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On the behaviour of solutions of xenon in liquid cycloalkanes: Solubility of xenon in cyclopentane

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ABSTRACT

The solubility of xenon in liquid cyclopentane has been studied experimentally and theoretically. Measurements of the solubility of xenon in liquid cyclopentane are reported as a function of temperature from 254.60 K to 313.66 K. The imprecision of the experimental data is less than 0.3%. The thermodynamic functions of solvation of xenon in cyclopentane, such as the standard Gibbs energy, enthalpy, entropy and heat capacity of solvation, have been calculated from the temperature dependence of Henry's law coefficients. The results provide further information about the differences between the xenon + cycloalkanes and the xenon + *n*-alkane interactions. In particular, interaction enthalpies between xenon and CH_2 groups in *n*-alkanes and cycloalkanes have been estimated and compared. Using a version of the *soft*-SAFT approach developed to model cyclic molecules, we were able to reproduce the experimental solubility for xenon in cyclopentane using simple Lorentz-Berthelot rules to describe the unlike interaction.

1. Introduction

Cyclic molecular structures are very common in nature. Consequently, the study of their thermodynamic behaviour, in particular cycloalkanes, has always been a matter of great interest and an attractive research field from both experimental and theoretical points of view [1]. However, the number of theoretical approaches, which can provide a reliable and accurate description of the thermodynamic behaviour of cyclic molecules and their mixtures, is rather small, compared with those dealing with linear molecules. *n*-Alkanes and cycloalkanes, though essentially formed by the same type of chemical units (CH_2 groups), display rather different physical behaviour either as pure substances or in mixtures. Many studies have compared the thermodynamic behaviour exhibited by cycloalkanes with that of their corresponding *n*-alkanes, i.e., linear molecules with the same number of carbon atoms. In general, it is found that cycloalkanes are less volatile, denser and have higher vapourization enthalpies than their linear analogues. This has been interpreted as a result of stronger attractive interactions between cyclic molecules, ultimately due to their different molecular structure (electronic structure and shape) and organization in the liquid state [1].

Cycloalkanes can be divided into three categories: (1) long chain cycloalkanes, with more than 9 carbon atoms. These adopt molecular conformations that basically resemble double chain linear alkanes; (2) medium chain cycloalkanes, 6–9 carbon atoms. These molecules, of which cyclohexane is by far the most studied one, are quasi-spherical globular molecules. They can act as 'structure breakers' when mixed with long *n*-alkanes, i.e., they disrupt the short-range orientational order of *n*-alkanes, giving rise to positive contributions to the excess enthalpies and entropies; (3) short cycloalkanes, with 5 carbon atoms or less. These are rigid, plate like anisotropic rotors. Rotations around C–C bonds are hindered, resulting in almost eclipsed conformations of the CH_2 groups. The distortion of the bond angles causes a large strain and displaces the electronic density out of the ring. These important differences at the molecular level could be expected to influence the intermolecular interactions between CH_2 groups of small cycloalkanes [1].

Liquid state properties are known to depend considerably on the organization of the fluid, for which molecular shape (repulsion forces) is a key factor. With that in mind, we have undertaken a number of studies with the purpose of assessing the

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effect of the molecular shape on the thermodynamic behaviour of liquid mixtures, in particular those involving cyclic molecules [2,3]. From the experimental point of view, binary mixtures such as xenon + cyclopropane [4] and xenon + cyclobutane [5] have been investigated and the results compared with those of mixtures containing the linear analogues xenon + propane [6] and xenon + butane [7]. In general, we have found that mixtures containing a cyclic component exhibit larger positive deviations from Raoult's Law (and consequently larger values of G^E), but more negative excess volumes and enthalpies than those containing a linear analogue. These results have been explained using the so-called "condensation" effect proposed in the 1970s by Patterson et al. [8]. According to this effect, linear alkanes would "condense" at the surface of highly branched, rigid and sterically hindered molecules, with a restriction of its molecular motion and hence giving rise to negative contributions to excess enthalpies and entropies and positive additions to excess heat capacities. This effect was also used to explain the results exhibited by mixtures involving cyclopentane [9,10], whose plate-like anisotropic molecular structure would favour the condensation of *n*-alkanes on its surface. Since cyclopropane and cyclobutane are also plate-like anisotropic rotors, it was suggested that a "condensation" type phenomenon could arise between these molecules and xenon, a particle with a high polarizability, which enhances the dispersion forces [4,5].

In order to accurately predict the thermodynamic properties of complex systems from a theoretical point of view, it is essential to incorporate explicitly the molecular features of a given system. There are in the literature a number of approaches to predict the thermodynamic properties of complex substances and their mixtures. In this work we focus on the use of a molecular-based formalism, the so-called *soft*-SAFT equation of state proposed by Blas and Vega [11,12]. We suggest the book of Sengers et al. [13] for readers interested on the details of this and other molecular theories.

