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Behaviour of organoarsenic compounds in contact with natural zeolites

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Batch experiments were conducted on aqueous solutions containing arsenite, arsenobetaine, methylarsonic acid or phenylarsonic acid in contact with natural zeolites to examine their interaction. The concentration of the arsenic species in the liquid phase at equilibrium before and after contact was measured by means of liquid chromatography coupled with inductively coupled plasma mass spectrometry detection. Clinoptilolites completely removed arsenobetaine from the solution and the resulting amounts of dimethylarsinic acid were detected. The methylarsonic acid maximum concentration diminution was reached at a mass—to volume *V* value of $m/V = 0.2$. Phenylarsonic acid solution decreased its concentration 75% after treatment with clinoptilolites. Untreated mordenites in contact with arsenite solutions led to the formation of arsenate, whereas acid-washed mordenites practically removed arsenobetaine and were less effective for methylarsonic acid. To show the incompatibility of molecular dimensions with the zeolite windows, the molecular parameters of surface area, molecular volume, molecular length, and the width and depth of arsenite, arsenate and a series of ten organic arsenic compounds were calculated. Since sorption onto the external zeolite surface rather than a sieve process defined the interaction, an acid-catalysed reaction mechanism is proposed to explain the transformation results. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: arsenite; arsenate; organoarsenicals, methylarsonic acid; dimethylarsinic acid; arsenobetaine; phenylarsonic acid; natural zeolites; speciation; HPLC–ICP-MS

INTRODUCTION

Methylarsenicals are commonly found in the environment.[1] They can be formed by fungi, yeasts and bacteria,[2] but also by humans from inorganic arsenic.[3] In marine water, the concentrations of methylarsonic acid and dimethylarsinic acid are small, but they are higher in the photic zone due to the algae population;[2] arsenobetaine (AsB) is also the major arsenic compound in a large domain of marine animals, like crustaceans, molluscs, echinoderms, sponges and fish.[4] AsB is ingested by humans *via* this route; it is easily absorbed[5] and readily excreted,[6] although there is one report concerning the formation of AsB by humans.[7] The metabolic modification of inorganic arsenic into organoarsenic compounds fortunately leads to dramatic changes in the arsenic toxicity, and is generally considered as a detoxification mechanism. Most of the transformation information is gained from studies using experimental animals, and synthetic work has also been required in order to obtain standards for determining the metabolic products. However, no work has been described in the literature concerning the interaction of organoarsenicals with solids, which can lead to chemical transformations.

Zeolite utilization has become popular in the last decade in water and industrial waste[8] treatment on account of their cation exchange properties.[9] In catalytic applications, the success of zeolites is due to their molecular sieve properties and their acidity. The crystalline structure of zeolite determines a number of properties that are specific and favourable for catalytic reactions, but the adsorption processes observed, both in the pores system and on the framework, may predispose a chemical transformation. The interactions present during adsorption may involve the pairs (i) adsorbate molecules–interchangeable zeolite cations, (ii)

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Table 1. Zeolite types studied and their compositions[a]

Zeolite	Type	Si/Al	Na_2O (%)	CaO (%)	K_2O (%)	MgO (%)	Fe_2O_3 (%)	Origin
ZH-C	55% clinoptilolite + 30% mordenite	6.3	1.06	1.98	3.54	0.03	0.6	Hungary, natural
ZMT-C	clinoptilolite	6.4	0.73	1.53	2.00	0.64	1.4	Mexico, natural
ZMA-C	55% clinoptilolite + 35% erionite	8.8	0.63	1.05	2.02	0.77	1.4	
ZME-C	40% clinoptilolite + 30% mordenite	5.2	3.22	1.04	2.65	0.31	1.8	
ZMT-M	mordenite	7.5	0.39	1.11	0.30	0.61	0.8	
ZMT-M*	mordenite	6.4	2.88	2.02	0.57	0.85	1.0	
ZS-M	mordenite	7.4	0.78	0.05	0.02	0	0.2	Synthetic
ZS-M*	mordenite	7.0	6.16	0.10	0.04	0	0.2	

[a] Asterisk indicates no acid treatment.

