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Solubility Modeling of Refrigerant/Lubricant Mixtures

H. Harvey Michels and Tobias H. Sienel
United Technologies Research Center, East Hartford, CT 06108

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Abstract

A general model for predicting the solubility properties of refrigerant/lubricant mixtures has been developed based on applicable theory for the excess Gibbs energy of non-ideal solutions. In our approach, flexible thermodynamic forms are chosen to describe the properties of both the gas and liquid phases of refrigerant/lubricant mixtures. After an extensive study of models for describing non-ideal liquid effects, the Wohl [3]-suffix equations, which have been extensively utilized in the analysis of hydrocarbon mixtures, have been developed into a general form applicable to mixtures where one component is a POE lubricant. In the present study we have analyzed several POEs where structural and thermophysical property data were available. Data were also collected from several sources on the solubility of refrigerant/lubricant binary pairs. We have developed a computer code (NISC), based on the Wohl model, that predicts dew point or bubble point conditions over a wide range of composition and temperature. Our present analysis covers mixtures containing up to three refrigerant molecules and one lubricant. The present code can be used to analyze the properties of R-410a and R-407c in mixtures with a POE lubricant. Comparisons with other models, such as the Wilson or modified Wilson equations, indicate that the Wohl [3]-suffix equations yield more reliable predictions for HFC/POE mixtures.

Introduction

The addition of lubricants to refrigerants, either single component hydrofluorocarbons or the newer multicomponent blends, is necessary to reduce bearing friction and to minimize gas leakage at gaskets and fittings. The primary considerations in choosing a lubricant are its chemical compatibility with the refrigerant type and the required viscosity for the service application. In the case of refrigerant blends, a new problem arises since the individual refrigerant components may exhibit different solubilities in the lubricant. These different component solubilities can give rise to fractionation (distillation) effects in the evaporator, condenser or compressor sump which differ from the vapor-liquid equilibrium conditions in the absence of a lubricant. The effects of refrigerant/lubricant interactions may impact both cycle analysis and system performance. If these interactions are significant (non-ideal solution behavior), they may result in detrimental performance and lower system operating efficiency.

In the present program, an analysis of applicable theory for predicting the solubility of refrigerant-oil mixtures has been carried out. Models based on both non-ideal solution theory and on an equation-of-state have been examined. The former require a large amount of experimental VLE data; the latter model involves the difficult task of describing the PVT behavior of two substances with drastically different boiling points. We have mainly based our analysis on solution theory models. Several solution theory models have been described in the literature which relate non-ideal behavior, as measured for example by the excess Gibbs energy, to composition, temperature and pressure of the mixture.[1] A solution theory model for refrigerant/lubricant mixtures can be parameterized using limited data sets for the solubility of refrigerant/lubricant pairs. Owing to the large size differences between refrigerant and lubricant molecules, the model must account for differences in their effective molar volumes. In addition, the model should also be capable of predicting immiscible regions. Finally, the model should rely mainly on data for binary refrigerant/refrigerant and refrigerant/lubricant pairs. Ternary mixture interaction parameters are difficult to extract from experimental solubility data and the most useful model will be based on a theoretical description of the interaction parameters that minimizes the need for ternary or quaternary mixture data. Solution theory models are generally reliable under the temperature and pressure conditions normally encountered in system operation. For operation near the critical point of a refrigerant, however, an EOS model would be more applicable. We have examined experimental solubility data for HFC-32/POE, HFC-125/POE and HFC-134a/POE mixtures. The POEs examined were mainly pentaerythritol esters, of both branched and straight chain formulations, with average molecular weights ranging from 500-800. Experimental data for mixtures of these lubricants with HFC-32, HFC-125 and HFC-134a were obtained from literature reports,[2-7] from manufacturer's tabulations[8-9] and from experimental data collected in our laboratory. These data were reduced to pressure-composition isotherms, as required for rigorous themodynamic solution modeling.

