CALCULATION OF ELECTROSTATIC POTENTIALS AND FIELDS INSIDE ZEOLITE CAVITIES

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

We present a modification of our bond increment method for the calculation of molecular electrostatic potentials and fields inside zeolite cavities. Introducing a variant of the Mulliken approximation for the off-diagonal matrix elements of the potential and optimizing the parameters of the modified formula, we achieved much better agreement with *ab initio* STO-3G minimal basis set results than with the original version. For a representative set of 10 small molecules the standard mean deviation between potentials calculated on the van der Waals surface with the *ab initio* and approximate methods is 9·1 kJ/mol. The relative error decreases from 21 to 9 per cent for the lone-pair regions of molecules modelling zeolite cavities. Applying the modified bond increment method for a realistic faujausite model we have found that the potential and field are almost exclusively of long-range origin. This means that, if using appropriate atomic charges, the monopole approximation gives correct results for electrostatic potentials and fields inside zeolite cavities.

Rudolf Zahradník and his coworkers were among the first who recognized the importance of quantum chemical calculations in elucidation of structure and properties of zeolites.[1−4] The brilliant lecture given by him in Eger, Hungary, some years ago[5] gave a major impetus to some of us to start theoretical calculations on zeolites. The more so, since molecular recognition, intensively studied in our laboratory, plays an important role in zeolite chemistry, too. It seems that theoretical aspects of recognition have a common basis even in case of apparently very different phenomena, like host–guest complexation, packing in molecular crystals, protein–ligand binding or interaction of small molecules with zeolite cavities.

Molecular electrostatic potentials and fields are observable quantities and can be calculated theoretically relatively easily.[6,7] They are directly related to interaction energies in a broad class of non-covalent molecular complexes and can be determined even for very large systems, like proteins,[8,9] nucleic acids[10] or molecular crystals.[11] Zeolites are strongly ionic therefore it is important to calculate their electrostatic properties in order to get a correct description of their macroscopic and microscopic behaviour. Since appropriate zeolite models are pretty large in size, approximations have to be introduced that allow considerable reduction of the computational work.

Until now relatively few electrostatic calculations have been done for zeo-lites.[2,12-16] In this paper we present an improved version of a method proposed earlier for the calculation of electrostatic potentials of very large systems,[9] the theoretical background is outlined in the next section. Later on, we compare our results to *ab initio* calculations using an STO-3G minimal basis set and at last the adequacy of the point-charge approximation will be tested on a realistic faujausite model.

THEORETICAL

Improvement of the Bond Increment Method

Previously we have proposed the bond increment (BI) method for the calculation of molecular electrostatic potentials (MEP) and fields (MEF) for large systems.[9,17,18] The method is based on a strictly localized molecular orbital (SLMO) expansion of the total wave function. The ϕ_i SLMO's representing two-centre σ or π, one--centre lone-pair and many-centre delocalized π bonds are supposed to be trans-ferable from one molecule to the other. The electrostatic potential is then obtained from the following expression

$$V(\boldsymbol{r}) = V_{\mathrm{el}} + V_{\mathrm{nucl}} \tag{1}$$

with

$$V_{\mathrm{el}} = -2\sum_{ij} T_{ij} V_{ij}(\boldsymbol{r}) \tag{2a}$$

$$V_{\mathrm{nucl}} = \sum_a Z_a |\boldsymbol{r} - \boldsymbol{R}_a|^{-1} , \tag{2b}$$

where $\boldsymbol{T} = \boldsymbol{S}^{-1}$ the inverse overlap matrix and

$$V_{ij}(\boldsymbol{r}) = \int \phi_i(1) |\boldsymbol{r} - \boldsymbol{r}'|^{-1} \phi_j(1) \, \mathrm{d}v' \tag{3}$$

the corresponding matrix element of the electronic part of the electrostatic potential operator. Originally we introduced the assumption that $T_{ij} = 1$ if $i = j$ and $T_{ij} = 0$ otherwise. As a result, we obtained an approximate expression for V_{el} where summa-tion runs over one index instead of two therefore the computational work increases linearly with the number of bonds in the molecule.

