

## ABSORPTION OF REFRIGERANT MIXTURES IN LUBRICANT OIL

**Tobias R. Gessner**

Universidade Federal de Santa Catarina, Departamento de Engenharia Mecânica, Florianópolis, SC, 88040-900, Brazil.  
[tobias@nrva.ufsc.br](mailto:tobias@nrva.ufsc.br)

**Jader R. Barbosa Jr.**

Universidade Federal de Santa Catarina, Departamento de Engenharia Mecânica, Florianópolis, SC, 88040-900, Brazil.  
[jrb@nrva.ufsc.br](mailto:jrb@nrva.ufsc.br)

**Abstract.** A methodology is proposed to calculate the absorption of a binary refrigerant mixture in lubricant oil. The model is based on an apparent diffusion coefficient formulation that accounts for both molecular diffusion and macroscopic motion due to density instability in the liquid phase. Diffusion in the vapour and liquid phases are coupled with a thermodynamic model for interfacial equilibrium. Results are compared with experimental data available in the literature for absorption of R410a in a stagnant layer of Polyol-Ester Oil (POE68). The adequacy of the formulation will be assessed in light of the basic assumptions and performance of the model.

**Keywords:** Absorption, apparent diffusion coefficient, refrigerant-oil mixtures.

### 1. Introduction

In refrigeration systems where capillary tubes are used as expansion devices, the problem of refrigerant (vapour) absorption in the lubricant oil in the compressor is of crucial importance to the determination of the system equalizing pressure. In reciprocating compressors, for example, high absorption rates of refrigerant are desirable since lower equalizing pressure means reduced torque and power required for compressor start-up.

Solubility and vapour-liquid equilibrium data for refrigerant-oil mixtures, as well as information on the transient behaviour during absorption, are important parameters in the selection of the most appropriate lubricants, especially those for HFC refrigerants and their mixtures, i.e., the polyol esters (POE) and poly-alkylene glycols (PAG).

The present paper extends the theory advanced by Sell and Barbosa (2004) for absorption of pure refrigerants in lubricant oil using an apparent diffusivity formulation (Fukuta *et al.*, 1995). A review of the literature on diffusion of refrigerants in lubricant oil and on the development of the apparent diffusion theory is available in Sell and Barbosa (2004) and will not be repeated here.

Rates of absorption of refrigerants by a polyol ester (ISO 68) were measured by Goswami *et al.* (1998) over a wide range of constant pressure and temperature conditions. The following pure refrigerants and mixtures were analysed: R-134a, R-143a, R-125, R-32, R-404a (44% of R-125, 52% of R-143a and 4% of R-134a by mass), R-407c (23% of R-32, 25% of R-125 and 52% of R-134a by mass) and R-410a (50% of R-32 and 50% of R-125 by mass). Goswami *et al.* correlated the instantaneous volume averaged liquid mass fraction as follows

$$\langle x_R \rangle = x_I (1 - e^{-Kt}) \quad (1)$$

where  $x_R$  is the refrigerant mass fraction,  $\langle \rangle$  is a volume average operator,  $x_I$  is the refrigerant solubility,  $K$  is an absorption rate and  $t$  is time.

The work presented here employs the apparent diffusivity formulation to predict the absorption of R-410a in POE68. It is postulated that interaction effects (Toor, 1957) are not present and the effective apparent diffusivity of each component (R-32 or R-125) in the liquid mixture is equal to that of each component if it were alone in the oil. The apparent diffusivity for each oil-refrigerant pair is obtained from a one dimensional absorption theory that utilizes the instantaneous volume averaged mass fraction data of Goswami *et al.* (1998) in conjunction with an error minimization procedure (Sell and Barbosa, 2004). Section 2 of this manuscript presents the model geometry and governing equations for the binary (single refrigerant plus oil) and ternary (binary refrigerant plus oil) cases. The implementation of the binary and ternary cases is discussed in Section 3 and the results for the ternary case are presented in Section 4. The adequacy of the formulation in predicting absorption of refrigerant mixtures is assessed in the light of the basic assumptions and performance of the model. Finally, conclusions are presented in Section 5.

