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# A New Method for Calculating Viscosity and Solubility of Lubricant-Refrigerant Mixtures

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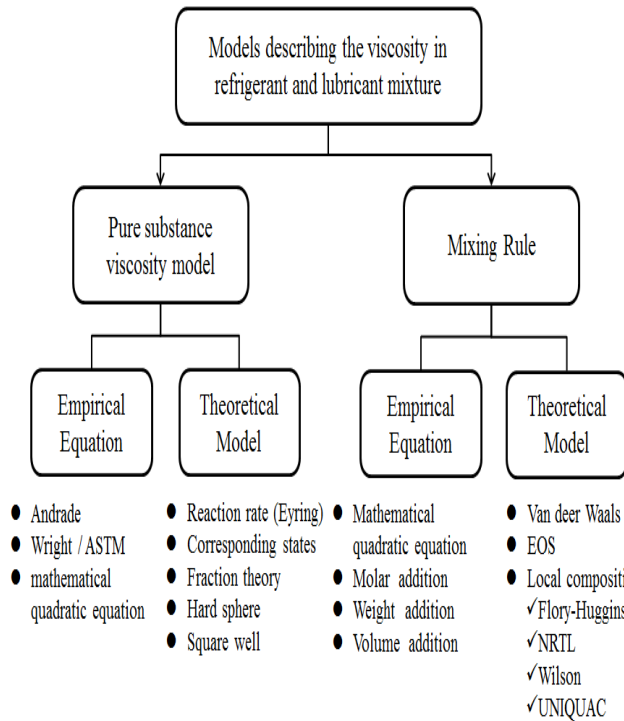
## ABSTRACT

A new model – Pseudo Ideal Solution Model (PISM) – was developed to determine viscosity and solubility of lubricant-refrigerant mixture, using concepts from lattice model in liquid state, reaction rate theory for viscosity, and local composition theory. The computing results from our new model showed high degree of accuracy, and are comparable to the results from NRTL model and Flory-Huggins model. Various type of POE lubricants (viscosity ranges from 68~220cst) in R134a refrigerant have been fitted for the new model to describe the viscosity and pressure of binary systems. The tests were conducted in temperature ranging from 0°C to 100°C. Typical average absolute deviation (AAD%) of these calculation results in the model is between 1.0~3.5%.

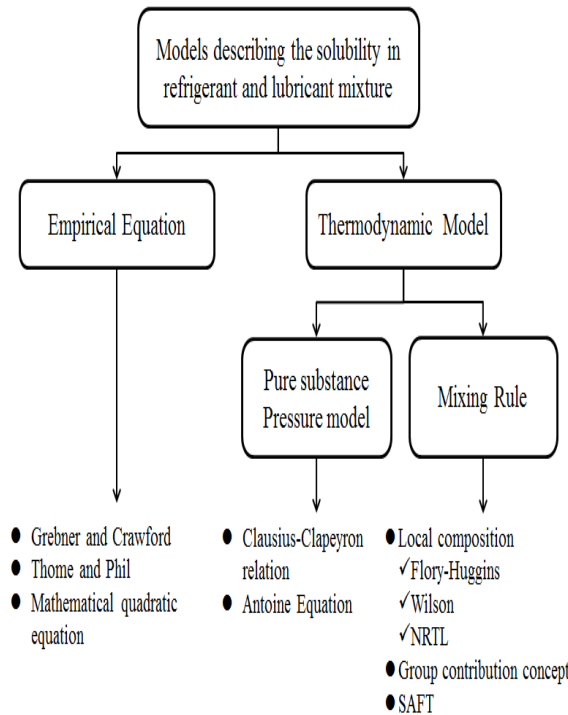
## 1. INTRODUCTION

The understanding and correlation of thermo-physical properties of lubricant-refrigerant mixtures is not only highly important for the design of refrigeration and air-conditioning systems, but also for the selection of proper lubricants for compressors. There are two primary thermo-physical properties: viscosity of lubricant in compressor operating condition, and the solubility of refrigerant in lubricant. The solubility of refrigerant in lubricant, often referred to as vapor-liquid equilibrium (VLE), can significantly change the viscosity and characteristics of lubricant. In case of too much refrigerant dissolving into lubricant under compressor operation, the dissolved refrigerant may substantially lower the viscosity of the oil-rich phase, resulting in lower lubrication properties and giving rise to a potential breakdown of the compressor mechanical parts. On the other hand, too little refrigerant dissolving into lubricant will increase the viscous drag in compressor operation, and thus increase compressor power consumption. Therefore, good knowledge of both viscosity and phase behavior is of a fundamental importance. In order to correlate and to predict the viscosity and phase behavior at various compressor operating conditions, proper models for solubility data correlation and for viscosity data correlation must be developed for lubricant-refrigerant mixtures.

