Modeling of AlPO4-8, VPI-5, and related structures

Citation for published version (APA):

DOI:
10.1021/j100204a063

Document status and date:
Published: 01/01/1992

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 03. Apr. 2019
Modeling of AlPO₄-8, VPI-5, and Related Structures

A. J. M. de Man, R. A. van Santen,*
Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

and E. T. C. Vogt

AKZO Chemicals BV, Research Centre Amsterdam, P.O. Box 26223, 1002 GE Amsterdam, The Netherlands
(Received: October 14, 1991; In Final Form: June 25, 1992)

The structure and infrared spectrum of AlPO₄-8, the 18-ring aluminophosphate VPI-5, and related structures are simulated using atomistic potentials and a generalized valence force field. The various topologies theoretically possible for the VPI-5 structure indicate that hexagonal prisms and cubes in the structure increase its lattice energy, thus decreasing the plausibility of the structure. This is not the only energy-determining feature; the relative orientation of neighboring tetrahedra also has an effect. The calculated differences in lattice energy between the 14-ring structure AlPO₄-8, the 18-ring structure VPI-5, and a hypothetical 24-ring structure are mainly due to density differences; no direct effect of the ring size on the lattice energy has been observed. Both VPI-5 and AlPO₄-8 show a shift of layers when their lattice energy is minimized by optimizing the crystallographic coordinates and unit cell parameters. The hypothetical 24-ring structure does not show such a shift. This is probably due to the flexibility of the 24-rings that can completely accommodate strains in the initial structure. This is also indicated by the large loss of symmetry of the structure. The simulated infrared spectrum of the hypothetical 24-ring structure is clearly distinguishable from that of VPI-5.

Introduction

One of the most spectacular zeolitic structures known today is VPI-5. This AlPO₄ material has pores with rings existing of 18 tetrahedra (called 18-rings), thus causing a pore diameter that is greater than 12 Å. The first reports of this structure,1,2 in 1988, received much interest because of the need for large-micropore, well-defined catalytic materials. The XRD pattern of VPI-5 is very similar to that of the SAPO structure MCM-9, which was patented in 1987.4 Analogies between VPI-5 and AlPO₄-8, which was first made in 1982,5 have been noted as well. At that time, it was suggested that MCM-9 and AlPO₄-8 also contain 18-membered rings. MCM-9 is a mixture of Si-VPI-5 and the 10-ring-containing structure SAPO-11.3,6 AlPO₄-8 has also been suggested to consist of 18-membered rings in layers that are shifted relative to each other(1 Figure 1), thus explaining its lower adsorption capacity.7 Although by now the sizes of the rings in AlPO₄-8 and VPI-5 are beyond discussion, the details of their structures are still uncertain. Experimental structure refinements have shown that AlPO₄-8 actually contains 14-rings,8 as was suggested for an early DLS structure.9 The observed transformation10 of VPI-5 to AlPO₄-8, be it reversible or not, also indicates a close relation between the two structures. Vine et al.11 observed that rather large conversions of VPI-5 to AlPO₄-8 result in minor changes in X-ray diffractograms, even though the pure VPI-5 and AlPO₄-8 structures each show some unique features. They hypothesise from powder XRD and HR-TEM the general existence of unarranged VPI-5 in AlPO₄-8, which of course obscures the structure determination of the latter. This apparently contradicts the conclusions of Davis et al.3 based on a combination of argon adsorption isotherms and powder XRD experiments that AlPO₄-8 does not contain extra large pores. The experimental data can also be explained by pore blocking. Another impurity often hindering the structure refinement of VPI-5 and AlPO₄-8 is the AlPO₂₄ hydrate H₃(PO₄)·13H₂O.12 Theoretical, modeling of AlPO₄ structures can help to solve these problems.

The VPI-5 topology is part of an infinite range of hexagonal (4,2) networks with increasing pore size designated 81, 81(1), and 81(2)14,15 (Figure 2). Net 81 corresponds to the 12-ring structure.
AIPO₄-8, which is discussed in a previous paper,⁶ net 81(1) equals VPI-5, and net 81(2) results in a 24-ring structure. There are several ways to generate a 24-ring structure,¹⁵ one of which will be discussed in this paper in order to investigate the feasibility of ultrawide pore structures. The 13 ways to derive an 18-ring structure in the enumeration of Richardson and co-workers¹⁷,²² will all be evaluated here. These structures look the same when projected along the c axis but differ significantly when viewed in other directions.

