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A drastic influence of the anion nature and concentration on high pressure intrusion–extrusion of electrolyte solutions in Silicalite-1

A. Ryzhikov,* H. Nouali, T. J. Daou and J. Patarin

High pressure intrusion–extrusion of concentrated solutions of sodium salts in a pure-silica MFI-type zeolite (Silicalite-1) was studied for potential applications in mechanical energy absorption and storage. It was discovered that the anion nature has a drastic influence on the behavior and the energetic performances of “Silicalite-1 – concentrated Na^+X^- solution” systems, where $\text{X}^- = \text{Cl}^-$, Br^- , I^- , NO_2^- , NO_3^- , ClO_4^- and CrO_4^{2-} . In the case of NaNO_2 , NaClO_4 , Na_2CrO_4 , and NaI a combination of bumper and shock-absorber behaviors with a partial irreversible solution intrusion was observed, whereas a fully reversible spring behavior is demonstrated for the intrusion–extrusion of NaBr , NaCl and NaNO_3 solutions. In comparison with water, the intrusion pressure increases for all the solutions except for NaClO_4 one. The irreversibility of intrusion decreases with a dilution rate, and the behavior of the corresponding systems with diluted solutions becomes very close. The variation of the system behavior and intrusion pressure values can be related to a different affinity of the corresponding anions for the pores of Silicalite-1. The samples before and after intrusion–extrusion experiments were characterized using several structural and physicochemical methods (XRD, TGA, solid-state NMR, and N_2 physisorption), but no significant structural difference was observed.

Introduction

One of the most important global challenges is low cost, efficient and sustainable energy production and storage. Heterogeneous Lyophobic Systems (HLS) based on high pressure intrusion of a nonwetting liquid in a porous lyophobic matrix are some of the promising technologies for storage,^{1,2} absorption^{3–9} and low temperature generation of mechanical energy.^{10–12} They can also be used for industrial security¹³ and are the systems with volume-memory¹⁴ or a negative expansion coefficient.¹⁵ The operating principle of HLS is as follows. Under high pressure, the nonwetting liquid penetrates into the pores with transformation into a multitude of molecular clusters (intrusion). Thus, the supplied mechanical energy during the compression step is converted into solid–liquid interfacial energy. When the pressure is released, the system can induce an expulsion of the liquid out of the pores (extrusion), thus, restoring the mechanical energy.

Various porous materials such as mesoporous silicas,^{16–18} zeolites¹⁹ and later metal–organic frameworks^{20,21} and porous

carbons^{22,23} were studied as porous matrices of HLS. The systems based on hydrophobic all-silica zeolites (zeosils) and water as nonwetting liquids are among the most promising for the applications in energy storage. Since our pioneering work¹⁹ many zeosils of different structure types were studied in intrusion–extrusion experiments.^{24–33} Depending on the zeolite structure, the “zeosil–water” system is able to restore, dissipate or absorb mechanical energy and therefore, it displays a spring, shock-absorber, or bumper behavior.

The energetic performances of heterogeneous lyophobic systems based on zeosils and hydrophobic high-silica zeolites can be improved by the use of electrolyte solutions.^{34–45} It was found that highly concentrated aqueous solutions of salts such as LiCl , NaCl , and MgCl_2 enhanced the intrusion pressure in MFI-type zeosil (Silicalite-1) up to 3 times (in the case of the “Silicalite-1- LiCl 20M” system).³⁴ Similarly, an increase of energetic performances was observed in high-silica faujasite and ZSM-5 zeolites.^{37–40} The studies of the influence of the LiCl concentration on energetic performances were performed recently by our team for MFI-, FER- and CHA-type zeosils, where a strong increase of intrusion pressure with the salt concentration was found.^{41,43,44} The improvement of energetic performances of HLS with electrolyte aqueous solutions was also observed for other hydrophobic porous materials, such as mesoporous silicas^{46–49} and Metal–Organic Frameworks (MOFs).^{50–53}

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The increase of intrusion pressure with the increase of the electrolyte concentration can be explained by a higher solid-liquid interfacial tension, by osmotic phenomena^{52,53} and by the ion desolvation.^{35,39}