adsorbate molecules–anionic zeolite framework, (iii) zeolite–water and (iv) adsorbate molecules–water when a heterogeneous system consisting of a zeolite in contact with an aqueous solution of solute is considered. Recently, we reported the adsorption and desorption of arsenite and arsenate from aqueous solution by natural zeolites.[10] An oxidative process of arsenite in contact with mordenite and some clinoptilolite zeolite types was also found. As part of our research on arsenic removal, the present paper deals with evidence of the chemical transformation of organoarsenicals in solution induced by zeolites. The procedure adopted for this study was to calculate molecular parameters of known organoarsenic compounds in order to compare them with the pore windows dimensions in zeolites. Selected batch adsorption experiments carried out in an aqueous medium were chosen as examples. The resulting solution in each assay was analysed and the identification of the products was followed by speciation analysis using the coupling of chromatographic separation and inductively coupled plasma mass spectrometery (ICP-MS) detection.

EXPERIMENTAL

Chemicals

Stock solutions of the individual arsenic compounds with different concentrations were prepared from arsenic trioxide (Fluka), arsenate solution (Titrisol, Merck), methylarsonic acid, dimethylarsinic acid (DMAs) trihydrate (Merck), AsB and phenylarsonic acid (PhAs; Fluka). The concentration of the arsenic species is always given as the concentration of elemental arsenic. The pH of the solutions was adjusted to pH 4 by adding 1×10^{-4} M HCl. Deionized water (Milli-Q, Millipore) was used in every solution.

Analytical procedures

The total amount of arsenic was determined by ICP atomic emission spectroscopy using a Spectroflame P/M (Spectro A.I.) with nebulization (cross-flow nebulizer). The high-performance liquid chromatography (HPLC) ICP-MS system for the determination of arsenic species consisted of an LC 250 binary pump (Perkin Elmer) coupled with an Elan 5000 ICP mass spectrometer (Perkin Elmer) *via* a cross-flow nebulizer. A volume of 200 µl was always injected. The guard and separation columns used were Ion Pac AG7 and Ion Pac AS7 (Dionex) respectively. The mobile phase was nitric acid without an organic modifier and the same gradient elution as in Ref. 11 was applied.

Zeolites

The zeolites used in this work were natural Mexican and Hungarian zeolites and synthetic mordenite with mesh sizes of 60 and 20 and are described in Table 1. They were characterized[12] by X-ray diffraction, fluorescence spectroscopy and IR spectroscopy. All of them correspond with clinoptilolite and mordenite zeolite types. Their activation, as published in Ref. 10, comprised an acid wash with 2 M HCl with agitation at 50 °C for 2 h, keeping them for 24 h in the acid solution, decanting and washing with water until pH 5 was obtained and the chloride test proved negative, followed by drying at 200 °C for 2 h. On account of this pretreatment, we consider the zeolites to be their hydrogenated forms. Synthetic and natural mordenite were used in both untreated and acid washed forms.

Procedures

A given volume of arsenic solution was equilibrated with a weighed amount of zeolite for a definite time and was initially shaken in an ultrasonic bath. Initial elemental arsenic solution concentration was 600 µg l^{-1}, comparable to that in polluted water from Zimapán, Mexico.[13] The experiments were carried out at 22 °C, using glass containers as batch reactors. In the first trials the solid-to-solution ratio was varied and then it was maintained at 1:10. After equilibration, the final pH was measured and 2 ml of the supernatant was used for species analysis by HPLC–ICP-MS. Solutions were analysed after 24 h, 7 days and 30 days contact. The chromatograms were evaluated quantitatively by integrating the peaks corresponding to arsonic acid

[As(III)], arsenic acid [As(V)], monomethylarsonic acid (MMAs), DMAs and AsB applying the peak-fitting module of the Microcal Origin 5.1 software.

Calculations

The molecular parameters surface area, molecular volume, hydrophobicity, molecular length, width and depth, global maximum and global minimum of the molecules were calculated for undissociated As(III) and As(V), MMAs, DMAs, trimethylarsinic oxide (TMAs), tetramethylarsonium (4MAs), AsB, arsenocholine (AsC), PhAs, *o*-aminophenylarsonic acid (oAPhAs), *p*-aminophenylarsonic acid (pAPhAs) and tetraphenylarsonium (4PhAs). For the calculation the program Physical!Property Pro™ from ChemSW was used. Molecular length is the distance along the *x* axis between the left and rightmost atoms plus their van der Waals' radii. The width is considered as the *y* axis and the depth the *z* axis. The global maximum and the global minimum are defined as the longer and shorter side respectively of a rectangle that can envelop the molecule considering the van der Waals radius of all the atoms. Input parameters with correct values for bond lengths and bond angles were considered by the program automatically. After drawing, the low-energy conformation of the molecule was calculated and the strain energy in the molecule was minimized by the corresponding operation.

