the bimolecular reaction $RO^{-*} + H_3O^+$, the probability of which being practically nil during the lifetime of the excited state. The rate that is measured in water is possibly the rate of geminate recombination from a small fraction of the ion pairs (RO^{-*},H_3O^+), while the proton is still within the Coulomb radius;[52,53] for most of the ion pairs, the proton diffusion leads to complete dissociation and then the recombination takes place in the ground state, after the fluorescence decay of RO^{-*}.[18]

In reversed micelles ($w \lesssim 12$), the proton recombination is faster than in bulk water, owing to the higher probability of geminate recombination with respect to the dissociation of the ion pair. As a matter of fact, the dissociation is hampered because of the peculiar structure of the aqueous core (little amount of hydrogen bonding, lower mobility of the oxygen atoms of water molecules, and relatively high viscosity of the medium). It is also of interest to consider the size parameters involved in this system: pyranine has a hydrodynamic radius of 4.7 Å;[54] the Debye radius[42] is 28 Å[18] in water and less than 10 Å in a 0.1 M salt solution;[21] the radius of the water pool is about 9 Å at $w = 3$ and about 20 Å at $w = 11.5$.[15] All these considerations lead us to think that, during the lifetime of the excited state, the ejected proton remains more or less in the vicinity of RO^{-*} at low water contents. This cavity effect is to be compared with the observations of Gutman et al.[30] concerning the behavior of pyranine in the apomyoglobin binding site.

Conclusion

Kinetics of proton transfer in reversed micelles brings interesting information on the relation between structure and reactivity and permits a better understanding of the acidity in the aqueous core and an evaluation of the water activity. In the present work, fluorescence probing around the center of the water pool reveals that the proton-transfer efficiency and the water activity become similar to those in bulk water beyond a water content of $w \sim 12$. However, at a closer distance to the interface and even more at the interface, proton transfer is expected to be less efficient because water molecules close to the interface participate in the hydration of sodium ions and ionic heads of surfactant. Appropriate probes will be used in the future for this study. Experiments are also in progress in our laboratory for investigating the effects of injected buffered solutions and basic or acid solutions on proton-transfer dynamics in the water pool of reversed micelles.

Acknowledgment. We are grateful to Dr. M. T. Le Bris for her help in the difficult purification of pyranine.

Registry No. AOT, 577-11-7; pyranine, 6358-69-6.

Supplementary Material Available: Derivation of the equations used in differential phase fluorometry in the case of reversible and irreversible proton transfer (2 pages). Ordering information is available on any current masthead page.

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[52] M. Hauser, H. P. Haar, and U. K. A. Klein, *Ber. Bunsenges. Phys. Chem.*, **81**, 27 (1977).

[53] H. P. Haar, U. K. A. Klein, and M. Hauser, *Chem. Phys. Lett.*, **58**, 525 (1978).

[54] H. P. Haar, U. K. A. Klein, F. W. Hafner, and M. Hauser, *Chem. Phys. Lett.*, **49**, 563 (1977).

Enthalpies, Free Energies, and Entropies of Transfer of Phenols from Nonpolar Solvents to Water

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The enthalpies of transfer of seven phenols from 1-octanol to water and from toluene to water were determined by calorimetry. In the case of two phenols, whose rate of solution in water was found to be too slow for measurement by the usual heat of solution method, a new two-phase titration method was employed. The free energies of transfer between these solvents were determined by measuring the appropriate partition coefficients. The nature of the nonpolar solvent (toluene or 1-octanol) was found to cause large changes in the average values of the thermodynamic parameters of transfer into water, as well as changes in the ordering of the phenols in the series with respect to these transfer parameters. A curious correlation was observed between the octanol-water partition coefficients and the toluene → water entropies of transfer.

Introduction

The importance of hydrophobic interactions for the understanding of a variety of biological problems such as the stabilization of protein structures has long been recognized and is the subject of continuing study.[1-6] The very nature of the hydrophobic effect is at present a subject of active investigation[7-10] as is the associated question of the water structure enhancing capacity of nonpolar solutes in water[11,12] and the consequences this may have for chemical[13] and biological[14] phenomena. One of the most interesting and useful demonstrations of the importance of the hydrophobic effect is to be found in the Hansch analysis[15,16] of drug

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[1] Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 507.

