Ab initio pair potentials for the ionic lithium-formate system

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The potential energy surfaces for the interatomic interaction in the Li^+HCOO^- system have been investigated by *ab initio* methods within the rigid-molecule approximation. Analytical potential expressions were fitted to 133 calculated SCF energies for the Li^+-HCOO^- interaction, 42 SCF energies for the Li^+-Li^+ interaction, and 332 SCF energies for the $HCOO^--HCOO^-$ interaction. The global minimum on the Li^+-HCOO^- surface is -170 kcal/mol and corresponds to the lithium ion lying on the C_2 axis of the formate ion at 2.2 Å from the carbon atom on the oxygen side. The cation-cation and anion-anion interactions are repulsive everywhere, although the potential surface is markedly anisotropic for the $HCOO^--HCOO^-$ interaction.

Key words: Lithium formate—Potential surface—SCF calculation

1. Introduction

Reliable potential energy functions for the interaction between ions are of vital importance for the theoretical modelling of ionic systems in solid, melt, solution or gas. A vast literature exists on the construction of potential functions to model the structure and physical properties in alkali halide solids and melts (see, for example, [1, 2]). Computer simulations have been performed on dilute aqueous solutions of the alkali, alkaline earth and ammonium halides [3-10]. The molecular ordering in alkali cyanide [11] and lithium sulphate [12] crystals has been investigated in computer simulations. The structures of different minerals have been studied using empirical model potentials [13]. In this laboratory molecular dynamics simulations have recently been performed on an aqueous lithium formate system, the results of which are reported elsewhere [14, 15]. The

present paper deals with the potential energy surfaces for the three different ionic interactions in the lithium formate system: Li^+-$HCOO^-$, Li^+-Li^+ and $HCOO^-$-$HCOO^-$. To the best of our knowledge no quantum mechanical calculations nor any potential function have previously been published for the interactions in this system.

The layout of the paper is as follows. Details of the calculations are given in Sect. 2. The results are discussed in Sect. 3 and a summary is given in Sect. 4.

2. Method

2.1. SCF calculations

Ab initio MO-LCAO-SCF calculations were carried out for 133 geometrical configurations for the Li^+-$HCOO^-$ system, 42 for Li^+-Li^+ and 332 for the $HCOO^-$-$HCOO^-$ surface using the IBMOL program [16]. The internal geometry of the formate ion was kept fixed in all calculations and was taken to be planar, with the C-O distances equal to 1.250 Å, the C-H distance 1.085 Å and the O-C-O angle 125.0°. The values were chosen as typical values for a bonded formate ion based on available diffraction studies of crystalline formates [17].

The basis sets used for carbon, oxygen and hydrogen were of double-zeta plus polarization quality. Dunning's [18] $[4s2p/2s]$ contraction of Huzinaga's [19] $(9s5p/4s)$ Gaussian basis sets were used for carbon, oxygen and hydrogen, augmented with polarization functions according to Roos and Siegbahn [20], i.e. a set of $3d$ functions with exponent 0.63 on carbon, 1.33 on oxygen and a $2p$ function with exponent 0.8 on hydrogen. The energy of a free formate ion at the geometry used in this work is -188.232067 hartree (h). The optimized free formate geometry using this same basis gives a C-O distance of 1.236 Å, a C-H distance of 1.124 Å and an O-C-O angle of 130.6° with a total energy of -188.235404 h.

For Li^+ three different basis sets were tested: (i) the $(7s1p)/[3s1p]$ basis set of Clementi and Popkie [21], (ii) the $(10s)/[4s]$ basis set of Dunning [22], augmented with the same polarization function as in (i); and (iii) the $(10s4p)/[4s2p]$ basis set of Dunning and Hay [23]. The Li^+-$HCOO^-$ interaction energies calculated with the three basis sets are very similar: for the most attractive configuration included in the SCF calculations (which is, in fact, very close to the global minimum; see curve *A* in Fig. 1a) the *total energies* are -195.736288 h, -195.739412 h, and -195.742592 h for (i), (ii) and (iii), respectively, and the *interaction energies* (BSSE corrected; see below) are -166.9, -167.2, and -168.6 kcal/mol. The largest basis set, (iii), was selected in the final calculations of the potential surfaces.