### 2. Modelling

#### 2.1. The binary case

As done previously (Sell and Barbosa, 2004), the problem geometry (see Fig. 1) models itself on the experiments of Goswami *et al.* (1998). Initially, the liquid layer is comprised by oil only and this initial amount of oil is always known.

For simplicity, it is assumed that the oil is a single species. Pressure and temperature are kept constant for every experimental run. A one-dimensional model for the transport of a single component refrigerant in the liquid phase is given by

$$\frac{\partial}{\partial t} \rho_{RL} - v_{zL} \frac{\partial}{\partial z} \rho_{RL} = \frac{\partial}{\partial z} \left( D \frac{\partial}{\partial z} \rho_{RL} \right) \quad (2)$$

where  $\rho_{RL}$  is the mass concentration of refrigerant in the liquid phase,  $v_{zL}$  is the liquid phase velocity and  $D$  is the molecular diffusion coefficient of the refrigerant in the liquid mixture.

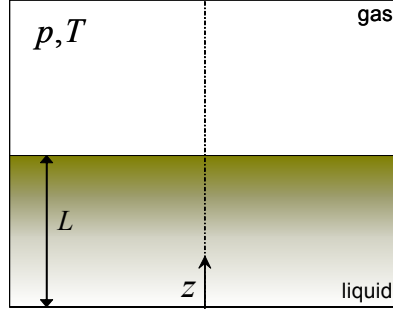


Figure 1. A schematic description of the problem geometry.

Through definition of an apparent diffusion coefficient,  $D_{ap}$ , it is possible to combine the advective and diffusive terms into an apparent diffusive term as follows

$$\frac{\partial}{\partial t} \rho_{RL} = \frac{\partial}{\partial z} \left( D_{ap} \frac{\partial}{\partial z} \rho_{RL} \right) \quad (3)$$

where initial and boundary conditions for Eq. (3) are given by

$$\rho_{RL} = \rho_{RL,0}; \quad \text{at } 0 \leq z \leq L(t) \text{ and } t = 0 \quad (4.a)$$

$$\rho_{RL} = \rho_{RL,i}; \quad \text{at } z = L(t) \quad (4.b)$$

$$\frac{\partial}{\partial z} \rho_{RL} = 0; \quad \text{at } z = 0 \quad (4.c)$$

In Eq. (4.a),  $\rho_{RL,0}$  is the initial mass concentration of refrigerant in the liquid (set to zero if the liquid layer is initially made up of oil only). Equation (4.b) reflects the assumption of phase equilibrium at the interface (subscript  $i$ ). Scaling analyses (Sell and Barbosa, 2004) revealed that the variation of the height of liquid layer,  $L(t)$ , as a result of refrigerant absorption was negligible in the experiments of Goswami *et al.* (1998). This is because the solubility of the refrigerant in the liquid is small. Therefore,  $L$  is assumed constant in the model. By definition, the local mass fraction is given by

$$x_R = \rho_{RL} / \rho_L \quad (5)$$

Therefore, Eqs. (3) and (4) can be written as (for a constant apparent diffusion coefficient)

$$\frac{\partial}{\partial t} x_R = D_{ap} \frac{\partial^2 x_R}{\partial z^2} \quad (6)$$

$$x_R = x_{R,0}; \quad \text{at } 0 \leq z \leq L \text{ and } t = 0 \quad (7.a)$$

$$x_R = x_i; \quad \text{at } z = L \quad (7.b)$$

$$\frac{\partial}{\partial z} x_R = 0; \quad \text{at } z = 0 \quad (7.c)$$

where  $\rho_L$  is the local liquid density and  $x_i$  is the refrigerant solubility obtained from the experimental results of Goswami *et al.* (1998) for each condition. Analytical solutions of Eqs. (6) and (7) are available in several texts (Crank, 1975; Mikhailov and Ozisik, 1994), and were used to model absorption of single component refrigerants in lubricant oil (Yokozeki, 2002; Sell and Barbosa, 2004).

