream of a carrier solution of a chosen concentration by throwing a six-way tap fitted with a sampling loop. The concentration of the sample was by 1 to 2% lower than that of the carrier solution. The resulting concentration profile was determined by means of a differential refractometer (Knauer) placed at the end of the stainless steel capillary thermostatted at  $25.0 \pm 0.05^\circ\text{C}$ . The reference cell of the refractometer always contained the carrier solution. The main capillary was connected with the inner cell of the refractometer through a 30 cm steel capillary of 0.2 mm inner diameter. The cell volume was *c.* 8 mm<sup>3</sup>. The evaluation was made on the assumption that this connection affected only the so-called effective radius of the capillary. This radius, which represents the apparatus constant, can be determined experimentally by measuring the response curve for a system of known diffusivity. As previously<sup>12</sup>, the calibration was made using a potassium chloride solution containing 1.8 wt.% KCl (in the vicinity of this concentration, the diffusivity of KCl in water,  $1.830 \cdot 10^{-9}$  m<sup>2</sup>/s, is little concentration dependent, as indicated by a plot of  $D$  against concentration which shows a flat minimum in this region<sup>26,27</sup>). The volume flow rate of the carrier solution was kept con-

TABLE I  
Measured values of the differential diffusion coefficient of potassium chlorate in water at 25°C

$m$	$D_m \cdot 10^9, \text{m}^2/\text{s}^a$	$c$	$D_c \cdot 10^9, \text{m}^2/\text{s}^b$	$c$	$D_c \cdot 10^9, \text{m}^2/\text{s}^b$
0	1.829	0.049	1.743	0.301	1.628
0.06	1.625	0.097	1.649	0.355	1.625
0.12	1.57	0.15	1.654	0.408	1.622
0.24	1.50	0.200	1.629	0.455	1.592
0.535	1.38	0.248	1.625	0.501	1.543

<sup>a</sup> Results of this work; <sup>b</sup> results of Kozlová<sup>11</sup>.

stant at  $20 \pm 1$  ml/h by means of a linear proportioner (Infumat, MLR); the corresponding average flow rate in the capillary was 0.3144 cm/s.

*Potassium chloride and potassium chlorate* of analytical grade were purified by triple fractional recrystallization from water redistilled in a quartz apparatus. Before use both salts were dried in a desiccator over  $P_2O_5$  for three weeks. The points of the response curve were recorded equidistantly at 5 and 16 s intervals, and were evaluated by numerical optimization using Marquardt's algorithm<sup>12</sup>. Four to six values were measured for each of the four concentration levels chosen; averages of the values are listed in Table I, along with data obtained by Kozlová<sup>11</sup>. A slight difference in the concentration dependence for the two sets of measurements can be seen in Fig. 1; the bar on each experimental point indicates the difference between the maximum and minimum measured values in the case of our data and an estimate of standard deviation for data of Kozlová<sup>11</sup>.

Other quantitative characteristics of the measurements and the conditions for applicability of mathematical relations used in evaluating the experimental results are summarized in Appendix I. Physicochemical properties of the system are listed in Table II.

## RESULTS AND DISCUSSION

A phenomenological model of the concentration dependence of the diffusion coefficient for electrolytes has been described in the literature: Hartley's and Crank's model of the concentration dependence of diffusivity for binary systems has been extended by Agar to completely dissociated electrolytes (cited according to Robinson

TABLE II

Values of physicochemical properties of aqueous solutions of  $KClO_3$  at 25°C used in calculating the concentration dependence of diffusivity

$c^a$	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5
$\alpha(c)$	0.978	0.969	0.952	0.933	0.910	0.866	0.827	0.780	0.703
$n_w/n_s^a$	4.096	2.048	1.024	512	128	32	8		
$\alpha$	1.000	0.977	0.972	0.959	0.932	0.875	0.797		
$m^b$	0.1	0.2	0.3	0.4	0.5	0.6	0.7		
$\gamma_{\pm}$	0.749	0.681	0.635	0.599	0.568	0.541	0.518		
$\phi$	0.913	0.887	0.867	0.849	0.832	0.816	0.802		
$c^c$	0.01054	0.02114	0.08675	0.25875	0.52516	0.05	0.10	0.333	
$\eta/\eta^0$	0.99979	0.99952	0.99810	0.99514	0.99242	0.99957	0.9985	0.994	
$p^a$	1	2	3	4	7.999		$m^a$ 0.5		
$q$	1.0034	1.0099	1.0165	1.0233	1.0484		$q^{(m)}$ 1.0338		

<sup>a</sup> Ref. <sup>37</sup>; <sup>b</sup> ref. <sup>5</sup>; <sup>c</sup> ref. <sup>4</sup>.

and Stokes<sup>5</sup>; for the derivation, see refs<sup>5,6,29,30</sup>, and for discussion of the final form, refs<sup>1,7,10</sup>), and subsequently by Wishaw and Stokes<sup>31</sup> to partly associated electrolytes. The final form for 1 : 1 electrolytes

$$D(m) = [\alpha(D^0 + A_1 + A_2) + 2(1 - \alpha) D_{12}] W(m) \cdot \left[ \left( 1 - \frac{M_w}{10^3} hm \right) \left( 1 + \frac{mM_w}{10^3} \left[ \frac{2D_w}{D^0} - h \right] \right) \right] \frac{\eta^0}{\eta} \quad (2)$$

is usually considered in the simplified form<sup>6,10</sup>

$$D(m) = [\alpha(D^0 + A_1 + A_2) + 2(1 - \alpha) D_{12}] W \cdot \left[ \left( 1 + \frac{2M_w}{1000} m [D_w/D^0 - h] \right) \right] \frac{\eta^0}{\eta} \quad (3)$$

