

An Investigation on the Dissociative Heat of Low-GWP Refrigerant/Lubricant Oil Mixtures for the Reliable Design of Refrigerant Compressors

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ABSTRACT

This study presents an investigation carried out to build an understanding of the dissociative heat of low-GWP refrigerant/lubrication oil mixtures. The dissociative heat is the heat that is generated (or absorbed) when the refrigerant gas dissolves in (or dissociates from) the refrigeration oil. Understanding of this behavior is important because the lubrication property of the lubricant oils is influenced by the thermal interactions with their surroundings. A theoretical model that predicts the dissociative heat was derived by combining a solubility model with the Clausius-Clapeyron equation and solving for the enthalpy change at the refrigerant-gas/lubricant phase equilibrium. Once the dissociative heat model was built, solubility data of low-GWP refrigerant/lubrication oil mixtures was collected from the literature and the model was tested. The considered mixtures were namely, R1234yf/POE(POE75), R1234ze(E)/POE(POE75), R1243zf/POE(RL68H), and R290/mineral oil mixtures. The calculated dissociative heat values were found to be generally consistent for all the mixtures. It was found that the dissociative heat is strongly affected by the system pressure. Analysis of the results seem to suggest that the further the state of the refrigerant gas from its corresponding saturation state at a given temperature, the higher the dissociative heat will be. Therefore, decrease in the system temperature at constant pressure or increase in the pressure at constant temperature will yield lower dissociative heat values. Generally, the results indicate that a significant quantity of heat (comparable to the latent heat of the refrigerant) is absorbed/released during the dissolution process of the refrigerant and lubricant oil. Such thermal interactions could influence the lubrication capability of the oil, and hence consideration of such effects could be a useful input towards the improvement of the reliability and performance of the refrigerant compressors. Because sustaining an effective oil film between the moving parts of the compressor is crucial to minimize the wear and the associated losses caused by the direct metal-to-metal contact.

1. INTRODUCTION

Global warming has caused a major challenge to the modern world with impacts across various aspects of human life, ecosystem, and the environment in general. The refrigeration and air conditioning industry is among the major contributors to this issue, due to the enormous quantity of refrigerant gases that are released to the atmosphere. The traditional refrigerants, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), not only have high global warming potential (GWP), but also have the potential to deplete the ozone layer. The later issue was solved by developing a class of refrigerants known as the Hydrofluorocarbons (HFCs) which offered very low (or zero) ozone layer depletion potential (ODP). However, the HFCs have high GWP. Therefore, the effort to develop refrigerants

with low GWPs and ODP has been underway. As a result, a new generation of refrigerants called the Hydrofluoroolefins (HFOs), have been developed. The HFOs have lower GWPs than the HFCs, and they are more environmentally friendly alternatives.

It is essential that the development of these new refrigerants be accompanied by the development and careful selection of compatible lubrication oils. Because the performance and longevity of the of the refrigeration system, such as the refrigerant compressor, will be strongly affected by the lubrication oil properties. One of such influencing properties is the solubility of the refrigerant in the oil. Depending on the solubility of the refrigerant in the oil, certain mass fraction of oil will be carried by the refrigerant vapor and will circulate in the refrigeration system, thereby causing some challenges such as on the heat transfer performance at the heat exchangers and the pressure loss in the system. On the other hand, depending on the solubility of the refrigerant in the oil, the lubrication property (viscosity) of the oil can be altered significantly due to the presence of the refrigerant in the oil. Reduction of the viscosity of the lubricant oil will break the vital lubricant film between the moving parts which will lead to the premature failure of the components and the system. Thus, the investigation of the phase behavior, thermophysical properties of the refrigerant/lubricant oil mixture, among others, are very vital.

Therefore, the main objective of the current study is, to be able to understand and estimate the thermal behavior of the refrigerant/lubricant oil mixture during the dissolution. More specifically, the research aims to estimate the dissociative heat of the refrigerant/lubricant oil mixtures. The dissociative heat is the heat that is generated (or absorbed) when the refrigerant gas dissolves in (or dissociates from) the refrigeration oil. Understanding of this behavior is important because the lubrication property of the lubricant oils is influenced by the thermal interactions with their surroundings. Therefore, in the present study, a theoretical model has been developed to estimate the dissociative heat. The vapor-liquid equilibrium between the refrigerant gas and the refrigeration oil has been modeled by combining a solubility model with the Clausius-Clapeyron equation. The solubility model was prepared based on experimental data from the literature, then, Clausius-Clapeyron equation was used to derive the enthalpy of dissociation of refrigerant gas from the refrigeration oil. Based on the literature data, the dissociative heat was estimated for several low-GWP refrigerant/lubricant oil mixtures.