Comparison of our approximation with *ab initio* minimal basis set results for small molecules has shown that, though trends are reproduced correctly, absolute value of the potential is overestimated by about fifty per cent in average.[18] Further-more, the fair linear correlation between BI and *ab initio* potential values was maintained only for separate subclasses of compounds (e.g. first-row, second-row molecules, charged species). In order to improve our approximation, we introduced

the following variant of the Mulliken approximation[19] for the V_{ij} matrix element that is formally similar to the formula proposed by Ruedenberg[20]

$$V_{ij} \approx S_{ij}(\alpha_i V_{ii} + \alpha_j V_{jj})/2 . \tag{4}$$

Introducing Eq. (4) in V_{el} of Eq. (2a) after some algebraic manipulation we get

$$V_{el} \approx = 2 \sum_i V_{ii} \left(T_{ii} + \alpha_i \sum_j {}' T_{ij} S_{ij} \right) =$$

$$= -2 \sum_i V_{ii} \left[T_{ii}(1 - \alpha_i S_{ii}) + \alpha_i \sum_j T_{ij} S_{ij} \right] =$$

$$= -2 \sum_i V_{ii} \left[T_{ii}(1 - \alpha_i) + \alpha_i \right] . \tag{5}$$

The prime over the summation symbol means that the $i = j$ term has to be omitted. Expanding T in a power series and retaining terms up to the second order $T_{ii} \approx$ $\approx 1 + \delta_i^2$ and the quantity in square brackets of Eq. (5) can be written as follows

$$V_{el} \approx -2 \sum_i V_{ii}(1 - \beta_i) \tag{6}$$

with $\beta_i = \delta_i^2(\alpha_i - 1)$. Owing to the normalization condition of the wave function the

$$\sum \beta_i = 0 \tag{7}$$

condition has to be fulfilled within a molecule. In the following we consider β_i as an empirical parameter and use a fitting procedure to obtain its best value.

Fitting Procedure

We fitted the approximate potential V^{app} from Eqs (1), (2b) and (6) to *ab initio* STO-3G results by minimizing the following sum

$$I = \sum_a [V^{3G}(r_a) - V^{app}(r_a)]^2 . \tag{8}$$

Summation runs over 12 to 30 reference points selected in characteristic regions (lone pairs, CH, NH, OH and SH bond directions, π-bond region) around the molecule.[18] We divided the reference points in two groups, one is outside the van der Waals envelope of the molecule, the other is inside.

Considering Eq. (6), Eq. (8) can be rewritten as follows

$$I = \sum_a [V^{3G}(r_a) - V^{BI}(r_a) - 2 \sum_i \beta_i V_{ii}(r_a)]^2 , \tag{9}$$

where V^{BI} is the potential calculated by the original BI method. Minimization of I in Eq. (9) with the constraint in Eq. (7) defines a linear least-square fit problem, the

solution of which is described in standard textbooks.[21] The same procedure has been accepted in their point charge fitting of electrostatic potentials by Cox and Williams.[22] We wrote a computer program for the IBM PC/AT microcomputer that allows to introduce some symmetry constraints and fix the value of some β_i's. Ab initio calculations were done with the MONSTERGAUSS program package.[23]

Calculation of the Madelung Potential

In order to obtain the MEP and MEF inside faujausite cavities we combined the BI method for the close environment (eight sodalite units belonging to the unit cell) and the Ewald summation[24,25] of the Madelung potential for the long-range electrostatic effect of the crystal environment. For the latter we used transferable atomic point charges coresponding to bond polarities in the BI method (Si 1·163, Al 0·448, O −0·653, Na⁺ 1·000).

In our approach the potential of the zeolite crystal is described at three different levels of approximation. At large distances (from about $1·0 − 1·2$ nm to infinity) a point-charge approach is used in the framework of the Ewald method to sum up the conditionally convergent Madelung series. At intermediate distances (from 0·25 to 1·0 nm) the BI method strictly corresponds to an atomic point-multipole description of the charge distribution where the highest order multipole is the quadrupole (p–p orbital product). At the closest vicinity of the points of interest the spatial extension of the atomic charge densities becomes nonnegligible and the exponential decay of the potential (instead of $1/r$ behaviour) should be taken into account.