Mathematical Model for Solubility of Refrigerant/Lubricant Mixtures

The vapor-liquid equilibria of a mixture can be described in terms of the component fugacities in the liquid and vapor phases.[1] At equilibrium, we have

$$f_i^v = y_i P_T \phi_i^v = f_i^\ell = x_i \gamma_i P_i^v \phi_i^* \mathcal{P}_i^\ell \qquad (1)$$

where y_i = vapor phase molar composition of component i,
P_T = total system pressure at temperature T,
ϕ_i^v = vapor phase fugacity coefficient which, for moderate pressure, can be estimated from second virial coefficient data,
x_i = liquid phase molar composition of component i,
γ_i = liquid phase activity coefficient,
P_i^v = vapor pressure of pure component i at temperature T,
ϕ_i^* = fugacity coefficient for pure i at the system T and P,
$\mathcal{P}_i^\ell$ = Poynting factor for compressibility of the liquid phase.

For $\phi_i^v = \gamma_i = \phi_i^* = \mathcal{P}_i^\ell = 1.0$, this analysis reduces to ideal solution behavior (Raoult's Law). Choosing a fixed value of the system temperature, the fugacity coefficients are evaluated in terms of the vapor phase virial expansion as follows:

$$\ln \phi_i^v = \frac{P_T}{RT}[2\sum_j y_j B_{ij} - B_{mix}]; \qquad B_{mix} = \sum_i \sum_j y_i y_j B_{ij} \qquad (2)$$

Correspondingly, for pure component i, we have

$$\ln \phi_i^* = \frac{B_{ii} P_T}{RT} = Z_{ii} - 1 \tag{3}$$

The Poynting factor is normally negligible for moderate pressures, but may be estimated from molar volume data for pure liquid component i :

$$\ln \mathcal{F}_i^{\ell} = \int_{P_i^V}^{P_T} \frac{V_i^{\ell}}{RT} dP = \frac{V_i^{\ell} (P_T - P_i^V)}{RT} \tag{4}$$

Finally, we combine the fugacity coefficients and Poynting factor into a correction term, F_i, as

$$F_i = \exp\left[\frac{B_{ii} P_T}{RT} + \frac{V_i^{\ell} (P_T - P_i^V)}{RT} - \frac{P_T}{RT}\left(2\sum_j y_j B_{ij} - B_{mix}\right)\right] \tag{5}$$

The vapor-liquid equilibria for component i (Eq. 1) can then be written as

$$y_i P_T = x_i \gamma_i P_i^V F_i \tag{6}$$

The correction term, F_i, can be evaluated from liquid density and second virial coefficient data for pure refrigerants. One convenient source is the tabulation given in the NIST REFPROP database.[10] The difficult part of this analysis is the representation of the liquid phase activity coefficients, γ_i. These liquid activity coefficients may be extracted from experimental data or estimated using group additivity models such as UNIFAC.[11] The latter approach is difficult at present due to limited knowledge of the chemical formulations of the POEs and the lack of reliable functional group interaction parameters.

Preliminary evaluation of the non-ideal behavior of HFC-32/POE, HFC-125/POE and HFC-134a/POE binary mixtures indicated both positive and negative deviations from ideal solution behavior. Many of the proposed forms for liquid phase activity coefficients cannot mathematically represent such behavior. The Wilson model[12] for the excess Gibbs energy, for example, is not applicable over the entire refrigerant/lubricant composition range. Various modifications of the Wilson model have been proposed, including those described in the literature as the Heil,[13] NRTL,[14] and T-K[15] equations. All of these equations represent local composition models in an attempt to incorporate effects of molecular size as well as mixture concentration. Their derivations, however, are mainly empirically based, and can lead to computed solution parameters that lack physical meaning. After an extensive study of models for describing non-ideal liquid phase effects, the Wohl [3]-suffix equations[16] were chosen. Using the Wohl [3]-suffix expansion, the excess Gibbs energy can be represented as:

$$\frac{g^E}{RT\sum_j^n x_j q_j} = 2\sum_{\substack{i,j\\ i\neq j}}^n a_{ij} z_i z_j + 3\sum_{\substack{i,j\\ i\neq j}}^n a_{iij} z_i^2 z_j + 6\sum_{\substack{i,j,k\\ i\neq j\neq k}}^n a_{ijk} z_i z_j z_k \tag{7}$$

where z_i = generalized volume fraction (q-fraction) = $\dfrac{x_i q_i}{\sum\limits_{j}^{n} x_j q_j}$; q_i = effective volume of species i upon collision. The a_{ij}, a_{iij}, a_{ijk} are the interaction parameters describing binary and ternary interaction strengths. For binary pairs, this leads to the following form for the liquid phase activity coefficients:

$$\ln\gamma_1 = z_2^2[A_{12} + 2z_1(\frac{q_1}{q_2}A_{21} - A_{12})] \; ; \quad \ln\gamma_2 = z_1^2[A_{21} + 2z_2(\frac{q_2}{q_1}A_{12} - A_{21})] \qquad (8)$$