2. METHODOLOGY

2.1 Solubility model

In a multicomponent mixture system, when the gas phase is treated as an ideal gas and the liquid phase is treated as an ideal solution, the relation outlined in equation (1) holds true. Because the gas phase obeys Dalton's law, and the liquid phase side obeys Raoul's law.

$$Py_i = P_i^s x_i \quad (1)$$

where, P represents the total pressure, P_i^s : represents the saturated vapor pressure when component i exists alone, x_i represents the mole fraction of component i in the liquid phase, and y_i represents the mole fraction of component i in the gas phase.

In the case of a mixture of the refrigerant ($i = 1$) and the refrigeration oil ($i = 2$), the vapor pressure of the refrigeration oil is considered to be very small compared to the vapor pressure of the refrigerant. Thus, the mole fraction of the refrigerant and the lubrication oil in the gas phase will be, $y_1 = 1$ and $y_2 = 0$, respectively. Therefore, the following equation holds true.

$$P = P_i x_i \quad (2)$$

Multiplying both sides of equation (2) by a factor that takes into account the non-ideality of the gas and liquid phases, respectively, the resulting equation will be as follows:

$$P\phi_1 = \gamma_1 P_i x_i \quad (3)$$

where, ϕ_1 is the fugacity coefficient and γ_1 is the activity coefficient of the refrigerant.

From the equation of state of a real gas, the fugacity coefficient can be expressed by the following equation.

$$\phi_1 = \exp \left[\frac{(B_{11} - \bar{v}_{L1})(P - P_1^s)}{RT} \right] \quad (4)$$

where, B_{11} is the second virial coefficient, \bar{v}_{L1} is the saturated liquid molar volume. These values can be obtained from the REFPROP 10.0 database. The system temperature and the universal gas constant are denoted by T and R , respectively.

The Non-Random Two Liquid (NRTL) activity coefficient model is chosen to model the solubility of the refrigerant and lubricant oil mixture. The model is given by the following equations (5) to (9):

The activity coefficient is given by:

$$\ln \gamma_1 = x_2^2 \left(\tau_{21} \left[\frac{\exp(-\alpha \tau_{21})}{x_1 + x_2 \exp(-\alpha \tau_{21})} \right]^2 + \frac{\tau_{12} \exp(-\alpha \tau_{12})}{[x_2 + x_1 \exp(-\alpha \tau_{12})]^2} \right) \quad (5)$$

The non randomness parameter is denoted by α and the binary interaction parameters for the refrigerant/lubricant oil mixture are defined as follows:

$$\tau_{12} = \frac{\Delta g_{12}}{RT} \quad (6)$$

$$\tau_{21} = \frac{\Delta g_{21}}{RT} \quad (7)$$

$$\Delta g_{12} = a_{12} + 10^{-3} b_{12} T + 10^{-5} c_{12} T^2 \quad (8)$$

$$\Delta g_{21} = a_{21} + 10^{-3} b_{21} T + 10^{-5} c_{21} T^2 \quad (9)$$

The constants a_{ij} , b_{ij} & c_{ij} are empirical temperature-dependent parameters and they are determined by the fitting of experimental data.

2.2 Estimation model of the dissociative heat

The estimation of the dissociative heat is carried out by building on the solubility model developed for the mixtures. The solubility equations will be combined with the Clausius-Clapeyron equation to estimate the vapor-liquid-equilibrium behavior.

The Clausius-Clapeyron equation is given as follows:

$$\frac{dP_1^s}{dT} = \frac{h_{fg}}{(v_v - v_L)T} \quad (10)$$

where P_1^s is the saturated vapor pressure, T is the system temperature, v_v and v_L denote the saturated vapor and saturated liquid specific volume. The latent heat of vaporization is represented by h_{fg} . Using the Clausius-Clapeyron

equation, the latent heat of evaporation can be obtained from dP/dT , which is the slope of the saturated vapor pressure curve.

