An AOT Reverse Micelle in a Medium of Supercritical Carbon Dioxide

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Received December 3, 2014

Abstract—Reverse micelles of Aerosol OT in the medium of supercritical carbon dioxide have been simulated by the molecular dynamics method. For the first time, a micelle in ternary water–Aerosol OT–supercritical CO_2 has been simulated by describing the surfactant and the supercritical liquid in terms of the coarse-grained approach. It has been shown that the structural and energetic characteristics of the micelle are, with a good accuracy, described within the framework of simplified models.

INTRODUCTION

Supercritical carbon dioxide (SCCD) is an available and environmentally safe solvent that works well with an efficient technology of regeneration. This is the reason for the wide interest in its application for supercritical fluid extraction. Micellar extraction is one of the most promising fields related to this problem. In view of the development of industrial separation processes [1], increasing attention is being focused on the study of extraction based on reverse micelles in the investigations of both applied and fundamental character [2–12].

Aqueous cavities in micellar aggregates serve as reservoirs for polar components of a solubilisate, into which these components penetrate from a supercritical solvent. Therewith, the solvation ability of a solvent is controlled by technological conditions. The most efficient solubilization of a solute can be achieved under optimal conditions of system treatment. Then, by varying temperature and pressure, the supercritical solvent is transferred to the gaseous state, thereby completely removing it from the system; then, it is returned to a technological process without any additional purification.

The chemical stability and relatively low values of the critical parameters (pressure $P_{cr} = 7.38$ MPa, temperature $T_{cr} = 304$ K, and bulk density $\rho = 465$ g/L) make carbon dioxide a very promising extractant. Because of the similar properties of supercritical fluids and liquids, they are frequently referred to as supercritical liquids, although their kinetic state corresponds to a gaseous phase. These features have underlain the development of novel SCCD models within the framework of computer simulation. The necessity to study the prospects of using supercritical fluids has caused the interest in the study of them using computer simulation, primarily, by the molecular dynamics (MD) method, because it enables one not only to determine the main structural and thermodynamic parameters, but also to investigate the dynamics of a system at the molecular level [13].

At present, several models of carbon dioxide have been described in the literature [14–24]. The three following main principles of describing molecules may be distinguished among them:

• Full-atom models with a partly distributed charge. Within the framework of this approximation, three partial charges correspond to the force centers of the atoms in CO_2. The EPM2 three-point model [15–18] is most commonly used among them.

• Simplified models that take into account the quadrupole moment [19–22]. One force center of interaction corresponds to the three-atom CO_2 molecule. The internal energy of the system is calculated as the sum of the contributions from the Lennard-Jones potential and the quadrupole component of the molecule.

• Simplified models under spherical approximation without the quadrupole moment that take into account only the Lennard-Jones dispersion interaction [23, 24].

The full-atom description of carbon dioxide molecules makes it possible to calculate the thermodynamic characteristics of examined systems with a high accuracy and determine the contribution of the electrostatic component to the interaction energy. Such interactions are essential in solutions of reverse micelles and water-in-oil (w/o) microemulsions. Detailed descriptions of carbon dioxide molecules are common in works devoted to the simulation of reverse micelles and w/o microemulsions [25–28]. Works [25–27] were devoted to studying micellization, while the structural and dynamic characteristics of water

located in the confined space of a micellar core were selected as objects for study in [28].

In [27], the MD method was employed to study the aggregation of a fluorine-containing surfactant, the molecule of which consists of two nonpolar tails and a polar group, in an SCCD medium. The results obtained have shown that the surfactant is prone to spontaneous aggregation into aggregates with the shape and structure similar to those of reverse micelles. In the absence of the surfactant, the system contains small water clusters, which are at equilibrium with monomers.

Molecular aggregation of an ionic liquid (IL)—guanidine acetate—in the medium of supercritical carbon dioxide has been considered in [26]. It has been shown that randomly distributed particles of the ionic liquid and a fluorine-containing surfactant spontaneously form a unified ensemble over 200 ns. The resulting micelles have an almost ellipsoidal shape. The calculations of the internal interaction energy have suggested that there is a high degree of bonding between the IL and the polar groups of the surfactant.

