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Journal of Colloid and Interface Science 316 (2007) 996–1002
Journal of Colloid and Interface Science
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Effects of a static magnetic field on water and electrolyte solutions

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Received 18 May 2007; accepted 14 August 2007

Abstract

Water and electrolyte solutions were exposed for 5 min to a weak static magnetic field ($B = 15$ mT). Their conductivity and the amount of evaporated water were then measured as a function of time. Simultaneously, these quantities were determined for magnetically untreated samples, as reference systems. It was found that a magnetic field influences these two parameters and their changes depend on the thermodynamic functions of hydration of these ions. A roughly linear change in conductivity versus 'scaled' functions was obtained. On this basis it was concluded that the magnetic field causes changes in the hydration shells of the ions.

Keywords: Magnetic field; Water; Electrolyte solutions; Conductivity; Evaporation

1. Introduction

Numerous papers about the influence of static or alternating magnetic (MF) and electromagnetic (EMF) fields on the physicochemical properties of water or aqueous solutions and suspensions have been published [1–22]. The effects of these fields still attract much research. The changes caused by MF depend on many factors, such as the field strength [1–3,17], the direction of the applied field [13], the time of the magnetic exposure [1,16,17], the flow rate of the solutions [9,10,24], the additives present in the system [6–8,11], and the pH [12,15]. The effects caused by external MF lasted even up to 200 h after the field had ceased [9]. This phenomenon is called a memory effect.

Especially, MF effects on calcium carbonate and calcium sulfate precipitation processes and their suspensions have been investigated extensively [1–15]. This is because of the problem of hard scale formation. It was found that the presence of static MF increases aragonite formation, which is less adhesive than calcite [2,3], altered the ζ potential of colloidal particles [6,7,11,17], and promoted homogeneous precipitation of $CaCO_3$ [21]. However, reproducibility of carried out experiments was very often low.

Different hypotheses regarding the influence of magnetic fields on water and aqueous solutions have been taken into account [5,21,22]. Colic and Morse [21] suggested that effects caused by electromagnetic fields could originate form a perturbation at the gas/liquid interface and the effects disappeared after the system was degassed.

Madsen [5] investigated the influence of a magnetic field on the precipitation of some inorganic salts. He calculated that the Lorenz force on moving ions in solution is too weak to influence a crystallization process to any measurable degree. Also, any perturbation of the electronic structure of the ions may be ruled out. He concluded that a magnetic field might significantly influence only proton spin and MF effects could be seen for diamagnetic salts of weak acids. The longitudinal relaxation time (T1) of proton spin in pure water is about 3 s and it can decrease for paramagnetic ions in the presence of external MF; for example, in 0.05 M Mn^{2+} it may amount less than 1 ms.

Higashitani and Oshitani [22], using AFM, examined the influence of MF on the short-range interaction force between a mica surface and an AFM probe tip in electrolyte solutions. They found that magnetic effects appeared mostly in solutions consisting of structure-disordering cations. They suggested that water molecules weakly bonded at such cations were quasi-stabilized and structured and that applied MF thickened the layer of the structured cations on the mica surface.

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doi:10.1016/j.jcis.2007.08.026

Murad [23], based on molecular simulations, examined the effect of external MF on transportation of water molecules across membranes using reverse osmosis. He concluded that magnetic fields, like electric ones, could play an important role in weakening water and hydrated ion clusters.

In our earlier paper [11] studying simple inorganic electrolytes, we found a linear relationship between changes in their electric conductivity and the entropy or Gibbs free energy of the ion hydration. The aim of this work is to investigate whether a relatively weak static magnetic field ($B = 15$ mT), originating from a stack of magnets, could influence conductivity and the evaporation of water from aqueous solutions of selected inorganic electrolytes.

2. Experimental

2.1. Materials

The inorganic salts NaCl, KCl, Na_3PO_4, and $CaCl_2$ were of p.a. grade from POCH S.A., Poland and were used as received. All the solutions were prepared using doubly distilled water, which was then deionized using a Millipore Q-Plus 185 system. All solutions were stored in polyethylene flasks to avoid any contamination coming from glass surfaces.

