MONTE CARLO CALCULATIONS OF SOLVENT EFFECT IN THE REACTION $F^- + CH_3F = F...CH_3...F^-$

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A new approach is suggested and tested to calculation of solvent effect on chemical reactivity based on the statistical-thermodynamic Monte Carlo simulation of models of aqueous solutions devised by Metropolis. The results of computer experiments are presented for the following systems: $F^-.26\,H_2O$, $CH_3F.26\,H_2O$, $FCH_3F^-.52\,H_2O$, $26\,H_2O$, $52\,H_2O$ at a temperature of 300 K at the conditions of canonical ensemble. The pair potentials MCY–CI (for water–water interactions) and 4-31G (for solute–water interactions) have been used. The 4-31G potentials have been derived from the SCF calculations of the interaction energies of the systems: $F^-.H_2O$, $CH_3F.H_2O$, and $FCH_3F^-.H_2O$. Internal energies, radial distribution functions, and snapshots of the configurations have been calculated. The calculated partial molar internal energies depend strongly on quality of the solute–water pair potentials and are overestimated with respect to experiment. On the basis of the results obtained, further possibilities of the suggested approach are discussed.

Theoretical studies of solvent effect on structure, properties, and reactivity of molecules were developed especially in the last decade. Various approaches to solution of the mentioned problem were suggested and applied (see *e.g.* the reviews[1–3]). For the *ab initio* calculations the available theoretical approaches are usually classified as follows: (*I*) the pair interaction energies in connection with the statistical-thermodynamic treatment[4] (the Monte Carlo simulation, molecular dynamics), (*II*) the supermolecular approach and its approximations (various modifications using the point charges[5,6]), (*III*) the continuum models (described in detail, *e.g.*, in ref.[7]), (*IV*) combinations of the *II* and *III* approaches[8]. The mentioned papers mostly deal with the solvent effects on structure and properties of molecules, whereas the field of chemical reactivity was less studied in this respect. This situation obviously follows from the fact that the analysis of reacting systems (*e.g.*, study of the potential energy hypersurface at a level of "chemical accuracy") represents a difficult task even in gas phase. So far the solvent effect on chemical reactions has only been investigated for selected points of the hypersurface either by the (*II*) approach[6,9–12] or by the (*III*) approach[13–16]. Such calculations, however, do not give full information about the reacting systems: *e.g.*, little can be learnt about the solvent structure from the supermolecular calculations, and nothing from the continuum models. Another serious drawback consists in that they do not allow to take into account the temperature effect. Therefore, the (*I*) approach appears to be the most suitable alternative, because it gives a microscopical view on structure of the considered systems at a defined temperature and statistically averaged quantities. The Monte Carlo (MC) calculations for pure water, solution models, but also for complex systems involving biologically active compounds[4,17–22] gave valuable results of high quality, hence it is possible to propose their application to chemical reactivity, too.

The aim of the present work was to test the MC method in the model system

$$F^- + CH_3F = F...CH_3...F^- \qquad (A)$$

in aqueous solution and to evaluate its efficiency in calculation of the activation enthalpy of the reaction (*A*), as well as to investigate the solvent structure in the vicinity of both the reactants and the activated complex. Out of the systems involved in the reaction (*A*), the hydration of F^- was studied by Clementi and Barsotti[23] and by Mezei and Beveridge[20]. The former paper mostly deals with determination of the coordination number, the latter communication investigates the hydration energetics and structure of the hydration shell in terms of the distribution functions. The MC simulation of the hydration of the CH_3F and FCH_3F^- systems has not been published yet. Out of these two systems, a special problem is presented by the MC calculation of the activated complex FCH_3F^- – as far as we know the first application of the MC simulation to an activated state. It is impossible to use any of the standard pair potential functions (PPF) for this system, because these functions are usually chosen in such a way that they conform stable molecules in ground states and equilibrium geometries. Obviously, no empirical potential may be used, too. As it is likely that the PPF calculation will present a serious problem in all further applications of the MC simulation to the activated complex, we have chosen the most simple way to determination of PPF, *viz.* the SCF method and the 4–31G basis set, with the aim of testing such PPF. As mentioned below, PPF of such quality cannot be expected to give a precise calculation of the internal energy of the solvated system. If, however, there is approximately the same error in the calculations of reactants and of the activated complex, then one can expect a compensation of the errors and, hence, a realistic assessment of the solvation contribution to the activation barrier.

The proper applicability of the MC simulation to the activated state presents another problem, which is connected with separability of motions of electrons and nuclei of the activated complex from those of solvent molecules during the activation process[24]. In this communication we assume such separation to be possible, *i.e.* the geometry of the activated complex of the reaction (*A*) is practically unchanged by solvent effect. This assumption is supported by the solvation rule suggested by Westaway[25] for the S_N2 reactions of the type (*A*).