To a first approximation, the diffusion coefficient  $D_{12}$  of an ion pair may be estimated on the basis of simple geometrical and hydrodynamic considerations (see, *e.g.*, the treatment used by Wishaw and Stokes<sup>31</sup> to estimate  $D_{12}$  for ammonium nitrate). Alternatively, it may be evaluated as the only empirical parameter by optimization in fitting experimental values of the function  $D(m)$  to a theoretical relation of the type of Eq. (3).

For complete dissociation of an electrolyte, in which case  $\alpha = 1$ , experimental data on  $D_c(m)$  can be used to determine the hydration number from the slope of a linear plot according to the relation

$$f_1(D) = 1 + 0.036m(D_w/D^0 - h), \quad (4)$$

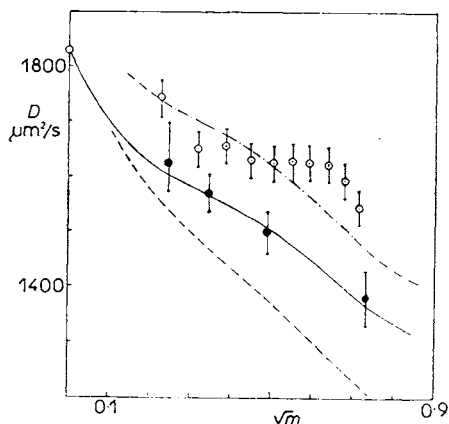


FIG. 1

Concentration dependence of diffusion coefficient of potassium chlorate in water at 25°C. Experimental points: ○ theoretical limiting values of  $D^0$ ; ● results of this work; ○ results of Kozlová and Samohýl. Calculated lines (Eq.3): - - - -  $h = 0, \alpha = 1$ ; ———  $h = 0, D_{12} = 887 \mu\text{m}^2/\text{s}$ ; ·····  $h = 0, D_{12} = 950 \mu\text{m}^2/\text{s}$

where

$$f_1(D) = D_e / [(D^0 + \Delta_1 + \Delta_2) W], \quad (5)$$

or a viscosity-corrected relation  $f_2(D)$ ,

$$f_2 = f_1 \eta / \eta^0. \quad (6)$$

The hydration numbers  $h_1$  and  $h_2$  evaluated from the functions  $f_1$  and  $f_2$  may differ significantly, depending on the nature of the function  $\eta^0/\eta$ . Using Eqs (4) to (6), Campbell and Oliver<sup>10</sup> have evaluated experimental data on  $D_e(m)$  for sodium and lithium chlorates (Table III). A check on their procedure has shown a negative value of  $h_2$  for  $\text{NaClO}_3$  (for details, see the second part of Table III). The concept of negative hydration is synonymous to increased mobility of solvent molecules in the vicinity of some ions (the so-called structure breakers), and is still a subject of interest (see, *e.g.*, a recent discussion presented by Geiger<sup>35</sup>). Campbell and Oliver<sup>10</sup> have noted that the positive values obtained by them for the hydration number  $h_2$  represent the lower limits of the hydration number estimates (*i.e.*, they include the influence of the secondary hydration layers, whereas the  $h_1$  values likely reflect the nature of the first hydration shell only). A definite conclusion that may be drawn from their results is that the sodium salt is less hydrated than the lithium salt<sup>10</sup>. From our data on the concentration dependence of diffusivity  $D_e(m)$  for  $\text{KClO}_3$  we first evaluated the hydration number  $h$  from Eqs (4) and (5), *i.e.* on the assumption that  $\alpha = 1$ . The viscosity correction  $\eta/\eta^0(m)$  is negligible for  $\text{KClO}_3$  (Table II or IV) and the  $h_1$  and  $h_2$  values almost coincide. The data for the concentration dependences of the required physicochemical properties are summarized in Table II (see also Table V). The calculations of  $D^0$  and of the electrophoretic terms  $\Delta_1$  and  $\Delta_2$  are described in detail in Appendix II. The position of the line representing the concentration dependence of diffusivity is seen from Fig. 2 to depend strongly on the value of  $h$ . The hydration number that leads to a satisfactory fit of the theoretical line corresponding to Eq. (3) for  $\alpha = 1$  is negative,  $h = -8.6$ . In the same situation, when interpretation of the  $f(D)$  dependence for  $\text{NH}_4\text{NO}_3$  also led to negative values of  $h$ , Wishaw and Stokes<sup>31</sup> introduced the assumption of zero hydration of ions,  $h = 0$ . According to their reasoning, the increased diffusivity measured may be explained on the basis of partial ion association by assuming that the associated species moves effectively faster than in the form of two separate particles (even when its diffusivity is smaller than that for the dissociated electrolyte). In further calculations of the concentration dependence we used experimentally determined degrees of association  $\alpha(m)$  (Tables II and V) and also introduced  $h = 0$ . The assumption of zero hydration receives some support from comparison of limiting diffusivities  $D^0$  for the other alkali metal salts (and also the analogous silver and ammonium

