Surface tension of O$_2$-Ar, N$_2$-Ar and O$_2$-N$_2$-Ar mixtures

Tensión superficial de las mezclas O$_2$-Ar, N$_2$-Ar y O$_2$-N$_2$-Ar

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Abstract

The surface tension of some binary and ternary mixtures was calculated by means of molecular dynamics simulations in a canonical set. The analyzed mixtures were oxygen-argon, nitrogen-argon and oxygen-nitrogen-argon. The force field for argon was recalculated in order to reproduce the experimental surface tension. The corresponding force fields for O$_2$ and N$_2$ were taken from a previous work [Mol. Simul. 45 (2019) 958-966], where it was shown that such force fields reproduce the experimental surface tension curves, as pure fluids. The nitrogen-argon surface tension was calculated for several mole fractions of argon. The obtained curve was compared with those experimental data and a good agreement was found. The standard Lorentz-Berthelot combining rules were employed. For the oxygen-argon mixture it was necessary to modify the cross term of the combining rules in order to reproduce theoretical and experimental data. The surface tension of the ternary mixture was also estimated varying the mole fraction of argon at a certain concentration of oxygen and nitrogen, previously adjusted. Several temperatures were used in order to show a tendency mostly at relatively low temperatures. After comparing the available experimental data, which are scarce, a good agreement was observed.

Surface tension, Molecular dynamics, Force field

Resumen

La tensión superficial de algunas mezclas binarias y ternarias se calculó mediante simulaciones de dinámica molecular en un conjunto canónico. Las mezclas analizadas fueron oxígeno-argón, nitrógeno-argón y oxígeno-nitrógeno-argón. El campo de fuerza para el argón se re-estimó aquí para reproducir la tensión superficial experimental como fluido puro. Los campos de fuerza correspondientes para O$_2$ y N$_2$ se tomaron de un trabajo anterior [Mol. Simul. 45 (2019) 958-966], donde se demostró que tales campos de fuerza reproducen las curvas experimentales de tensión superficial, como fluidos puros. La tensión superficial de nitrógeno-argón se calculó para varias fracciones molares de argón. La curva obtenida se comparó con los datos experimentales y se encontró un buen acuerdo. Las reglas de combinación estándar de Lorentz-Berthelot fueron utilizadas. Para la mezcla de oxígeno-argón fue necesario modificar el término cruzado de las reglas de combinación para reproducir resultados teóricos y experimentales. La tensión superficial de la mezcla ternaria también se estimó variando la fracción molar de argón a una cierta concentración de oxígeno y nitrógeno ajustada previamente. Se exploraron varias temperaturas para mostrar una tendencia principalmente a temperaturas relativamente bajas. Luego de comparar con los datos experimentales disponibles, que son escasos, se observó un buen acuerdo.

Tensión superficial, Dinámica molecular, Campo de fuerza

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Introduction

Molecules such as nitrogen, oxygen and argon are important air compounds. The surface tension of these relatively simple fluids has been subject to theoretical, experimental and computer simulation studies. From the point of view of molecular simulation, we can see in the literature that there is more than one model for each, but not all of them reproduce the experimental surface tension. Garcia et al. (2019) have proposed force fields for oxygen and nitrogen that reproduce the experimental data as pure fluids, where the interaction function is composed of the potentials of Lennard-Jones (L-J) and Colulomb.

In the case of argon, Goujon et al. (2014) proposed a correction to the L-J function to reproduce the experimental surface tension as a function of temperature, that is, they added an extra term to the interaction potential. We believe it would be convenient to use the L-J and Coulomb potentials in all molecular models to calculate the surface tension of the mixture of these same fluids.

The surface tension of the binary mixtures oxygen-argon and nitrogen-argon has been estimated with a theoretical procedure by Kim et al. (1969). They compared their results with the experimental data generated by Blagoi (1960), and by Blagoi and Rudenkov (1959), as a result, they found a good degree of coincidence. This interfacial property was estimated at T = 83.85K for all mixtures. Eckert and Prausnitz (1964) have estimated by theoretical calculations the surface tension of the same binary mixtures, and as a result they found a good agreement. However, there is no data of the same interfacial property at different temperatures. We believe that with molecule models that reproduce the experimental surface tension as pure fluids, it is possible to obtain good results when calculating the same interfacial property of the mixtures at T = 83.85K and for a wide range of temperatures.