During the intrusion-extrusion of water and electrolyte solution into the pores of *BEA-type zeosil, it was discovered that the system “*BEA-type zeosil – LiCl solution” changed its behavior from a bumper for water and low concentrated solutions (<15 M) to a shock-absorber for highly concentrated LiCl solutions.⁵⁴ It was supposed that this transformation was related to a change in the nature of the intruded liquid: at a low LiCl concentration, water molecules are not bounded or weakly bounded (2nd coordination sphere) with Li^+ and Cl^- ions and the intruded liquid is water, whereas at a high concentration it was hypothesized that the highly concentrated solutions (>15 M) are reversibly intruded into the pores. In these solutions the number of water molecules per Li^+ cation is close or less than the coordination number (c.n.) of the lithium cation. Our hypothesis of different nature of the intruded liquid was proven indirectly using physicochemical characterization. It was shown using TGA and solid-state NMR methods that the intrusion of water and low concentrated LiCl solution led to the breaking of siloxane bridges with the formation of silanol defects, since the intruded water molecules are corrosive to the *BEA structure. At the same time almost no defects are formed under intrusion of highly concentrated solutions. A similar phenomenon was observed in the case of LiCl solution intrusion in LTA-type zeosil.³⁰ A change in the system behavior with the LiCl concentration was also demonstrated for BEC,³² CHA,⁴⁴ and -OKO-type zeosils.³¹ Thus, the intrusion-extrusion behavior of highly concentrated solutions can be completely different to the one of diluted solutions. It should be noticed that in spite of concentrated LiCl solutions in our works,^{30–34,40–44,54} all other studies were carried out with relatively diluted solutions which had a number of water molecules per cation ($\text{H}_2\text{O}/\text{M}^+$ molar ratio) higher than its coordination number (c.n.). In this work we present the first systematic study of the influence of the anion nature and electrolyte concentration on the behavior and energetic performances of “Silicalite-1 – sodium salt aqueous solution” systems.

Results and discussion

Intrusion-extrusion isotherms. The sodium salts were chosen because of their very high solubility, thus, the influence of different anions can be compared for highly concentrated solutions. Except NaCl, all the salts used in this work are sufficiently soluble to obtain aqueous solutions, where the number of water molecules per cation ($\text{H}_2\text{O}/\text{Na}^+$ ratio) is close or lower than the sodium coordination number (c.n. = 6).^{55,56} For some salts a study of the influence of the concentration ($\text{H}_2\text{O}/\text{Na}^+$ molar ratio) on the system behavior and energetic performances of “Silicalite-1 – solution” systems was performed, for this the saturated solutions were diluted consequently. The NaCl solution

Fig. 1 Intrusion-extrusion isotherms of the “Silicalite-1 – saturated Na^+X^- solution” systems, where $\text{X} = \text{ClO}_4^-$, CrO_4^{2-} , NO_2^- , NO_3^- . For clarity, the intrusion-extrusion isotherms are shifted along the Y axis.

(minimal $\text{H}_2\text{O}/\text{Na}^+$ molar ratio = 9.0) and pure water have been studied for comparison.

The pressure-volume diagrams (intrusion-extrusion isotherms) of some “Silicalite-1 – sodium salt aqueous solution” systems are reported in Fig. 1 and 2. One cycle is shown, when all three cycles are overlapping, two cycles are shown in the case, when only the 2nd and 3rd cycles are overlapping. The isotherms of different systems are shifted along the y-axis for better visibility. The corresponding data are reported in Table 1. In the case of saturated solutions of sodium salts, the nature of anion changes drastically the behavior of the systems. The “Silicalite-1 – NaBr and NaNO_3 saturated solutions” systems demonstrate a spring behavior with a fully reversible extrusion and a small hysteresis between the intrusion and extrusion isotherms. This behavior is the same as the one observed previously for water and solutions

Fig. 2 Intrusion-extrusion isotherms of the “Silicalite-1 – NaBr solution” and “Silicalite-1 – NaI solution” systems with different rates of dilution: $\text{H}_2\text{O}/\text{Na}^+$ molar ratio of 4.5 (NaI), 9.0 (NaI, $C_{\text{max}}/2$), 18.0 (NaI, $C_{\text{max}}/4$). For clarity, the intrusion-extrusion isotherms are shifted along the Y axis.

