Experimental Investigation and Modeling of Moisture Solubility in R-12 and R-134a

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Abstract

Worldwide reactions to global warming and ozone depletion have led to social responses and legislative measures that have serious implications for refrigeration and associated industries. Some refrigerants used in refrigeration industries were reported as contributing factors to atmospheric degradation. In phasing out these gases alternatives were sought as replacements. Research is going on in order to determine the thermodynamics, physical and thermal properties as well as ozone depletion potentials of these alternative refrigerants, but not much attention had been paid to the control of moisture and other contaminants in these alternative refrigerants. This article examines the moisture solubility in R-12 and one of its established alternatives, namely R-134a. The result obtained for R-12 was compared with existing data and the deviation was within 20%. The moisture solubility for both R-12 and R-134a followed a similar trend at higher temperatures, but there was a serious deviation at sub-zero temperate. Solubility curves, from the obtained data, were used to develop models for predicting moisture solubility in both R-12 and 134a refrigerants at various temperatures.

Keywords: Refrigerant, atmospheric degradation, modeling, CFCs, R-12, R-134a.

Introduction

Chlorofluorocarbon (CFC) compounds are used as aerosol propellants, blowing, cleaning agents and refrigerants. These compounds had been in use since the 17th century. Examples of these compounds are: R-11; R-12; R-113; R-114; to mention but a few. These compounds contain no Hydrogen atoms because they are fully halogenated organic compounds. All the hydrogen atoms had been replaced by either chlorine or fluorine atom(s).

The search for alternatives to these compounds began in 1974 when a theory was proposed by two American scientists (Rowland and Monila), that fully halogenated chlorofluorocarbons (CFCs) released into the troposphere could cause a reduction of ozone in the stratosphere. As a result, steps were taken to stop the release of these compounds into the atmosphere. This led to the emanating of regulations such as Montreal and Kyoto Protocols. The Montreal Protocol restricted the production of the individual chemicals of concern, leading to their ultimate phase out for most uses (Calm 2002). The Kyoto Protocol imposed national limits on emissions of important greenhouse gases (GHGs), these encompassing six specific gases or grouped of gases. The most critical gas among them is CO₂ (Ko, et al. 1993).

The severe consequences of ozone depletion are being averted through international adherence to Montreal and Kyoto protocols. These are done by search for alternatives to CFCs. It has been discovered that no fully halogenated compounds are good alternatives to the fully halogenated CFCs. These are called HFCs (hydrogen-fluorocarbon) (Kutter 1988; Calm, et al. 1999). Examples of these compounds are: R–123, R-141b, R-22, R-124, R-1529, etc. Research is going on in order to determine the thermodynamics and physical properties, as well as ozone depletion potentials, of these alternatives (Lorentzen 1988; Kutter 1988; and Clark 1999).
In an attempt to study the thermodynamics properties of alternatives to R-22, Wijuya and Spatz (1995) measured average heat transfer coefficients for R-410 and pure R-22. Tests were conducted in a 3.05m long, 7.75 mm diameter tube. They expected the mixture (R-410a) to perform slightly better than pure R-22 based on its thermal properties. By comparing the semi-local heat transfer coefficients they found that, over the entire range, the mixture performed 2% to 6% better than R-22. Chitti and Anand (1996) also compared the performance of R-22 and R-410a in an 8.0 mm smooth tube. They found that R-410a had higher heat transfer coefficients at higher mass fluxes but also found that R-22 had significantly higher heat transfer coefficients at the lower mass fluxes. They attributed some of the differences to the high experimental uncertainty at the lower mass fluxes. Eckels and Tesene (2003) compared the thermodynamic properties of R-22, R-134a, R-410a and R-407c. In their work, the performances of refrigerants R-22, R-13a, R-410a and R-407c were compared in a range of typical condenser tubes. The average heat transfer coefficients were measured at a saturation temperature of 40°C and over a mass flux range of 125 kg/m².s to 600 kg/m².s. Local heat transfer coefficients were measured in the 9.52 mm outer diameter smooth tube and micro-fin tube. A comparison of the performance of the different refrigerants reveals that R-134a has the highest performance, in both the smooth tube and the micro-fin tube, of all the refrigerants tested. R-22 and R-410a had similar performances that were slightly less than R-134a. In general, R-407c had the lowest performance of the refrigerants tested. A similar experiment was performed by Eckels and Tesene (2004) where it was reported that R-134a and R-12 indicated similar thermodynamic characteristics. Their work also corroborates the works of Kutter (1988) and Goncalves (1999). More works about the thermodynamic properties of alternative refrigerants can be seen in the works of: Akintunde, et al. (2005); Kedzierski and Goncalves (1999) and McMullan (2002).