RESULTS AND DISCUSSION

Transformation of organoarsenic compounds

Solutions of AsB and MMAs in contact with the zeolites described in Table 1 were monitored for a period of 30 days. The mass-to-volume ratio in this set of experiments was kept exact and constant at a value of 1:10. After 24 h the arsenic concentration of the original compound decreased considerably in the batch solution containing natural clinoptilolite-type zeolites, as can be appreciated from Fig. 1. We found DMAs (Fig. 1A, dotted lines) and small amounts of As(V) after 24 h in the experiment initially containing AsB and clinoptilolite ZME-C. In the case of the MMAs solution, formation of As(III) (Fig. 1B, dotted lines) was also observed after this time. The sorption of MMAs is reported for goethite and haematite,[14] but no evidence of a chemical transformation was given in that work. Figure 2 shows this result and demonstrates that after 7 days the AsB was completely extinguished (Fig. 2A, continuous line), whereas in the MMAs solution a small amount of MMAs (Fig. 2B, continuous line) was still present together with the As(III) formed. As Fig. 1A shows, clinoptilolites completely removed AsB from the solution, transforming it in 30 days by up to 40% into DMAs using zeolite ZME-C. In the case of MMAs, its concentration did not reach a zero value (Fig. 1B) and its transformation into As(III) by the sample ZME-C presented the highest value after 7 days. Then a decrease of the arsenite concentration occurred as a result of its adsorption, as has already been reported by us[10] for clinoptilolites. So, the first step in MMAs removal by clinoptilolites can be conceived as transformation into arsenite and, subsequently, adsorption. In the case of clinoptilolite ZME-C, for example, after 7 days and 30 days in the 600 μg l^{-1} original MMAs solution there were 200 μg l^{-1} MMAs + 400 μg l^{-1} As(III) and 190 μg l^{-1} MMAs + 330 μg l^{-1} As(III) respectively. In contrast, the clinoptilolite ZMT-C formed 50 μg l^{-1} MMAs + 100 μg l^{-1} As(III) after 7 days and 60 μg l^{-1} MMAs + 20 μg l^{-1} As(III) after 30 days, which means an 87% diminution of the arsenic content in the MMAs solution.

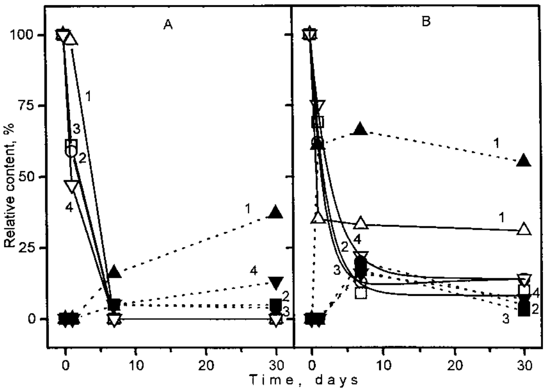


Figure 1. Decrease (solid lines) of AsB (A) and MMAs (B) concentration with time after contact with four clinoptilolite-type natural zeolites. Dotted lines represent formation of DMAs (A) and of As(III) (B). 1: ZME-C; 2: ZMA-C; 3: ZMT-C; 4: ZH-C.

Dependence on zeolite mass

In connection with the result obtained with MMAs in contact with the clinoptilolite ZME-C, we examined the effect of the zeolite mass-to-solution volume ratio in the interval 1:10–4:10. Figure 3A demonstrates an exponential decrease of the MMAs concentration and a symmetrical increase of the arsenite content after 7 days, reaching an asymptotic amount of 20% and 80% respectively. After this time, no formation of arsenate was observed. Remembering the kinetics of chemical transformations, these curves resemble a reversible first-order reaction. Half the value of the MMAs concentration is already reached at a Mass *M* to volume V value of $m/V = 0.06$, and at $m/V = 0.2$ it practically reached constancy. Figure 3B shows that, after 30 days contact, additional small amounts of arsenate were detected in the solution and the highest concentration of arsenite formed corresponded to $m/V = 0.2$ and 0.3. This set of curves resembles the kinetic curves characteristic for consecutive reactions.

