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# EXTERNAL TRANSVERSE MAGNETIC FIELD EFFECT ON ELECTROLYTE DIFFUSION IN ALKALI CHLORIDE–WATER SOLUTIONS

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## ABSTRACT

The observed external transverse magnetic field effect on electrolyte diffusion in diamagnetic alkali chloride (LiCl, NaCl; KCl and CsCl)–water solutions, expressed as the fractional arithmetic average integral diffusion coefficient, $\bar{D}^* = [(\langle \bar{D}^{\circ}_{H}\rangle - \langle \bar{D}^{\circ}\rangle)/\langle \bar{D}^{\circ}\rangle] \times 10^2$; has been correlated with structural (hydration number, viscosity and ionic limiting equivalent conductance) and microdynamical (proton nuclear magnetic relaxation times and proton nuclear magnetic resonance shifts) parameters expressing the configurational rearrangement modes of the solvent and solute molecules forming the aqueous solution.

## INTRODUCTION

Lielmezs and co-workers[1-5] by means of modified[*] fritted glass diaphragm–cell method[1-7] (Fig. 1) have found that an applied transverse magnetic field of 5 kG strength, at 25 °C and at the ambient pressure; influences the integral diffusion coefficient values of alkali chloride (LiCl, NaCl, KCl and CsCl)–water solutions at various concentrations. The obtained results (including the previously discussed[3] HCl–$H_2O$ system) in the form of the integral diffusion coefficient and the corresponding arithmetic mean fractional diffusion coefficient; have been summarized in Figs. 2 and 3. In all integral diffusion coefficient value calculations it has been assumed that the applied transverse magnetic field does not in any way alter the physico-chemical properties (density, electric conductance) of water[**] and the salt used. The observed external transverse magnetic field effect on electrolyte diffusion in alkali chloride–water solutions[1-5]; expressed through the fractional arithmetic average integral diffusion coefficient.

$\bar{D}^* = [(\langle \bar{D}^{\circ}_{H}\rangle - \langle \bar{D}^{\circ}\rangle/\langle \bar{D}^{\circ}\rangle] \times 10^2$ has been correlated[**] (Table 1, Figs. 5–10) with a series of microscopic structural and microdynamical parameters of the alkali

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[*] The apparatus of two parts: the Varian Associates 9-in. electromagnet system and the diffusion cell assembly (Fig. 1).

[**] Lielmezs et al.[8] have shown that transversally applied magnetic field of 5 kG strength increases the distilled water viscosity up to 0.056 %; while Lielmezs and Aleman[9] have presented evidence that the external magnetic field will, for instance, increase the viscosity of 0.01 N KCl–$H_2O$ solution by 0.242 % at 25 °C temperature and at $H = 12$ kg strength. Since these viscosity increases represent

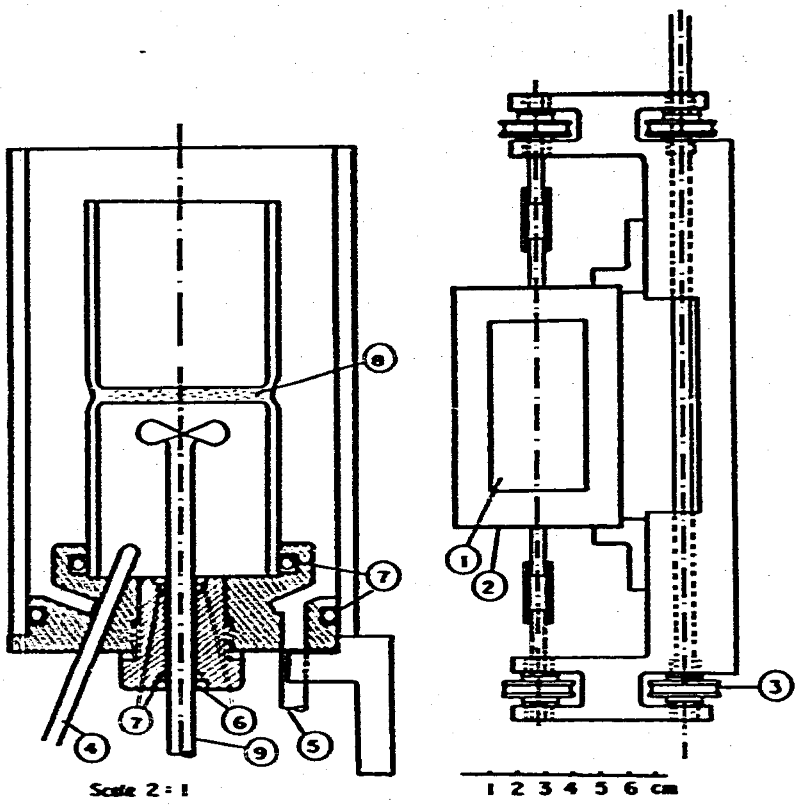

Fig. 1. Details of diffusion cell: (1) cell (glass); (2) cell cooling water jacket with cooling water circulated through constant temperature bath; (3) drive pulley (brass); (4) thermistor jacket (glass) placed inside the cell; (5) inlet and outlet for water circulated through constant temperature bath; (6) plastic retaining ring; (7) rubber sealing (O) ring; (8) fritted glass diaphragm; (9) glass stirrer, rotating with 60 r.p.m. Stirrer and drive pulley are connected with tygon tubing. Note that the diffusion cell is drawn in detail only for the bottom part. The cell top part is symmetric to the bottom part of the diffusion cell.

chloride–water solution at 0.04; 0.08; 0.4 and 0.8 N salt concentration. These correlations (Figs. 5–10) show that this effect characterized by the changes in the magnetic state of the given diamagnetic state of the given diamagnetic salt–water system; appear to be a complex measure of the involved structural bulk rearrangements and microdynamic molecular processes.

## DISCUSSION

### *General*

The presented alkali chloride–water solutions are the simplest of all aqueous electrolyte systems since they are completely dissociated in dilute solution except

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fixed background; the salt diffusion coefficient values were calculated without considering this effect. Figure 4 shows the relation between those two observed effects ($D^*$ and $\nu^*$) for KCl–$H_2O$ solution. In expression for $D^*$; superscript "o" denotes the "no-applied" field (except for the presence of the earth magnetic field) condition; while subscript "$H$" represents the transversally applied magnetic field of $H = 5$ kg state.