TABLE III

Differential diffusion coefficients of lithium and sodium chlorates in water at 25°C measured and calculated by Campbell and Oliver<sup>10</sup>

<i>m</i>	$D_e$	$D_1$	$D_2$	<i>W</i>	$\eta/\eta^0$	$f_1$	$f_2$
LiClO <sub>3</sub>							
0	1.288	1.288	1.288	1.000	1.000	1.000	1.000
0.0929	1.212	1.202	1.199	0.937	1.012	0.994	1.006
0.201	1.205	1.215	1.210	0.961	1.025	0.962	0.986
0.354	1.218	1.213	1.207	0.982	1.042	0.952	0.992
0.729	1.251	1.248	1.239	1.074	1.090	0.895	0.975
1.658	1.302	1.298	1.299	1.325	1.220	0.757	0.924
2.570	1.341	1.200	1.251	1.495	1.360	0.693	0.942
8.575	1.239	neg	0.767	2.478	2.700	0.389	1.049
19.02	0.578	neg	0.704	2.265	8.20	0.199	1.632
33.48	0.143	neg	0.036	1.251	28.9	0.089	2.581
35.01	0.120	neg	neg	1.308	32.6	0.072	2.337
NaClO <sub>3</sub>							
0	1.502	1.502	1.502	1.000	1.000	1.000	1.000
0.126	1.365	1.384	1.387	0.905	1.008	0.980	0.988
0.356	1.358	1.340	1.347	0.877	1.024	0.998	1.022
0.537	1.341	1.324	1.328	0.870	1.040	0.990	1.030
0.727	1.325	1.308	1.310	0.866	1.058	0.981	1.038
1.207	1.296	1.288	1.285	0.870	1.104	0.954	1.153
1.877	1.270	1.260	1.246	0.878	1.175	0.927	1.089
3.750	1.667	1.219	1.123	0.931	1.470	0.805	1.183
5.699	1.041	1.138	0.957	0.966	1.896	0.693	1.134
5.843	1.036	1.130	0.945	0.967	1.932	0.689	1.331
7.400	0.865	1.041	0.806	0.978	2.396	0.570	1.366
8.594	0.690	0.985	0.718	1.000	2.840	0.445	1.264

The values of measured ( $D_e$ ) and calculated ( $D_1, D_2$ ) diffusivities are quoted in  $10^{-9}$  m<sup>2</sup>/s.  $D_1 = (D^0 + A_1 + A_2) W \{1 + 0.036 m [D_w/D^0 - h]\}$ ;  $D_2 = (D^0 + A_1 + A_2) W \{1 + 0.036 m [D_w/D^0 - h]\} \eta^0/\eta$ ;  $W = 1 + m d \ln \gamma_{\pm}/dm$ ;  $f_1 = D_e/[(D^0 + A_1 + A_2) W]$ ;  $f_2 = f_1 \eta/\eta^0$ . Hydration numbers  $h$  in calculating  $D_1$  were  $h = 6.0$  for LiClO<sub>3</sub> and  $h = 28$  for NaClO<sub>3</sub>, and in calculating  $D_2$ ,  $h = 3.2$  for LiClO<sub>3</sub> and  $h = 0.6$  for NaClO<sub>3</sub> (see ref.<sup>10</sup>, Table IV). Slopes of linear plots based on Eqs (4) and (6) (denoted by  $\beta_1$  and  $\beta_2$ , respectively) and the corresponding hydration numbers  $h_1$  and  $h_2$ , as read by us from Figs 2 and 3 of the work of Campbell and Oliver<sup>10</sup>:  $h_1 = (D_w/D^0) - \beta_1/0.036$ ; for LiClO<sub>3</sub>:  $\beta_1 = -0.1491$ ,  $\beta_2 = -0.0525$ ,  $\beta_1/0.036 = -4.14$ ,  $\beta_2/0.036 = -1.458$ ,  $D_w/D^0 = 1.895$ ,  $h_1 = 6.035$ ,  $h_2 = 3.353$ ; for NaClO<sub>3</sub>:  $\beta_1 = -0.0925$ ,  $\beta_2 = +0.08735$ ,  $\beta_1/0.036 = -2.57$ ,  $\beta_2/0.036 = +2.428$ ,  $D_w/D^0 = 1.626$ ,  $h_1 = 4.196$ ,  $h_2 = -0.802$ . From Fig. 2 of ref.<sup>10</sup> it is obvious that  $\beta_1 \approx -\beta_2$ ; Eq. (9) shows that  $\beta > 0$  only for non-negative  $h < D_w/D^0$  (for non-negative values of  $h$ , the slope takes the highest value at  $h = 0$ ).

uni-univalent salts), see Table VI. Regardless of the nature of the anion, the  $D^0$  values for the lithium, sodium and potassium salts always increase in pronounced

TABLE IV

Differential diffusion coefficients of potassium chlorate in water at 25°C evaluated in this work, and parameters used in the calculations