CALCULATIONS

The following model was chosen:

$$F^-.26\,H_2O + CH_3F.26\,H_2O = FCH_3F^-.52\,H_2O\,; \qquad (B)$$

The MC calculations of the systems considered were carried out in canonical [NVT] ensemble by the Metropolis procedure[26] whose modification for aqueous solutions is well-described

e.g. in refs[19,21]. Further information on the MC method in statistical mechanics is also given in ref.[27].

The molecular clusters were characterized by the following parameters: Temperature 300 K, numerical density of H_2O molecules (W) $\varrho_N = 0{\cdot}0333 \cdot 10^{-30}$ m^{-3} ($\varrho = 996{\cdot}514$ kg m^{-3}). Transfer of a solute molecule (S) into a sample of pure water causes a little change of the volume (about 1·5%) which can be neglected with respect to the total sample volume, hence we did not make the respective correction of the cube magnitude. The configurational potential energies $E_{sw}(X^s, X^w)$ and $E_{ww}(X^w)$ were calculated in periodical boundary conditions by the SC (spherical cutoff) method with the approximation of pairwise additivity.

$$E_{sw}(X^s, X^w) = \sum_i^{N_w} E_i(X^s, X_i^w), \tag{1}$$

$$E_{ww}(X^w) = \sum_i^{N_w} E_{ij}(X_i^w, X_j^w), \tag{2}$$

where E_i and E_{ij} mean the PPF of the $S \ldots W_i$ and $W_i \ldots W_j$ molecules, respectively, and the symbols X^s and X^w stand for an abbreviated notation of the configurational coordinates of S and W molecules, respectively. The potential was calculated for the molecular distance equal to $L/2$, where L is the length of the cube edge. For the $W \ldots W$ interaction we used the PPF by Matsuoka and coworkers[28] (the MCY potential), for the $S \ldots W$ interaction we developed the PPF from the SCF 4-31G calculations[29] of the systems $F^-.H_2O$, $CH_3F.H_2O$, $FCH_3F^-.H_2O$. Since the economic reasons compelled us to use the 4-31G basis of lower quality in the calculations of the PPF of the $S \ldots W$ systems, the energy quantities of our simulations can be expected to be less precise. In the simulations we chose cyclic procedure of selection of molecules[30], *i.e.* one step of the simulation involved N_w moves of water molecules. Each simulation consisted of an equilibration and an production phases, the ratio of number of the generated configurations (= number of motions) "equilibration": "production" being equal to 1 : 2. The maximum translation Δr of a molecule in one simulation step and the maximum rotation angle $\Delta\varphi$ were chosen in such way that the acceptance ratio (*i.e.* ratio of the numbers of accepted to excluded configurations) was equal to 0·2–0·4. The resulting values were $\Delta r = 0{\cdot}3 \cdot 10^{-10}$ m and $\Delta\varphi = 10°$. The acceptance ratio chosen is lower than the usual value (50% in most simulations published so far), but it enables a more rapid convergence of the distribution functions and energies (as shown by Kincaid and Scheraga[18]).

In the following text we shall use the energy symbols according to ref.[19]. The direct result of a computer experiment for a solution is the value of the total internal energy $U_{sw}(N_w, N_s)$ for a cluster of N_w solvent molecules and 1 solute molecule:

$$U_{sw}(N_w, N_s) = \int \ldots \int E(X^s, X^w)\, P(X^s, X^w)\, \mathrm{d}X^s\, \mathrm{d}X^w, \tag{3}$$

or for the pure solvent:

$$U_w(N_w) = \int \ldots \int E(X^w)\, P(X^w)\, \mathrm{d}X^w, \tag{4}$$

where $E(X^s, X^w)$ is the configurational potential energy of the system

$$E(X^s, X^w) = E_{sw}(X^s, X^w) + E_{ww}(X^w),$$

[$N_s = 1$, $N_w = 26, 52$], $P(X^s, X^w)$ is the probability that the system will be found in the $\{X^s, X^w\}$ configuratiom. The quantities $E(X^w)$ and $P(X^w)$ are analogous for pure water. According to Ben-Naim[31], the partial molar internal energy of transfer of one S molecule from dilute gas into liquid is

$$U_s = U_{sw}(N_w, N_s) - U_w(N_w) . \tag{5}$$

Also it is possible[19] to express U_s as follows:

$$U_s = U_{s'} + U_{rel} , \tag{6}$$

where the contribution $U_{s'}$ is:

$$U_{s'} = \int \dots \int E_{sw}(X^s, X^w) P(X^s, X^w) \, dX^s \, dX^w , \tag{7}$$

and U_{rel} means the relaxation energy:

$$U_{rel} = U_{w'}(N_w) - U_w(N_w) . \tag{8}$$

The term $U_{w'}(N_w)$ represents the configurational potential energy of N_w water molecules in the presence of the S molecule. It is evaluated as a $W-W$ component in the calculation of $U_{sw}(N_w, N_s)$. From refs[19-21] it is known that the U_s quantity is very sensitive to quality of PPF of $W \dots W$ and $W \dots S$ and to the convergence rate of U_{sw} in the MC simulation. Moreover, an important role in the U_s calculation is also played by its dependence on N_w. Several authors showed[18-22] that the calculation of partial molar internal energy represents a key problem in further application of the MC methods to solutions and that it necessitates the PPF models of the highest possible accuracy.

