

Transport Properties of Nitrogen and *n*-Alkane Binary Mixtures

José Luis Rivera¹

and

José Alejandro^{1,2*}

June 12, 2000

- (1) Departamento de Química,
Universidad Autónoma Metropolitana-Iztapalapa,
Apdo. Postal 55-534; 09340 México D.F. México.
(2) Simulación Molecular, Instituto Mexicano del Petróleo,
Eje Central Lázaro Cárdenas 152, Apdo. Postal
14-805, 07730 México D.F., México

Pages: 14

Tables: 2

Figures: 4

*Author for correspondence

Abstract

We have performed molecular dynamic simulations of nitrogen/*n*-alkane binary mixtures in the liquid phase to obtain the diffusion coefficient and the shear viscosity. The states are chosen to be in the liquid-vapor equilibrium, in this case, the liquid density at 310.93 K is around 0.65 and 0.74 g/cm³ for mixtures containing *n*-hexane and *n*-decane, respectively. For these mixtures the composition of nitrogen varies until 0.25. We obtained the transport properties using Green-Kubo relations. As the mol fraction of nitrogen increases, the diffusion coefficient of nitrogen in *n*-hexane decreases and has a maximum in *n*-decane. The diffusion is greater in mixtures with *n*-hexane than in mixtures with *n*-decane. The shear viscosity of nitrogen/*n*-hexane mixtures is smaller than those of nitrogen/*n*-decane mixtures and in general decreases with nitrogen concentration.

Keywords: molecular simulation; viscosity; diffusion coefficient; nitrogen; hydrocarbon; mixture

1 Introduction

When pressure decreases in an oil reservoir a common practice is to inject gas to maintain high pressure to favor the extraction of oil [1]. Nitrogen can be extracted from the atmosphere and is not a reactive molecule. The knowledge of how nitrogen will modify the gas and oil properties will allow to develop strategies in oil extraction, separation and refining processes. The experiments at high pressure and temperature are expensive and time consuming. Thermodynamic properties in the liquid-vapor equilibrium have been reported for some binary mixtures involving *n*-alkanes from methane to *n*-decane [2, 3, 4, 5, 6, 7, 8, 9], but transport properties are scarce for these systems.

We have started a systematic investigation on nitrogen/*n*-alkane mixtures. In a previous work, we optimized an intermolecular potential model for nitrogen [10] which gives good agreement with the experimental orthobaric densities, surface tension and viscosity in a wide range of temperatures. We used this model to simulate nitrogen/*n*-alkane binary mixtures in the liquid-vapor equilibrium at high pressure [11]. The intermolecular interaction for hydro-

carbons was given by the NERD [12] or by the TraPPE [13] models. Both potentials gave essentially the same results for the vapor pressure-composition and vapor pressure-density curves and good agreement was found with available experimental results.

In this work we performed molecular dynamic simulations of binary mixtures of nitrogen containing *n*-hexane or *n*-decane to learn about the behaviour on the diffusion and shear viscosity coefficients on the liquid phase of the liquid-vapor equilibrium. No comparison with experimental data is done because there is not available results.

This paper is organized as follows. Section 2 gives the potential model, the simulation details are given in section 3. The results and discussion are given in section 4. Finally conclusions and references are provided.

2 Potential model and properties

The nitrogen molecule has two sites and the *n*-alkane molecules are simulated using the united atom model for methyl and methylene groups. During the molecular dynamic (MD) simulations the bond distances are kept constant at their equilibrium value by using a SHAKE procedure [14]. This allow us to eliminate short time vibrations and to increase the time step used to integrate the classical equations of motion.

The bond distance in nitrogen molecules is 1.0897 Å while in *n*-alkane molecules it is 1.54 Å for bonds between CH₃-CH₃, CH₃-CH₂ and CH₂-CH₂.

The bond angle potential for *n*-alkanes is given by a quadratic function

$$U(\theta) = \frac{k_{\theta}}{2}(\theta - \theta_0)^2 \quad (1)$$

where θ is the bond angle and subscript 0 denotes its equilibrium value, k_{θ} is the spring constant.

For *n*-alkane molecules θ_0 is 114° and $k_{\theta} = 62500 \text{ K rad}^{-2}$ and the torsional angle energy around every bond C-C is

$$U(\phi) = \sum_{i=0}^5 C_i \cos(\phi)^i \quad (2)$$

where ϕ is the torsional angle between four atoms and C_i are constants taken from Rickaert and Bellemans [15] ($C_0 = 1116 \text{ K}$, $C_1=1462 \text{ K}$, $C_2=-1578 \text{ K}$, $C_3=-368 \text{ K}$, $C_4=3156 \text{ K}$, $C_5=-3788 \text{ K}$). These values reproduce the

experimental n -alkane conformations in the gas phase. The same constant values were used for the different dihedral angles in a chain.

