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Solubilities of gases in cycloethers. The solubility of 13 nonpolar gases in 2,5-dimethyltetrahydrofuran at 273.15 to 303.15 K and 101.32 kPa

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ABSTRACT

The solubilities of gases in liquids are interesting, not only from a practical point of view, but also because they provide a rigorous touchstone to test the structural models on the liquid state. In this work the solubilities of 13 nonpolar gases, He, Ne, Ar, Kr, Xe, H_2, D_2, N_2, CH_4, C_2H_4, C_2H_6, CF_4, and SF_6, in 2,5-dimethyltetrahydrofuran at five temperatures between (273.15 and 303.15) K and 101.32 kPa partial pressure of gas were measured and the associated thermodynamic functions were calculated. Correlation of data has been made and the capacity of prediction of several typical molecular models of liquids, namely, SPT model, perturbation theory, UNIFAC and COSMO-RS, specifically applied to gas solubilities, has been checked.

Keywords:
Gas solubility
Nonpolar gases
2,5-Dimethyltetrahydrofuran
Cycloethers
SPT, Perturbation, UNIFAC, COSMO-RS models

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1. Introduction

A series of previous papers about solubilities of nonpolar gases in different cycloethers has been published by our research group [1-5] in order to show the influence of the ether group, ring size and substitutions, on the solubility of these gases, and ultimately, on the intermolecular potential of the solvent molecules. In this work we continue this series, now reporting the solubility of 13 nonpolar gases (He, Ne, Ar, Kr, Xe, H_2, D_2, N_2, CH_4, C_2H_4, C_2H_6, CF_4, and SF_6) in 2,5-dimethyltetrahydrofuran (2,5DMTHF) at several temperatures. Besides, we test the results of the extended series through the prism of several correlation and prediction models.

From a general point of view, it can be said that the solubilities of gases in liquids provide a rigorous touchstone to test any structural model to be proposed for the liquid state. This is so true that, to date, there is not any general method good enough to predict those solubilities in a fully satisfactory way.

In this frame, the correlation and prediction capacity of several methods has been tested along several decades. Apart from purely empirical models, such as that of the Factor Analysis by de Ligny [6] or purely thermodynamic ones such as the well-known and relatively successful of Hildebrand [7], different increasingly sophisticated molecular models have tried to bring the theoretical results closer and closer to the experimental values. In this way, the classical Scaled Particle Theory (SPT) for the solubility of gases [8, 9] not only allows to correlate and, to some extent, to predict solubility values, but by reversing the calculation, allows us to obtain an approximate description of the intermolecular potential. For its part, Perturbation models such as those developed by Neff and McQuarrie [10] or Goldman [11-14], have attempted to surpass the SPT results through a more rigorous formulation, especially specifying the so-called radial distribution function, but their improvement over the classical SPT has not been successful since, as it is admitted, the classic SPT enjoys the advantage of error compensation.

On the other hand, UNIFAC (UNIQUAC Functional-group Activity Coefficients) is a group contribution method, initially developed by Fredenslund et al. [15] to estimate activity coefficients in nonideal liquid-mixtures, which was extended by Nocon et al. [16] to the solubility of gases on the basis that the gas-liquid systems can be treated by the same thermodynamic equations used for the vapor liquid equilibrium of liquid mixtures. However, although the original UNIFAC model and its modifications, such as new-UNIFAC, UNIFAC-Dortmund, MHV2, or UNIFAC-FV, have been very effective in the study of phase equilibria, the satellite application of UNIFAC to gas solubility has not been widely used due to lack of the necessary parameters and the scarcity of suitable solubility data to estimate them.

Finally, more modern quantum/statistical thermodynamics hybrid methods, such as COSMO-RS [17], have been developed trying to overcome the current difficulties to predict the solubilities of gases when using exclusively quantum mechanics methods.

A detailed explanation of the application of the cited models to our data will be presented along the text.

2. Experimental

2.1. Materials

Specifications of the chemicals used in this work are gathered in Tables 1 and 2. All the gases were from Sociedad Española de1 Oxigeno (now, Air Liquid España S.A.), with the exception of Ne and CF_4, which were from J.T. Baker (Fisher Scientific). The liquid, 2,5DMTHF, was a Merck-Schuchardt product (purity 99%) consisting in a mixture of cis/trans isomers being their relation 1.1:1.0, respectively, as determined by 1H NMR (see Fig. S1 of the Supporting Information). Estimated relative standard uncertainty for this composition ratio is 5%. The refractive index n_D^{20} was measured and used together to its gas GLC chromatogram as purity criteria. Also our density and vapour pressure measurements can be compared with the existing data of literature [18-24] (Table 2). A Zeiss refractometer with interchangeable thermostated prisms was used for refractive index measurements, with an standard uncertainty of ±0.0001. The chromatogram was carried out using a semicapillary column (O.D. 530 μm) of methylsilicone. All the chemicals were used without further purification.

2.2. Apparatus and procedure

Details of the equipment and the experimental procedure used for the solubility measurements were described elsewere [5, 25]. Our apparatus is an adaptation of that of Ben Naim and Baer [26] and essentially consists of a solution vessel (volumes about 25 and 100 mL, depending on the gas), a gas burette system and a Hg manometer to measure adequately pressures from a few mbar to somewhat higher than one bar. The apparatus was located in a thermostatic air bath, the temperature of which was controlled within ±0.2 K. The temperature of the solution vessel was controlled within ±0.05 K and the total pressure above the liquid phase is chosen for the partial pressure of gas to be about 101.32 kPa (values between 100.12 and 102.53 kPa). The actual total and partial pressures of gas (effective pressures in the experiments) together with the corresponding standard uncertainties are gathered in Table S1 of the supplementary file.

Mole fraction of the dissolved gas is determined from both the volume change at constant pressure of saturated gas in the burettes, and the mass of liquid in the solution vessel determined by weighing.

Densities and vapour pressures of 2,5DMTHF were also determined in the working temperature interval and fitted by least squares to the equations shown in Table 2. Densities, ρ, of the liquid were measured using an Anton-Paar DMA-58 vibrating-tube densimeter calibrated with deionized doubly destilled water and dry air. The repeatability of the density measurements was $\pm 1\cdot 10^{-5}$ g·cm^{-3}, but following Chirico et al. [27] about the influence of other factors in the estimates of standard uncertainty, the value of this could reach the figure of almost 0.8 kg·m^{-3} on the basis of the purity of the sample (99%).

Vapor pressure of pure solvent was measured isothermically with a separated Hg manometer (I.D. 3 cm) and using a Wild 338 cathetometer with an standard uncertainty of ±0.02 mm.

The value of the dipole moment of 2,5DMTHF, μ_1, necessary when applaying the SPT theory tour data, was obtained from dielectric permittivity measurements using a WTM Dipolimeter impedance bridge of Khal Scientific, DMOS model, resulting in a value μ_1 = 1.67 D.