In a similar manner, the Clausius-Clapeyron equation can be applied to the vapor-liquid-equilibrium of the refrigerant/lubricant mixture.

$$\frac{dP}{dT} = \frac{h_D}{(v_g - v_{abs})T} \quad (11)$$

where the h_d refers to the dissociative heat, and refrigerant/lubricant mixture equilibrium pressure is denoted by P . The molar volume of the superheated refrigerant vapor is denoted by v_g . On the other hand, the molar volume of the refrigerant gas that is dissolved in the lubricant oil is represented by v_{abs} .

The solution for the dissociative heat can be started by rearranging equation (11) as shown in the following equation and solving the pressure derivative with respect to the temperature.

$$h_D = (v_g - v_{abs})T \frac{dP}{dT} \quad (12)$$

The NRTL solubility model is used to find the solution for the derivative in the above equation. The analysis is explained as follows:

Considering the non-ideal behavior of the refrigerant/oil mixture, if the equation (3) is rewritten in a logarithmic form, the following will be obtained:

$$\ln \phi_1 + \ln P = \ln \gamma_1 + \ln P_1^s + \ln x_1 \quad (13)$$

After re-arranging the equation (13) and differentiating both sides of the equation with respect to the temperature:

$$\frac{d \ln P}{dT} = \frac{d \ln P_1^s}{dT} + \frac{d \ln \gamma_1}{dT} - \frac{d \ln \phi_1}{dT} \quad (14)$$

Performing the derivative on the left-hand side of equation (14), the derivative of the pressure with respect to the temperature can be stated as:

$$\frac{dP}{dT} = P \left(\frac{d \ln P_1^s}{dT} + \frac{d \ln \gamma_1}{dT} - \frac{d \ln \phi_1}{dT} \right) \quad (15)$$

The first term in the bracket in equation (15) can be obtained by applying the Clausius-Clapeyron equation as follows:

$$\frac{d \ln P_1^s}{dT} = \frac{d \ln P_1^s}{dP^s} \cdot \frac{dP^s}{dT} = \frac{1}{P^s} \cdot \frac{h_{fg}}{(v_v - v_L)T} \quad (16)$$

The second term is expressed as follows:

$$\frac{d\ln\gamma_1}{dT} = x_2^2 \cdot \left(E_1 \cdot E_2 + \frac{E_3(E_4 - E_5)}{E_6} + \frac{E_7 - E_8}{E_9} \right) \quad (17)$$

where E_1 to E_{10} are given by:

$$E_1 = \frac{1}{R} \left(C_{21} \cdot 10^{-5} - \frac{a_{21}}{T^2} \right) \quad (a)$$

$$E_2 = \left(\frac{\text{EXP}(-\alpha\tau_{21})}{x_1 + x_2 \text{EXP}(-\alpha\tau_{21})} \right)^2 \quad (b)$$

$$E_3 = 2\tau_{21} \cdot \frac{\text{EXP}(-\alpha\tau_{21})}{x_1 + x_2 \text{EXP}(-\alpha\tau_{21})} \quad (c)$$

$$E_4 = \text{EXP}(-\alpha\tau_{21}) \cdot (-\alpha) \cdot [x_1 + x_2 \text{EXP}(-\alpha\tau_{21})] \cdot E_1^2 \quad (d)$$

$$E_5 = -\alpha \cdot E_1^2 \cdot x_2 \cdot [\text{EXP}(-\alpha\tau_{21})]^2 \quad (e)$$

$$E_6 = [x_1 + x_2 \text{EXP}(-\alpha\tau_{21})]^2 \quad (f)$$

$$E_7 = [\text{EXP}(-\alpha\tau_{12}) - \alpha\tau_{12} \cdot \text{EXP}(-\alpha\tau_{12})] \cdot (E_9)^{0.5} \cdot (E_{10})^2 \quad (g)$$

$$E_8 = -2\alpha \cdot \tau_{12} \cdot x_1 \cdot E_9 \cdot (E_{10} \cdot [\text{EXP}(-\alpha\tau_{12})])^2 \quad (h)$$

$$E_9 = [x_2 + x_1 \text{EXP}(-\alpha\tau_{12})]^4 \quad (i)$$

$$E_{10} = \frac{1}{R} \cdot \left(C_{12} \cdot 10^{-5} - \frac{a_{12}}{T^2} \right) \quad (j)$$

