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SOLUBILITY AND VISCOSITY OF REFRIGERANT-OIL MIXTURES

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ABSTRACT

So far in the literature, refrigerant-oil solubility data have been correlated with empirical forms. The correlations require much experimental data with a large amount of adjustable parameters, and are limited to use within the experimental condition. Often, the correlations are unable to represent all data with temperature, pressure, and compositions at the same time. This situation becomes particularly serious for the case of multicomponent refrigerants with oil. More versatile and theoretical models are needed.

General and practical models, based on thermodynamic theory, have been developed for the refrigerant-oil solubility and successfully applied for various systems for the first time. In addition, the viscosity of refrigerant-oil mixtures has been studied, and a simple mixing rule has been proposed. By combining these solubility and viscosity models, viscosity charts as functions of pressure, temperature, and compositions are constructed. Several examples and applications based on the present models will be discussed.

INTRODUCTION

In common refrigeration equipment, the compressor is literally the heart of the system. In order for the compressor to perform properly, oil requires to lubricate compressor bearings and other moving parts, as well as minimizing gas leakage during compression. Oil properties must meet this purpose suitably. However, selecting a proper oil is complicated due to the presence of refrigerant, which dissolves in the oil. The oil properties will be significantly changed by this process. The viscosity of the oil/refrigerant mixture, which is one of the most important factors, may decrease as much as an order of magnitude, since the refrigerant viscosity is typically 2-3 order of magnitudes smaller than that of oil. The suitable degree of solubility is also important. Too much solubility of refrigerant in the compressor oil is harmful, causing low viscosity, oil foaming, etc., while partial immiscibility (liquid-liquid separation) may also cause problems, since both (oil rich and refrigerant rich) liquids could have very low viscosities. Oil also circulates with refrigerant throughout the system. Large amounts of oil in the system create problems: reduction of heat transfer in heat exchanger and clogging of capillary tubes. To prevent the system from excessive oil accumulation, a high degree of mutual solubility may be required, but at the same time it must provide a proper viscosity of the mixture in the compressor.

Solubility depends not only on the type of refrigerant/oil combination but also strongly on temperature (T) and pressure (P), as does viscosity of the mixture. To understand these relations quantitatively is of upmost importance for designing the system and selecting lubricants. There have been time-consuming experimental efforts and empirical correlations based on laboratory data. Developing purely empirical correlations requires a large amount of data covering a wide range of experimental conditions (T, P, and compositions), as well as a large amount of fitting parameters. The extrapolation and interpolation of such correlations are often severely limited. In some cases, empirical correlations can not fit all observed data with the same correlation form; different equations may be needed for different regions of data. Perhaps, one of the most serious shortcomings will be that it is highly impractical to correlate the case of multicomponent refrigerants with oil.

Although the properties, such as vapor pressure and viscosity, of oil and refrigerant are quite different, the mutual solubility is nothing but the thermodynamic phase equilibrium: vapor-liquid or vapor-liquid-liquid equilibrium (VLE or VLLE). It must be correctly modeled within the thermodynamic theory. However, no successful model has been reported in the literature. In the present study, we have developed general and practical models based on the equation-of-state (EOS) theory and/or the activity-model (solution) theory. Concerning the viscosity of oil/refrigerant mixtures, a simple mixing rule has been developed and successfully tested for various observed systems. The solubility and viscosity models are then combined to construct an entire chart of viscosity with T, P, solubility, and compositions. Several selected examples and applications based on the present model will be given.

MODELING

A) Solubility (VLE/VLLE)

Various solution (activity) models have been known in the literature. Among them, Wilson⁽¹⁾ and modified Wilson equations⁽²⁾ are commonly used. With two or three adjustable parameters for each binary pair, any multicomponent system may be reliably predicted. Here, we use the following modified Wilson activity model⁽²⁾ for the "Gamma-Phi" phase-equilibria equations⁽³⁾.