The quality of the formate basis set used here was tested by comparison with a considerably more extended basis set, made up of $(12s8p2d)/[5s4p2d]$ for oxygen [25], $(6s2p)/[3s2p]$ for hydrogen [25], and $(10s6p)/[5s3p]$ for carbon [19, 22]. The latter is augmented with a polarization function with exponent 0.72. The free formate ion energy calculated with this basis set is -188.267433 hartree. The resulting effect on the potential energy curves was checked for the lithium-formate
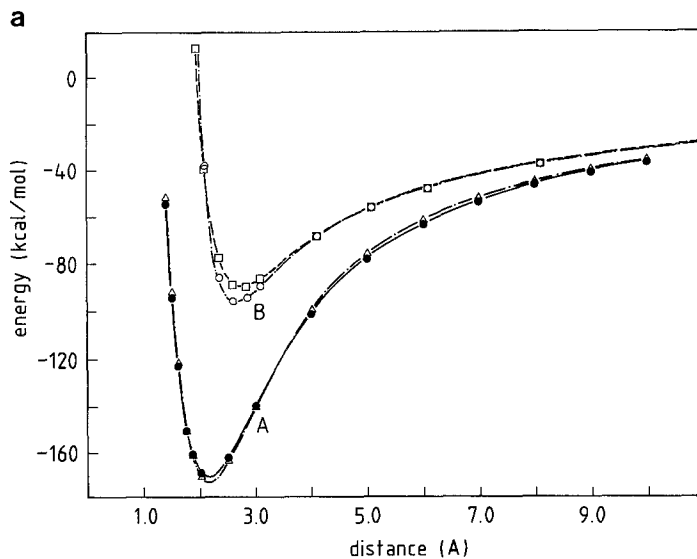
Fig. 1. a Lithium-formate potential energy curves from the SCF calculations and from the fitted analytical function (expressions (1) and (2a)) for two different geometries of approach. The quantity on the *horizontal axis* is the Li^+-C distance. The curves are second-order spline functions through the SCF points and the analytical points, respectively. b The geometries corresponding to the curves in a. ─●─ and ──□── are the SCF results; ─·△─· and ─·○─· are the fitted results
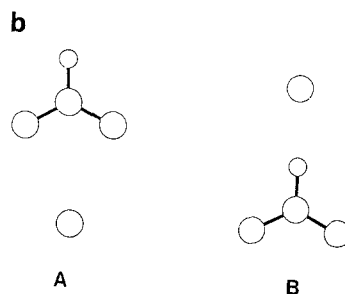
curve A in Fig. 1a, and the formate-formate curve B in Fig. 3a. The lithium-formate interaction energies for Li–C distances of 1.5, 2.0 and 4.0 Å in the A conformation are −98.0, −172.3, and −102.4 kcal/mol, respectively, calculated with the smaller basis set (not corrected for BSSE), while the large basis set (not corrected for BSSE) gives −99.7, −168.6 and −99.5 kcal/mol. The formate-formate interaction energies for C–C distances of 5.5 and 7.5 Å in the B conformation are 76.3 and 51.5 kcal/mol, respectively, calculated with the smaller basis set, and 74.9 and 51.1 kcal/mol with the larger basis. The errors introduced by using smaller basis sets are thus in general quite small (on the order of 2% of the interaction energies). The double-zeta-plus-polarization basis sets are hence adapted in all the calculations as a reasonable compromise between accuracy and computational speed and resources.

The *interaction energies*, defined as $E(complex) - E(Li^+) - E(HCOO^-)$ and similarly for the other ion pairs, were in all cases corrected for *basis set superposition errors* (BSSE's) using the counterpoise method [24]. Figure 1a shows the varation of the interaction energy with C–Li^+ distance for two different directions of approach in the *lithium-formate* system. In fact, these two directions represent