In order to obtain the solubilities of the gases, the data reduction of temperature, pressure and the dissolved volume of wet gas (mixture of gas and vapor of the liquid solvent) were carried out following a modification [1] of the method proposed by Tominaga et al. [28], modification which takes into account the particularities of our experimental design. Gas-liquid equilibrium is determined using a method of trial and error making use of the equations:

$$(1 - y_2)P\phi_1^V(T,P,y_2) \; = \; x_1\gamma_1(T,P,x_2)P_{S,1}(T)\mathcal{P}_1(T,P)\phi_{S,1}^{0V}(T,P_{S,1}) \qquad (1)$$

$$y_2P\phi_2^V(T,P,y_2) \; = \; x_2\gamma_2^{\prime}\,(T,P,x_2\,)K_{H\,2,1}(T,P_{S,1})\mathcal{P}_2(T,P) \qquad (2)$$

where the asymmetric convention is assumed. In these equations T and P have their usual meaning; 1 and 2 refer to solvent and solute, respectively; y_2 is the molar fraction of solute in the gas phase; γ_i is the activity coefficient of component i in the liquid phase; $\mathcal{P}$, the Poynting correction; Φ_i, the fugacity coefficient of i component in the gas phase; $\phi_{S,1}^{0V}$, the fugacity coefficient of pure solvent vapor, and $K_{H2,1}(T,P_{S,1})$, the Henry constant at the pressure of pure solvent $P_{S,1}$.

When applying the data reduction, P, $P_{S,1}$ and T, are known and the calculations are simplified assuming three approximations. On the one hand, it can be considered that both activity coefficients γ_1 and $\gamma_2^{\prime}$ equal one, which is a reasonable approximation for low solubilities as those involved in the present cases, only leading to minor errors in the reported quantities; on the other hand, at such low pressures as in this work, fugacity coefficients can be obtained through the approximate Eq. (3), making use of the virial coefficients, B:

$$ln\ \phi_i^V = P\cdot(B_{ii} + y_j^2\Delta_{12})/RT \qquad \text{(i,j =1,2; i}\neq\text{j)} \qquad (3)$$

being Δ_{12} = $2B_{12}$-B_{11}-B_{22}. Finally, for our P and T conditions, the Poynting corrections were calculated assuming the molar volumes as constant within the limits of the corresponding integrals, $P_{S,1}$ and 1 bar. For the solvent, its molar volume at atmospheric pressure is adopted, whereas for the solute their partial molar volumes at infinite dilution in the liquid phase are employed, being their values those provided by Prausnitz and Shair [29], or when necessary they are calculated through the equation of Wing and Walkley [30].

3. Results

3.1. Densities and vapour pressures of solvent

Our experimental values for densities, ρ_1, and vapour pressures, $P_{s,1}$, of solvent are reported in Table 2 and were fitted to linear equations appearing in this table. Because the relatively short temperature interval considered, the simpler form of the Antoine equation with only two coefficients (ec. Clausius-Clapeyron) was used to fit the vapour pressure to temperature. Also a linear relation suffices for ρ_1 *vs.* T.

In Table 2 it can be observed that the values of ρ_1 in this work are in line with that previously reported in the literature. However, the differences (5% average) between our experimental values for $P_{s,1}$ and the bibliographic ones, significantly exceed those based on their corresponding uncertainties. Nevertheless, at least in part, these differences could be attributed to the different origin of the commercial products, since this circumstance could imply a different ratio between the contents of *cis trans* isomers and also in the nature of the impurities.

3.2. The solubility of gases in 2,5-dimethyltetrahydrofuran

The solubilities, expressed as molar fraction, x_2, of the nonpolar gases He, Ar, Kr, Xe, H_2, D_2, N_2, O_2, CH_4, C_2H_4, C_2H_6, CF_4, SF_6, in 2,5DMTHF, between 273.15 and 303.15 K and at 101.32 kPa partial pressure of gas, are gathered in Table 3. For every gas, its solubility, x_2, as a function of temperature T, was fitted by least squares by the equation:

$$\ln x_2 = \mathrm{a} + \mathrm{b}/T \qquad (4)$$

where a and b are constants which are reported also in Table 3 together the standard deviations, σ, defined according to:

$$\sigma = \left\{ \left[\sum \left(\ln x_2 - \mathrm{a} - \mathrm{b} \cdot T^{-1} \right) \right] / \left(n - 2 \right) \right\}^{1/2} \qquad (5)$$

Estimated relative combined standard uncertainty for the solubility data here reported is less than 1% for most of the gases considered. For the less soluble gases, He and Ne, the dissolved gas volume is very small and then, because the size of the division in the graduate burettes, this uncertainty is larger but, in any case, less than 2%.

In Fig. 1 the values of *ln* x_2 vs. 1/T for all the considered gases are represented.

3.3. Thermodynamic functions associated with the solution processes

The coefficients a and b corresponding to equation (4) can be used for the calculation of several standard partial molar thermodynamic functions $\Delta\overline{G}_{m,2}^{0}$, $\Delta\overline{H}_{m,2}^{0}$, $\Delta\overline{S}_{m,2}^{0}$, for the hypothetic solution process considered by Clever and Battino [31] and by Wilhelm et.al. [32]:

$$Z_2\left(gas,\ 1.01325\ bar, T\right) \longrightarrow Z_2\left(solution,\ x_2 = 1,\ P,\ T\right) \qquad (6)$$

These functions were calculated according to:

$$\Delta\overline{G}_{m,2}^{0} = -RT ln x_2(sat) = -RT\left(a + b \cdot T^{-1}\right) \qquad (7)$$

$$\Delta\overline{H}_{m,2}^{0} = -RT\left(\partial ln x_2(sat)/\partial lnT\right) = -R \cdot b \qquad (8)$$

$$\Delta\overline{S}_{m,2}^{0} = -R\left[\left(\partial ln x_2(sat)/\partial lnT\right) + ln x_2(sat)\right] = R \cdot a \qquad (9)$$

In these equations ideal behavior of the gas and the validity of the laws for dilute solutions are assumed.

As usual, we consider the so called Hildebrand entropy, corresponding to the process [31, 32]:

$$Z_2\left(gas,\ 1.01325\ bar, T\right) \longrightarrow Z_2\left(solution,\ x_2(sat),\ P_2 = 1.01325\ bar,\ T\right) \qquad (10)$$

being calculated according to:

$$\Delta\bar{S}_{H,2} = -R\left[\left(\partial lnx_2(sat)/\partial lnT\right)\right]_{sat,P} = R\cdot b\cdot T^{-1} = \Delta\bar{S}^{\,0}_{m,2} - RTlnx_2 \qquad (11)$$

The values of all these thermodynamic quantities for the gases dissolved in 2,5DMTHF are gathered in Table 4.

An overall view of the solubilities data of the gases considered in this work, point out that solubilities in 2,5DMTHF increase according with the following series

$$He<Ne<H_2\sim D_2<N_2<CF_4<Ar<<CH_4<Kr<SF_6<<Xe\sim C_2H_4<C_2H_6$$

which is very similar to that observed in other cycloethers [1-5] as well as in many other organic solvents.

When comparing the solubilities in 2,5DMTHF with those in 2-methyltetrahydrofuran (2MTH) [2] and in tetrahydrofuran (THF) [3], it can be seen that the solubility of any of the studied gases is always higher in 2,5DMTHF than in 2MTHF and higher in this solvent that in THF whitin the temperature interval studied. Consequently, the more methyl groups the basic pentagonal ring has, the higher the solubility of gases and the lower the partial molar Gibbs energy for the solution process are. The same pattern has been observed for the similar cycloketone series cyclohexanone, 2-methylcyclohexanone, and 2,6-dimethylcyclohexanone [33-35].

4. Discussion

During several decades, a very significant progress has been made in the correlation and prediction of properties of fluid mixtures by applying different methods, from those purely empirical [6] to the most sophisticated including theoretical methods which involve advanced formulations from the fields of quantum chemistry and statistical mechanics [36]. In the following sections several theoretical and semiempirical methods will be considered in relation with the correlation and prediction of the solubilities of the chosen nonpolar gases in 2,5DMTHF and other cycloethers.