$$P\phi_i y_i = \gamma_i x_i P_i^0 \phi_i^0 \exp\left(\int_{P_i^0}^P \frac{V_i}{RT} dp\right) = \gamma_i x_i P_i^0 \phi_i^0 \exp\left\{\frac{V_i (P - P_i^0)}{RT}\right\}$$

$$\ln(\gamma_i) = -\ln\left(\sum_{j=1}^n x_j \Lambda_{ij}\right) - \sum_{k=1}^n \left(\frac{x_k \Lambda_{ki}}{\sum_{j=1}^n x_j \Lambda_{kj}}\right) + \ln\left(\sum_{j=1}^n x_j V_j / V_i\right) + \sum_{k=1}^n x_k \left(\frac{V_i / V_k}{\sum_{j=1}^n V_j x_j / V_k}\right)$$

$$\text{where } \Lambda_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{\lambda_{ij}}{RT}\right), \text{ with } \Lambda_{ii} = \Lambda_{jj} = 1$$

n: number of species; P: pressure; T: temperature; V: molar volume; x, y: mole fraction; R: gas constant; subscripts: each species; superscript of o: pure compound's properties.

The vapor phase fugacity coefficients, ϕ_i , for refrigerants are calculated by the equation-of-state discussed later. The Gamma-Phi method has a special advantage for the solubility correlation of oil/refrigerant mixtures, where the physical properties of oil, such as vapor pressure, critical point, etc. that are usually unknown, are not required, since the vapor pressure of oil may be ignored under the typical experimental conditions. Only a nominal (or average) molecular weight of oil is needed to correlate the experimental solubility data. For each oil/refrigerant binary mixture, three adjustable parameters, λ_{12} , λ_{21} (Wilson's binary interaction parameters), and the molar volume of oil, V_{oil} , will be determined from the experimental solubility (TPx, temperature, pressure, composition) data.

Although the above method is convenient to use for the oil/refrigerant solubility, there are some limitations. It is only safely used well below the critical temperature of refrigerants. Often, the binary interaction parameters have strong temperature dependences in order to fit data with a wide range of temperatures. This introduces more fitting parameters and makes it difficult to extrapolate beyond the experimental data.

A more rigorous and versatile formulation of phase equilibria is to use a proper EOS for both liquid and vapor phase fugacities. For this purpose, the following EOS has been developed based on the SRK (Soave-Redlich-Kwong) equation⁽⁴⁾.

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)}$$

$$\text{where } a = \sum_{i,j=1}^n \sqrt{a_i a_j} (1 - k_{ij}) x_i x_j, \quad a_i = 0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} \alpha_i(T)$$

$$\alpha_i(T) = \sum_{i=0}^3 \beta_i \left(\frac{T_{ci}}{T} - \frac{T}{T_{ci}} \right)^k, \quad k_{ij} = \frac{l_{ij} l_{ji} (x_i + x_j)}{l_{ji} x_i + l_{ij} x_j}$$

$$b = \frac{1}{2} \sum_{i,j=1}^n (b_i + b_j) (1 - m_{ij}) (1 - k_{ij}) x_i x_j, \quad b_i = 0.086640 \frac{RT_{ci}}{P_{ci}}$$

subscript of ci: critical point of i-th species; all other notations are the same as previous equations.

The temperature dependence of the above "a" parameter, $\alpha(T)$, is no longer the acentric factor (ω) form commonly used⁽⁵⁾:

$$\alpha(T)^{0.5} = 1 + (1 - \sqrt{T/T_c})(0.48508 + 1.5517\omega - 0.15613\omega^2)$$

The present modification has significantly improved the vapor pressure correlation of various refrigerants, since the coefficients, β , are determined so as to fit observed vapor pressure data of each pure compound. As for oil, the above acentric factor equation is applied with properly estimated T_c and P_c . A simple method to estimate critical constants has been recently proposed by Vetere⁽⁶⁾. Since the critical T of oil is very high w.r.t. that of any refrigerant and its vapor pressure is essentially zero under the present interest, a rough estimation of T_c and P_c of oil may be sufficient. It is, however, found that the acentric factor must be suitably set up. Here, we treat it as an adjustable parameter, to be determined from oil/refrigerant VLE data.

Another development, at the present study, is to adopt a new type of binary interaction parameters. The ordinary k_{ij} , which is symmetric ($k_{ij} = k_{ji}$), is modified in order to take into account the different size of refrigerant and oil, since the molecular sizes of the two kinds of compounds are very different and the ordinary random mixing theory⁽⁷⁾ may not be applied. Here, the k_{ij} can be asymmetric when the l_{ij} and l_{ji} in the above equation are different; when the l_{ij} and l_{ji} are the same, the mixing rule is reduced to be the usual one. The mixing rule in the "b" parameter is also included with this asymmetric interaction, since the "b" parameter is theoretically related to the molecular size.