The authors of [25] were the first to employ the MD method for studying micellization. Computer experiments were performed under the conditions of an *NVT* ensemble at 310 K in a cubic cell with periodic boundary conditions. Molecules of a fluorine-containing surfactant were described in terms of the "united atom" approximation. In addition, the SPC/E model was used for water and the EPM2 triatomic model taken from [15] was applied to describe SCCD molecules; the density of the supercritical solvent was 0.482 g/cm^3.

The simulation results have indicated that, over a time period of nearly 1036 ps, three spherical aggregates with almost the same sizes and compositions are formed in a cell containing 30 surface-active particles, 132 water molecules, and 2452 SCCD molecules. The radial density profiles of individual aggregates have been calculated, and the local structure of micelles has been investigated. The data obtained have shown that substantial amounts of molecules of both solvents are present in a surface layer.

The structural and dynamic characteristics of water under the conditions of a confined space in a micelle core have been studied in [28]. The structure of micelles was characterized with the use of the radial profiles of the partial densities and pair distribution functions. The water diffusion coefficient was calculated by the Einstein relation.

Additional information on these and other works devoted to computer simulation of reverse micelles and w/o microemulsions is available from review [29].

The main drawback of atomistic models is the large expense of computational resources. The use of simplified models markedly increases the potential of simulation, and, when simulating extraction pro-

cesses, this factor may appear to be essential, because multicomponent microheterogeneous systems are considered in the case of supercritical micellar extraction. Therefore, a simplified approach has been selected for the nonpolar solvent in this work.

This study has been devoted to the computer simulation of reverse micelles of Aerosol OT (AOT, sodium bis(2-ethylhexyl) sulfosuccinate) in SCCD in terms of a coarse-grained description of the surfactant. The selected anionic surfactant is widely applied for micellar catalysis, synthesis, and extraction, because it can form reverse micelles and microemulsions without the addition of cosurfactants.

SIMULATION CONDITIONS

In the presence of an ionic surfactant, the ionic strength of a solution makes it necessary to take into account the contribution of the quadrupole interaction of solvent molecules. Therefore, SCCD molecules were described in the coarse-grained approximation using a model [20] that takes into account the quadrupole moment of CO_2 molecule.

The scheme of multilevel simulation in terms of the *NVT* ensemble was realized in this work. While the active medium of SCCD was described under the coarse-grained approximation, the components of the aqueous cavity of a micelle were specified with the accuracy of full-atom models. Water molecules were represented within the framework of the SPC/E three-point model with partial charges located at each atom [30]. AOT molecules (Fig. 1) were simulated in terms of the coarse-grained approximation [32]. The denotations of the force centers of AOT molecule are presented in Fig. 1.

The internal energy of the system was described in the approximation of the pair additivity. For all types of particles, the specific interaction was described using Lennard-Jones potential U_1 [13], the electrostatic energy was represented by Coulomb potential U_2 [13], and dipole–quadrupole U_3 and quadrupole–quadrupole U_4 components were expressed via the isotropic intermolecular potentials [20] as follows:

$$U_1 = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6],$$

$$U_2 = q_i q_j / r_{ij},$$

$$U_3 = \beta\mu^2 Q^2 / (r_{ij})^8,$$

$$U_4 = \beta Q^4 / (r_{ij})^{10}.$$

Here, r_{ij} is the distance between particles *i* and *j*; ε and σ are the energetic and geometric Lennard-Jones parameters, respectively; q is the AOT ion charge and/or a partial charge in a water molecule; μ is the dipole moment of water (7.84×10^{-30} C m) [31]; Q is the quadrupole moment of CO_2 molecules $- 1.367 \times 10^{-39}$ C m^2); and $\beta = 1/k_B T$, where k_B is the Boltzmann constant and *T* is the system temperature.
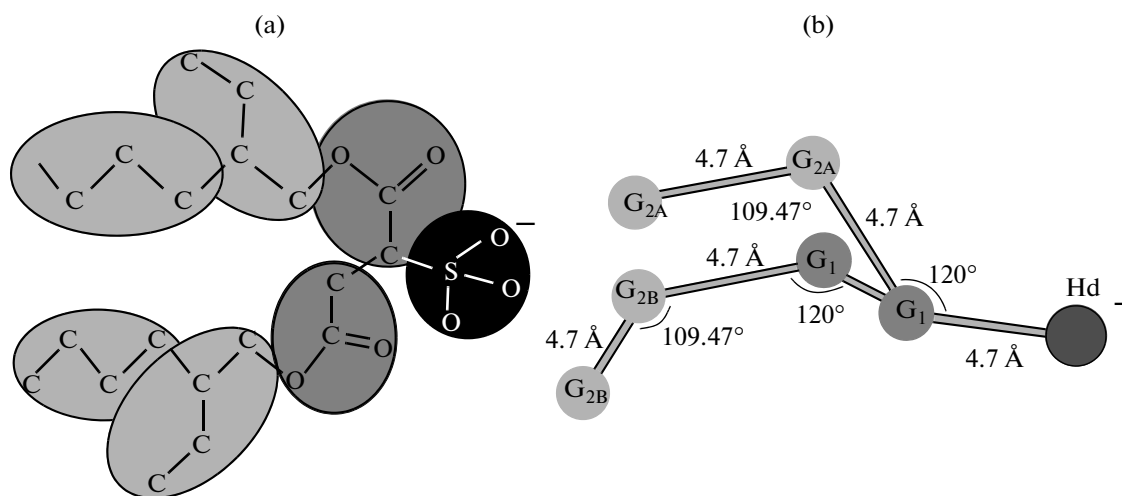
(a)

(b)

Fig. 1. (a) Detailed and (b) coarse-grained models of AOT anion.

The values of the parameters of the interaction potentials are listed in Table 1.

A micelle with a composition of 32 Na-AOT and 320 H_2O was placed into the center of a spherical cell with an impermeable shell and a radius of 80 Å. The space between the aggregate and the cell wall was filled with 2000 CO_2 molecules. All components of the system could freely move within the preset volume of the simulation. The simulation was implemented at a temperature of 318 K, the constancy of which was maintained with the help of a Nose–Hoover thermostat [13]. Periodic boundary conditions were not used. The simulation was performed with a step of 1 fs, the time of system equilibration was about 3 ns, and the total time of system monitoring was 6 ns. In accordance with to the simulation conditions, the micellar aggregate was placed into the center of the sphere and surrounded with a layer of the supercritical fluid with an average particle density of 0.008 Å^{-3}, which corresponded to nearly 0.580 g/mL and was in good agreement with the data obtained in [25, 28].

Table 1. Parameters of energetic potentials U_1 and U_2

Center	m, a. m. u.	q, e	σ, Å	ε/k_B, K
O	16.0	−0.8476	3.166	78.17
H	1.0	0.4238	−	−
Na$^+$	23.0	1.0	2.275	58.01
$(SO_3)^-$	80.0	−1.0	6.0	251.6
G_1	72	−	4.7	342.0
G_2	72.0	−	4.7	409.06
SCCD	44.0	−	3.658	232.2

SIMULATION RESULTS

The equilibrium shape of the micelle was almost spherical. The deviations from the sphericity can be characterized by the eccentricity value calculated based on the principal moments of inertia for micelle components by the following equation:

$$e = \sqrt{1 - a/c},$$

where a and c are minor and major axes of an ellipsoid, respectively. The eccentricity value was 0.43, which was substantially lower than that of a micelle with the same composition in the medium of a hydrocarbon ($e = 0.56$) [33]. Moreover, the visual observation of the system showed slight fluctuations of the aggregate surface, which were accompanied by mixing of the two solvents in the surfaced layer. This was also evident from the noticeable overlap of the radial density profiles of water and carbon dioxide (Fig. 2).

