

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 legislature measures, which have serious implications for refrigeration and associated industries. Some gases (called Refrigerants) used in the refrigeration industries were sported as contributing factor to this atmospheric degradation. In phasing out these gases alternatives were sought as replacement. Researches are going on, on the thermodynamics and physical properties as well as ozone depletion potentials of these alternatives, but no much attention had been paid to the control of moisture and other containments in these alternative Refrigerant systems. This study examines the moisture solubility in R-12 and one of its established alternatives, namely R-134a. The result for R-12 was compared with an existing data and the deviation was within 20%. The moisture solubility in both R-12 and R-134 follows similar trend at higher temperatures but there is a serious deviation at sub-zero temperature. Looking at the trend of solubility curves, models for predicting moisture solubility in both refrigerants were predicted.

Key words: Moisture solubility, investigation, R-12, R-134a

INTRODUCTION

Chloro- Fluoro –Carbon (CFC) compounds (other wise known as refrigerants in Refrigeration industries) are used as aerosol propellants, blowing and cleaning agents and refrigerants. These compounds had been in use since 17th century. Examples of these components are, R-11, R-12, R-113, R-114, to mention but a few. These compounds contains no Hydrogen atom, hence are called fully halogenated organic compounds. All the hydrogen atoms had been replaced by either chlorine or fluorine atom(s).

As a result of the two U-S scientists (Rowland and Monila) in 1974, that proposed a theory that fully halogenated Chloro-Fluoro-Carbons (CFCs) release into the troposphere could cause a reduction of ozone in the stratosphere, steps were taken to stop the release of these compounds. This leads to the emanating of regulations such as Montreal and Kyoto Protocols. The functional measures of the Montreal and Kyoto Protocols – beyond those addressing scientific assessments and international assistance – differ. The Montreal Protocol restricts the production of the individual chemicals of concern, leading to their ultimate phaseout for most uses^[1]. The Kyoto Protocol imposes national limits on emissions of important Green-House-Gases (GHGs), but does not by a collective approach encompassing six specific gases or group of gases. The most critical gas among them is CO₂^[2]. HFCs and PFCs are groups constitute two of the six GHGs in the Kyoto Protocol bracket.

The severe consequences of ozone depletion are being averted through international adherence to Montreal and Kyoto protocol. These are done by search

for alternative to CFCs. It has been discovered that none fully halogenated compounds are good alternatives to the fully halogenated CFCs. These are called HCFs,^[3,4]. Examples of these compounds are: R – 123, R-141b, R-22, R-124, R-1529 etc. Researches are going on, on their thermodynamics and physical properties as well as ozone depletion potentials^[5,6].

In an attempt to study the thermodynamics properties of alternative to R-22,^[7] 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^[8]. also compared the performance of R-22 and R-410a in a 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^[9]. 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 m⁻².s to 600 kg m⁻².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

3 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^[10] where it was reported that R-134a and R-12 indicated similar thermodynamic characteristics. More works about the thermodynamic properties of alternative refrigerants can be seen in the works of:^[11-13].

Works on the ozone depletion potentials of refrigerants and their alternatives can be found in the works of^[1-3,13-16] Haagan smit^[17] use *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^[18]. In this method, a measured amount of refrigerant vapour was passed through two tubes connected in series, each containing phosphorous pent-oxide (P_2O_5). Moisture present in the refrigerant reacts chemically with the P_2O_5 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.*,^[19] 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^[20] but requires a large sample for precise results and is subject to interference if lubricant is present in the refrigerant.

In this study moisture contents of R-12 and one of its alternatives (R-134a), was examined at various temperatures. The objectives of this study are to obtain solubility data for R-134a at various temperatures and to ascertain its substitute for R-12 in relation to moisture retention and to present model for the determination of their moisture contents.

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 through-out 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

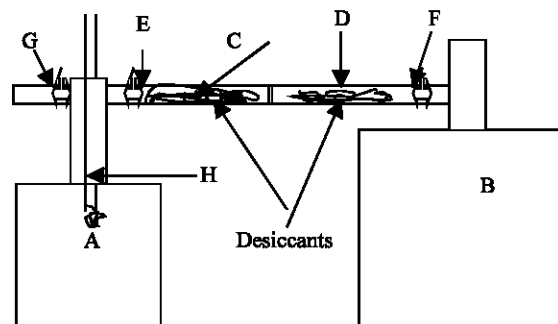


Fig. 1 Simplified Experimental set-up

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 connect 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 and A kept on it until the temperature is adjudged 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 continuing until water beginning to appear at the base of bottle A.

Tubes C and D were connecter in series has shown in Fig. 1. Tube C contains 20 g of activated silica gel while tube D contains 10 g of activated alumina. 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 form A to B (which was initially evacuated) 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 200g.

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 has stated above. Experimentation becomes unreliable at temperature below $-60^{\circ}C$, since it becomes difficult to keep the refrigerants in the liquid phase.