Information about the solvent structure in the vicinity of the reactants and the activated complex is obtained from the radial distribution functions (RDF):

$$g_{xy}(R) = \Delta N_{xy}(R)/4\pi R^2 \, \Delta R \varrho_y , \tag{9}$$

where $\Delta N_{xy}(R)$ means the occurrence number of the Y atoms in the ΔR layer at the distance R from the X atom (average value for a great number of configurations), ϱ_y is the numerical density of the Y atoms. These functions were calculated for several distribution types, the steric relations of CH_3F and FCH_3F^- being taken into account. The distributions with respect to F and H atoms were only calculated for selected sections of the configurational space, so that, *e.g.*, the distribution of oxygen atoms with respect to F might not be affected by the distribution of the same atoms with respect to hydrogen atoms of the methyl group (see the following section and Fig. 1).

RESULTS

The MC simulations were carried out for following samples: $F^-.26\,H_2O$, $CH_3F.26\,H_2O$, $FCH_3F^-.52\,H_2O$, $26\,H_2O$, $52\,H_2O$. The resulting energy values are listed in Table I.

$F^-.26\,H_2O$. The initial configuration was obtained by generating a cluster of 27 H_2O molecules in simple cubic lattice from which the water molecule located in the origin of coordinates was removed and substituted by F^- ion. The equilibration

phase was begun at $T = 500$ K. After having generated 1 000 configurations, the temperature was decreased to $T = 300$ K. The simulation involves 335 000 configurations, out of which the initial 105 000 configurations were excluded from the averaging. During the production phase the $U_{sw}(N_w, N_s)$ value became relatively constant at $-3\,343$ kJ mol^{-1} *i.e.* -129 kJ mol^{-1} per one H_2O molecule. The calculated radial distribution functions are given in Fig. 2; Fig. 3 compares the $\Delta N_0/\Delta R$ function of our system $F^-.26\,H_2O$ [4–31G] with that[23] of $F^-.300H_2O$. Additional information is given in Fig. 4 representing a snapshot of the cluster in the perspective view. The oxygen atoms nearest to the observer are represented by the largest circles.

$CH_3F.26\,H_2O$. The parameters of this run differ from the above ones only by the configurations number 390 000, out of which the initial configurations (130 000)

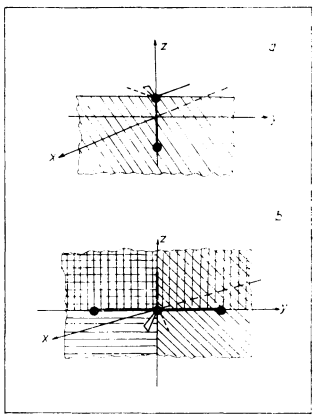

FIG. 1

The definition of the sub-spaces for: *a*) CH_3F, *b*) FCH_3F^-. The position of CH_3F was chosen in such way that the absolute values of *z* coordinates of the H and F atoms might be equal. *a*) The plane separating the two sub-spaces has the *z* coordinate equal to $0{\cdot}537 \cdot 10^{-10}$ m, the hatched part corresponds to the distribution F—O or F—H_w; *b*) the three sub-spaces for the activated complex differ in the hatchure used: oblique — the distribution with respect to $F_{(1)}$, horizontal — the distribution with respect to $F_{(2)}$, vertical — the distribution with respect to H_m

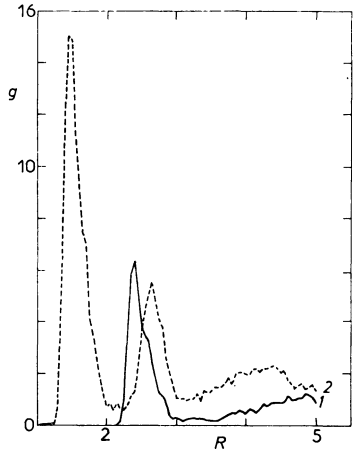

FIG. 2

The RDF of the $F^-.26\,H_2O$ system, g(F—O) ... 1, g(F—H_w) ... 2, the distances in 10^{-10} m, the g(F—H_w) values are scaled by a factor of 2 to be synoptical