Table 1 Intrusion–extrusion characteristics of “Silicalite-1 – sodium solution” systems as a function of the anion nature: intrusion (P_{int}) and extrusion (P_{ext}) pressures, intruded (V_{int}) and extruded (V_{ext}) volumes, systems’ behavior

Solution	H ₂ O/Na ⁺ molar ratio	P_{int} (MPa)	P_{ext} (MPa)	V_{int} (mL g ⁻¹)	V_{ext} (mL g ⁻¹)	Behavior ^d
H ₂ O	—	96	94	0.10	0.10	S
NaCl	9.0	138	133	0.10	0.10	S
NaCl, $C_{int}/2^a$	18.0	113	110	0.10	0.10	S
NaBr	6.0	178	165	0.085	0.085	S
NaBr, $C_{int}/1.5^a$	9.0	127	118	0.10	0.10	S
NaBr, $C_{int}/3^a$	18.0	112	108	0.10	0.10	S
NaI	4.5	146 ^b /144 ^c	142 ^b /141 ^c	0.12 ^b /0.07 ^c	0.07	B + S ^b /S ^c
NaI, $C_{int}/2^a$	9.0	132	126	0.10	0.10	S
NaI, $C_{int}/4^a$	18.0	111	107	0.10	0.10	S
NaNO ₂	4.5	164 ^b /130 ^c	129 ^b /119 ^c	0.095 ^b /0.06 ^c	0.06	B + SA ^b /SA ^c
NaNO ₃	5.2	145	136	0.085	0.085	S
NaClO ₄	3.4	77 ^b /75 ^c	63	0.12 ^b /0.035 ^c	0.035	B + SA ^b /SA ^c
NaClO ₄ , $C_{int}/1.34^a$	4.5	77/76	63	0.11/0.06	0.06	B + SA ^b /SA ^c
Na ₂ CrO ₄	5.4	143 ^b /105 ^c	112 ^b /96 ^c	0.10 ^b /0.06 ^c	0.06	B + SA ^b /SA ^c

^a C_{int}/x -saturated solution (maximal concentration) diluted by x times ($x = 1.8, 2$ or 4). ^b 1st intrusion–extrusion cycle. ^c 2nd and 3rd intrusion–extrusion cycles. ^d Behavior: S = spring, B = bumper, SA = shock-absorber.

of LiCl, NaCl and MgCl₂.³⁴ In the case of NaI, NaNO₂, NaClO₄ and Na₂CrO₄ saturated solutions, a drastic change in the HLS behavior is observed. For the 1st cycle, these systems demonstrate a partially irreversible intrusion; a part of the intruded liquid remains inside the pores after the extrusion step. Another part of the liquid is extruded with a more or less pronounced hysteresis between the intrusion and extrusion isotherms. Thus, the systems display a combination of a bumper and a shock-absorber or a spring behavior. In the following cycles the systems show a spring or shock-absorber behavior with no additional irreversibility. The maximal irreversibility (~80% of intruded volume remains in the pores) was observed for the NaClO₄ solution, for other solutions the part of non-expelled liquid is about 40% of the intruded volume. This difference can be related to a lower H₂O/Na⁺ molar ratio (3.4) of NaClO₄ solution. It might be possible that in this case lower solvated ions interact more easily with pore walls. In our solutions all water molecules are in the coordination sphere of Na⁺ cations and the corresponding anions, thus, the intruded liquid has probably the same composition as the initial solution. It could be supposed that the variation of behaviors is related to a different affinity of the solutions to the pores of Silicalite-1 and this affinity being determined by the nature of the anion.

A correlation between the system behavior and the Lewis basicity of some anions, as well as their charge density, is observed for the NO₃⁻–NO₂⁻ and Br⁻–I⁻ couples. The anions Br⁻ and NO₃⁻ are known to be stronger Lewis bases and have higher charge density than I⁻ and NO₂⁻, respectively. The anions with a higher charge density (stronger bases) lead to a spring behavior under intrusion of the corresponding solutions, the ones with a lower charge density (I⁻, NO₂⁻) correspond to the combination of bumper and shock-absorber/spring behaviors. This reasoning does not allow explaining well the partially irreversible intrusion of NaClO₄ and Na₂CrO₄ solutions, where the anions have quite different charge densities, but it could be supposed that due to their structure ClO₄⁻ and CrO₄²⁻ anions have a higher affinity for the Silicalite-1 structure composed of SiO₄ tetrahedra, which facilitates their retention inside the pores.