Natural and synthetic mordenites

Zeolites exhibit cations and a framework, acting as two sorption centres, and the role of the accompanying materials in natural zeolites cannot be neglected. When an untreated

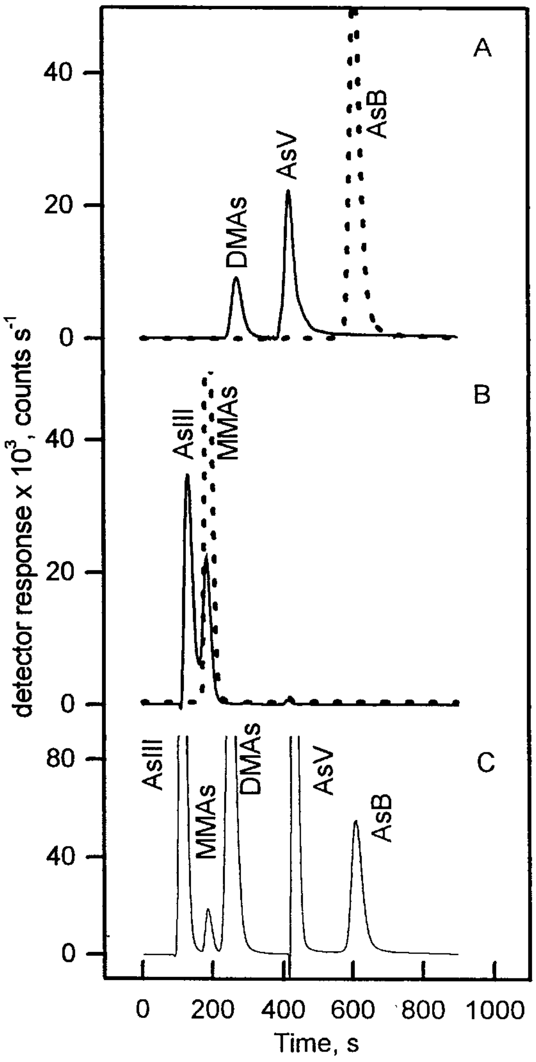


Figure 2. Chromatograms of AsB (A) and MMAs (B) solutions before (dotted lines) and after 7 days contact with zeolite ZME-CM (continuous lines). Chromatogram of a model mixture (C) used for peak identification.

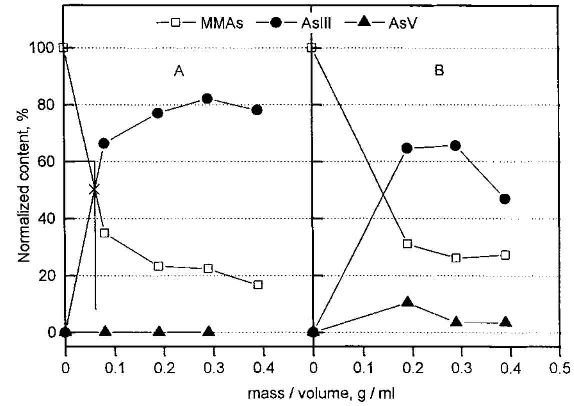


Figure 3. Dependence of the transformation of MMAs into As(III) and As(V) on the relation between zeolite mass and batch volume for the zeolite ZME-C after 7 days (A) and after 30 days (B).

synthetic mordenite ZS-M* was equilibrated with MMAs and AsB solutions, no removal of arsenic and no formation of new species, such as DMAs, As(III) and As(V), was observed. To be clear as to whether or not this zeolite type behaves differently from clinoptilolites, a more detailed study was carried out on synthetic washed ZS-M, synthetic unwashed ZS-M* and natural unwashed ZMT-M* mordenites. Figure 4 demonstrates that both natural ZMT-M* and untreated synthetic ZS-M* mordenites exhibit similar behaviour when chromatograms (d) and (f) are compared: a negligible diminution of the AsB concentration at the expense of the formation of As(V), whereby the extent of As(V) formed is higher in the experiments containing natural mordenite. Also, a small decrease of the MMAs concentration and formation of As(V) was observed [Fig. 4, chromatograms (e) and (g)] in experiments containing these samples. Furthermore, we considered the influence of the aqueous medium. An interesting observation in the two groups of zeolites studied was the pH change of the batch solutions, which had an initial value of pH 4. After 24 h, in both untreated mordenite experiments we obtained notably basic final solutions (Fig. 5). Among the clinoptilolites, the final solutions increased in pH value but remained in the acidic range. The explanation is that this is due to mordenite hydrolysis, since mordenites containing sodium can be