were discarded. The resulting value $U_{sw}(N_w, N_s) = -1\,095$ kJ mol^{-1} (-42 kJ mol^{-1} per one H_2O molecule). The analysis of configurations was carried out for two half-spaces (Fig. 1*a*): the distribution of F—O, F—H_w was investigated for $z < 0{\cdot}537 \cdot 10^{-10}$ m, that of H_m—O, H_m—H_w for $z > 0{\cdot}537 \cdot 10^{-10}$ m (the index m denotes a hydrogen atom of methyl group). The corresponding RDF are given in Figs 5 and 6. For comparison, we also calculated the overall C—O and C—H_m distributions for the whole configurational space (Fig. 7). As in the previous case ($F^-.26\,H_2O$) we give a random snapshot of the cluster in Fig. 8.

$FCH_3F^-.52\,H_2O$. This simulation started from a simple cubic lattice at $T = 500$ K which was decreased to 300 K after generating 5 200 configurations. Total 771 000 configurations were generated, out of which the initial ones (238 000) were excluded from the averaging. The resulting value $U_{sw}(N_w, N_s) = -3\,359$ kJ mol^{-1} (-65 kJ mol^{-1} per one H_2O molecule). The distribution functions were calculated for sections of the configurational space according to Fig. 1*b*. The distribution $F_{(1)}$—O, $F_{(1)}$—H_w for $y > 0$, $F_{(2)}$—O, $F_{(2)}$—H_w for $y < 0$, the distributions H_m—O, H_m—H_w for $z > 0$, and the distributions with respect to the carbon atom for the whole space. The corresponding RDF's are given in Figs 9–11, a random snapshot of the cluster is given in Fig. 12. For better resolution in this case we only give the water molecules whose oxygen atoms have their x coordinates within the interval

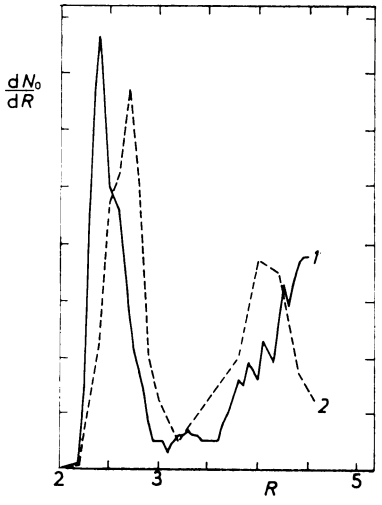

FIG. 3

The $\Delta N_0/\Delta R$ functions of the $F^-.26\,H_2O$ (1) and $F^-.300\,H_2O$ (2) systems (see ref.[23]). The distances in 10^{-10} m

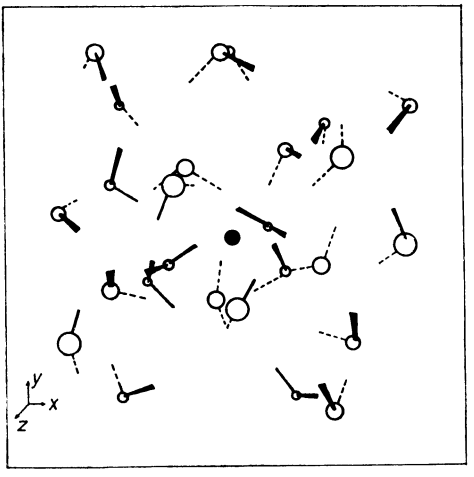

FIG. 4

The snapshot of the $F^-.26\,H_2O$ cluster taken at the end of the production phase of the MC run

(−5·5) in 10^{-10} m units. The oxygen atoms near the YZ plane are denoted by full circles, the empty circles denote the atoms with the maximum or the minimum x coordinate values.

26 H_2O, 52 H_2O. The calculation of U_{rel} (Eq. (*8*)) necessitated these two simulations of pure water. The calculations started, respectively, from the final configurations of the MC runs for $F^-.26\ H_2O$ and $FCH_3F^-.52\ H_2O$. Both in the equilibration and in the production phase 100 000 configurations were generated in each simulation. The resulting $U_w(N_w)$ values are given in Table I.

TABLE I

Energy contributions (kJ mol^{-1}) of individual components of Eq. (*B*), $N_s = 1$

Quantity	F^-	CH_3F	FCH_3F^-	ΔU_s
$U_{sw}(N_w, N_s)^a$	−3 343·6	−1 094·6	−3 359·2	
$U_w(N_w)^b$	− 951·6	− 951·6	−1 887·6	
$U_{w'}(N_w)^c$	− 528·8	− 930·8	−1 565·2	
$U_{s'}(N_w)^d$	−2 815·8	− 163·8	−1 794·0	
$U_{rel}{}^e$	422·8	20·8	322·4	
$U_s{}^f$	−2 393·0	− 143·0	−1 471·6	1 064·4
ΔH_{hydr}	− 502·4[g]	− 65·6[h]	—	

[a] The total configurational potential energy of the system, $U_{sw}(N_w, N_s)$; [b] the configurational potential energy of pure water for N_w molecules; [c] the configurational potential energy of water in the presence of S; [d] the total averaged $W...S$ interaction, $U_{s'}(N_w)$; [f] the relaxation contribution $U_{rel} = U_{w'}(N_w) - U_w(N_w)$; [f] the partial molar internal energy of transfer of S into water. $U_s = U_{sw}(N_w, N_s) - U_w(N_w)$; [g] see ref.[39] [h] see ref.[40].

