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Absorption processes of gases in liquids: new perspectives from ferrofluids?

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Abstract

Absorption is one of the fundamental unit operations in industrial processes; it is particularly used for gas purification. Constant research is carried out for finding and characterizing new absorption fluids with higher absorption capability and selectivity, less energy requirements for regeneration, and lower environmental impact. In the context of this work, the potential use of ferrofluids as absorption means for separating gaseous mixtures of paramagnetic and diamagnetic components has been investigated for the first time. An experimental apparatus has been designed and tested to measure the impact of an external magnetic field on the solubility of gases in ferrofluids.

Introduction

Oxygen solubility in different liquid solvents has been widely investigated (1-7). A correct knowledge of oxygen solubility in different solvents is important in many fields, such as underground storage where salty water is involved, medical application according to the concentration of oxygen in blood and cells (8), thermal stability of petroleum fractions (9). However, the use of the paramagnetic behavior of oxygen for increasing its affinity with the solvent has not been investigated for the moment. Ferrofluids are magnetic liquid solutions composed of magnetic nanoparticles solvated in a liquid solvent. Ferrofluids have various applications. They can be used for medical application in hyperthermia treatments (10) or drug delivery (11), and also for dynamic sealing (12). The nanoparticles in the ferrofluids act as nano-magnet under the influence of magnetic field. As paramagnetic elements are attracted by magnetic field, there may be a magnetic interaction between the nanoparticle and the oxygen. This hypothesis can be verified through the study of the variation of the solubility of oxygen in a ferrofluid with and without an external magnetic field. The present work describes the conception, construction, and validation of an experimental unit for the measurement of the solubility of oxygen in ferrofluids in the presence of an external magnetic field.

Theory

Under the influence of an external magnetic field, the electronic cloud of a molecule will be affected, creating a response to this magnetic field. Two cases are possible. If the repartition of the electrons in their quantum level of energy is symmetrical the molecule does not have a

permanent magnetic moment and the magnetic response will be a “counter-current” effect, producing a magnetic field in the opposite direction with respect to the external magnetic field. Those molecules are diamagnetic. If the repartition of the electrons presents an asymmetry, then the molecule presents a permanent magnetic moment. However, the orientation of this permanent moment is not fixed in time and space, so the temporal mean value of the magnetic moment of those molecules is null. This magnetic moment will react to an external magnetic field, tending to align with it. This will create a magnetic field in the same direction than the external magnetic field. This behavior describes a paramagnetic molecule.

A description of the distribution of the magnetic moment with and without an external magnetic field is represented in Figure 1.

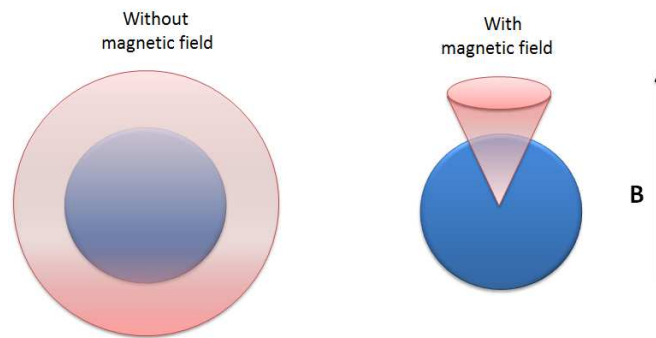


Figure 1. Representation of the distribution of the magnetic moment. In blue the paramagnetic molecule. In red the surface of the equiprobability of the direction of the magnetic moment.

The magnetization induced by an external magnetic field is described by Eq. (1).

$$\vec{M} = \chi \vec{H} \quad (1)$$

For a diamagnetic element χ is negative, whereas in the case of paramagnetic element it is positive.

This magnetic susceptibility is a statistics mean which represents the competition between the magnetic force and the thermal agitation. This value is then not a constant but it varies with the temperature. The expression of the susceptibility for a pure paramagnetic element is given by Curie’s law, Eq. (2):

$$\chi = \frac{C}{T} \quad (2)$$

C is the Curie constant. This constant only depends of the quantum characteristics of the molecules and the molecular density. Its value can be calculated through Eq. (3).

$$C = \frac{\mu_0 \mu_B^2}{3k_B} N_m g^2 J(J + 1) \quad (3)$$

μ_0 : Permeability constant
 μ_B : Bohr magneton
 J : Angular momentum quantum number
 g : Lande g-factor
 N_m : Number of magnetic molecules per volume unit

When a magnetic moment \vec{m} is under the influence of an external magnetic field \vec{B} a torque $\vec{\tau}$ and a force \vec{F}_m are applied on the magnetic moment.