The local structure of the micelle has was described by a set of radial profiles of the partial densities with respect to the center of mass of the micelle (Figs. 2, 3) and pair correlation functions (Figs. 4, 5). As can be seen from the comparison of the profiles of the partial densities of AOT force centers with those obtained in [33], the replacement of a nonpolar solvent by SCCD has resulted in widening of the polar core. Two resolved peaks are seen in the density profile of the head groups of surfactant ions (curve *1*). Seemingly, this pattern of the profile results from the mutual dissolution of water and carbon dioxide in the surface layer, while the second peak is related to ions surrounded by CO_2 molecules.

Na$^+$ counterions dissolved in the aqueous cavity are displaced into the surface layer, and their profile is actually overlapped with the profile of the local density of surfactant head groups (Fig. 3). All counterions are involved in the formation of the micelle surface, as well as the surface-active ions.
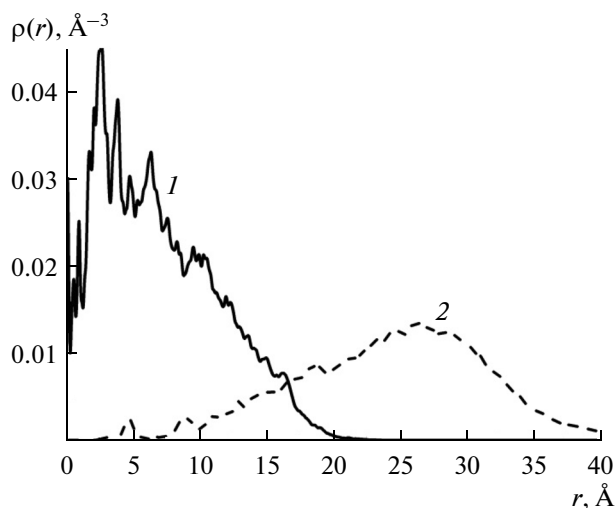
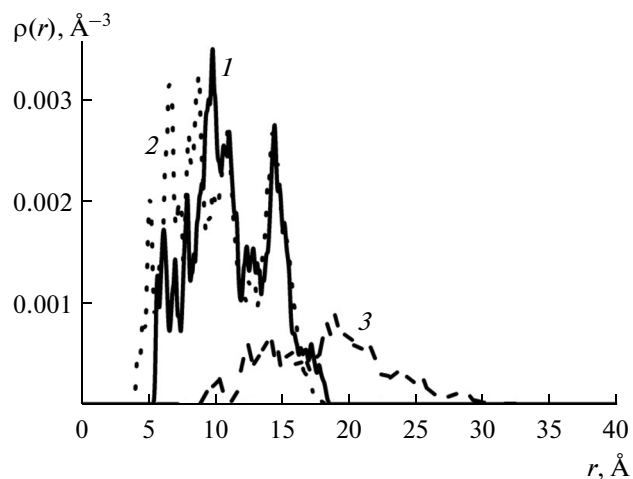**Fig. 2.** Radial profiles of partial densities for (*1*) water and (*2*) SCCD in a micelle.