A slight increase of the intruded volume (0.12 mL g⁻¹) was observed for NaI and NaClO₄ saturated solutions in comparison with that of pure water (0.10 mL g⁻¹). It might be explained by a higher affinity of the intruded solution that increases the size of clusters of solvated ions inside the pores or by a more compact organization of solvated ions there.

The influence of the anion nature on the values of intrusion and extrusion pressure was significant, but no clear dependence was found. The intrusion pressure values are higher than the one of water ($P_{int} = 96$ MPa) for all the salt solutions except for NaClO₄ one ($P_{int} = 77$ MPa). In the latter case the system shows a decrease of intrusion pressure in comparison with pure water that has never been observed previously. In order to better compare the intrusion pressure of the solutions with different anions, the most concentrated solution (NaClO₄) was diluted to a H₂O/Na⁺ molar ratio of 4.5. The values of intrusion pressure for the solutions of similar concentrations ($4.5 < \text{H}_2\text{O}/\text{Na}^+ < 6.0$) are reported in Fig. 3. The highest value (178 MPa) is observed for NaBr solution with H₂O/Na⁺ = 6.0, followed by the NaNO₂ one (164 MPa). For the most part of other solutions (NaI, NaNO₃ and Na₂CrO₄) the intrusion pressure values are very close (143–146 MPa), whereas the lowest one (77 MPa) was found for NaClO₄ solutions. It should also be noticed that the dilution does not change significantly the intrusion pressure in the latter case, which reinforces the hypothesis on the key role of the anion affinity in the behavior and the performances of “Silicalite-1 – solution” systems. However, this small dilution (1.34 times for NaClO₄) leads to a decrease of intrusion irreversibility. The extruded volume in the first cycle increases from 0.035 to 0.06 mL g⁻¹, when the H₂O/Na⁺ molar ratio passes only from 3.4 to 4.5. The influence of the H₂O/Na⁺ ratio was studied more thoroughly for NaCl, NaBr, NaI solutions. It was observed that the decrease of the salt concentration (increase of the H₂O/Na⁺ ratio) changes the behavior of “Silicalite-1 – NaI solution” systems: from a combination of spring and bumper behaviors with a partially irreversible intrusion for saturated NaI solution (H₂O/Na⁺ = 4.5) to a fully reversible spring one for diluted solutions. It can be supposed that the change in the

Fig. 3 Intrusion pressure values (1st cycle) of "Silicalite-1 – sodium salt solution" systems with a similar H_2O/Na^+ molar ratio varied between 4.5 and 6.0.

Fig. 4 Intrusion pressure values of "Silicalite-1 – Na^+X^- solution" systems, where X = halogen anions: Cl^- , Br^- , I^- with H_2O/Na^+ molar ratios of 9.0 and 18.0.

intrusion–extrusion behavior with the dilution rate is related to the appearance of weakly bounded free water molecules in the solutions with the H_2O/Na^+ molar ratio $> Na^+$ c.n. These molecules can significantly modify the solution properties and change the nature of the intruded liquid. Earlier it was supposed that for diluted solutions the water was intruded into the pores instead of solvated ions in saturated solutions. This hypothesis was proposed to explain the change in the behavior of "BEA – LiCl solution" systems.⁵⁴ However, recent experiments using *in situ* X-ray diffraction demonstrated that in the case of intrusion of relatively diluted solution of $MgCl_2$ (H_2O/Mg^{2+} molar ratio = 21) in FER-type zeosil, the intruded liquid was saturated $MgCl_2$ solution (H_2O/Mg^{2+} = 10).⁵⁷ Thus, the difference between the intrusion–extrusion behavior of saturated and diluted solutions is established, but not well explained. This subject merits a more detailed study using *in situ* methods in order to better understand the nature of the intruded liquid.

