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Experimental investigation of R134a adsorption on silica gel for cooling system applications

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Abstract

The aim of this study is to assess adsorption characteristics of R134a on a commercially available silica gel. Experimental study is performed by a constant volume variable pressure method. Adsorption process are realized at different temperatures between 293.15 and 320.15 K and for pressures up to 500 kPa. Parameters in the Dubinin-Astakhov (DA) equation for the silica gel – R134a pair is computed by the use of measured experimental data. Adsorption isotherms are obtained by using DA equation for the silica gel – R134a pair. Further, the adsorption enthalpy are provided for the specimen investigated. It is observed that the value of the heat of adsorption is always quite higher than the vaporization enthalpy of the adsorbent in the range of 1.2 to 1.8 depending on the specific adsorbed mass of R134a. Obtained data from the present experimental study can be used for the design of cooling and refrigeration systems in which adsorption process is employed.

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1. Introduction

Adsorption refrigeration and cooling systems can be run with the low grade heat sources such as solar energy and waste heat sources in industry [1]. Since, they uses thermal compression to pressurize the vapor, adsorption refrigeration systems do not have mechanical vapor compressor. Therefore, they are an alternative to conventional refrigeration with vapor compressor. In addition to that the effects of the common refrigerants onto the ozone depletion and global warming have attracted more attention to research on adsorption refrigeration systems which can be considered as environment friendly, low cost and simple in construction. In contrast to vapor absorption cycles, adsorption cycles dispense with the heat exchangers [2]. The properties of adsorbent/adsorbate pairs as well as the operating conditions have significant effects on the system performance [3]. The isosteric heat of adsorption is a specific combined property of an adsorbent/adsorbate combination. Meanwhile, an important motivation present to use natural and/or ozone friendly refrigerants on the cooling and refrigeration sector.

In recent years, adsorption refrigerators driven by solar energy have been receiving much attention as a replacement for conventional vapor compression refrigeration cycles driven by electricity [4]. In the adsorption refrigeration systems, silica gel is the one of the adsorbent used to adsorb the vapor of the refrigerant and promote its evaporation [5]. The solar energy derived adsorption refrigerators with a silica gel–water pair were investigated and their performance reported by several researcher such as Lu et al. [5], Habib et al.[6], Zhai et al. [7], Lu et al. [8], Alam et al.[9] and Pan et al.[10]. However, this pair requires to work under vacuum conditions. If the need is to use refrigerants that
result in system pressures above atmospheric pressures, that are also non-toxic and ozone friendly, the choice narrows down to partly halogenated hydro fluorocarbon refrigerant R-134a (tetrafluoroetan CF₃CH₂F). Thus, R-134a based adsorption refrigeration cycles provide a good match for the current aspirations and expectations from adsorption cooling systems. The design of these refrigeration systems requires data on isotherms and the heats of adsorption for indenting heating inventories. Detailed literature review on adsorption working pairs for refrigeration is given by Wang et al. [11]. A review on adsorption technology is reported by Wang et al. [12]. Habib et. al. [6] also published a paper about the various adsorbent-adsorbate pairs for the application of solar driven adsorption cooling in tropical climates. In that study, experimentally validated adsorption data for the corresponding adsorbent/adsorbate combinations were considered.

IsostERIC heat of adsorption is commonly expressed as a function of specific adsorbed mass of adsorbate due to its dependence on temperature is relatively weaker [13]. For adsorption of refrigerants below their thermodynamic critical point, its magnitude is larger than the heat of vaporization of the adsorbate, which has a strong temperature dependence [14]. As a result, the difference between the two is a property of relevance in the design of adsorption refrigeration systems. However, adsorption data are usually unavailable from the manufacturers of adsorbents [15]. The characteristics of a new adsorbent like a kind of silica gel may different than the known ones. In order to design a cooling system based on adsorption the knowledge is required about the adsorption isotherms and the isosteric heat of adsorption for the adsorbent/adsorbate pair used in the system [16].

Although, a number of studies have been published about adsorption parameters of the pair of silica-gel and water, to the best of our knowledge, there is not any published study that has been devoted to study on the adsorption parameters for a commercially available silica-gel and R134a pair. From the above mentioned perspectives, the present paper reports an experimental study to obtain isotherm data during an adsorption process for the pair of R-134a and a commercially available silica gel. The isosteric heat of adsorption data is extracted from the present experiments. The presented results can be used on the design of an adsorption based cooling cycle systems in which a silica gel – R134a pair is employed.

2. Material and Method

The CVVP experimental test rig system comprises two tanks, heating/cooling water circulation units, several valves, pipes, pressure and temperature sensors, a computer and a vacuum pump. The volumes of both the adsorption and charging tanks were 3000 cc. The volume of both charging and adsorption tanks are inclusive of the volumes of related piping and valves. Temperatures of the both the charging and adsorption vessels could be controlled independently by the separate water circulation units. Pressures in the system were measured by the pressure transducers with an uncertainty of 0.15% of full scale and a pressure ranging from 0 to 1.6 MPa. Temperatures in the system were measured by separate Pt 100 type thermometers with an uncertainty of 0.2%. Valves and pipes were used to control fluid flows in the system. A computer was used to control the test system and record the data during the measurements. A vacuum pump that achieves vacuum level of 0.05 kPa was used during evacuation processes.
Table 1. Physical properties of the silica gel used in the test.