The intermolecular interactions are given for a truncated and shifted Lennard Jones potential. The interaction between atom a in molecule i and atom b in molecule j is

$$U(r_{iajb}) = 4\epsilon \left[\left(\frac{\sigma}{r_{iajb}} \right)^{12} - \left(\frac{\sigma}{r_{iajb}} \right)^6 \right] - U(R_c) \quad (3)$$

where σ is the diameter of a site, ϵ is the well depth, R_c is the cut-off distance and r_{iajb} is the distance between site a in molecule i and site b in molecule j . The potential is zero for distances greater than R_c .

The σ and ϵ parameters for sites in nitrogen are taken from Ref. [10] while for methyl and methylene groups are taken from Ref. [12]. Atoms in the same molecule beyond three bond distances interact by a potential given in equation (3). The Lorentz-Berthelot mixing rule was used for the cross interaction between unlike atoms. The Lennard Jones parameters used to simulate nitrogen and n -alkanes in the binary mixtures are given in Table 1. The diffusion coefficient and shear viscosity were obtained from Green-Kubo equations [16] for the velocity autocorrelation function and the off-diagonal components of the pressure tensor autocorrelation function, respectively.

The diffusion coefficient is

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{V}(t) \cdot \mathbf{V}(0) \rangle dt \quad (4)$$

where \mathbf{V} is the velocity of the center of mass of a molecule and t is the time. The shear viscosity is

$$\eta = \frac{1}{VkT} \int_0^\infty \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt \quad (5)$$

where V is the volume of the system, k is the Boltzmann's constant, T is the absolute temperature and $P_{\alpha\beta}$ is the component $\alpha\beta$ of the molecular pressure tensor given by

$$VP_{\alpha\beta} = \sum_i^N M_i (\mathbf{V}_i)_\alpha (\mathbf{V}_i)_\beta + \sum_i \sum_{j>i} \sum_a \sum_b (\mathbf{R}_{ij})_\alpha (\mathbf{F}_{iajb})_\beta \quad (6)$$

where N is the number of molecules, M_i is the molecular mass, $(\mathbf{V}_i)_\alpha$ is the velocity of the center of mass in the α direction, $(\mathbf{R}_{ij})_\alpha$ is the distance

between the centres of masses of molecules i and j in the α direction. The force between atom a in molecule i and atom b in molecule j is

$$\mathbf{F}_{iajb} = -\frac{\mathbf{r}_{iajb}}{r_{iajb}} \left[\frac{dU(r_{iajb})}{dr_{iajb}} \right] \quad (7)$$

3 Simulation details

All simulations were carried out using 256 molecules in the liquid phase with the Verlet algorithm using a time step of 2 fs. Binary mixtures between nitrogen and n -alkane molecules were prepared at different composition. Periodic boundary conditions in the three directions and a neighbour list was used. The liquid densities and compositions are taken from simulation results of the liquid-vapor equilibrium obtained before [11]. The temperature in all the simulations was kept constant at 310.93 K. This temperature and mixtures containing n -hexane and n -decane were chosen because there are experimental and simulation results of the orthobaric densities in the liquid-vapor equilibrium. The potential was truncated at 15.72 Å. The thermodynamic conditions are given in Table 2. After an equilibration period of 50 000 steps the average properties are obtained for additional 300 000 steps. The components of the pressure tensor and velocities of the center of mass were stored every 10 steps. The corresponding autocorrelation functions were obtained at the end of the simulation and the diffusion coefficient and shear viscosity were calculated using equations (4) and (5), respectively.

4 Transport properties results

This section contains the results for the diffusion and shear viscosity coefficients of nitrogen/ n -alkane binary mixtures.

4.1 Diffusion coefficient

Figure 1 shows a typical velocity autocorrelation function, VACF, of nitrogen mixed with n -hexane and n -decane with total liquid densities of 0.647 g/cm³ and 0.741 g/cm³, respectively at 310.93 K. The VACF decreases monotonically to zero for all mixtures with n -hexane while the VACF of mixtures with n -decane change sign because the high density, the molecules change

the velocity in successive time correlations. The diffusion coefficient of nitrogen are calculated by integration of the VACF and they are given in Table 2 and shown in Figure 2 for all the mixtures studied in this work. As the mol fraction of nitrogen increases the mixtures contain less molecules of n -alkane. One would expect that diffusion coefficient of nitrogen increases with the amount of nitrogen in the mixture, but it seems that there is a balance between liquid density and pressure. The diffusion coefficient of nitrogen in n -hexane decreases while in n -decane has a maximum.