two extreme cases: the deepest and the least deep minima on the potential surface. The corresponding geometrical configurations are displayed in Fig. 1b. Figure 2 shows the variation of the interaction energy with interatomic distance for the *lithium-lithium* system. The variation of the interaction energy with C-C distance for the two extreme (in terms of interaction energy) directions of approach for the *formate-formate* system are shown in Fig. 3a, and Fig. 3b displays the corresponding geometries. The potential curves will be discussed in more detail in the next section; here we just wish to comment on the effect of the BSSE correction on the interaction energy. For the shortest distance of approach (i.e. the most repulsive point) displayed in Fig. 3a the BSSE is 2.4 kcal/mol (out of a total interaction energy of +140.0) for curve A and 2.5 kcal/mol (out of +121.7) for curve B. The Li^+-Li^+ calculations show no BSSE's. For the shortest distance of approach displayed in Fig. 1a the BSSE is 4.5 kcal/mol (out of −54.1) for curve A and 3.1 kcal/mol (out of +13.3) for curve B. At the minimum in curve A the BSSE is 3.7 kcal/mol and 2.0 kcal/mol in curve B. Although not vanishingly small, the BSSE's are thus quite small on a relative scale for all points included in the calculations.

2.2. Geometrical configurations

A proper selection of the configurations is necessary to ensure that the derived potential function represents any general geometrical configuration of the two ions. Both the translational and rotational (where applicable) degrees of freedom in the energy hypersurface have to be covered as completely as possible. To this end, the *formate-formate* configurations were selected in such a manner that the "second" formate ion was translated along "rays" originating at the C atom on
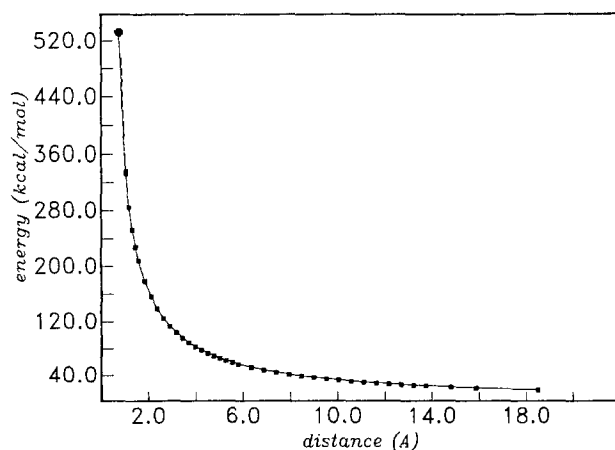

Fig. 2. Lithium-lithium potential energy curves from the SCF calculations and from the fitted analytical function (expressions (1) and (2b)). The curves are second-order spline functions through the SCF points and the analytical points, respectively: —●— SCF, – –■– – fitted
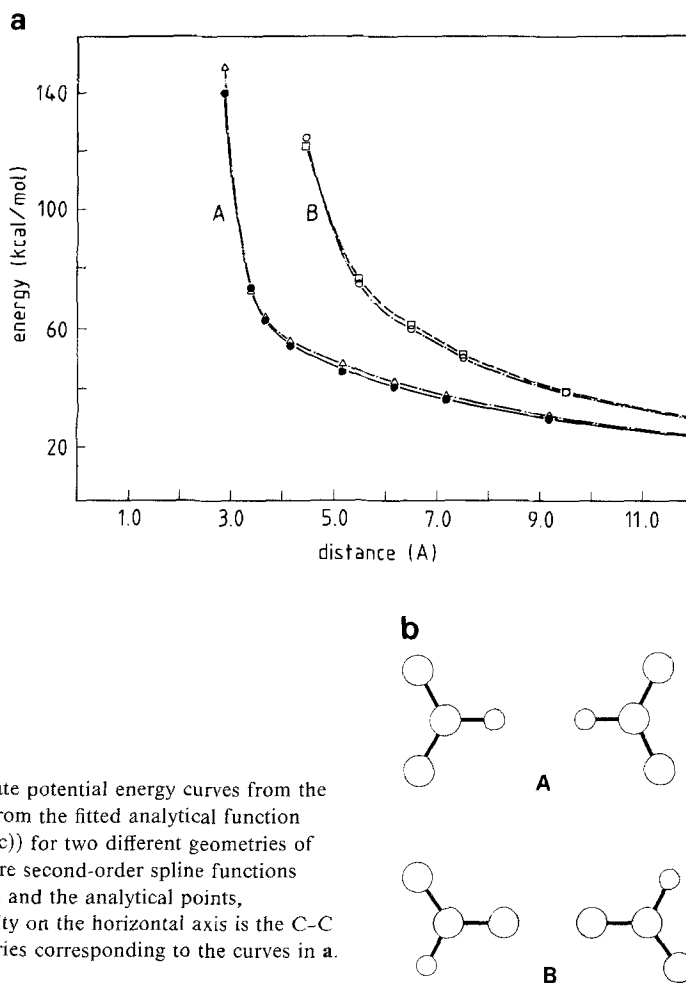
Fig. 3. a Formate-formate potential energy curves from the SCF calculations and from the fitted analytical function (expressions (1) and (2c)) for two different geometries of approach. The curves are second-order spline functions through the SCF points and the analytical points, respectively. The quantity on the horizontal axis is the C-C distance. **b** The geometries corresponding to the curves in a. Symbols as in Fig. 1