We wrote a microcomputer program that is based on the above principles and calculates the Madelung potential relatively rapidly. The calculation of the MEP in one point needs 4 min time on the IBM PC/AT. The same program calculates MEF values and field gradients, as well.

RESULTS AND DISCUSSION

Small Model Molecules

Results of fitting for groups I and II (outside and inside the van der Waals envelope) are given in Tables I and II while comparison of our corrected BI potential values to the reference ab initio STO-3G ones are depicted in Figs 1 and 2. The fit is good outside the van der Waals envelope, the mean deviation from the ab initio values is 9·1 kJ/mol, about three times as large as that obtained by Singh and Kollman applying a monopole fit to the MEP.[26] Comparing their results to ours, it has to be borne in mind that they calculated the MEP on successive shells of various multiples of the van der Waals radii ranging from 1·2 to 2·0 times the radius. Our fitting included the van der Waals envelope itself (1·0 times the van der Waals radius). It

TABLE I

β Parameters from Eq. (6) for some selected model molecules. Reference points outside the van der Waals surface. σ^{old}, σ^{new} and σ^{rel} denote standard deviations from *ab initio* STO-3G values before and after fitting (kJ/mol), and relative error after fitting (in per cent)

| Molecule | Bond (X = C, Si; Y = N, O, S) | | | | σ^{old} | σ^{new} | σ^{rel} |
	lp on Y	X—Y(Y—Y)	Y—H	X—H			
CH_3OH	−0·074	0·120	0·027	0^a	30·8	2·8	4·4
CH_3NH_2	−0·054	0·003	0·026	0^a	23·1	15·5	17·6
CH_3SH	−0·122	0·123	0·122	0^a	76·1	6·8	15·2
H_2S_2	−0·144	0·336	0·121	—	84·6	5·1	9·1
N_2H_4	−0·103	0·222	−0·004	—	26·6	10·8	10·6
H_2O	−0·042	—	0·042	—	21·9	2·9	3·5
NH_3	−0·031	—	0·010	—	16·5	5·3	4·1
SiH_3OH	−0·125	0·202	0·049	—	30·6	12·9	30·4
	C—C$^\sigma$	C—C$^\pi$					
C_2H_4	0·071	0·098	—	−0·042	31·6	12·4	33·7
C_6H_6	0·114	−0·167	—	−0·030	20·5	6·5	25·9
all					39·3	9·1	20·6

^{a} By constraint.

TABLE II

β Parameters from Eq. (6) for some selected model molecules. Reference points inside the van der Waals surface. For notations see Table I

| Molecule | Bond (X = C, Si, Y = N, O, S) | | | | σ^{old} | σ^{new} | σ^{rel} |
	lp on Y	X—Y	Y—H	X—H			
CH_3OH	−0·054	0·036	0·072	0^a	104	72	49
CH_3NH_2	−0·056	−0·069	0·062	0^a	100	68	27
CH_3SH	−0·066	0·089	0·044	0^a	140	110	62
H_2O	−0·052	—	0·052	—	92	50	25
NH_3	−0·035	—	0·012	—	93	83	33
SiH_3OH	−0·077	0·047	0·107	0^a	99	35	22
	C—C$^\sigma$	C—C$^\pi$					
C_2H_4	0·090	0·136	—	−0·057	129	37	19
all					114	79	37

^{a} By constraint.

seems probable that including bond polarities and lone-pair orientations in the fitting procedure the agreement with the reference *ab initio* values will improve. A further appealing feature of our parametrization is that at least a qualitative agreement between the corrected BI and *ab initio* potentials can be achieved even inside of the van der Waals surface (cf. Table II and Fig. 2). Using the regression equation, given in the caption of Fig. 2 the agreement between approximate and reference *ab initio* values can be improved.