The performances of diluted solutions of three sodium halogen salts (NaCl, NaBr, and NaI) with the same H_2O/Na^+ molar ratios of 9.0 and 18.0 have been compared (see Fig. 4). In their case the "MFI-type zeosil – solution" systems demonstrate a spring behavior, and the intrusion pressure becomes very close for all the anions. For H_2O/Na^+ = 9.0 its values are situated between 127 and 138 MPa, and for H_2O/Na^+ = 18.0 – between 111 and 113 MPa. Taking into account the drastic difference of the intrusion–extrusion behavior of saturated NaBr and NaI solutions with a considerable variation of the intrusion pressure, it can be concluded that in the case of diluted solutions the anion nature does not have such an importance as in the case of the saturated ones.

Characterization

The XRD patterns of the Silicalite-1 samples before and after three intrusion–extrusion cycles of saturated aqueous solutions

Fig. 5 X-ray diffraction patterns of Silicalite-1 samples before and after intrusion–extrusion experiments with saturated solutions of NaI and $NaClO_4$.

of NaI and $NaClO_4$ are shown in Fig. 5. All diffractograms are very close that means that the MFI structure is not affected at the long range order. A study of the crystal morphology using scanning electron microscopy shows that the nonintruded Silicalite-1 sample consists of twinned coffin shaped crystals with a length of 20–25 μm , a width of 8–15 μm and a thickness of 1–4 μm (Fig. S1, ESI†). After the intrusion–extrusion tests, most of the crystals are broken (Fig. S1b, ESI†), that is typical for the intrusion–extrusion experiments in MFI-type zeosil.⁴¹

Thermogravimetric curves corresponding to the samples after intrusion–extrusion of saturated $NaClO_4$ and NaI solutions and diluted NaI solutions with H_2O/Na^+ molar ratios of 9.0 and 18.0 ($C_{max}/2$ and $C_{max}/4$, respectively) are reported in Fig. 6. The samples were washed after intrusion–extrusion tests that leads to not well-controlled removal of nonextruded solutions. That is why the TG results should be taken with care, but nevertheless

Fig. 6 Thermogravimetric curves of the sample before and after intrusion–extrusion tests with NaClO_4 and NaI saturated solutions and NaI solutions with $C_{\text{max}}/2$ and $C_{\text{max}}/4$ ($\text{H}_2\text{O}/\text{Na}^+$ molar ratio = 9.0 and 18.0, respectively).

some correlations have been observed. The total weight loss for the nonintruded Silicalite-1 sample is quite low (1.0 wt%), which confirms the hydrophobic character of the material. After intrusion–extrusion tests, the total weight loss is considerably higher – 2.0–2.5 wt% for the most part of intruded samples, and even 4.6 wt% in the case of saturated NaI solution. In the latter case, such a result is expected since for the saturated NaI solution a mixed bumper/spring behavior is observed and a part of the intruded liquid (0.05 mL g^{-1}) is not expelled from the solid after the extrusion step. All the samples demonstrate an additional weight loss step starting at approximately 250°C . In the case of NaClO_4 solution this step is less pronounced and shifted to a higher temperature. It can be supposed that this weight loss is related to salt ions adsorbed inside the pores and with water molecules strongly bounded with them. As mentioned above the washing procedure seems to strongly affect the TG results. According to the intrusion–extrusion experiments, the volume of non-expelled liquid is larger (0.085 mL g^{-1}) for NaClO_4 than NaI (0.05 mL g^{-1}) while the weight loss is lower.

The N_2 adsorption–desorption isotherms of the nonintruded sample and those intruded with NaI solutions are shown in Fig. S2 (ESI†). Before intrusion the isotherms are close to type I characteristic of microporous solids with the presence of a step for relative pressures near $p/p_0 = 0.15$, which is typical for Silicalite-1 and attributed to a density change of the adsorbed phase.⁵⁸ The BET surface area and microporous volume of samples degassed at 300°C and 90° are quite similar. They are equal to $378 \text{ m}^2 \text{ g}^{-1}$ and $0.17 \text{ cm}^3 \text{ g}^{-1}$ for the sample degassed at 300°C and to $360 \text{ m}^2 \text{ g}^{-1}$ and $0.16 \text{ cm}^3 \text{ g}^{-1}$ for the one degassed at 90°C . The above-mentioned step is less pronounced and situated at slightly higher pressure in the case of the samples intruded with NaI solutions. For MFI-type zeosil intruded with saturated NaI solution the values of the BET surface area ($338 \text{ m}^2 \text{ g}^{-1}$) and microporous volume ($0.15 \text{ cm}^3 \text{ g}^{-1}$) are lower than for the nonintruded one, that could be related to the

irreversible character of intrusion and, thus, the presence of NaI traces in the pores. When more diluted solution (NaI , $C_{\text{max}}/2$) is intruded, the corresponding characteristics are very close to the ones of the nonintruded sample that is in correlation with a fully reversible spring behavior observed under intrusion–extrusion of this solution.