The typical methods for modelling the thermo-physical properties of lubricant-refrigerant mixture can be classified into two categories: empirical and thermodynamic approaches (Fig 1 and Fig 2). For empirical approaches: Grebner and Crawford (1992) developed purely empirical models for vapor-liquid equilibrium in specific refrigerants with particular oils. Thome and Phil (1995) presented a generalized empirical approach in which an empirical equation is modified to fit with the pure refrigerant data for a blend of interest. Seeton and Hrnjak (2006) correlated VLE data and viscosity data of CO<sub>2</sub>/POE mixtures by using empirical quadratic formulation. A major drawback of the empirical approaches is that the correlations require many experimental measurements with a large number of adjustable parameters, and their use is limited to the range of experimental conditions. For thermodynamic approaches: models based on thermodynamic consideration can be divided into two separate categories, ‘local composition’, also known as heterogeneous models, and homogeneous models based on the ‘cubic equation of State’. The basic foundation of thermodynamic approaches is calculation of excess Gibbs energy, which means the deviation between real solution and ideal solution. McAllister (1960) calculated excess Gibbs energy by using an empirical cubic composition-dependent function. His equation is based on three-body interactions and requires at least three adjustable parameters for ternary systems. The friction theory (f-theory), a theory for viscosity modeling based on friction concepts of classical mechanics and equation of state, has been introduced by Quinones-Cisneros et al. (2000). Monsalvo (2006) correlated viscosity data of lubricant-refrigerant mixtures based on friction theory. In this paper, we will try to develop a new model to describe a concept of ‘pseudo-ideal solution’(PISM), and discuss the AAD% differences between several correlation models for lubricant-refrigerant mixture.



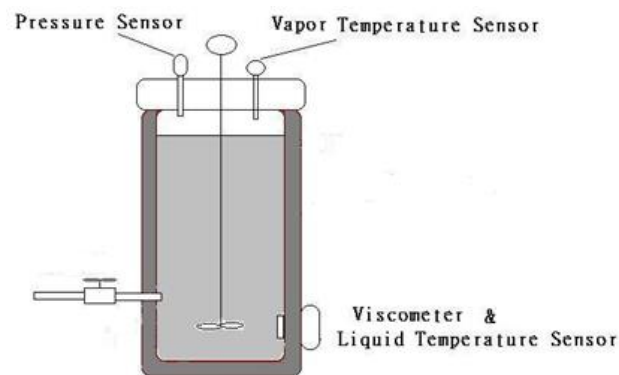
**Fig 1.** Viscosity modeling of lubricant-refrigerant mixture



**Fig 2.** Solubility modeling of lubricant-refrigerant mixture

## 2. VISCOSITY AND SOLUBILITY TEST SYSTEM

An experimental test facility has been constructed, tested and calibrated for measurement of lubricant-refrigerant mixture properties. The lubricant is first charged into the test system ( $\pm 0.1$  grams) and then the refrigerant is charged ( $\pm 0.1$  grams) into test system under condition:  $-10^{\circ}\text{C}$  and high vacuum. The mixture system is stirred and heated to suitable temperature based on the type of refrigerant. Sampling and measuring the related solubility and viscosity data only when vapor-liquid equilibrium has been achieved in mixture system.



**Fig 3.** Viscosity and solubility test system

## 3. DESCRIPTION OF EXISTING MODELS

### 3.1 Empirical Quadratic Equation for Viscosity Correlation of Mixture

Seeton and Hrnjak (2006) proposed an empirical quadratic equation for kinematic viscosity correlation of  $\text{CO}_2$  and POE mixture in refrigeration system.

$$\ln(\ln(\nu + 0.7 + \exp(-\nu)K_0(\nu + 1.244068))) = a_1 + a_2 \ln(T) + a_3 \ln^2(T) + \omega(a_4 + a_5 \ln(T) + a_6 \ln^2(T)) + \omega^2(a_7 + a_8 \ln(T) + a_9 \ln^2(T)) \quad (1)$$

Where  $\omega$  is mass fraction of refrigerant,  $K_0$  is zero order modified Bessel function of second kind,  $\nu$  is kinematic viscosity, and  $a_1 \sim a_9$  are adjustable parameters determined by experimental data.

### 3.2 Thermodynamic Theory for Viscosity Correlation of Mixture

**3.2.1 Absolute Reaction Rate Theory:** The reaction rate theory of Eyring and coworkers (1941) states that a liquid is densely populated by molecules with a few "holes", which give the liquid a new degree of translation. Viscous flow is considered a "reaction" in which a molecule sometimes acquires the activation energy necessary to slip over a potential energy barrier and move to the next equilibrium position. The resulting equation for liquid viscosity is:

$$\eta V = Nh \exp\left(\frac{\Delta G^*}{RT}\right) \quad (2)$$

Where  $\eta$  is viscosity,  $V$  is molar volume,  $N$  is Avagadro's number,  $h$  is Planck's constant, and  $\Delta G^*$  is energy change of activation for a molecule to jump to a hole.