[2] Kauzmann, W. *Adv. Protein Chem.* **1959**, *14*, 1.

[3] Franks, F. Ed. "Water, a Comprehensive Treatise"; Plenum Press: New York, 1972-1982; Vol. 1-7.

[4] Hopfinger, A. J. "Intermolecular Interactions and Biomolecular Organization"; Wiley: New York, 1977.

[5] Tanford, C. "The Hydrophobic Effect: Formation of Micelles & Biological Membranes"; Wiley: New York, 1980.

[6] Nemethy, G.; Peer, W. J.; Sheraga, H. A. *Ann. Rev. Biophys. Bioeng.* **1981**, *10*, 459.

[7] Abraham, M. H. *J. Am. Chem. Soc.* **1982**, *104*, 2085.

[8] Mirejovsky, D.; Arnett, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 1112.

[9] Wertz, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 5316.

[10] Stillfinger, F. H. *Science* **1980**, *209*, 451.

[11] Savaminathan, S.; Beveridge, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 5832.

[12] Jorgensen, W. L. *J. Chem. Phys.* **1982**, *77*, 5757.

[13] Engbersen, J. F. J.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1975**, *97*, 1563.

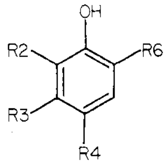
[14] Haberfield, P.; Kivuls, J. *J. Med. Chem.* **1973**, *16*, 942.

[15] Hansch, C.; Muir, R. M.; Fujita, T.; Maloney, P. P.; Geiger, F.; Streich, M. *J. Am. Chem. Soc.* **1963**, *85*, 2817.

[16] Hansch, C.; Leo, A. "Substituent Constants for Correlation Analysis in Chemistry and Biology"; Wiley: New York, 1979.

0022-3654/84/2088-1913$01.50/0

TABLE I: Heats of Solution, ΔH_S, of Phenols in Toluene, 1-Octanol, and Water and Enthalpies of Transfer, $\delta\Delta H_{S_1 \rightarrow S_2}$, from the Organic Solvents to Water at 25 °C



phenol	R2	R3	R4	R6	ΔH_{tol}, kcal/mol	ΔH_{oct}, kcal/mol	ΔH_{H_2O}, kcal/mol	$\delta\Delta H_{oct \rightarrow H_2O}$, kcal/mol	$\delta\Delta H_{tol \rightarrow H_2O}$, kcal/mol
1	H	H	H	H				2.6^b	-1.5^b
2	H	H	CH_2OH	H	6.02	3.22	5.27	2.05	−0.75
3	H	CH_2OH	H	H	9.48	3.08	5.49	2.41	−3.99
4	CH_2OH	H	H	H	8.29	3.96	4.97	1.01	−3.32
5	CH_2OH	H	CH_3	H	8.06	4.02	4.54	0.52	−3.52
6	CH_2OH	H	Cl	H	7.55	1.85	4.79	2.94	−2.76
7	CH_2OH	H	Br	H	7.67	2.40		1.14^c	-4.13^d
8	CH_2OH	H	Cl	Cl	8.22	2.58		2.06^c	-3.58^d

[a] Integral heats of solution, measured at concentrations ranging from 5×10^{-4} to 10^{-2} M; standard deviations from the mean were 0.2 kcal or better. [b] From ref 17. [c] $\delta\Delta H_{oct \rightarrow H_2O} = \Delta H_{tol} - \Delta H_{oct} + \delta\Delta H_{tol \rightarrow H_2O}$. [d] Obtained by using the titration–extraction procedure; see Experimental Section.

action. This method utilizes octanol–water partition coefficients of homologous series of biologically active substances as a measure of their relative hydrophobicity. Recent work by Breslauer[17] on the thermodynamics of solvent transfer of phenol and aniline has shown that the thermodynamic parameters of transfer into water differ widely, depending on the choice of the organic solvent. This has grest significance for problems such as Hansch analysis or for studies where the thermodynamic parameters of transfer from an organic solvent to water in a series of solutes are taken as a measure of their relative hydration parameters.[18]