2.2. Magnetic exposure

The equipment for exposure to magnetic fields consisted of two identical polyethylene columns of diameter 60 mm and length 500 mm (Fig. 1A). Inside one of them a stack of permanent magnets of total height 410 mm and diameter 35 mm was placed ($B = 15$ mT). The "tubular magnetic apparatus (RAM)" was kindly supplied by Poland Feniks, Gliwice, Poland (Patent PL 155856). The stack consisted of 29 magnets and nonmagnetic separating elements arranged convertibly as shown in Fig. 1B. To protect the solution from the contact with the metal surface of the magnet, it was laminated with a polyethylene foil. Experiments were conducted simultaneously, one in the column without any magnets (the reference system), and another in the column with the magnetic stack. A sample of 0.5 dm^3 of the examined solution was poured into each of the polyethylene columns and sealed to avoid any contact with air. After a due time the examined solutions were removed via a Teflon tap, and conductivity and amount of evaporated water were investigated. For each solution tested the experiments were repeated five to seven times at 20 ± 1 °C.

2.3. Measurements

The conductivity was measured using a multiparametric system (ELMETRON CX-731) equipped with probe electrodes (the cell constant $K = 0.5\ cm^{-1}$). Right after the solution flowed out from the column a part of it was taken in a polyethylene vessel, which was immediately covered with a cap to avoid contact with air. Then the conductivity of the solution was measured for 30 min.

Simultaneously with the conductivity measurements, the amounts of evaporated water were also measured. For this purpose 20 cm^3 of the same MF-treated or MF-untreated samples were poured into polyethylene vessels. The surface of the evaporating water (the cross-section of the vessel) equaled ca. 17 cm^2. After 3 min since the moment the solution was placed in the vessel, it was covered and weighed (Sartorius BP 211 D, sensitivity 0.1 mg) for the first time. This weight of MF-treated or MF-untreated sample was the reference system for the next weighing. The next weighings were done after 7, 17, 27, and 37 min. The vessel with water or tested solution was covered only during the time of weighing. Then the evaporated amounts of water, from both the MF-treated and MF-untreated samples, were calculated as the differences between the sample weights. The differences in the weights were determined after 10–3, 20–10, 30–20, and 40–30 min; i.e., the determined water evaporation time intervals were 7, 10, 10, and 10 min.

3. Results and discussion

Prior to experiments with the electrolyte solutions, it seemed interesting to learn whether any MF effect would appear in

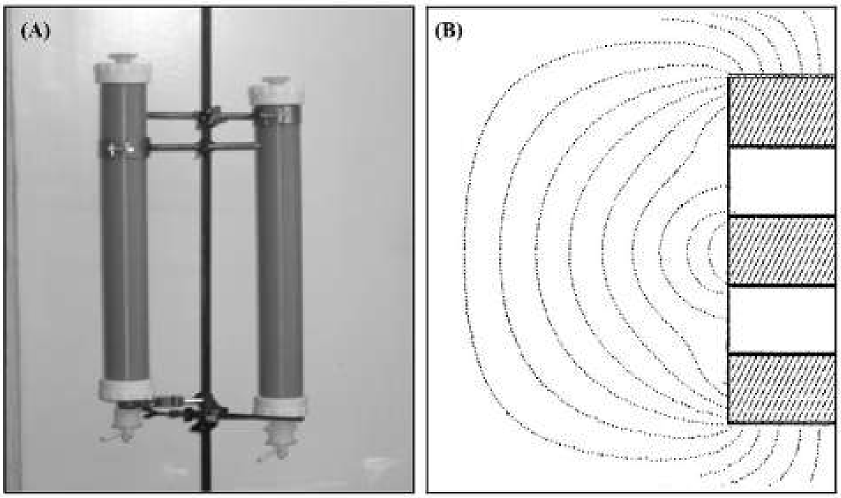

Fig. 1. (A) Photograph of the equipment for magnetic field treatment; (B) the direction of the applied magnetic field.