The structure of VPI-5 is strongly influenced by adsorbed species, e.g., water.¹⁹-²¹ Usually a small amount of silicon is present (about 5%). This study, however, is restricted to the bare AIPO₄ framework, which is also called AIPO₄-5⁴,¹⁷

Methods and Models

To select from a set of comparable structures, the most plausible one, generally lattice energy, is used as a criterion.²²-²⁸,²⁹ For silica systems, a wide variety of potential parameter sets have been developed in order to calculate this energy. For AIPO₄'s, this is not the case. In this study, a potential set is used that is derived by van Beest et al. on the basis of quantum chemical calculations of the potential surface of small molecular entities⁶,³¹ in combination with some crystal data. The model consists of Coulomb terms using partial charges (1.4 for Al, 3.4 for P, and -1.2 for O) and two-body terms of the Buckingham type for Si-O and O-O interactions. The potential parameters have been applied before to some zeolitic AIPO₄'s.²⁵,³² They form a consistent set with parameters for silica derived in a similar way.

Because of the low ability of this model to predict vibrational spectra,³¹ a generalized valence force field (GVFF³³) has been applied for the calculation of infrared spectra. This force field consists of harmonic nearest-neighbor stretching and bending forces and interactions between them. The force constant values have been derived by us from the experimental spectra of α-berlinite.

Lattice energy minimizations are done with the THBREL code.³²,³⁴,³⁵ A "constant pressure" relaxation was performed; i.e., the unit cell vectors as well as the atomic positions are optimized to minimize the lattice energy. No symmetry constraints are used in the relaxation. Ewald summations are applied for the Coulomb term in the energy. The short-range terms are only calculated within a region of 10 Å around each atom of the unit cell.

Calculations of spectra using a generalized valence force field are performed with the VIBRAT program of Dowty.²⁵,³⁶ The program uses the harmonic approximation for zero wave vector modes. Symmetry is explicitly used for solving the dynamical matrix. Infrared line strengths are calculated using formal ionic charges. For all spectral peaks, line widths of 10 cm⁻¹ and a Gaussian line shape were assumed. Unrelaxed and energy-minimized structures are both used for the calculation of infrared spectra.

### Table I: Results of the Lattice Energy Minimization of AIPO₄-8

<table>
<thead>
<tr>
<th>exp</th>
<th>8° DLS</th>
<th>8° ND</th>
<th>9 DLS, XRD</th>
<th>calc h.l.</th>
</tr>
</thead>
<tbody>
<tr>
<td>energy, kl/mol TO₂</td>
<td>-5609.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>symmetry</td>
<td>Cs</td>
<td>Cs</td>
<td>Cs</td>
<td>Cs</td>
</tr>
<tr>
<td>density, T/1000 Å¹</td>
<td>17.72</td>
<td>17.54</td>
<td>17.75</td>
<td>17.13</td>
</tr>
<tr>
<td>a, Å</td>
<td>33.0894</td>
<td>33.2900</td>
<td>33.29</td>
<td>34.275</td>
</tr>
<tr>
<td>c, Å</td>
<td>8.3630</td>
<td>8.3660</td>
<td>8.257</td>
<td>8.364</td>
</tr>
</tbody>
</table>

Table II: Root-Mean-Square Deviations from the Ideal Tetrahedral Angle (α₁) for Dense AIPO₄ Phases

<table>
<thead>
<tr>
<th>structure</th>
<th>ref</th>
<th>α₁</th>
<th>α₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-berlinite</td>
<td>42</td>
<td>2.4568</td>
<td>1.7962</td>
</tr>
<tr>
<td>β-berlinite</td>
<td>41</td>
<td>0.9326</td>
<td>1.5304</td>
</tr>
<tr>
<td>AIPO₄-cristobalite</td>
<td>43</td>
<td>2.7221</td>
<td>0.0392</td>
</tr>
</tbody>
</table>

Experimental Section

VPI-5 was prepared as described in ref 37. AIPO₄-8 was prepared from VPI-5 by heating the sample at 110 °C in air overnight. Infrared spectra of AIPO₄-8 and VPI-5 were recorded on a Biorad FTS 60 FTIR spectrometer.