On the other hand, Pandey et al. (2004) have estimated the surface tension of the ternary mixture Ar-O_2-N_2 at different temperatures, from 90K to 110K, and at different pressures. They developed a theoretical approach using the Brock-Bird relation, where critical properties, such as pressure, volume and temperature of pure fluids, were considered in the calculations.

These authors compared their results with experimental data and observed a good agreement. Experimental data were obtained using the capillary ascent method estimated by Kai et al. (1994), where they considered temperatures from 90.1K to 114.8K, which are equivalent to those used in the aforementioned contribution. However, they do not do a systematic study where the concentration of each species in the mixture is fixed and the temperature is varied. We believe it is convenient to have a database that can serve as a reference.

In this paper, the surface tension of the binary mixtures O_2-Ar and N_2-Ar, as well as the ternary mixture O_2-N_2-Ar, was calculated by molecular dynamics simulations using appropriate force fields that reproduce the surface tension of each species as pure fluids. We determined the numerical values of the L-J parameters for argon that reproduce the experimental surface tension as a pure fluid. We assume that it is necessary to have good force fields for pure components. The force field for oxygen and nitrogen was taken from the work of García et al. (2019).

As far as we know, there is no database of such interfacial property covering a wide range of temperatures, in fact, a similar comment was made by Pandey et al. (2004). An immediate extension of the present work is the analysis of the influence of the air in the measurement of the apparent surface tension of aqueous solution of hydrophilic solutes. Docoslis et al. (2000) analyzed the case of sugars, where they showed that the experimentally measured surface tension did not correspond to the cohesion-free energy of the aqueous solution. The rest of this paper is distributed as follows: Section 2 is dedicated to explaining the molecule models and the relevant equations used. Section 3 contains the details of the simulation. Section 4 shows the relevant results and Section 5 presents the final conclusions.

Relevant equations

The force fields used for nitrogen and oxygen were taken from the work of García et al. (2019), which consists of models of three sites, these interaction sites are along a given axis. For binary molecules, two atoms are attached at a certain separation distance *L*, and a virtual site is included between the two atoms.

The experimental quadrupole moment was used as an input data to adjust the partial charges, the relation between both properties is quite simple due to linear symmetry, $\Theta=Lq/2$. A partial charge $+2q$ is located in the virtual site in the center of the molecule and two partial charges, $-q$, are located at the ends of the molecule. The L-J and Coulomb potential make up the law of interaction between molecules.

$$u=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]+\frac{1}{4\pi\varepsilon_0}\frac{q_iq_j}{r} \qquad (1)$$

ε and σ are the depth of the attraction well and the diameter of the atom, respectively. ε_0 is the vacuum permittivity, r is the separation distance between two interaction sites, and q_i is the partial charge related to the i-site. The L-J parameters were adjusted to recover the experimental surface tension as a function of the temperature of each fluid. Particularly, the diameter of each atom σ was used to modify the slope of the surface tension curve and the intensity of the attraction well ε was used to raise or lower the entire curve. This last procedure was followed to reproduce the experimental surface tension of argon.

The surface tension is calculated using the difference between the components of normal and tangential pressure with respect to the interfacial area found in the x − y plane as follows:

$$\gamma=\frac{L_z}{2}\left[\langle P_{zz}\rangle-\frac{1}{2}\langle P_{xx}+P_{yy}\rangle\right] \qquad (2)$$

Lz is the longest side of the simulation cell, and the angular brackets denote a set average $\langle\cdots\rangle$ in the thermodynamic property. Equation (2) is divided by 2 because two interfaces are considered, as detailed by Allen and Tildesley (1987). P_{ii} are the pressure components estimated using virial expression

$$VP_{\alpha\beta}=\sum m_i\,(v_i)_\alpha(v_i)_\beta+\sum\sum(r_{ij})_\alpha\left(f_{ij}\right)_\beta \qquad (3)$$

where v_i and m_i are the velocity of atom i and the mass of the same atom, respectively. **r** = **r**$_i$ - **r**$_j$ is the distance vector between two atoms. **f**$_{ij}$ is the interaction force between atoms and V is the volume occupied by the fluid.

Atom	σ(A)	ε(kJ/mol)	L(A)	q_i(e)
O	3.11	0.4015	1.23	-0.1101
N	3.375	0.29508	1.098	-0.482
Ar	3.484	0.9556		0

Table 1 Parameters of the potentials of L-J and Coulomb. The charges are presented in units of the electron charge. The oxygen and nitrogen data were taken from the work of García et al. (2019).