The third term in the bracket of equation (16) is expressed as follows:

$$\frac{d\ln\phi_1}{dT} = \frac{d\ln\phi_1}{d\phi_1} \cdot \frac{d\phi_1}{dT} = \frac{d}{dT} \left[\frac{(B_{11} - \bar{v}_{L_1})(P - P_1^s)}{RT} \right] \quad (18)$$

By substituting the equations (16) through equation (18) to the equation (15), the derivative of the pressure (dP/dT) can be obtained. As a result, the dissociative heat can be calculated by the equation (12).

2.3 Experimental data

The experimental data that is necessary for the analysis was obtained from the literature. Table 1. provides a summarized overview of the extracted data and Table 2 provides the information about the refrigerants.

Table 1: Summary regarding the data extracted from the literature

Mixture	Refrigerant	Lubricant oil	Data source
1	R1234yf	POE (POE75)	X. Jia et al., (2020)
2	R1234ze(E)	POE (POE75)	
3	R1243zf	POE (RL68H)	H. Jia et al., (2023)
4	R290	Mineral oil (3GS)	X. Wang., (2021)

The solubility data is obtained as mole fraction of the refrigerant and lubricant oil, except for the 4th mixture (R290/Mineral oil). Therefore, the corresponding mole fraction data was calculated for it using the following equation.

$$x_1 = \frac{\frac{w_1}{M_1}}{\frac{w_1}{M_1} + \frac{1 - w_1}{M_2}} \quad (18)$$

Where w_1 is the mass fraction of the dissolved refrigerant and the lubricant oil. M_1 and M_2 represent the molecular mass of the refrigerant and lubricant oil, respectively. The molecular mass of the oil was taken to be $316.62 \text{ g} \cdot \text{mol}^{-1}$ (X. Wang., (2021))

Table 2: Information regarding the refrigerants used in the study

	R1234yf	R1234ze(E)	R1243zf	R290
Ozone depletion potential	0	0	0	0
Global warming potential *	4	6	1	3
Molecular weight [g/mol]	114.040	114.040	96.051	44.096
Critical temperature [K]	368	382	379	370
Critical pressure [MPa]	3.382	3.635	3.609	4.2512
Normal boiling point [K]	244	254	248	231
Latent heat of vaporization [J/mol]**	16578	19036	17404	14804
[kJ/kg]	145	167	181	336

* 4th IPCC

** Evaluated at 298.15 K using REFPROP ver. 10.0

3. RESULTS AND DISCUSSION

The solubility model that is discussed in section 2.1 has been applied for all the experimental data and the corresponding solubility equation were obtained. Then the dissociative heat was estimated by solving the model presented in section 2.2. The solubility correlation equations obtained for each mixture serve as the input to the dissociative heat calculation process along with the experimental solubility data. Results of the calculations are presented in the following figures.