4.1. Scaled Particle Theory (SPT)

The central objective in the statistical mechanics treatment of solubilities is to calculate the thermodynamic properties of the solution process from the forces between molecules, being a key point for this purpose the determination of the so-called radial distribution function. In this theoretical frame, following the line of Pierotti [37] in its approximation to the solubilities of nonpolar gases in liquids, one can use the equations derived by Reiss, Frisch, Helfand and Lebowitz [38-40] to calculate the reversible work, $\overline{G}_{cav}$, needed to create a cavity able to host a solute molecule, considered as a hard sphere, into the solvent. This formulation named the **S**caled Particle Theory (SPT) is complemented, according with Pierotti [37], using an intermolecular potential of Lennard-Jones (12,6), corrected with a term for the dipole-induced dipole interactions when necessary, to calculate the interaction energy, $\overline{G}_i$, between the solute molecule and the surrounding solvent. Then the solubility of the nonpolar gases can be obtained. Several major approximations are applied: radial distribution function equal to one, pairwise additivity for the total potential, mean arithmetic and mean geometric single rules for the distance and energy parameters, respectively, among others.

The calculation can be performed in a reverse way in order to estimate the effective Lennard-Jones (LJ) pair potential parameters for the solvent (σ_1 and ε_1) from the gas solubility data using the corresponding parameters of the gases obtained from the literature [41]. First of all, the distance parameter of σ_1 of the solvent is calculated; this involving the extrapolation of the Henry´s law constants, $K_{H\,2,1}$, of the noble gases at zero polarizability, that is, when the interaction term,$\overline{G}_i$, is considered to be null. At zero polarizability it is assumed that the rigid sphere diameter of a hypothetical noble gas has a value of a_2^0 = 0.258·10^{-10} m [36]. Fig. 2 left, represents $\ln K_{H\,2,1}$ as a function of polarizability for the noble gases [41] at 298.15 K. From the extrapolated value, $lnK_{H\,2,1}^{\,0}$, the distance parameter for the intermolecular potential identified with the rigid sphere diameter, $a_1 = \sigma_1$, is obtained through the equations:

$$ln\,K_{H\,2,1}^{\,0} = \lim_{\substack{\alpha\to 0\\ a_2\to a_2^0}} ln\,K_{H\,2,1} = \frac{\overline{G}_{cav}}{RT} + ln\left(\frac{RT}{V_1^0}\right) \qquad (12)$$

$$\frac{\overline{G}_{cav}}{RT} = 6\frac{y}{1-y}\left[2\left(\frac{a_{12}}{a_1}\right)^2 - \left(\frac{a_{12}}{a_1}\right)\right] + 18\left(\frac{y}{1-y}\right)^2\left[\left(\frac{a_{12}}{a_1}\right)^2 - \left(\frac{a_{12}}{a_1}\right) + \frac{1}{4}\right] - \ln(1-y) + f(p) \qquad (13)$$

$$y = \frac{\pi a_1^3 \rho}{6} \qquad (14)$$

$$\rho = \frac{N_A}{V_1^0} \qquad (15)$$

being f(p) is a function of P, and also of a_1 and a_{12}, function that can be approximated to 0 at pressures until 1 bar.

On the other hand, the estimation of the LJ energy parameter for the solvent, ε_1, needs the values of $K_{H\,2,1}$ for the different gases, the polarizability α_2 of solutes, and their LJ distance parameter, σ_2, this last in order to deduce σ_{12} using the arithmetic mean rule, as well as the LJ energy parameter (ϵ_1/k).

Following Wilhelm and Battino [35]:

$$RT lnK_{H\,2,1} - \overline{G}_c - RT\ln\left(\frac{\mathrm{RT}}{V_1^0}\right) + 1.333\pi\rho N_A\left(\frac{\mu_1^2\alpha_2}{\sigma_{12}^3}\right)$$
$$= -\,3.55\pi\rho R\sigma_{12}^3\,(\epsilon_1/k)^{1/2}(\epsilon_2/k)^{1/2} \qquad (16)$$

the values of ε_1/k can be deduced directly from the slope of the straight line (Fig. 2, right) obtained by plotting the values of the left side on Eq. 16 versus the values of -3. $55\pi\rho R\sigma_{12}^3\,(\varepsilon_2/k)^{1/2}$ for all considered gases.

Using this method, we have obtained the following LJ (12,6) intermolecular potential parameters for 2,5DMTHF:

$\sigma_1 = 5.85\cdot10^{-10}$ m $\varepsilon_1/k = 574$ K

The consistency and correlation capacity of the model for these systems can be deduced by inverting the calculation, starting from these σ_1 and ε_1, to obtain the theoretical predicted values of the solubility or that of the thermodynamic functions for the solution process, and inspecting their deviations from the experimental values. The results for the theoretical $\Delta G^o_{m,2}$ (indicated as $\Delta G^o_{m,2}(SPT, l = 0)$) are shown in Table 4, and it can be said that the agreement between the calculated and experimental values for x_2 and for thermodynamic $\Delta\overline{X}^o_{m,2}$ follow a pattern similar to that observed for other solvents [1-5].

4.2.The attempts to improve the SPT. The dependence of the rigid sphere diameter with the temperature.

A potential improvement of the model previously described, was proposed by Monfort and Perez [42], and Cosgrove and Walkley [43] in order to avoid the fact that the SPT provides, in general, worse results when the measurement temperature range increases. These authors considered the effect of the temperature on the value of the rigid sphere diameter introducing the named linear expansion coefficient, defined by:

$$l_1 = (1/a_1)(\partial a_1/\partial T)_P \qquad (17)$$

From our data, it was obtained directly using the values of a_1 achieved at the different temperatures, $l_1 = -1.82\cdot10^{-4}$ K^{-1}. Alternatively, it can be calculated, following Cosgrove [43], from enthalpy results, $\Delta\overline{H}^o_{m,2}$, and in this case it turns out to be $l_1 = -1.61\cdot10^{-4}$ K^{-1}. Anyway, in our temperature interval, there is only a slight improvement in the agreement between calculated and experimental values of x_2 and $\Delta\overline{X}^o_{m,2}$. As an example, the RMSD of the theoretical SPT values of $\Delta\overline{G}^{o}_{m,2}$ with respect to the experimental ones reaches a value of 0.95 kJ·mol^{-1} when $l = 0$, while it only decreases to a value of 0.93 kJ·mol^{-1} when the value $l_1 = -1.61 \cdot 10^{-4}$ K^{-1} is assumed.

4.3. Perturbation Theory

In an attempt to obtain better correlations for the solubilities in cycloethers, we have tested the perturbation theory according the method of Leonard-Henderson-Barker (LHB) [44].

As occurred in the SPT model, in this method it is accepted that the potential energy of the cluster of molecules including solute and solvent may be expressed simply as a sum of pair interaction energies. They are also assumed the arithmetic and geometric means combining rules, respectively, for size and energy parameters of interactions between unlike pair molecules. In the corresponding formulation, Helmholtz energy is expressed as a Taylor series around the value of a reference system. The adopted reference potential between pairs of molecules is that of rigid spheres and a LJ (12,6) potential is introduced as the perturbation potential in order to adjust the reference value to the actual one.