A major advantage of the β_i parameters in Eq. (6) is that negative MEP regions above and under aromatic systems, like ethylene and benzene, are correctly reproduced while in the original version of the BI method these regions were incorrectly described to be positive.[17] At the expense of the improvement in accuracy the transferability of the β values is not maintained. The only trend in the set of molecules used for fitting is that β's for lone pairs are always negative.
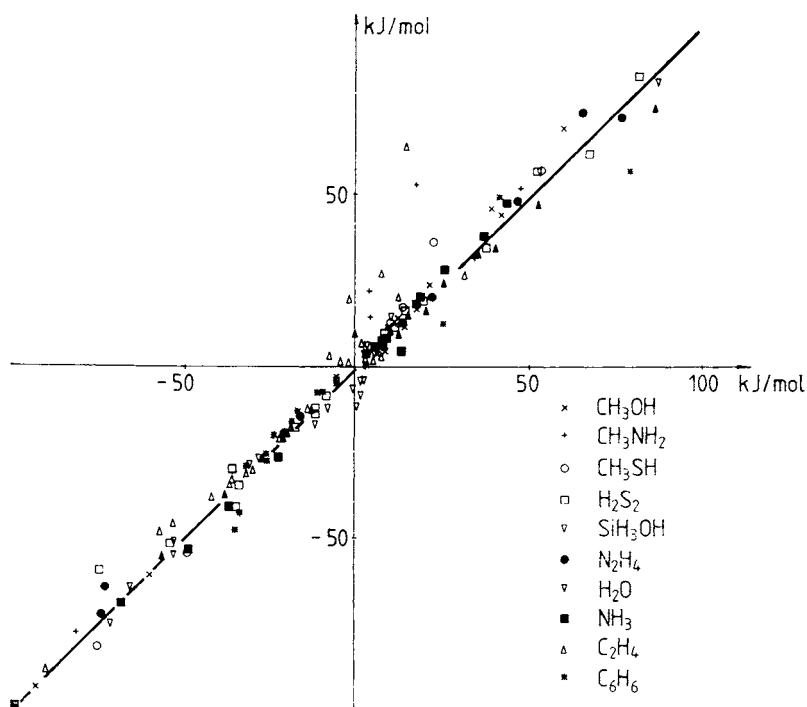

FIG. 1

Comparison of *ab initio* STO-3G and modified BI MEP values. Reference points outside the van der Waals surface. The heavy line corresponds to perfect agreement between fitted and *ab initio* values

Since in this paper we focus our attention to zeolites where the important regions for calculating the MEP and MEF are inside the cavities, we introduced a special parametrization for $H_3SiOSiH_3$ and $H_3SiOAlH_3^-$, model molecules for neutral and charged zeolite fragments. We selected for these molecules reference points only in the lone-pair region that is oriented towards the cavity. Results in Table III and Fig. 3 indicate that this restriction allows to achieve a good accuracy. The standard deviation is 17 kJ/mol, the relative error is only 9 per cent.

At last, we checked the accuracy of MEF values using β_i parameters obtained from the fitting of the potential. The agreement is much worse for the molecules in Table I than in case of the potential. The standard mean deviation between fitted and *ab initio* values is 2·3 V/nm (40 per cent). However, the situation is better for the molecules modelling the cavity in zeolites (Table III), the deviation is 2·1 V/nm (18 per cent).
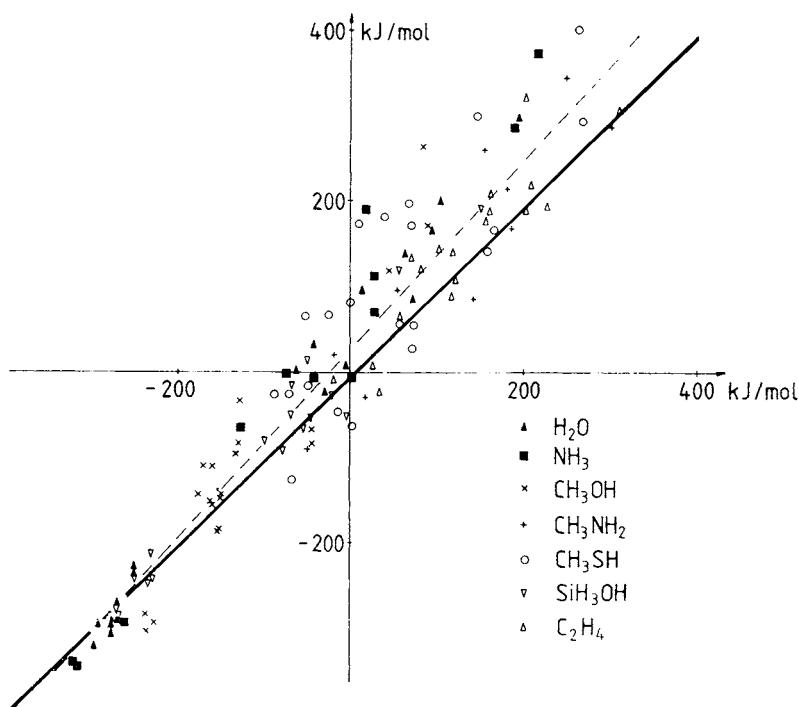