Detailed information on the ozone depletion potentials of refrigerants and their alternatives can be found in the works of Calm and Didion (1998); Ko, et al. (1993); Calm (2002); Kutter, (1988); McMullan, (2002); Sand, et al. (1997); and Spauschas (1991).

Haagan-Smit, et al. (1970) used coulometric titration method to determine the moisture contents of some hydrocarbon refrigerants such as R-11 and R-22. In their experiment, water was titrated with iodine that was generated electrochemically. The instrument used measured the quantity of electric charge used to produce the iodine and then back titrated with water through which the amount of moisture content was calculated. The gravimetric method for measuring moisture content of refrigerants was described in ASHRAE Standards (2002). In this method, a measured amount of refrigerant vapour was passed through two tubes connected in series, each containing phosphorous pent-oxide (P₂O₅). Moisture present in the refrigerant reacts chemically with the P₂O₅ and appears as an increase in mass in the first tube. The second tube is used as a tare. In this method, approximately 200 g of refrigerant is required for accurate results.

Thrasher, et al. (1993) used nuclear magnetic resonance spectroscopy to determine the moisture solubility of R-123 and R-12. Another method, infrared spectroscopy, was used for moisture analysis of some refrigerants, (Cohen 1994) but requires a large sample for precise results and is subject to interference if lubricant is present in the refrigerant.

In the research outlined here, the moisture contents of R-12 and one of its alternatives (R-134a) were examined at various temperatures. The objectives of this work were to obtain data for moisture solubility in R-12 and R-134a at various temperatures to ascertain R-134a as a substitute for R-12 in relation to moisture retention and to present model for the prediction of moisture contents in both R-12 and R-134a at various temperatures.

Materials and Methods

The simplified experimental rig is shown in Fig.1, the rig consists of two refrigerant glass bottles labeled “A” and “B”. Bottle “B” was kept at the atmospheric condition...
throughout the experimentation and its volume is twice that of “A”, while the Temperature of bottle “A” was varied. Both bottles were weighted before and in between the experimentation. Bottles “A” and “B” were equipped with one directional non-return valves “E” and “F”, respectively. Bottle “A” was further equipped with water inlet valve (G) the entering water was spared in the bottle to facilitate proper contact and mixing with the refrigerant. Bottle “A” was kept on a regulated electric heater. Bottle “A” was connected to a refrigerant bottle until its mass was increased by 500 g. The electric heater, on which bottle “A” was kept, was set to the required temperature. “A” was kept on the heater until the temperature is justified uniform by the use of mercury in glass thermometer (H). Moisture was then introduced through value “G” and spray inside the refrigerant while the set temperature was maintained. This process was continued until water began to appear at the base of bottle “A”.

Tubes “C” and “D” were connected in series as shown in Fig. 1. Tube “C” contains 20 g of activated silica gel while tube “D” contains 10 g of activated alumina as suggested by Cohen and Blackwell (1995). Both tubes were of the same material and weighted together with their contents before installation.

Valves “F” and “E” were then opened simultaneously. The refrigerant then passes from “A” to “B” very slowly, because of the cooling effect so as to maintain the required temperature. It takes between 8 to 10 hours to increase the weight of “B” by 200 g.

The tubes were then disconnected and their ends corked to prevent entering of atmospheric moisture. The tubes were weighted on an electronic balance, which has a resolution of 0.005 mg. It was only tube “C” that shows change in weight while that of D was constant. In any case of change in the weight of tube D, the amount of desiccant in C would have to be increased and the experiment repeated.

For sub-zero temperatures, A was transferred to a 10 kW deep freezer and the temperature was regulated via thermostats. The experiment was repeated as stated above. Experimentation becomes unreliable at temperature below -60°C, since it becomes difficult to keep the refrigerants in the liquid phase.

Results and Discussions

Fig. 2 shows the moisture solubility of R-12 and R-134a in 200 g of the respective refrigerant. Fig. 3 shows the comparison of moisture solubility of R-12 measured in this work (R12M) as compared with that of Thrasher, et al. (1993) (R12T) in mg/kg. Fig. 4 shows the comparison of moisture solubility of R-12 and R-134a in mg/kg; while Fig. 5 shows the relative moisture solubility of R-12 and R-134a.