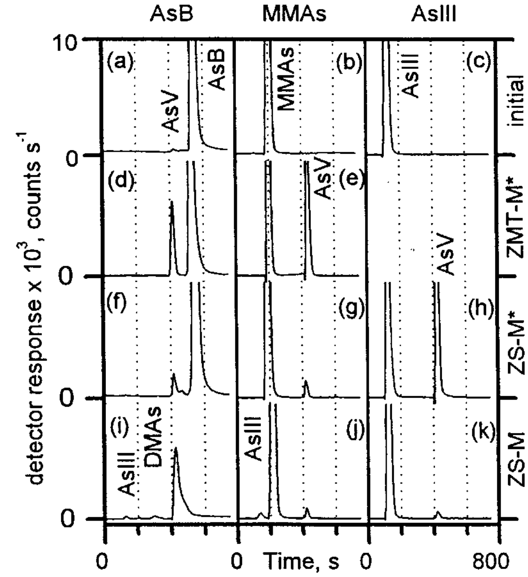


Figure 4. Chromatograms of batch solutions of AsB, MMAs and As(III) after 7 days contact with mordenite-type zeolites: natural ZMT-M*, synthetic unwashed ZS-M* and synthetic washed ZS-M; *m*/*V* = 0.1.

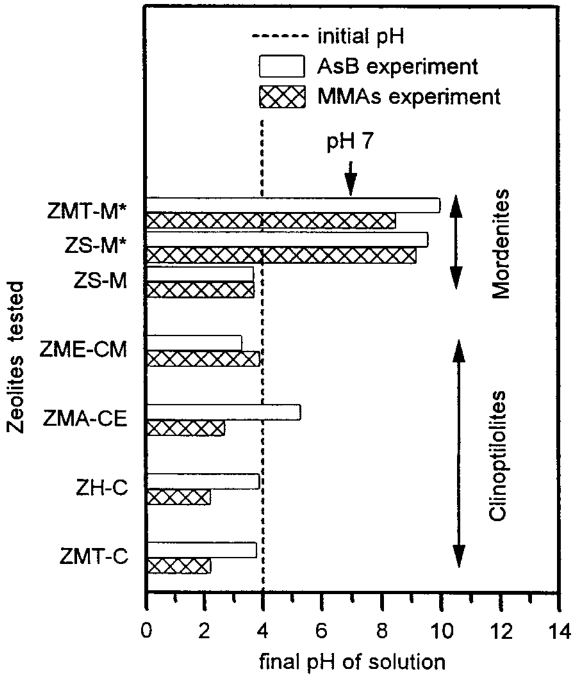


Figure 5. Variation of the pH after 24 h in the batch solutions of the systems zeolite/AsB solution and zeolite/MMAs solution using zeolites described in Table 1.

regarded as a salt producing free base and zeolite acid on the surface (Eqn. [(1)]):

$$[\mathrm{Na}^+ \cdots {}^-\mathrm{O{-}(Si, Al)}] + \mathrm{H_2O} \longleftrightarrow \mathrm{NaOH} + \mathrm{HO{-}(Si, Al)} \quad [1]$$

or a more acidic —OH group in the intracrystalline hydrolysis.