## 2.2. The ternary case

In dealing with absorption of a binary refrigerant mixture (e.g., R-410a) in lubricant oil, one must model the mass transfer processes in the liquid and vapour phases as well as the interfacial mass balance. In the present work, the apparent diffusivities in the liquid phase are modelled as effective diffusivities as follows (Taylor and Krishna, 1993)

$$\frac{\partial}{\partial t}(x_R) = [D_{ap}] \frac{\partial^2(x_R)}{\partial z^2} \quad (8)$$

where the liquid phase mass fraction and the apparent diffusivity matrix are given by

$$(x_R) = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}; [D_{ap}] = \begin{bmatrix} D_{ap1,3} & 0 \\ 0 & D_{ap2,3} \end{bmatrix}. \quad (9.a,b)$$

The effective diffusivity formulation assumes that interaction effects (Toor, 1957) do not contribute to mass transfer in the mixture, i.e., the mass transfer of a given species depends only on its concentration gradient and not on that of the other components. In other words, it implies that the diffusion of components 1 and 2 in the mixture takes place as if they were alone in an arbitrarily chosen species (e.g., species 3) at the same concentration. The solution of the system of equations for the liquid phase (Eq. 8) is thus simpler for the effective diffusivity approach because the assumption of zero non-diagonal diffusivities in Eq. 9.b results in uncoupled mass fraction profiles for species 1 and 2. This simplified approach, however, tends to be valid only when the species are chemically alike. This is certainly not true for refrigerants and lubricant oil and a justification for using the effective diffusivity method in the present study will be provided later in the manuscript.

Initial and boundary conditions for Eq. 8 are identical to those for the binary case

$$(x_R) = (x_R)_0; \quad \text{at } 0 \leq z \leq L \quad \text{and } t = 0 \quad (10.a)$$

$$(x_R) = (x_R)_I; \quad \text{at } z = L \quad (10.b)$$

$$\frac{\partial}{\partial z}(x_R) = 0; \quad \text{at } z = 0 \quad (10.c)$$

Solving Eqs. 9-10 for the liquid phase mass fractions of components  $i = 1, 2$  gives

$$\frac{x_i - x_{i,0}}{x_{I,i} - x_{i,0}} = \sum_{n=1}^{\infty} C_n \exp\left(-\zeta_n^2 \frac{D_{ap1,3} t}{L^2}\right) \cos\left(\zeta_n \frac{z}{L}\right) \quad (11)$$

where

$$C_n = \frac{4 \sin(\zeta_n)}{2\zeta_n + \sin(2\zeta_n)}; \quad \zeta_n = \pi \frac{(2n-1)}{2} \quad (12.a,b)$$

The instantaneous volume averaged mass fraction of component  $i$  is given by

$$\langle x_i \rangle = x_{I,i} + (x_{i,0} - x_{I,i}) \sum_{n=1}^{\infty} C_n \exp\left(-\zeta_n^2 \frac{D_{ap1,3} t}{L^2}\right) \frac{\sin(\zeta_n)}{\zeta_n} \quad (13)$$

In the vapour phase, assumed semi-infinite, diffusion is governed by Fick's Second Law as follows

$$\frac{\partial}{\partial t} y_1 = D_G \frac{\partial^2 y_1}{\partial z^2} \quad (14)$$

$$y_1 = y_{1,0}; \quad \text{at } L \leq z \leq \infty \quad \text{and } t = 0 \quad (15.a)$$

$$y_1 = y_{I,1}; \quad \text{at } z = L \quad (15.b)$$

$$y_1 = y_{1,0}; \quad \text{at } z = \infty \quad (15.c)$$

In the above equations,  $x_i$  and  $y_i$  stand for the liquid and vapour phase mass fractions of component  $i$ . Subscripts 1 and 2 refer to the two species of refrigerant that form the refrigerant blend and subscript 3 denotes the oil. Subscript  $I$  denotes to the property evaluated at the liquid-vapour interface. Solving the equations for the vapour phase gives

$$\frac{y_1 - y_{I,1}}{y_{I,0} - y_{I,1}} = \text{erf} \left[ \frac{(z - L)}{2\sqrt{D_G t}} \right] \quad (16)$$