**3.2.2 Eyring-Based Local Composition Viscosity Model:** Wei and Rowley (1985) proposed a method based on Eyring's Equation (2) which requires pure component viscosity data, NRTL binary information and excess enthalpy. Novak *et al.*(2004) established a new viscosity model for polymer and suggested that component-based Eyring-NRTL viscosity model should be replaced with segment-based Eyring-NRTL viscosity model.

$$\Delta G^* = RT(x_1 \ln x_1 + x_2 \ln x_2) + \Delta G^E = \Delta G_1^{ideal} + \Delta G_2^{ideal} + \Delta G^E \quad (3)$$

$$\eta_{mix} V_{mix} = Nh \exp\left[\frac{x_1 \Delta G_1^{ideal} + x_2 \Delta G_2^{ideal} + \Delta G^E}{RT}\right] \quad (4)$$

$$\ln(\eta_{mix} V_{mix}) = x_1 \underbrace{\ln(\eta_1 V_1)}_{\text{Ideal solution part}} + x_2 \underbrace{\ln(\eta_2 V_2)}_{\text{Ideal solution part}} + \underbrace{\frac{\Delta G^E}{RT}}_{\text{Interaction part (non-ideal solution)}} \quad (5)$$

Equation (5) can be divided into two parts: ideal solution part and non-ideal solution part (interaction part). In order to calculate viscosity of mixture, excess Gibbs energy  $\Delta G^E$  should be obtained first. Some models based on local composition are common used, such as NRTL (non-random two-liquid) model and Flory-Huggins model.

**3.2.2.1 Component-based NRTL model:** We can calculate  $\Delta G^E$  and get the viscosity of mixture by combining Equation(5) with well-known NRTL model (Renon and Prausnits,1968) shown in Equation (6) ~ (10),

$$\frac{\Delta G^E}{RT} = x_1 x_2 \left( \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \quad (6)$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \quad (7)$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \quad (8)$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}) \quad (9)$$

$$G_{21} = \exp(-\alpha_{12} \tau_{21}) \quad (10)$$

**3.2.2.2 Segment-based NRTL model:** Chen's segment-based NRTL model (1993) was successfully used for polymer solution-phase equilibria. A segment-based model should be more physically realistic for large molecules. Because diffusion and flow are viewed to occur by a sequence of small individual segment jumps into vacancies, rather than large molecule jumps into large vacancies. When we deal with lubricant-refrigerant mixture by using this model, segments are defined as the ratio of molecular weight of lubricant (large molecule) to molecular weight of refrigerant (small molecule), which is normally treated as component. We can calculate  $\Delta G^E$  and get the viscosity of mixture by combining Equation(5) with segment-based NRTL model shown in Equation (7) ~ (13),

$$X_2 = \frac{nx_2}{x_1 + nx_2} \quad (11)$$

$$X_1 = \frac{x_1}{x_1 + nx_2} \quad (12)$$

$$\frac{\Delta G^E}{RT} = X_1 X_2 \left( \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \quad (13)$$

Where n is number of segments on each lubricant molecule,  $X_1$  is segment-based molar fraction of refrigerant, and  $X_2$  is segment-based molar fraction of lubricant.

**3.2.3 Eyring-Flory-Huggins viscosity model:** Flory–Huggins theory is a lattice model based mathematical model for mixture of polymer and solvent. The basic concept is that individual polymer segments and individual solvent molecules occupy sites on a lattice. Each site is occupied by exactly one molecule of the solvent or by one monomer of the polymer chain. It is a physically realistic model for mixtures containing both large and small molecules such as lubricant and refrigerant.

$$\Delta G^E = x_1 \Phi_2 \chi_{12} \quad (14)$$

$$\chi_{12} = \frac{\Delta \omega}{\kappa T} \quad (15)$$

$$\Phi_2 = \frac{nx_2}{x_1 + nx_2} \quad (16)$$

Where n is number of segments on a lubricant molecule,  $\kappa$  is Boltzmann's constant,  $\Delta \omega$  is the interchange energy between refrigerant molecules and lubricant segments,  $\chi_{12}$  is interchange energy parameter.  $\Phi$  is segment fraction. It is easy to calculate  $\Delta G^E$  and get the viscosity of mixture by combining Equation(5) with Flory-Huggins model shown in Equation (14) ~ (16)

### 3.3 Empirical Quadratic Equation for Solubility Correlation of Mixture

Seeton and Hrnjak (2006) proposed an empirical quadratic equation for vapor pressure correlation of CO<sub>2</sub> and POE mixture in refrigeration system.

$$\text{Log}_{10}(P) = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} + \text{Log}_{10}(\omega) \left[ a_4 + \frac{a_5}{T} + \frac{a_6}{T^2} \right] + \text{Log}_{10}^2(\omega) \left[ a_7 + \frac{a_8}{T} + \frac{a_9}{T^2} \right] \quad (17)$$

Where  $\omega$  is mass fraction of refrigerant, P is vapor pressure, and  $a_1 \sim a_9$  are adjustable parameters determined by VLE data.