$m$	$D$	$D^0 + \Delta_1 + \Delta_2$	$D_a$	$W$	$\eta/\eta^0$	$D_{na}$	$f$
0.1	1.592	1.683	1.781	0.879	0.998	1.490	1.812
0.15	1.552	1.661	1.784	0.861	0.997	1.445	1.803
0.2	1.528	1.645	1.786	0.844	0.996	1.407	1.811
0.25	1.504	1.632	1.788	0.827	0.995	1.373	1.818
0.3	1.479	1.621	1.788	0.811	0.995	1.340	1.824
0.35	1.453	1.611	1.789	0.795	0.994	1.309	1.827
0.4	1.428	1.602	1.788	0.779	0.994	1.280	1.833
0.45	1.403	1.595	1.787	0.764	0.993	1.253	1.836
0.5	1.381	1.588	1.786	0.749	0.993	1.228	1.845
0.55	1.360	1.582	1.785	0.737	0.992	1.206	1.846
0.6	1.343	1.576	1.783	0.726	0.992	1.187	1.850

The diffusivities are quoted in  $10^{-9} \text{ m}^2/\text{s}$ .  $D_a = \alpha(D^0 + \Delta_1 + \Delta_2) + 2(1 - \alpha)D_{12}$ ;  $W = 1 + d \ln \gamma_{\pm} / d \ln m = \phi + d\phi/d \ln m$ ;  $D = D_a W H \eta^0 / \eta$ ;  $H = 1 + 2mM_w(D_w/D^0 - h)/10^3$ ;  $D_{na} = (D^0 + \Delta_1 + \Delta_2) W H \eta^0 / \eta$ ;  $f = D/W$ . For  $m \in (0.1, 0.6)$ ,  $1.004 < H < 1.029$ . Values of constants used in the calculations<sup>5</sup>:  $RT/F^2 = 2.6612 \cdot 10^{-7} \Omega \text{ mol s}^{-1}$ ;  $\alpha = (8Ne^2 I/10^3 kT)^{1/2} = 0.3291 \sqrt{c}$ ;  $M = 122.549$ ;  $r_{K^+} = 1.33 \cdot 10^{-10} \text{ m}$ ;  $r_{ClO_3^-} = 2.88 \cdot 10^{-10} \text{ m}$ ;  $a = r_{K^+} + r_{ClO_3^-}$ ;  $M_w = 18.0153$ ;  $\eta^0 = 0.8903 \text{ cP}$ ;  $a = 4.21 \cdot 10^{-10} \text{ m}$ ;  $\lambda_1^0 = \lambda^0(K^+) = 73.5 \cdot 10^{-4} \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ ;  $\lambda_2^0 = \lambda_{ClO_3^-} = 64.6 \text{ cm}^2 \cdot 10^{-4} \Omega^{-1} \text{ mol}^{-1}$ .

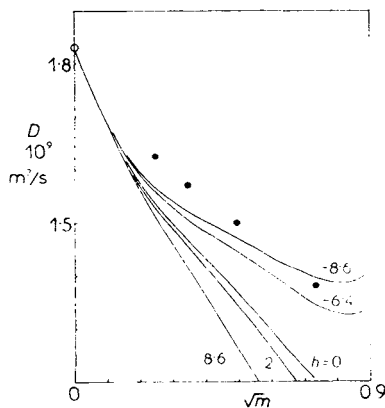


FIG. 2

Illustration of sensitivity of the concentration dependence of diffusivity of  $KClO_3$  in water to the value of hydration number  $h$  according to Eq. (3) with  $\alpha = 1$

steps with increase in the atomic number of the cation. The rubidium and cesium salts, on the other hand, show only slight increases in diffusivity relative to potassium salts. If the differences in diffusivity are due mainly to the degree of hydration it may be concluded that the  $K^+$ ,  $Rb^+$  and  $Cs^+$  ions are hydrated to approximately the same extent. Assuming that the degree of hydration decreases and that a negative hydration number represents a physically unreal situation<sup>31,33-35</sup>, we may take it that starting from potassium,  $h = 0$ . It should be pointed out, however, that other

TABLE V

Coefficients of polynomials of the form  $f(x) = \sum_{i=1}^s a_i x^{(i-1)/2}$ ,  $0.1 < m < 0.7$ , representing data for various properties of aqueous solutions of  $KClO_3$  at 25°C. The density of aqueous solution of  $KClO_3$  was expressed as  $\rho(p) = 0.9972 + 0.0064p$  or in the equivalent form  $\rho(m) = 0.9972 + 0.64m/(m + 1000/M)$ . The conversion from the molality to molarity scale was made using the relation  $c(m) = \rho(m)m/(1 + mM/1000)$

Property	$x$	$s$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	(%)
$\alpha$	$c$	4	1.0014	-0.7508	0.75708	-0.41299	—	0.09
$\eta/\eta^0$	$m$	3	1.0008	-0.00875	-0.00408	—	—	—
$\phi$	$m$	4	0.96978	-0.17172	-0.02027	-0.01742	—	0.06
$\gamma_{\pm}$	$m$	4	0.9572	-0.7829	0.44427	-0.16304	—	0.1
$W$	$m$	4	0.8391	0.50697	-1.4615	0.8007	—	0.17
$W$	$m$	5	1.0337	-1.0111	2.770175	-4.2269	2.16033	0.01

TABLE VI

Limiting diffusion coefficients of aqueous solutions of some alkali metal, silver and ammonium salts at 25°C (in  $10^{-9} \text{ m}^2/\text{s}$ ). The values were obtained from the Nernst equation  $D^0 = (RT/F^2) \cdot (\nu_1 + \nu_2) \lambda_1^0 \lambda_2^0 / [\nu_1 |z_1| (\lambda_1 + \lambda_2)]$  using limiting equivalent conductivities given by Robinson and Stokes<sup>5</sup>