4.2 Shear viscosity

A typical stress correlation function of nitrogen/ n -alkane mixtures is shown in Figure 3. The results correspond to the same systems shown in Figure 2. The functions oscillate around zero after few picoseconds. The nitrogen/ n -decane system has more oscillations and has negative values. The viscosity is obtained by integration of this correlation function. The results are given in Table 2 and they are also shown in Figure 4. The shear viscosity in general decreases with nitrogen composition, except in the nitrogen/ n -decane mixture where the diffusion coefficient was maximum. The nitrogen/ n -hexane mixtures has lower shear viscosities than the nitrogen/ n -decane mixture because it has lower liquid density.

5 Conclusions

We have obtained the diffusion coefficient and shear viscosity of nitrogen/ n -alkane binary mixtures at 310.93K. The systems are in the liquid phase of the liquid-vapor equilibrium. For the nitrogen compositions studied in this work, the liquid density is around 0.65 g/cm³ for all the nitrogen/ n -hexane mixtures and 0.74 g/cm³ for all the nitrogen/ n -decane mixtures. The diffusion coefficient of mixtures containing n -hexane is higher than mixtures with n -decane and the shear viscosity is lower, this is because the differences in the liquid density. As nitrogen composition increases the diffusion coefficient decreases in n -hexane mixture while in n -decane mixture increases. The shear viscosity in general decreases with nitrogen composition.

6 List of symbols

D diffusion coefficient
 F_{ij} force between atoms i and j
 k Boltzmann's constant
 k_θ spring constant
 N number of molecules
 M molecular mass
 $P_{\alpha\beta}$ components of the pressure tensor
 r distance between particles
 R_{ij} distance between molecules i and j
 t time
 T absolute temperature
 U Potential energy
 \mathbf{V} velocity of the center of mass
 V volume
 ϵ potential well depth
 η viscosity
 θ bond angle
 ϕ torsional angle
 σ diameter of a site

Acknowledgments

We thank CONACyT for financial support. JA thanks Instituto Mexicano del Petr3leo for facilities given during his sabbatical period.

References

- [1] L.K. Thomas, T.N. Dixon, R.G. Pierson, H. Hermansen. Ekofisk Nitrogen Injection. SPE Formation Evaluation, June, (1991), page. 1951
- [2] R. Stryjek, P.S. Chappellear, R. Kobayashi. Low-temperature vapor-liquid equilibria of nitrogen-methane system. J. Chem. Eng. Data. 19 (1974) 334
- [3] M.K. Gupta, G.C. Gardner, M.J. Hegarty, A.J. Kidnay. Liquid-vapor equilibria for the $N_2 + CH_4 + C_2H_6$ system from 260 to 290 K. J. Chem. Eng. Data. 25 (1980) 313

- [4] L. Grauso, A. Fredenslund, J. Mollerup. Vapor-liquid equilibrium data for the systems $C_2H_6 + N_2$, $C_2H_4 + N_2$, $C_3H_8 + N_2$, and $C_3H_6 + N_2$. Fluid Phase Equilib. 1 (1977) 13
- [5] M.K.F. Malewski, S.I. Sandler. High-pressure vapor-liquid equilibria of the binary mixtures nitrogen + n-butane and argon + n-butane. J. Chem. Eng. Data. 34 (1989) 424
- [6] H. Kaira, D.B. Robinson, G.J. Besserer. The equilibrium phase properties of the nitrogen/*n*-pentane system. J. Chem. Eng. Data. 22 (1977) 215
- [7] R.S. Poston, J.J. Mcketta. Vapor-liquid equilibrium in the *n*-hexane-nitrogen system. J. Chem. Eng. Data., 11 (1966) 364.
- [8] D. Legret, D. Richon, H. F.Renon. Vapor liquid equilibria up to 100 Mpa : A new apparatus. AIChE J. 27 (1987) 203.
- [9] A. Azarnoosh, J.J. Mcketta. Nitrogen/*n*-decane system in the two-phase region. J. Chem. Eng. Data. 8 (1963) 494.
- [10] J.L.Rivera, J. Alejandre, S.K. Nath, J.J.dePablo. Thermodynamic and transport properties of nitrogen-butane mixtures. Molec. Phys. 98 (2000) 43
- [11] J.L. Rivera, J. Alejandre. Simulation of nitrogen/*n*-alkane binary mixtures. submitted to Molec. Phys. 2000.
- [12] S.K. Nath, F.A. Escobedo. J.J. de Pablo. J. Chem. Phys. 108 (1998) 9905.
- [13] M.G. Martin, J.I. Siepmann. 1998, J. Phys. Chem. B., 102 (1998) 2569.
- [14] J.P. Ryckaert, G. Ciccoti, J.C. Berendsen. J. Comp. Phys., 23 (1977) 327
- [15] J.P. Ryckaert, A. Bellemans. Discuss. Faraday. Soc., 66 (1978) 1978.
- [16] M.P. Allen, D.J. Tildesley. Computer Simulations of Liquids. Oxford University Press, Oxford, 1987