The species conservation at the interface is governed by the following set of equations

$$\dot{m}_I (y_{I,1} - x_{I,1}) = -\rho_G D_G \left. \frac{\partial y_1}{\partial z} \right|_{z=L} - \rho_L D_{ap1,3} \left. \frac{\partial x_1}{\partial z} \right|_{z=L} \quad (17.a)$$

$$\dot{m}_I (y_{I,2} - x_{I,2}) = -\rho_G D_G \left. \frac{\partial y_2}{\partial z} \right|_{z=L} - \rho_L D_{ap2,3} \left. \frac{\partial x_2}{\partial z} \right|_{z=L} \quad (17.b)$$

where the interfacial gradients of liquid and vapour mass fractions are evaluated through Eqs. (11) and (16). Thermodynamic equilibrium is assumed at the phase interface. Thus

$$x_{I,1} + x_{I,2} + x_{I,3} = 1 \quad (18)$$

$$y_{I,1} + y_{I,2} = 1 \quad (19)$$

$$K_1 = \frac{\tilde{y}_{I,1}}{\tilde{x}_{I,1}} \quad K_2 = \frac{\tilde{y}_{I,2}}{\tilde{x}_{I,2}} \quad (20.a,b)$$

In the relationships above, the superscript  $\sim$  denotes molar quantities and  $K_i$  are the equilibrium ratios calculated from (Bett et al., 1975)

$$K_i = \frac{\gamma_i p_i^{sat} \phi_i^{sat} Pe}{p \phi_i} \quad (21)$$

where  $Pe$  is the Poynting factor,  $p$  is the system pressure,  $p_i^{sat}$  is the saturation pressure of component  $i$  at the system temperature ( $T$ ),  $\phi_i$  is the fugacity coefficient of component  $i$  at  $p$  and  $T$ ,  $\phi_i^{sat}$  is the fugacity coefficient of component  $i$  at  $p_i^{sat}$  and  $T$  and  $\gamma_i$  is the activity coefficient of component  $i$ .

### 3. Implementation

#### 3.1. The binary case

The purpose of the binary case analysis in the present paper is to determine the apparent diffusion coefficient for each refrigerant-oil pair as a function of pressure and temperature (Sell and Barbosa, 2004). This is performed through a minimization procedure of an objective function (Eq. 22) using the instantaneous volume averaged mass fractions calculated through Eq. (13) and the instantaneous average refrigerant mass fractions obtained experimentally by Goswami *et al.* (1998) (Eq. 1)

$$Ob = \frac{1}{N} \sum_{i=1}^N \left| \langle x_R \rangle_{cal,i} - \langle x_R \rangle_{exp,i} \right| \quad (22)$$

where  $N$  is the number of experimental points obtained at different times along an absorption experiment and the subscripts *calc* and *exp* stand for calculated and experimental, respectively. The apparent diffusion coefficients for the oil-refrigerant pairs are then used in the main diagonal of the apparent diffusion coefficient matrix of the ternary case. Table 1 summarizes the apparent diffusion coefficients for the binary pairs.

Table 1. Apparent diffusion coefficients for the binary oil-refrigerant pairs.

R-134a			
$p$ [kPa]	$x_i$ [-]	$D_{ap}$ [ $10^{-10} \text{ m}^2/\text{s}$ ]	$Ob$ [ $10^{-3}$ -]
239	0.0856	2.142	1.9971
308	0.1252	2.374	2.7879
446	0.2109	3.394	3.5258
R-32			
$p$ [kPa]	$x_i$ [-]	$D_{ap}$ [ $10^{-10} \text{ m}^2/\text{s}$ ]	$Ob$ [ $10^{-3}$ -]
239	0.0160	2.243	0.5195
446	0.0272	1.831	0.5902
584	0.0670	2.569	1.3552
R-125			
$p$ [kPa]	$x_i$ [-]	$D_{ap}$ [ $10^{-10} \text{ m}^2/\text{s}$ ]	$Ob$ [ $10^{-3}$ -]
239	0.0675	4.202	0.4187
446	0.1060	1.994	1.6970
584	0.1536	2.136	3.2902

Figures (2), (3) and (4) illustrate the absorption of R-32, R-125 and R-134a in lubricant oil POE68, respectively. Results are presented in terms of the volume averaged liquid mass fraction of refrigerant as a function of time (Sell and Barbosa, 2004). The temperature is maintained constant at 24°C in all cases, whereas the variation of pressure is assessed at three different levels according to Table 1.