We thought if would be useful to examine the enthalpies, free energies, and entropies of transfer of a series of related compounds from two organic solvents into water to see not only the gross changes in these parameters on changing the organic solvent but also to see what changes, if any, took place in the relative order of the compounds with respect to each parameter. The solvents employed were 1-octanol (because of its extensive use in biological structure activity studies) and toluene, a more lipophilic as well as a nonhydrogen-bonding solvent.[19] As solutes, we chose a series of phenols for which some early structure–activity data[20] and analysis[21] are available.

Results and Discussion

The enthalpies of transfer of the phenols were determined calorimetrically and are listed in Table I. The enthalpies of transfer of phenols **2**–**6** (see Table I for structures) were determined by measuring their heats of solution in water, in 1-octanol, and in toluene, the enthalpy of transfer between any pairs of these solvents being the difference between the heats of solution in the two solvents:

$$\delta\Delta H_{oct \rightarrow H_2O} = \Delta H_{H_2O} - \Delta H_{oct}$$

The rates of solution of compounds **7** and **8** in water were too slow for an accurate measurement of their heats of solution in water. For these compounds, the enthalpies of transfer between toluene and water were determined by measuring the heat of mixing of a toluene solution of the phenol and an aqueous solution of NaOH. Subtraction of the (aqueous) heat of neutralization of the phenol from the above two-phase titration heat yielded the heat of transfer of the phenol from toluene to water (see Experimental Section for details). This method, which is similar to that of Breslauer,[17] gave good results and is to be recommended for enthalpies of transfer of organic acids or bases which suffer from slow rates of dissolution in water. The enthalpies of transfer of these two compounds from 1-octanol to water can then be calculated by subtracting the heat of solution in 1-octanol from the sum of the toluene → water transfer enthalpy plus the heat of solution in toluene (see Table I). For purposes of comparison, Table I also contains the transfer enthalpies of phenol itself (compound **1**) as measured by Breslauer, Witkowski, and Bulas.[17]

On examining the enthalpies of transfer of these phenols from the two nonpolar solvents to water (last 2 columns in Table I), the first observation that can be made is that these quantities are clearly not principally a measure of solute–water interactions. This is so because, as has been noted before,[17] the nature of the particular nonpolar solvent used has a substantial effect on the enthalpy of transfer. In fact, the $\delta\Delta H$ values into water from these two solvents do not even have the same sign, the differences between the two organic solvents ranging from 2.8 to 6.4 kcal/mol. One possibility is that these large differences reflect the differences between the cavity formation energies in toluene and in 1-octanol. However, this is not likely. A measure of the cavity formation energy differences between these two solvents is the enthalpy of transfer of an "inert" molecule such as CH_4 or SF_6. The enthalpy of transfer of these two compounds from toluene to octanol ($\delta\Delta H_{tol \rightarrow oct}$) is 0.23 and −0.30 kcal/mol, respectively.[7] These values are an order of magnitude smaller than $\delta\Delta H_{tol \rightarrow oct}$ values for our phenols, and hence it is reasonable to suppose that our differences are due to specific solute–solvent interactions between the phenols and octanol (and/or toluene) rather than to major differences in the cavity formation energies of these two organic solvents.

The difference between the two organic solvents is probably due to hydrogen bonding between the 1-octanol and the phenols. The enthalpies of transfer of the phenols from toluene to octanol (Table IV, column 3) show values which are reasonable for an O–H–O hydrogen bond. The enthalpies of transfer of the phenols from toluene to water (Table I, last column), on the other hand, seem to reflect mainly the cavity formation energy difference between toluene and water. (This can be seen by again considering the CH_4 and SF_6 models, which have $\delta\Delta H_{tol \rightarrow H_2O}$ values of −2.1 and −3.5 kcal/mol, respectively.) The positive $\delta\Delta H_{tol \rightarrow H_2O}$ values are then seen to arise from the difference between the ~3 kcal/mol water cavity formation energy and the ~5 kcal/mol octanol–solute hydrogen bond.

