international journal of refrigeration 34 (2011) 2109–2117

available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/ijrefrig

# Solubility of nitrogen in one-component refrigerants: Prediction by PC-SAFT EoS and a correlation of Henry's law constants

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ARTICLE INFO

*Article history:*
Received 5 March 2011
Received in revised form
10 July 2011
Accepted 13 July 2011
Available online 23 July 2011

*Keywords:*
Equation of state
Nitrogen
Non-condensable gas
Refrigerant
Solubility

ABSTRACT

Even small amount of non-condensable gas – mostly air or nitrogen – present inside a compression refrigerating circuit may decrease the efficiency of the cooling system. So far, a quantitative assessment of the effect of dissolved gases on the cooling circuit performance is hindered by unavailability of suitable thermodynamic models. In this study, we analyzed the solubility of nitrogen in the following refrigerants: hydrochlorofluorocarbons (HCFC) R22, R123, R124; hydrofluorocarbons (HFC) R23, R32, R125, R134a; perfluorocarbons (PFC) R14, R116, R218, R-3-1-10; and hydrocarbons (HC) R290, R600a. Perturbed-Chain (PC) Statistical Associating Fluid Theory (SAFT) and its modification for polar fluids PCP-SAFT were used to model the temperature dependence of the Henry's law constant of nitrogen. A simple correlation of the Henry's law constants valid over large temperature ranges was developed, suitable for assessment of the adverse effects of dissolved nitrogen (and approximately air) on the performance of compression cooling systems.



# Solubilité de l'azote dans les frigorigènes à un seul composant : prévision par l'équation d'état PC-SAFT et par corrélation des constantes de la loi de Henry

*Motsclés* : Équation d'état ; Azote ; Gaz non condensable ; Frigorigène ; Solubilité

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doi:10.1016/j.ijrefrig.2011.07.002

**Nomenclature**

| | |
|---|---|
| $A$ | coefficient |
| $C$ | number of carbons |
| $k_B$ | Boltzmann constant (J $K^{-1}$) |
| $k_H$ | Henry's law constant (Pa) |
| $m$ | segment number |
| $N$ | number of data points |
| $p$ | pressure (Pa) |
| $s$ | standard deviation (%) |
| $T$ | temperature (K) |
| $x$ | mole fraction |
| $y$ | mole fraction |
| $z$ | general variable |

*Greek letters*

| | |
|---|---|
| $\delta$ | average deviation (%) |
| $\varepsilon$ | energy parameter (J) |
| $\phi$ | fugacity coefficient |
| $\mu$ | dipole moment (D) |
| $\rho$ | density (mol $m^{-3}$) |
| $\sigma$ | segment diameter (Å = $10^{-10}$ m) |

*Subscripts*

| | |
|---|---|
| A | solvent (refrigerant) |
| B | solute (nitrogen) |
| cal | calculated value |
| cond | condensation |
| crit | conditions at the critical point |
| i | index |
| exp | experimental value |
| H | Henry |
| L | liquid phase |
| min | minimum |
| max | maximum |
| r | reduced |
| V | vapor |

# 1. Introduction

## 1.1. *Non-condensing gases in cooling circuit*

As it has been discussed by Downing (1988), Cecchinato et al. (2007), or Cavestri and Seeger-Clevenger (2008), the refrigerant charge of a cooling circuit may get contaminated by non-condensing gases after some operational time. Moreover, some amount of dry air, nitrogen, or other gases may remain inside the circuit already during its manufacturing (Cavestri and Seeger-Clevenger, 2008). Even a small amount of non-condensing gases inside the refrigerant charge can result in a significant decrease of the cooling efficiency and can cause a damage of the system (Cecchinato et al., 2007). Presence of the non-condensing gases inside the cooling circuit can be detected by increased condensing pressure $p_{cond} > p_{A,V}(T_{cond})$. Cecchinato et al. (2007) stated that the main effect of non-condensing gases on the performance of a small vapor cooling circuit is the clogging effect of gaseous bubbles generated during the throttling process inside the capillary tube. However, as reported in our previous studies (Vinš and Vacek, 2009; Vinš et al., 2010), the non-condensing gases accumulated inside the condenser or liquid receiver partially dissolve in the liquid refrigerant and travel along the whole cooling system. Therefore, the gas impurities can affect large cooling units and not only the small systems with reduced internal volumes.

The main property describing the solubility of non-condensing gases in the liquid refrigerant is the Henry's law constant $k_H$. The Henry's law is written in its simplified form as follows:

$$p_B = p - p_A = k_H x_B \quad (1)$$

where $x_B$ denotes the mole fraction of non-condensing gas in the liquid phase, $p$ is the total pressure, $p_A$ is the solvent (refrigerant) partial pressure, and $p_B$ marks the solute (gas impurity) partial pressure. Because the molar fraction of dissolved nitrogen is small in cases relevant to refrigeration, it is mostly sufficient to consider the Henry's law in the form of Eq. (1). However, the Henry's law constants computed and correlated in this work are based on the proper thermodynamic definition of $p_H$ for non-ideal mixtures.

In general, knowledge of the temperature-dependent Henry's law constant can improve the prediction and mitigation of the unfavorable effect of non-condensing gases on the cooling circuit performance.

## 1.2. *Nitrogen dissolved in refrigerants*

In many applications, the nitrogen and dry air are found as the main gases polluting the refrigerant charge (Cavestri and Seeger-Clevenger, 2008). These gases are used for the pressure tests or as the surrounding environment of the evaporator structures (Attree et al., 2008). Unfortunately, the availability of Henry's law constant correlations for nitrogen and dry air dissolved in various refrigerants is very limited. Besides, most correlations are not valid over sufficient temperature ranges, which makes them unsuitable for cooling applications.

Battino et al. (1984) introduced a comprehensive database of correlations for nitrogen solubility in various substances, including some common refrigerants. However, extrapolations of the correlations outside the temperature and pressure ranges of the fitted experimental data are rather questionable. Recently, Vrabec et al. (2009) and Huang et al. (2009) used the approach of molecular simulation to predict vapor–liquid equilibrium (VLE) of a large number of binary mixtures. In addition, Vrabec et al. (2009) evaluated binary interaction parameters for Peng and Robinson (1976) equation of state (EoS) for 267 binary mixtures, including 16 mixtures with nitrogen. Huang et al. (2009) predicted the Henry's law constant from molecular simulation for 95 binary systems including some CFC refrigerants, namely R113 and R114.

In the present study, we focus on nitrogen. Nitrogen solubility is also considered as a reasonable estimate for the