the "first" ion. These rays were distributed quite evenly in space, within and out of the plane of the first formate ion. At each position the second formate ion was allowed to rotate in a stepwise fashion. Fortunately, the formate ion exhibits C_{2v} symmetry, which greatly reduces the space to be covered. For *lithium-formate* no rotations had to be performed and, hence, fewer geometries were necessary. Altogether, 332 SCF points were caculated for the formate-formate complex and 133 for the lithium-formate. For the *lithium-lithium* interaction 42 energies were calculated with an ion-ion distance between 1.1 and 18.5 Å.

2.3. Fitting procedure

The intermolecular potential functions were expressed as sums of site-site pair potentials representing both the Coulombic and the non-Coulombic interactions.

If U is the total potential energy of a system it is thus written as

$$U = \sum_{1 \leq i \leq j \leq N} U_{ij},$$ (1)

where the sum includes all pairs of sites i and j on the different ions. The sites chosen were the atomic sites for both the lithium and the formate ion.

Many different forms of the potentials were tested. Based on the success of the fittings and the simplicity of the functional form, the final expressions used were the following

$$\text{Li}^+\text{-HCOO}^-: \qquad U_{ij} = \frac{q_i q_j}{r_{ij}} - A_{ij}\, e^{-B_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^4}$$ (2a)

$$\text{Li}^+\text{-Li}^+: \qquad U_{ij} = \frac{q_i q_j}{r_{ij}} - A_{ij} e^{-B_{ij} r_{ij}}$$ (2b)

$$\text{HCOO}^-\text{-HCOO}^-: \qquad U_{ij} = \frac{q_i q_j}{r_{ij}} - A_{ij} e^{-B_{ij} r_{ij}},$$ (2c)

where r_{ij} is the site-site separation, q_i and q_j are the site charges and the coefficients A_{ij}, B_{ij}, and C_{ij} are the fitting parameters. Different values for the formate charges were tested, based on the result of the Mulliken population analysis for different lithium-formate and formate-formate geometries. As is often the case with analytical potential expressions, the charges have to be interpreted with caution and should be seen as fitting constants rather than true effective charges. The charges and the fitting coefficents are listed in Tables 1–3.

Table 1. Parameters for the analytical pair potential (2a) for the Li$^+$-HCOO$^-$ interaction. Both oxygen atoms in the formate ion have the same charges and coefficients. Distances are given in Å and energies in kcal/mol. Note that the q values in the table are given in a.u. and thus have to be converted to give the energy in kcal/mol

C-Li	A	554.940608
	B	0.8393816
	C	−249.651025
O-Li	A	−509.32822
	B	0.99828424
	C	−453.72615347
H-Li	A	−292.07704307
	B	0.94805706
	C	−99.40491297
Li	q	+1.0
C	q	−0.150
O	q	−0.500
H	q	+0.150

Table 2. Parameters for the analytical pair potential (2b) for the Li$^+$-Li$^+$ interaction. See text for the actual expression. Same unit conventions as in Table 1