A_{12} and A_{21} are defined as follows:

$$A_{12} = q_1(2a_{12} + 3a_{122}) \; ; \qquad A_{21} = q_2(2a_{12} + 3a_{112}) \qquad (9)$$

We note that $A_{12} \neq A_{21}$ in this analysis. Eq. (8) was utilized to reduce the experimental solubility data for the six binary pairs: HFC-32/HFC-125, HFC-32/HFC-134a, HFC-125/HFC-134a, HFC-32/POE-ISO 68, HFC-125/POE-ISO 68 and HFC-134a/POE-ISO 68.

The derived form of the Wohl [3]-suffix equations for component 1 in a quaternary mixture becomes:

$$\begin{aligned}
\ln\gamma_1 = {} & z_2^2[A_{12} + 2z_1(\frac{q_1}{q_2}A_{21} - A_{12})] + z_3^2[A_{13} + 2z_1(\frac{q_1}{q_3}A_{31} - A_{13})] + z_4^2[A_{14} + 2z_1(\frac{q_1}{q_4}A_{41} - A_{14})] \\
& + z_2 z_3[\frac{1}{2}(\frac{q_1}{q_2}A_{21} + A_{12} + \frac{q_1}{q_3}A_{31} + A_{13} - \frac{q_1}{q_2}A_{23} - \frac{q_1}{q_3}A_{32}) \\
& + z_1(\frac{q_1}{q_2}A_{21} - A_{12} + \frac{q_1}{q_3}A_{31} - A_{13}) + (z_2 - z_3)(\frac{q_1}{q_2}A_{23} - \frac{q_1}{q_3}A_{32}) - (1-2z_1)C_{123}^{*}] \\
& + z_2 z_4[\frac{1}{2}(\frac{q_1}{q_2}A_{21} + A_{12} + \frac{q_1}{q_4}A_{41} + A_{14} - \frac{q_1}{q_2}A_{24} - \frac{q_1}{q_4}A_{42}) \\
& + z_1(\frac{q_1}{q_2}A_{21} - A_{12} + \frac{q_1}{q_4}A_{41} - A_{14}) + (z_2 - z_4)(\frac{q_1}{q_2}A_{24} - \frac{q_1}{q_4}A_{42}) - (1-2z_1)C_{124}^{*}] \\
& + z_3 z_4[\frac{1}{2}(\frac{q_1}{q_3}A_{31} + A_{13} + \frac{q_1}{q_4}A_{41} + A_{14} - \frac{q_1}{q_3}A_{34} - \frac{q_1}{q_4}A_{43}) \\
& + z_1(\frac{q_1}{q_3}A_{31} - A_{13} + \frac{q_1}{q_4}A_{41} - A_{14}) + (z_3 - z_4)(\frac{q_1}{q_3}A_{34} - \frac{q_1}{q_4}A_{43}) - (1-2z_1)C_{134}^{*}] \\
& + 2 z_2 z_3 z_4 C_{234}^{*}
\end{aligned} \qquad (10)$$

For a quaternary mixture (3 refrigerants plus 1 lubricant), 18 binary parameters plus 4 ternary parameters are required. The expressions for γ_2, γ_3 and γ_4 can be obtained from Eq. (10) by cyclic permutation of subscripts. All of the required A_{ij} can be evaluated from the binary pair data alone. The C*'s, which contain only non-identical 3-body collision terms, are initially taken as zero. They can be adjusted for a better overall description by analysis of ternary VLE data. This Wohl [3]-suffix model has been developed into a computer code (NISC) that, in its present form, describes HFC-32/HFC-125/HFC-134a/POE-ISO 68 mixtures over the entire composition range.