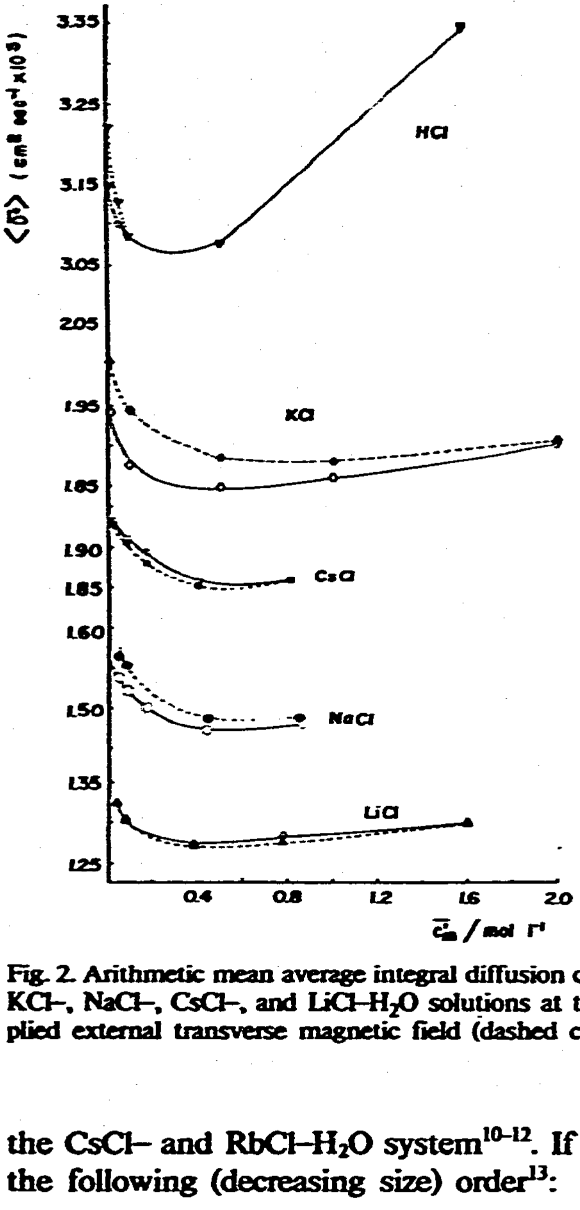

Fig. 2. Arithmetic mean average integral diffusion coefficient and concentration plot at 25 °C for HCl–, KCl–, NaCl–, CsCl–, and LiCl–$H_2O$ solutions at the ambient earth field (solid curve) and at the applied external transverse magnetic field (dashed curve) conditions. Data from refs. 1–5.

the CsCl– and RbCl–$H_2O$ system[10–12]. If the ionic radii for alkali metal ions form the following (decreasing size) order[13]:

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ \tag{1}$$

then the transport properties of alkali chloride–water solution series increase with the increasing cationic radius with the only exception for the RbCl salt which has the largest conductance self-diffusion coefficient and cationic transport number[10–14]. However, the alkali chloride ionic $B$-coefficients for viscosity[15,16] fall in the series as follows (ranging from positive to negative values):

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ \tag{2}$$

Equation (2) implies that the structural disordering effect is greater the smaller is the charge to radius ratio[13]. Yet, recent solvation spectra studies[17] of the proton

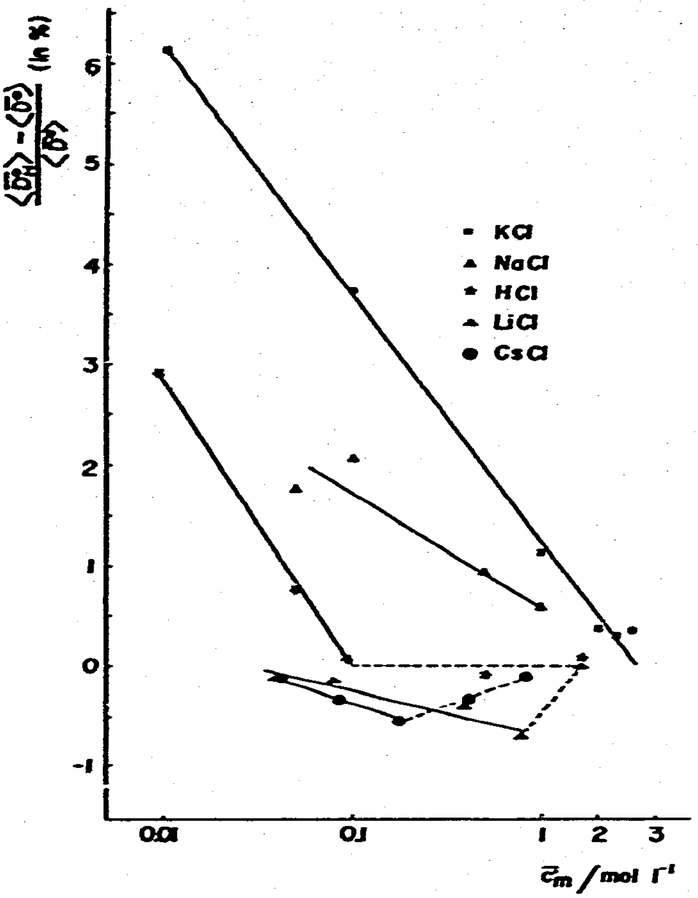

Fig. 3. Arithmetic mean average fractional diffusion coefficient and concentration plot in semi-logarithmic coordinates for HCl–, KCl–, NaCl–, CsCl–, and LiCl–$H_2O$ solutions at 25°C. Data from ref. 1–5.

magnetic resonance shifts of water protons in the presence of the alkali metal ions (Table 1, Fig. 10) show the following ionic sequence at the infinite dilution.

$$Cs^+ < Rb^+ < K^+ > Na^+ > Li^+ \tag{3}$$

Equation (3) indicates the presence of maximum disorder for $K^+$-ion (upfield shift). Table 1 shows that $\bar{D}^*$ (dimensionless measure of the magnetic field effect on the electrolyte diffusion behavior in alkali chloride solutions) forms the following series for all salt concentrations:

$$KCl > NaCl > CsCl \approx LiCl \tag{4}$$

Comparing the sequence of the proton magnetic resonance shifts for water protons as induced by cations and anions in aqueous solution (eq. (3)) with the series of $\bar{D}^*$-values (eqn (4)); we observe that for both of these series, property associated with the KCl–$H_2O$ solution, has the largest magnitude. It appears that the applied magnetic field may cause the largest effect on salt diffusion behavior in

TABLE 1

SUMMARY OF DATA

| *Alkali chloride* | *Alkali chloride concentration in water,* | *Arithmetic mean average fractional diffusion coefficient*[1-5] | | *Proton nuclear magnetic relaxation time ratios in solution*[23] | | *Proton nuclear magnetic resonance molal*[17] *salt shift (ppm)* | *Hydration number*[18] | *Coefficient of structural change in solvent*[19] | *Ion limiting equivalent conductance*[20] | *Relative*[a] *viscosity*[15] | *Relative viscosity*[b] *at magnetic state H*[8,9] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LiCl | 0.04 | −0.090 | −2.25 | 2.0 | 6.0 | +0.047 | 4.3 | −0.10 | 38.67 | 1.0069 | |
| | 0.08 | −0.200 | −2.50 | | | | | | | 1.0130 | |
| | 0.40 | −0.600 | −1.50 | | | | | | | 1.0615 | |
| | 0.80 | 0.000 | 0.00 | | | | | | | 1.1246 | |
| NaCl | 0.04 | 2.140 | 53.50 | 1.4 | 2.2 | +0.096 | 2.9 | −0.51 | 50.09 | 1.0044 | |
| | 0.08 | 1.820 | 22.75 | | | | | | | 1.0081 | |
| | 0.40 | 0.950 | 2.38 | | | | | | | 1.0369 | |
| | 0.80 | 0.730 | 2.91 | | | | | | | 1.0739 | |
| KCl | 0.04 | 4.675 | 116.88 | 0.9 | 0.9 | +0.111 | 1.5 | −0.56 | 73.48 | 1.0005 | 0.9905 |
| | 0.08 | 3.925 | 49.06 | | | | | | | 1.0004 | 0.9885 |
| | 0.40 | 2.210 | 5.23 | | | | | | | 0.9987 | 0.9718 |
| | 0.80 | 0.975 | 1.22 | | | | | | | 0.9962 | 0.9517 |
| CsCl | 0.04 | −0.125 | −3.13 | 0.7 | 0.8 | −0.080 | 0.9 | −0.31 | 77.23 | 0.9990 | |
| | 0.08 | −0.310 | −3.88 | | | | | | | 0.9975 | |
| | 0.40 | −0.390 | −0.98 | | | | | | | 0.9847 | |
| | 0.80 | −0.100 | −0.13 | | | | | | | 0.9708 | |

[a] Viscosity units in centipoises. [b] Viscosity units in centistokes.