Ion	$F^-$	$Cl^-$	$Br^-$	$I^-$	$NO_3^-$	$ClO_3^-$	$IO_3^-$	$ClO_4^-$	$IO_4^-$	$OH^-$	$SO_4^{2-}$	$CO_3^{2-}$
$Li^+$	1.212	1.366	1.377	1.369	1.336	1.288	1.053	1.308	1.204	1.72	1.041	0.991
$Na^+$	1.400	1.610	1.625	1.614	1.568	1.501	1.193	1.529	1.390	2.13	1.230	1.611
$K^+$	1.681	1.993	2.016	1.999	1.929	1.830	1.391	1.871	1.666	2.86	1.529	1.424
$Rb^+$	1.722	2.051	2.075	2.058	1.983	1.879	1.419	1.992	1.707	2.97	1.575	1.463
$Cs^+$	1.717	2.044	2.068	2.050	1.986	1.873	1.415	1.915	1.702	2.96	1.569	1.458
$Ag^+$	1.556	1.819	1.838	1.825	1.765	1.682	1.304	1.717	1.543	2.51	1.393	1.305
$NH_4^+$	1.682	1.994	2.016	2.000	1.929	1.831	1.391	1.871	1.667	2.86	1.530	1.424



considerations lead to a markedly higher estimate of the radius of hydrated potassium ion compared with the crystal and Stokes ionic radii (Table VII taken from Nightingale<sup>36</sup>).

TABLE VII  
Ionic radii for selected ions<sup>36</sup> (in units of  $10^{-10}$  m)

Ion	$r_c$	$r_s$	$r_h$
$\text{Li}^+$	0.60	2.38	3.82
$\text{Na}^+$	0.95	1.84	3.58
$\text{K}^+$	1.33	1.25	3.31
$\text{Rb}^+$	1.48	1.18	3.29
$\text{Cs}^+$	1.69	1.19	3.29
$\text{NH}_4^+$	1.48	—	—
$\text{Cl}^-$	1.81	1.21	3.32
$\text{ClO}_3^-$	2.88	1.42	3.41
$\text{NO}_3^-$	2.64	1.29	3.35

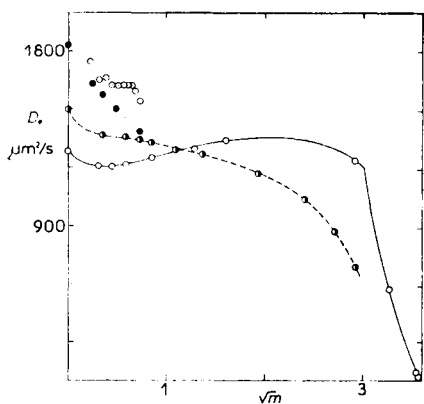


FIG. 3

Plots of diffusivity against concentration for chlorates.  $\circ$   $\text{LiClO}_3$ , (Campbell and Oliver<sup>10</sup>);  $\bullet$   $\text{NaClO}_3$  (Campbell and Oliver<sup>10</sup>);  $\bullet$   $\text{KClO}_3$  (this work);  $\circ$   $\text{KClO}_3$  (Kozlová<sup>11</sup>)

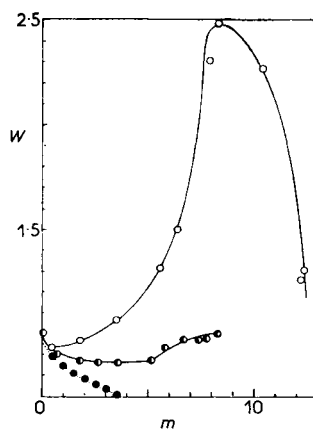


FIG. 4

Plots of the activity term  $W$  against concentration for chlorates in aqueous solutions.  $\circ$   $\text{LiClO}_3$  (Campbell and Oliver<sup>10</sup>);  $\bullet$   $\text{NaClO}_3$  (Campbell and Oliver<sup>10</sup>);  $\bullet$   $\text{KClO}_3$  (Robinson and Stokes<sup>5</sup>)

Fitting experimental data for the concentration dependence of diffusivity to Eq. (3) for  $h = 0$  has yielded  $D_{12} = 0.887 \cdot 10^{-9} \text{ m}^2/\text{s}$ . The position of the curve portraying the function  $D(m)$  defined by Eq. (2) or (3) depends very strongly on the value of  $D_{12}$  (Fig. 1). Once again, the known observation<sup>10,31</sup> has been confirmed that the  $D(m)$  values are not very sensitive to the values of the parameter  $a$ .