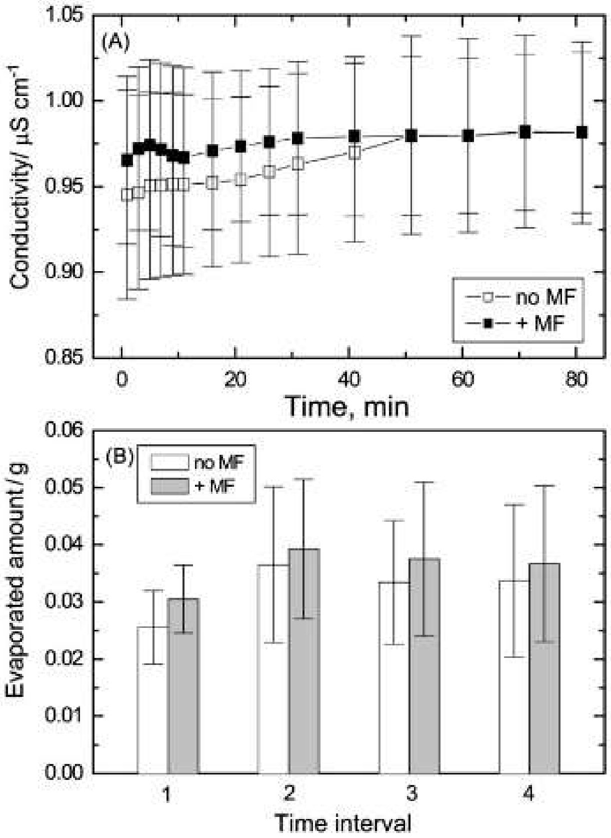

Fig. 2. Changes of conductivity (A) and evaporated amount (B) of water caused by exposure to MF for 5 min vs time.

changes of conductivity and evaporation of pure water. The results are presented in Figs. 2A and 2B, respectively. The conductivity changes and their calculated standard deviations are obtained on the basis of five replicated experiments for 5-min MF-treated and MF-untreated samples. It is seen that for MF-treated samples some increase in the conductivity relative to MF-untreated samples appears. However, the changes are within standard deviations and after 50 min, and up to 80 min, both samples show exactly the same conductivity. Moreover, it should be noted that the conductivity of MF-untreated samples increases slightly during the first 50 min, while that of MF-treated samples is practically constant (Fig. 2A). The conductivity measurements were performed in closed polyethylene vessels. The increase in conductivity of untreated water, whose pH was 6.0, is actually very small, $2 \times 10^{-8}\ \mathrm{S\,cm^{-1}}$ (that is, its resistance decreases from 1.053×10^6 to $1.031 \times 10^6\ \Omega\,\mathrm{cm}$). This might be due to some ionic impurities that can dissolve from the electrodes and/or adsorb onto the polyethylene vessel surfaces. Also, possibly some CO_2 from the atmosphere of the closed vessel would dissolve in the solution during the experiment. Practically constant conductivity of MF-treated water may result from a compensating effect of the above-mentioned reasons. Therefore, it seems that the lower arithmetic mean conductivity of untreated water sample observed during the first 50 min can be ascribed to MF effect. The large standard deviations suggest that changes, if they occur at all, reflect their highly dynamic character.

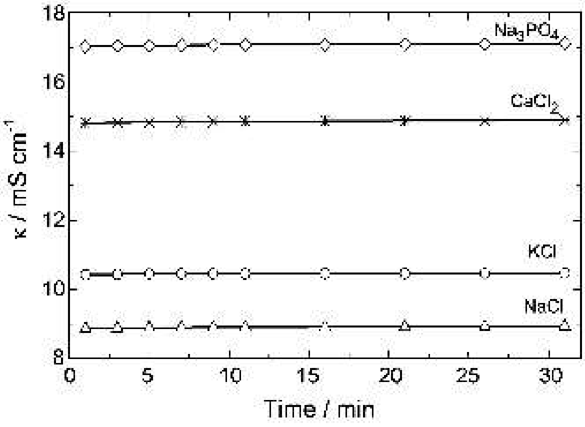

Fig. 3. Changes in the conductivity of 10^{-1} M electrolyte aqueous solutions as a function of time.

In Fig. 2B, the changes in evaporated amounts are depicted for MF-treated and untreated water samples. The changes are presented in the form described earlier in Section 2. Similarly, in the case of conductivity the standard deviations are relatively high, and they overlap for both samples. But again, a clearly visible trend is observed that evaporated amounts are higher for MF-treated samples and the differences are practically constant during the 37 min of the experiment. Because evaporation of a liquid is related to the work of cohesion, which for water equals $W_c = 2\gamma_L = 2 \times 72.8 = 145.6\ \mathrm{mN\,m^{-1}}$ at 20 °C, the increase in evaporated amount of water after MF treatment during the same time period can be regarded as a weakening of the intermolecular forces, in this case the hydrogen bonding. The conductivity of pure water is due to the presence of tiny amounts of H^+ ions, i.e., about 10^{-6} M, and even fewer OH^- ions (10^{-8} M) and/or HCO_3^- ions. Hence, it can be hypothesized that the slight increase in the conductivity seen in Fig. 2 may be due to weakening of the hydration shell around these ions [5,11,22,24]. If this mechanism really takes place after MF treatment one may expect that this effect can be magnified in an electrolyte solution. Therefore, in Fig. 3 there are shown conductivities of 10^{-1} M investigated solutions, which were measured for 31 min. The conductivities are constant during this time, which means that the measured experimental conditions are stable. During the same time, the amounts of evaporated water from the same electrolyte solutions are shown in Fig. 4A. In this figure is also plotted the evaporated amount of pure water. Only in the case of KCl is more water evaporated from the solution than from pure water. These changes can be related to the presence of so-called structure-ordering or -disordering ions in the solutions. In Table 1 is shown which ions are water-structure-ordering or -disordering [24,25].