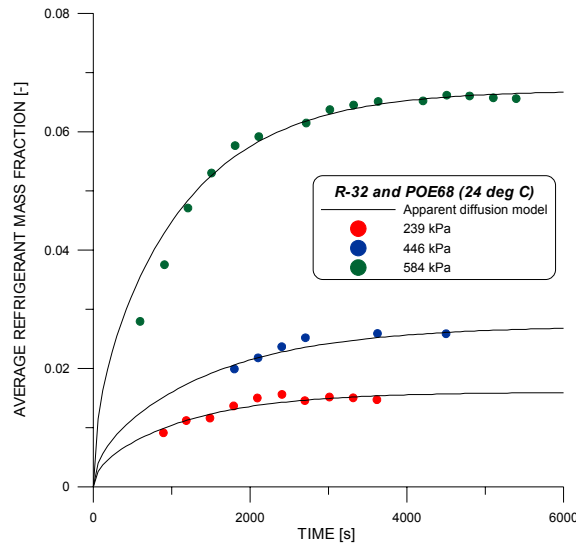


Figure 2. Absorption of R-32 in POE68 at 24°C and different pressures.

### 3.2. The ternary case

In the ternary case, the solution strategy is to use the adjusted binary apparent diffusion coefficients in the mass transfer model for the liquid phase. In this model, the governing equations for the liquid (Eq. 11) and for the vapour (Eq. 16) are solved simultaneously and, at each time step, boundary conditions are provided by interfacial transport and equilibrium relationships (Eqs. 17-20). The interfacial concentrations in both phases and the total interfacial mass flux are calculated from Eqs. (17)-(20) through a multidimensional Newton-Raphson algorithm as described in Taylor and Krishna (1993). The vapour diffusion coefficient is calculated with the Wilke and Lee model (Poling *et al.*, 2000).

#### 4. Results

This section presents the results for absorption of R-410a in POE-68. Figure 5 shows the instantaneous volume averaged liquid phase mass fraction of refrigerant as a function of time for two different pressures. As can be seen, the experimental data are represented well by the formulation. However, the experimental data are consistently underpredicted and, therefore, the deviations are more pronounced than in the binary cases from which the binary apparent diffusion coefficients were derived. Such discrepancies may be justified by the existence of interaction effects (neglected with the assumption of non-diagonal coefficients equal to zero) associated with the lack of similarity between the refrigerants and oil species, or even with the influence of natural convection effects. In a sense, the use of the effective apparent diffusion formulation may be justified by the lack of knowledge about the true molecular diffusivity of refrigerants in oils.

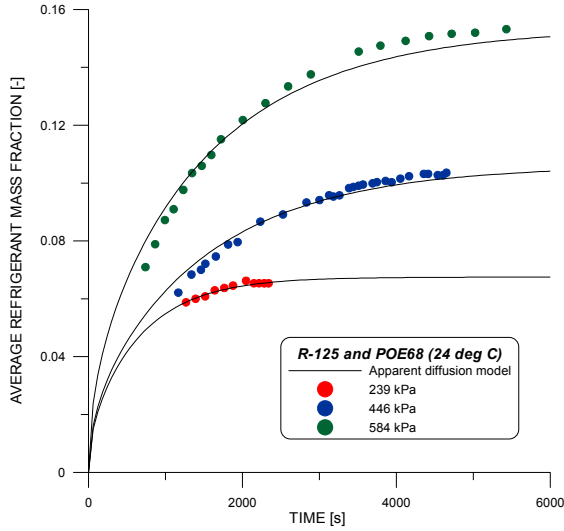


Figure 3. Absorption of R-125 in POE68 at 24°C and different pressures.

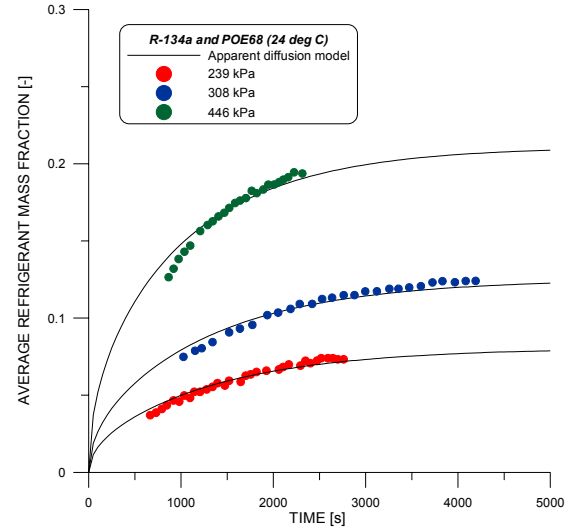


Figure 4. Absorption of R-134A in POE68 at 24°C and different pressures.