Methodology

Molecular dynamics simulations were performed in a canonical set as explained by Allen and Tildesley (1989). N = 8000 molecules were placed in a cubic crystalline arrangement centered on the faces, which forms a liquid plate that is surrounded by vacuum, forming a parallelepiped cell. The free GROMACS-5.2.1 software was used for all our simulations. Typical dimensions of the simulation box used here were Lx = Ly = 5.0nm and Lz = 30nm for argon, with Lz = 40nm for the binary mixtures and Lz = 50nm for the ternary mixture.

The algorithm called *frog jump* was used to predict the trajectories of all molecules. Periodic boundary conditions and minimum image criteria were considered in all three directions. The passage time was 1fs in all our simulations. The Particle mesh Ewald method was used to estimate Coulomb interactions using a 0.2nm grid for reciprocal vectors with a spline of 4, as explained by Essmann et al. (1995). A cut-off distance of Rc = 2.5nm was used in real space for Coulomb and the dispersive term of the L-J potential. The LINCS method (LINear Constraint Solver) proposed by Hess et al. (1997) was used to keep diatomic molecule bonds rigid.

To reach equilibrium, 1×10^5 steps were performed and 1.9×10^6 additional steps were performed to estimate the averages. A similar procedure was followed to simulate the binary mixtures, but N = 7000 molecules were used instead; the concentration of both species varied, keeping the total number of molecules constant. For all cases, the Lorentz-Berthelot combination rules commented by Allen and Tildesley (1987) were used

$$\varepsilon_{ij}=\eta\sqrt{\varepsilon_{ii}}\sqrt{\varepsilon_{jj}} \qquad (4)$$

$$\sigma_{ij}=\eta\frac{\sigma_{ii}+\sigma_{jj}}{2} \qquad (5)$$

ε_{ij} and σ_{ij} are the cross terms of the L-J potential and model the interaction of different species. η is an external parameter that allows to modify the cross terms and in the case that said parameter is equal to the unit, the standard combination rules will be used.

Results

The surface tension of argon as a function of temperature was calculated using the parameters $\varepsilon=0.9556kJ/mol$ and $\sigma=0.3484nm$ to reproduce the experimental data, see Figure 1. The data of Goujon et al. (2014) were included for comparison, and it can be seen that the agreement is excellent. The surface tension of both pure fluids, oxygen and nitrogen, was also included, these data were taken from the work of García et al. (2019).
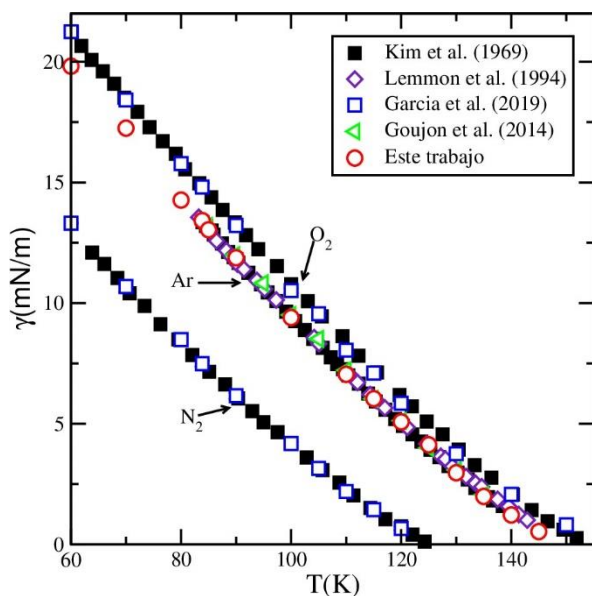

Figure 1 Surface tension as a function of temperature. The symbols are explained in the box in the figure

The parameters of the interaction potential that characterize the nitrogen and argon molecules are contained in Table 1, these data will be used in the molecular simulation of the binary nitrogen-argon mixture. In Figure 2, the data obtained of the surface tension of the mixture already described as a function of the mole fraction of argon in a temperature range of 70K to 100K is shown. In the literature, we found 83.85K temperature experimental data compiled by Kim et al. (1969). These same data coincide with those that were generated by theoretical calculations reported by Eckert and Prausnitz (1964), as well as the theoretical calculations reported by Kim et al. (1969).