The torque is defined by Eq. (4):

$$\vec{\tau} = \vec{m} \times \vec{B} \quad (4)$$

The force is defined by Eq. (5):

$$\vec{F}_m = \nabla(\vec{m} \cdot \vec{B}) \quad (5)$$

A potential magnetic energy can be expressed by Eq. (6):

$$E_m = -\vec{m} \cdot \vec{B} \quad (6)$$

According to those equations, when a magnetic field is applied to a ferrofluid, the magnetic moment of the iron molecules composing the nanoparticles will align with the external magnetic field, creating a nano-magnet. Those magnets will produce a local magnetic field with a high gradient localized close to the surface of the nanoparticle. This high gradient could attract another paramagnetic molecule such as oxygen.

A representation of the interaction between the nanoparticles and the oxygen molecule is represented in Figure 2.

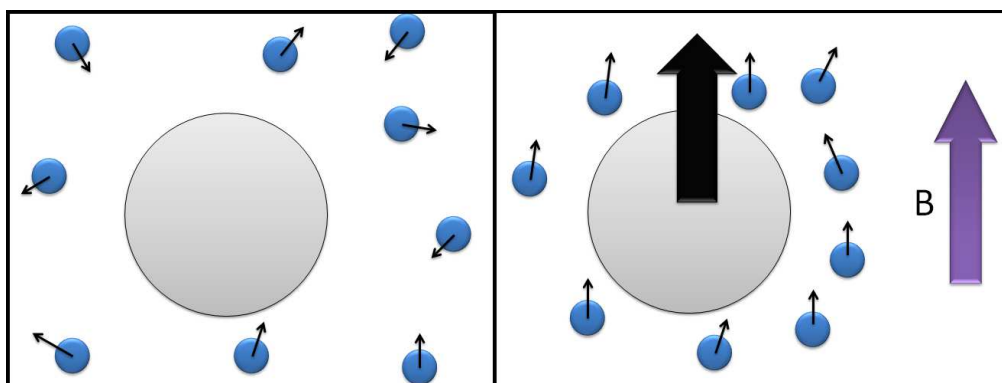


Figure 2. Influence of a magnetic field on the repartition of the oxygen molecules around to the nanoparticles. In grey, the nanoparticle, in blue the molecules of oxygen, black arrays represent their magnetic moments.

This interaction may be evaluated by measuring the change of the solubility of oxygen in the ferrofluid under the influence of an external magnetic field.

Materials

The preparation of the ferrofluid used in this work was made by dissolving commercial nanoparticles into a solvent, n-heptane. The commercial nanoparticles are the EMG1200 series, supplied by the company Ferrotec. The n-heptane used has a purity of 99.5%. The protocol for making the ferrofluids is to weight some grams of the nanoparticles, put them in a vacuum balloon, and then add the solvent. Once the solution is mixed and homogeneous, the balloon is degassed by a vacuum pump to eliminate any air that could have been dissolved in the liquid. The experimental apparatus that has been designed to measure the solubility of oxygen in different solvents, for different values of pressure, temperature and external magnetic field is presented in Figure 3.

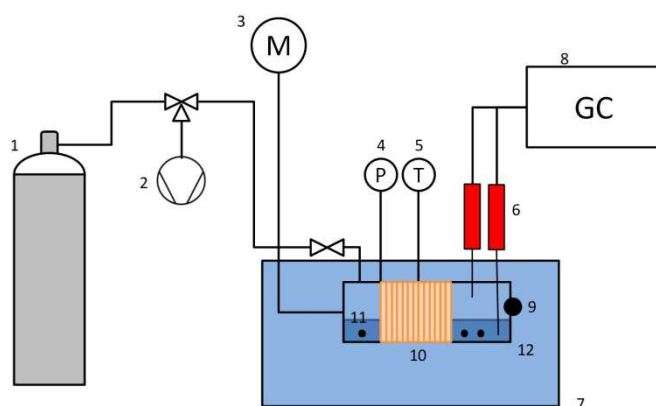


Figure 3. Scheme of the experimental apparatus

- (1) Oxygen cylinder, (2) Vacuum pump, (3) Driving motor, (4) Pressure transducer, (5) Temperature probe, (6) ROLSI® sampler, (7) thermostated bath, (8) Gas chromatograph, (9) Pivot, (10) Electromagnetic coil, (11) Polymer beads, (12) Equilibrium cell.