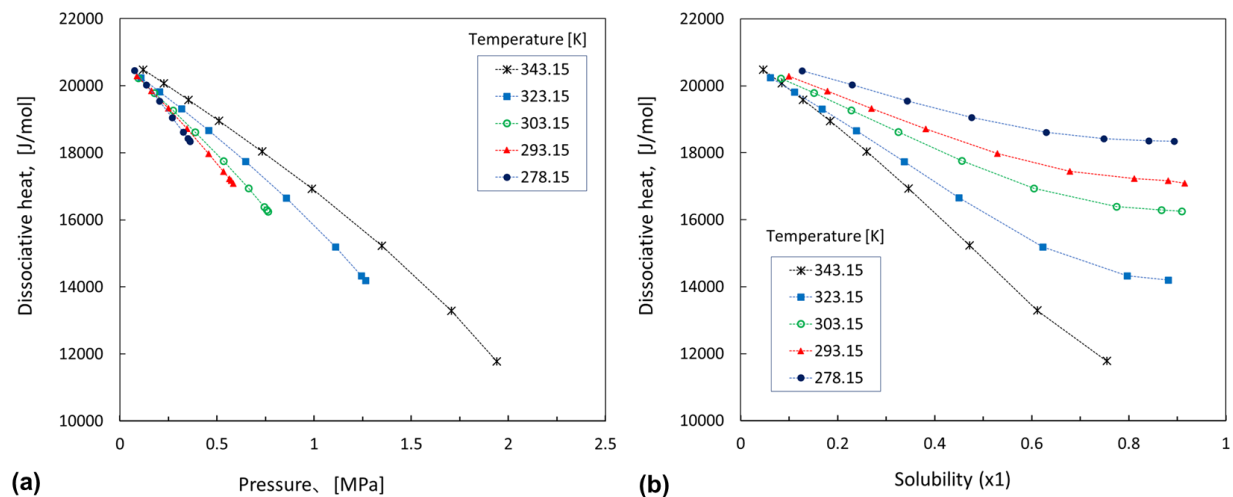


Figure 1: Calculation result of the dissociative heat for the **R1234yf/POE** mixture

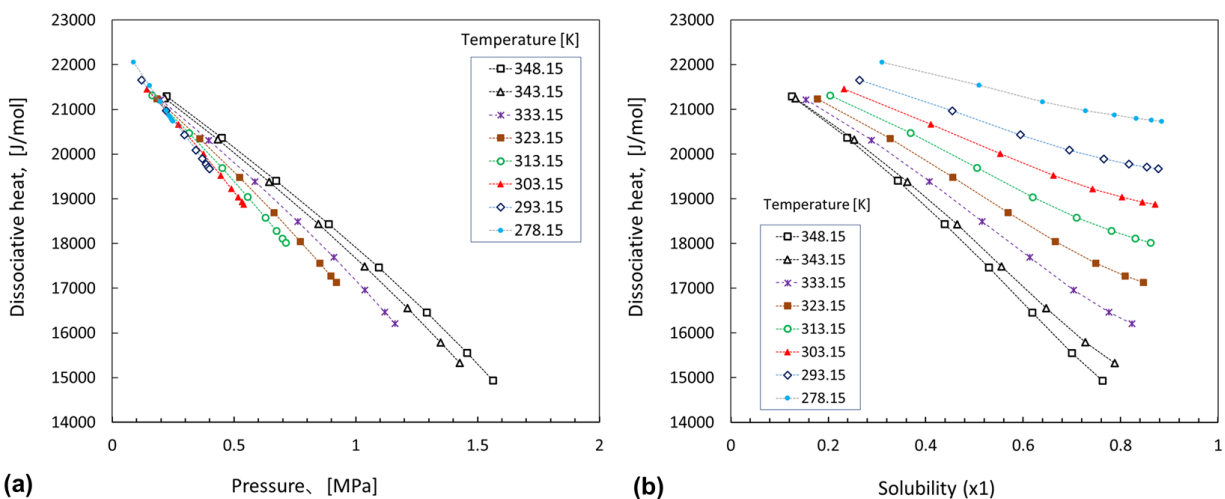


Figure 2: Calculation result of the dissociative heat for the **R1234ze(E)/POE** mixture