According to Neff and McQuarry [10] and Goldman [45, 46], the application of the LHB theory leads to the following expression of Henry's coefficient:

$$\ln K_{H\,2,1} = \ln \frac{RT}{V_1^0} + \beta\mu^{\cdot HS}_{2} + I^{\cdot}_{11} + I^{\cdot}_{12} \qquad (18)$$

In this equation,

$$\beta\mu^{\cdot HS}_{2} = \beta f^{\cdot HS} + N_1 \left(\frac{\partial \beta f^{HS}}{\partial N_2}\right)_{\dot{N}_1,T,V} \qquad (19)$$

$$I^{\cdot}_{11} = 2\pi\rho N_1 \beta \frac{\partial}{\partial N_2} \left(\int_{a_{11}}^{\infty} r_2 u_{11}(r) g_{11}^{HS}(r)\,dr\right)_{\dot{N}_1,T,V} \qquad (20)$$

$$I^{\cdot}_{12} = 4\pi\rho_1\beta\int_{a_{12}}^{\infty} r^2 u_{12}(r) g^{\cdot HS}_{12} dr \qquad (21)$$

$$\beta f = \frac{F(N_1,N_2,T,V) - F^{id}(N_1,N_2,T,V)}{(N_1 + N_2)K_{H\,2,1}T} \qquad (22)$$

being N_1 and N_2 the number of molecules of 1 (solvent) and 2 (solute) in a volume V at temperature T.

The first term in Eq. (18), $\ln\left(RT/V_1^0\right)$, is associated to the different standard states of solute for liquid and vapor phases. $\beta\mu^{\cdot HS}_{2}$ corresponds to the reversible energy for creating a cavity of diameter a_{22} in a system of rigid spheres having a diameter a_{11}; and it is calculated using the EOS of Mansoori-Carnahan-Stirling [47] for a system of rigid spheres. The term $I^{\cdot}_{11}$ corresponds to changes in the solvent structure around the cited cavity; and finally $I^{\cdot}_{12}$ is associated to the solute-solvent interaction, this being the most inaccurate term because its estimation involves an adequate knowledge of the radial distribution function $g^{\cdot HS}_{12}$ which is quite problematic.

The solution of Lebowitz [48] for the Percus-Yevick EOS corresponding to a mixture of rigid spheres [49] was used to obtain the Laplace transform of factor $\mathrm{r}g_{ij}^{HS}(r)$ appearing in the previous equations. The integrals in the calculus scheme were solved using the Gauss method, dividing the total integration interval in seven subintervals with 20 points each and using double precision for the figures. The minor integrals from a_{ij} to σ_{ij} as limits were calculated according the approximation proposed by Neff and McQuarrie [10] that assumes a linear variation of the integrand.

Taking THF as a model for the cycloethers, the solubilities for the 13 gases considered in this study have been calculated. When comparing with the results of SPT, it can be observed that the deviations are of the same order, not only with no improvement but actually a worsening in the average value (45%, Perturbation theory; 35% SPT). This can be explained by the limited existing knowledge for a full application of that Perturbation theory.

4.4. Group contribution models. The UNIFAC model

In a previous paper [50] we described the details of the application of the UNIFAC method to gas solubilities according to Nocon et al.[16, 51], and reported the interaction parameter gas-alkane and alkane-gas for most gases included in this work obtained through the correlation of a large amount of solubility data of gases in alkanes. Now, in order to test the possibilities of the model with our solubilities in cycloethers, we have calculated the necessary new parameters for its application, and also have recalculated those for the pairs alkane-gas.

In this methodology the starting thermodynamic equation for the solubilities of gases is that relative to the equilibrium of the solute between the two phases involved:

$$x_2 \gamma_2 f_2^{0L} = y_2 \phi_2^G \mathrm{P} \qquad (23)$$

where γ_2 represents the activity coefficient of solute when using as reference state the Raoult law, f_2^{0L} is the standard fugacity of the solute as a hypothetical liquid, ϕ_2^G is the fugacity coefficient in the gas phase, and P, x_2 and y_2 have their usual meaning. For our experimental conditions and at the level of this approximation, the second member of Eq. 23 can be approximated to a value of one.

Another key aspect in the calculation process is the estimation of the standard fugacities for the gases as hypothetical liquids. They were estimated by using the extrapolation proposed by Nocon et al. [16, 51]. In this way, the coefficients of Antoine's equation were obtained from the TRC Tables [52] and the critical constants were taken from Reid et al. [53]. Soave equation [54] was chosen to calculate the fugacity coefficient; and the molar volume of solute as hypothetical liquid was determined by the method of Zellner et al. [55]. A third-degree polynomial has been used to fit the fugacities as a function of temperature. The corresponding coefficients of the polynomial for most of the gases used in this work were reported in [50]; He, H_2 and D_2 are not included in the series because of the bad results provided by the extrapolation. Finally, the UNIFAC method was properly used in order to calculate the activity conﬀicents.

In the original UNIFAC [15], $ln\gamma_2$ is considered to be the sum of two terms according to the equation:

$$ln\gamma_2 = ln\gamma_2^C + ln\gamma_2^R \quad (24)$$

where the superscript C refers to the combinatorial term associated to the differences in size and shape of the molecules in the solution, and R corresponds to the residual term that accounts for the interactions between the structural groups in the molecules.

In the so called UNIFAC-free volume (UNIFAC-FV) [51] (also considered in references [16] and [50]), a third term, $ln\gamma_2^{FV}$, introduced by Oishi and Prausnitz [56], is added at the right side of Eq. (24), this term arising from the volume effects in the solution process.

In order to calculate the combinatorial term, the required structural parameters R_k and Q_k (relative van der Waals, volumes and areas, respectively) for liquid (main groups 1 and 13, subgroups, 1, 2 and 26), and gases (main groups 57, 59, 60 68, 70, 71 72, 78, 80), were obtained from the data of Bondi [57] and are gathered in Table5.

Calculation of the residual term requires to know the a_{mn} and a_{nm} interaction parameters between the gas molecules and the structural groups of molecules (main groups "CH_2", "CH_2O"). These interaction parameters were determined by means of a correlation of activity coefficients obtained from experimental data. A Simplex method modified by Nedler and Mead [58] was performed minimizing the function:

$$F = \sum_{j}^{N_S} \frac{1}{2N_W}\left[\sum_{k}^{N_W}\sum_{i}^{n}\left(\frac{\gamma_{ijk,exp} - \gamma_{ijk,cal}}{\gamma_{ijk,exp}}\right)^2\right] \qquad (25)$$

In this equation, N_S is the number of different systems, N_w is the number of experimental points for a given system, n is the number of components and γ refers to the experimental or calculated activity coefficients.

Data series of VLE for 13 binary mixtures consisting in a cycloether (THF, 2MTHF, 2,5DMTHF, THP, OHM) plus a hydrocarbon (cyclopentane, cyclohexane, cyclooctane, hexane heptane, octane and nonane), including a total of 202 points were used in the calculation of the interaction parameters $a_{CH_2-CH_2O}$, $a_{CH_2O-CH_2}$. A total of 427 points corresponding to 138 binary systems gas plus hydrocarbon, within the temperature interval 272-316 K were considered in the calculation of the interaction parameters a_{CH_2-gas}, a_{gas-CH_2}. Finally, on the basis of our experimental studies of gas solubilities in cycloethers (THF,THP, OHM, 2MTHF, 2,5DMTHF) between 273 and 303 K, a total of 180 points for 45 systems gas-ether were considered in order to calculate the interaction parameters a_{CH_2O-gas}, a_{gas-CH_2O}. All these parameter are gathered in Table 5.