As is seen, both K^+ and Cl^- are water-structure-disordering, contrary to Na^+ and PO_4^{3-}, which are water-structure-ordering. The amounts of evaporated water from NaCl and $CaCl_2$ solutions are a little lower than those from pure water. In these solutions Na^+ and Ca^{2+} are water-structure-ordering and Cl^--disordering. These results clearly show that evaporation of water from the solutions depends on the water-ordering or -disordering role of the cations and anions present. The MF

Table 1

The radius r, the radius of the hydration shell Δr, the scaled shell thickness $\Delta r/r$, a hydration number n (water molecules hydrating the ion), and the molar Gibbs free energy, enthalpy, entropy, and heat capacity of hydration of water-structure-ordering or -disordering ions [24,25]

Ion	Water-structure-ordering (+) or -disordering (−)	r [Å]	Δr [Å]	$\frac{\Delta r}{r}$	n	$-\Delta\text{hyd}G^*$ [kJ mol^{-1}]	$-\Delta\text{hyd}H^*$ [kJ mol^{-1}]	$-\Delta\text{hyd}S^*$ [J K^{-1} mol^{-1}]	$-\Delta\text{hyd}C_p^*$ [J K^{-1} mol^{-1}]
K^+	(−)	1.38	0.74	0.54	2.6	295	330	93	72
Na^+	(+)	1.02	1.16	1.14	3.5	365	415	130	42
Ca^{2+}	(+)	1.00	1.71	1.71	7.2	1505	1600	271	183
Cl^-	(−)	1.81	0.43	0.24	2.0	340	365	94	70
PO_4^{3-}	(+)	2.38	0.54	0.23	4.5	2765	2875	440	341

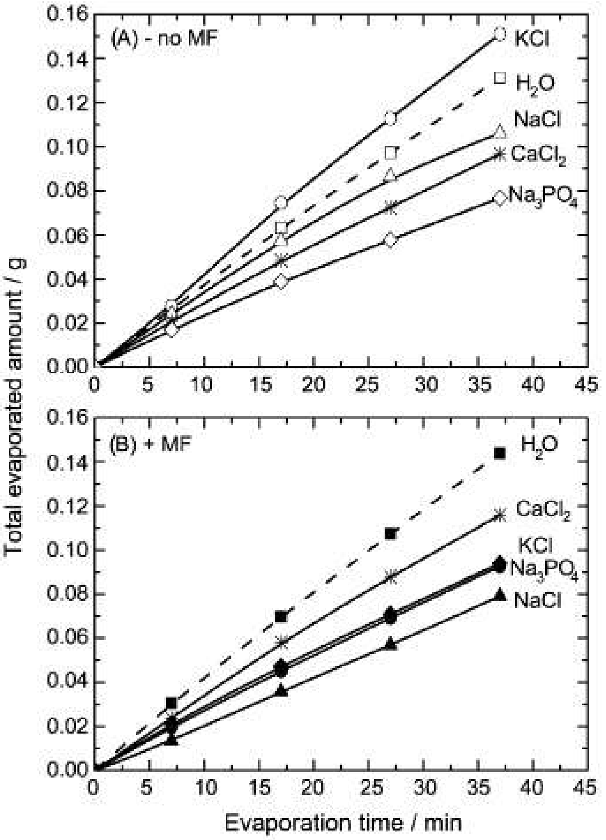

Fig. 4. Changes in the total amount of water evaporated from MF-untreated (A) and MF-treated (B) pure water and 10^{-1} M electrolyte aqueous solutions as a function of time.