The other observation that can be made on examining these enthalpy values is that there is clearly no correlation whatever

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[17] Breslauer, K. J.; Witkowski, L.; Bulas, K. *J. Phys. Chem.* **1978**, *82*, 675.

[18] Arnett, E. M.; Small, L. E.; Oancea, D.; Johnston, D. *J. Am. Chem. Soc.* **1976**, *98*, 7346.

[19] Some relevant physical properties of these solvents are: dielectric constant, 1-octanol 10.3, toluene 2.4 (Maryott, A.; Smith, E. "National Bureau of Standards Circular 514"; US Government Printing Office: Washington, DC, 1951); dipole moment, 1-octanol 1.60 D, toluene 0.37 D (McClellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, CA, 1963).

[20] Dunning, B.; Dunning, F.; Reid, E. E. *J. Am. Chem. Soc.* **1936**, *58*, 1565.

[21] Hansch, C.; Kerby, R. *J. Med. Chem.* **1970**, *13*, 957.

TABLE II: Partition Coefficients, P, and the Corresponding Free Energies of Transfer, $\Delta G^\circ_{S_1 \rightarrow S_2}$, of Phenols from Toluene to Water and n-Octanol to Water at 25 °C

phenol[a]	P(toluene-H_2O)[b]	$\Delta G^\circ_{tol \rightarrow H_2O}$, kcal/mol	P(oct-H_2O)[b]	$\Delta G^\circ_{oct \rightarrow H_2O}$, kcal/mol
1		0.27[c]		1.80[c]
2	1.79	0.35	1.78	0.34
3	0.0089	−2.80	3.18	0.69
4	0.13	−1.20	3.62	0.76
5	0.47	−0.45	9.40	1.33
6	0.92	−0.05	27.5	1.96
7	1.56	0.26	52.2	2.34
8	9.35	1.32	199	3.14

[a] For structures, see Table I. [b] Partition coefficients measured at concentrations ranging from 10^{-4} to 10^{-3} M; standard deviations from the mean were 3% or better. [c] From ref 17.

TABLE III: Entropies of Transfer of Phenols, $\Delta S^\circ_{S_1 \rightarrow S_2}$, from Octanol to Water and Toluene to Water at 25 °C

phenol[a]	$\Delta S^\circ_{oct \rightarrow H_2O}$, cal/(deg mol)	$\Delta S^\circ_{tol \rightarrow H_2O}$, cal/(deg mol)
1	2.8[b]	−5.9[b]
2	5.73	−3.68
3	5.77	−4.01
4	0.85	−7.09
5	−2.73	−10.32
6	3.27	−9.09
7	−4.03	−14.73
8	−3.61	−16.44

[a] For phenol structures, see Table I. [b] From ref 17.

between the order of the octanol → water enthalpies of transfer of compounds **2**–**8** and their toluene → water enthalpies of transfer.

The free energies of transfer of the phenols, determined by measuring their 1-octanol–water and toluene–water partition coefficients, are shown in Table II. Phenol aggregation has been found to be negligible at the concentrations used in this work.[22] As in the case of the enthalpies of transfer, it can be seen that the choice of the nonpolar solvent substantially modifies the magnitude of the free energies of transfer into water. This suggests that the phenol–organic solvent interactions are as important as the phenol–water interactions and the water cavity formation energy in determining the magnitude of the free energies of transfer into water. However, the manner in which the ΔG° of transfer values are affected by structural changes in the phenols is about the same for the two organic solvents. Compounds **2**–**8** are listed in the order of increasing octanol–water partition coefficient (i.e., the order of their Hansch π values[16,21]). This order is maintained when one looks at the toluene–water partition coefficients, except for compound **2** which is out of place to a spectacular degree.[24] Thus, Hansch structure–activity correlation analysis should give roughly similar results even when substantially different nonpolar solvents are used to provide the partition coefficients.