Li–Li	A	402 685.034476
	B	9.26491126
Li	q	+1.0

Since we are here dealing with ions it is to be expected that an overwhelming part of the intermolecular interaction at medium and long range is accounted for by the coulombic part of the potentials. So, for example, in the case of the *lithium-formate* interaction, the absolute value of the non-coulombic contribution to the interaction energy (i.e. the second and third terms in (2a)) for curve *A* in Fig. 1 is less than 1 kcal/mol for Li^+-C distances greater than 5.0 Å. At the minimum (Li^+-C equal to 2.2 Å) the non-coulombic contribution is +22.0 kcal/mol out of −170.9 kcal/mol. For the *lithium-lithium* interaction, the non-coulombic contribution is less than 1 kcal/mol for inter-ionic distances greater than about 1.5 Å. At 1.06 Å the non-coulombic contribution is +22 kcal/mol out of 336 kcal/mol. For the *formate-formate* interaction, the non-coulombic contribution is less than 1 kcal/mol for C-C distances greater than about 4.0 Å for curve *A* and 5.2 Å for curve *B* in Fig. 3a. For the most repulsive point on curve *A* the C-C distance is 2.92 A and the non-coulombic energy contributes 78 kcal/mol to the total interaction energy of 148 kcal/mol.

The standard deviation of the fitting, defined as $[\sum (E_{SCF} - E_{fit})^2/N]^{1/2}$, is equal to 5.0 kcal/mol for the *lithium-formate* case when all 133 points are included in the calculation of the standard deviation and 3.1 kcal/mol for the 122 geometries with interaction energies less than −30 kcal/mol. For *lithium-lithium* the standard devation is equal to 0.07 kcal/mol counting all 42 points. The standard deviation for *formate-formate* is 2.6 kcal/mol for the 316 geometries with interaction energies less than +150 kcal/mol and 1.5 kcal/mol for the 291 geometries with interaction energies less than +100 kcal/mol. We note that due to the non-coulombic

Table 3. Parameters for the analytical pair potential (2c) for the $HCOO^-$-$HCOO^-$ interaction. See text for the actual expressions. All oxygen atoms have the same charges and coefficients. Same unit conventions as in Table 1

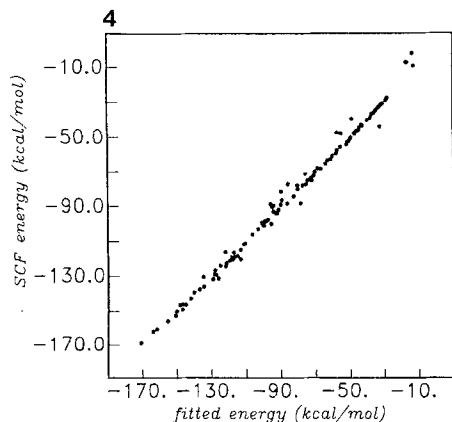|		
C-C	A	0.
	B	1.000
C-O	A	0.
	B	1.000
C-H	A	27 426.263121
	B	4.382489
O-O	A	61 024.586490
	B	4.366657
O-H	A	83 992.394802
	B	5.650649
H-H	A	1 439.962718
	B	4.236823
C	q	−0.150
O	q	−0.500
H	q	+0.1500

Fig. 4. Correlation between lithium-formate interaction energies from the SCF calculations and those derived from expressions (1) and (2a) and the parameters in Table 1
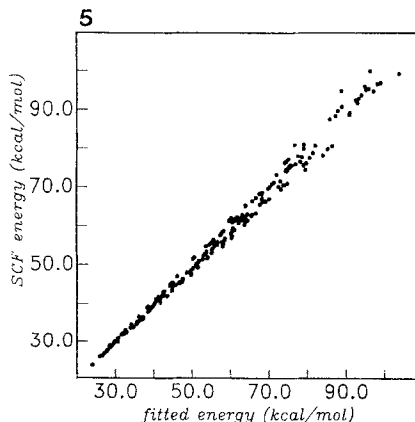
Fig. 5. Correlation between formate-formate interaction energies from the SCF calculations and those derived from expressions (1) and (2c) and the parameters in Table 3

nature of interaction, the standard deviations for the complex ions are much larger than that for the lithium-lithium.

The quality of the fitting is also displayed by the correlation curves between the SCF and fitted energies in Fig. 4 (lithium-formate) and Fig. 5 (formate-formate). These plots show that the fits are indeed quite satisfactory for all different geometries included in the fittings. No correlation plot is shown for the *lithium-lithium* interaction since it can readily be seen from Fig. 2 that the SCF and fitted energies essentially overlap.

The fittings were done with a program adapted from the LSQ8A program written by Probst and Clementi [26].