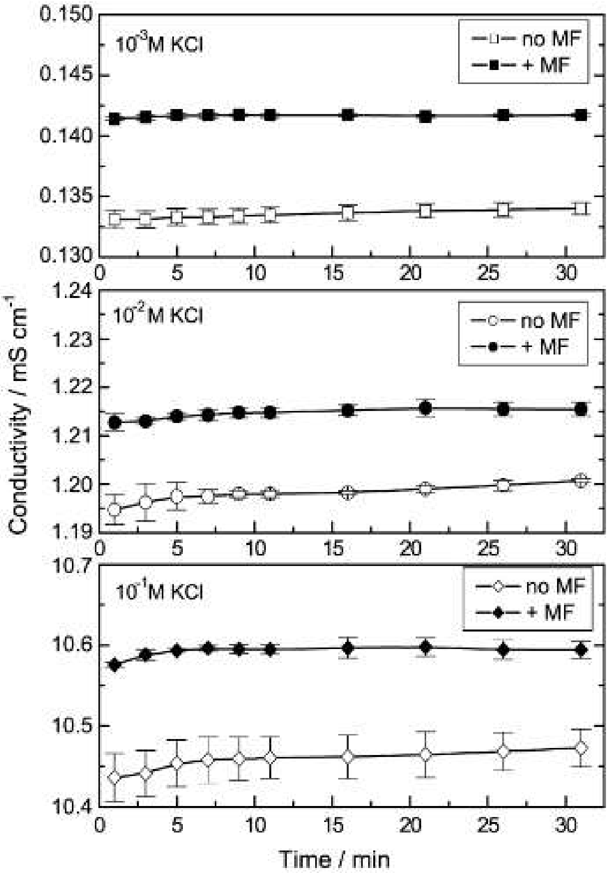

Fig. 5. Changes in conductivity for 10^{-3}–10^{-1} M KCl solutions for MF-untreated and MF-treated solutions vs time.

effects on total evaporated amount of water from 10^{-1} M solutions treated for 5 min are presented in Fig. 4B, where from all the solutions the evaporated amounts of water are less than for pure water. Here the weakest MF effect is observed for $CaCl_2$ and the strongest appears for NaCl. In the solutions Ca^{2+} and Na^+ cations are water-structure-ordering and Cl^- anions disorder it. In the case of KCl and Na_3PO_4, in which both ions are water-structure-disordering or -ordering, respectively, the MF effect is the same in comparison to pure water. However, from KCl MF-untreated solution the water evaporated amounts are greater than those from pure water, so for the evaporation from MF-treated solutions the amounts of evaporated water are lower. After 37 min they are 0.1815 and 0.0927 g, respectively. The evaporated amounts from pure water are 0.1313 and 0.1439 g for MF-untreated and -treated samples, respectively.

Again, the observed changes in the evaporation (total amount) of water can be explained assuming weakening and/or strengthening of the cohesion forces between water molecules, i.e., hydrogen bonding.

As an example, to better visualize the MF effect, in Figs. 5 and 6 are plotted changes in the conductivity and evaporated amounts of water from 10^{-3}–10^{-1} M solutions of KCl, for which the greatest changes in evaporated amount of water appeared (Figs. 4A and 4B). Parallel relative changes in the conductivity in all three studied KCl solutions are seen in Fig. 5 for MF-treated and MF-untreated solutions. In fact, the differences in the amount of evaporated water from these solutions are also roughly constant during 10-min periods, which are shown in Fig. 6. It is worth noting that the standard deviations in Figs. 5 and 6 are small and the changes are statistically significant.

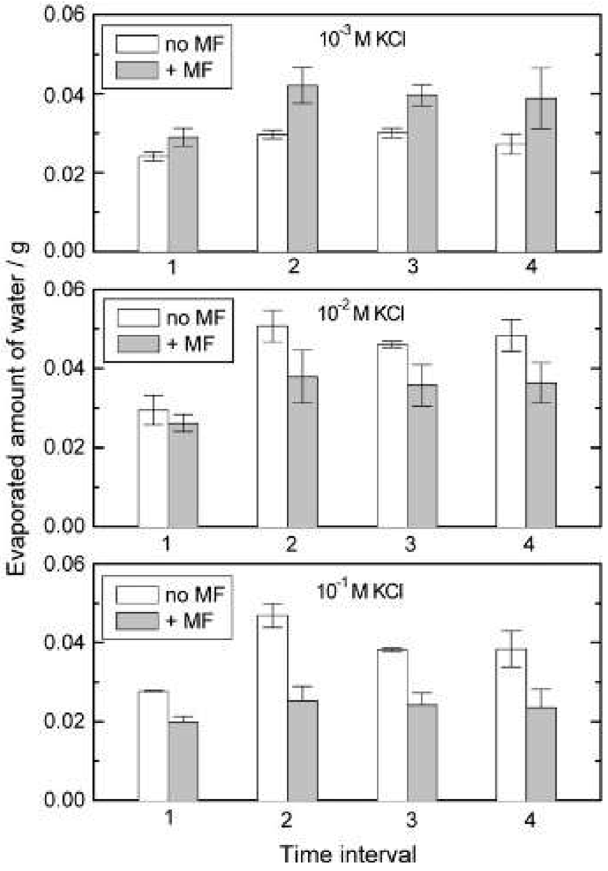

Fig. 6. Changes in the amounts of water evaporated from MF-untreated and MF-treated 10^{-3}–10^{-1} M KCl solutions in subsequent 10-min intervals, expect for 1, which deals with the 7 min after the MF ceased.