Results

The results of the lattice energy minimization of AIPO₄-8 are given in Table I together with the data of the original structure refinements. The structure given by Richardson and Vogts⁸ based on powder neutron diffraction data at 200 °C is used as a start for the energy minimization. The relaxed structure shows a larger distortion of the AI₀₄ tetrahedra than of PO₄ tetrahedra, which agrees with the NMR experiments on AIPO₄-5 by Möller et al.⁸ This is quantified in Table II by means of σ₄, the root-mean-square deviation from the tetrahedral angle. The DLS structural data on AIPO₄-8 of Dessau et al.⁹ show the opposite. The cause of this discrepancy is very clear. If water is adsorbed, some octahedral aluminum atoms can be present in most AIPO₄'s, as indicated by NMR.⁹,¹⁰ Both Möller et al. and Dessau et al. give no information about the water content of their samples. Diffraction methods¹¹-¹⁴ and NMR experiments¹⁵ on dense, water-free, AIPO₄ phases do not show a distortion of the AI₀₄ tetrahedra of the size found in zeolitic AIPO₄ systems (Table II). So water can account for the differences in AI₀₄ distortion between various experiments. Our calculations, however, represent dehydrated structures and should therefore show small AI₀₄ distortions compared to most experiments.

Structural data on VPI-5 are listed in Table III. Also in this case, diffraction methods give lower tetrahedral distortions for AI₀₄ than for PO₄. An exception is the structure given by McGeer et al.¹¹ in which aluminum atoms on one of the three crystallographic sites are coordinated by four framework oxygens.
TABLE III: Results of the Lattice Energy Minimization of VPI-5

<table>
<thead>
<tr>
<th>ref</th>
<th>expt</th>
<th>46° DLS</th>
<th>57° XRD</th>
<th>21° XRD</th>
<th>20° XRD</th>
<th>20° XRD</th>
<th>calc h.l.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_{ex}</td>
<td>C_{ex}</td>
<td>C_{ex}</td>
<td>C_{ex}</td>
<td>C_{ex}</td>
<td>C_{ex}</td>
<td></td>
</tr>
<tr>
<td>symmetry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-5680.35</td>
</tr>
<tr>
<td>density, T/1000 Å^3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
<td>14.21</td>
<td>14.22</td>
<td>14.25</td>
<td>14.54</td>
<td>14.18</td>
<td>13.71f</td>
<td></td>
</tr>
<tr>
<td>c, Å</td>
<td>8.113</td>
<td>8.1155</td>
<td>8.1044</td>
<td>8.332</td>
<td>8.123</td>
<td>8.479</td>
<td></td>
</tr>
<tr>
<td>mean, Å</td>
<td>1.698</td>
<td>1.728</td>
<td>1.771</td>
<td>1.695</td>
<td>1.697</td>
<td>1.751</td>
<td></td>
</tr>
<tr>
<td>min, Å</td>
<td>1.687</td>
<td>1.692</td>
<td>1.704</td>
<td>1.691</td>
<td>1.694</td>
<td>1.747</td>
<td></td>
</tr>
<tr>
<td>max, Å</td>
<td>1.690</td>
<td>1.747</td>
<td>1.857</td>
<td>1.699</td>
<td>1.700</td>
<td>1.754</td>
<td></td>
</tr>
<tr>
<td>mean, deg</td>
<td>160.0</td>
<td>154.4</td>
<td>148.7</td>
<td>160.6</td>
<td>160.9</td>
<td>158.0</td>
<td></td>
</tr>
<tr>
<td>min, deg</td>
<td>125.0</td>
<td>124.4</td>
<td>136.6</td>
<td>118.4</td>
<td>123.1</td>
<td>130.1</td>
<td></td>
</tr>
<tr>
<td>max, deg</td>
<td>176.7</td>
<td>178.4</td>
<td>166.7</td>
<td>179.7</td>
<td>177.2</td>
<td>178.9</td>
<td></td>
</tr>
<tr>
<td>σ_{Al}, deg</td>
<td>3.938</td>
<td>3.445</td>
<td>16.61</td>
<td>3.116</td>
<td>4.431</td>
<td>5.520</td>
<td></td>
</tr>
</tbody>
</table>