FIG. 2

Comparison of *ab initio* STO-3G and modified BI MEP values. Reference points inside the van der Waals surface. The heavy line corresponds to perfect agreement between fitted and *ab initio* values, the light line represents the regression equation $V^{3G} = 1·106 V^{app} + 30·1$ kJ/mol ($r = 0·967$)

TABLE III

β Parameters from Eq. (6) for the lone-pair region of zeolite model molecules. Reference points outside and inside the van der Waals surface. For notations see Table I

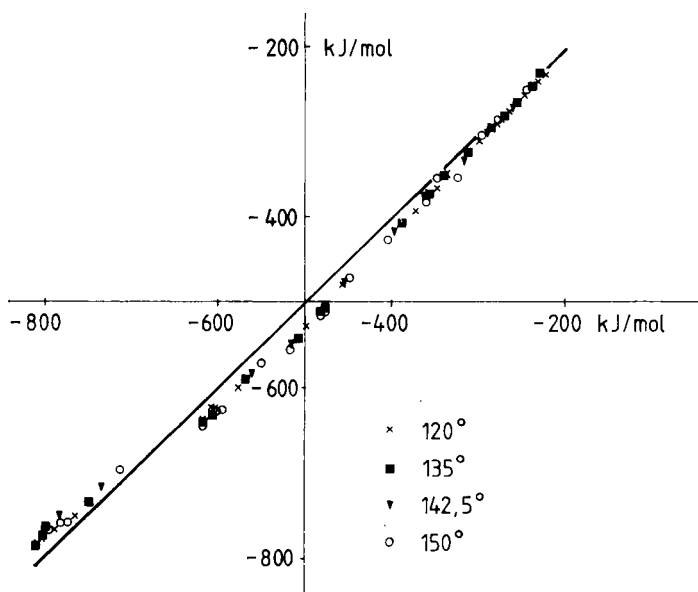| Molecule	Bond angle (°)	Bond			σ^{old}	σ^{new}	σ^{rel}
		lp on O	Si—O	Al—O			
$H_3SiOSiH_3$	120	−0·106	0·106	—	110	11	9
	135	−0·090	0·090	—	83	12	11
	142·5	−0·080	0·080	—	69	13	12
	150	−0·069	0·069	—	54	13	14
$H_3SiOAlH_3^-$	120	−0·132	0·251	0·012	136	19	4
	135	−0·120	0·218	0·023	112	21	5
	142·5	−0·114	0·204	0·025	98	22	4
	150	−0·108	0·190	0·025	85	23	4
all					97	17	9

FIG. 3

Comparison of *ab initio* STO-3G and modified BI MEP values for lone pair regions near zeolite model molecules. Reference points outside and inside the van der Waals surface. The heavy line corresponds to perfect agreement between fitted and *ab initio* values

Summing up the above results it can be stated that the modified BI method yields semiquantitative agreement with *ab initio* STO-3G minimal basis set potentials outside the van der Waals surface. Though the agreement is worse in case of molecular electrostatic fields, it seems plausible that the method can be parametrized in order to improve field values, as well. A separate parametrization is needed inside the van der Waals envelope.