### 3.4 Thermodynamic Theory for Solubility Correlation of Mixture

A fundamental relation between vapor pressure and activity coefficient is shown in Equation (18)

$$y_i \times P \times \Phi_i = (\gamma_i \times x_i) \times P_i^{sat} \times \Phi_i^{sat} \times P_e \quad (18)$$

Where  $\Phi$  is fugacity coefficient,  $\gamma$  is activity coefficient, and  $P_e$  is Poynting effect. Local composition theory and lattice theory, such as NRTL, Wilson, UNIQUAC, and Flory-Huggins equation, are well-known theories for calculation of activity coefficient. Activity coefficient means the deviation between real vapor pressure and theoretical vapor pressure. It is important to estimate and calculate activity coefficient of mixture by using thermodynamic model.

**3.4.1 NRTL model:**

$$\ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (19)$$

Where  $\tau_{12}$ ,  $\tau_{21}$ ,  $G_{12}$  and  $G_{21}$  can be calculated by using Equation (7)~(10)

**3.4.2 Flory-Huggins model:**

$$\ln \gamma_1 = \ln \left[ 1 - \left( 1 - \frac{1}{n} \right) \Phi_2 \right] + \left( 1 - \frac{1}{n} \right) \Phi_2 + \chi_{12} \Phi_2^2 \quad (20)$$

Where n is number of segments on a lubricant molecule, and  $\chi_{12}$  and  $\Phi$  can be calculated by Equation (15)~(16)

## 4. NEW MODEL DEVELOPMENT

### 4.1 Ideal Solution and Non-Ideal Solution

An ideal solution is a solution with thermodynamic properties analogous to those of a mixture of ideal gases. The enthalpy of mixing is zero as is the volume change on mixing (This is so-called 'random mixing'); the closer to zero the enthalpy of solution is, the more "ideal" the behavior of the solution becomes. The vapor pressure of the solution obeys Raoult's law, and the activity coefficient of each component (which measures deviation from ideality)

is equal to unity. For an ideal mixture of molecule A and B, the interactions between unlike-neighbors (A-B) and like-neighbors (A-A and B-B) must be of the same average strength. In lubricant-refrigerant mixture, lubricant is much bigger than refrigerant, A-B interaction becomes geometrically asymmetric and the mixing is non-random, so thermodynamic properties of mixture are far from ideal. Yokozeki (2001) provided a method to apply the random mixing concept in lubricant-refrigerant mixture. He suggested the molecular size must be re-scaled so that the number of neighboring interactions becomes geometrically symmetric. In this paper, we try to develop a new method based on this concept to eliminate the “non-ideal” part in Equation (5), thus the lubricant-refrigerant mixture can be considered as an “ideal solution”.

$$\ln(\eta_{mix} V_{mix}) = \theta_1 \ln(\eta_1 V_1)^* + \theta_2 \ln(\eta_2 V_2) \quad \begin{matrix} \theta_1 \text{ is 'pseudo' molar fraction of refrigerant in ideal solution} \\ \theta_2 \text{ is 'pseudo' molar fraction of lubricant in ideal solution} \end{matrix} \quad (21)$$

Only ideal solution parts, no interaction parts

### 4.2 Pseudo Ideal Solution Model (PISM)

Suppose two type of molecules in mixture have very different molecular sizes: small size A (refrigerant) and large size B (lubricant)

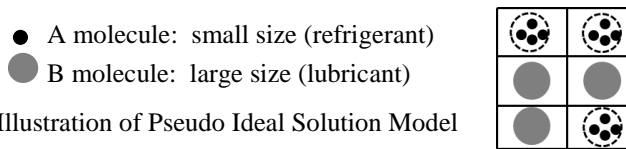


Fig 4. Illustration of Pseudo Ideal Solution Model

Basic assumptions and descriptions of PISM (Fig 4):

- ✓ A pseudo lattice is created inside the mixture.
- ✓ Combine n molecules of A into a new pseudo molecule A', and the new pseudo molecule A' occupies exactly one site.
- ✓ B molecule (large size) occupies exactly one site.
- ✓ All molecules occupy sites on a lattice obey the ideal solution rule, and interaction forces between different kinds of molecules are the same. (A'-A' = A'-B = B-B)
- ✓ Molar volume VA' = VB (volume change on mixing is zero)

#### 4.2.1 PISM for viscosity of mixture :

Summary of properties in PISM are listed in Table1. “n” molecules of refrigerant are combined to form a new “pseudo refrigerant molecule”. The new molar volume of pseudo refrigerant molecule ( $V_1^*$ ) is the same as molar volume of lubricant ( $V_2$ ), the molecular number of pseudo refrigerant molecule decrease from  $x_1$  to  $x_1/n$  and the molecular weight increase from  $Mw_1$  to  $nMw_1$ . Viscosity of pseudo refrigerant molecule is expressed as  $\eta_1^*$ . The key points of PISM are how to calculate the “n” value, and to verify the relationship among viscosity, molecular weight and molar volume.