An equilibrium cell (50 ml of internal volume) made of Hastelloy is placed in a temperature controlled bath of water. The cell is connected to a 0-50 bar Keller pressure transducer. Temperature is measured through a PT100 probe inserted into the body of the equilibrium cell. The cell is first evacuated through a vacuum pump and then filled with the magnetic fluid. To this purpose the magnetic fluid is loaded into a previously evacuated glass balloon connected to the loading line of the equilibrium cell. The magnetic fluid is transferred by gravity and pressure gradient into the equilibrium cell. Then a certain amount of gaseous oxygen is loaded from the 200 bar cylinder (Messer, 99.999% oxygen purity) into the cell to achieve the pressure of measurement. In order to enhance mass and heat transfer to achieve phase equilibrium, the equilibrium cell is made oscillating by a rotary motor with a pivot. Some polymer beads introduced in the cell allow agitating the ferrofluid thanks to the oscillation movement. Some microliters of the liquid phase are sampled through ROLSI® devices, vaporized into the carrier gas, and then transported to a Shimadzu gas chromatograph 2014 to measure the quantity of oxygen absorbed in the ferrofluid. The external magnetic field is produced by an electromagnetic coil settled around the equilibrium cell and it has a calculated value of about 50mT. The small amount of liquid phase sampled for each analysis allows taking several samples with a negligible influence on the phase equilibrium. As a result, the obtained solubility values are the average of several samples

taken at each temperature and pressure. The achievement of thermodynamic equilibrium is inferred by the analysis of the evolution of pressure with time. The system is considered at equilibrium when the pressure variation in one hour is less than the uncertainty of the pressure measurement, i.e. 10 mbar. In order to assess this criterion for determining the achievement of phase equilibrium, tests have been carried out by analyzing the mixture composition 24 hours after the pressure stabilization, revealing a difference in composition within the experimental error of the measurement.

Results

The first step has been to validate the apparatus and the experimental procedure measuring the solubility of oxygen for different pressure at 298.15 K in n-octane and checking the consistency with literature data (5). The results are represented in Table 1 and the graphical comparison with literature data is shown in Figure 4.

Table 1. Experimental values for the solubility of oxygen in n-octane at 298.14 K \pm 0.01 K.

Pressure (bar)	Solubility $\times 10^3$ (moles/moles)
3.256 \pm 0.001	6.9 \pm 0.2
3.849 \pm 0.001	8.8 \pm 0.7
5.013 \pm 0.003	10 \pm 1.6
6.019 \pm 0.002	13.3 \pm 0.5
7.852 \pm 0.004	16.7 \pm 0.6
9.019 \pm 0.005	20 \pm 1.2
10.840 \pm 0.005	23 \pm 1.1
11.526 \pm 0.004	25 \pm 1.1
13.635 \pm 0.007	30 \pm 1.5
14.515 \pm 0.006	30.8 \pm 0.9
17.599 \pm 0.010	39 \pm 2.1
19.558 \pm 0.003	41 \pm 2.6

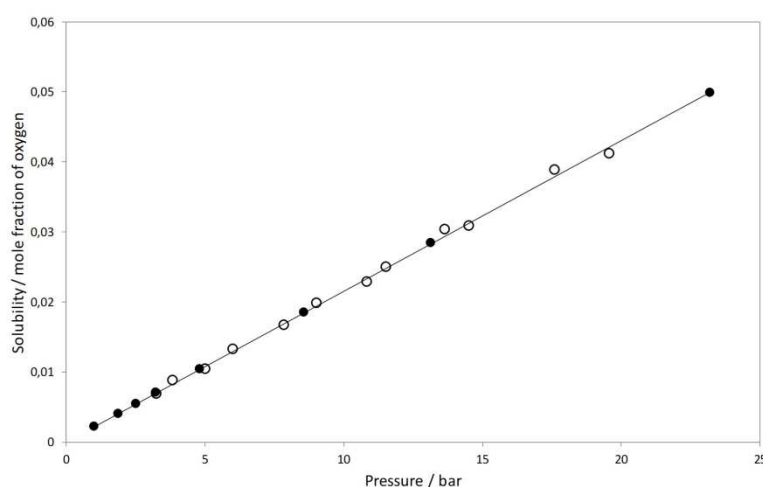


Figure 4. Solubility measurements of oxygen in n-octane at 298.15K at various pressures (•): literature data; (◦): this work; (—) linear correlation of the literature data (5).

Figure 4 shows that the experimental values obtained in this work lay on the curve correlating the literature data (5), which validate the apparatus and the experimental procedure.

The second test done was to measure the solubility of oxygen in n-heptane for various pressures at 298.15K, and to compare it with the solubility of oxygen in a ferrofluid composed of EMG1200 commercial nanoparticles and n-heptane, with and without an external magnetic field. The solubility calculation was considering the solvent as pure n-heptane, free of nanoparticles. The results are represented in Table 2 and Figure 5.

Table 2. Experimental values for the solubility of oxygen in n-heptane 298.14 K \pm 0.01 K.