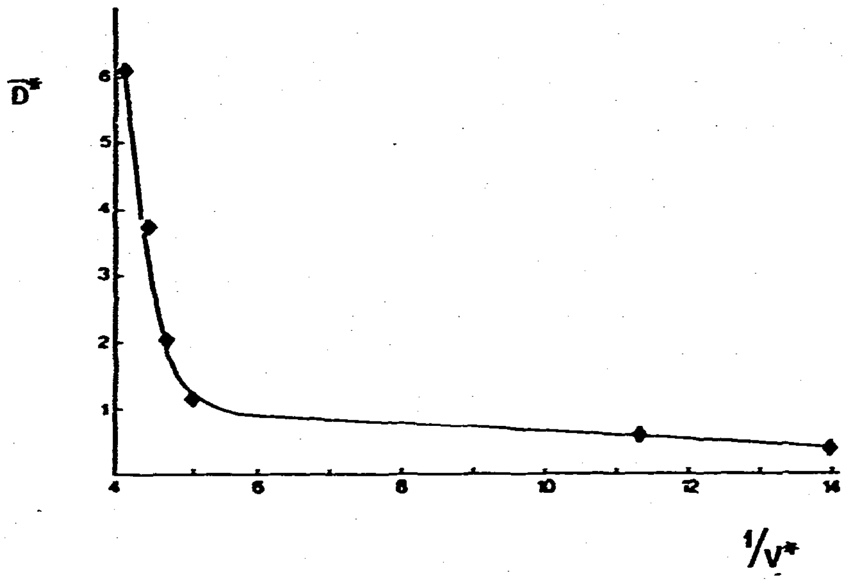

Fig. 4. The $\bar{D}^*-\nu^{*-1}$ plot for KCl$-H_2O$ solution at the same concentration and at 25°C. $\bar{D}^*$ is defined as: $\bar{D}^* = [(<\bar{D}^0_H> - <\bar{D}^0>)/<\bar{D}^0>] \times 100$ while $\nu^* = [(\nu^H - \nu^0)/\nu^0] \times 100$. The diffusion measurements were performed[1] at 5 kG while the viscosity measurements[9] at 12 kG strenght of the applied magnetic field.

these alkali chloride solutions which have the maximum disorder and highest degree of structural disturbance. Exactly how the applied magnetic field (or perhaps better, the magnetic state change of the system) influences the salt diffusion process cannot be said with any certainty at this time. However, an examination of the presented correlations (Figs 5–10) shown to exist between the $\bar{D}^*$-values and the salt–water molecule parameters characterizing the aqueous solution structural (hydration number[18]; coefficient of structural change in solvent[19]; ion limiting conductance[20]; relative solution viscosity[15,16]) and microdynamical (proton nuclear magnetic relaxation time[21-25] and proton nuclear magnetic resonance shifts[17]) properties (Table 1) may at least yield partial understanding of the complexities associated with the observed magnetic field effect on the diffusional processes of alkali chloride–water solutions.

### *Structural property correlations*

Figure 5 shows that fractional diffusion coefficient, $\bar{D}^*$ correlates with the hydration number of the given alkali chloride aqueous solution. The hydration number is considered to be the effective number of water molecules attached to the ion as it moves through the solution. The presented hydration numbers (Table 1, Fig. 5) were obtained from activity coefficient values[18]. The relation found between the $\bar{D}^*$-values and the corresponding hydration numbers (Fig. 5) seems to follow the pattern of proton magnetic resonance shift sequence (eqn (3)). In this context, Fig. 5 implies that the magnitude of the total binding of water molecules to the salt molecule alone does not sufficiently describe the observed

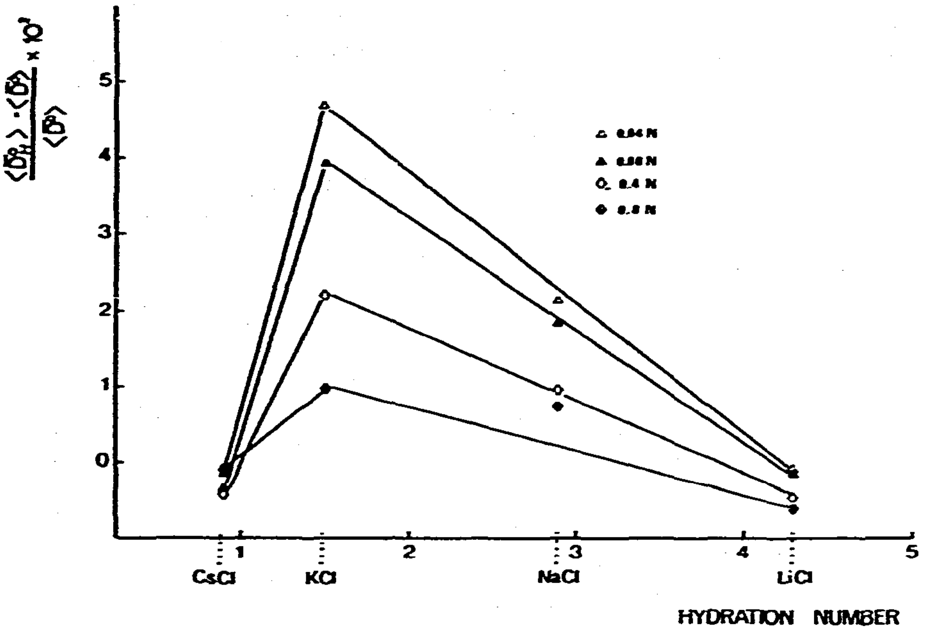

Fig. 5. $\bar{D}^*$ plot versus the hydration number. Data taken from ref. 18.

magnetic field effect on the diffusion of electrolytes in aqueous solution. In its simplest form this is expressed by $\zeta_i/\zeta^{**}$, the dimensionless ratio[26] of the times of residence of water molecule near to an ion and in solution surrounded only by other water molecules. Conditions $\zeta_i/\zeta^* \gtrsim 1.0$ describe the hydrated complex structural stability. For $\zeta_i/\zeta^* > 1.0$ (such as found in LiCl— and NaCl+$H_2O$ solutions), the water molecule spends more time in the vicinity of the ion than in the neighborhood of another water molecule yielding more effective binding and hence more stable configuration of water molecules about the ion than in pure water. When $\zeta_i/\zeta^* < 1.0$, the water molecule near the ion becomes more mobile than in pure water; the effective binding decreases and the resulting configuration of water molecules around the ion is less stable as in pure water and should become more unstable with an increase in the ionic size[13,2,6]. If the ionic size sequence (eqn (1)); the measure of structural disorder (eqn (3)), and the configurational stability and the mobility of water molecules in the hydrated ion complex ($\zeta_i/\zeta^*$ ratio) are considered; then the $\bar{D}^*$-hydration number relation (Fig. 5) brings clearly out that the largest $\bar{D}$-value should be expected for systems of maximum structural disorder, i.e., solutions characterized by configurationally least stable hydrated ion complexes. Indeed, the largest $\bar{D}^*$ value is found for KCl–$H_2O$ system with sequential $\bar{D}^*$ decrease for NaCl–, LiCl– and CsCl–$H_2O$ solutions. While for KCl–, NaCl– and LiCl–$H_2O$ solutions the observed $\bar{D}^*$ values appear