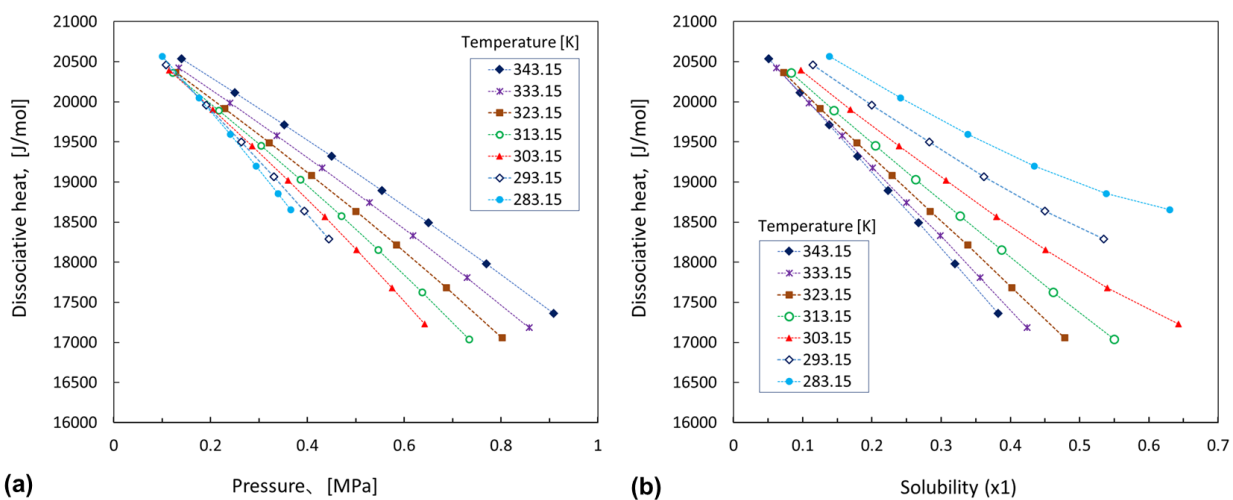


Figure 3: Calculation result of the dissociative heat for the **R1243zf/POE** mixture

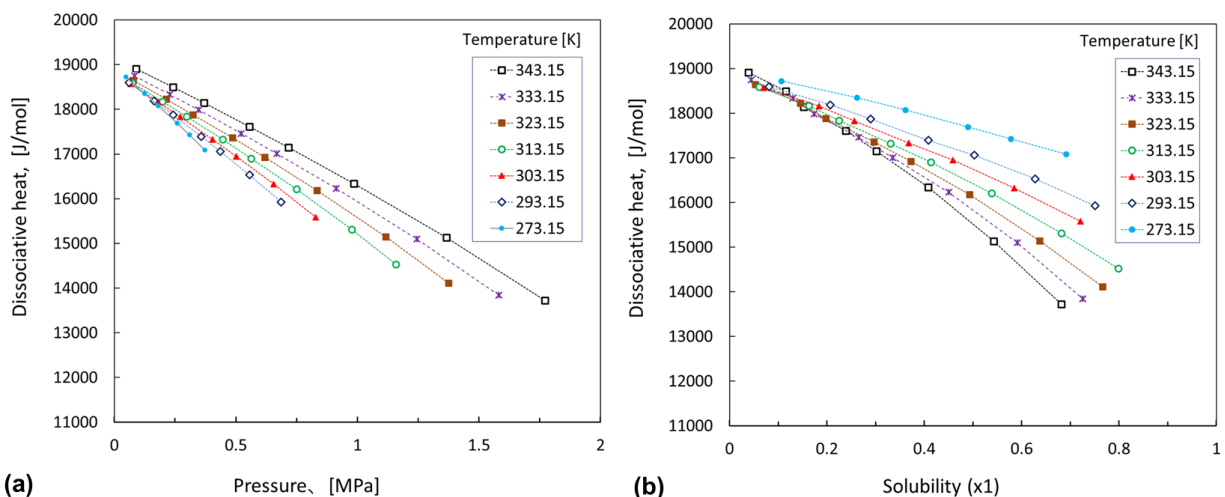


Figure 4: Calculation result of the dissociative heat for the **R290/Mineral oil** mixture

As it is shown in the results above, all the refrigerant/lubricant oil mixtures exhibit a declining trend of the dissociative heat as the refrigerant pressure increases. This tendency seems to follow the increasing trend of the solubility of the mixtures with respect to the system pressure.

All the calculated dissociative heat values were compared to the latent heat of the refrigerants at each temperature levels. It was found that all the estimated dissociative heat values are higher than the latent heat of vaporization. For instance, considering the R1234yf/POE mixture data; at the temperature of 293K and system pressure of 0.087MPa, the dissociative heat is about 19% higher than the corresponding latent heat of the refrigerant. However, this deviation gradually decreases and reaches to only 0.4% when the system pressure is increased to 0.583MPa. The same tendency is observed for the other temperature points as well.

For the other refrigerant/lubricant oil mixtures are well, similar behavior is observed. For instance, considering the R290/mineral oil mixture data; at the temperature of 293K and system pressure of 0.06MPa, the dissociative heat is about 22% higher than the corresponding latent heat of the refrigerant. However, the deviation quickly drops to about 5% when the system pressure is increased to 0.686MPa.

