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Comparative analysis of molecular interactions in quaternary fluid system performed by classical and *ab initio* molecular dynamics

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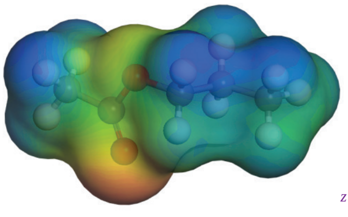
Molecular interactions in the quaternary fluid system acetic acid–*n*-propanol–*n*-propyl acetate–water were analyzed by classical and *ab initio* molecular dynamics methods. It was shown that *ab initio* molecular dynamics simulation can reproduce the molecular mobility tendency and structural features of a multicomponent system without empirical parameters.



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Intermolecular interactions in multicomponent fluid systems are of complex nature, and even their qualitative evaluation is a difficult task. Regardless of the nature of the components, aspects such as multiparticle interactions and concentration dependence, among others, should be taken into account. Molecular dynamics is a very efficient computational tool for the theoretical analysis of interactions at the atomic-molecular level.[1–4] Despite certain achievements in the field of classical molecular dynamics,[5] relatively adequate quantitative results have been obtained for simpler systems and models, including those using the Lennard–Jones potential.[6,7] It should be noted that the use of even simple models that take into account only pair interactions gives some real picture of the phase behavior of systems, including the main features of phase diagrams (binodals, spinodals, critical points).

A more adequate description of molecular interactions should be expected when experimental data on thermodynamic characteristics are used in calculations,[8–12] for example, the values of the excess Gibbs energy and its concentration dependence. Such a joint analysis of macroscopic parameters and characteristics of molecular interactions is one of the central problems in natural science and requires direct experimental information on thermodynamic properties.[13] Other possibilities are related to the estimation of the molecular interaction energy based on quantum chemical calculations, *i.e.*, using *ab initio* molecular dynamics.

In the present communication, some results of such calculations of interactions between the components of a quaternary system (consisting of four substances) are discussed, primarily in comparison with the results obtained in the framework of classical molecular dynamics.

The choice of the components is related to our studies of quaternary systems, which offer promising possibilities for the development of *ab initio* molecular dynamics calculations using or comparing with the obtained thermodynamic characteristics. The thermodynamic properties of binary and multicomponent systems formed by selected components, acetic acid, *n*-propanol, *n*-propyl acetate and water, have been well studied.[14–16] These substances are part of the ester synthesis/hydrolysis reaction mixture, but in the absence of a catalyst and in a limited time interval, the reaction processes can be neglected. Taking into account the possibilities of the methods of classical molecular dynamics and *ab initio* molecular dynamics, the main target indicators reflecting the specifics of intermolecular interactions are the parameters of self-diffusion and the values of the radial distribution functions. The first maximum of the radial distribution function is larger than the others and shows the closest distance between atoms. The self-diffusion coefficient is an important parameter for assessing the state of thermodynamic equilibrium.

Molecular dynamics calculations were performed using the Forcite module, and *ab initio* molecular dynamics calculations were performed using the DMol^3 module of the Materials Studio software package.[17]

For calculations by the method of classical molecular dynamics, at the first stage, the electronic structure of all four components of the system was determined by the DFT method (DMol^3 module) with full optimization of the molecular geometry. The dnp 4.4 basis and the PBE[18] functional were used. After the completion of the calculations, the Mulliken analysis of the orbital populations was carried out and the values of the charges of all atoms were determined.

Then a cell was built (Amorphous Cell module), filled with an equimolar number of molecules, 25 for each component [Figure 1(*a*)]. It was assumed that the equimolar composition and amounts of substances are sufficient to determine the values of the radial distribution functions and the mobility of the components. The

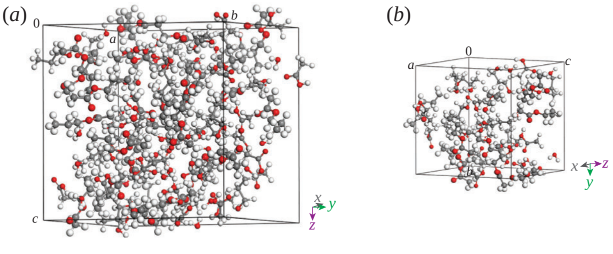

Figure 1 Cells used in (*a*) classical and (*b*) *ab initio* molecular dynamics simulations.