In the calculation of the contributions of terms C, R and FV to $ln\gamma_2$, some secondary parameters appear whose values are chosen according Nocon et al. [16,51].

Both models, original UNIFAC and UNIFAC-FV, in general, correlate the experimental data very acceptably. Fig. 3 presents the correlations corresponding to Ar and CH_4 as solutes in the THF, THP, 2MTHF, 2,5DMTHF solvent series.

In order to test the performance of the calculated interaction parameters when applied to other system gas-cycloethers, the solubilities of the gases Ar and CH_4 in 1,4-dioxane (1,4DO) were calculated and compared with the experimental ones [5]. It must be pointed out that this can be considered a hard test because of the particular structure of this compound which has two ether groups on opposite ends of the cycle. In Fig. 4, calculated data are compared with experimental values. It can be said that both, original UNIFAC and UNIFAV-FV predict well the solubilities of Ar. However, for methane solubilities, UNIFAC-FV become poorer than the original model.

4.4 COSMO-RS model. An hybrid quantum/statistical thermodynamics method.

Up to date, pure quantum chemical methods have shown inefficiencies to estimate adequately the solubilities of gases in liquids. According to Shiflett et al. [59], this is because of the intrinsic complexity of the specific intermolecular interactions and, on the other hand, by the large number configurations of solute and solvent molecules to be sampled. Then, the calculations become prohibitively expensive for an exclusive quantum chemical method. Due to these difficulties, some researchers have used quantum calculations considering only the interactions between the solute-solvent pairs of molecules [60,61] or, at most, considering small cluster models in order either to report trends or to obtain semi-quantitative results of solubilities of gases [59]. To advance in this purpose, quantum chemical calculations are used in combination with other approximations or models to predict the solubilities.

A modern and common approach to obtain values of solubility of gases is that based on the COSMO model developed by Klamt and Schürmann [62]. As in the case of

UNIFAC, COSMO, conveniently implemented, has been widely used in the last years to correlate and predict the solubility of CO_2 and other gases in liquids, especially in relation with the CO_2 capture by reversible ionic liquids and other solvents [61, 63], but in this work, electrically neutral solvents are considered. In this way, calculations with the version COSMO-RS (short for COnductor like Screening MOdel for Real Solvents) [64-66], a quantum mechanical continuum solvation model with DFT (Density Functional Theory), were performed in order to predict the solubility of gases in the cycloethers. Solubilities are calculated making use of the so called "screening charge densities" by means of statistical thermodynamics. The method follows a two-step procedure: 1) the geometry of molecules was optimized by adjustment of polarization charge density, σ, at the BP86/TZVP/DGA1 level. 2) statistical thermodynamics of the polarization charge density was applied to quantify the molecular interactions in the liquid phase. The parameterization BP_TZVP_C21_0111 was then used.

As an advance of our study about the application of this hybrid quantum/statistical thermodynamics method, in Fig. 4 we present a comparison between some of our experimental data and the data predicted by COSMO-RS.

5. Conclusions

This paper continues our work about experimental data series on solubilities of nonpolar gases in cycloethers reporting the solubilities of He, Ne, Ar, Kr, Xe, H_2, D_2, N_2, CH_4, C_2H_4, C_2H_6, CF_4, and SF_6 in 2,5DMTHF at five temperatures between 273.15 and 303.15 K and 101.32 kPa partial pressure of gas. When comparing with the less methylated cycloethers 2MTHF and THF, it can be observed that the solubilities of every of the studied gases progressively increase as the methylation of the pentagonal ring of THF increases.

From the experimental results, partial molar Gibbs energy, partial molar enthalpy, and partial molar entropy for the solution process were calculated.

The ability of several structural models to predict the solubility of the gases in 25-DMTHF has been tested. Using SPT model according to the formulation of Pierotti, we have obtained the effective LJ (12,6) intermolecular potential parameters of 2,5DMTHF molecules whose values are $\sigma_1 = 5.85 \cdot 10^{-10}$ m and ε_1/k = 574 K. Also a SPT variation which takes into account the linear expansion coefficient, $l_1 = (1/\sigma_1)(\partial\sigma_1/\partial T)_P \approx 1.7\ K^{-1}$ has been considered. SPT correlates acceptably well the experimental values of solubility within the usual limitations but the use of the linear expansion coefficient does not lead to a significant improvement.

Perturbation methods at the level of the approximations proposed by Neff and Goldman do not improve the results of the SPT model for our systems, although the order of the deviations is not very different. More rigorous approximations would be necessary in order to achieve better predictions.

For the application of the original-UNIFAC and UNIFAC-FV models, the interaction parameters alkane-ether, ether-alkane, gas-alkane, alkane-gas, gas-ether and ether-gas were calculated from a quite extensive set of experimental data. With these parameters, and following the Nocon and McQuarrie procedure, a relatively good correlation of our results of gas solubilites in the cycloethers was achieved, especially for UNIFAC-FV.

To determine the quality of the parameters as well as that of the model, the solubilities of Ar and CH_4 in a different cycloether, 1,4-dioxane (1,4DO), not included in the deduction of parameters, were calculated. In the case of original UNIFAC acceptable predictions were obtained.

Finally, COSMO-RS was tested as predictive model by calculating the solubilities of Ar and CH_4 in 1,4DO. Although the predictions are too poor in the case of Ar, the approximation is acceptable in the case of CH_4, especially when considering the difficulties that other purely predictive methods have to achieve a good quantitative agreement and not only a qualitative correlation.

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Tables

TABLE 1. Gases description: Sources, purities and analysis of the pure component.

GASES	Source	[a] Purity %	Purification	Analit. Meth.
He	Sigma-Aldrich	99.995	None	-
Ne	J.T. Baker	99.9	None	-
Ar	Air Liquide	99.9990	None	-
Kr	Air Liquide	99.95	None	-
Xe	Air Liquide	99.995	None	-
H_2	Air Liquide	99.99	None	-
D_2	Air Liquide	99.4	None	-
N_2	Air Liquide	99.998	None	-
CH_4	Air Liquide	99.95	None	-
C_2H_4	Air Liquide	99.90	None	-
C_2H_6	Air Liquide	99.0	None	-
CF_4	J.T. Backer	99.0	None	-
SF_6	Air Liquide	99.5	None	-

[a] As molar fraction.

TABLE 2. Solvent description. Densities, ρ, vapour pressure, $P_{S,1}$, and refractive index, n_D, of 2,5-dimethyltetrahydrofuran at 273.15 to 303.15, deviations ($\Delta Y = Y - Y_{calc}$, $Y = \rho_1$, $P_{S,1}$), and comparison with literature data.

T/K		ρ_1/ kg·m^{-3}	[a]$\Delta\rho$ /kg·m^{-3}	$P_{S,1}$/ Pa	[a]$\Delta P_{S,1}$/ Pa	n_D
273.15	[b] expt.	848.22	-0.04	2066	3	
	[c] lit.			[d,e] 2284		
283.15	[b] expt.	838.53	0.01	3618	-19	
	[c] lit.			[d,f] 3949		
293.15	[b] expt.	828.71	-0.02	6180	10	1.4043
	[c] lit.	[g] 830		[d,f] 6581		[h] 1.405
	[i]lit					[j] 1.4
298.15	[b] expt.	823.89	0.04	7909	-20	
	[c] lit.	[k] 825.27		[c,f] 8390		
	[c] lit.	[l] 825.3				
	[m] lit.	[n] 825.25				
303.15	[b] expt.	818.91	-0.06	10112	6	
	[c] lit.			[c,f] 10608		

Standard uncertainties are $u(\rho) = 0.8$ kg·m^{-3}, $u(P_{S,1}) = 17$ Pa, $u(n_D) = 0.0001$. Standard uncertainties for temperatures are $u(\mathrm{T}) = 0.02$ K for ρ and for $n_{D,}$ and $u(\mathrm{T}) = 0.05$ K for $P_{S,1}$. Density and refractive index were measured at atmospheric pressure $p = (0.1 \pm 0.002)$ MPa.