Our results are identified with the empty circles at T = 83.85K and, as observed, the agreement with the experimental and theoretical data is excellent. We also included predictions of surface tension as a function of the concentration of argon at temperatures 70K, 90K and 100K. Unfortunately, we did not find experimental data with which a comparison could be made.
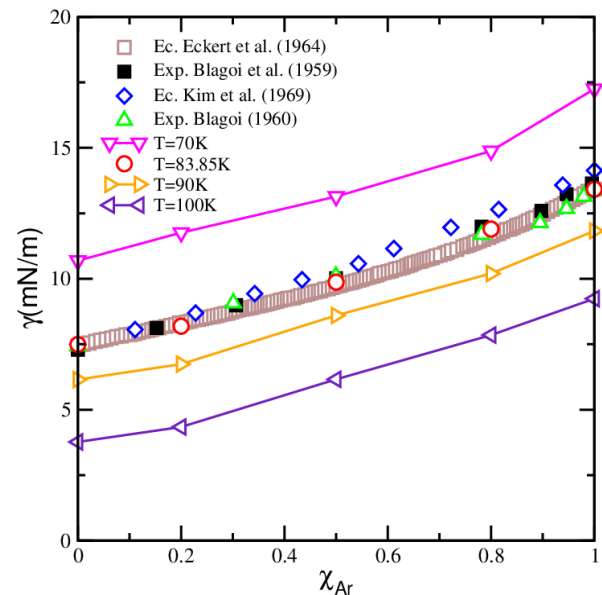

Figure 2 Surface tension of the binary nitrogen-argon mixture as a function of the concentration of argon, at different temperatures. The experimental and theoretical data were obtained at T = 83.85K. The symbols that identify the data are explained in the same figure. The empty circles at T = 83.85K are results of this work, as well as the data shown for temperatures 70K, 90K and 100K

Figure 3 shows the surface tension of the binary oxygen-argon mixture in a temperature range [70--100] K. Experimental data are included at T = 83.85K reported by Saji and Okuda (1963), and by Blagoi and Rudenkov (1959). Theoretical data are also included in the same figure as those reported by Eckert and Prausnitz (1964). The data generated in this work are shown with empty circles at T = 83.85K, and when compared with the aforementioned data, we found good agreement. It is important to note that the cross terms of the combination rules were modified with the intention of reproducing the experimental data, so the values used were $\eta_\varepsilon= 0.979$ and $\eta_\sigma= 1.0193$. This means that the van der Waals type attraction between species is weakened and the size of the interaction between different species grows slightly. This indicates that the oxygen-argon mixture deserves separate attention to analyze its L-J cross-interactions.

The corresponding data generated for temperatures 70K, 90K and 100K have been included in Figure 3. So far, we have not found experimental data with which to compare.
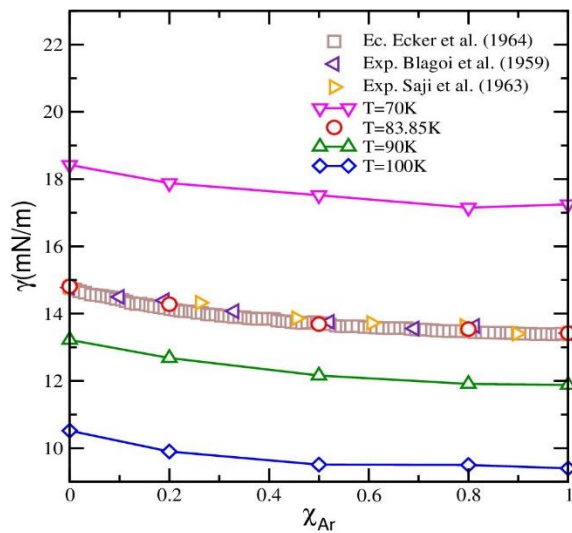

Figure 3 Surface tension of oxygen-argon at different temperatures. The symbols are identified in the figure. Empty circles are data generated in this work at T = 83.85K. The data corresponding to 70K, 90K and 100K temperatures were also generated in this work.