Table 1. Summary of properties in PISM

	Viscosity $\eta$	Molar Volume $V$	Molecular number	Molecular weight
●	$\eta_1$	$V_1$	$x_1$	$Mw_1$
⊙	$\eta_1^*$	$V_1^* = V_2$	$\frac{x_1}{n}$	$nMw_1$
●	$\eta_2$	$V_2$	$x_2$	$Mw_2$

Due to the similarity between the interaction forces in ideal solution and that of dilute gas state, the relationship among viscosity, molecular weight and molar volume in ideal solution could be analogous to those of dilute gas. A general form for viscosity of a dilute gas is provided by kinetic theory as described in Reid *et al* (1987). The gas is assumed to be consist of non-interacting rigid particles of diameter  $\sigma$ . An expression for the momentum flux between two layers in relative motion yields the following expression for viscosity.

$$\eta \propto \frac{Mw^{0.5}}{\sigma^2} \quad (22)$$

In order to calculate key factor ‘n’ in table 1, a new factor K should be introduced:

$$\bullet \quad \eta_1, V_1 \quad \rightarrow \quad \odot \quad \eta_1^*, V_1^*, n \quad K = \frac{\eta_1^* V_1^*}{\eta_1 V_1} \quad (23)$$

Combine Equation (23) with (22)

$$K = \frac{\eta_1^* V_1^*}{\eta_1 V_1} = C^* \times \frac{(Mw_1^*)^{0.5} \times (\sigma_1^*)^3}{(\sigma_1^*)^2 \times (\sigma_1^*)^3} = C^* \times \frac{(Mw_1^*)^{0.5} \times \sigma_1^*}{(Mw_1^*)^{0.5} \times \sigma_1} = C^* \times \frac{(Mw_1^*)^{0.5} \times (V_1^*)^{\frac{1}{3}}}{(Mw_1^*)^{0.5} \times (V_1)^{\frac{1}{3}}} = C^* \times \frac{(nMw_1)^{0.5} \times (V_2)^{\frac{1}{3}}}{(Mw_1)^{0.5} \times (V_1)^{\frac{1}{3}}} = C^* \times n^{0.5} \left( \frac{V_2}{V_1} \right)^{\frac{1}{3}} \quad (24)$$

Then  $n$  value can be expressed in terms of  $K$  factor

$$n = \frac{K^2}{(C^*)^2 \times \left( \frac{V_2}{V_1} \right)^{\frac{2}{3}}} = \frac{K^2}{C \times \left( \frac{V_2}{V_1} \right)^{\frac{2}{3}}} \quad \text{C is an adjustable parameter determined by PISM correlation} \quad (25)$$

Starting from Eyring's equation,  $K$  factor can be

$\eta V = Nh \exp\left(\frac{\Delta G^*}{RT}\right)$ , then  $\ln(\eta V) = \ln\left(Nh \exp\left(\frac{\Delta G^*}{RT}\right)\right) = A + \frac{B}{T}$  Combine this equation with  $K$  factor definition

$$\ln(K) = \ln\left(\frac{\eta_1^* V_1^*}{\eta_1 V_1}\right) = \ln(\eta_1^* V_1^*) - \ln(\eta_1 V_1) = \left(A_1^* + \frac{B_1^*}{T}\right) - \left(A_1 + \frac{B_1}{T}\right) = (A_1^* - A_1) + \frac{(B_1^* - B_1)}{T} = A + \frac{B}{T}$$

then  $K = \exp\left(A + \frac{B}{T}\right)$  A, B are adjustable parameters determined by PISM correlation (26)

Calculation of new molar fraction  $\theta$  in Equation (21) is shown in Equation (27):

$$\theta_1 = \frac{\frac{x_1}{n}}{\frac{x_1}{n} + x_2} \quad \theta_2 = \frac{x_2}{\frac{x_1}{n} + x_2} \quad \begin{array}{l} \theta_1 \text{ is 'pseudo' molar fraction of refrigerant in ideal solution} \\ \theta_2 \text{ is 'pseudo' molar fraction of lubricant in ideal solution} \end{array} \quad (27)$$

Molar volume of mixture ( $V_{mix}$ ) in Equation (21) can be obtained by the following steps:

For convenience of calculation, we assume the viscosity of new molecules is the same as that of the original molecules. Thus, we must expand  $V_1^*$  to a pseudo new molar volume  $V_1^{**}$



From the definition of  $K$

$$K \eta_1 V_1 = \eta_1^* V_1^* = \eta_1^* V_2 \quad (\because V_1^* = V_2) = \eta_1 V_1^{**} \quad \text{then new molar volume} \quad V_1^{**} = KV$$

Thus the molar volume of mixture in Equation (21) can be derived

$$V_{mix} = \theta_1 V_1^{**} + \theta_2 V_2 = \theta_1 KV_1 + \theta_2 V_2 \quad (28)$$

Viscosity of pure substances can be written in Equation (21) as the following forms

$$\ln(\eta_1) = A_1 + \frac{B_1}{T + C_1} \quad A_1, B_1, C_1 \text{ are coefficients for pure refrigerant} \quad (29)$$

$$\ln(\eta_2) = A_2 + \frac{B_2}{T + C_2} \quad A_2, B_2, C_2 \text{ are coefficients for pure lubricant} \quad (30)$$