[a] Differences between experimental and values Y_{calc} fitted to following linear equations: ρ / (kg·m^{-3}) = 1115.0±0.6 – (0.9765 ± 0.0021)·(T/K), and ln (P/Pa) = 23.689±0.041 – (4386±12)·(T/K)$^{-1}$. [b] Merck-Schuchardt product (purity of 99%, indicated by the supplier, was confirmed by GC in this work), mixture of isomers, relationship cis to trans 1.1:1.0, as determined by ^{1}H NMR. [c] Aldrich product, >99%, mixture of cis and trans isomers; composition not declared. [d,e] Reference [18], extrapolated value (5 ºC). [d,f] Reference [18], interpolated value. [g] Reference [19]. [h] Reference [20]. [i] Unspecified origin/composition of the chemical. [j] Reference [21]. [k] Reference [22]. [l] Reference [23]. [m] Acros product, 99%, mixture of cis and trans isomers; composition not declared. [n] Reference [24].

TABLE 3. Solubility of gases ($10^4 \cdot x_2$) in 2,5-dimethyltetrahydrofuran at various temperatures and adjusted to a partial gas pressure of exactly 101.32 kPa, coefficients a and b for Eq. (4), and standard deviations, σ, as defined according Eq. (5).

	x_2 10^4					Parameters		
Gas	**273.15K**	**283.15K**	**293.15K**	**298.15K**	**303.15K**	**a**	**b**	σ
He	1.13	1.28	1.46	1.54	1.66	-5.21±0.10	-1058±30	0.0088
Ne	1.77	1.99	2.16	2.28	2.35	-5.74±0.11	-791±31	0.0092
Ar	16.99	16.76	16.69	16.50	16.43	-6.70±0.03	89±11	0.0032
Kr	56.10	52.53	48.96	47.31	45.89	-7.22±0.03	559±10	0.0029
Xe	255.1	227.6	203.0	192.4	179.9	-7.15±0.09	952±27	0.0078
H_2	3.87	4.14	4.39	4.58	4.71	-5.86±0.05	-554 ±16	0.0046
D_2	3.97	4.27	4.54	4.70	4.84	-5.83±0.03	-545±8	0.0023
N_2	8.44	8.59	8.74	8.81	8.90	-6.55±0.02	-144±7	0.0020
CH_4	41.28	38.91	37.12	36.15	35.34	-7.05±0.02	426±7	0.0019
C_2H_4	277.5	235.6	201.3	188.9	175.8	-8.20±0.05	1260±13	0.0039
C_2H_6	365.5	302.9	254.5	237.6	217.1	-8.53±0.07	1425±20	0.0060
CF_4	14.22	13.95	13.78	13.70	13.61	-6.99±0.02	119±5	0.0016
SF_6	88.66	79.22	71.71	68. 60	63.95	-7.96±0.08	885±24	0.0069

Standar uncertainty is $u(T) = 0.05$ K and relative combined standard uncertainties are $u_r(x_2) = 0.02$ for He and Ne, and $u_r(x_2) = 0.01$ for all the other gases. Combined standard uncertainties for coefficients a and b are reported in the table togheter with the values of these coefficients.

TABLE 4. Experimental and theoretical (SPT) standard partial molar thermodynamic quantities, $\Delta\overline{X}^{o}_{m,2}$, $\Delta\overline{X}^{o.SPT}_{m,2}$, for the solution process of gases in 2,5-dimethyltetrahydrofuran at 298.15 K and 101.32 kPa partial pressure of gas.

Gas	$\Delta\overline{G}^{o}_{m,2}$ kJ mol^{-1}	$\Delta\overline{H}^{o}_{m,2}$ kJ mol^{-1}	$\Delta\overline{S}^{o}_{m,2}$ J K^{-1}mol^{-1}	$\Delta\overline{S}_{H,2}$ J K^{-1}mol^{-1}	$\Delta\overline{G}^{o,SPT}_{m,2}$ kJ mol^{-1}	$\Delta\overline{H}^{o,SPT}_{m,2}$ kJ mol^{-1}	$\Delta\overline{S}^{o,SPT}_{m,2}$ J K^{-1}mol^{-1}
He	21.73±0.43	8.80±0.25	-43.38±0.87	30.4±1.1	20.80	5.04	-53.3
Ne	20.80±0.42	6.58±0.26	-47.71±0.90	22.7±1.7	18.30	2.58	-53.0
Ar	15.88±0.16	-0.75±0.09	-55.76±0.31	-2.59±0.53	14.56	-0.93	- 52.5
Kr	13.27±0.13	-4.65±0.08	-60.09±0.29	-16.18±0.34	12.81	-2.56	-52.2
Xe	9.81±0.10	-7.92±0.22	-59.45±0.76	-27.56±0.97	10.85	-4.38	-51.1
H_2	19.07±0.19	4.52±0.13	- 48.78±0.45	15.70±0.76	19.04	3.35	-53.2
D_2	19.00±0.19	4.54±0.06	-48.50±0.22	15.75±0.40	18.89	3.20	-53.0
N_2	17.44±0.17	1.20±0.06	-54.47±0.20	4.18±0.13	16.77	1.42	-51.3
CH_4	13.94±0.14	-3.54±0.05	-58.62±0.19	-12.32±0.45	13.40	-1.95	-51.6
C_2H_4	9.85±0.10	-10.48±0.11	-68.16±0.38	-36.42±1.00	10.33	-4.83	-51.4
C_2H_6	9.29±0.09	-11.85±0.17	-70.90±0.59	-41.21±1.26	10.09	-4.87	-50.8
CF_4	16.35±0.16	-0.99±0.04	-58.15±0.15	-3.42±0.33	16.23	1.47	-49.6
SF_6	12.38±0.12	-7.36±0.20	-66.21±0.68	-25.44±1.44	12.60	-1.44	-47.0

Combined standard uncertainties for the experimental quantities are included in the table.