In order to correlate experimental VLE (PTx) data of each binary oil/refrigerant mixture in this model, at most four parameters, l_{ij} , l_{ji} , m_{ij} , and ω (oil) are required. Once the ω of a particular oil is determined, it should be a constant for that oil, and then any refrigerant with that oil will need at most three adjustable parameters to correlate the experimental binary VLE data. All multi-component mixtures with that oil may be reasonably calculated by the determined binary interaction parameters in the present model.

B) Viscosity

The liquid viscosity (η) for a pure compound has often been correlated by the following empirical form⁽⁸⁾:

$$\ln(\eta) = A + \frac{B}{T} + CT + DT^2$$

For oils, the first two terms are sufficient, while for refrigerants three or four terms are needed for a wide range of T. Liquid viscosities of most of pure compounds including oils are available in the literature. However, the viscosity of mixtures is not commonly available. Here, a simple mixing rule has been developed for the mixture viscosity.

$$\ln(\eta_{mix}) = \sum_i \xi_i \ln(\eta_i), \quad \text{where } \xi_i = \frac{m_i^k x_i}{\sum_j m_j^k x_j}$$

It may be called an effective weight fraction average of pure compounds, since ξ_i becomes a weight fraction when $k=1$; m is molecular weight, and x is mole fraction for each compound. It has been found that k is nearly a constant of 0.58 for many refrigerant mixtures studied. In the present study, it is fixed to 0.58 for refrigerant-only mixtures, while for oil and refrigerant (pure or mixtures) mixtures, k is treated as an adjustable parameter to be determined from experimental data. For various oil/refrigerant mixtures, so far studied, it ranges from about 0.6 to 1.0. In some cases, a small T dependence in k exists for a wide range of T, where it is modeled as a linear function of T.

RESULTS AND DISCUSSIONS

In order to test the present model, we have examined several published VLE/VLE data⁽⁹⁻¹²⁾. Figs.1 and 2 show the examples of the present correlation. Both cases fit the experimental data within a standard deviation of 0.7% in P, with the three binary interaction parameters and the oil acentric factor: for R123, $l_{ij} = l_{ji} = 0.01861$, $m_{ij} = -0.0242$, $\omega = 1.134$, and for R22, $l_{ij} = 0.04596$, $l_{ji} = 0.05664$, $m_{ij} = -0.02899$, $\omega = 0.9437$, respectively for the EOS model.

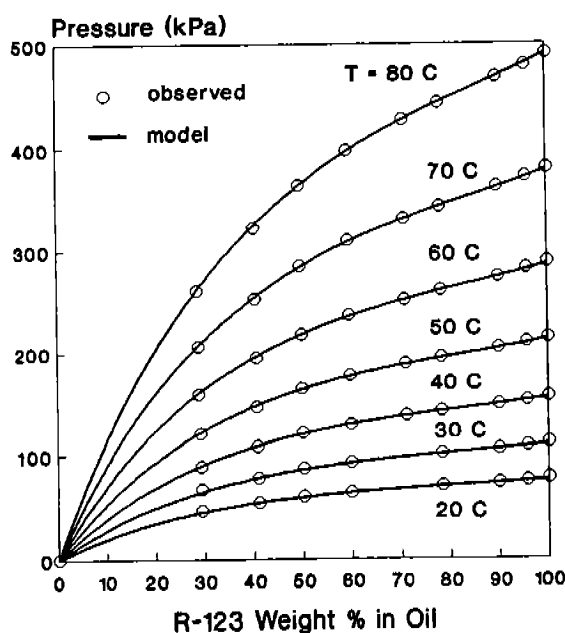


Fig.1. Solubility of R123 in naphthenic base mineral oil.

