

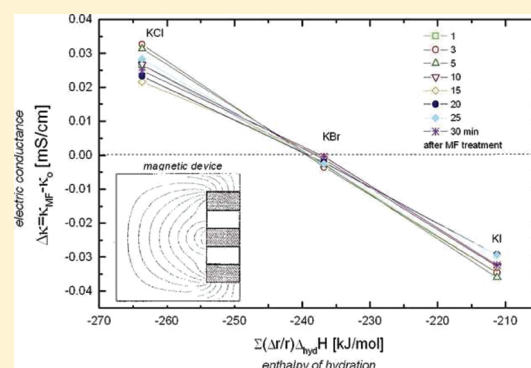
# Effects of Static Magnetic Field on Electrolyte Solutions under Kinetic Condition

A. Szcześ,<sup>\*,†</sup> E. Chibowski,<sup>†</sup> L. Hołysz,<sup>†</sup> and P. Rafalski<sup>‡</sup>

<sup>†</sup>Department of Physical Chemistry-Interfacial Phenomena, Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin 20-031, Poland

<sup>‡</sup>Institute of Agrophysics Polish Academy of Sciences, Doswiadczalna 4, Lublin 20-290, Poland

**ABSTRACT:** Electrolyte solutions were exposed for different time to weak static magnetic field (MF) generated from a stack of magnets ( $B = 15$  mT) at the flow rate of 1.4 mL/s. The conductivity was measured as a function of time following the application of MF. It was found that the changes in conductivity depend on the kind of electrolyte and the magnetic exposure time and are related to the thermodynamic function of hydration.



## 1. INTRODUCTION

Magnetic water treatment is of great interest as a nonchemical and inexpensive method that can be used to prevent the scaling problem. Because of its practical aspect, MF influence on the calcium carbonate crystallization is well-described.<sup>1–9</sup> Recently, also the positive influence of the stationary magnetic field on the plant seeds was established.<sup>10,11</sup> Besides many papers dealing with this problem,<sup>12–27</sup> magnetic field effect on water and aqueous solutions is still controversial, and its mechanism is investigated.

On the basis of the infrared adsorption spectrum and Raman spectrum of magnetized water, Pang and Deng<sup>12,13</sup> found that static magnetic field causes changes only in the distribution and polarization of the molecules but not in the constitution of water.

Comparing the theoretical calculation with measurement of viscosity, enthalpies, and surface tension of water after MF treatment, Toledo et al.<sup>14</sup> concluded that MF induces breaking of the larger clusters and forming smaller ones, with stronger intercluster hydrogen bonds. Nakagawa et al.<sup>15</sup> found that the MF enhances the water vaporization in air, and the magnitude of these effects depends on the field gradient product  $B \cdot dB/dx$ , and the maximum of the vaporization rate increment is asymmetric to the field axis. Moreover, this effect does not appear in nitrogen. Similar effect was also obtained by Szcześ et al.<sup>20</sup> Colic and Morse<sup>16</sup> suggested that the electromagnetic field perturbs the gas/liquid interface.

Cefalas et al.<sup>3,17</sup> explained MF action on water on the basis of quantum field theory. According to this model, the energy of the electromagnetic field is amplified locally by an ensemble of individual water molecular rotors first, forced by the external MF to rotate coherently; then, it is stored in a water's antisymmetric

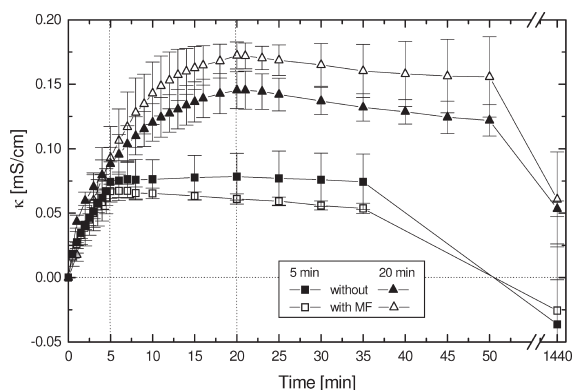
coherent state due to a symmetry-forbidden transition between the excited antisymmetric coherent state and the ground symmetric coherent one. Therefore, the water molecules and other solubles are placed in a local thermodynamic state of different free energy (Gibbs) than the thermodynamic state at zero magnetic field. The model interprets both the descaling processing of water flow surfaces by forming aragonite in water solutions instead of calcite and the memory effects.