TABLE 5. The R_k and Q_k reduced van der Walls parameters, and the parameters for the interactions between gases and structural subgroups of solvent molecules.

m (n) n (m)	**1** **“CH$_2$”**	**13** **“CH$_2$O”**	**57** **CH$_4$**	**59** **Ar**	**60** **N$_2$**	**68** **SF$_6$**	**70** **Ne**	**71** **Kr**	**72** **Xe**	**78** **C$_2$H$_6$**	**80** **CF$_4$**
1 **“CH$_2$”**	0	211.8	1339 842	416.9 719.6	2154 1912	869.7 705.9	2844 2488	817.5 555.5	165.9 -34.97	214.6 293.8	1431 678.9
13 **“CH$_2$O”**	-6.700	0	1019 479.2	610.0 765.5	1616 1577	682.3 679.2	2445 2382	638.7 891.4	166.9 554.3	742.6 1009	1075 1360
57 **CH$_4$**	-412.4 -324.2	-78.00 4705									
59 **Ar**	-105.5 -327.0	145.8 9.102									
60 **N$_2$**	-525.6 -499.9	2.700 -42.76									
68 **SF$_6$**	-325.4 -282.9	-26.12 -9.923									
70 **Ne**	-446.7 -435.8	-58.60 10.91									
71 **Kr**	-329.2 -286.1	7.280 -84.26									
72 **Xe**	-85.34 10.78	194.3 58.33									
78 **C$_2$H$_6$**	-94.86 -199.0	-40.78 -75.90									
80 **CF$_4$**	-433.2 -241.7	30.26 8.75									

Group	**Subgroup**	**nº**	**R$_k$**	**Q$_k$**
1	CH$_3$	1	0.9011	0.8480
	CH$_2$	2	0.6744	0.5400
	CH	3	0.4469	0.2280
	C	4	0.2195	0.0000
13	CH$_3$O	25	1.1450	1.088
	CH$_2$O	26	0.9183	0.780
	CHO	27	0.6908	0.468
	CH$_2$O	28	0.9183	1.1
57	CH$_4$	111	1.1290	1.124
59	Ar	113	1.1050	1.070
60	N$_2$	114	0.9340	0.985
68	SF$_6$	121	2.9743	2.600
70	Ne	123	0.6074	0.718
71	Kr	124	1.3708	1.2353
72	Xe	125	1.677	1.4151
78	C$_2$H$_6$	131	1.8022	1.696
80	CF$_4$	133	1.7277	1.760

FIGURE CAPTIONS

Fig 1. Logarithm of the solubilities for nonpolar gases in 2,5DMTHF, as a linear function of the inverse of temperature *T*. Experimental points: ∀ He, – Ne, Ξ H_2, □ D_2, ν N_2, □ CF_4, 8 Ar, ψ CH_4, X Kr, % SF_6,M Xe, □ C_2H_4, and , C_2H_6.

Fig 2. Left: Extrapolation of the values of the Henry´s law constant for noble gases at 298.15 K to obtain the value of $lnK_{H}{}_{2,1}^{0}(298.15\ \mathrm{K})$. Right: Straight line obtained by plotting the values of the left side on Eq. 16 versus the values of -3.55$\pi\rho R\sigma_{12}^{3}$ $(\epsilon_2/k)^{1/2}$ for all gases considered, at 298.15 K.

Fig.3. Left: Comparison between experimental and theoretical (UNIFAC, dot line and UNIFAC-FV, straigth line) solubilities of Ar in cycloethers (THF, −; THP, ∀; 2MTHP, 8; 2,5DMTHP, M) at 273.15 to 303.15 K and 101.32 kPa partial pressure of gas. Right: ib. for CH_4

Figure 4. Comparison between experimental and theoretical (UNIFAC, dot line; UNIFAC-FV, straight line, and COSMO-RS, dash line models) solubilities of Ar, ,, and CH_4, 7, in 1,4DO at temperatures 273.15 to 303.15 K and 101.32 kPa partial pressure of gas.

FIGURES

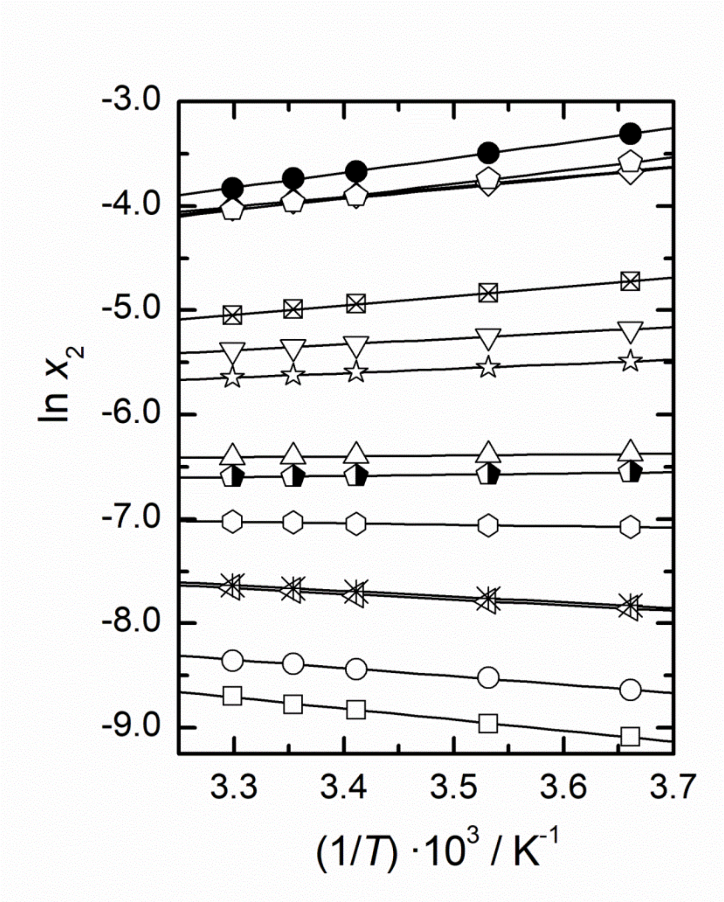


Figure 1

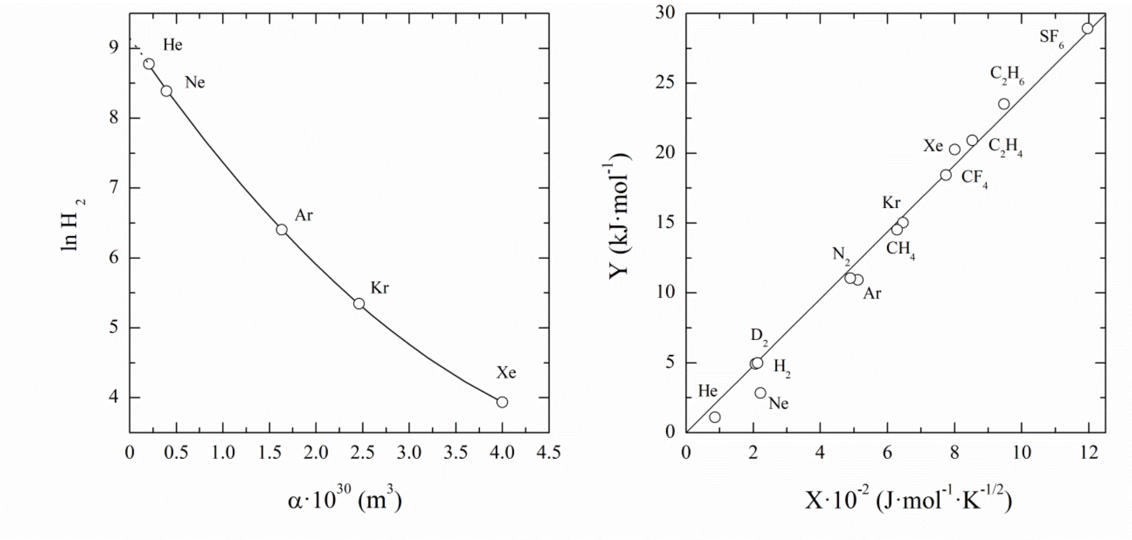

He
Ne
Ar
Kr
Xe
9
8
7
6
5
4
ln H 2
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
α·10^30 (m^3)
SF6
C2H6
Xe
C2H4
CF4
Kr
CH4
N2
Ar
D2
H2
He
Ne
30
25
20
15
10
5
0
Y (kJ·mol^-1)
0
2
4
6
8
10
12
X·10^-2 (J·mol^-1·K^-1/2)