Entropies of solvent transfer, calculaed from the above enthalpies and free energies, are shown in Table III. They exhibit a substantial range. The entropies of transfer of SF_6 and CH_4 from toluene to water are −24.9 and −16.1 cal/(deg mol), respectively. Taking these values as a measure of the difference between the cavity formation entropies of these two solvents for cavities of corresponding sizes, we can see that the $\Delta S^\circ_{tol \rightarrow H_2O}$ values of our phenols seem to approach these values, though they do appear to be smaller per unit volume. The $\Delta S^\circ_{oct \rightarrow H_2O}$ values are much more positive, reflecting a substantial contribution from the entropy of formation of the solute–octanol hydrogen bond.

TABLE IV: Thermodynamics of Transfer of Phenols from Toluene to Octanol at 25 °C

phenol[a]	$\Delta G^\circ_{tol \rightarrow oct}$, kcal/mol	$\Delta H^\circ_{tol \rightarrow oct}$, kcal/mol	$T\Delta S^\circ_{tol \rightarrow oct}$, kcal/mol
1	−1.53	−4.1	−2.56
2	0.01	−2.79	−2.81
3	−3.49	−6.40	−2.92
4	−1.96	−4.33	−2.37
5	−1.78	−4.04	−2.26
6	−2.02	−5.60	−3.69
7	−2.08	−5.27	−2.99
8	−1.81	−5.63	−3.83

[a] See Table I for structures.

A most curious feature of these entropy values is the fact that, for phenols **2**–**8**, the order of their octanol–water partition coefficients (the "Hansch order") is the same[25] as the order of their toluene → H_2O (but not their octanol → H_2O) entropies of transfer. If the entropy of transfer from toluene to water is taken to reflect mainly the water structuring effect on dissolving the organic solute in water, i.e., its "hydrophobicity", then this correlation with Hansch π values, which in turn correlate various biological phenomena, is of some interest. It remains to be seen whether this correlation of $\Delta G^\circ_{oct \rightarrow H_2O}$ with $\Delta S^\circ_{tol \rightarrow H_2O}$ holds for other classes of compounds.

To highlight the difference between the two nonpolar solvents used in this study, we list their thermodynamic parameters of transfer from one organic solvent to the other in Table IV. The most notable feature is the constancy of the $\Delta S^\circ_{tol \rightarrow oct}$ values which evidently reflect the magnitude of the solute–octanol hydrogen bond and appear to be only slightly perturbed by electronic effects or the size of the solute molecules.

Experimental Section

Materials. 1-Octanol (Aldrich) was washed and distilled. Toluene (Aldrich, A.C.S. reagent) was used without further purification. 4-Hydroxybenzyl alcohol (**2**) (Aldrich) was recrystallized from water, mp 124–125° (lit.[20] mp 124°). 3-Hydroxybenzyl alcohol (**3**) (Aldrich) was recrystallized from benzene, mp 67–68° (lit.[20] mp 71°). 2-Hydroxybenzyl alcohol (**4**) (Aldrich) was recrystallized from benzene, mp 86–87° (lit.[20] mp 87°). 2-Hydroxy-5-chlorobenzyl alcohol (**5**) was prepared from the corresponding aldehyde by hydrogenation at 20 lbs/in.^{2} pressure over 3% PtO_2 Adam's catalyst in 95% ethanol solvent. The product was recrystallized from water, mp 89–90° (lit.[20] mp 90°). 2-Hydroxy-5-bromobenzyl alcohol (**7**) was prepared in the same manner. Recrystallization from benzene yielded material of mp 108–109° (lit.[20] mp 109°). 2-Hydroxy-3,5-dichlorobenzyl alcohol (**8**) was also prepared by hydrogenation of the aldehyde. Recrystallization from benzene yielded product of mp 82–83° (lit.[20] mp 83°). 2-Hydroxy-5-methylbenzyl alcohol (**6**) was prepared by reduction of the corresponding benzoic acid with $NaBH_4$–BF_3 in THF. Recrystallization from water yielded material of mp 104–105° (lit.[20] mp 105°).