Recently, computer simulations have also been used as a valuable tool to study the external magnetic field influence on water systems at the molecular level.<sup>25,26</sup> Using Monte Carlo, simulations Zhou et al.<sup>25</sup> showed that at a magnetic flux density of 0.2 T changes greatly the internal energy and heat capacity of water. Chang and Weng<sup>26</sup> performed molecular dynamic simulations to investigate MF effects on aqueous NaCl solution at 298 K. They found that the magnetic field enhances the  $\text{Na}^+$  and  $\text{Cl}^-$  ions mobility in both low (1 M) and high (5 M) concentrations. However, the average number of hydrogen bonds increases in a solution of low concentration, and on the contrary, the field decreases the number of bonds in the highly concentrated solution.

Cheng et al.<sup>27</sup> exposed NaCl solutions to stationary and alternating MF for 1 h, and they recorded the electrical conductivity increase at different solution concentrations. On the basis of these results, they suggest that the hydrated layer of the ions is broken and the electrophoretic effect in electrolyte solutions is weakened. Hołysz et al.<sup>18</sup> examined the conductivity

Received: March 1, 2011

Revised: April 28, 2011



**Figure 1.** Changes in conductivity of 0.1 M  $\text{CH}_3\text{COONa}$  solution caused by exposure to MF for 5 and 20 min versus time.

of water and simple inorganic electrolytes under static conditions, and they found after the static magnetic field action a roughly linear change in the conductivity versus “scaled” thermodynamic functions of the ion hydration. The biggest increase in conductivity after MF action was detected for the electrolytes containing “water structure disordering ions”, which was in agreement with the results obtained by Higashitani and Oshitani.<sup>19</sup>

It seemed interesting whether such effect would appear in the case flowing condition. Therefore, in this Article, the effect of static MF on the conductivity of 0.1 M aqueous solutions of different electrolyte under flow conditions has been investigated.

## 2. EXPERIMENTAL SECTION

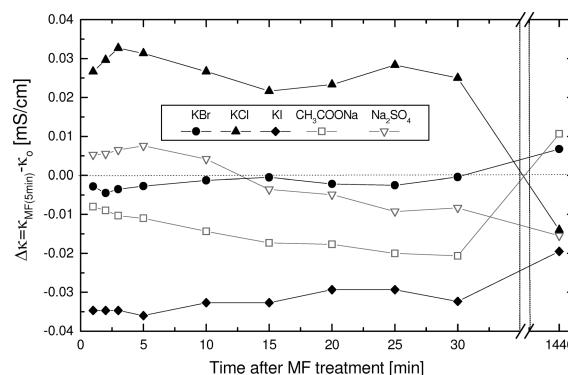
**Materials.** The inorganic salts KCl, KBr, KI,  $\text{Na}_2\text{SO}_4$ , and  $\text{CH}_3\text{COOH}$ , were of p.a grade from POCH S.A., Poland and were used as received. Doubly distilled water, deionized with a Millipore Q-Plus 185 system was used for the experiments. All solutions were stored in polyethylene flasks to avoid any contamination coming from glass surface.

**Magnetic Exposure and Measurements.** A magnetic stack ( $B = 15$  mT) consisting of 29 magnets separated by nonmagnetic elements arranged alternately, 3.5 cm in diameter and 41 cm long, was kindly supplied by Feniks, Gliwice, Poland (patent PL 155856). The magnetic system arrangement and the details of measurements were described in our previous paper.<sup>20</sup> In brief, all tested samples (100 mL each) circulated by means of peristaltic pumps in a plastic silicone tube (internal diameter 3 mm, external diameter 5 mm, length 240 cm) at the linear flow rate of 1.4 mL/s for 5 and 20 min through the MF system.

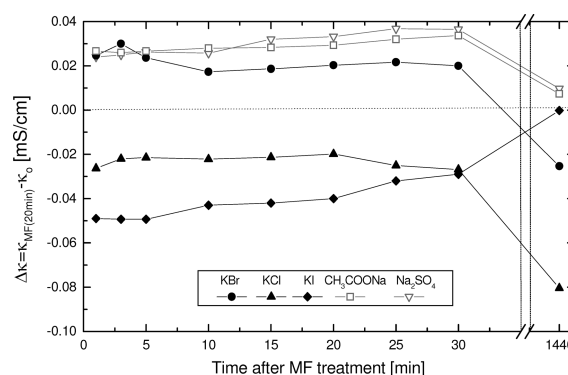
The conductivity was measured prior to the circulation of the electrolyte solutions, during the circulation, and up to 24 h after the circulation, respectively. The experiments were repeated three to five times at  $23 \pm 1$  °C.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the change in conductivity versus time for a 0.1 M solution of sodium acetate circulated in the presence of the magnetic field for 5 and 20 min as well as without MF. It is seen that the conductivity changes depend on the time of MF treatment. However, after shorter exposition to the magnetic field (5 min), the conductivity is lower in comparison with the reference system (without MF), but prolongation of the



**Figure 2.** Differences in conductivity of 0.1 M electrolyte aqueous solutions caused by the exposure to MF for 5 min versus time after exposure.