Fig. 3 shows plots of  $D$  as a function of concentration for all the three chlorates. In Fig. 4 are plots of activity coefficient against concentration; for all the three salts, the plots essentially follow the shapes of the  $D$ - $m$  curves. From Tables III and IV it is seen that as for other salts<sup>5,6</sup>, the values of the so-called thermodynamic diffusion coefficient,  $f = D/W$ , for all the three chlorates are considerably less concentration dependent than the diffusivity  $D$  defined by Fick's law. Considering the simplifications made in deriving Eqs (2) and (3), the agreement between the experimental and theoretical dependences of diffusivity on concentration may be regarded as satisfactory, particularly for the purpose of predicting the shape of the concentration profile from a few experimental values. On the other hand, the predictive power of Eq. (2) is somewhat restricted by the strong sensitivity of  $D(m)$  values to the parameters  $h$  and  $D_{12}$ . As only a few systems have as yet been treated in this way, it is premature to assess the usefulness of Eqs (2) and (3) in correlating diffusivities as a function of concentration. For partly associated and at the same time strongly hydrated electrolytes, however, it would be useful to obtain information about the parameters  $h$  and  $D_{12}$  by other, independent approaches based on more realistic models of ion hydration and ionic mobility. Optimization techniques by themselves may lead to good agreement between theoretical and experimental values of diffusivity for a wide range of acceptable values of the parameters  $h$  and  $D_{12}$ .

Further measurements will be carried out to elucidate the causes of the discrepancy between data obtained by the Taylor dispersion method and by the diaphragm-cell technique. It is interesting to note that very accurate measurements of integral diffusion coefficients have been made which do not lead to satisfactorily accurate differential values<sup>34</sup>. In principle, it is also possible that dielectric inhomogeneity of the boundary layers of solution in a diaphragm cell plays such an important role that the measurements of diffusivity in electrolyte solutions by the diaphragm-cell technique cannot give results comparable with those obtained by methods in which this effect is not involved. This problem has not, to our knowledge, been satisfactorily resolved although the wide application of the diaphragm-cell technique to measurements of diffusivities in electrolyte solutions makes such an effort worthwhile.

#### APPENDIX I

Quantitative characteristics of the apparatus and evaluation of criteria according to recommendations given by Alizadeh and coworkers<sup>32</sup>

Parameters of the apparatus:

Capillary:

Length	$L$	2.80 m
Inner diameter	$d$	1.50 mm
Loop radius	$R_c$	0.25 m
Volume	$V_c = \pi d^2 L / 4$	4.948 $\mu\text{l}$
Measured diffusivities	1.400–1.600	$\mu\text{m}^2/\text{s}$
Sample volume	$V_i$	5 $\mu\text{l}$
Cell volume	$V_r$	8 $\mu\text{l}$
Volume flow rate		20 ml/h
Mean velocity	$V$	3.144 mm/s
Mean time	$\bar{t}$	890 s

1) In order for the capillary curvature to be negligible, the conditions  $De^2 Sc < 20$  and  $2R_c/d \geq 100$  must be satisfied.

$$De = Re(d/2R_c)^{1/2} = 0.257; \quad De^2 Sc = 0.032125 \times 500 = 16.06$$

$$Re = dV/\eta = 4.7$$

$$2R_c/d = 333.3$$

$$Sc = \eta/(\rho D) = 500$$

Thus, both the conditions are satisfied.

2) Requirements of laminar flow:  $Re < 2000$ ,  $Pe > 700$ ,  $S > 10$ .  $Pe = d \cdot V/(2D) = 1290$  to 1700;  $Re \approx 5$ ;  $S = 2.2$  to 2.9. Thus, the first two conditions are fulfilled. For  $S$ , the original indefinite theoretical inequality  $S > 1$  was empirically extended by Giddings and Seager<sup>25</sup> to  $S > 3.5$ , and later by Alizadeh and coworkers<sup>32</sup> to  $S \geq 10$ . For our apparatus,  $S \geq 2.2$  was found to be a sufficient condition.

3) Corrections of the first two normalized moments  $\delta\bar{t}_1$  and  $\delta\sigma_1^2$  for the following departures of the apparatus from ideality:

a) finite width of pulse:

$$\delta\bar{t}_1 = -(L/V) V_i/2V_c = -0.45$$

$$\delta\sigma_1^2 = -(L/V)^2 (V_i/V_c)^2 = -0.793$$

b) mixing of the refractometer cell contents:

$$\delta\bar{t}_1 = -(L/V) [3F - V_r/V_c] = -22.22$$

$$\delta\sigma_1^2 = -(L/V)^2 \{13F - (V_r/V_c)^2 - (V_r/V_c) 2F\}$$

$$F = Vd^2/(192LD) = 0.00877$$

c) correction for the effect of the connecting refractometer capillary of length  $L_r$  and radius  $a_r$ :

$$\delta\bar{t}_1 = (L_r/V) (d_r/d)^2 \{1 + (d/d_r)^2 (LF/L_r) [1 + (d_r/d)^2]\} = 0.4242$$

$$\delta\sigma_1^2 = (L_r/V) (d_r/d)^4 \{(2LF/L_r) (d/d_r)^2 + (dLF/d_r L_r)^2 [3(d_r/d)^2 + 2]\} = 1.5 \cdot 10^{-5}$$