Figure 4 shows the surface tension of the oxygen-nitrogen-argon ternary mixture at different temperatures for various concentrations of each species. As far as we know, there is no systematic study of the dependence of the surface tension of the ternary mixture at the same concentration and at different temperatures. When comparing with data available in the literature, we found data of the surface tension of the experimentally measured ternary mixture, 10.87mN / m, where they used mole fractions of $\chi_{O2}= 70.4\%$, $\chi_{N2}= 11.6\%$ and $\chi_{Ar} = 18\%$, that we will call mixture 1, at T = 96.7K and at a vapor pressure of 2.3atm.

The data obtained in this work for the same interfacial property at the same conditions was 9.80mN / m, which is 9.8% below the experimental. It is important to mention that the vapor pressure we obtained was 2.8atm, which is 18 % above the experimental measure. This deviation may be due to the force fields used and/or the combination rules. In this calculation we maintained the modification in the cross-interactions of oxygen-argon, that is, we included the external parameters in the Lorentz-Berthelot combination rules to calculate the cross terms $\eta_\varepsilon= 0.979$ and $\eta_\sigma= 1.0193$, because with these modifications we could reproduce the experimental curve of the surface tension of the same binary mixture at T = 83.85K.

In the nitrogen-argon and nitrogen-oxygen interactions we used the standard Lorentz-Berthelot combination rules.

Additionally, we include a surface tension curve for another species concentration, different from the previous case, $\chi_{O2}= 21\%$, $\chi_{N2}= 78\%$ and $\chi_{Ar}= 1\%$, which we will call mixture 2. It is mentioned in the literature that this concentration of species corresponds to that found in the troposphere, which is the "breathable" layer, Gálvez et al. (1996). Unfortunately, we found no experimental data in the literature with which we could make a comparison. Particularly, we obtained a surface tension of 5.43mN / m at temperature of 96.7K. On the other hand, if we compare the surface tension obtained at T = 96.7K for mixtures 1 and 2, we find that the data for the second mixture is 50% below the data corresponding to the first mixture. This is because the highest concentration in the first mixture is nitrogen, which has a lower surface tension than oxygen, which is the majority species in the second mixture.
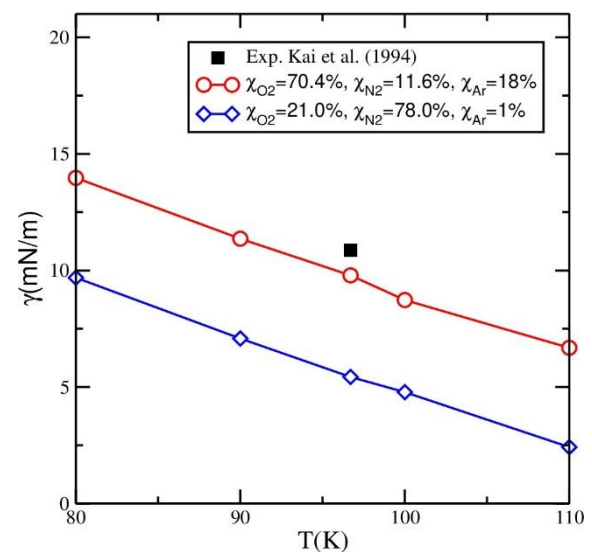

Figure 4 Surface tension of the oxygen-nitrogen-argon ternary mixture at different temperatures. Concentration of the different species $\chi_{O2} = 70.4\%$, $\chi_{N2}= 11.6\%$ and $\chi_{Ar} = 18\%$, the full table is an experimental data and the empty circles are data generated in this work. Empty diamonds are data generated in this work for the concentration $\chi_{O2}=21\%$, $\chi_{N2}=78\%$ y $\chi_{Ar}=1\%$.

Acknowledgments

Conclusions

The L-J potential parameters determined allowed us to reproduce the experimental argon surface tension curve.

The surface tension curve is shown as a function of the temperature of the ternary mixture that can be considered as an initial or controlled model of air.

The force fields that reproduce the surface tension of pure fluids provide the opportunity to obtain good results in binary and ternary mixtures. In addition, surface tension curves of binary and ternary mixtures at temperatures where we have not found experimental data were calculated and presented.

Some mixtures are difficult to model because cross interactions introduce inaccuracies. This is the case of the oxygen-argon mixture, where the cross term of both combination rules had to be modified. Even with all the inaccuracies found, computer simulation is a useful tool for generating reference data where there is no existing data.

We believe that a simple air model will allow a good analysis of its influence on the apparent surface tension of aqueous solutions of hydrophilic components.

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