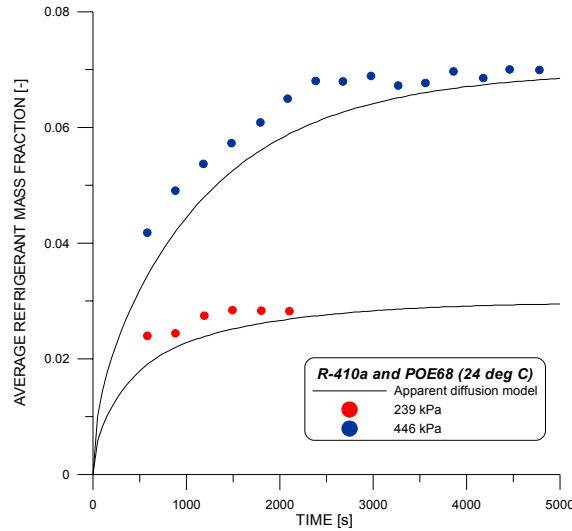


Figure 5. Absorption of R-410a in POE68 at 24°C at different pressures.

Despite continued efforts, there is a dearth of experimental data and calculation methodologies for predicting vapour-liquid equilibrium (VLE) in oil-refrigerant mixtures, especially for the case of refrigerant blends such as R-410a and R-407c. One of the few databases available for such cases is that of Burton *et al.* (1999), where VLE data for R-32

and R-410a with POE68 were generated for a range of pressure and temperature conditions and were correlated successfully by several activity models. As far as the present methodology is concerned, it was concluded that the activity models correlated by Burton *et al.* (1999) could not be used because the pressure and the liquid refrigerant compositions (i.e., solubility) in the experiments of Goswami *et al.* (1998) were much lower than (and therefore outside the range covered by the adjusted model parameters) those correlated by Burton *et al.* (1999). As a best estimate, the activity coefficients for each refrigerant used here (Eq. 21) were obtained directly from an extrapolation of the graphical data of Burton *et al.* (1999) at 24°C.

The interfacial mass fluxes (total and of R-32 and R125) in the high pressure case (446 kPa) are shown in Fig. 6. As absorption of the refrigerant components in the liquid mixture takes place, the driving forces for mass transfer become smaller and the components mass fluxes tend asymptotically to zero as time increases.

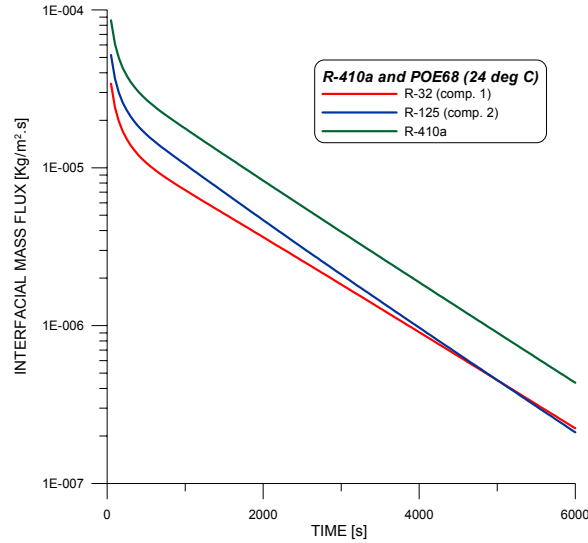


Figure 6. Behaviour of interfacial mass fluxes with time. High pressure case.