2.4. Iso-energy contour maps

Figures 6 and 7 show the iso-energy maps calculated from the potential functions in (2a) and (2c). The purpose of these maps is to provide a more comprehensive picture of the potential surfaces than do the one-dimensional plots in Figs. 1a and 3a. In addition, these maps serve as a way of checking the optimized analytical expressions to ensure that no spurious features occur between the point included in the fittings.

The maps were constructed in the following way. One formate ion was positioned at the center of the map and the center of the other ion was translated to each point in a user-defined grid in the plane studied. In the formate-formate case, at each grid point the second ion was allowed to rotate in such a way that the interaction energy was minimized. The energy contour maps were constructed from the final grid values. The program used was a modified version of EMIMAP written by Probst and Clementi [26].
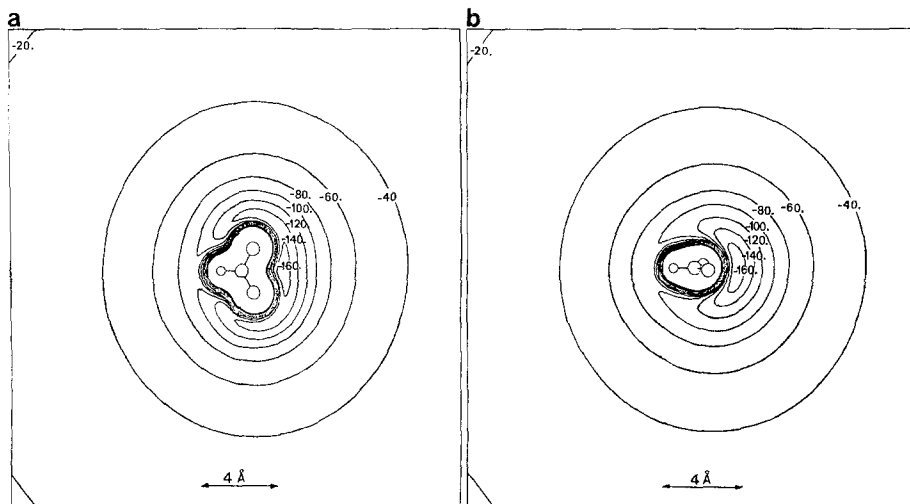
Fig. 6. Iso-energy plots for the lithium-formate interaction (see text) **a** in the formate plane; **b** perpendicular to the formate plane, through the C–H bond
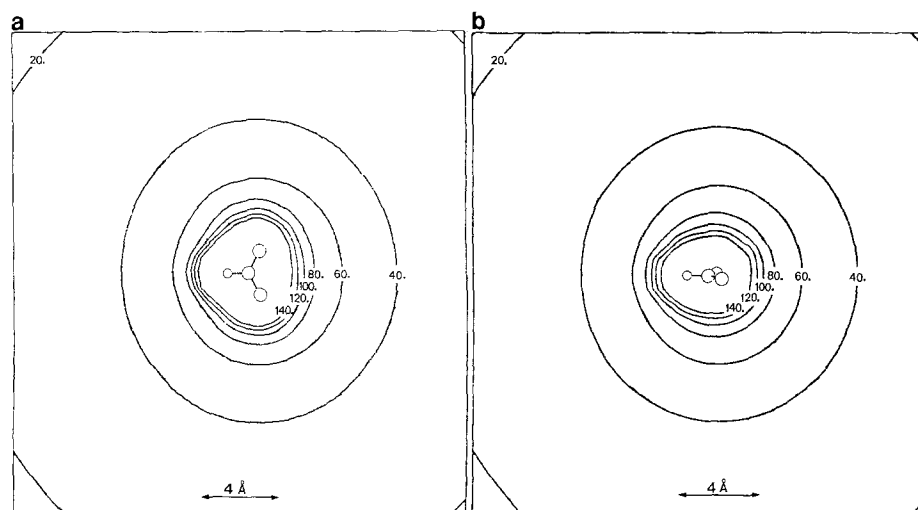

Fig. 7. Iso-energy plots for the formate-formate interaction (see text) **a** in the formate plane; **b** perpendicular to the formate plane, through the C–H bond

3. Results and discussion

The feature of the lithium-formate, lithium-lithium and formate-formate potential curves will be discussed in turn.