Pure n-heptane		n-heptane+nanoparticles		Nanoparticles+magnetic field	
Pressure (bar)	Solubility $\times 10^3$ (moles/moles)	Pressure (bar)	Solubility $\times 10^3$ (moles/moles)	Pressure (bar)	Solubility $\times 10^3$ (moles/moles)
3.717 \pm 0.003	7.32 \pm 0.02	3.857 \pm 0.002	7.2 \pm 0.2	3.859 \pm 0.003	7.63 \pm 0.02
6.518 \pm 0.002	12.87 \pm 0.09	4.916 \pm 0.001	9.87 \pm 0.05	4.922 \pm 0.002	9.93 \pm 0.02
10.726 \pm 0.004	20.77 \pm 0.08	5.147 \pm 0.003	11 \pm 1.1	5.135 \pm 0.002	10.2 \pm 0.2
15.094 \pm 0.003	29.9 \pm 0.2	5.904 \pm 0.002	11.4 \pm 0.2	10.018 \pm 0.004	19.74 \pm 0.05
		10.011 \pm 0.002	20.15 \pm 0.02	14.580 \pm 0.002	29.22 \pm 0.06
		14.583 \pm 0.001	29.51 \pm 0.05	19.886 \pm 0.003	39.96 \pm 0.07
		19.864 \pm 0.003	39.81 \pm 0.05		

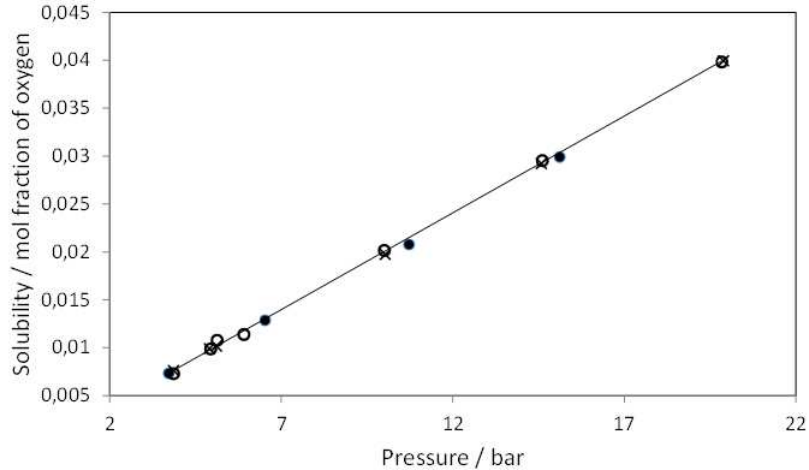


Figure 5. Solubility measurements of oxygen at 298.15K at various pressure in [n-heptane+EMG1200 nanoparticles]

(•) Pure n-heptane; (◦) n-heptane+nanoparticles; (x) n-heptane+nanoparticles+magnetic field; (—) linear correlation of the data.

In this test no evidence of the influence of the solvation of the nanoparticle nor the magnetic field has been found. However the concentration of nanoparticle in n-heptane is far from saturation and the magnetic field used is around 50mT. Tests with different solvents, and nanoparticles with a higher magnetic field will be conducted to verify if those preliminary results are definitive.

Conclusions

A first attempt of investigating the potential use of ferrofluids to absorb paramagnetic gases is presented in this work. A description of the magnetic properties of ferrofluids and a potential mechanism of interaction with a paramagnetic gas have been proposed. An experimental apparatus was designed, constructed and tested for the measure of solubility of oxygen. Preliminary results have not shown any evidence of an influence of the magnetic field on the solubility; however multiple parameters, such as the intensity of magnetic field, the concentration of the nanoparticles, the type of the solvent, will be modified in order to investigate the potential impact of the magnetic field on the solubility of oxygen in a ferrofluid. The theoretical change in the solubility of oxygen in the ferrofluid due to the presence of a magnetic field is related to the difference between the sum of the energies of interaction of the oxygen molecules with the ferrofluid in presence and absence of the magnetic field. These energies are: the potential energy (due to van der Waals forces) of interaction between the oxygen molecules and the solvent molecules (n-heptane), the potential energy of interaction between the oxygen molecules and the magnetic field, the potential energy (due to van der Waals forces) of interaction between the oxygen molecules and the surface of the nanoparticles. A potential interpretation of the obtained results is that the potential energy due to the interaction of the oxygen molecules with the magnetic field and the surface of the nanoparticles is negligible with respect to the energy of interaction with the solvent molecules. However, the theoretical values of these energies are hard to obtain. The interaction between the oxygen molecules and the ferrofluid cannot be determined without a proper knowledge of the surface of the nanoparticles (at molecular level), nor the repartition of the solvent molecules around the nanoparticles. Furthermore, the evaluation of the magnetic interaction needs a complete description of the variation of the magnetic field around the nanoparticles.

One of the perspectives of this work is to study the eventual influence of the magnetic field on the kinetics of absorption of oxygen in ferrofluids. If the magnitude of the energy of the interaction of the oxygen molecules with the magnetic field is not sufficient for affecting the solubility value at thermodynamic equilibrium, the diffusion rate through the liquid and the molecular mixing can be improved with the magnetic field.

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