Enthalpies of Transfer. Heat of Solution Method. An LKB-8700 solution calorimeter was used to measure the integral molar heats of solution of the phenols in water, 1-octanol, and toluene. At least five determinations were made for each compound in each solvent at concentrations ranging from 5×10^{-4} to 10^{-2} M. The standard deviation of the mean was 0.2 kcal/mol or better. The enthalpy of transfer from one solvent to another, $\delta\Delta H_{tol \rightarrow H_2O}$, was then calculated as the difference between the heats of solution in the two solvents:

$$\delta\Delta H_{tol \rightarrow H_2O} = \Delta H_{H_2O} - \Delta H_{tol}$$

The results are listed in Table I.

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[22] Anderson, B. A.; Rytting, J. H.; Higuchi, T. *J. Am. Chem. Soc.* **1979**, *101*, 5194.

[23] Breslauer, K. J.; Terrin, B.; Sturtevant, J. B. *J. Phys. Chem.* **1974**, *78*, 2363.

[24] A plot of $\Delta G^\circ_{tol \rightarrow H_2O}$ vs. $\Delta G^\circ_{oct \rightarrow H_2O}$ yields a least-squares line whose slope has a standard deviation of 53%. Eliminating the first point, compound **2**, gives a standard deviation of the slope of 21%.

[25] Not exactly the same, phenols **5** and **6** being reversed. However, a plot of $\Delta G^\circ_{tol \rightarrow H_2O}$ vs. $\Delta S^\circ_{tol \rightarrow H_2O}$ is fairly linear, the least-squares slope of the line having a value of -4.6×10^{-3} deg^{-1} and a standard deviation of this value of 0.70×10^{-3} or 15%.

Two-Phase Titration Method. Slow rates of solution of phenols **7** and **8** in water made the measurement of their heats of solution in water difficult. We, therefore, measured the enthalpy of transfer of these two compounds from toluene to water by a method similar to one developed by Breslauer.[17,23] An LKB 8700 titration calorimeter was used to measure the heat produced when a 1-5-mL portion of 0.02 M phenol in toluene was added to a stirred solution of 95 mL of 0.1 N aqueous NaOH (ΔH_1). (This value (ΔH_1) has to be corrected for the (small) heat effect produced on mixing a 1-5-mL portion of pure toluene with 95 mL of 0.1 N aqueous NaOH.) In a separate experiment, the heat of neutralization of the phenol was measured by adding a 1-5-mL portion of 0.02 M aqueous phenol to 95 mL of 0.1 N aqueous NaOH (ΔH_2).

$$\begin{array}{ll}
\mathrm{ArOH_{tol}} + \mathrm{OH^-{}_{H_2O}} \rightarrow \mathrm{ArO^-{}_{H_2O}} + \mathrm{H_2O_{H_2O}} & \Delta H_1 \\
\mathrm{ArOH_{H_2O}} + \mathrm{OH^-{}_{H_2O}} \rightarrow \mathrm{ArO^-{}_{H_2O}} + \mathrm{H_2O_{H_2O}} & \Delta H_2 \\
\hline
\mathrm{ArOH_{tol}} \rightarrow \mathrm{ArOH_{H_2O}} \qquad \delta\Delta H_{\mathrm{tol}\rightarrow\mathrm{H_2O}} = \Delta H_1 - \Delta H_2 &
\end{array}$$

The enthalpy of transfer from toluene to water is then calculated from the difference of the above two heats of mixing.

Free Energies of Transfer. Partition coefficients of the phenols from toluene to water and from octanol to water were measured as follows. A weight of phenol was dissolved in water to make a solution which was approximately 10^{-3}–10^{4} M. The long-wavelength absorbance of this solution (ca. 285 nm) was measured, and then a precise volume of this solution was placed into a water-jacketed flask maintained at 25.0 °C. A precise volume of toluene or octanol was then added and the flask was shaken for 15 min and then allowed to settle for another 15 min. A portion of the aqueous layer was removed, filtered (to remove any tiny droplets of organic phase), and its absorbance was determined. The partition coefficient, P, was then calculated from the relation

$$P = \left(\frac{A_\mathrm{i} - A_\mathrm{f}}{A_\mathrm{f}}\right)\left(\frac{V_\mathrm{H_2O}}{V_\mathrm{org}}\right)$$

where A_i is the initial absorbance of the aqueous phase, A_f is the final absorbance of the aqueous phase, $V_\mathrm{H_2O}$ is the volume of the aqueous phase, and V_org is the volume of organic phase.