Results and Discussion

In the present study we have analyzed in detail a POE-ISO 68 formulated as mixed esters of pentaerythritol with both straight and branched chain acids since structural and thermophysical property data are available for this POE. Data were collected from several sources[2-9] on the solubility of the binary pairs: HFC-32/POE, HFC-125/POE, and HFC-134a/POE. In addition, refrigerant/lubricant solubility data for twelve different POE formulations, ranging in molecular weight from 525 to 1500, were examined in some detail. These included all of the mixtures reported by Henderson,[4] Cavestri,[5] Martz and Jacobi,[6] and Grebner and Crawford,[2] as well as data supplied by the manufacturers.[8-9] There are scatter in the data from these separate sources, which covered a temperature range of 0°-80°C. We relied most heavily on the data supplied by the POE manufacturers which seemed internally to be more consistent. Data on the refrigerant pairs: HFC-32/HFC-125, HFC-32/HFC-134a, HFC-125/HFC-134a, were also collected from several sources and compared with the predictions of the CSD equation-of-state model in REFPROP.[10] All experimental data have been analyzed within the Wohl [3]-suffix model.

Using the solution theory model described above, we have analyzed the P-T-X solubility data for binary mixtures to extract the liquid phase activity coefficients. As shown in Fig. 1, γ_{HFC-32} exhibits both positive and negative deviations from an ideal solution (γ=1.0), illustrating the difficulty in modeling HFC/POE mixtures, which exhibit such behavior as a common characteristic. Few data are available for HFC-32/POE and HFC-125/POE mixtures since HFC-32 requires special handling owing to its flammability characteristics and HFC-125 is currently not used as a single component refrigerant. Henderson[4] has reported data for several HFC-32/POE mixtures for both low refrigerant concentrations: 0-30 weight percent, and for high refrigerant concentrations: 80-100 weight percent. HFC-32 shows immiscibility regions with several of the mainly straight chain POEs for high refrigerant concentration mixtures. The HFC-32/HFC-125, HFC-32/HFC-134a, and the HFC-125/HFC-134a binary pairs exhibit small deviations from ideal liquid phase behavior. For internal consistency, these refrigerant pairs were also analyzed using the Wohl [3]-suffix model.

The non-ideal liquid behavior of the refrigerant/lubricant binary pairs is illustrated in Fig. 2 where we represent the logarithm of the activity coefficients of HFC-32, HFC-125 and HFC-134a (components 1) as functions of the q-fraction of POE-ISO 68 (component 2). A straight line fit indicates that the [3]-suffix form, represented by Eq. (8), is a satisfactory representation. The parameters for the data fit are the A_{ij} and the q-ratios. We find that measuring concentration in molar units is not satisfactory, since the refrigerant and lubricant molecules exhibit large size and volume differences. Fig. 3 illustrates that the q-ratio is poorly represented as 1.0, which would be the case for molecules of similar size. Further, identifying the q-ratio as the molar volume ratio of the molecules, which would be an appropriate choice for small molecule/polymer solutions, is also unsatisfactory. HFC/POE mixtures have properties somewhere between these two limiting cases and the q-ratios must be treated as adjustable parameters. Experimental data for the binary pairs: HFC-32/POE, HFC-125/POE and HFC-134a/POE were all least-squares reduced to the functional form represented by Eq. (8) for the temperature range: 0°- 60°C. The activity coefficients, γ_i, indicated a temperature dependence over this range but the q-ratios were relatively constant with temperature. This is physically reasonable since the q-ratios are a measure of the relative size of the refrigerant and lubricant molecules, which should be nearly temperature independent. The coefficients, A_{ij}, are often taken to be either independent of temperature (athermal-solution behavior) or inversely proportional to temperature (regular-solution behavior). Neither limit is accurate for the refrigerant/lubricant pairs under study and we have chosen to fit the A_{ij} to the empirical form: $A_{ij}(T) = a + b/T$.