**Figure 3.** Differences in conductivity of 0.1 M electrolyte aqueous solutions caused by exposure to MF for 20 min versus time after the treatment.

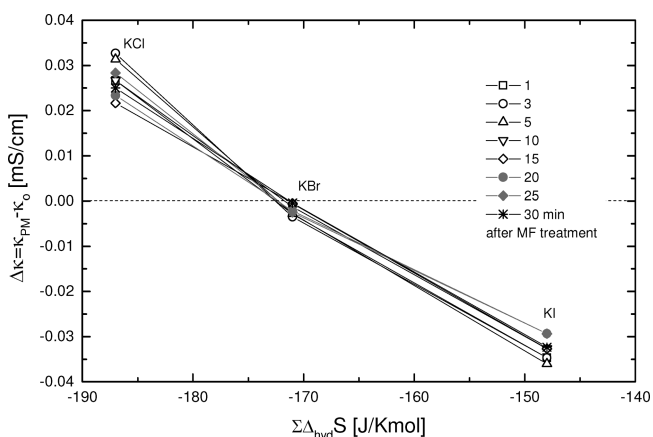
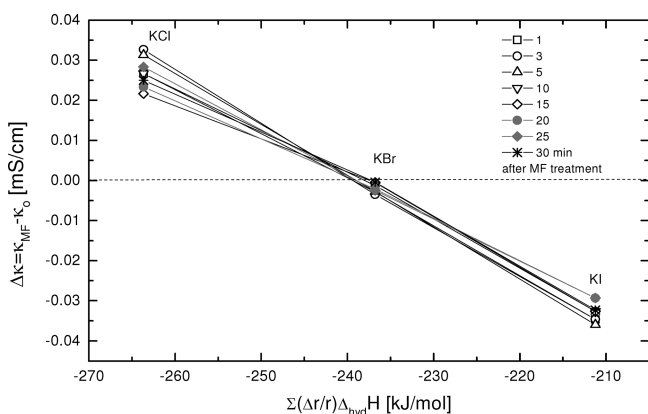
circulation time and the magnetic exposure causes the conductivity increase relative to the reference system. It is worth noticing that the changes in conductivity after the MF action are greater than the standard error. Moreover, conductivity of the reference system increases after 20 min of circulation relative to after 5 min of circulation. This is probably caused by some conducting impurities originating from the plastic pipe material. However, some “dynamic effects”, for example, temporary affecting the ions hydration, also seem to be possible. Therefore, in the Article to follow we will investigate the effect of the pipe material (using soft Teflon pipes) and more durations of the circulation of the solutions without and with the MF presence.

To better visualize the effect, in Figures 2 and 3 is shown the difference in conductivity ( $\Delta\kappa = \kappa_{\text{MF}} - \kappa_0$ ) of the 0.1 M aqueous solutions of the tested electrolytes exposed to MF for 5 and 20 min, respectively, and at the flow rate of 1.4 mL/s. Conductivity of the magnetized sample is denoted as  $\kappa_{\text{MF}}$  and that of the sample without MF action is denoted as  $\kappa_0$ .

After the given time period, the solution flow was stopped, and the sample conductivity was measured up to 24 h. The investigated electrolytes consist of both “water structure ordering ions” ( $\text{Na}_2\text{SO}_4$  and  $\text{CH}_3\text{COONa}$ ) and “water structure disordering ions” (KI, KBr, KCl). From these figures, it can be seen that only for the KI solution did MF cause the conductivity decrease irrespectively of the duration to magnetic field exposition. Moreover, the change in  $\Delta\kappa$  for KI solution is the biggest in comparison with the other investigated electrolytes solution.