*Uncalcined sample. hydration. Richardson et al., 17 investigating the thermal and hydrothermal stability of the silicon-free AlPO_4-54, found values of 19.009 and 8.122 Å for a hydrated sample and 18.549 and 8.404 Å for the dehydrated one. This shows there is virtually no influence of the (small) amount of silicon on the unit cell dimensions. A very striking difference between the experimental and calculated structures is the large increase of unit cell size for the latter and the decrease of symmetry. The length of the c axis is in reasonable agreement with the experimental data. Figure 4. Unrelaxed and relaxed structures of VPI-5 viewed along the a and c axes. From top to bottom: the structure of McCusker et al., 21 the structure of Crowder et al., 26 and the relaxed one. Globes represent aluminum atoms.
agreement with the value for the dehydrated structures, but the a axis is too large and tends to go to the value for hydrated VPI-5. This is partly explained by the net increase of the T-O distance due to the fact that the lengthening of the Al-O bond is larger than the decrease in the P-O distance.

In the relaxed structures of AlPO₄-8 and VPI-5, one observes a shift of layers (Figures 3 and 4). This shift is about 0.8 Å in the a direction for AlPO₄-8 and 0.7 Å in the same direction for VPI-5. Dessau et al.² also found a shift for AlPO₄-8 (see Figure 3), but in this structure, the phosphorus atoms are shifted to the pore, while in the relaxed structure the aluminum atoms are. The latter situation seems more reasonable in view of the usual water coordination of aluminum.¹⁹,⁴⁰,⁴⁵ The presence of a deviation from C₂ᵥ symmetry of VPI-5 is in accordance with the observation of McCusker et al.,²¹ but the direction of the shift of layers is not.

Figure 4 shows the VPI-5 structure of McCusker et al. that the one given by Crowder et al. and the relaxed VPI-5 structure. The shift of layers explains why the net increase in T-O distance has a larger effect on the length of the a unit cell vector than on the c vector.

Table IV shows structural data and calculated lattice energies for the nets enumerated by Richardson et al. The symmetries and unit cell dimensions apply to the AlPO₄ systems. The energies are given for the AlPO₄ and silica systems. The calculated energy shows a spurious density dependence, which can be corrected by the following empirical formula for AlPO₄ systems:²⁸

\[ E_c = E + 3.79207n_a \]  
(1)

where \( E_c \) is the corrected energy (kJ/mol of TO₂), \( E \) is the calculated energy (kJ/mol of TO₂), and \( n_a \) is the framework density (T atoms/1000 Å³). The density dependence is due to an overestimation of the \( r^2 \) term in the Buckingham potential for nonbonded atoms because these parameters were essentially derived for bonded interactions. In general, the correction can be expressed by

\[ \frac{4\pi}{3} (2C_{OO} + C_{TO}) \left( \frac{1}{R_i} - \frac{1}{R_{CO}} \right) n_a \]  
(2)

where \( C_{OO} \) is the O-O \( r^{-6} \) potential parameter, \( C_{TO} \) is the T-O \( r^{-6} \) potential parameter (T = Al, P, Si), \( R \) is the upper limit of the range of the \( r^{-6} \) terms, \( R_{CO} \) is the cutoff radius of short-range potential (10 Å), \( n_a \) is the framework density (T atoms/1000 Å³). The energy correction does not influence the internal coordinates of the relaxed structure because of its low geometry sensitivity. Previous studies on the relaxation of silica polymorphs²²-²⁹,30,31,47-⁴⁹ have shown that the uncorrected potential predicts crystal structures very well. For silica polymorphs, the need for the energy correction can easily be verified because of the availability of experimental data for the lattice energy. This is illustrated in Figure 5, where the correction is applied to the density.

silica partial charge potential, which is consistent with the AlPO₄ potential applied here, and to the so-called silica shell model. The corrected values of the lattice energy are also included in Table IV. From this table, one can conclude that net 520 is the most plausible. This is in complete agreement with a comparison between simulated and experimental powder diffraction patterns of the nets and AlPO₄-54 (the pure aluminumphosphate analogue of VPI-5), respectively. The table also shows the influence of double rings (hexagonal prisms and cubes) on the lattice energy. The presence of these substructures, however, is not the only factor determining the lattice energy. More subtle structural differences must account for the energy gap between net 520 and the nets 521, 523, and 524 and the presence of net 313 in the intermediate energy range. The structural feature playing a major role in this case is the presence of crankshaft¹⁵ chains which, in contradistinction to the suggestion of Brunner,⁵⁰ play a more favorable role. Only net 520 shows a complete alternation of tetrahedra pointing "up" and "down" (with respect to the c axis), while in all other nets adjacent tetrahedra pointing in the same direction occur. In other words, net 520 is the only structure in this enumeration that is completely composed of crankshaft chains. The energy trends for silica and AlPO₄ systems are comparable. The corrected