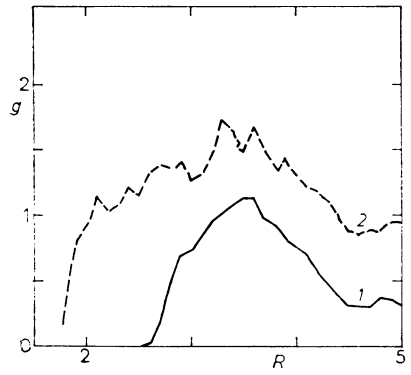

FIG. 5

The RDF $g(F—O)...1$, $g(F—H_w)...2$ of the $CH_3F.26\ H_2O$ system. The distances in 10^{-10} m, the $g(F—H_w)$ values are scaled by the factor of 2

DISCUSSION

Analysis of our energy results will start from the values given in Table I. At first sight differences are obvious between the theoretical and experimental U_s values. The U_s value is overestimated by the factor of 4·8 and 2·2 in the cases of F^- and CH_3F, respectively. In principle, these differences can be due to two reasons: *1*) convergence in the MC algorithm, *2*) imperfectness of PPF. The U_s value is obtained as a difference of two relatively large values (Eq. (*5*)) whose absolute magnitudes are comparable especially for weak interactions (*e.g.*, $CH_4 \ldots H_2O$[18]). In these cases the $U_{sw}(N_w, N_s)$ and $U_w(N_w)$ values do not differ very much, and (as already shown by Kincaid and Scheraga[18]) the small energy fluctuations (about 0·8 kJ mol^{-1} per one H_2O molecule in pure water) inherent in the MC algorithm with $10^5 - 10^6$ configurations can cause relatively large differences between theory and experiment. Our simulations involve systems with strong ion–dipole and dipole–dipole interactions. Considering the energy fluctuations about 1 kJ mol^{-1}, we get a scattering of ± 26 kJ mol^{-1} for a cluster of 26 molecules. The found differences between experiment and U_s are, however, much greater, especially so for F^-. Therefore, we presume that the dominant source of the deviations consists in quality of the 4–31G PPF used in our simultations. As the 4–31G basis set overestimates the dipole moment of the water molecule, it follows that the main electrostatic component of the interaction energy will decide the question of quality of 4–31G PPF and, hence, of the U_s value. This result makes itself felt most distinctly in ion–dipole interactions, *i.e.* $F^- \ldots H_2O$, to a lesser extent in dipole–dipole interactions, *i.e.* $CH_3F \ldots H_2O$. The calculated contribution of hydration to the activation barrier of (*B*) is $\Delta U_s =$

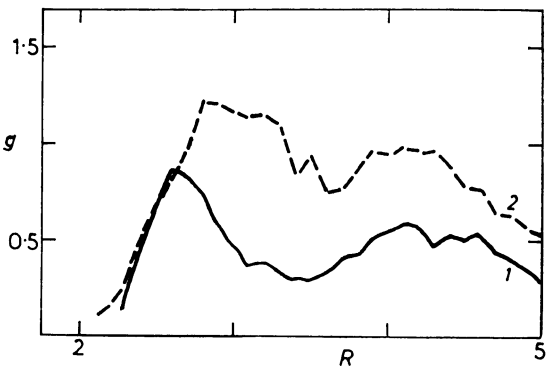

FIG. 6

The RDF $g(H_m—O) \ldots 1$, $g(H_m—H_w) \ldots 2$ of the $CH_3F.26\ H_2O$ system. The distances in 10^{-10} m, the $g(H_m—H_w)$ values are scaled by the factor of 2

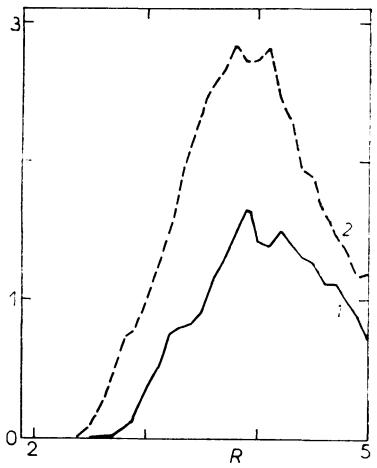

FIG. 7

The RDF $g(C—O)...1$ and $g(C—H_w)...2$ of the $CH_3F.26\,H_2O$ system. The distances in 10^{-10} m, the $g(C—H_w)$ values are scaled by the factor of 2