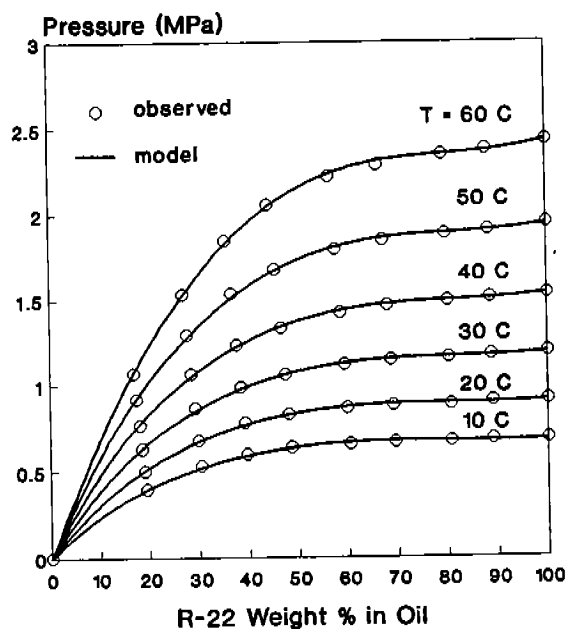


Fig.2. Solubility of R22 in alkyl benzene base synthetic oil.

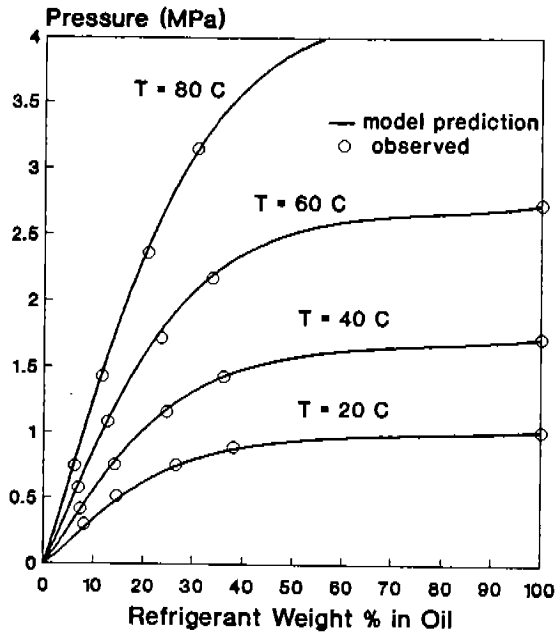


Fig.3. Vapor pressure of R32/R125/R134a in polyol ester oil (VG 56).

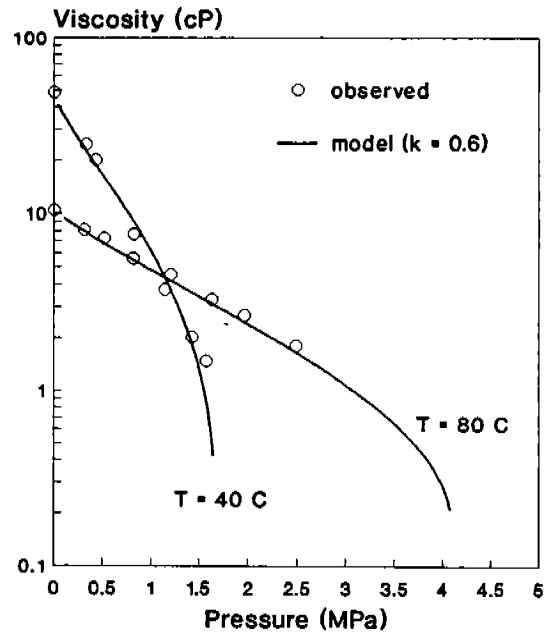


Fig.4. Viscosity vs. pressure of R32/R125/R134a in polyol ester oil (VG 56).