It can also be observed from the figures that, at a given system pressure, the increase in the system temperature corresponds to a higher dissociative heat value. Therefore, the indication of these observations seems that, the further the state of the refrigerant gas from the corresponding saturation state, the higher the dissociative heat value. As a result, for each isotherm, when the system pressure is increased, the dissociative heat approaches the latent heat of the refrigerant.

It can be observed from the results that the dissociative heat is significant in quantity that it is comparable to the latent heat of the refrigerant. Hence, the absorption/release of such quantity of heat to the lubrication oil would influence the lubrication capability of the oil. This observation is important from the point of view of the lubrication of the moving parts of the compressor. Because knowledge of the thermal influences that are imposed on the lubricant is vital to attain the proper lubrication system for the moving parts. The lubricant oil properties, such as the viscosity are strongly affected by temperature and hence better knowledge of the thermal effects on the lubricant oil is important. The proper lubrication system design would make it possible to sustain an effective oil film between the moving parts of the compressor thereby minimizing the wear and the associated losses caused by the direct metal-to-metal contact.

Even though the findings of the current study are based on few low-GWP refrigerants and lubricant oil mixtures, the estimation of the dissociative heat can be extended for other refrigerant and lubricant oil mixtures as well. Including the existing systems, such as those utilizing the R134a, the estimation of the dissociative heat can be carried out to estimate the thermal contribution of the refrigerant gas dissolution in the lubricant oil upon availability of the solubility data. For the case of R134a, the dissociative heat might be expected to behave in similar manner to that of the R1234yf due to the similarity of the corresponding properties of the R134a and R1234yf.

6. CONCLUSIONS

A theoretical model has been developed for the estimation of the dissociative heat of the refrigerant gas that is dissolved in the lubrication oil of the refrigerant compressors. The model has been developed based on the Clausius-Clapeyron equation, the NRTL (non-random two liquid) solubility model and successfully tested using literature data. The concluding remarking of the study are outlined as follows.

- The dissociative heat estimation model seems to provide consistent results for the various low-GWP refrigerant/lubricant oil mixtures that were investigated, namely, R1234yf/POE(POE75), R1234ze(E)/POE(POE75), R1243zf/POE(RL68H), and R290/mineral oil mixtures.
- The dissociative heat seems to be strongly affected by the system pressure. For all the mixtures that were evaluated at various temperature, a decrease in the system pressure has resulted in an increase in the dissociative heat.
- At constant system pressures, the dissociative heat increases as the system temperature increases.
- The lower limit to the dissociative heat seems to be the latent heat of vaporization of the pure refrigerant. All the calculated dissociative heat values were found to be higher than the corresponding latent heat of vaporization of each isotherm.
- The results seem to suggest that the further the state of the refrigerant gas from its corresponding saturation state at a given temperature, the higher the dissociative heat will be. Therefore, decrease in the system temperature at constant pressure or decrease in the pressure at constant temperature will yield low dissociative heat values.
- Generally, the results indicate that a significant quantity of heat (comparable to the latent heat of the refrigerant) is absorbed/released during the dissolution process of the refrigerant and lubricant oil. Such thermal interactions could influence the lubrication capability of the oil, and hence consideration of such effects could be a useful input towards the improvement of the lubrication of the moving parts of the compressor thereby enhancing its reliability and performance.

NOMENCLATURE

B_{11}	second virial coefficient	(m ³ /mol)
GWP	global warming potential	
h_d	dissociative heat	(J/mol)
h_{fg}	latent heat of vaporization	(J/mol)
M	molar mass	(g/mol)
NRTL	non-random two liquid model	
ODP	ozone depletion potential	
P	pressure	(MPa)
P^s	saturation pressure	(MPa)
R	universal gas constant	(J/mol/K)
T	temperature	K
w	mass fraction in liquid phase	
x	mole fraction in liquid phase	
Y	mole fraction in gas phase	

Subscript

1, 2	component 1, and 2, respectively
a_{ij}, b_{ij}, c_{ij}	empirical temperature-dependent parameters
abs	absorbed gas.
g	gas phase of the refrigerant
L	saturated liquid state
v	saturated vapor state

Greek

α	non randomness parameter
γ	activity coefficient
v	molar volume (J/mol/K)
τ_{ij}	binary interaction parameters
ϕ	fugacity coefficient

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