Solid-state NMR spectroscopy

The ^{29}Si MAS and ^1H – ^{29}Si CPMAS (insert) NMR spectra of Silicalite-1 before and after intrusion–extrusion of saturated NaClO_4 and NaI solutions are shown in Fig. S3 (ESI†). The ^{29}Si MAS spectra of nonintruded and intruded samples exhibit 8 resonances in the -108 to -118 ppm range, which can be ascribed to the 24 nonequivalent crystallographic silicon sites of the MFI-type zeosil structure. No signals assigned to Q_3 groups [$\text{Si}(\text{OSi})_3\text{O}^-$] or [$\text{Si}(\text{OSi})_3\text{OH}$] expected at about -100 ppm are observed. The spectra of nonintruded and intruded samples are very close. An apparition of a broad peak at -103 ppm is observed on the ^1H – ^{29}Si CPMAS (not visible on ^{29}Si MAS) spectra of the NaClO_4 solution intruded sample that can be explained by the formation of a small number of Q_3 groups. Thus, no significant structural changes and defect formation are found after intrusion–extrusion tests.

Experimental

Silicalite-1 was prepared in a fluoride medium according to a procedure similar to that described in ref. 41. This route allows the synthesis of a material having a strong hydrophobic character. The synthesis requires the presence of tetrapropylammonium (TPA) cations as structure-directing agents (TPABr, Fluka, purum). Aerosil 130 (Degussa) was used as the silica source. The reaction gel had the following molar composition: $1 \text{ SiO}_2 : 0.1 \text{ TPABr} : 0.1 \text{ NH}_4\text{F} : 20 \text{ H}_2\text{O}$. The mixture, transferred into PTFE-lined stainless-steel autoclaves, was heated at 100°C for 7 days. After synthesis, the solid was calcined at 550°C for 6 hours in order to remove the organic template.

The intrusion–extrusion experiments of saturated aqueous solutions of several sodium salts in the Silicalite-1 sample in the form of compressed pellets were performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV), as described in our previous works.⁴¹ The concentration of studied solutions and their $\text{H}_2\text{O}/\text{Na}^+$ molar ratio are given in Table 2. Before the intrusion–extrusion experiments, the pellets were outgassed at 300°C under vacuum. The compressibility of pure water or the corresponding aqueous solution was subtracted from the experimental intrusion–extrusion curves. The values of the intrusion (P_{int}) and extrusion (P_{ext}) pressures correspond to that of the half volume total variation. The pressure is expressed in megapascals (MPa) and the volume variation in milliliters (mL) per gram of the outgassed samples. The experimental error is estimated to 1% on the pressure and on the volume.

After intrusion–extrusion experiments, generally the samples were washed with water to remove traces of salts, then dried at

Table 2 Concentrations of sodium salt solutions (20 °C)

Salt	Concentration (g/100 g of H ₂ O)	H ₂ O/Na ⁺ molar ratio
NaCl	36	9.0
NaCl, $C = C_{\text{max}}/2$	18	18.0
NaBr	94.3	5.4
NaBr, $C = C_{\text{max}}/1.5$	62.9	9.0
NaBr, $C = C_{\text{max}}/3$	31.4	18.0
NaI	184	4.5
NaI, $C = C_{\text{max}}/2$	92	9.0
NaI, $C = C_{\text{max}}/4$	46	18.1
NaNO ₂	84.8	4.5
NaNO ₃	91.2	5.2
NaClO ₄	201	3.4
NaClO ₄ , $C = C_{\text{max}}/1.34$	150.6	4.5
Na ₂ CrO ₄	84	5.4

70 °C overnight, and rehydrated in a 80% relative humidity atmosphere for 24 h in order to set the hydration state.