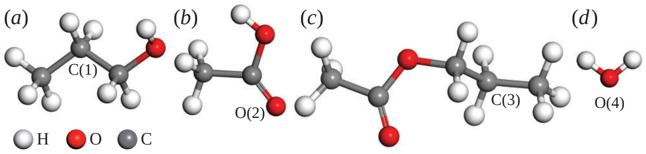

Figure 2 Molecular models of the components of the quarternary system with selected atoms in interacting molecules: (*a*) *n*-propanol, (*b*) acetic acid, (*c*) *n*-propyl acetate and (*d*) water.

force field of interacting molecules was built on the basis of the universal force field potentials. In this case, the short-range forces were determined by the parameters of this field, and the electrostatic interaction was determined using the calculated charges on the atoms. The calculation of such a cell with imposed periodic boundary conditions was carried out by the method of classical molecular dynamics (Forcite module) at a temperature of 298 K in the NVT ensemble with a simulation time of 50 ns and a step of 1 fs.

For *ab initio* molecular dynamics, a smaller cell was constructed due to the large computational requirements for such calculations. An equimolar mixture of 10 molecules of each component of the quaternary system was placed into the constructed cubic cell [Figure 1(*b*)]. The calculation was carried out by the DFT method implemented in the DMol^3 module. The PBE functional, dnp 4.4 basis, calculation duration 5 ps, step 1 fs and temperature 300 K were used for calculations. For detailed information on classical and *ab initio* molecular dynamics simulations, see Online Supplementary Materials.

The self-diffusion coefficients of the components were calculated from the obtained values of the root-mean-square displacement (Table 1). As can be seen, the absolute values of the self-diffusion coefficients calculated by different methods differ by several times, but the trends in the difference in their values are completely preserved. Thus, despite the semi-empirical choice of parameterization of molecular interaction in classical molecular dynamics and the completely non-empirical nature of such an interaction in *ab initio* molecular dynamics, this indicator successfully represents the relative dynamic trends in the given system. It should be noted that, due to the nature of the system under consideration (its components participate in esterification/hydrolysis reactions), *n*-propanol and acetic acid (the components involved in the esterification reaction) have similar values of self-diffusion coefficients, while for *n*-propyl acetate and water (the components that enter into the ester hydrolysis reaction), there are much greater differences in this value. This fact seems to be quite interesting and requires further investigation, which is beyond the scope of the present study.

The structural characteristics of the system and the nature of the interaction of molecules with each other were determined using the radial distribution functions. The atoms in the interacting molecules were chosen according to different types of interactions (Figure 2). The values of the maxima for pair interactions, corresponding to the stable preservation of the minimum distance between the atoms of molecules, are presented in Table 2.

Table 1 Self-diffusion coefficients of the components of the quaternary system *n*-propanol–acetic acid–*n*-propyl acetate–water.

Molecular dynamics method	Self-diffusion coefficient/Å^2 ps^{-1}			
	n-Propanol	Acetic acid	*n*-Propyl acetate	Water
Ab initio	0.243	0.241	0.236	0.249
Classical	0.0279	0.0257	0.0207	0.0741

Table 2 Values of the maxima of the pairwise distribution functions of the quaternary molecules system, calculated by the methods of classical and *ab initio* molecular dynamics.

Pair of atoms in interacting molecules[a]	Maximum of pairwise distribution function/Å	
	Classical method	*Ab initio* method
C(1) in *n*-propanol – O(2) in acetic acid	4.71	4.30
C(1) in *n*-propanol – C(3) in *n*-propyl acetate	5.10	4.65
C(1) in *n*-propanol – O(4) in water	3.81	3.57
O(2) in acetic acid – C(3) in *n*-propyl acetate	4.72	4.25
O(2) in acetic acid – O(4) in water	3.35	2.75
C(3) in *n*-propyl acetate – O(4) in water	4.11	4.69

[a] The numbering of atoms is shown in Figure 2.

As can be seen from Table 2, the closest contact is established between water molecules and molecules of *n*-propanol and acetic acid, *i.e.*, pairs with relatively small values of the maxima of the distribution function. Probably, in this case, this is due to the small size of water molecules and their ability to approach the regions of molecules with acceptor characteristics without steric hindrance. The approach of water molecules to *n*-propyl acetate is associated with steric hindrances and screening of oxygen atoms by hydrocarbon residues. In general and in other cases, the largest distances with other molecules are observed for *n*-propyl acetate. It is important that, as in the case of dynamic characteristics (self-diffusion values), the general trend in the calculations of the intermolecular interaction parameters by the methods of classical and *ab initio* molecular dynamics is preserved.

Thus, the use of the *ab initio* molecular dynamics method, despite resource-intensive calculations, makes it possible to reproduce important indicators of interactions in the *n*-propanol–acetic acid–*n*-propyl acetate–water system without involving experimental parameters. Note that at this stage we have obtained the above characteristics for equimolar quaternary mixtures, but we can assume that they also reflect a more complete picture of interactions in a quaternary system. Accordingly, on the basis of *ab initio* molecular dynamics, a fully automated computer calculation scheme can be created, which makes it possible to avoid the ambiguity in the choice of the force field due to different approaches to fitting parameters to experimental data in the classical approach.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.04.036.

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