**Table 1.** Radius,  $r$ , the Width of Hydration Shell,  $\Delta r$ , the Scaled Shell Width,  $\Delta r/r$ , the “Hydration Number”,  $n$ , and the Molar Gibbs Free Energy, Enthalpy, Entropy, and Heat Capacity of Hydration of Water Structure Ordering or Disordering Ions<sup>28</sup>

ion	$r$ [Å]	$\Delta r$ [Å]	$\Delta r/r$	$n$	$-\Delta_{\text{hyd}}G$ [kJ mol <sup>-1</sup> ]	$-\Delta_{\text{hyd}}H$ [kJ mol <sup>-1</sup> ]	$-\Delta_{\text{hyd}}S$ [J K <sup>-1</sup> mol <sup>-1</sup> ]	$-\Delta_{\text{hyd}}C_p$ [J K <sup>-1</sup> mol <sup>-1</sup> ]
K <sup>+</sup>	1.38	0.74	0.54	2.6	295	330	93	72
Cl <sup>-</sup>	1.81	0.43	0.24	2.0	340	365	94	70
Br <sup>-</sup>	1.96	0.35	0.18	1.9	315	335	78	74
I <sup>-</sup>	2.20	0.26	0.12	1.6	275	290	55	64

**Figure 4.** Difference in conductivity of 0.1 M electrolyte aqueous solutions caused by exposure to MF for 5 min versus summed ( $\Delta_{\text{hyd}}S$ ) for appropriate ions.**Figure 5.** Difference in conductivity of 0.1 M electrolyte aqueous solutions caused by exposure to MF for 5 min versus summed ( $(\Delta r/r)\Delta_{\text{hyd}}H$ ) for appropriate ions.

However, on the basis of the obtained results, it is difficult to see a straight correlation between the changes in conductivity and the kind of investigated salts or the magnetization time. An interesting question is whether there is any dependence between the MF field effect and the thermodynamic function of the ion hydration. It appeared that for the aqueous solutions of the salts consisting of the water structure disordering ions, that is, KBr, KCl and KI, the conductivity changes caused by the 5 min exposition to the MF are a linear function of the calculated total (cation plus anions) thermodynamic function of hydration, such as enthalpy ( $\Delta_{\text{hyd}}H$ ), Gibbs free energy ( $\Delta_{\text{hyd}}G$ ), and entropy ( $\Delta_{\text{hyd}}S$ ) as well as the bare ion radius ( $r$ ) and the ratio  $\Delta r/r$  (where  $\Delta r$  is the

width of the hydration shell) (Table 1). No correlation between the conductivity changes and the number of water molecules hydrating the ion (the hydration number “ $n$ ”) and heat capacity of hydration ( $\Delta_{\text{hyd}}C_p$ ) as well was found.

In Figure 4 are shown changes in the conductivity ( $\Delta\kappa = \kappa_{\text{MF}} - \kappa_0$ ) caused by 5 min of exposition to the MF as a function of the summed entropy (of the respective cation and anion) of hydration, whereas in Figure 5 are plotted the same changes versus the product of the summed scaled thickness ( $\Delta r/r$ ) and the summed enthalpy of hydration of the respective cation and anion.

From these Figures, it is seen that up to 30 min since the MF has ceased the changes in conductivity ( $\Delta\kappa$ ) are preserved and they are roughly linear functions of the summed entropy or enthalpy of hydration.

However, if the MF was acting on the aqueous solution for 20 min, then the changes in conductivity ( $\Delta\kappa = \kappa_{\text{MF}} - \kappa_0$ ) are roughly linear function only of the heat capacity of hydration of the ions (the results not presented here). Moreover, this linear relation was observed for only  $\sim 25$  min after the MF ceased.

From the results presented above, it is clearly seen that the MF effect on the solution conductivity is greater the higher the entropy of hydration  $\Delta_{\text{hyd}}S$ . It means that the MF more greatly affects the ions with less ordered water hydrating shell. Because for the circulation time extended up to 20 min the changes in  $\Delta\kappa$  are a linear function of only the heat capacity of hydration, it seems that the observed changes may be due to two effects: ordering of the water structure around the ions in the presence of the magnetic field and its destruction by the solution flow. Although the changes in the thermodynamic function of hydration caused by MF cannot be evaluated from these experiments, the obtained results point out that magnetic field influences the hydration shell of “water disordering ions” and the results confirm the “memory effect” presence.

## 4. CONCLUSIONS

The obtained results show that the magnetic field affects the electrolyte solution conductivity. If the solutions were circulated for 5 min for the “water structure disordering ions”, then this effect changed linearly versus total (cation plus anion) thermodynamic functions of hydration, that is,  $\Delta_{\text{hyd}}H$ ,  $\Delta_{\text{hyd}}G$ , and  $\Delta_{\text{hyd}}S$ , as well as the bare ion radius ( $r$ ) and the  $\Delta r/r$  ratio (where  $\Delta r$  is the width of the hydration shell). However, if the circulation lasted 20 min, then changes were roughly a linear function of the heat capacity of hydration only. These results indicate that the ion’s hydration shell is responsible for the observed magnetic field effect.