From this observation, and considering the effect of pH on the stability of the inorganic arsenic species, it can be expected that when the basicity of the solution grows, arsenite produces detectable amounts of arsenate. A solution of As(III) in contact with untreated synthetic mordenite ZS-M* confirmed this, as can be appreciated from Fig. 4, where 50% of the arsenite species transformed into arsenate [chromatogram (h)]. On the other hand, the similar behaviour of the untreated natural ZMT-M* and synthetic ZS-M* mordenites against AsB and MMAs could be interpreted on the basis of the obstruction of the 'large port' channels, whose windows are (6.5 × 7.0 Å) in the synthetic mordenite, since natural mordenites present mostly 'small port' (2.6 × 5.7 Å) channels. It is known that synthetic varieties may be either small or large port types, depending on the synthesis conditions and washing procedures. In order to obtain 'large port' synthetic mordenite, acid washing of zeolite ZS-M* was performed to produce ZS-M, and solution systems containing AsB, MMAs or As(III) were studied [see chromatograms (i)–(k) in Fig. 4]. Solutions in contact with ZS-M now produced the following results: AsB was absent in the solution, whereas up to 20% of As(V) emerged, together with detectable amounts of As(III), MMAs and DMAs. The MMAs content in the solution was reduced by just 10% and As(V) and As(III) were also detected. In the As(III) solution, no appreciable As(V) formation could be detected and arsenite concentration was reduced by 25%. The similarity between the behaviour of the mordenite and clinoptilolite zeolite types can be attributed to active sites present on both zeolites, and no sieve effect can be ascribed to the interaction, since any of the organic anions can penetrate into the clinoptilolites, as will be discussed below.

Molecular characteristics of organoarsenic compounds

The calculated molecular dimensions length, width and

Table 2. Calculated molecular characteristics of the arsenic species studied

Compound	Code	Molecular weight	Formula	Molecular parameters				
				Volume V_w ($\mathrm{cm^3\,mol^{-1}}$)	Surface A_w ($10^9\,\mathrm{cm^2\,mol^{-1}}$)	Length (Å)	Width (Å)	Depth (Å)
Arsonic acid	As(III)	125.94	H_3O_3As	37.6	5.8	6.64	5.32	5.47
Arsenic acid	As(V)	141.94	H_3O_4As	42.3	6.4	5.42	6.69	6.35
Monomethylarsonic acid	MMAs	139.97	CH_5O_3As	47.0	7.0	7.24	5.91	6.33
Dimethylarsinic acid	DMAs	137.99	$C_2H_7O_2As$	51.6	7.6	6.26	6.19	5.59
Tetramethylarsonium	4MAs	135.061	$C_4H_{12}As$	56.3	8.2	5.80	7.41	6.55
Trimethylarsinic oxide	TMAs	136.025	C_3H_9OAs	64.3	9.1	7.38	6.42	5.71
Arsenocholine	AsC	165.087	$C_5H_{14}OAs$	77.4	11.8	8.86	7.28	6.71
Arsenobetaine	AsB	178.06	$C_5H_{11}O_2^-As^+$	79.4	11.9	7.59	7.81	7.18
Phenylarsonic acid	PhAs	202.04	$C_6H_7O_3As$	79.8	10.2	9.51	6.36	7.21
o-Aminophenylarsonic acid	oAPhAs	217.056	C_6H_8NOAs	86.5	11.2	6.31	10.01	7.08
p-Aminophenylarsonic acid	pAPhAs	217.056	C_6H_8NOAs	86.5	11.2	11.05	7.20	5.54
Tetraphenylarsonium	4PhAs	383.344	$C_{24}H_{20}As$	194.7	22.0	11.36	11.85	11.49

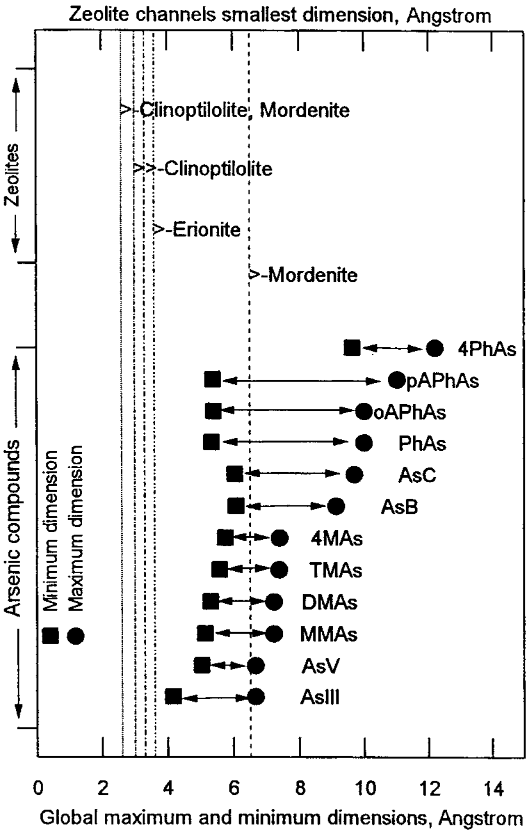


Figure 6. Dimensions range of organoarsenic compounds in comparison with zeolite channels smallest dimension.