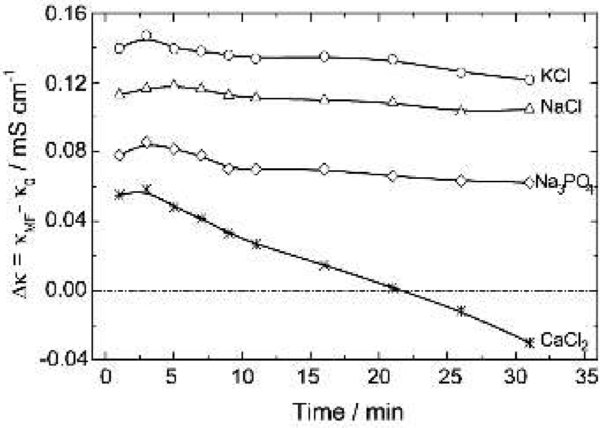

Fig. 7. Differences between conductivity of MF-treated and MF-untreated 0.1 M electrolyte aqueous solutions as a function of time after the MF ceasing.

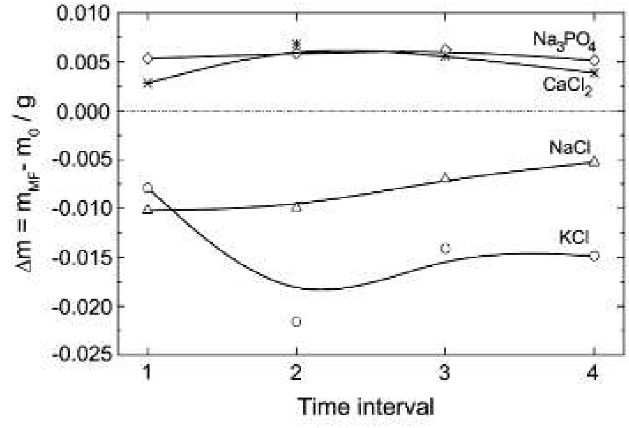

Fig. 8. Differences between the amounts of water evaporated from MF-untreated and MF-treated 0.1 M electrolyte aqueous solutions in subsequent 10-min intervals, expect for 1, which deals with the 7 min after the MF ceased.

Next, in Fig. 7 are plotted differences in conductivity between MF-treated and MF-untreated 10^{-1} M solutions of the investigated electrolytes that were measured during 37 min. Expect for $CaCl_2$ solutions, $\Delta\kappa$ values are positive and practically constant during this time. Only in the case of $CaCl_2$ do initially positive differences in conductivity decrease during 20 min, and then $\Delta\kappa$ values become increasingly negative. The conductivity of an electrolyte solution is inversely proportional to the diameter of the hydrated cation and anion and proportional to their valency. As seen in Fig. 7, increase in conductivity ($\Delta\kappa > 0$) for particular electrolytes can be regarded as due to change in the ion hydration shell thickness, as well as some changes in the water structure in the shell. The greatest $\Delta\kappa$ change appears for KCl solution (Fig. 7), in which both ions are water-structure-disordering (Table 1). Then $\Delta\kappa$ is less for NaCl, in which Na^+ is the structure-ordering and Cl^- is the structure-disordering ion. Next, smaller changes in $\Delta\kappa$ are observed for Na_3PO_4, in which $3Na^+$ and PO_4^{3-} ions are water-structure-ordering. However, considering this mechanism, it is difficult to explain the changes in the conductivity of $CaCl_2$ solution and their dynamic nature. In Fig. 8, differences in the amounts of evaporated water from 0.1 M solutions due to MF treatment for the subsequent three 10-min time intervals and the 7-min first one are plotted. It is seen that to fourth intervals differences are practically the same for Na_3PO_4 and $CaCl_2$ and are positive, while those for NaCl and KCl are negative and different, although also roughly constant for these three time periods. It may be noted that MF treatment of Na_3PO_4 and $CaCl_2$ solutions causes an increase in the evaporated water, while in the case of KCl and NaCl the field depresses the amount of evaporated water. Moreover, there is not a straight correlation between $\Delta\kappa$ and Δm (Figs. 7 and 8), although some general features of the solutions behavior can be seen.