## AUTHOR INFORMATION

### Corresponding Author

\*Phone: +48-81-537-56-39. Fax: +48-81-537-56-56. E-mail: aszczes@poczta.umcs.lublin.pl.

## ACKNOWLEDGMENT

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

## REFERENCES

- (1) Chang, M.-C.; Tai, C. Y. *Chem. Eng. J.* **2010**, *164*, 1.
- (2) Alimi, F.; Tlili, M. M.; Ben Amor, M.; Maurin, G.; Gabrielli, C. *Chem. Eng. Process.* **2009**, *48*, 1327.
- (3) Cefalas, A. C.; Kobe, S.; Dražić, G.; Sarantopoulou, E.; Kollia, Z.; Stražišar, J.; Meden, A. *Appl. Surf. Sci.* **2008**, *254*, 6715.
- (4) Madsen, H. E. L. *J. Crystal Growth.* **2007**, *305*, 271.
- (5) Alimi, F.; Tlili, M. M.; Gabrielli, C.; Georges, M.; Ben Amor, M. *Water Res.* **2006**, *40*, 1941.
- (6) Chibowski, E.; Hołysz, L.; Szcześ, A. *Colloids Surf., A.* **2003**, *222*, 41.
- (7) Kobe, S.; Dražić, G.; McGuinness, P. J.; Meden, T.; Sarantopoulou, E.; Kollia, Z.; Cefalas, A. C. *Mater. Sci. Eng., C* **2003**, *23*, 811.
- (8) Kobe, S.; Dražić, G.; Cefalas, A. C.; Sarantopoulou, E.; Stražišar, J. *Cryst. Eng.* **2002**, *5*, 243.
- (9) Gabrielli, C.; Jaouhari, R.; Maurin, G.; Keddad, M. *Water Res.* **2001**, *35*, 3249.
- (10) Aladjadjian, A. *Int. Agrophys.* **2010**, *24*, 321.
- (11) Martínez, E.; Carbonell, M. V.; Flórez, M.; Amaya, J. M.; Maqueda, R. *Int. Agrophys.* **2009**, *23*, 45.
- (12) Pang, X. F.; Deng, B. *Physica B* **2008**, *403*, 3571.
- (13) Pang, X. F.; Deng, B. *Sci. China, Ser. G: Phys., Mech. Astron.* **2008**, *51*, 1621.
- (14) Toledo, E. J. L.; Ramalho, T. C.; Magriotis, Z. M. *J. Mol. Struct.* **2008**, *888*, 409.
- (15) Nakagawa, J.; Hirota, N.; Kitazawa, K.; Shoda, M. *J. Appl. Phys.* **1999**, *86*, 2923.
- (16) Colic, M.; Morse, D. *Colloids Surf., A.* **1999**, *154*, 167.
- (17) Cefalas, A. C.; Sarantopoulou, E.; Kollia, Z.; Riziotis, C.; Dražić, G.; Kobe, S.; Stražišar, J.; Meden, A. *J. Comput. Theor. Nanosci.* **2010**, *7*, 1800.
- (18) Hołysz, L.; Szcześ, A.; Chibowski, E. *J. Colloid Interface Sci.* **2007**, *316*, 996.
- (19) Higashitani, K.; Oshitani, J. *J. Colloid Interface Sci.* **1998**, *204*, 363.
- (20) Szcześ, A.; Chibowski, E.; Hołysz, L.; Rafalski, P. *Chem. Eng. Process.* **2011**, *50*, 124.
- (21) Amiri, M. C.; Dadkhah, A. A. *Colloids Surf., A.* **2006**, *278*, 252.
- (22) Coey, J. M. D.; Cass, S. J. *Magn. Mater.* **2000**, *209*, 71.
- (23) Alkhazan, M. M. K.; Saddiq, A. A. N. *J. Evol. Biol. Res.* **2010**, *2*, 7.
- (24) Sueda, M.; Katsuki, A.; Nonomura, M.; Kobayashi, R.; Tanimoto, Y. *J. Phys. Chem. C* **2007**, *111*, 14389.
- (25) Zhou, K. X.; Lu, G. W.; Zhou, Q. C.; Song, J. H.; Jiang, S. T.; Xia, H. R. *J. Appl. Phys.* **2000**, *88*, 1802.
- (26) Chang, K.-T.; Weng, C.-I. *Comput. Mater. Sci.* **2008**, *43*, 1048.
- (27) Cheng, S.; Chen, L.; Li, N.; Chai, F. *Gaojishu Tongxun* **2010**, *20*, 1091.
- (28) Marcus, Y. *Biophys. Chem.* **1994**, *51*, 111.