The optimum refrigerant/lubricant q-ratios were found to be:

$$\frac{q_{\text{HFC-32}}}{q_{\text{POE}}} = 0.28 \qquad \frac{q_{\text{HFC-125}}}{q_{\text{POE}}} = 0.62 \qquad \frac{q_{\text{HFC-134a}}}{q_{\text{POE}}} = 0.58$$

There are three refrigerant/refrigerant q-ratios that can be derived from the above data.

$$\frac{q_{\text{HFC-32}}}{q_{\text{HFC-125}}} = 0.45 \qquad \frac{q_{\text{HFC-32}}}{q_{\text{HFC-134a}}} = 0.48 \qquad \frac{q_{\text{HFC-125}}}{q_{\text{HFC-134a}}} = 1.07$$

These refrigerant/refrigerant q-ratios can be compared with ratios of the molecular structure parameter, r, of the UNIQUAC[11] solution theory model:

$$\frac{r_{\text{HFC-32}}}{r_{\text{HFC-125}}} = 0.59 \qquad \frac{r_{\text{HFC-32}}}{r_{\text{HFC-134a}}} = 0.63 \qquad \frac{r_{\text{HFC-125}}}{r_{\text{HFC-134a}}} = 1.07$$

The UNIQUAC r-parameters are interpreted as a measure of the size of a molecule. These r-ratios indicate good agreement with the q-ratios derived from our optimum fit of experimental refrigerant/lubricant data. The internal consistency and physically meaningful interpretation of solution parameters in the Wohl model is evident. This situation is in contrast to modified Wilson solution theory models, where fitted refrigerant/lubricant interaction parameters can even change sign, depending on the exact form of the Wilson model equations.

Calculated solubility data for three refrigerant/lubricant mixtures: 1) HFC-134a/POE, 2) R-410a/POE, and R-407c/POE, are shown in Figs. 4-6, respectively. The data are presented as P-X diagrams for several isotherms. Isothermal vapor-liquid equilibrium data facilitate the evaluation of the vapor phase fugacity coefficients. Experimental data from several tabulated sources[6,8,9] are shown on these figures. The performance of the Wohl [3]-suffix model in describing the solubility of HFC-32/HFC-125/HFC-134a/POE mixtures is clearly satisfactory. Further improvements in the model through adjustment of the ternary interaction parameters, are currently being undertaken.

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Figure 1 - Liquid Phase Activity Coefficient for HFC-32 / POE-ISO 68 Mixture