To find any reason for the changes observed in Figs. 7 and 8 it may be expected that the thickness of the hydration shell (Δr) (Table 1) can shed a light. Among the investigated ions Ca^{2+} possesses the greatest Δr, amounting to 1.71 Å, while that of Cl^- is only 0.43 Å. On the other hand, Δr for the PO_4^{3-} ion is also small, 0.54 Å, and for Na^+ it is 1.16 Å [24]. Comparing these values, it is seen that the Ca^{2+} ion possesses the thickest hydration shell, while Cl^- has the thinnest. Hence, it may be concluded that the small MF effect on the conductivity of $CaCl_2$ solution is somehow due to the thick and ordered water shell around the Ca^{2+} ion. Because around Cl^- the water shell is thin and water is disordered (Table 1), the resulting MF effect on the solution conductivity may change on this time scale. Verification of this hypothesis needs more analogous experiments with other electrolyte solutions.

As was mentioned in the Introduction, Higashitani and Oshitani [22] have also found that magnetic effects appeared mostly in solutions containing structure-disordering cations. They hypothesized that "around structure-disordering ions" the hydrating water molecules "are quasi-stabilized and structured by magnetic exposure" and that thickening of the adsorbed layer on mica, as determined with AFM, was caused by adsorption of those structured ions. Because any change in the electrolyte conductivity at constant temperature, pressure, and solution composition in fact results from the change in the hydrated ion radius, we concluded that the increases in conductivity observed after MF treatment were due to decrease of the radius. In other words, the hydrating water might be more structured, which is actually in agreement with the hypothesis of Higashitani and Oshitani [22]. However, as was discussed above, the MF seems to weaken cohesive forces between water molecules at water/air interface.

Finally, we looked for some relationship between the observed changes in the conductivity of the solutions and thermodynamic functions describing the ion hydration in aqueous solution. First, in Fig. 9A are plotted changes in $\Delta\kappa$ measured after 3 and 31 min versus the sum of the water-molecule-hydrating cations and anions, which were taken from the paper by Marcus [24] (Table 1). It appeared that the relationship for the three chlorides is quite linear, but $\Delta\kappa$ of the Na_3PO_4 solution, in which both cations and anions are water-structure-ordering (Table 1), deviates from this relationship. Then, in Fig. 9B are plotted $\Delta\kappa$ values versus the sum of entropy of hydration of the cation and anion constituting a particular salt, also for $\Delta\kappa$ after 3 and 31 min since the MF was removed. Again, expect for Na_3PO_4, the relationship is linear. With increasing negative $\Delta\mathrm{hyd}S^*$ of the ions the MF effect on the conductivity is lower. The lower negative values of $\Delta\mathrm{hyd}S^*$ mean that the water structure around the ions is more ordered, and therefore MF influences it less. However, $\Delta\mathrm{hyd}S^*$ for Na_3PO_4 is more negative than that for $CaCl_2$ (Table 1), but $\Delta\kappa$ is higher than in $CaCl_2$ solution. As was mentioned above, in Na_3PO_4 solution there are four water-structure-ordering ions in each molecule. It should be mentioned that in our previous paper [11] similar linear relationships were found for a larger number of chloride salts of mono and bivalent cations. However, the $\Delta\kappa$ values were somewhat different, which might result from the fact that those solutions were treated for 20 min with a stronger MF (0.4 T) and the solutions were outgassed prior to MF treatment. These relationships indicate that the changes in the electrolytes' conductivity after MF treatment can be related to changes in the hydration shell around the ions, and it seems that they may last for a period of time. It was intriguing why $\Delta\kappa$ of Na_3PO_4 solution does not fit into the linear dependence of $\Delta\kappa$ vs number of water molecules hydrating the ions, as well as changes in the total entropy. Seeking for some explanation of this behavior, we took into account the scaled shell thicknesses, which were defined as $\Delta r/r$, where Δr is the thickness of the shell and r is the radius of bare ion. The calculated total (anions plus cations) hydration $\Delta\mathrm{hyd}G^*$, $\Delta\mathrm{hyd}H^*$, and $\Delta\mathrm{hyd}C_p^*$ functions are plotted in Figs. 10A–10C. Now, surprisingly, for all four electrolytes the relationships of $\Delta\kappa$ vs the quantities thus calculated are roughly linear, both those measured after 3 and 31 min of the MF ceasing. The best linear fit is that of $\Delta\kappa$ vs $\Delta\mathrm{hyd}C_p^*$. These results again support the hypothesis that magnetic fields cause changes in the hydrating water structure. Although the changes in the hydration thermodynamic functions caused by MF cannot be evaluated in these experiments, the linear changes in the solution conductivity versus their original values clearly indicate that they are determining parameters. The effect is proportional to the relative thickness of the shell and depends also upon the nature of the ion, i.e., whether it is water-structure-ordering or -disordering.