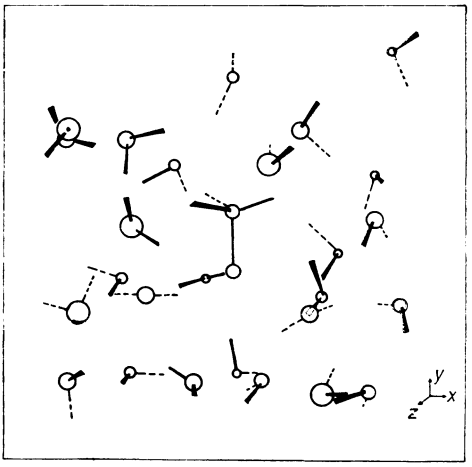

FIG. 8

The snapshot of the $CH_3F.26\,H_2O$ cluster taken at the end of the production phase of the MC run

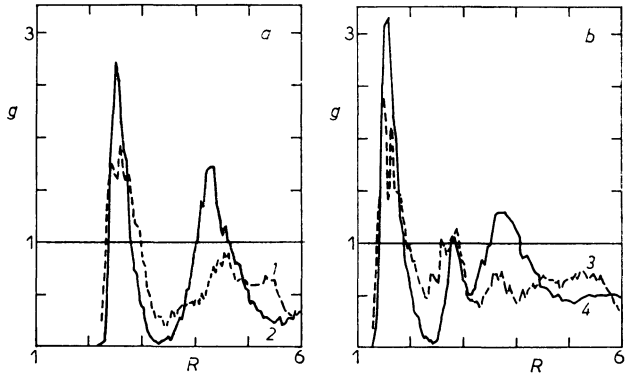

FIG. 9

The RDF for the system $FCH_3F^-.52\,H_2O$. *a*) $g(F_{(1)}—O)...1$, $g(F_{(2)}—O)...2$, *b*) $g(F_{(1)}—H_w)...$ $...3$, $g(F_{(2)}—H_w)...4$. The distances in 10^{-10} m

$= 1\,064{\cdot}4\ \mathrm{kJ\ mol^{-1}}$. This value is rather overestimated when compared with the hitherto calculations or assessments. Berthier and coworkers[32] assess this contribution at $80\ \mathrm{kJ\ mol^{-1}}$, Cremaschi and coworkers[9] give $290\ \mathrm{kJ\ mol^{-1}}$. Miertuš and coworkers[33] obtained the value of $378\ \mathrm{kJ\ mol^{-1}}$ using the continuum model. As it turned out, it is impossible to expect the presumed compensation of errors in U_s when calculating the hydration effect on the activation barrier. Obviously, the reason lies in non-uniform overestimation of the partial molar internal energy of the reactants (expecially F^-) and the activated complex. Quantitative estimation of the hydration effect on the reaction (*B*) consists in two steps: *1*) calculation of U_s and *2*) calculation of ΔU_s. Each step involves differences of large numbers, hence it is necessary to use the best PPF. Development of the PPF represents an exacting and extensive piece of calculation work, which is a considerable limiting factor to possible selection of the basis for calculation of the data base of the interaction energies. For small systems it presents no difficulties to use a large base which may give correct U_s values. Such unambiguous accordance with experiment is seen, *e.g.*, in the results by Mezei and Beveridge[20] who obtained for $F^-.215\ H_2O$ $U_s = -597\ \mathrm{kJ\ mol^{-1}}$ with the *W...S* PPF obtained from extensive SCF calculations with the basis

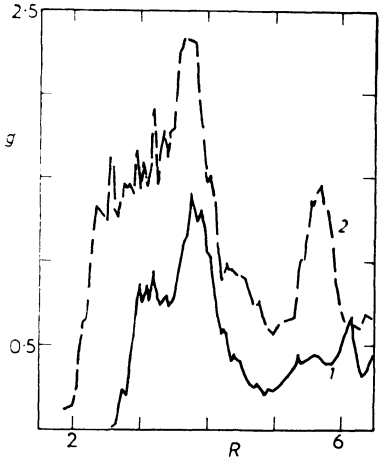

FIG. 10

The RDF $g(H_m—O)...1$ and $g(H_m—H_w)...2$ for the system $FCH_3F^-.52\ H_2O$. The distances in 10^{-10} m