Table 1: Intermolecular Lennard Jones parameters for nitrogen and *n*-alkane molecules

molecule	site	$\sigma(\text{\AA})$	$\epsilon/\text{k(K)}$	reference
nitrogen	N	3.310	36.0	[10]
<i>n</i> -alkane	CH ₂	3.93	45.8	[12]
	CH ₃	3.91	104.0	

Table 2: Transport properties of nitrogen/*n*-alkane binary mixtures in the liquid phase at 310.93 K. The units of vapor pressure are bars, g cm⁻³ for densities, cm² s⁻¹ for diffusion coefficients and g cm⁻¹ s⁻¹ for viscosities.

<i>n</i> -alkane	P_v	ρ_L	x_{N_2}	$D_{N_2}/10^{-5}$	$\eta/10^{-3}$
hexane	95.7	0.646	0.141	8.45	2.87
	142.9	0.648	0.184	8.37	2.61
	189.7	0.647	0.250	8.21	2.38
decane	68.4	0.735	0.055	7.13	3.87
	113.2	0.739	0.113	7.78	3.88
	156.4	0.738	0.184	7.98	4.29
	203.8	0.741	0.227	7.61	3.46

Figure Captions

Figure 1: Velocity autocorrelation function at 310.93 K: dashed line is for nitrogen in *n*-hexane at 0.647 g/cm³ and continuous line is for nitrogen in *n*-decane at 0.741 g/cm³.

Figure 2: Diffusion coefficient of nitrogen/*n*-alkane mixtures at 310.93 K. full circles and full squares for mixtures containing *n*-hexane and *n*-decane, respectively. The line is given to guide the eye.

Figure 3: Stress autocorrelation function of nitrogen/*n*-hexane and nitrogen/*n*-decane. Symbols and thermodynamic conditions are the same as in Figure 1.

Figure 4: Shear viscosity of nitrogen/*n*-alkane mixtures at 310.93 K. Symbols are the same as in Figure 2.