Figure 2

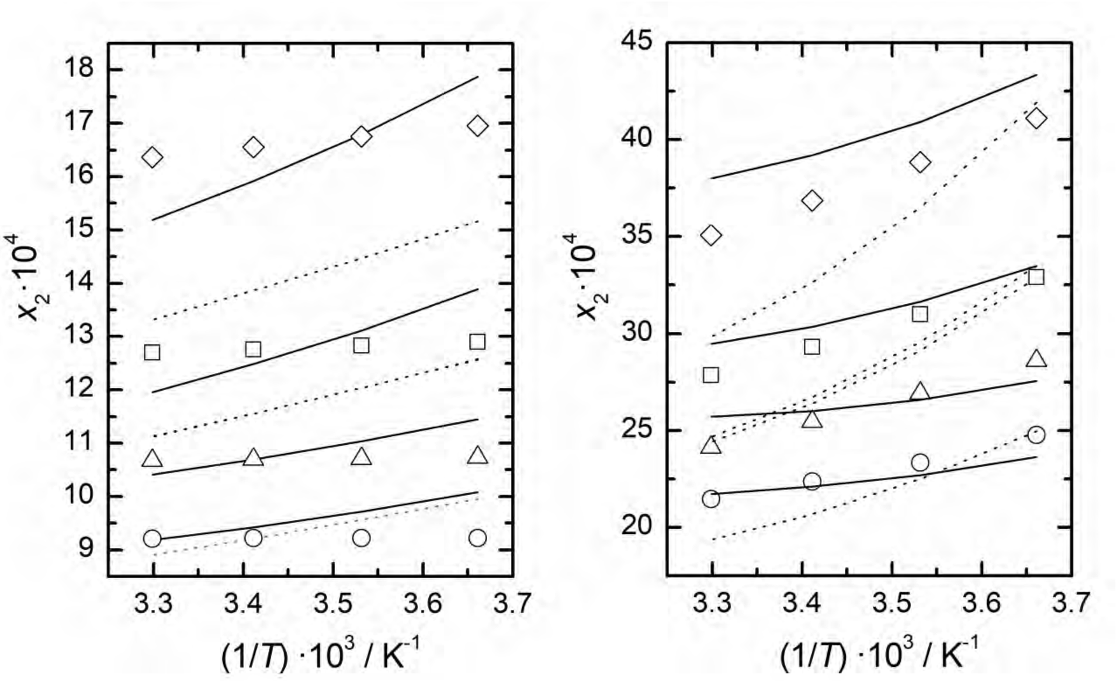

$x_2 \cdot 10^4$
18
17
16
15
14
13
12
11
10
9
3.3
3.4
3.5
3.6
3.7
$(1/T) \cdot 10^3$ / K^{-1}
$x_2 \cdot 10^4$
45
40
35
30
25
20
3.3
3.4
3.5
3.6
3.7
$(1/T) \cdot 10^3$ / K^{-1}

Figure 3

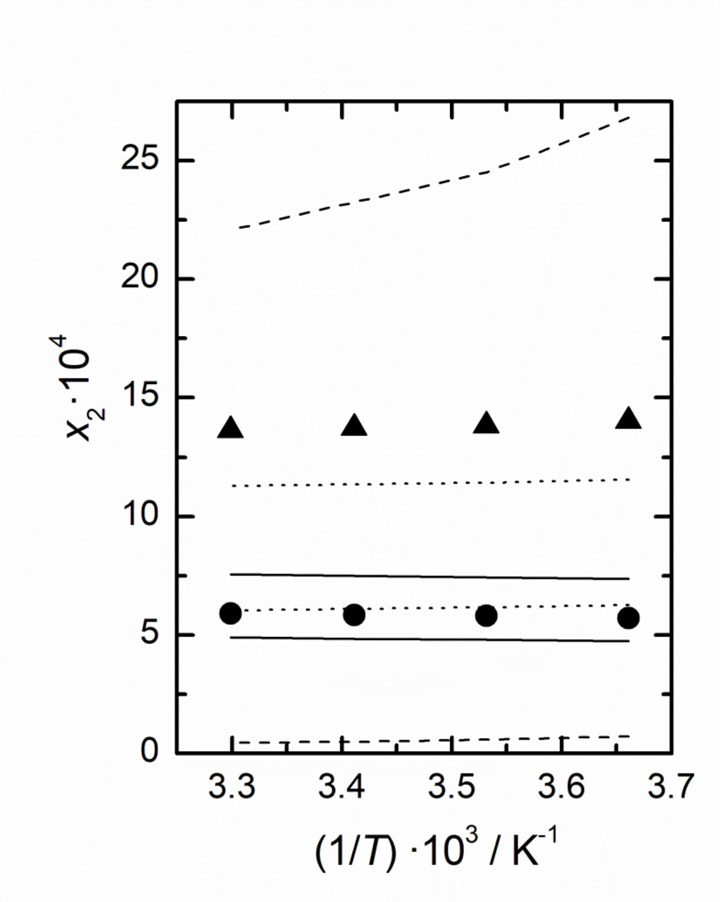
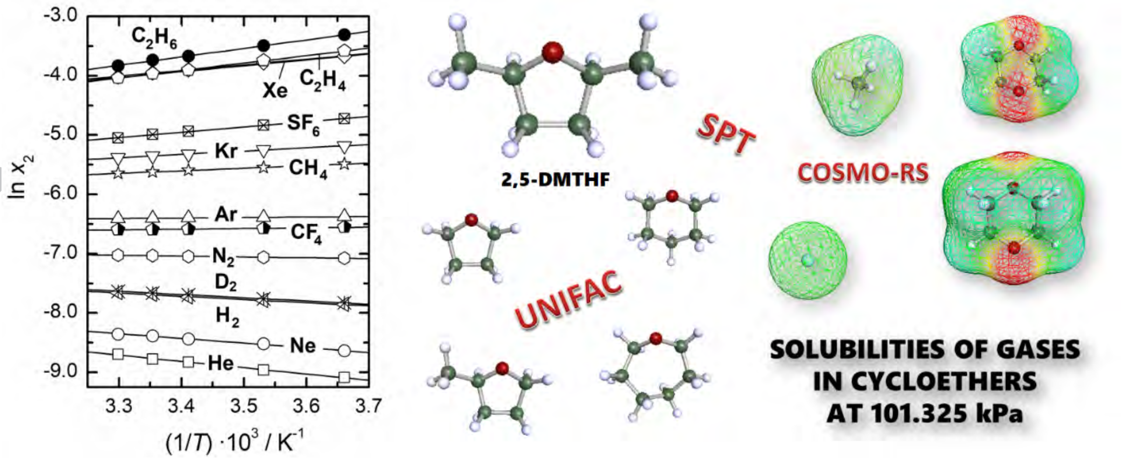


Figure 4



Highlights

Solubilities of gases in cycloethers. The solubility of 13 nonpolar gases in 2,5-dimethyltetrahydrofuran at 273.15 to 303.15 K and 101.32 kPa

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- Solubilities of 13 nonpolar gases in 2,5-dimethyltetrahydrofuran at 101.32 kPa and *T*= (273.15 - 303.15) K were measured
- The ability of several methods (SPT, Perturbation, UNIFAC, COSMO-RS) to correlate or predict gas solubilities in cycloethers was tested
- New interaction parameters to predict solubilities of nonpolar gases in cycloethers according the UNIFAC model are proposed
- SPT model provides the parameters of the Lennard-Jones (12,6) potential for 2,5-dimethyltetrahydrofuran