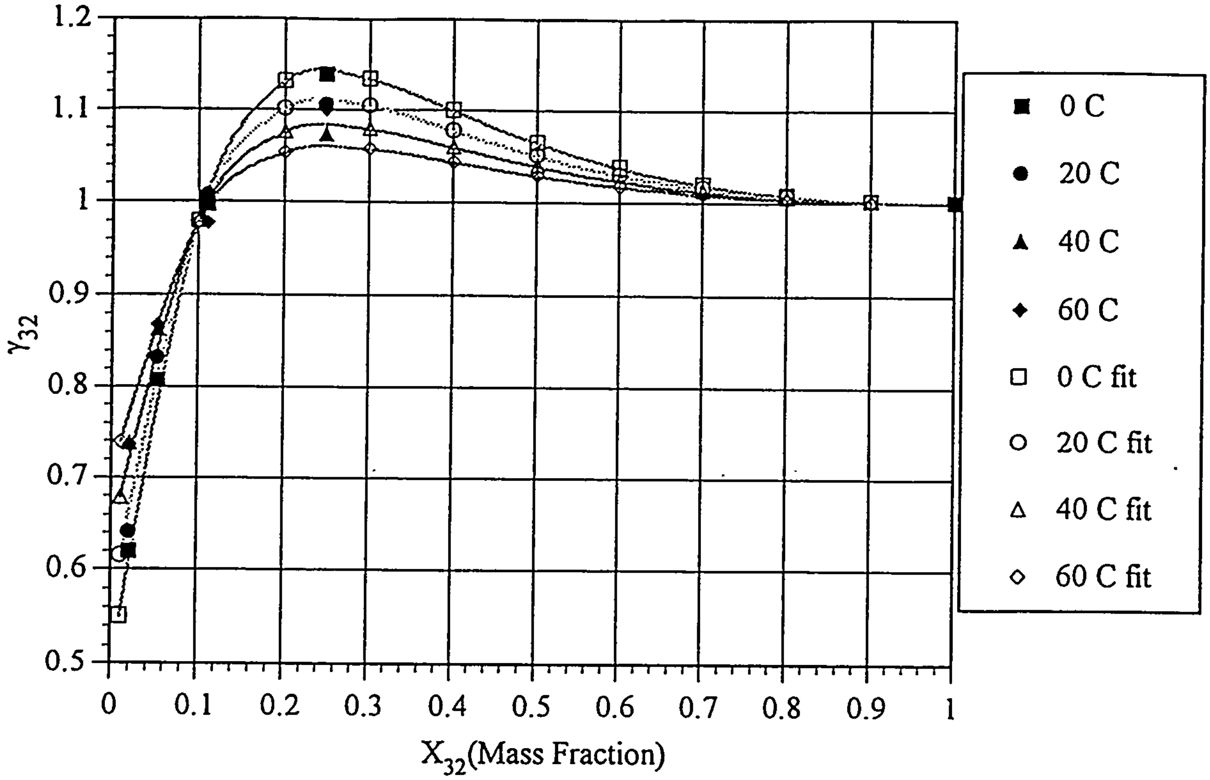

Figure 2
Binary Activity Coefficients for HFC-32 / HFC-125 / HFC-134a / POE-ISO 68 Mixtures
Based on Wohl 3-Suffix Equation (T=20 C)

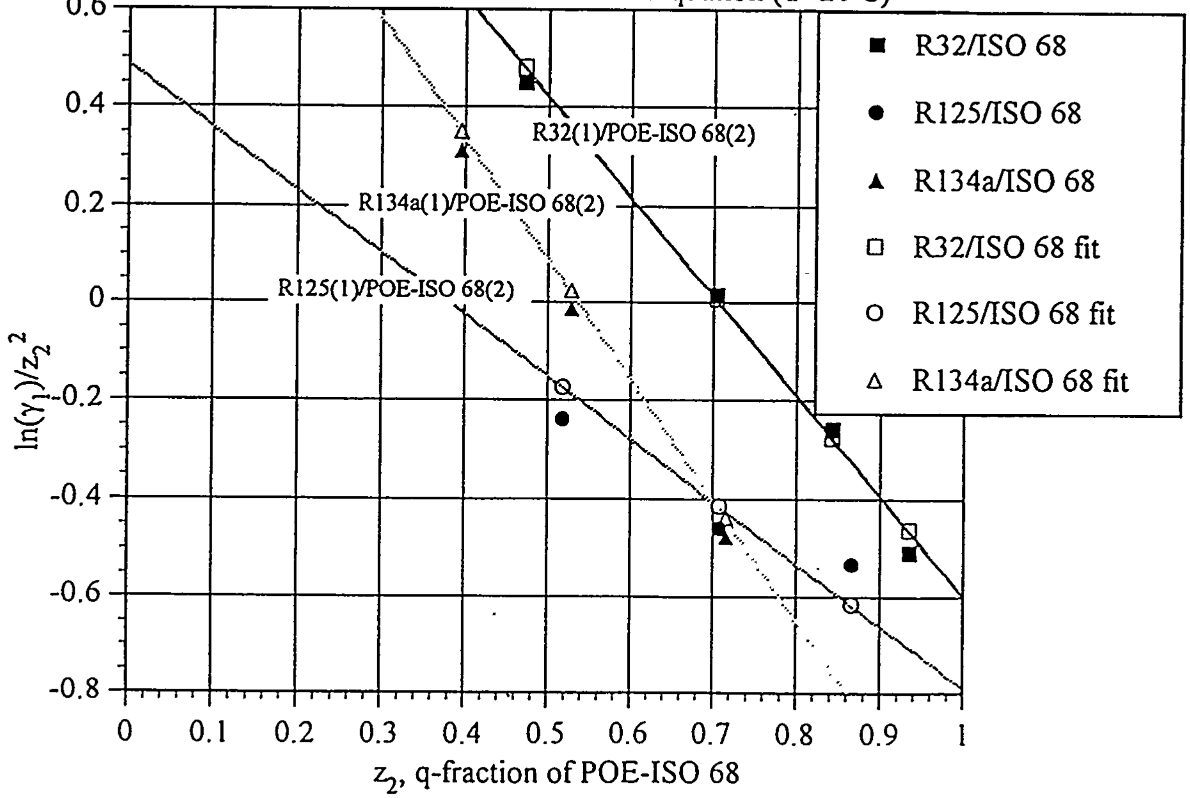

Figure 3 - Experimental HFC-32(1)/POE-ISO68(2) Liquid Phase Activity Coefficients (T=40 C)