RESULTS AND DISCUSSIONS

Figure 2 shows the solubility of R-12 and R-134a in 200 g of the respective refrigerants. Fig 3 shows the solubility of R-12 measured in this study (R12M) as compared with that of^[19] (R12T) in mg kg^{-1} . Fig. 4 shows the comparison of solubility of R-12 and R-134a in mg kg^{-1} ; while Fig.5 shows the relative solubility of R-12 and R-134a.

As could be seen in all the figures the general trend is the same. The solubility increases with increase in temperature and that of R-134a is always higher than that of R-12

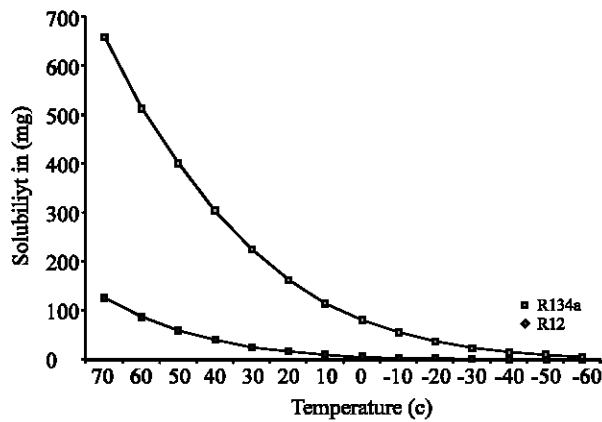


Fig. 2: Moisture solubility in 200 g of R-12 and R-134a

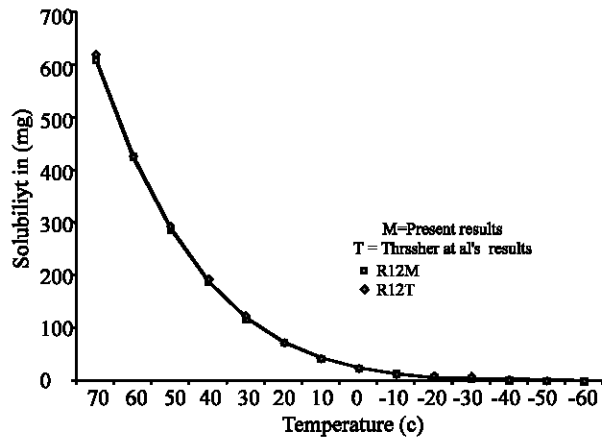


Fig. 3: The measured solubility of moisture in 1 kg of R-12 compared with that of^[19]

In Figure 3, which shows the comparison of solubility of R-12 as measured in this study with that of^[19], shows that the experimental method used in this study was reliable, since both results agreed. Although the values of solubility measured by^[19] were about 20% (averagely) higher than that of the present work. Since

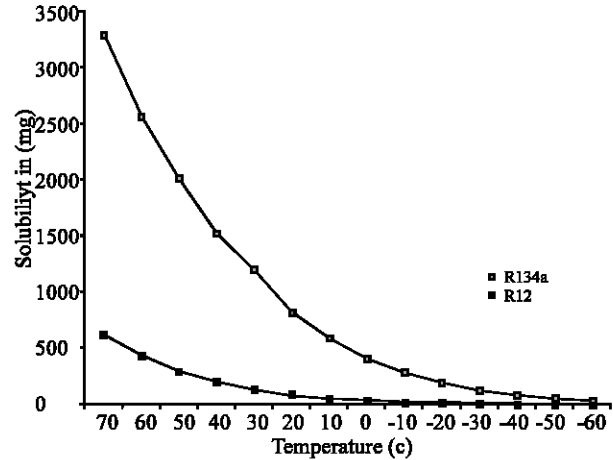


Fig. 4: Moisture solubility in the mg kg^{-1} of R-12 and R-134a

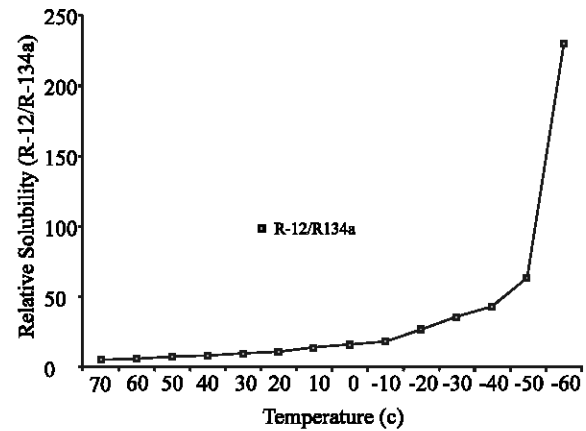


Fig. 5: Relative moisture solubility in R-12 and R-134a

the solubility of moisture in R-134a is very high, the refrigerant should not be exposed when used to charge a system. It is still advisable to pass the refrigerant through desiccant before it is charged into a system. This will prevent corrosion and copper plating and thereby extend the life of the 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 an 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 or Hyperbola). Eq. 1 to 4 were then suggested.

$$S = al^{bT} \quad (1)$$

$$S \propto \log_e T \quad (2)$$

$$S = \alpha \cosh bT (= \alpha \sinh bT) \quad (3)$$

$$S = \alpha T^2 \quad (4)$$

Where: S = solubility in mg kg^{-1} at a given temperature T in $^{\circ}\text{C}$. a and b are constants to be determined using the experimental data.