Realistic Faujausite Models

We calculated the MEP and MEF in some points of a faujausite cavity (cf. Fig. 4) with Si : Al ratios 1 : 1 (model a) and 1·18 : 1 (model b). The models were built according to Dempsey.[12] Cartesian coordinates were taken from the X-ray data of Mortier et al.[27] The twelve unit negative charges per sodalite unit were compensated by point charges placed on cation sites I, I' and II (ref.[28]). Sites I were filled with divalent-, sites I' and II with monovalent cations (point charges). Though the simultaneous occupation of adjacent sites I and I' are usually avoided in faujausite models, since after filling sites I and II the remaining cations are placed at sites III, we did not follow this procedure. Our reasons for doing so are the following: (i) no direct experimental evidence supports the occupation of site III by a cation, (ii) X-ray diffraction data indicate that the simultaneous occupation of sites I and I' is possible.[29] Model b was obtained from model a by replacing an Si atom by Al atom in each sodalite unit. Simultaneously with the replacement of an aluminium by silicon atom we dropped a cation from class I' site.

The potential and field were calculated along the bisector of the TOT angle (T = Si, Al). There are three different types of such lines. Types **1** and **2** start from the oxygen atom on the central hexagon (denoted by the numbers 1 and 2 on Fig. 4), while type **3** crosses the centres of two sodalite units. All occupied cation sites lie on one of the above lines.
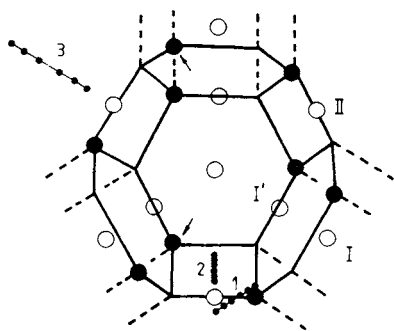

FIG. 4

Schematic model of a sodalite unit in faujausite. Empty circles represent cations bearing unit positive charges. Full circles represent Al atoms in model a. Three of them, lying on the opposite face of the unit in a triangular arrangement rotated by 60° around the six-fold axis, are omitted for the sake of clarity. Arrows denote Al–Si substitutions in model b. Dotted lines denoted by arabic numbers represent the sites where MEP and MEF were calculated (cf. Figs 5 and 6)

TABLE IV

Variation of the MEF along the line of type 1 for model a in the point-charge (PC) and point-charge plus BI (PC + BI) approximations (in V/nm)

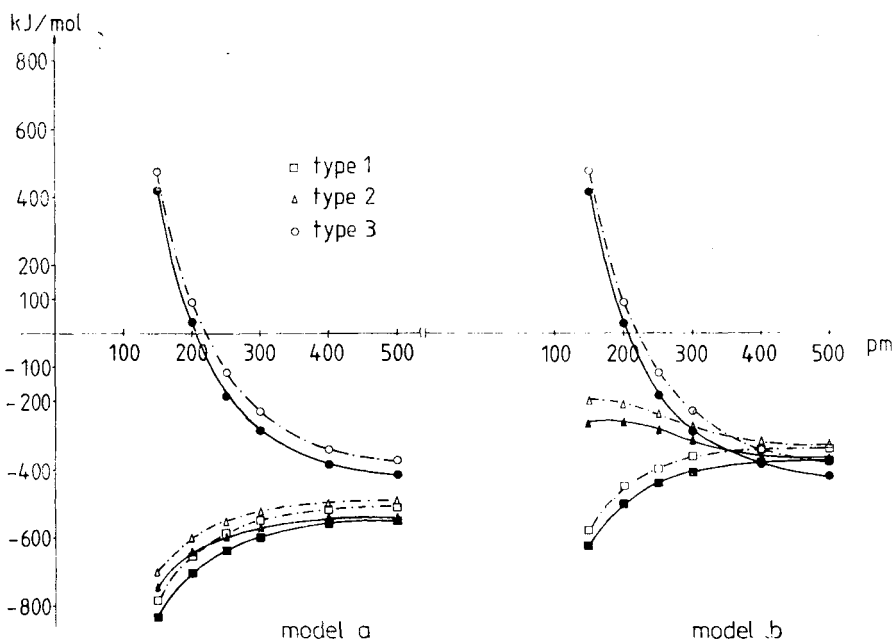| Distance pm	Component						Field	
	x		y		z			
	PC	PC + BI	PC	PC + BI	PC	PC + BI	PC	PC + BI
150	−9·07	−6·99	−63·19	−60·65	43·43	44·89	77·21	75·78
200	−3·77	−3·04	−28·51	−27·90	19·39	20·16	34·68	34·56
250	−1·30	−0·99	−15·00	−14·73	11·16	11·46	18·74	18·70
300	−0·32	−0·15	−8·63	−8·45	7·20	7·32	11·24	11·18
400	0·16	0·22	−2·96	−2·86	2·86	2·88	4·12	4·06
500	0·00	0·002	−0·10	0·00	0·10	0·05	0·14	0 05