Fig. 3. Radial profiles of partial densities of (*1*) head groups of AOT^- anions, (*2*) Na^+ counterions, and (*3*) hydrophobic tails of AOT.
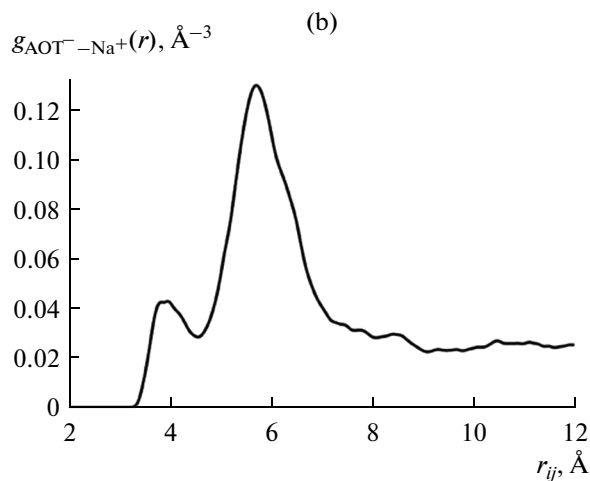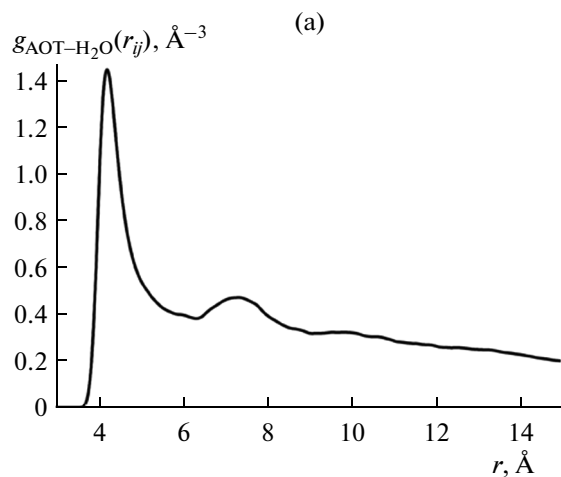

Fig. 4. Pair correlation functions for (a) $AOT-H_2O$ and (b) AOT^--Na^+.

An aqueous cavity with an average density close to the average density of bulk water remains preserved in the center of the micelle. The profile of the partial densities of water and SCCD shows some penetration of water molecules onto the external side of the micelle (Fig. 2), where the mixing of the two solvents takes place, which has not previously been observed for a hydrocarbon [32, 33]. Distributions at which the charged head groups of the surfactant and counterions were located only in the aqueous cavity of the aggregate were obtained in [32, 33]. The replacement of the nonpolar solvent by carbon dioxide, the molecules of which have their own quadrupole moment, facilitates the penetration of surfactant ions into the solvent. Therewith, the density profile of the solvent itself suggests that there is a uniform distribution between the micelle and the external wall, while the average density

of the fluid (0.580 g/mL) is, within the determination error, close to the full-atom simulation data [25, 28]. Moreover, it may be concluded that, in the presence of SCCD, water penetrates into the external part of the surface layer of the micelle to form a denser hydration shell of surfactant ions. All counterions are concentrated in the surface layer, which also increases the AOT^--Na^+ coordination number.

The general pattern of the pair correlation functions (Figs. 4, 5) is similar to that obtained for a micelle in the medium of a nonpolar hydrocarbon [33]. The positions of the peaks are almost the same; however, their heights and the values of the coordination numbers (Table 2) are larger than those found for the micelle in the nonpolar solvent [33]. The $AOT^--O_{H_2O}$ pair correlation function (Fig. 4a) shows that the first hydration shell of anions is located at a distance of

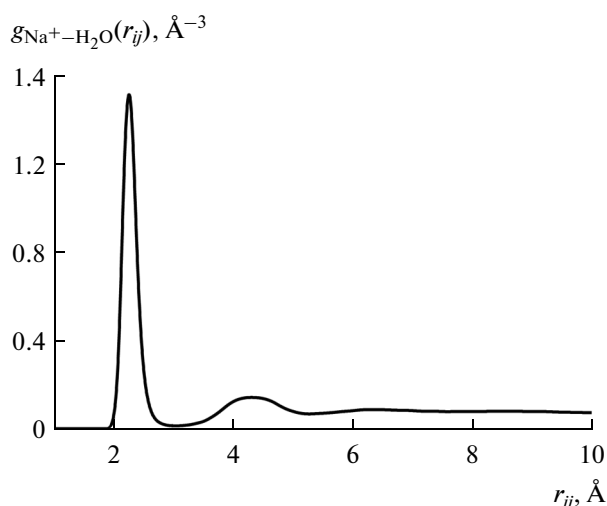$g_{\text{Na}^+-\text{H}_2\text{O}}(r_{ij})$, Å^{-3}

Fig. 5. Pair correlation function for $\text{Na}^+-\text{H}_2\text{O}$.