---

**TABLE IV: Results of the Lattice Energy Minimization of 18-Ring Nets**

<table>
<thead>
<tr>
<th>net</th>
<th>rings</th>
<th>units</th>
<th>symmetry</th>
<th>( a/a' )</th>
<th>( c/c' )</th>
<th>energy, kJ/mol of TO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>520</td>
<td>18</td>
<td>C₅</td>
<td>C₅</td>
<td>1.048</td>
<td>0.999</td>
<td>36.37 -4.66 49.49</td>
</tr>
<tr>
<td>523</td>
<td>8, 18</td>
<td>C₅</td>
<td>C₅</td>
<td>1.056</td>
<td>1.050</td>
<td>42.63 -1.47 56.63</td>
</tr>
<tr>
<td>521</td>
<td>18</td>
<td>C₅</td>
<td>C₅</td>
<td>1.065</td>
<td>1.033</td>
<td>43.08 -1.02 57.12</td>
</tr>
<tr>
<td>524</td>
<td>18</td>
<td>C₅</td>
<td>C₅</td>
<td>1.066</td>
<td>1.029</td>
<td>44.81 0.82 59.13</td>
</tr>
<tr>
<td>542</td>
<td>10, 18</td>
<td>C₅</td>
<td>C₅</td>
<td>1.060</td>
<td>0.990</td>
<td>44.87 3.12 59.13</td>
</tr>
<tr>
<td>525</td>
<td>8, 18</td>
<td>1h</td>
<td>D₅</td>
<td>1.062</td>
<td>0.995</td>
<td>45.55 0.77 60.53</td>
</tr>
<tr>
<td>313</td>
<td>8, 18</td>
<td>2h</td>
<td>D₅</td>
<td>1.044</td>
<td>1.069</td>
<td>45.83 0.78 61.32</td>
</tr>
<tr>
<td>560</td>
<td>18</td>
<td>C₅</td>
<td>C₅</td>
<td>1.078</td>
<td>1.032</td>
<td>51.06 5.82 67.31</td>
</tr>
<tr>
<td>561</td>
<td>14, 18</td>
<td>1h 2c</td>
<td>D₅</td>
<td>1.066</td>
<td>0.938</td>
<td>52.00 13.25 68.81</td>
</tr>
<tr>
<td>528</td>
<td>10, 18</td>
<td>1h</td>
<td>D₅</td>
<td>1.078</td>
<td>1.025</td>
<td>52.73 7.84 66.77</td>
</tr>
<tr>
<td>527</td>
<td>10, 18</td>
<td>2h</td>
<td>D₅</td>
<td>1.084</td>
<td>0.972</td>
<td>54.24 11.43 66.28</td>
</tr>
<tr>
<td>526</td>
<td>10, 18</td>
<td>2h</td>
<td>D₅</td>
<td>1.090</td>
<td>0.875</td>
<td>54.57 16.69 71.94</td>
</tr>
<tr>
<td>529</td>
<td>8, 12, 18</td>
<td>2h 2c</td>
<td>D₅</td>
<td>1.062</td>
<td>1.091</td>
<td>54.92 5.85 68.91</td>
</tr>
</tbody>
</table>

* Lattice energy for AlPO₄, density-corrected AlPO₄ (formula 1), and silica, respectively, relative to the energies of α-berlinite (5716.59 kJ/mol of TO₂) and α-quartz (5628.76 kJ/mol of SiO₂). ² Number of T atoms in ring. Each net has four-membered and six-membered rings. Structural units per unit cell: h = hexagonal prism (double six-ring), c = cube (double four-ring). Symmetry before and after lattice energy minimization. \( a/a' \) and \( c/c' \) are the ratios between the lattice vectors of the minimized and hypothetical structures. The \( a \) values are 18 Å for all structures. The \( c \) length is 9 Å for nets 313, 525, and 529 and 8.5 Å for the other nets, but the relaxations were all straited with \( c \) axes of 8.404 Å. ³ The average of \( a \) and \( b \) is taken.