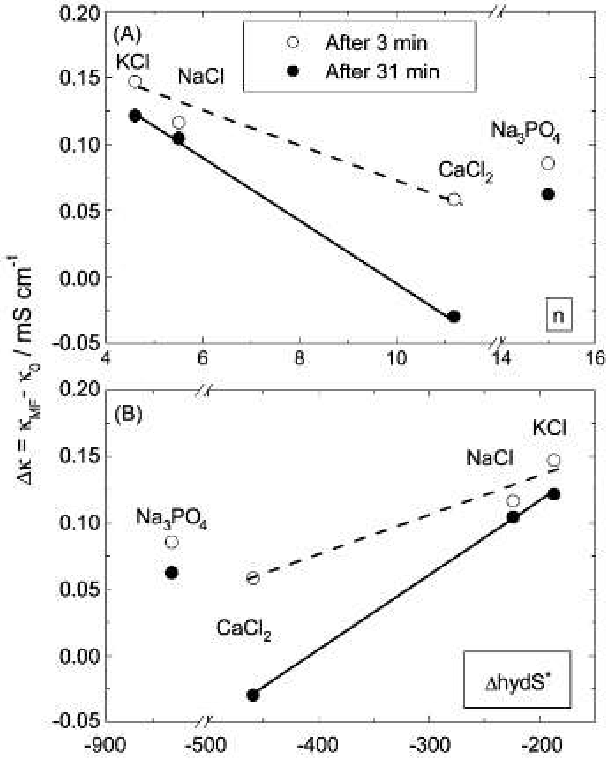

Fig. 9. Differences between the conductivity of MF-treated and MF-untreated 0.1 M electrolyte aqueous solutions as a function of the sum of water-molecule-hydrating cations and anions and the entropy of hydration of ions after 3 and 31 min from the MF ceasing.

4. Conclusions

The results presented show that magnetic fields cause changes in the conductivity of electrolyte solutions, as well as in the amounts of evaporated water from the solutions. These effects depend on the nature of the ions present in the solutions and are proportional to the thickness of the hydration shell around the ions and thermodynamic functions of hydration. It is suggested that MF treatment causes changes in the hydrating water structure around the ions.

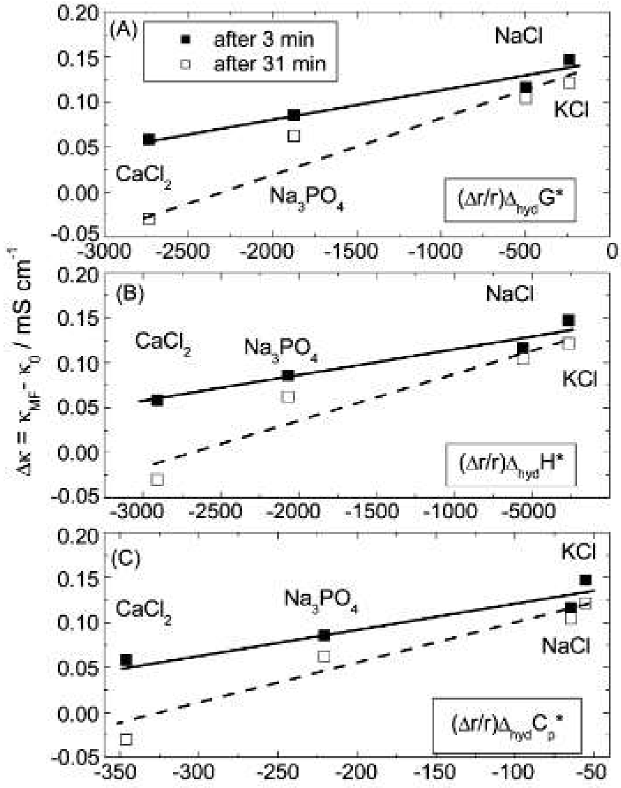

Fig. 10. Differences between conductivity of MF-treated and MF-untreated 0.1 M electrolyte aqueous solutions as a function of the scaled shell thickness $(\Delta r/r)$ and the molar Gibbs free energy, enthalpy, and heat capacity of hydration of cations and anions after 3 and 31 min from the MF ceasing.

Acknowledgment

We thank Jerzy Wazny for his kind supply of the magnetic device used in these experiments.

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