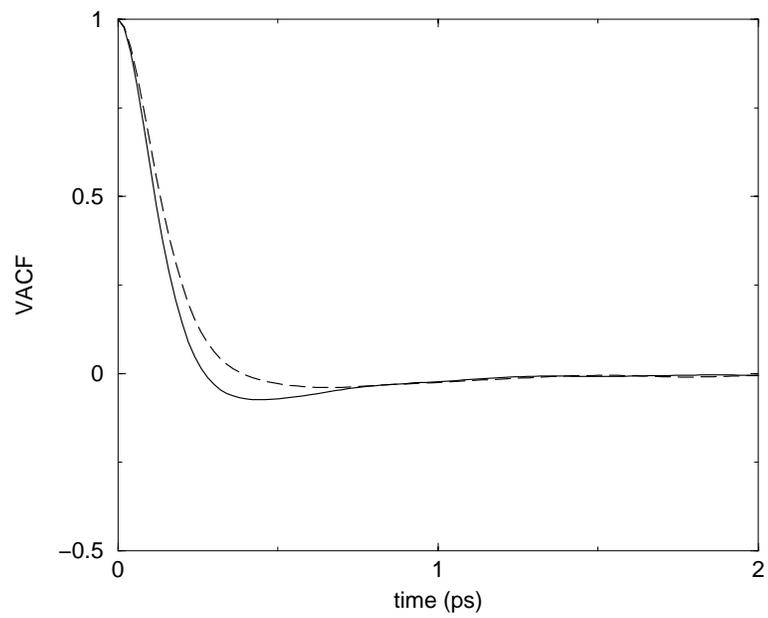


Figure 1.
J. L. Rivera and J. Alejandre

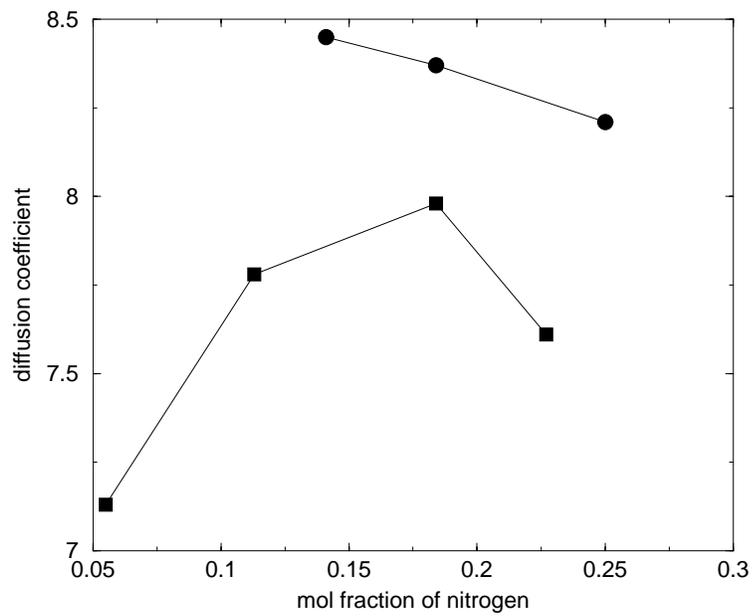


Figure 2.
J. L. Rivera and J. Alejandre

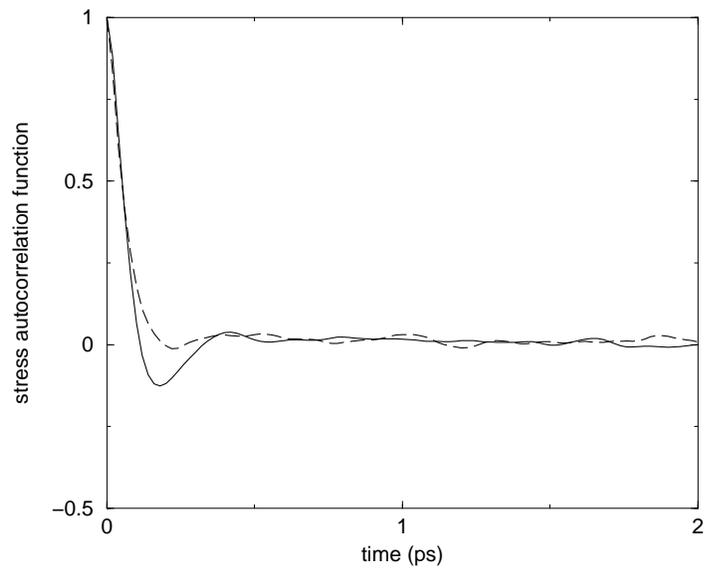


Figure 3.
J. L. Rivera and J. Alejandre

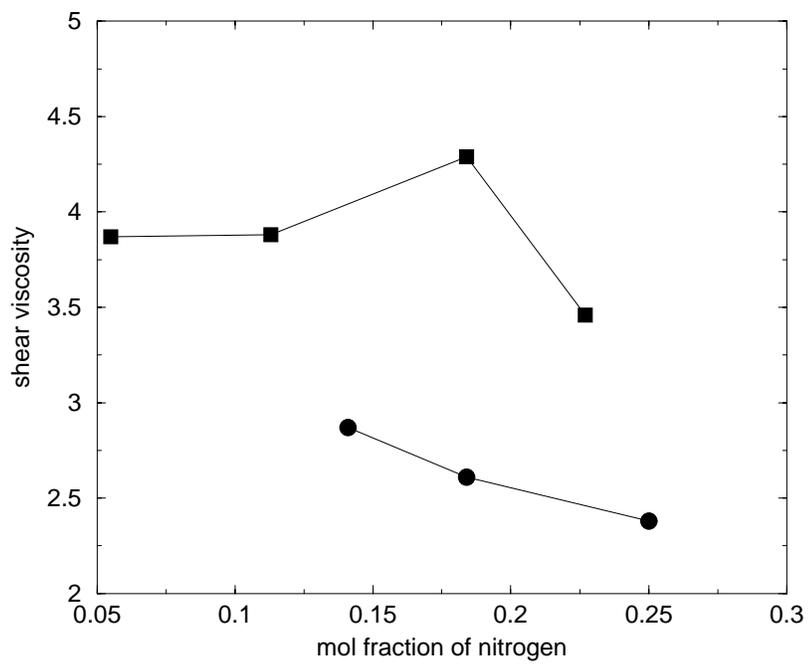


Figure 4.
J. L. Rivera and J. Alejandre