Figures 1 and 6 illustrate the final potential energy surfaces for the *lithium-formate* interaction. The interaction is markedly anisotropic. The global minimum is
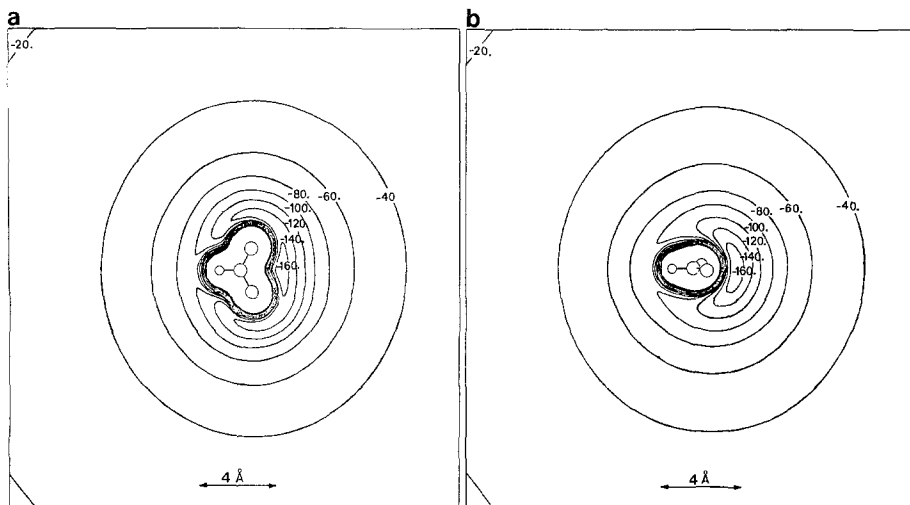
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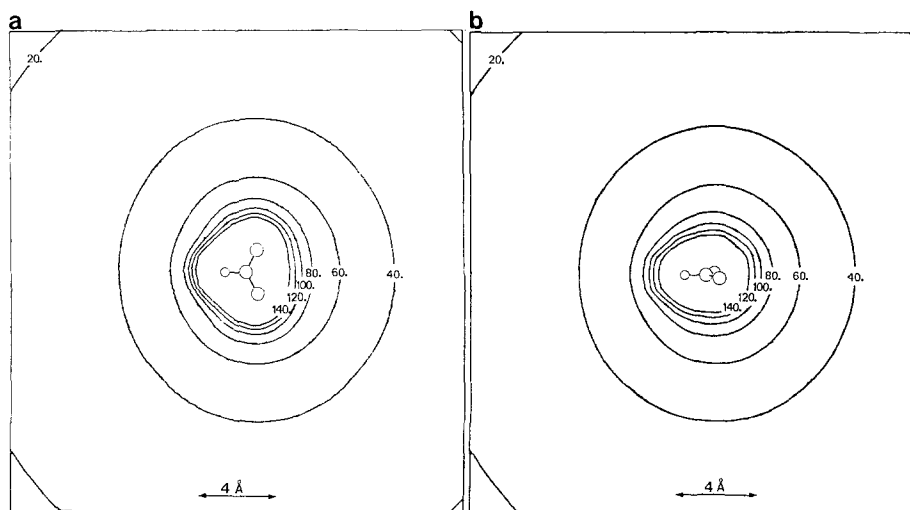

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The SCF-calculated energies and the atomic coordinates can be obtained from the authors on request.

4. Summary

The potential surfaces for the interaction between a rigid formate ion and a lithium ion and between the like ions have been derived by quantum-mechanical methods. All interaction energies were corrected for basis set superposition errors. Analytical potential expressions were constructed to fit the SCF energies.

For the *lithium-formate* interaction the minimum in the potential energy curves varies between -170 and -90 kcal/mol for different directions of approach. The *formate-formate* interaction is everywhere repulsive, but is highly dependent on the mutual orientation of the two ions. The interaction energy is substantially less repulsive when a formate ion points its hydrogen atom, rather than its oxygen atom(s), towards the other formate ion. For the *lithium-lithium* interaction the potential curve agrees with that of two unit point charges for distances greater than about 1.5 Å.

Finally, it should be stressed that the present work, as a beginning, has addressed only the two-body component of the lithium-formate interaction. The many-body corrections in ionic systems are well known to be important [28] and therefore a two-body approach will likely limit the molecular dynamics and Monte Carlo simulations to qualitative rather than quantitative results.

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