---

**Figure 5.** Calculated lattice energies as a function of framework density of relaxed structures. The crosses represent the shell model results, the triangles give the partial charge model values, and the dots represent experimental data. The structures used are the same as those in ref 28. The energies are given relative to α-quartz (the absolute energy of α-quartz is -12417.28 kJ/mol of SiO₂ for the shell model and -5628.76 kJ/mol of SiO₂ for the partial charge model). (a) Not corrected for density dependence. (b) Corrected for density dependence.
energy values suggest that some structures might be more stable than a-berlinite. The influence of the initial symmetry on the structure relaxation was tested by randomizing the initial atomic coordinates of net 520 with an amplitude of 0.1 Å in each direction. Relaxation resulted in the same structure as found before.

A 24-ring structure, here referred to as Super-VPI-5, can be made from the 18-ring structure by replacing the crankshaft common to the 24-rings in VPI-5 by a double crankshaft. A double crankshaft has the same external connectivity as a single one, so this procedure could be repeated infinitely. This Super-VPI-5 structure is not equal to net 81(2) of Smith and Dytrych because it does not show a complete alternation of up- and down-pointing vertices. The topological symmetry of the Super-VPI-5 structure is $D_{6h}$ while net 81(2) has $D_{3d}$ symmetry. When the alternation of aluminum and phosphorus is taken into account, this reduces to $C_{6i}$ for Super-VPI-5 and $C_{2h}$ for net 81(2). Smith estimated the 24-ring pore diameter to be 15 Å. The relaxed structure of Super-VPI-5 is shown in Figure 6. Its symmetry is very low ($C_1$), but the unit cell is still hexagonal. No shift of layers occurs. The results of the energy minimization are given in Table V. The lattice energy difference between AlPO$_4$-8 and VPI-5 is equal to the difference between VPI-5 and Super-VPI-5 (10 kJ/mol of TO$_2$). The lattice energies corrected according to formula 1 are $-5625.96$, $-5628.36$, $-5628.27$, and $-5628.66$ kJ/mol of TO$_2$ for AlPO$_4$-8, VPI-5, net 520, and Super-VPI-5, respectively. So the energy differences decrease significantly by the correction; AlPO$_4$-8 is now the less stable structure. This indicates that a reversible VPI-5$\rightarrow$ AlPO$_4$-8 transformation is thermodynamically allowed. The 24-ring Super-VPI-5 is energetically allowed, so ultralarge-pore AlPO$_4$ structures might exist.

The infrared spectra of AlPO$_4$-8 and VPI-5 are shown in Figures 7 and 8. The spectra are calculated for both unrelaxed and relaxed (energy-minimized) structures. The calculated bending and symmetrical stretching modes (those below 800 cm$^{-1}$) are in good agreement with experiment. The asymmetrical stretching modes, however, differ extensively from experiment. The spectra obtained from the relaxed structures are slightly better than those obtained from the experimental, unrelaxed structures. This is probably due to the more feasible angles and distances present in the relaxed structures and the influence of water on the samples used for the experimental spectra. The calculated infrared spectrum of relaxed AlPO$_4$-8, VPI-5, and Super-VPI-5 structures, one observes a merging of the two peaks in the bending region (400-550 cm$^{-1}$) and an increase of the number of peaks that can be distinguished in the symmetrical stretch region (650-800 cm$^{-1}$).

Conclusions and Discussion

For various structures presented here, relaxation results in a lower symmetry than used in the experimental structure determinations. The question arises whether this is due to artifacts in the potential set or to inaccuracies in the experiments. In the structure determination of AlPO$_4$-8, five T sites are present in a 1:2:2:2:2 crystallographic multiplicity ratio. The $^{31}$P NMR spectra of hydrated samples show three peaks at a 1:2:6 ratio. This is not necessarily a contradiction; three crystallographic sites may show a close resemblance. For AlPO$_4$'s and alumin-
silicates, a relation exists between the average of the T-O-T angles a T atom takes part in and the NMR shift of that atom. So the mean T-O-T angles can be used to estimate whether NMR peaks of various T sites will differ. Multiplicities and average T-O-T angles for the P sites in AlPO$_4$-8 are given in Table VI. The experimental and calculated structures do not exactly result in three 31P NMR peaks with the intensity ratio given above. From diffraction data, a 1:2:2:4 ratio seems most probable, while our calculations suggest three peaks in a 2:2:5 intensity ratio. The diffraction data are not really incompatible with the NMR experiment.