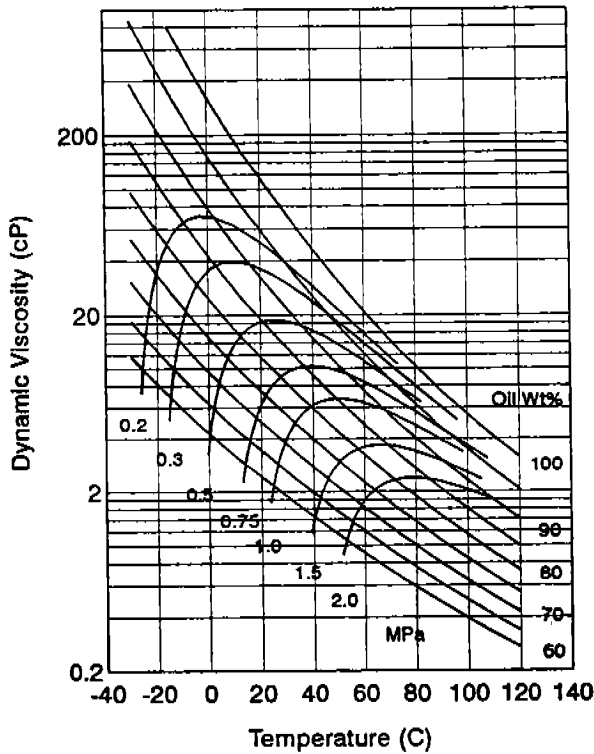


Fig.5. Viscosity chart of R32/R125/R134a in polyol ester oil (VG 56).

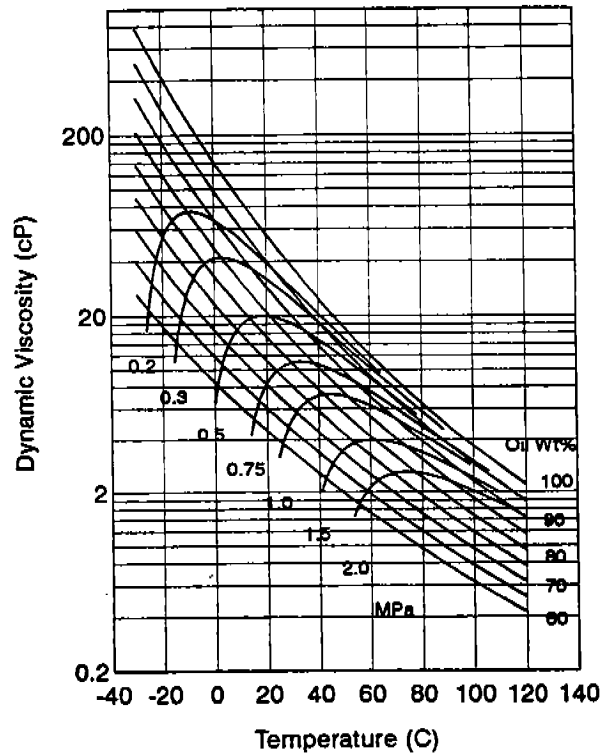


Fig.6. Viscosity chart of R32/R125/R134a in polyol ester oil (VG 22).

The solution (Γ/Φ) model also fits equally well for the R123 case, while for the R22 case, the binary interaction parameters were no longer independent of T in order to fit all the T data simultaneously. This situation was generally true for other systems studied and expected, since this model is known to be valid for low P VLE. The rest of the results are all based on the EOS model. As mentioned earlier, the present model is able to predict the solubility behavior of multicomponent refrigerants with oil based on each binary data. Fig. 3 shows one of such examples. A ternary mixture of R32/R125/R134a (30/10/60wt%) with a polyol ester oil (VG 56 with molecular weight of 554) has been successfully predicted for the experimental data⁽¹³⁾. The viscosity model of mixtures have been examined for various systems with the fitting parameter of k. All systems studied so far correlate reasonably well using a constant k parameter. Fig. 4 shows an example for the same ternary refrigerant and the oil. A constant k of 0.60 fits the observed data⁽¹³⁾ fairly well. If necessary, the k can be used with a linear function of T.

By combining the EOS solubility model with the viscosity model, a viscosity chart with T, P, and solubility such as Figs. 5 and 6 can be constructed. Fig. 5 is the case for the above-mentioned ternary refrigerant and the oil. Here, the composition of each refrigerant is kept constant (30/10/60wt%) in the oil. The present model, however, can calculate any composition changes due to T and P and the corresponding viscosity. Fig. 6 shows a similar chart of the same ternary refrigerant components (23/25/52wt%) with a different polyol ester oil (VG 22 with molecular weight of 560). Again, all binary VLE have been measured⁽¹⁴⁾ and the multicomponent properties are calculated. It is interesting to see the significantly different behavior between the two polyol ester oils; here the effect due to the different refrigerant compositions is minor.

CONCLUSIONS

The solubility model based on thermodynamic theory has been developed and successfully applied for various refrigerant/oil mixtures. It not only correlates binary VLE data with 2-4 parameters, but also can predict multicomponent thermodynamic properties. A simple mixing rule for oil/refrigerant viscosities has been proposed and tested.

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