The evaluation is made using the corrected values  $\bar{i}_i = i_c + \sum_i \delta \bar{i}_i$ ;  $\sigma_i^2 = \sigma_c^2 + \sum_i \delta \sigma_i^2$ . The  $p$ -th moments defined by  $\mu_p = (L/V)^p \int_0^\infty T^p C dT / \int_0^\infty C dT$  may then be expressed as

$$\begin{aligned}\mu_1 &= \bar{i}_i = (L/V)(1 + 2F) = i_0 T \\ \mu_2 &= (L/V)^2 [1 + 6F + 12F^2] \\ \sigma_i^2 &= (L/V)^2 (2F + 8F^2) = \frac{2F + 8F^2}{(1 + 2F)^2} \bar{i}_i^2 \\ F &= \frac{Vd^2}{192LD} = 2\sigma_i^2 - \bar{i}_i^2 + \sqrt{(\bar{i}_i^4 + 4\bar{i}_i^2 \sigma_i^2)/(8\bar{i}_i^2 - 4\sigma_i^2)} \\ D &= \frac{d^2}{96\bar{i}} \frac{\sqrt{(1+E)+3}}{\sqrt{(1+E)+E/2-1}} \left[ \frac{1}{2} + \frac{1}{2} \sqrt{(1-\delta_a)} \right],\end{aligned}$$

where  $E = 4\sigma_i^2/\bar{i}_i^2$  and  $\delta_a = 12.79977F$ .

If  $Dt/d^2 > 2.5$ , the value of  $D$  may be estimated to an accuracy of 1% from the simple relation

$$D = d^2 \bar{i}_i / 96 \sigma_i^2.$$

## APPENDIX II

### Evaluation of the limiting diffusivity and its electrophoretic corrections

1) The limiting diffusivities are obtained from the expression<sup>5-7</sup>

$$D^0 = RT \lambda_1^0 \lambda_2^0 \nu [F^2 \nu_1 |z_1| (\lambda_1^0 + \lambda_2^0)]^{-1}.$$

The limiting equivalent conductivities  $\lambda_i^0$  of the individual ions are available, for example, in a book of Robinson and Stokes<sup>5</sup>.

2) The electrophoretic correction terms  $A_1$  and  $A_2$  for 1:1 electrolytes are given by<sup>5,6</sup>

$$\begin{aligned}A_1 &= -\frac{kT}{6\pi\eta} (i_2^0 - i_1^0)^2 \frac{x}{1+xa} = -8.07 \cdot 10^{-6} T \frac{\sqrt{c}}{1+0.3291a\sqrt{c}} \\ A_2 &= \frac{kT}{12\pi\eta} \frac{e^2}{\epsilon kT} (xa)^2 \left( \frac{\exp(xa)}{1+xa} \right)^2 Ei(2xa) = 8.77 \cdot 10^{-21} \phi_2(xa)/a^2\end{aligned}$$

3) Evaluation of the integral exponential function and of the function  $\phi_2 = x^2[\exp x/(1+x)]^2 \cdot Ei(2x)$

The evaluation is accomplished simply and rapidly by using the polynomial

$$\phi_2 = b_1 + b_2 x + b_3 x^2 + b_4 x^3 + b_5 x^4.$$

For  $x$  in the interval (0.5, 1.8), the maximum relative error in the obtained values is less than 0.1%.

$$\begin{aligned}b_1 &= -0.0116962 & b_3 &= -0.2146649 & b_5 &= -0.0143819 \\ b_2 &= 0.2429208 & b_4 &= 0.0881460\end{aligned}$$

The calculations were performed using an algorithm for evaluating the integral exponential function  $Ei(p)$  in the form

$$Ei(p) = -0.577\,215\,665 - \ln p + p - p^2/4 + p^3/18 \dots (-1)^{k+1} \frac{p^k}{k \cdot k!},$$

the summation being terminated at terms smaller than  $10^{-7}$ .

#### LIST OF SYMBOLS

$a$	mean distance of closest approach of ions <sup>5</sup>
$a_i$	coefficients of fitting polynomials
$b_i$	coefficients of polynomial in Appendix II
$c$	molar concentration
$c_0$	initial concentration
$d$	diameter of measuring diffusion capillary
$d_r$	diameter of refractometer capillary
$D$	differential diffusion coefficient
$D_c$	measured value of diffusivity
$D_{12}$	diffusivity of ion pair
$D_{Na}^a, D_{Na}^b$	defined in Table VII
$D^0$	limiting Nernst diffusivity
$D_w$	self-diffusion coefficient of water
$e$	electron charge
$E = (2\sigma_i/\bar{r}_i)^2$ ,	defined in Appendix I
$f = D/W$ ,	thermodynamic diffusivity
$F$	Faraday constant, Appendix II
$h$	hydration number in Eqs (2) and (3)
$H$	hydration term in Eq. (3), Table IV
$L$	length of measuring diffusion capillary
$m$	molal concentration
$M$	molar mass of salt
$M_w$	molar mass of water
$n_w$	number of moles of water
$n_s$	number of moles of salt
$N$	total of measured points
$p$	concentration (weight per cent)
$p = x - Vt$ ,	coordinate
$Pe = aV/D$ ,	Peclet number
$r$	radial coordinate
$r_c$	crystal ionic radius
$r_s$	Stokes ionic radius
$r_h$	effective radius of hydrated ion
$R_c$	radius of capillary loop
$Re = 2aVQ/\eta$ ,	Reynolds number
$S = D\bar{t}/a^2$ ,	dimensionless time (Fourier number)
$t$	time
$t_i^0$	limiting transfer number
$T$	absolute temperature