31P NMR spectra obtained by Davis et al. indicate that the symmetry of VPI-5 is lower than given by diffraction experiments. The original structures based on XRD or neutron diffraction have two P sites, the one in the six-membered ring (Si site) and the one in the two adjacent four-rings, in a ratio of 2:1. Davis observed three 31P NMR peaks in a 1:1:1 ratio due to splitting of the Si site. This splitting is not caused by template molecules but still might originate from occluded water because it is not seen at high temperatures (150 °C). A NMR peak due to POH is sometimes observed, but can be easily discriminated from the "pure" structural peaks. The VPI-5 structure derived by McCusker et al. from powder XRD does contain three crystallographic P sites with equal multiplicities. Our relaxed structure, however, has five crystallographic P sites. This may be consistent with the change of the intensity ratio of the NMR peaks that is observed by Stöcker et al. for a carefully dried VPI-5 sample.

Table VII shows the multiplicity and mean P-O-Al angles of the P sites. It is clear that the relaxed VPI-5 structure gives at least four and most probably five peaks in the 31P NMR spectrum.

If we ascribe the distortion of the AlO$_4$ tetrahedra found in some experiments to the presence of water, the large distortion of the AlO$_4$ tetrahedra compared with PO$_4$ tetrahedra in our calculations has to be caused by a flaw in the interatomic potential. For silica, the presence of an O-T-O bond-bending term has been shown to be essential, at least for potentials using formal charges. The potential applied here does not have a bending term, but this does not have to be the reason for the distortion of the tetrahedra. A slight change of the (partial) charges used may have a large influence on the structural features. This has been observed for the absolute charge in the silica potential that is compatible with the AlPO$_4$ potential and for the P-Al charge difference in the AlPO$_4$ potential. An improvement of the potential by changing the charges is preferred over the inclusion of a O-T-O three-body term. This will also affect the magnitude of the shift of layers. The absence of a layer shift in the relaxed Super-VPI-5 structure and the presence of such a shift in the relaxed AlPO$_4$-8 and VPI-5 structures can probably be explained by a higher flexibility of the 24-rings compared with the 14- and 18-rings. Whereas the strain in the initial Super-VPI-5 structure can be accommodated by a deformation of the 24-rings (resulting in a very low symmetry), the rings in AlPO$_4$-8 and Super-VPI-5 are not changed and the reduction of energy is performed by the shift of layers.

The discrepancy between calculated and observed infrared spectra can partly be caused by the silicon present in the experimental samples, although silicon-containing models are low, and by an artifact of the procedure for obtaining the generalized valence force field. The parameters for the AlPO$_4$ force field were derived by fitting the spectrum of α-berlinite. Some peaks in the experimental spectra of α-berlinite used are subject to discussion, especially the one at 1230 cm$^{-1}$. Inclusion of the latter peak in the fitting procedure may have caused an overestimation of a stretching force constant. The discrepancy in bandwidth between calculated and experimental spectra has been observed before in the case of pure silica systems. Theoretically, the Al-O-P angle size and distribution are reflected in the position and shape of the stretching peaks. This cannot be the cause of the discrepancy between calculated and experimental spectra because both the average and the extrema of the calculated angles are in good agreement with experiment and the experimental line widths would require angles that are improbable. The use of relaxed structures in the spectra simulations is to be preferred. The differences between experimental and calculated spectra do not obstruct the use of these calculations for identifying structures because the main differences between the experimental spectra of AlPO$_4$-8 and VPI-5 are reflected in the simulations.

Acknowledgment. We thank J. W. Richardson, Jr., for providing detailed information concerning the hypothetical networks related to VPI-5 and L. B. McCusker for sending a preprint of ref 21.

Registry No. AlPO$_4$, 7784-30-7.

References and Notes

(18) Richardson, J. W. Private communication.
(29) Grant, G. H.; Abrahams, R. J. Catal. 1990, 9, 68.
(34) Leslie, M. Daresbury Laboratory Technical Memorandum, in preparation.
(52) Klinowski, J. Prog. NMR Spectrosc. 1984, 16, 237.
(57) Rudolf, P. R.; Crowder, C. E. Zeolites 1990, 10, 163.