approximately 4.5 Å from the center. According to the data in Table 2, the hydration number in it is 5.5. At a distance of 7.5 Å, a subsequent small peak can be seen, which corresponds to the second hydration shell. The first peak of the correlation function for the AOT^--Na^+ pair in Fig. 4b corresponds to contact ion pairs, while the second one reflects the solvent-separated pairs, i.e., those separated by molecules of water or CO_2. The majority of counterions with their own hydration shells form a coordination sphere at a distance of 6 Å from the center of the negatively charged head group (Fig. 4b). The $\text{Na}^+-\text{H}_2\text{O}$ pair function (Fig. 5) shows that these hydration shells are actually isolated and located at a distance of nearly 2.5 Å from the center of a counterion.

Table 3 presents the data calculated for the partial potential energy per force center. In the calculation, the interaction energy of dissimilar centers was equally divided between them. These data show that the use of SCCD as a solvent leads to a reduction in the potential energy of the components, which may also be explained by the allowance for the ion–quadrupole and dipole–quadrupole components of the energy and a decrease in the hydrophobic effect. This primarily affects a reduction in the energy of the interaction between CO_2 and water. This value is responsible for

the highest percentage of the decrease in the energy. Therewith, within the determination error, the value for SCCD is in good agreement with the value presented in [15] as the configurational energy for the EPM2 three-point model (≈ 20 kJ/mol).

CONCLUSIONS

An MD simulation has been performed for an AOT reverse micelle in the medium of SCCD. The complexity of the system justifies the simplified description of CO_2 molecules. Allowance for the quadrupole component of the interaction energy decreases the hydrophobic effect and facilitates the formation an aqueous cavity in the micelle center, with the density inside the cavity being close to that of bulk water. Therewith, all surfactant ions are located near the surface to form an ionic layer. Due to the mutual dissolution of water and SCCD, the thickness of the surface layer increases and the eccentricity of the aggregate decreases to compare with a micelle formed in a hydrocarbon [32, 33]. The micelle retains its layered molecular structure and energetic stability.

The presence of the supercritical fluid molecules possessing a quadrupole moment and sizes close to the sizes of water molecules promotes their mutual penetration into the region of water/SCCD interface. This result is not a drawback of the simplified representation of the model, because an analogous effect was observed in [25, 28], when using the full-atom model for the supercritical solvent.

The penetration of water into the region of the supercritical liquid enhances its contact with AOT ions, thereby increasing the coordination numbers and the heights of the peaks in the pair distribution curves. At the same time, the calculation of the potential interaction energy in the system has shown a trend

Table 2. Coordination numbers N_{ij} of micelle components

Pair	Hd$^-$−Na$^+$	Hd$^-$−H$_2$O	Na$^+$−H$_2$O	H$_2$O−H$_2$O
N_{ij}	5(0.4)	1.4	7.1(9)	6.4

Table 3. Potential energy of components (kJ/mol, with an accuracy of ± 3 kJ/mol) in different systems

System \ Component	H_2O	Na^+	Hd^-	Nonpolar solvent molecule
Water−AOT−hexane [32]	−45	−342	−358	−22
Water−AOT−SCCD	−67	−370	−421	−18

toward a reduction in the internal energy of the system in the medium of supercritical carbon dioxide.

REFERENCES

1. *Handbook of Microemulsion Science and Technology*, Kumar, P. and Mittal, K.L., Eds., New York: Marcel Dekker, 1999.

2. Gale, R.W., Fulton, J.L., and Smith, R.D., *J. Am. Chem. Soc.*, 1987, vol. 109, p. 920.

3. Fulton, J.L. and Smith, R.D., *J. Phys. Chem.*, 1988, vol. 92, p. 2903.

4. Hu, Z. and Gulari, E., *J. Chem. Technol. Biotechnol.*, 1996, vol. 65, p. 45.

5. Rabie, H.R. and Vera, J.H., *Sep. Sci. Technol.*, 1998, vol. 33, p. 1181.

6. Jimenez-Carmona, M.M. and De Castro, M.D.L., *Anal. Chim. Acta*, 1998, vol. 358, p. 1.

7. Soni, K. and Madamwar, D., *Proc. Biochem.,* 2000, vol. 36, p. 311.

8. Pérez, E., Sanchez-Vicente, Y., Cabanas, A., Pando, C., and Renuncio, J.A.R., *J. Supercrit. Fluids*, 2005, vol. 36, p. 23.