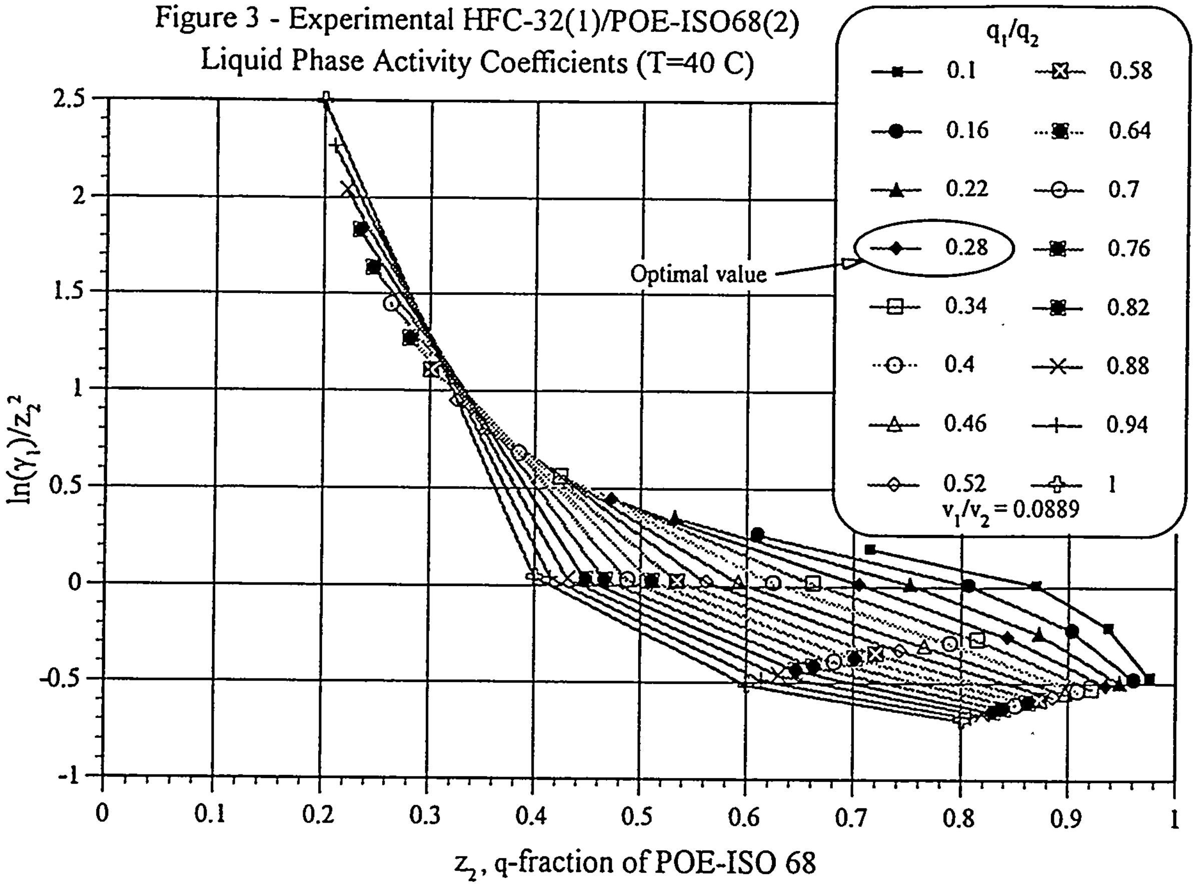

Figure 4 - R134a Experimental Data vs. NISC Predictions

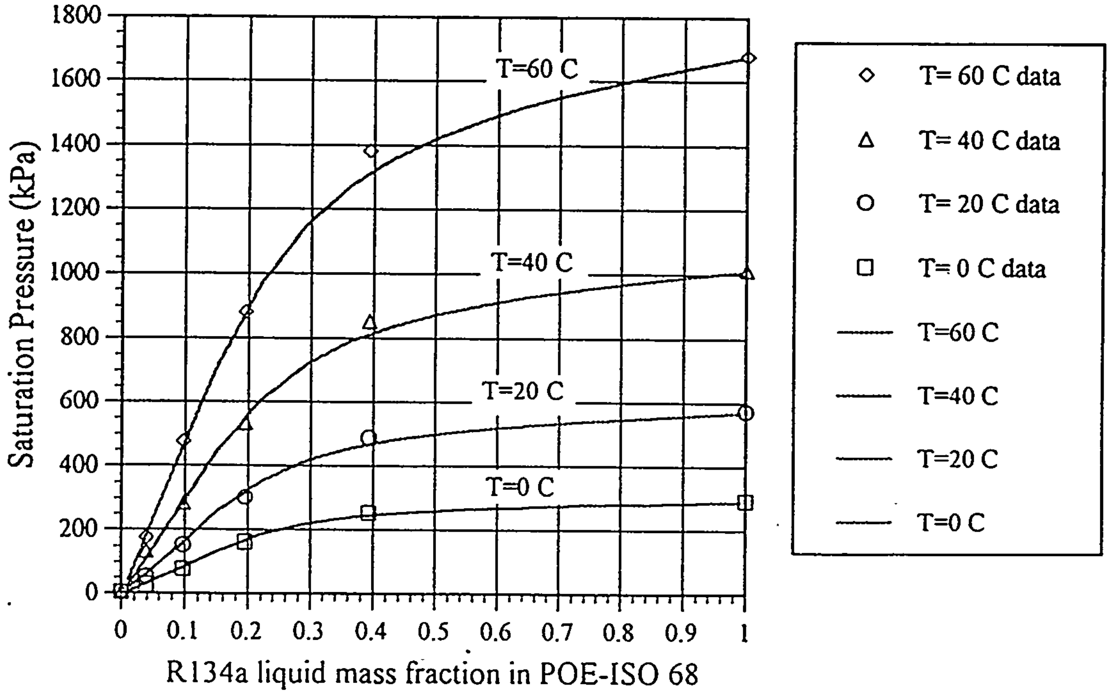