Transition of Mixing Scheme in the Water-Rich Region of Aqueous 2-Butoxyethanol:
Partial Molar Volumes and Their Derivatives†

Yoshikata Koga
Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1
(Rceived: February 14, 1992; In Final Form: September 8, 1992)

The mixing scheme boundary proposed in paper 1 (J. Phys. Chem. 1990, 94, 3879) was extended to high temperatures. Using the data of the excess partial molar volumes in aqueous solutions of 2-butoxyethanol (BE), $V_m^E(i)$ (i = BE or H2O), reported in paper 2 (J. Chem. Thermodyn., in press), the composition derivatives of $V_m^E(BE)$, $(\partial V_m^E(BE)/\partial n_{BE})_{n_H2O}$, were calculated. These partial molar quantities provide direct information about the actual contribution of the i-th substance to the mixture in terms of enthalpy and entropy, respectively. They were determined accurately and in small increments in composition. It was therefore possible to evaluate composition derivatives,

$$(\partial H_m^E(i)/\partial n_{i})_n = [(1-x)/N]|(\partial H_m^E(i)/\partial x)|$$

and

$$(\partial S_m^E(i)/\partial n_{i})_n = [(1-x)/N]|(\partial S_m^E(i)/\partial x)|$$

with a reasonable accuracy, within several percent. N is the total amount of the mixture, and x is the mole fraction of the i-th substance. Thus, it has been argued intuitively that they provide a measure of the i-i interaction in terms of enthalpy and entropy. Using these quantities, we have pointed out that there are three composition regions in the single-phase domain, in each of which the mixing scheme is qualitatively different from those in the other regions. Furthermore, we have pointed out that the crossovers between the neighboring regions are associated with anomalies in the third or the fourth derivatives of the Gibbs free energy. In particular, the transition of mixing scheme from the water-rich to the intermediate regions is associated with peak anomalies in the third derivatives of the Gibbs free energy. In ref 1 (called paper 1 hereinafter) we contrasted these anomalies in the third derivatives with those associated with bulk phase transitions. Namely, the latter are accompanied by various anomalies in response functions, the second derivatives of Gibbs free energy. Since bulk phase transitions involve some changes in long-range order, we suggested that the transition in mixing scheme from the water-rich to the intermediate regions of BE-H2O mixes is related to a transition in short- to medium-range order and that it is associated with anomalies in the third derivatives of Gibbs free energy. In paper 1, we also presented the mixing scheme boundary in the temperature–mole fraction field (Figure 3 in paper 1) that separates the water-rich from the intermediate regions as the loci at which all the available thermodynamic quantities proportional to the third derivatives of Gibbs free energy show peak or cusp anomalies.

We have therefore started a program of determining various thermodynamic quantities proportional to the third derivatives of Gibbs free energy in the water-rich region of aqueous solutions of BE. Recently, we measured the thermal expansivities (the second derivative) of the BE-H2O mixtures in small increments in mole fraction and took mole fraction derivatives thereof. The latter, the third derivative, showed peak anomalies at the same loci shown in Figure 3 of paper 1.

Introduction

In the previous studies from this laboratory on aqueous solutions of 2-butoxyethanol (abbreviated as BE), the excess partial molar enthalpies, $H_m^E(i)$, and the excess partial molar entropies, $S_m^E(i)$, were determined. Here i stands for BE or H2O, and nH2O is the amount of i-th substance in solution. These partial molar quantities provided direct information about the actual contribution of the i-th substance to the mixture in terms of enthalpy and entropy, respectively. They were determined accurately and in small increments in composition. It was therefore possible to evaluate composition derivatives,

$$(\partial H_m^E(i)/\partial n_{i})_n = [(1-x)/N]|(\partial H_m^E(i)/\partial x)|$$

and

$$(\partial S_m^E(i)/\partial n_{i})_n = [(1-x)/N]|(\partial S_m^E(i)/\partial x)|$$

with a reasonable accuracy, within several percent. N is the total amount of the mixture, and x is the mole fraction of the i-th substance. Thus, it has been argued intuitively that they provide a measure of the i-i interaction in terms of enthalpy and entropy.

$^1$This paper is dedicated to Professor Loren G. Hepler on the occasion of his retirement.

0022-3654/92/2096-10466$03.00/0 © 1992 American Chemical Society