9. Ji, J., Ding, Y., Yang, Ch., Huang, H., and Ding, Y., *Adv. Mater. Res.,* 2011, vols. 233−235, p. 585.

10. Ibrahim, T.H., *Sep. Sci. Technol.*, 2011, vol. 46, p. 2157.

11. Zhou, B., Wan, J., Wang, J., and Cao, X., *Proc. Biochem.,* 2012, vol. 47, p. 229.

12. Chuo, S.C., Mohd-Setapar, S.H., Mohamad-Aziz, S.N., and Starov, V.M., *Colloids Surf. A*, 2014, vol. 460, p. 137.

13. Allen, M.P. and Tildesley, D.J., *Computer Simulation of Liquids*, Oxford: Clarendon, 1991.

14. Lentini, E. and Vicentini-Missoni, M., *J. Chem. Phys.*, 1973, vol. 58, p. 91.

15. Harris, J.G. and Yung, K.H., *J. Phys. Chem.,* 1995, vol. 9, p. 12021.

16. Demurov, A., Radhakrishnan, R., and Trout, B.L., *J. Chem. Phys.*, 2002, vol. 116, p. 702.

17. Skarmoutsos, I., Dellis, D., and Samios, J., *J. Chem. Phys.*, 2007, vol. 126, p. 224503.

18. Vlcek, L., Chialvo, A.A., and Cole, D.R., *J. Phys. Chem. B*, 2011, vol. 115, p. 8775.

19. Moller, D. and Fischer, J., *Fluid Phase Equilib.*, 1994, vol. 100, p. 35.

20. Albo, S. and Muller, E.A., *J. Phys. Chem. B*, 2003, vol. 107, p. 1672.

21. Mognetti, B.M., Yelash, L., Virnau, P., Paul, W., Binder, K., Muller, M., and Macdowell, L.G., *J. Chem. Phys.*, 2008, vol. 128, p. 104501.

22. Mognetti, B.M., Virnau, P., Yelash, L., Paul, W., Binder, K., Muller, M., and Macdowell, L.G., *J. Chem. Phys.*, 2009, vol. 130, p. 044101.

23. Virnau, P., Muller, M., Macdowell, L.G., and Binder, K., *J. Chem. Phys.,* 2004, vol. 121, p. 2169.

24. Sanghi, T. and Aluru, N.R., *J. Chem. Phys.,* 2012, vol. 136, p. 024102.

25. Salaniwal, S., Cui, S.T., Cummings, P.T., and Cochran, H.D., *Langmuir,* 1999, vol. 15, p. 5188.

26. Chandran, A., Prakash, K., and Senapati, S., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 12511.

27. Lu, L. and Berkowitz, M.L., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 10254.

28. Senapati, S. and Berkowitz, M.L., *J. Phys. Chem. B*, 2003, vol. 107, p. 12906.

29. Mudzhikova, G.V. and Brodskaya, E.N., *Colloid J.,* 2012, vol. 74, p. 269.

30. Berendsen, H.J.C., Grigera, J.R., and Straatsma, T.P., *J. Phys. Chem.*, 1987, vol. 91, p. 6269.

31. Kusalik, P.G. and Svishchev, I.M., *Science* (Washington, D. C.), 1994, vol. 265, p. 1219.

32. Brodskaya, E.N. and Mudzhikova, G.V., *Mol. Phys.,* 2006, vol. 104, p. 3635.

33. Mudzhikova, G.V. and Brodskaya, E.N., *Colloid J.,* 2009, vol. 71, p. 803.

Translated by A. Kirilin