Eq. 2 could not be used because T has some negative value and Eq. 4 failed because S is not a doubled valued parameter. The values obtained when Eq. 3 was applied were too outrageous and was dropped.

Eq. 1 was subjected to least square method to determine the value of the constants. The process of least square method is summarized as follows using Eq. 1

$S = a e^{bT}$ (5)

Eq. 1 can be written in linear form by taking the

logarithms of both sides, this is given in Eq. 4.

$$\ln S = \ln a + bT \quad (5).$$

If we let $y = \ln S$ and $\ln a = c$ we have Equation (6)

$$y = c + bT \quad (6)$$

The difference of ordinates (D) using Eq. 6 is given by Eq. 7 and the summation of its squares, at a given point, say (y_i, T_i) is given by Eq. 8

$$D = y_i - c - bT_i \quad (7)$$

$$\psi = \sum D^2 = \sum \{y_i - c - bT_i\}^2 \quad (8)$$

Eq. 8 was then differentiate with respect to c and b and rearranged to get Eq. 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 Eq. 9 and 10 simultaneously to obtain the values of b and c . Then the value of a from Eq. 11

$$a = e^c \quad (\text{see Eq. 5}) \quad (11)$$

The resulting models for R-12 and R-134a were given in Eq. 12 and 13 respectively.

$$S_{12} = 15.534 e^{0.0641T} \quad (12)$$

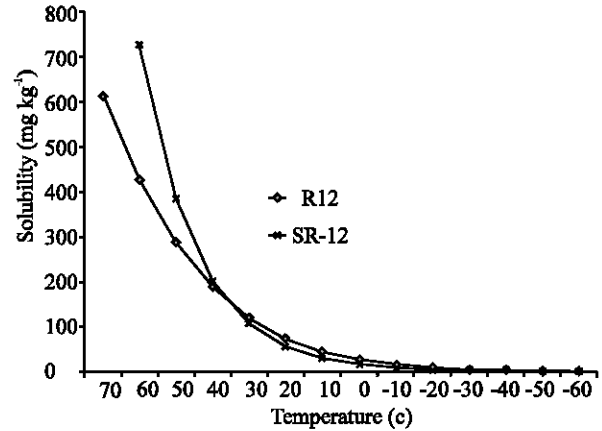


Fig. 6: Moisture solubility model and measured results for R-12

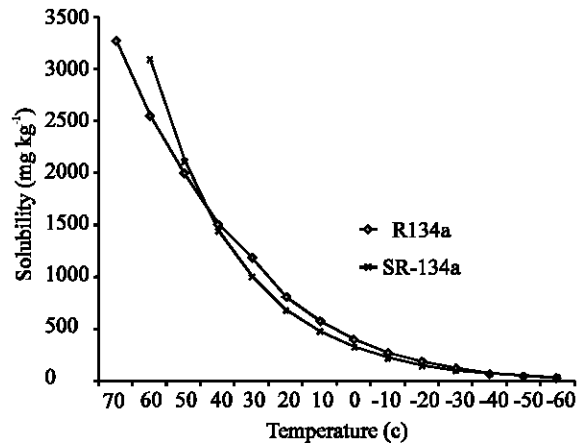


Fig. 7: Moisture solubility model and measured results for R-134a

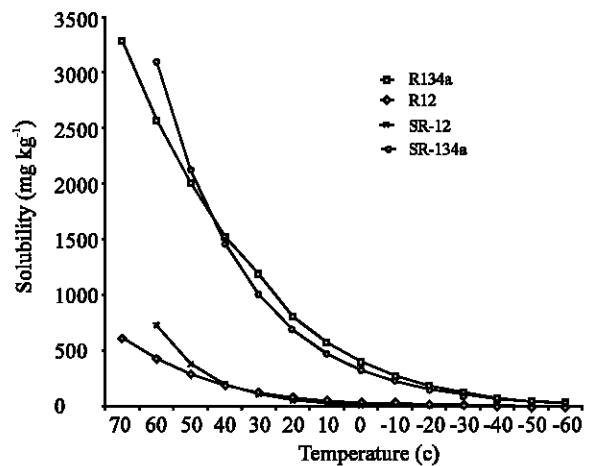


Fig. 8: Summary of model results for R-12 and R-134a

$$S_{134} = 324.867 e^{0.0376T} \quad (13)$$

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

CONCLUSIONS

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 R-134a shows the R-134a absorb 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^[1-21], 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.

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