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*For alkali chlorides, Samoilov[26] specifies the following values for $\zeta_i/\zeta^*$ ratio: $Li^+$, $\zeta_i/\zeta^* = 3.48$; $Na^+$, $\zeta_i/\zeta^* = 1.4$; $K^+$, $\zeta_i/\zeta^* = 0.65$; $Cs^+$, $\zeta_i/\zeta^* = 0.57$ and $Cl^-$, $\zeta_i/\zeta^* = 0.63$.

to be directly associated with restraints of Equations (1) and (2) and the $\zeta_i/\zeta^*$ ratio; the understanding of the hydrated complex behavior for CsCl–$H_2O$ solution requires additional consideration. It seems that the description of molecular motion in the solution under the influence of an applied magnetic field should include the particle size in such a way as to indicate that upon reaching a certain critical particle diameter; the unstable hydrated ion complex of that aqueous solution starts to become more stable. This molecular motion can be described by the Stokes–Einstein relation:

$$D = kT/6\pi a\eta \qquad (5)$$

where "$a$" is the radius of the moving particle while $\eta$ is the shear viscosity (in centistokes) of the medium. Equation (5) indicates that the molecular motion may be affected first, directly by the particle size "$a$"; and secondly, indirectly through the assumption that shear viscosity "$\eta$" is function of the diffusing particle size; i.e., $\eta = \eta(a)$. If we consider the product "$a\eta$"; and assume that $\bar{D}^*$ represents the molecular motion in the same way as $D$ in eqn (5); than for systems of weak interactions and large molecular size, the product "$a\eta$" will be large (since $a\eta = a\eta = a\eta(a)$) yielding small $\bar{D}^*$-value. For a system of small molecules with strong interactions; the product "$a\eta$" will again be large and the resulting $\bar{D}^*$

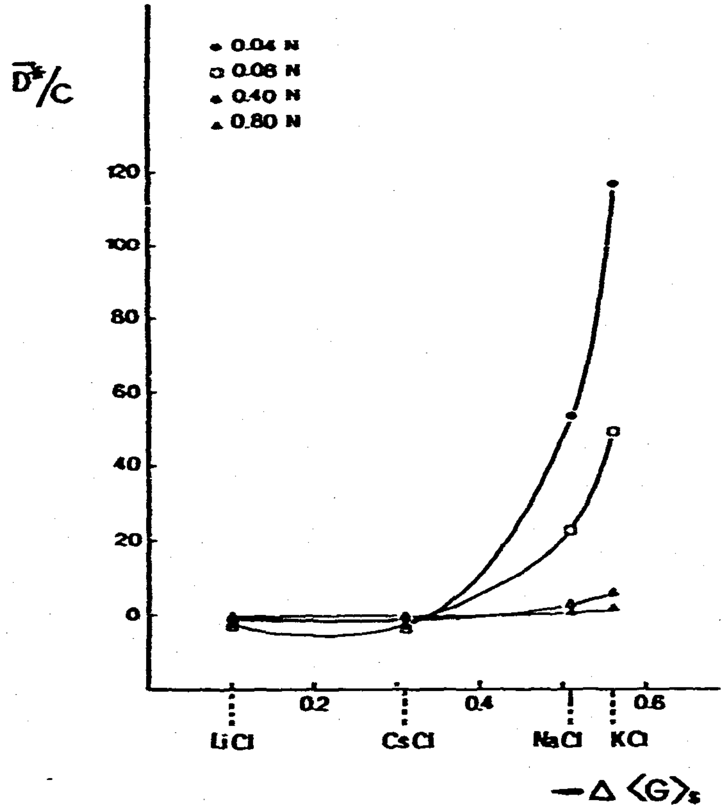

Fig. 6. The $D^*/C$plot versus the structural parameter $-\Delta\langle G\rangle_s$. Diffusion coefficient data taken from ref. 1–5 while the structural parameter $-\Delta\langle G\rangle_s$ values taken from ref. 19.

small. Indeed, both limiting solutions, $CsCl-H_2O$ and $LiCl-H_2O$, follow this relation between the solution structure (strength of interactions) and the molecular size and show small $\bar{D}^*$-values (Fig. 5, Table 1). On the other hand, Fig. 6 gives $\bar{D}^*$-value plot against $-\Delta\langle G\rangle_s$; where $-\Delta\langle G\rangle_s$; represents a parameter introduced by Ben Naim[19] to measure the structural changes in the solvent induced by the dissolution of solute (compare with structure breaker–structure promotor concept[21-26]) in aqueous solutions. If we accept the correctness* of the given $-\Delta\langle G\rangle_s$-values (Table 1); then the relation between $\bar{D}^*$ and $-\Delta\langle G\rangle_s$ (Fig. 6) reaffirms the previously made observation that the largest applied magnetic field effect on the diffusional behavior of electrolytes, should be found for the least stable hydrated complex configurations. The appearance of negative $\Delta\langle G\rangle_s$ values[19] (Table 1) indicates that the addition of salt to the aqueous solution has destabilizing (the more negative $\Delta\langle G\rangle_s$; the less stable the water structure) effect on the structure of water. How the applied magnetic field influences the stability of water structure and how this influence changes the diffusional process of salts in aqueous solution, is a topic which clearly deserves further study. Figure 7 shows correlation between the measure of the magnetic field effect on the diffusion of the salts in solution, the $\bar{D}^*$-values and the natural logarithm of the product of limiting equivalent conductance of cations[20] and the relative viscosity (Table 1) of solution[15,16] when this product is divided by the concentration of the electrolytes. It is seen (Fig. 7) that the observed magnetic field effect on diffusion of electrolytes ($\bar{D}^*$-values) tends to fall into two distinct groups: the positive high $\bar{D}^*$-values associate with the KCl and NaCl salts; while the negative low $\bar{D}^*$-values are found for LiCl and $CsCl-H_2O$ solutions. The product $\Lambda_o^+\eta_r$, represents the ion mobility and electrolyte viscosity effect on the medium in which ions move when referred to the given electrolyte concentration. This $\Lambda_o^+\eta_r$-product represents two separate changes: the limiting equivalent conductance $\Lambda_o^+$-values increase[20] following the ion sequence $Cs^+ > K^+ > Na^+ > Li^+$, while the reduced solution viscosity increases[15,16] in concentration for LiCl– and $NaCl-H_2O$ solutions but decreases[15,16] for KCl– and $CsCl-H_2O$ solutions (Table 1). Relative viscosity, $\eta_r$, is defined as:

$$\eta_r = \frac{\eta_{\text{solution}}}{\eta_{H_2O}} \tag{6}$$

Expansion of eqn (6) in concentration yields the modified Jones–Dole equation[15,16]:

$$\eta_r = \frac{\eta_{\text{solution}}}{\eta_{H_2O}} = 1 + Ac^{\frac{1}{2}} + Bc + Dc^2 \tag{7}$$