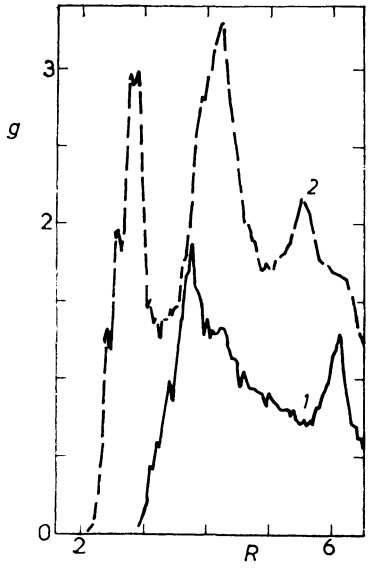

FIG. 11

The RDF $g(C—O)...1$, $g(C—H_w)...2$ for the $FCH_3F^-.52\ H_2O$ system. The distances in 10^{-10} m, the $g(C—H_w)$ values are scaled by the factor of 2

F[7*s*4*p*1*d*], O[4*s*3*p*1*d*], H[2*s*1*p*] (ref.[34]). For larger systems, as *e.g.* FCH_3F^- or CH_3F, application of an extended basis to generation of extensive data bases of interaction energies is connected with considerable calculation problems. Future development in the field of numerical MC experiments in chemical reactivity will depend on the development of high-quality PPF for the large systems, too (as *e.g.* the activated complex FCH_3F^-). It appears that a suitable alternative of solution of the problem of PPF consists in their scaling which improves the energy results without decreasing quality of the distribution functions[35,36].

Bearing the mentioned results in mind we also judge our calculations which enable determination of only qualitative hydration effect on the activation barrier of reaction (*B*). More real results can be expected from the scaled PPF which, however, necessitate to carry out – at important points of the interaction energy hypersurfaces – several calculations with extended basis set and therefrom to derive a suitable form of the scaling function. In our laboratory the corresponding investigation is in its initial phase.

The second part of this discussion will be focused on the radial distribution functions which enable a microscopical view on structure of the solvation shells of the systems investigated. Two types of the curves are given for the system $F^-.H_2O$, *viz.* the RDF in Fig. 2 and the derivative curves in Fig. 3, the latter being compared with the work by Clementi and Barsotti[23]. The first hydration sphere is well reproduced in our simulation. Position and height of the first maximum at the curve with 26 H_2O molecules are affected by the used PPF which causes a mild contraction of the first hydration layer, however, the agreement with the reference curve is satisfactory. Also the comparison with ref.[20] allows a similar conclusion – the 4–31G

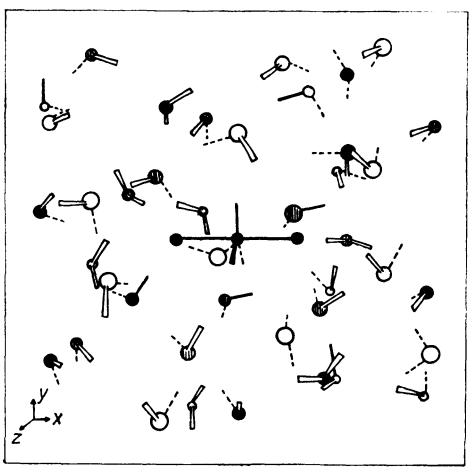

Fig. 12

The snapshot of the cluster of the hydrated FCH_3F^- structure taken at the end of the production phase of the MC run

PPF stresses the first maximum, and its position is closer to F^- ion by about 0·5 . 10^{-10} m. The position and height of the second maximum are affected by magnitude of the sample, in our case it should lie at the distance R_{OF} = (4·2 to 4·3) . 10^{-10} m which is, however, in close vicinity of the cube edge $L/2$. The effects at the edge of the simulation cube were observed earlier, *e.g.*, by Mezei and Beveridge [20]. The RDF g(F—O), g(F—H) indicate a relatively firm coordination of F^- and the H_2O molecules of the first hydration sphere, but the remainder of the cluster represents a transition between structural and macroscopic water (Fig. 4).

Another situation is encountered in the CH_3F. 26 H_2O cluster (Figs 5–7). The curve $g(H_m—O)$ of oxygen atom with respect to methyl hydrogen atom (H_m) and the curve g(F—O) of the oxygen atom with respect to fluorine atom differentiate well the first maximum from the rest of the cluster. The first maximum at the g(F—O) curve lies at R_{OF} = 3·5 . 10^{-10} m which is substantially farther than the first maximum for F^-.26 H_aO. This result agrees with the physical picture of the $F^-...H_2O$ and $CH_3F...H_2O$ interactions and with the very different charges at the fluorine atoms in the two systems. The second maximum is only slightly developed due to very small number of water molecules in the sample, which is similar to the F^-.26 H_2O cluster at the edge of the simulation cube.