$V$	mean velocity of flow in capillary
$W = 1 + d \ln \gamma_{\pm} / d \ln m$	activity term
$z$	quantity proportional to measured concentration
$z_1$	cation charge
$\alpha$	degree of electrolyte dissociation
$\beta$	slope of linear plot according to Eq. (4)
$\gamma_{\pm}$	mean molal activity coefficient
$\epsilon$	dielectric constant of solvent, Appendix II
$\delta$	correction term
$\Delta_1$	electrophoretic term defined in Appendix II
$\lambda^0$	limiting equivalent conductivity
$\phi$	osmotic coefficient
$\eta$	viscosity of electrolyte solution
$\eta^0$	viscosity of pure solvent
$\rho$	specific mass
$\kappa$	term proportional to ionic strength, Appendix II
$\nu$	stoichiometric number of ions in electrolyte molecule
$\nu_1$	number of cations in electrolyte molecule
$\nu_2$	number of anions in electrolyte molecule

## REFERENCES

1. Spiro M., King F. in the book: *Ionic Liquids* (D. Inman, D. G. Lovering, Eds). Plenum Press, New York 1981.
2. Lobo V. M. M.: *Electrolyte Solutions: Literature Data on Thermodynamic and Transport Properties*. Coimbra Editors, Coimbra 1975.
3. Janz G. J., Mayer G. E.: United States Dept. of the Interior Office of Saline Water, Research and Development Progress Rept. No 196, 1966.
4. Landolt Börnstein *Zahlenwerte und Funktionen. Eigenschaften der Materie in Ihren Aggregatzuständen*, 5. Teil, Bdteil a: *Transportphänomene I — Viskosität und Diffusion* (K. Schäfer, Ed.). Springer Verlag, Berlin 1969.
5. Robinson R. A., Stokes R. H.: *Electrolyte Solutions*, 2nd Ed., Ch. 11. Butterworths, London 1959.
6. Harned H. S., Owen B. B.: *The Physical Chemistry of Electrolyte Solutions*. Reinhold, New York 1958.
7. Erdey-Grúz T.: *Transport Phenomena in Aqueous Solutions*, Ch. 3.2. Akadémiai Kiadó, Budapest 1974.
8. Nývlt J., Pekárek V.: *Z. Phys. Chem. (Frankfurt/M)* 122, 199 (1980).
9. Harano Y., Nakano K., Saito M., Imoto T.: *J. Chem. Eng. Jap.* 9, 373 (1976).
10. Campbell A. N., Oliver B. G.: *Can. J. Chem.* 47, 2681 (1969).
11. Kozlová A.: *Thesis*. Prague Institute of Chemical Technology, Prague 1981.
12. Hančil V., Rod V., Rosenbaum M.: *Chem. Eng. Commun.* 3, 155 (1979).
13. Taylor G. I.: *Proc. Roy. Soc. Ser. A* 219, 186 (1953); *A* 223, 446 (1954).
14. Taylor G. I.: *Proc. Roy. Soc. Ser. A* 225, 473 (1954).
15. Taylor G. I.: *Proc. Phys. Soc.* 42, 857 (1955).
16. Reejsinghani N. S., Gill W. N., Bardhun A. J.: *AIChE J.* 12, 916 (1966); 14, 100 (1968).
17. Komiyama H., Smith J. M.: *J. Chem. Eng. Data* 19, 384 (1974).
18. Ouano A. C.: *Ind. Eng. Chem., Fundam.* 11, 268 (1972).

19. Baldauf W.: *Thesis*. Technische Universität, Berlin 1981.
20. Ferrel R. T.: *Thesis*. University of Texas 1966.
21. Marrero T. R.: *Thesis*. University of Maryland 1970.
22. Alizadeh A.: *Thesis*. Imperial College, London 1980.
23. Bournia A., Coull J., Houghton G.: *Proc. Roy. Soc. London A* 261, 227 (1961).
24. Evans E. V., Kenney G. N.: *Proc. Roy. Soc., Ser A* 284, 540 (1965).
25. Giddins J. C., Seager S. L.: *Ind. Eng. Chem. Fundam.* 1, 277 (1962).
26. Marrero T. R., Mason E. A.: *J. Phys. Chem. Ref. Data* 1, 3 (1972).
27. Grushka E., Maynard V. R.: *J. Phys. Chem.* 77, 1437 (1973).
28. Wakeham W. A.: *Faraday Symposia* 15/12, 1 (1980).
29. Pommersheim J. M., Greskovich E. J., Kenner R. C.: *AIChE J.* 23, 118 (1977).
30. Rard J. A., Miller D. G.: *J. Chem. Eng. Data* 25, 211 (1980).
31. Wishaw B. F., Stokes R. H.: *J. Amer. Chem. Soc.* 76, 2065 (1954).
32. Alizadeh A., Nieto de Castro C. A., Wakeham W. A.: *Int. J. Thermophys.* 1, 243 (1980).
33. Crank J.: *The Mathematics of Diffusion*. Clarendon Press, Oxford 1956.
34. Rard J. A., Miller D. G.: *J. Solution Chem.* 8, 755 (1979).
35. Geiger A.: *Ber. Bunsenges. Phys. Chem.* 85, 52 (1981).
36. Nightingale E. R., jr: *J. Phys. Chem.* 63, 1381 (1959).
37. *Gmelins Handbuch der Anorganischen Chemie*, 8. Aufl. Kalium, Syst. No 22 (E. Pietsch, Ed.). Verlag Chemie, Berlin 1938.

Translated by M. Škubalová.