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*Ben Naim[19] derived the presented $\Delta\langle G\rangle_s$ values (Table 1) neglecting the salt dissociation effects. If the salt dissociation into ions in water is accounted for; the given tentative results may change since CsCl– and RbCl– salts dissociate in water.

where $A$ is a constant depending on the long range Coulombic forces; $B$ is a complex measure of structural solvation and hydrodynamical (size, shape) effects, and may include higher terms of the long range Coulombic forces; while $D$ is again a mixed parameter, describing solute–solute and solute–solvent interactions with concentration; and representing higher terms of the hydrodynamic effect and the long range Coulombic forces. It is possible* to express the relative contributions of parameters $A$, $B$ and $D$ at 25 °C temperature by means of fractional parameters, $a$, $b$ and $d$, defined as:

$$a = \frac{|A|-|B|}{|A|}; \qquad b = \frac{|A|-|D|}{|A|}; \qquad c = \frac{|B|-|D|}{|B|} \tag{8}$$

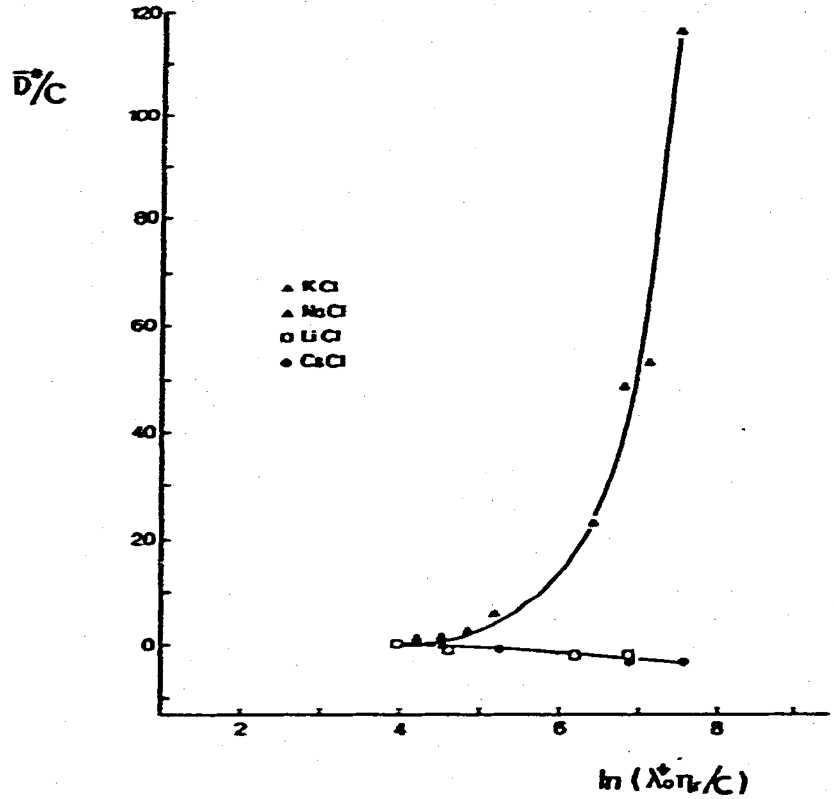

Fig. 7. The $D^*/C$ plot versus the ln ($\Lambda_+^0 \eta_r$/c) the diffusion coefficient data from ref. 1–5; while the ion limiting equivalent conductance $\Lambda_+^0$ data from ref. 20 and the relative viscosity $\eta_r$ values from ref. 15.

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*Values taken from ref. 15.

The calculated fractional parameters $a$, $b$ and $d$ are:

$$\begin{array}{llll} \text{LiCl:} & a=-19.9; & b=-0.97; & d=+0.91 \\ \text{NaCl:} & a=-12.3; & b=\ \ 0.17; & d=+0.91 \\ \text{KCl:} & a=\ \ -1.4; & b=+0.60; & d=+0.83 \\ \text{CsCl:} & a=\ \ -9.20; & b=-1.04; & d=+0.80 \end{array} \tag{9}$$

It is of interest to note (eqn (9)) that parameter $A$ (may be estimated from ionic equivalent conductivities[15]) is of the same order of magnitude as parameter $D$ at 25 °C temperature. Indeed for KCl–$H_2O$ solution, $A$-value exceeds that of $D$-value. On the other hand, $B$-values are larger than $A$-values; however, again for KCl–$H_2O$ solution this observed difference between the $A$ and $B$-values, is the smallest. Finally, $B$-value contributions exceed those of $D$-value for all alkali chloride–water solutions. If we consider the $\eta_r$–$c$ behavior (eqn (7)); then the $A$-term (long range Coulombic forces) predominates at very low salt concentrations (up to 0.002 M); while other interaction mechanisms (chiefly $B$-term) are found to predominate up to 0.1 M salt concentration in water. For higher concentrations there appears[15] at least one extra term in $c^2$ (coefficient $D$). In view of this, it seems that the largest long range Coulombic contribution is found for the KCl–$H_2O$ solution (eqns (7) and (9)). Indeed it appears that the results of Fig. 7 indicate that the largest measure of the applied magnetic field effect on the alkali chloride diffusion behavior should be expected in these aqueous solutions which possess the strongest available (over other interaction mechanisms) long range Coulombic forces to interact with the externally applied magnetic field. As a matter of fact, the largest $\bar{D}^*$-values occur (Table 1, Figs. 5–7) at very low concentrations for KCl– and NaCl–$H_2O$ solutions.

### *Microdynamic structural correlations*

Table 1, Figs. 8 and 9 indicate that the observed measure of the magnetic field effect on the diffusional behavior of salts ($\bar{D}^*$-values) may be related to the microdynamical relaxation processes occurring in the hydrated complex of the ion in the aqueous solution. In turn, the relaxation processes of the diamagnetic alkali chloride–water solution are expressed through the reorientational and translational correlation times ($\tau_c$ and $\tau_t$) of the water molecules of this solution. Assuming the validity of the theory of Brownian motion in the diagnetic salt–water solutions, it is possible[21-25] to obtain the well known proportionalities between the total proton relaxation time $T_1^{-1}$ (for alkali chloride–water solutions the longitudinal relaxation time $T^{-1}$ is approximately the same[21-25] as the transverse relaxation time, $T_2^{-1}$), the self-diffusion coefficient of water molecule in solution, $D$, and the shear viscosity, $\eta$, as*:

$$T_1^{-1} \propto D^{-1} \propto \eta \tag{10}$$

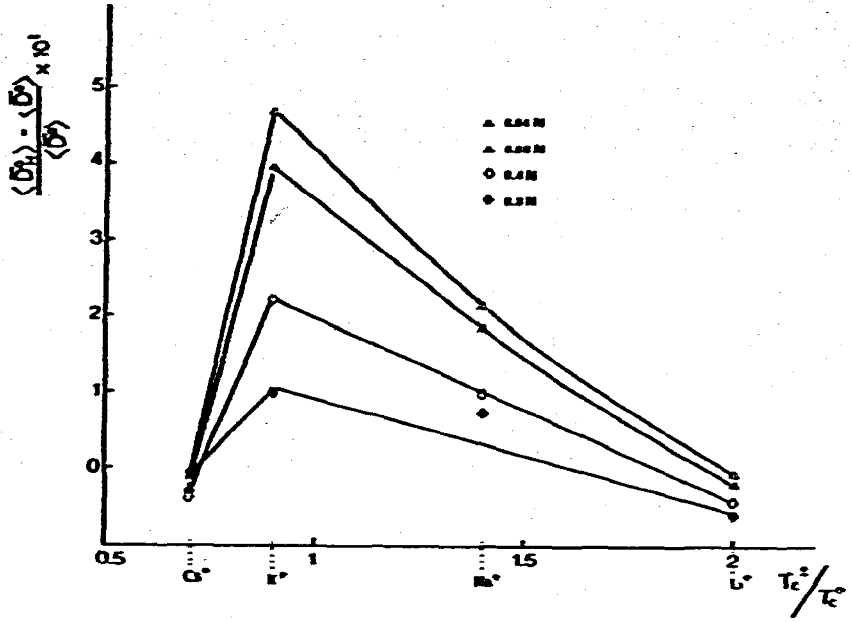

Fig. 8. The $\bar{D}^* = [(\langle \bar{D}_H^o \rangle - \langle \bar{D}^o \rangle)/\langle \bar{D}^o \rangle] \times 100$ plot against the reorientational correlation time ratio, $\tau_c^{\pm}/\tau_c^{o}$. The reorientational correlation time, $\tau_c^{\pm}$ and $\tau_c^{o}$ values taken from ref. 23.

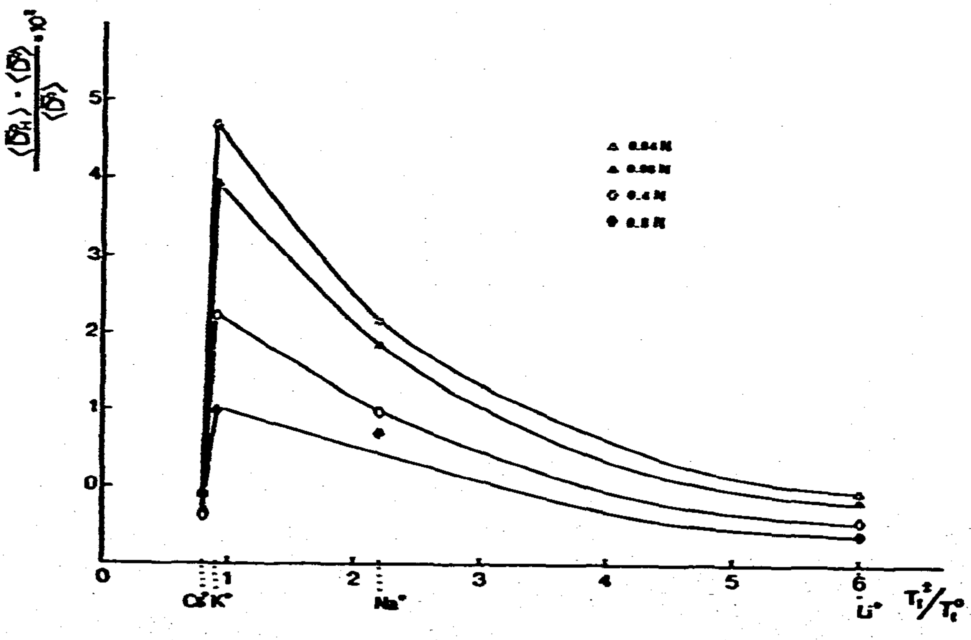

Fig. 9. The $\bar{D}^* = [(\langle \bar{D}_H^o \rangle - \langle \bar{D}^o \rangle)/\langle \bar{D}^o \rangle] \times 100$ plot against the translational correlation time ratio, $\tau_t^{\pm}/\tau_t^{o}$. The translational correlation time, $\tau_t^{\pm}$ and $\tau_t^{o}$, values have been taken from ref. 23.

The experimental total proton spin-lattice relaxation time $T_1^{-1}$ can be separated into two independent contributions:

$$(T_1^{-1})_{\mathrm{exp}} = (T_1^{-1})_{\mathrm{intra}} + (T_1^{-1})_{\mathrm{inter}} \tag{11}$$

where: exp = experimental
intra = intramolecular
inter = intermolecular

The intramolecular relaxation rate, $(T_1^{-1})_{\mathrm{intra}}$ is due to the magnetic dipole–dipole interaction of two protons within the same rotating molecule and following Hertz[21-25], can be written as:

$$\left(\frac{1}{T_1}\right)_{\mathrm{intra}} = \frac{2}{5}\frac{\gamma^4 \hbar^2}{r^6} I(I+1)\left\{\frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+\omega^2\tau_c^2}\right\} \tag{12}$$

where:

$\gamma$ = nuclear gyromagnetic ratio

$I$ = nuclear spin (equal protons, $I=\frac{1}{2}$)

$r$ = intramolecular distance between the two interacting protons in the molecule. It is constant throughout the solution.

$\hbar$ = $h/2\pi$, Planck's constant/$2\pi$.

$\omega$ = nuclear magnetic resonance frequency

$\tau_c$ = rotational ($\approx$ reorientational) correlation time of the water molecule in the hydrated complex (hydration sphere) around the ion.

The high fluidity liquids (water, aqueous solutions) may be characterized by the so-called "extreme narrowing"; that is product $\omega^2\tau_c^2 \ll 1$. Subject to this limiting constraint (letting $\omega^2\tau_c^2 \to 0$), Equation (12) for the diamagnetic alkali chloride–water solution can be rewritten as[21-25]:

$$\left(\frac{1}{T_1}\right)_{\mathrm{intra}} = \left\{(1-x^+-x^-)\left(\frac{1}{T_1^{\circ}}\right)_{\mathrm{intra}} + x^+\left(\frac{1}{T_1^{+}}\right)_{\mathrm{intra}} + x^-\left(\frac{1}{T_1^{-}}\right)_{\mathrm{intra}}\right\}$$

$$= \frac{3}{2}\frac{\gamma_I^4 \hbar^2}{r^6}\left[(1-x^+-x^-)\tau_c^{\circ} + x^+\tau_c^+ + x^-\tau_c^-\right] \tag{13}$$

with: $x^+ = \dfrac{\nu^+ \eta_k^+ c}{55.5}$; $\quad x^- = \dfrac{\nu^- \eta_k^-}{55.5}$

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*Relation (10) is subject to the validity of Bloembergen–Purcell–Pound[27] derivation of nuclear spin relaxation in liquids; the Stokes relation between viscosity $\nu$ and the rotational (reorientational) correlation time and the Stokes–Einstein relationship between viscosity and the translational self-diffusion coefficient

The following notation has been used:

$\left(\frac{1}{T_1^\circ}\right)_{\text{intra}}$ = intramolecular relaxation rate of the free water,

$\left(\frac{1}{T_1^\pm}\right)_{\text{intra}}$ = intramolecular relaxation rates in the hydration spheres of the cation and anion, respectively.