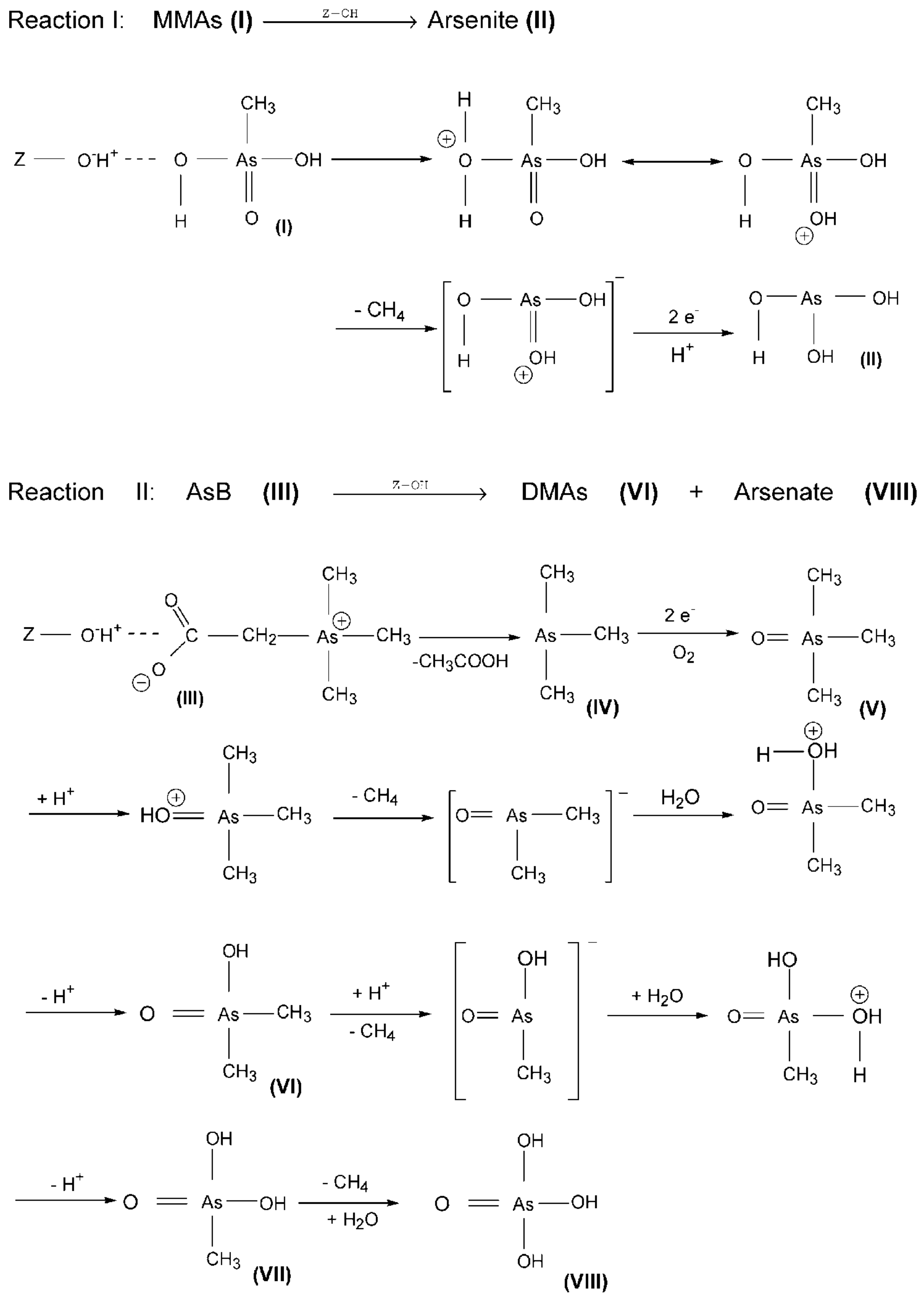
depth of 12 arsenic compounds are listed in Table 2. Bulkiness characteristics, like surface and volume, present a growing tendency with the number of carbon atoms in the molecule. We compared the calculated global minimum dimension and the global maximum dimension (not given in Table 2) with the channel dimensions of the zeolites clinoptilolite, erionite and mordenite in Fig. 6. It can be appreciated that the molecular range of the set of arsenic compounds is completely beyond the restrictive window dimension (dotted lines) of the three sized channels of clinoptilolite (2.6 × 4.7 Å), (3.0 × 7.6 Å), (3.3 × 4.6 Å), of the erionite channels (3.6 × 5.1 Å), and only within the broad window of the mordenite (6.5 × 7.0 Å), since its narrow window (2.6 × 5.7 Å) also presents a prohibiting width. The smallest minimum (4.2 Å) corresponds to As(III), and all molecules (except 4PhAs) present a global minimum smaller than the 6.5 Å mordenite window dimension. The 7 Å size of the (6.5 × 7.0 Å) window would determine that only As(III), As(V), MMAs, DMAs and TMAs with a smaller than 7 Å maximum depth could penetrate the broad windows of the mordenite, whereas the rest of the organoarsenicals cannot do it in any orientation. In the case where a molecule matches the window size, a perfect correspondence with its accessing orientation has to be accomplished.