As can be seen in all the figures, the general trend was the same. The solubility increased with increases in temperature and that of R-134a was always higher than that of R-12.
Fig. 3, which presents the comparison of moisture solubility of R-12 as measured in this work with that of Thrasher, et al. (1993), shows that the experimental method used is this work was reliable, since both results agreed, although the values of moisture solubility measured by Thrasher, et al. were about 20% (averagely) higher than that of the present work. Since the solubility of moisture in R-134a is very high, the refrigerant should not be exposed when used for system charging. It is still advisable to pass the refrigerant through desiccant before its charged into system. This will prevent corrosion and copper plating and thereby extend the life system.

Also, though the solubility decreases with temperature as shown in all the figures, the relative solubility of R12/R134a is outrageous at sub-zero temperatures (Fig.5). Care should be taken therefore when R-134a is used as alternative to R-12, at sub-zero temperature, because any leakage or opportunity for moisture to enter the system may be dangerous.

**Solubility Model**

Looking at the nature of the solubility curves, one can think of any of the following models, logarithmic, hyperbolic or conic section (i.e. parabola, hyperbola). Equations (1) to (4) were then suggested.

\[ S = a e^{bT} \]  
\[ S = a \log_e T \]  
\[ S = a \cosh bT = a \sinh bT \]  
\[ S = aT^2 \]

Where: \( S \) = moisture solubility in mg/kg at a given temperature \( T \) in °C, \( a \) and \( b \) are constants to be determined using the experimental data.

Equation (2) could not be used because \( T \) has some negative value and equation (4) failed because \( S \) in not a doubled valued parameter. The values obtained when equation (3) was applied were too outrageous and was dropped.

Equation (1) was subjected to least square method analysis to determine the value of the constants (“\( a \)” and “\( b \)”). The process of least square method is summarized as follows using equation (1)

\[ S = a e^{bT} \]  

(1)
Equation (1) can be written in linear form by taking the logarithms of both sides, this is given in equation (4).
\[
\ln(S) = \ln(a) + b\ln(T) \quad (4)
\]
If we let \( y = \ln(S) \), and \( \ln a = c \) we have equation (6)
\[
y = c + b\ln(T) \quad (6)
\]
The difference of ordinates (D) using equation (6) is given by equation (7) and the summation of its squares, at a given point, say \( (y_i, T_i) \) is given by equation (8)
\[
D = y_i - c - bT_i \quad (7)
\]
\[
\psi = \sum_{i=1}^{n} (y_i - c - bT_i)^2 \quad (8)
\]
Equation (8) was then differentiate with respect to \( c \) and \( b \), and rearranged to get equations (9) and (10) respectively.
\[
\sum_{i=1}^{n} y_i - b\sum_{i=1}^{n} T_i - nc = 0 \quad (9)
\]
\[
\sum_{i=1}^{n} y_i T_i - b\sum_{i=1}^{n} (T_i)^2 - c\sum_{i=1}^{n} T_i = 0 \quad (10)
\]
Experimental data were used to solve equations (9) and (10) simultaneously to obtain the values of \( b \) and \( c \). Then the value of \( a \) from equation (11)
\[
a = \beta \quad (11)
\]
The resulting models for R-12 and R-134a were given in equations (12) and (13), respectively.
\[
S_{12} = 15.534e^{0.0641T} \quad (12)
\]
\[
S_{134} = 324.867e^{0.0376T} \quad (13)
\]
Where: \( S_{12} \) and \( S_{123} \) are the moisture solubility for R-12 and R-134a, respectively.

Figs. 6 and 7 show the comparison of model results with the experimental data for R-12 and R-134a, respectively. The two results are summarized in Fig. 8.

**Conclusion**

The moisture solubility of R-12 and R-134a were examined within temperature range of typical condensers (35 °C to 60 °C) and evaporators (–60 °C to 10 °C). A comparison of the moisture solubility of R-12 and R134a shows the R-134a absorbed more moisture than R-12 at all temperatures.

Empirical models were developed for both R-12 and R-134a for the determination of their moisture contents at a given temperature. The developed models agreed very well with the measured values.

Although it has been established that R-134a is a good alternative to R-12 from thermodynamic point of view (Calm 2002; and Mahmoud, et al. 2001), care must be taken in the use of R-134a to prevent system rusting and copper plating which may result due to large moisture content in the refrigerant. It is advisable to pass R-134a through desiccant when charging and proper flushing during repair.
References