$\tau_c^\circ$ = correlation time of the reorientational motion of the water molecule in the free water,
$\tau_c^\pm$ = correlational time of the reorientational motion of the water molecule in the cationic and anionic hydration spheres, respectively,
$x^\pm$ = mole fractions
$\nu^\pm$ = stoidriometric number (cationic, anionic) of the electrolyte
$\eta_h^\pm$ = hydration numbers of the cation and anion
$c$ = concentration in moles per kg $H_2O$.

While it appears that within its feasibility range[21-25] ($\omega^2\tau_c^2 \rightarrow 0$), Equation (13) is an artifact referring to a set of uniformly distributed non-overlapping hydration spheres; yet the correlation times $\tau_c^\circ$, $\tau_c^\pm$ serve as measures of structure breaking and structure promoting processes in aqueous salt solutions[21-25]. Indeed in view of eqns (7), (10)–(13), Hertz[21-25] has expressed as a first approximation the ratio of reorientational correlation times $\tau_c^\pm$ to the reorientational correlational time in pure water, $\tau_c^\circ$, in terms of ionic coefficients $B^\pm (B = \nu^+ B^+ + \nu - B^-)$ as:

$$\frac{\tau_c^\pm}{\tau_c^\circ} = 1 + \frac{55.5}{\eta_h^\pm} B'^\pm \tag{14}$$

relating the reorientational correlation times in the hydration spheres to the measured initial slopes of the relaxation rates[21-25]. This ratio, when referred to the unity (pure water) classifies the structural properties of the aqueous solution as:

$$\frac{\tau_c^\pm}{\tau_c^\circ} \gtreqless 1.0 \tag{15}$$

Taking ratio $\tau_c^\pm/\tau_c^\circ > 1.0$ (slower reorientational motion than in the pure water) we speak of the structure forming of the solution; but when the ratio $\tau_c^\pm/\tau_c^\circ < 1.0$ (faster reorientational motion), we have structure breaking process of the aqueous solution. Hertz[23] showed that for an ion with a charge $Ze$, the ratio, $\tau_c^\pm/\tau_c^\circ$, may be expressed as a first approximation to be:

$$\frac{\tau_c^\pm}{\tau_c^\circ} = 1 + a' - b' \frac{|Z| e}{r^2} + c' \frac{Z^2 e^2}{r^4} \tag{16}$$

where $a'$, $b'$ and $c'$ are constants; $r$ is the ionic radius; while term $E = Ze/r^2$ is the electric field appearing at the periphery of the ion. From eqn (16), Hertz[23] identified the ionic coefficient $B'^{\pm}$ as:

$$B'^{\pm} = k[a'r^2 - b'e|Z| + c^1 \frac{Z^2e^2}{r^4} \tag{17}$$

Equations (14), (15) and (17) show that the ratio $\tau_c^{\pm}/\tau_c^{0}$ is a measure of the ionic charge (and the associated Coulombic force interactions) taken as a function of the ionic radius. This further indicates that the shape and the charge distribution of the ion are related to the ability of the ion to change the water structure to a configuration of molecules with faster or slower motions. Assuming that in $KCl–H_2O$ solution $B'(K^+) \approx B'(Cl^-)$ is the proper way of separating the $B'$-coefficient in its ionic contributions, $B'^{+}$ and $B'^{-}$, such that $B'\ \nu^+B'^{+} + \nu^-B'^{-}$; Hertz[23] has given for alkali chloride–water solutions a set of $B'^{\pm}$-coefficients:

$$\begin{gathered} Li^+ : B'^{\pm} = 0.14; \quad Na^+ : B'^{+} = 0.06; \quad K^+ : B'^{+} = -0.01; \\ C_s^+ : B'^{+} = -0.05; \quad Cl^- : B'^{-} = -0.01 \end{gathered} \tag{18}$$

Comparing data (Table 1, Equations (17) and (18)), $KCl–H_2O$ solution displays the following microdynamical parameter behavior at 25 °C: $B'^{+} \approx B'^{-}$; $\tau_c^{+} \approx \tau_c^{-}$; so that $B' < 0$ and $\tau_c^{\pm}/\tau_c^{0}$ 1.0. These limiting conditions indicate* that ionic microdynamical parameters of $KCl–H_2O$ solution are almost identical (at 25 °C temperature) with the corresponding quantities in pure water, i.e., it may be thought that the microdynamical behavior of the water molecules in the hydration sphere of $K^+$ and $Cl^-$ ions is alike to that of pure water. Comparing this $KCl–H_2O$ solution behavior with the values of the solution structural stability factor, $-2\langle G \rangle_s$; we recall that $KCl–H_2O$ solution in terms of the listed $-2\langle G \rangle_s$ value (Table 1, Fig. 6) represents the least stable hydrated sphere configuration; that is, the $KCl^-$ salt apparently has a very intense destabilizing effect on the structure of water in aqueous solution. Indeed, it appears that the $KCl–H_2O$ solution possessing almost the same (at 25 °C) correlation times ($\tau_c^{\pm}/T_c^{0} \approx 1.0$; with $B' \approx 0$) as pure water; should also possess the most unstable molecular configuration of the hydration sphere in the alkali chloride–water solution series. This is brought out by Fig. 8 which presents the $\bar{D}^*$-value relation with the reorientational correlation time ratio, $\tau_c^{\pm}/\tau_c^{0}$; once again showing that the highest** $\bar{D}^*$-value is found for

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*This observed nuclear magnetic resonance relaxation behavior has been described[21–25] by idealized models involving fixed hydration number values and well defined correlation times of the aqueous solution.

**That the applied magnetic field may increase the eletrolytic diffusion coefficient value is indirectly indicated by the calculated reduced solution viscosities, $\nu_r^H$ of $KCl–H_2O$ solution (Table 1, ref. 8, 9) obtained at $H = 12$ kG strength and at the 25 °C. The reduced solution viscosity in the applied magnetic field $H$ is defined as $\nu_r^H = \nu^*$ solution$/\nu^*_{H_2O}$; where $\nu^* = [(\nu^H - \nu^0)/\nu^0] \times 10^2$ and $\nu$ is given in centistokes. Comparing $\nu_r^H$ with the reduced solution viscosity $\eta_r$ (measured at the ambient earth magnetic field), we see that the applied magnetic field has decreased the reduced viscosity of solution $\nu_r^H$; even if the absolute values of the solution viscosity and of the pure water had been increased.

the configurationally least stable KCl–$H_2O$ solution. On the other hand, the intermolecular relaxation time, $(T_1^{-1})_{inter}$, (eqn (11)) contribution is thought to be due to the magnetic dipole–dipole interaction between protons on different water molecules diffusing translationally relative to one another in the liquid. Hertz[21–25] gives the following simplified relation for the intermolecular relaxation rate in diamagnetic aqueous solutions:

$$\left(\frac{1}{T_1}\right)_{inter} = \frac{3\pi\gamma_I^4\hbar^2 c_I \tau_t^{-(I)}}{d^3}\left(\frac{1}{3}+\frac{2}{15}\frac{d^3}{\bar{D}_I\bar{\tau}_t^I}\right)+ + \frac{8\pi\gamma_I^2\gamma_s^2\hbar^2 S(S+1)C_s\tau_t^{(Is)}}{3R_{Is}^2}\left(\frac{1}{3}+\frac{2}{15}\frac{R_s^2}{\bar{D}_s\bar{\tau}_t^{(Is)}}\right)+ + \frac{8\pi\gamma_I^2\gamma_s^2\hbar^2 S'(S'+1)c_s'\tau_t^{(Is')}}{3R_{Is'}^2}\left(\frac{1}{3}+\frac{2}{15}\frac{R_{Is'}^2}{\bar{D}_{Is'}\bar{\tau}_t^{(Is')}}\right) \qquad (19)$$

where:

$\bar{\tau}_t^{(I)}$ = average translational jumping time of the proton, concentration dependent
$\bar{\tau}_t^{(s)}$ = average translational jumping time of the ion in the solution, concentration dependent
$\tau_t^{(I,s)} = \frac{1}{2}(\bar{\tau}_t^{(I)}+\bar{\tau}_t^{(s)})$
$\bar{D}_s$ = self diffusion coefficient of the ion, concentration dependent
$\bar{D}_{Is} = \frac{1}{2}(\bar{D}_s+\bar{D}_I)$
$R_{Is}$ = distance of closest approach between the water proton and the ion nucleus. For further nomenclature, see ref. 23.

If $\tau_t^{\pm}$ and $\tau_t^o$ are the mean translational jumping times in the ionic hydration sphere and the free water, respectively, and $\langle r\rangle_\pm$ is the mean square displacement for one translational jump in the ionic hydration sphere; then we may write the following relations between the self-diffusion coefficient and the translational correlation times[21–25]:

$$\tau_t^{\pm} = \frac{1}{6}\frac{\langle r^2\rangle^{\pm}}{D_0^{\pm}} \qquad (20)$$

and:

$$\frac{\tau_t^{\pm}}{\tau_t^o} = \frac{1}{1+\dfrac{55.5}{n_h^{\pm}}D_0^o\left(\dfrac{dD}{dC}\right)^{\pm}_{c\to 0}}$$

where:

$$\left(\frac{dD}{dC}\right)_{c\to 0} = \nu^+\left(\frac{dD}{dC}\right)^+_{c\to 0}+\nu^-\left(\frac{dD}{dC}\right)^-_{c\to 0} \qquad (21)$$

Similarly[21-25] to reorientational correlation time ratios (eqn 1) we may write for the mean translational correlation times that:

$$\frac{\tau_t^{\pm}}{\tau_t^{o}} \gtreqless 1.0 \tag{22}$$

Equation (21) indicates that we have ions for which their translational correlation times are either shorter, longer or equal to those of pure water. Similarly to the behavior of the reorientational motion (eqn (15)); eqn (21) indicates that the aqueous solution structures depending on the added salt may be classified as structure breakers for which $\tau_t^{\pm}/\tau_t^{o}<1.0$; or again, as structure promotors, $\tau_t^{\pm}/\tau_t^{o}>1.0$. This correlation time similarity (eqns 15 and 21) in dynamic microstructural behavior is brought out by Fig. 9 representing the $\bar{D}^{*}$-value $\tau_t^{\pm}/\tau_t^{o}$ ratio plot. Similar to Fig. 8, Fig. 9 shows that the largest magnetic field effect on the electrolyte diffusion in solution is found for the KCl–$H_2O$ solution. Both, the reorientational and the translational correlation times correlate with $\bar{D}^{*}$-values in the same manner. This should not be regarded as a surprise since both of these modes of microstructural molecular motion are formally equivalent[21-25]; and seem to show the same type of configurational instability of the hydrated complex (Figs. 5–7); eqns (3), (8) and (9). The results of solvation spectra analysis[17] by means of the absolute proton magnetic resonance shifts for water protons in alkali chloride–water solutions support the contention that the structural instabilities of the hydrated complex may be largely responsible for the observed magnetic field effect on the electrolyte diffusion in alkali chloride aqueous solutions ($\bar{D}^{*}$-values, Table 1). Fi-

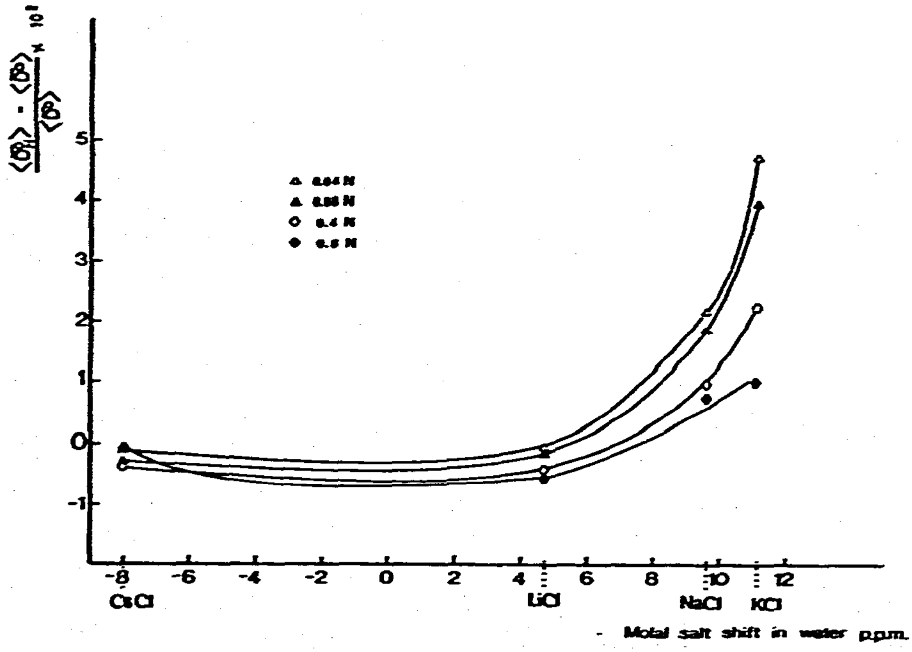

Fig. 10. The $\bar{D}^{*}=[(\langle\bar{D}_H^{o}\rangle-\langle\bar{D}^{o}\rangle)/\langle\bar{D}^{o}\rangle]\times 100$ plot against the molal salt shifts of alkali chlorides in water. The plotted NMR–molal salt shift data have been taken from ref. 17.

gure 10 indicates this by presenting a relation between the $\tilde{D}^*$-values and the molal salt shifts of alkali chlorides in water. The largest $\tilde{D}^*$-value occurs at the maximum disorder (upfield shift[17], compare with eqn (3)) for the KCl–$H_2O$ solution. Figure 10 shows that in terms of molal salt shifts the $\tilde{D}^*$-values increase from CsCl–, LiCl–, NaCl– to KCl–$H_2O$ solution. The microdynamical structural correlations (Figs. 8–10; eqns (11)–(21)) seem to confirm the interpretation of the presented structural property correlations (Figs. 5–7); eqns (3), (7)–(9) that the largest applied magnetic field effect on the salt diffusion in alkali chloride–water solutions should be expected for these solutions which have configurationally the least stable hydrated complexes (hydration spheres) and which appear to be associated with the strongest available residual (in relation to other interaction mechanisms) Coulombic force interactions. Indeed, it does not appear that the observed $\tilde{D}^*$-value changes will follow alone the pattern of somewhat strictly dividing the ionic solutions with reference to the pure water as structure breakers and structure formers[19].

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