Figure 5 - R410a Experimental Data vs. NISC Predictions

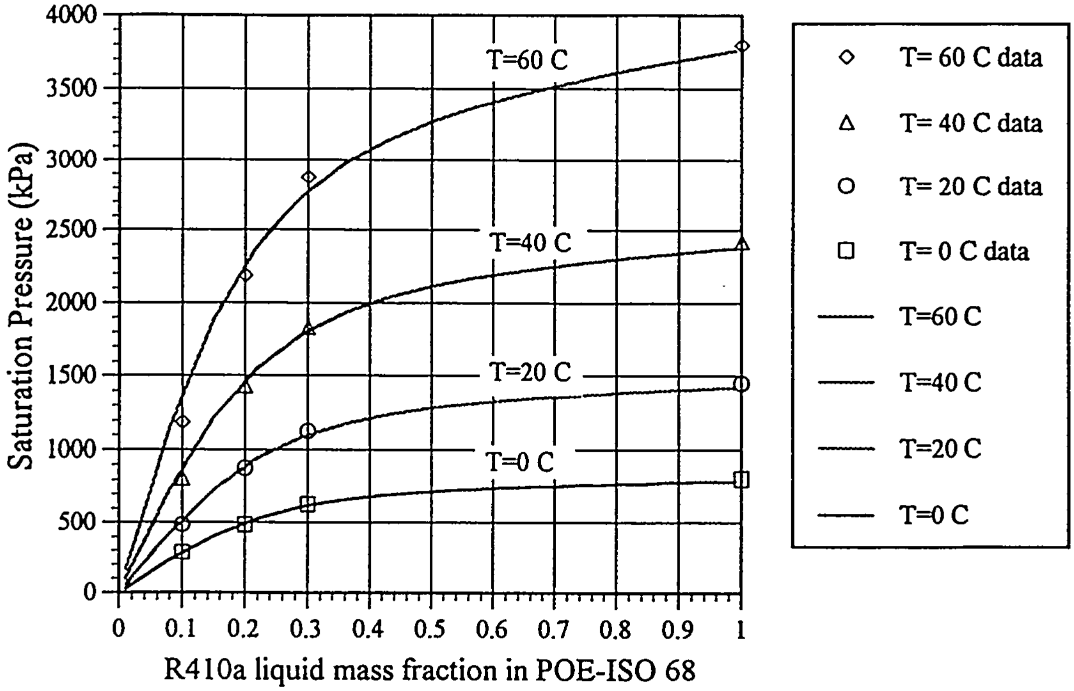

Figure 6 - R407c Experimental Data vs. NISC Predictions