Table 3. Relation between the organoarsenic compounds retained and formed in batch experiments after 7 days contact of AsB, MMAs and PhAs solutions with the zeolites described in Table 1; $m/V = 0.1$

Zeolite	$X \rightarrow Y + \mathrm{As(V)}$			
	Y formed	As(V) formed	X retained	X not retained
X = PhAs, Y = As(III)				
ZH-C	<1		72	28
ZMT-C	0		78	22
ZMA-C	<1	0	67	33
ZME-C	0		11	89
ZMT-M	0		20	80
ZS-M	0		23	76
X = MMAs, Y = As(III)				
ZH-C	16		62	22
ZMT-C	17		74	9
ZMA-C	20		67	13
ZME-C	66	<1	0.2	33
ZMT-M*	0.1		7	92
ZS-M*	0		4	95
X = AsB, Y = DMAs				
ZH-C	5	18	77	0
ZMT-C	5	8	87	0
ZMA-C	5	28	67	0
ZME-C	16	47	37	0
ZMT-M	0	13	3	84
ZS-M	0	2	13	85

Interaction with PhAs

After consideration of the infeasible penetration of MMAs and AsB into the channels present in the zeolites studied, we considered the study of PhAs, an organoarsenic molecule with almost the same volume as AsB. Table 3 presents these results, where it can be appreciated that no As(III) was formed. The clinoptilolites ZH-C, ZMT-C and ZMA-C retained 67–78% of PhAs, whereas the efficiency of the mordenites ZMT-M and ZS-M, together with the clinoptilolite ZME-C, is considerably lower. Taking into account the sieve effect of PhAs (see Fig. 6) into samples containing mordenite (see Table 1), e.g. into ZH-C and ZMT-M samples or clinoptilolite/30% mordenite zeolitic phase like the ZH-C and ZME-C samples, different removal of PhAs was obtained. However, ZME-C performed the transformations described above to a greater extent: greater amounts of As(III) were formed from MMAs and greater amounts of DMAs were formed from AsB. It is worth of mentioning that all clinoptilolites removed the original AsB, and that the DMAs formed was consumed in the formation of As(V), as presented above, and that this can be sorbed, as was demonstrated by us previously.[10] Examining Table 3, uptake of the initial arsenic compound by the group of three



Scheme 1.

clinoptilolites ZH-C, ZMT-C and ZMA-C, the sequence AsB >MMAs >PhAs can be established.

From the above results, we assume that the acid–base properties at specific sites of the external zeolite surface provide an explanation for the transformations observed. The proposed reactions taking place in solution in the presence of zeolites are shown in Scheme 1. Cleavage of bonds proceeds over acidic sites of the zeolites. Here, the zeolite could have functioned as a proton donor, as normally occurs in acid catalysis and which is favoured in the case of the organoarsenicals studied by the intermediate ionic species formed. The compounds **IV** and **V** are trimethylarsine and trimethylarsine oxide respectively, commonly occurring arsenic compounds. The products **VI, VII** and

VIII were observed in detectable amounts in the system AsB/ZS-M, whereas **VI** and **VIII** were observed in the systems AsB/clinoptilolites.

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