The CH_3F.26 H_2O system is characterized by a non-uniform distribution of water molecules between hydrophilic and hydrophobic sections of methyl fluoride. This non-uniformity is documented by the heights of the first maxima at the g(F—O), $g(H_m—O)$, as well as $g(F—H_w)$, and $g(H_m—H_w)$ curves and is distinct in the samples with small number of the solvent molecules. This interpretation is also supported by the general view given in the snapshot (Fig. 8). As compared with the previous system, the RDF maxima are broader and lower, which indicates formation of clathrate structures of the solvent around CH_3F. A similar RDF course is also encountered with the aqueous solutions of methane[18,19,21,22] and methanol[37].

The global distribution functions $g(C—O)$ and $g(C—H_w)$ represent the spherical arrangement of the water molecules, and differentiation of the hydration spheres is made difficult, because the hydration layers at the side of the F atom are overlapped by those at the side of CH_3 group, so that these RDF give a picture of their superposition.

In the case calculation of the distribution functions of the FCH_3F^- . 52 H_2O cluster, the situation is complicated by the form of the activated complex. The interatomic distance $F_{(1)}—F_{(2)}$ = 3·66 . 10^{-10} m is relatively large compared with the length of the cube edge L = 11·76 . 10^{-10} m, in other words, there remains less space for the water molecules forming the hydration shell. To check the statistical distribution at the both sides of the system, we calculated RDF with respect to the both fluorine atoms. The curves $g(F_{(1)}—O)$ and $g(F_{(2)}—O)$ (or $g(F_{(1)}—H_w)$ and $g(F_{(2)}—H_w)$) should be substantially identical, which was confirmed only partially. The course of the two g(F—O) curves (Fig. 9) is identical for R =

$= 3{\cdot}8 \cdot 10^{-10}$ m, *i.e.* for the first solvation layer. This layer with the maximum at $R = 2{\cdot}5 \cdot 10^{-10}$ m is ascribed to solvation of fluorine atom, which is supported by similar shape of the $g(F_{(1)}—O)$ and $g(F_{(2)}—O)$ curves to that of the $g(F—O)$ curve of F^- ion. Position of the maximum in the activated complex corresponds to such sequence of the positions which would be presumed according to the population analysis at the F atom in F^-, CH_3F, and FCH_3F^-. Table II can serve for better orientation about positions of the maxima and minima in the individual systems. The second maximum at the $g(F—O)$ curve corresponds obviously to the solvation layer near the CH_3 group and perhaps partially also to the contribution of the second hydration sphere being formed around the F atom. The position of the second maximum corresponds fully to this idea (*cf.* Table II, Figs 2, 5, and 9). The interpretation of $g(F—H)$ is identical with what was said about $g(F—O)$. Perhaps it would be worth mentioning that the shape of the curves for $R > 3 \cdot 10^{-10}$ m indicates lowered organization of solvent near the CH_3 group, similar as with CH_3F. The global RDF $g(C—O)$ and $g(C—H_w)$ in Fig. 11 confirms the hitherto picture of the hydration of FCH_3F^-.

CONCLUSION

Application of the MC method to solution of problems of chemical reactivity, as it was described in this communication, is at its beginning so far. The results obtained answered some questions connected with this task:

TABLE II

Positions of the maxima and the minima (distances in 10^{-10} m) on the RDF of the $F^-.26\ H_2O$, $CH_3F.26\ H_2O$, and $FCH_3F^-.52\ H_2O$ systems

System	Distribution	R_1[a]	r_1[b]	R_2
$F^-.26\ H_2O$	F—O	2·4	3·1	≈5
$CH_3F.26\ H_2O$	F—O	3·5	4·5	—
	C—O	3·9	—	—
	H_m—O	2·6	3·5	≈4
$FCH_3F^-.52\ H_2O$	F_1—O	2·6	3·45	≈4·5
	F_2—O	2·5	3·35	4·3
	C—O	3·75	5·5	≈6
	H_m—O	3·2[c]		
		3·8[d]	4·8	(≈6)

[a] Maximum; [b] minimum; [c] a plateau at the curve; [d] position of the first maximum after the plateau.

1) The semi-quantitative to quantitative calculations of the energy contributions will necessitate the PPF derived from high-quality *ab initio* SCF calculations (possibly with inclusion of the correlation energy). Application of less accurate PPF gives only qualitative results. In our case the errors introduced by inaccurate PPF into the results for the system at the left-hand and the right-hand sides of Eq. (*B*) were not mutually compensated.

2) The main result of our simulations is seen in the structural information which proves the well-developed first hydration layer in all the three cases also documented by the snapshot pictures. Such averaged structures can be used, *e.g.*, in the supermolecular calculations at the level of electrostatic approximation[38].

3) As far as the effect of PPF on the structural information is concerned, useful results can also be obtained with potentials of lower quality: when evaluating the RDF it is necessary to take into account some imperfections of the PPF which overestimate the interaction energy and affect the positions and, especially, the heights of the extremes.

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