The Statistical Associating Fluid Theory (SAFT) is a molecular-based equation of state, originally proposed by Chapman et al. [14,15] based on Wertheim's first-order Thermodynamic Perturbation Theory [16–21], specially suited to predict the thermodynamic properties of chain molecules and associating substances. In this approach, the different microscopic effects are accounted for in several contributions to the Helmholtz free energy. In particular, the theory explicitly takes into account the molecular non-sphericity of chain molecules, flexibility, and specific interactions (hydrogen bonding), among others. Since its development, the SAFT approach has been used to predict the phase equilibria of a wide variety of pure components and their mixtures, and it is presently considered one of the most powerful predictive tools for the study of the fluid phase equilibria. For a more detailed description, we recommend the reviews of Müller and Gubbins [22] and Radosz et al. [23]. More recently, there have been new developments related with the formalism of SAFT that are not included in the previous reviews [24–26].

In this work we have extended the study of systems involving xenon and cyclic molecules to consider xenon + cyclopentane solutions. The solubility of xenon in liquid cyclopentane has been measured as a function of temperature from 254 K to 314 K and Henry's law coefficients calculated. This system had been previously studied by Pollack et al. [27] in the range 278.15–303.15 K. The present work not only doubles the temperature range of the available results, but also provides experimental data with a precision that allows the calculation of the thermodynamic properties of solvation as a function of temperature and therefore the calculation of second derivative properties, such as the heat capacity of solvation.

The results were interpreted using an extension of the *soft*-SAFT equation of state that deals with ring molecular structures [3,28]. For comparison, we have also calculated the solubility of xenon in *n*-pentane. This procedure allows examining the effect of changing a linear alkane by a cyclic alkane on the thermodynamic properties of a given mixture.

2. Experimental

The cyclopentane used as solvent was from Acros, analytical reagent, with 99% (mol/mol) minimum stated purity. The liquid was purified by distillation in an inert atmosphere of dry nitrogen. The final purity was confirmed by checking its vapour pressure, after degasification, at two temperatures. Deviations from literature values [29] were found to be 0.39% at 258.33 K and −0.21% at 277.17 K. The xenon used was from Linde Gas with 99.99% (mol/mol) minimum stated purity. The gas was used as received from the manufacturer.

The experimental apparatus and procedure have been previously described in detail [30]. The solubility measurements involve the equilibration of known amounts of dry gas and degassed solvent at constant volume and the determination of the equilibrium pressure for the saturated solution maintained at a constant temperature.

The amount of gas is determined measuring its pressure in a calibrated glass bulb at constant temperature and correcting for gas non-ideality. Pressure is measured with a transducer (Paroscientific model 0–7 bar, precision 0.01% FS). The pure solvent is degassed by successive melting/freezing cycles, while vacuum pumping non-condensable gases. The amount of pure solvent is determined volumetrically. The equilibrium cell, based on the design of Carnicer [31], has two capillaries through which the liquid is forced to circulate during the equilibration process, promoting a close contact with the gas. The volume of the cell was previously determined with a precision of 0.01%. The readings of pressure during the dissolution process are recorded until a constant value is reached indicating that equilibrium has been attained. The final pressure, temperature and level of the solution in the capillaries are then measured. Equilibrium is typically attained within 72 h.

Temperature is maintained constant in a water thermostat to within 0.01 K by means of a Hart Scientific PID temperature controller, and is measured with a previously calibrated Pt100 platinum resistance thermometer. The measurement of solubility at different temperatures is done by simply changing the thermostat set point and waiting for a new thermodynamic equilibrium. With a single loading it is thus possible to make measurements over a large temperature range. Several runs were performed in order to check the reproducibility of the results, both increasing and decreasing temperature.

3. Experimental results

The solubility of xenon in cyclopentane was experimentally measured from 254.60 K to 313.66 K. The results are reported in Table 1. For each experimental point, the temperature, equilibrium pressure, molar fractions of xenon in the liquid and gaseous phases in equilibrium and Henry's law coefficients, $H_{2,1}(T, p_1^{sat})$, are indicated.

Henry's law coefficients were calculated from experimental data as follows. Henry's law coefficients are usually defined as [32],

$$H_{2,1}(T,p) = \lim_{x_2 \to 0}\left[\frac{f_2(p,T,x_2)}{x_2}\right] \tag{1}$$

where f_2 is the fugacity of the solute (component 2) and x_2 its molar fraction in the liquid solution. The fugacity of component 2 can then be determined in the usual way [33]:

$$f_2(p,T,x_2) = \varphi_2(p,T)y_2p \tag{2}$$