A series of density data at different temperature of pure substances are useful to get the coefficients in such molar volume equation:

$$V = \frac{Mw}{\rho} \quad \text{For refrigerant} \quad V_1 = b_1 + b_2 T + b_3 T^2 + b_4 T^3, \quad b_1 \sim b_4 \text{ are coefficients for pure refrigerant} \quad (31)$$

$$\text{For lubricant} \quad V_2 = c_1 + c_2 T, \quad c_1 \sim c_2 \text{ are coefficients for pure lubricant} \quad (32)$$

Combine Equation (21) and Equation (25)~ (32), then viscosity of mixture is expressed as below

$$\eta_{mix} = \exp\left[\theta_1 \ln(K \eta_1 V_1) + \theta_2 \ln(\eta_2 V_2) - \ln(V_{mix})\right] \quad (33)$$

In refrigeration system, the use of kinematic viscosity in most of equations instead of absolute viscosity has the obvious advantage of avoiding equations containing volume fractions, or volume changes on mixing, quantities which are not always known. It is easy to convert absolute viscosity to kinematic viscosity by the following way:

$$\eta \times V = \nu \times Mw \quad (34)$$

$$Mw_{mix} = \theta \times K \times Mw_1 + \theta_2 \times Mw_2 \quad (35)$$

$$\nu_{mix} = \exp[\theta_1 \ln(K \nu_1 Mw_1) + \theta_2 \ln(\nu_2 Mw_2) - \ln(Mw_{mix})] \quad (36)$$

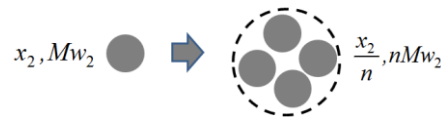
4.2.2 PISM for solubility correlation of mixture:

4.2.2.1 Saturated vapor pressure of pure refrigerant: The Antoine equation is a vapor pressure equation describing the relationship between vapor pressure and temperature for pure components. The Antoine equation is derived from the well-known Clausius–Clapeyron relation.

$$\text{Antoine equation} \quad \ln(P_1^{sat}) = A + \frac{B}{T+C} \quad A, B, C \text{ are coefficients for pure refrigerant} \quad (37)$$

$$\text{Clausius Clapeyron relation} \quad \ln(P) = -\frac{L}{RT} + C \quad L: \text{ specific latent heat, } C=\text{constant} \quad (38)$$

4.2.2.2 PISM solubility model: Instead of combining refrigerant molecules into pseudo molecule A', we re-normalize lubricant molecules by stretching or shrinking.



Then new molar fraction  $\theta$  should be

$$\theta_1 = \frac{x_1}{x_1 + \frac{x_2}{n}} \quad \theta_2 = 1 - \theta_1 \quad (39)$$

Therefore, vapor pressure correlation of PISM can be carried out by using Equation (37) ~ (41)

$$\ln P = \theta_1 \times \ln P_1^{sat} \quad P_{mix} = \exp(\theta_1 \times \ln P_1^{sat}) \quad (40)$$

$$n = \exp\left(a + \frac{b}{T+c}\right) \quad a, b, c \text{ are adjustable parameters determined by PISM correlation} \quad (41)$$

## 5. RESULTS AND DISCUSSION

Several viscosity and solubility experiments were conducted by the test instrument shown in Fig 3, with each test containing 45 to 50 data points. The tests were conducted in temperature ranging from 0°C to 100°C. Afterwards, analysis of the data was carried out by applying the above models to the pressure-versus-temperature data and viscosity-versus-temperature data, for five different initial compositions of the R134a-POE mixture. All of the investigated models have more empirical parameters that are specific for each mixture considered. These parameters were fitted by regression using minimization of the sum of squares:

$$\text{Sum of squares for kinematic viscosity correlation} \quad SS = \sum_{i=1}^{NP} \left(1 - \frac{Kv_{calc,i}}{Kv_{exp,i}}\right)^2 \quad (42)$$

$$\text{Sum of squares for vapor pressure correlation} \quad SS = \sum_{i=1}^{NP} \left(1 - \frac{P_{calc,i}}{P_{exp,i}}\right)^2 \quad (43)$$

Where  $k_{v,cal}$  is calculated kinematic viscosity,  $k_{v,exp}$  is experimental kinematic viscosity,  $P_{cal}$  is calculated vapor pressure,  $P_{exp}$  is experimental vapor pressure, and  $N_p$  is the number of experimental points. The result of the parameter estimation is expressed as relative AAD% (average absolute deviation) of the calculated equilibrium pressures and viscosity for each mixture, according to



$$\text{AAD\% of kinematic viscosity} = \frac{\sum_{i=1}^{N_p} \left| \frac{Kv_{calc,i} - Kv_{exp,i}}{Kv_{exp,i}} \right|}{N_p} \times 100\% \quad (44)$$

$$\text{AAD\% of vapor pressure} = \frac{\sum_{i=1}^{N_p} \left| \frac{P_{calc,i} - P_{exp,i}}{P_{exp,i}} \right|}{N_p} \times 100\% \quad (45)$$

The AAD% comparisons analyzed by different models are shown in Table 2 and Table 3. Kinematic viscosity deviation of ISO 220-D between raw data and calculated results are drawn in Fig 5~8.