The individual interfacial mass fluxes of R-32 (component 1) and R-125 (component 2) are calculated from Eqs. (17) as follows

$$\dot{m}_{I,1} = x_{I,1}(\dot{m}_{I,1} + \dot{m}_{I,2}) - \rho_L D_{ap1,3} \left. \frac{\partial x_1}{\partial z} \right|_{z=L} = y_{I,1}(\dot{m}_{I,1} + \dot{m}_{I,2}) - \rho_G D_G \left. \frac{\partial y_1}{\partial z} \right|_{z=L} \quad (23.a)$$

$$\dot{m}_{I,2} = x_{I,2}(\dot{m}_{I,1} + \dot{m}_{I,2}) - \rho_L D_{ap2,3} \left. \frac{\partial x_2}{\partial z} \right|_{z=L} = y_{I,2}(\dot{m}_{I,1} + \dot{m}_{I,2}) - \rho_G D_G \left. \frac{\partial y_2}{\partial z} \right|_{z=L} \quad (23.b)$$

Figures 7 and 8 illustrate the behaviour of the interfacial liquid and vapour mass fractions with time for the high pressure case (446 kPa). As can be seen, in both phases the behaviour of concentrations is asymptotic towards the equilibrium value.

## 5. Conclusions

This paper utilized the concept of apparent molecular diffusion (Fukuta *et al.*, 1995) to describe the absorption of pure and mixed refrigerants by stagnant oil. A one-dimensional absorption model combined with a minimization procedure were conformed to the experimental data of Goswami *et al.* (1998) in order to provide apparent diffusion coefficients for a given oil-refrigerant pair under different pressure-temperature conditions. The binary diffusion coefficients were used in a multicomponent diffusion model to predict absorption rates and average mass fractions in absorption of R-410a (50% of R-32 and 50% of R-125 by mass) in POE68.

The multicomponent method calculated the liquid and vapour mass transfer and both phenomena were coupled with an interfacial transfer model. The liquid phase mass transfer was modelled with an effective diffusivity formulation that neglects interaction effects (Toor, 1957). The results for average mass fraction agreed well with, but slightly underpredicted, the experimental data of Goswami *et al.* (1998).

More experimental and theoretical work is needed to provide a better understanding of VLE and absorption of pure refrigerants and refrigerant blends in lubricant.

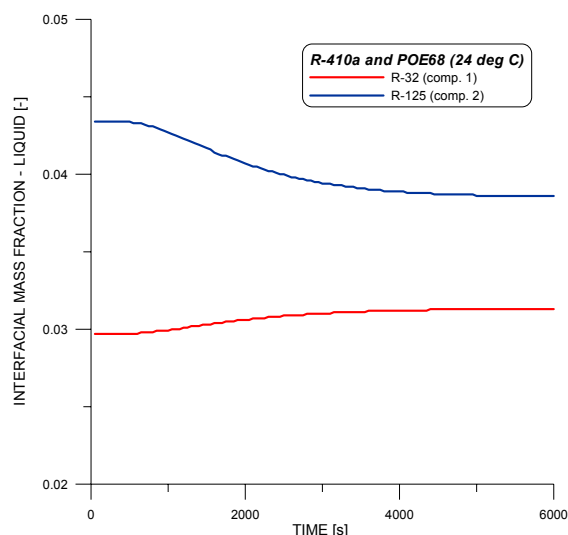


Figure 7. Interfacial concentration in the liquid phase. High pressure case.

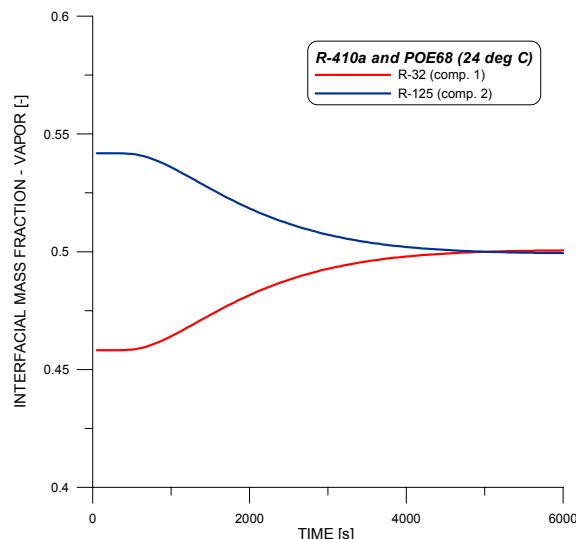


Figure 8. Interfacial concentration in the vapour phase. High pressure case.

## 6. Acknowledgements

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