In the case of toluene, it was found that some of the phenols (**2**-**4**) had their long-wavelength absorbance too close to that of toluene. In these cases, the solutions were diluted with an equal volume of 1 N aqueous NaOH before the absorbance measurement in order to shift the λ_max of the phenol to a longer wavelength. The free energies of transfer were then calculated in the usual way:

$$\Delta G^\circ{}_{\mathrm{org}\rightarrow\mathrm{H_2O}} = RT \ln P$$

Registry No. **1**, 108-95-2; **2**, 623-05-2; **3**, 620-24-6; **4**, 90-01-7; **5**, 4383-07-7; **6**, 5330-38-1; **7**, 2316-64-5; **8**, 6641-02-7; toluene, 108-88-3; 1-octanol, 111-87-5.

Influence of Temperature and Adsorption on the Cation Distribution in Ca–Y Zeolites

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Using X-ray powder-diffraction methods, we investigated the variation of the Ca-ion location as a function of the temperature and the adsorption of H_2O, NH_3, acetone, benzene, and ethanol. A general rule for the influence of the temperature could be formulated as follows: the occupancy of the "better"-coordinated sites is favored with rising temperature. These "better"-coordinated sites are (i) site I for the dehydrated zeolites, (ii) site I′ in the presence of H_2O or NH_3, and (iii) site II in the presence of molecules which are unable to penetrate in the small cavities, i.e., acetone and benzene.

Introduction

The location of extraframework cations depends on a number of factors, such as the framework type, the presence of adsorbed molecules, the framework composition, the ion-exchange degree, etc. All these parameters influence the surface structure and composition and are therefore important for the understanding of the physicochemical properties. Although several applications of zeolites require elevated temperatures, the impact of heating on the zeolite structure was hardly investigated. A Boltzmann-type formalism, relating the energy-level differences with the site-occupancy ratios, accurately predicts the Fe^{2+}/Mg^{2+} equilibrium distribution between two nonequivalent sites in orthopyroxes.[1] This formalism implies a more homogeneous distribution of the cations with rising temperature. A single-crystal study of dehydrated Ca–mordenite,[2] however, proved that this formalism cannot be applied to zeolites for predicting the site occupancies: the site populations become more and more unequal with increasing temperature. The present study of the distribution of Ca ions in Ca–Y zeolites, in the presence or absence of adsorbed molecules, is an attempt to rationalize the direct influence of the temperature on the distribution of the exchangeable cations in zeolite structures.

Experimental and Results

The Ca–Y sample ($Ca_{26.8}Na_{3.4}Al_{56.9}Si_{135.1}O_{384}\cdot 252H_2O$) was the same as described by Costenoble et al.[3] Disks (10 mm in diameter and weighing approximately 100 mg) were mounted in a HDK (Seifert) high-temperature X-ray diffractometer camera[4,5] and, after a first dehydration step, equilibrated at the recording temperature, eventually in a gas atmosphere. A summary of the pretreatment and recording conditions is given in Table I. The diffraction pattern was recorded in steps of 0.01° (2θ) (counting time 9 or 18 s) at constant temperature. The sample name contains the recording temperature and the type of atmosphere. Ethanol, benzene, and acetone were outgassed and dried by vacuum distillation onto activated 4A extrudes before adsorption. Dry NH_3 was introduced directly into the system from a gas cylinder. The X-ray data sampling and refinement was described

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(1) Mortier, W. J. *J. Phys. Chem.* **1975**, *79*, 1447.
(2) Mortier, W. J. *J. Phys. Chem.* **1977**, *81*, 1334.
(3) Costenoble, M. L.; Mortier, W. J.; Uytterhoeven, J. B. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 466.
(4) Politis, C. "Zur thermische Gitterdilatation einiger Ubergangsmetallverbindungen", Kernforschungszentrum Karlsruhe, 1975, report KFK 2168.
(5) Politis, C. *Prakt. Metallog.* **1970**, *8*, 328.