**Table 2.** AAD% of kinematic viscosity data correlation for POE in R134a

AAD%	Number of experimental points	Pseudo-Ideal-Solution Model (PISM)	Segment-Based Eyring-NRTL Model (SBEN)	Eyring-Flory-Huggins Model (EFH)	Empirical quadratic equation (EQE)
ISO-220-A	48	3.09	5.65	6.73	11.01
ISO-220-B	48	2.61	3.08	5.13	7.13
ISO-220-C	46	2.47	2.58	4.97	6.64
ISO-220-D	44	2.35	3.11	5.71	10.5
ISO-220-E	46	2.85	4.01	6.4	10.7
ISO-68-A	47	1.16	2.67	3.03	4.66
ISO-68-B	45	2.15	1.95	4.68	2.69
ISO-68-C	46	2.05	2.02	5.03	4.06

**Table 3.** AAD% of solubility data correlation for POE in R134a

AAD%	Number of experimental points	Pseudo-Ideal-Solution Model (PISM)	NRTL Model (NRTL)	Flory-Huggins Model (FH)	Empirical quadratic equation (EQE)
ISO-220-A	48	2.88	4.65	2.48	2.44
ISO-220-B	48	2.39	6.56	5.09	3
ISO-220-C	46	2.47	8.15	3.36	3.09
ISO-220-D	44	2.48	9.48	4.31	2.91
ISO-220-E	46	3.05	9.86	5.53	2.34
ISO-68-A	47	2.45	3.53	2.73	2.21
ISO-68-B	45	2.61	2.59	2.47	2.17
ISO-68-C	46	2.11	5.92	3.36	2.23

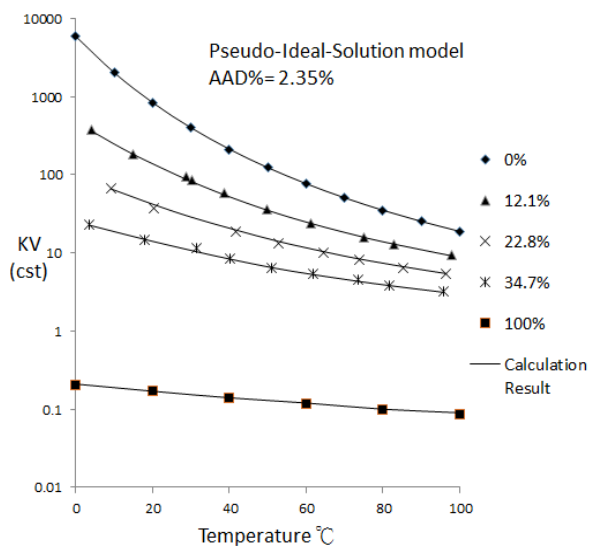
**Table 4.** Description of refrigeration lubricants using in these experiments

ISO-220-A	ISO-220-B	ISO-220-C	ISO-220-D	ISO-220-E	ISO-68-A	ISO-68-B	ISO-68-C
ISO 220 Fully branched acid POE	ISO 220 Mixed acid POE	ISO 220 Mixed acid POE	ISO 220 Mixed acid POE	ISO 220 Fully branched acid POE	ISO 68 Fully branched acid POE	ISO 68 Mixed acid POE	ISO 68 Mixed acid POE

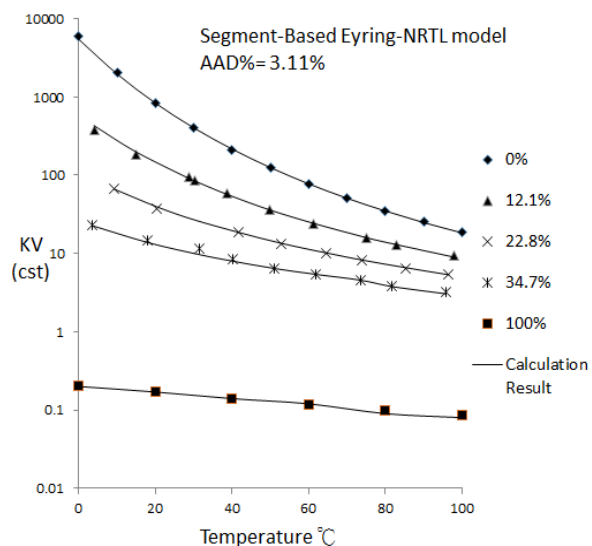
### 5.1 Comparison of Viscosity models:

AAD% of kinematic viscosity data correlation for POE in R134a is given in Table 2 and Fig 5~8. The correlation results from our new PISM viscosity model showed higher degree of accuracy than the other models