X-Ray diffraction patterns of the different samples were recorded in a Debye-Scherrer geometry on a STOE STADI-P diffractometer equipped with a curved germanium(111), primary monochromator, and a linear position-sensitive detector (6° 2 θ) using Cu K α_1 radiation ($\lambda = 0.15406$ nm). Measurements were achieved for 2 θ angle values in the 3–50 range, step 0.15° 2 θ , and time/step = 120 s.

The size and the morphology of the crystals were determined by scanning electron microscopy (SEM) using a Philips XL 30 FEG microscope.

Nitrogen adsorption-desorption isotherms were performed at –196 °C using a Micromeritics ASAP 2420 apparatus. Prior to the adsorption measurements, the samples were outgassed at 90 °C (90° and 300° for nonintruded one) overnight under vacuum to eliminate physisorbed water. Low degassing temperature was chosen to avoid the dehydroxylation process. The specific surface area (S_{BET}) and microporous volume (V_{micro}) were calculated using the BET and t-plot methods, respectively.

Thermogravimetric (TG) analyses were carried out on a TG Mettler Toledo STARE apparatus, under air flow, with a heating rate of 5 °C min^{–1} from 30 to 800 °C.

²⁹Si MAS and ¹H–²⁹Si CPMAS NMR spectra were recorded on a Bruker Avance II 300 MHz spectrometer, with a double-channel 7 mm Bruker MAS probe. The recording conditions are given in Table 3.

Table 3 Recording conditions of the ²⁹Si MAS and ¹H–²⁹Si CPMAS NMR spectra

	²⁹ Si MAS	¹ H– ²⁹ Si CPMAS
Chemical shift standard	TMS ^a	TMS ^a
Frequency (MHz)	59.6	59.6
Pulse width (μs)	1.87	4
Flip angle	π/6	π/2
Contact time (ms)	—	8
Recycle time (s)	80	10 ^b
Spinning rate (kHz)	4	4
Scans number	800	7000

^a TMS: tetramethylsilane. ^b The relaxation time t_1 was optimized.

Conclusions

A first systematic study of the influence of the anion nature on high pressure intrusion-extrusion of electrolyte solutions in hydrophobic pure silica zeolites was performed for possible applications in absorption and storage of mechanical energy. The intrusion-extrusion of concentrated and diluted NaCl, NaBr, NaI, NaNO₂, NaNO₃, NaClO₄ and Na₂CrO₄ aqueous solutions in a pure-silica MFI-type zeolite (Silicalite-1) was investigated. It was shown that the anion nature influences drastically the behavior and the energetic performances of “Silicalite-1 – sodium salt solution” systems for the solutions with a H₂O/Na⁺ molar ratio lower or close to the sodium coordination number (c.n. = 6). A combination of bumper and shock-absorber behaviors with a partially irreversible intrusion was observed in the first intrusion-extrusion cycle for NaNO₂, NaClO₄, Na₂CrO₄, and NaI solutions, whereas for NaBr and NaNO₃ ones the “Silicalite-1 – solution” systems demonstrate a fully reversible spring behavior. The maximal irreversibility (~80% of intruded volume remains in the pores) was demonstrated by the NaClO₄ solution, for other solutions the part of non-expelled liquid is about 40% of the intruded volume. The irreversible character of intrusion (non-expelled intruded liquid) decreases with the dilution rate. The behavior of the systems intruded with diluted solutions becomes fully reversible and very close to the one of “Silicalite-1 – water”. The intrusion pressure values are higher than that of water ($P_{\text{int}} = 96$ MPa) for all the salt solutions except for NaClO₄ ($P_{\text{int}} = 77$ MPa) and reach 178 MPa for the saturated NaBr solution. For the diluted solutions the influence of the anion nature becomes insignificant. It could be supposed that the variation of behavior is related to a different affinity of the solutions for the pores of Silicalite-1 and this affinity being determined by the nature of the anion. The change in the intrusion-extrusion behavior with the dilution rate can be related to the appearance of water molecules weakly bounded with the ions in the solutions with the H₂O/Na⁺ molar ratio > Na⁺ c.n. These molecules can significantly modify the solution properties and change the nature of the intruded liquid. No significant structural difference was observed between Silicalite-1 samples before and after intrusion-extrusion experiments according to XRD, TGA, solid-state NMR and N₂ physisorption measurements.

Conflicts of interest

There are no conflicts to declare.

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