FIG. 5

Alteration of the MEP inside a sodalite cavity of faujausite. For the definition of type 1, 2 and 3 lines and models a and b see text and Fig. 4. Full line: Madelung potential, dashed line: Madelung potential corrected using the BI method

Results of MEP and MEF calculations are shown on Figs 5 and 6 and, the MEF for an illustrative case, in Table IV. Both potential and field values are quite large as compared to free molecules[18] or proteins.[5,9] The large absolute values are due to the strongly ionic character of zeolites and are mainly of long-range origin. The field near $H_3SiOSiH_3$ and $H_3SiOAlH_3^-$ is about 2·5 V/nm in average, the absolute values in Table IV are an order of magnitude larger than this. Owing to the predominant role of long-range effects the corrections to the point-charge model, offered by the BI method, are negligible. Though in case of the MEP the absolute value of the correction is quite large (50 kJ/mol in average, cf. Fig. 5) the deviaton is practically constant therefore the variation of the potential remains unaltered if introducing the BI correction. For the MEF this correction is negligible for distances larger than 150 pm therefore we did no depict the BI corrected values on Fig. 6. As a consequence we may state that, at least for faujausite models discussed in this work, the point-charge approximation yields correct results for electrostatic potentials and fields inside the sodalite cavities. Clearly, numerical values depend strongly on the actual charges on Si, Al, and O atoms and counter ions. It is therefore of primary importance to apply correct charges in the monopole approximation. Work to derive correct charge distribution from *ab initio* calculations on zeolite models is in progress.
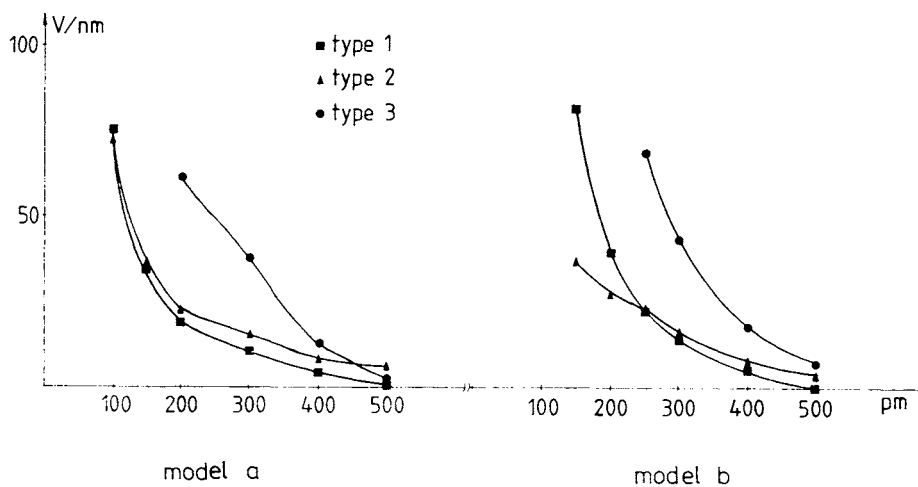

FIG. 6

Alteration of the MEF as obtained from the Madelung summation inside a sodalite cavity of faujausite. For definitions see Fig. 4

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