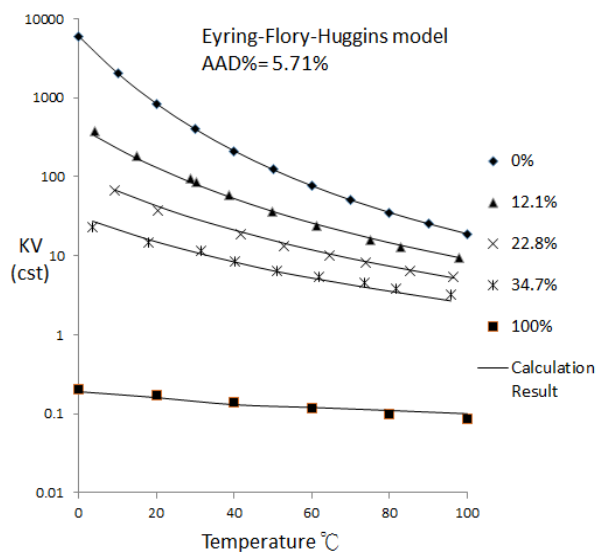
analyzed in this study. Table 2 illustrates that the accuracy of the models is significantly affected by viscosity differences between lubricant and refrigerant. Correlation accuracy will increase as viscosity of lubricant decreases in all test models. This is mainly due to the geometric asymmetry in lubricant-refrigerant mixture, and the non-randomness of mixing. Thus, thermodynamic properties of mixture are far from ideal. Since the main purpose of PISM is to make the mixture more 'ideal', PISM viscosity model would have good ability to correlate with both higher viscosity difference mixture (ISO 220-R134a) and lower viscosity difference mixture (ISO 68-R134a). The viscosity of lubricant-refrigerant mixture is typically composition-dependent. Therefore, it is of great importance for a model to be able to extrapolate the viscosities over a certain composition range, using the information obtained at a given composition. For nonpolar systems, such as lubricant-lubricant mixtures, all models should give very similar results. On the other hand, for polar systems, such as lubricant-refrigerant systems, difference of extrapolations obviously depends mainly on the flexibility of the mixing rule used. In the experimental conditions with wide range of refrigerant composition from high viscosity pure lubricant (0% refrigerant) to low viscosity pure refrigerant (100% refrigerant), PISM viscosity model demonstrated good potential to correlate the various viscosity over a wide composition range.



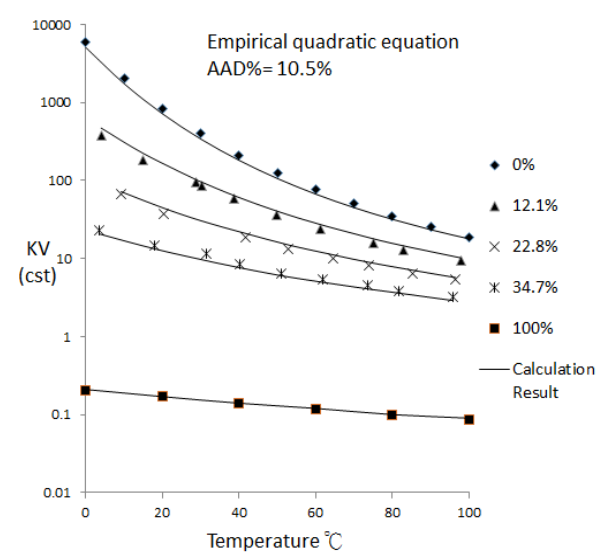
**Fig 5.** Viscosity correlation of POE ISO 220-D-R134a mixture by PISM model



**Fig 6.** Viscosity correlation of POE ISO 220-D-R134a mixture by SBEN Model



**Fig 7.** Viscosity correlation of POE ISO 220-D-R134a mixture by EFH model



**Fig 8.** Viscosity correlation of POE ISO 220-D-R134a mixture by EQE model

### 5.2 Comparison of solubility models:

The correlation results of solubility data are shown in Table 3. PISM solubility correlation showed high degree of accuracy, and are comparable to Flory-Huggins model and empirical quadratic equation. The correlation deviation of lubricant-refrigerant VLE data calculated by NRTL model seems larger than the deviation calculated by the other models in this study.

### 5.3 Physical meanings of PISM model:

In order to realize the physical meanings of PISM, we consider the following factor  $\alpha$

$$\alpha = \frac{K}{n} \quad (46)$$

Where K and n are parameters in PISM, which are defined in Equation (23) and (25). K factor implies expansion of refrigerant molar volume from original molecules to “new pseudo molecules”, and n value means the number of original molecules combined into a “new pseudo molecule”. Therefore, physical meaning of  $\alpha$  value should be degree of repulsion between lubricant and refrigerant. When  $\alpha$  value decrease, the affinity between refrigerant and lubricant will increase, while the vapor pressure decrease, and the viscosity obviously will increase. Based on PISM, at the same molar concentration of refrigerant in mixture, the more miscible mixture should have lower vapor pressure and higher viscosity than less miscible mixture. When  $\alpha$  value approaches unity, then the mixture can be considered as an ideal solution.

## 6. CONCLUSIONS

A new, comprehensive thermodynamic model incorporating the Eyring's equation and pseudo-ideal-solution concepts has been developed. The pseudo-ideal-solution model (PISM) gives a good correlation with viscosity and pressure data in lubricant-refrigerant mixtures. After testing in a various refrigerant composition mixtures, PISM shows good potential to extrapolate the viscosity and solubility over a certain composition range.

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