<table>
<thead>
<tr>
<th>Color</th>
<th>Grain size (mm)</th>
<th>Density (kg/m³)</th>
<th>MicroPore volume (cm³/g)</th>
<th>Specific surface area BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>3-5</td>
<td>720</td>
<td>0.276</td>
<td>556</td>
</tr>
</tbody>
</table>

Table 1 shows the physical properties of the silica gel used in the present experimental measurements. Fig.1 shows a picture of the silica gel used as adsorbent in the present study.

**Fig. 1. A picture of the silica gel used as adsorbent in the study.**

### 2.1. Methodology used in the experimental study

In this study, an experimental measurement procedure had been realized by following three stages. These were drying the specimen, evacuation or cleaning the system from any moisture or remedy gases and adsorption process. In the first stage, a drying process was performed to desorb moisture or any residual gas inside the specimen. For this aim, the silica gel specimen was put into an oven for 24 hour time. The temperature of the oven was maintained at 393.15 K. In the second stage, the specimen was placed into the adsorption tank. Air and any other gas content inside the test rig was evacuated and the inside pressure of the system was reduced to about 0.05 kPa by using a vacuum pump. Then, the tanks were heated by employing hot water circulation circuits. The temperatures of both the charging and the adsorption tanks were maintained at 333.15 K for 6 hour. Meanwhile, the evacuation process from the test rig was continued. At the end of regeneration work, the experimental test rig is pressurized up to 1.6 MPa with helium gas and discharged again to achieve desired low vacuum state. This process is repeated several times in order to obtain conditions that the system is free from moisture or any unwanted residual gases. It should be mentioned that there is no measurable interaction between the inert gas (helium) and the adsorbent. After the final evacuation, the charging cell is pressurized with the assorted refrigerant and left until it reaches a thermal equilibrium state. During charging the refrigerant, it should be necessary to keep the charging pressure lower than the saturation pressure of the refrigerant to ensure no condensation is occurred. After the charging procedure was completed, it was left until the tank reaches a thermal equilibrium state. Then, the initial pressure and temperature in the charging cell were measured before adsorption. The second stage was finished when the adsorption and charging vessel temperatures became uniform and steady. In the third stage, the adsorption process was performed. Once thermal equilibriums at the
desired temperatures were achieved for all the components in the system, the needle valve between the charging and adsorption tank is opened with maintaining the isothermal conditions in the adsorption tank. The isothermal adsorption process was continued until the temperature and pressure was not changed indicating that the adsorption process reaches into equilibrium condition. The pressures and temperatures in both the adsorption and charging tanks were recorded in every two seconds during all the stage. This process was repeated for each charging step until the high pressure was reached. By the use of a specimen, each isotherm was measured at a constant temperature over a range of pressure from 0 to 500 kPa.

With the known initial mass of dry specimen, the temperature of the test system is varied to calculate the uptake of the assorted refrigerant varying with time.

2.2. Evaluation for the overall uncertainty

The instrumentations used in the measurements have some uncertainties as given at the start of the section 2. These effect the accuracy of the obtained data during adsorption process. In addition to that some errors occur during the mathematical evaluations of the data. It is predicted that the overall uncertainty of the results given in this study is within 3%.

3. Mathematical modelling

The starting point for this analysis is the use of Dubinin–Astakhov (D–A) model of adsorption isotherm in the following form [14]:

\[ W = W_0 \exp \left\{ - \left[ \frac{RT}{E} \ln \left( \frac{p_s}{p} \right) \right]^n \right\} \] (1)

with

\[ W = Cv_a \quad \text{and} \quad W_0 = C_0v_0 \] (2)

Here \( E \) is the characteristic energy of the assorted adsorbent/adsorbate pair which can be evaluated experimentally. The parameter \( n \) is an exponential constant which gives the best fitting of the experimental isotherms. The quantity \( C \) represents the specific adsorbed mass of adsorption (kg of adsorbent per kg of adsorbate), and \( v_a \) is the specific volume of the adsorbed phase, which is given by

\[ v_a = v_b \exp( \Omega(T - T_b)) \] (3)

where

\[ \Omega = \ln(b/v_b)/ (T_c - T_b) \] (4)

The quantity \( b \) denotes the van der Waals volume, \( v_b \) is the saturated liquid specific volume at the normal boiling point. \( T \) is the temperature with suffixes \( c \) and \( b \) referring to critical and normal boiling points, respectively. The parameter \( v_0 \) can be obtained by using Eq. (3) at \( T = 273.15 \) K. Table 2 shows the properties and parameters of the adsorbate used in the present experimental study. Eq. (1) can be arranged as follows:

\[ \ln p = \ln p_s - E/(RT)[\ln(C_0v_0/Cv_a)]^{1/n} \] (5)

Differentiating Eq. (5) with respect to 1/T for the isosteric conditions (i.e. \( C \) is constant). Noting that \( v_s \) is also a function of temperature, one can get the following equation:

\[ \frac{\partial \ln p}{\partial (1/T)} = \frac{\partial \ln p_s}{\partial (1/T)} - \left( \frac{E}{R} \right) \left[ \ln(C_0v_0/Cv_a) \right]^2 - \left( \frac{E}{(1-n)/n} \right) \left[ \ln(C_0v_0/Cv_a) \right]^{(1-n)/n} \] (6)
Isosteric heat of adsorption is defined by the Clausius–Clapeyron relation as
\[ Q_{ads} |_{CC} = -R \frac{\partial (\ln p)}{\partial (1/T)} \] (7)
and the heat of vaporization defined as
\[ h_{fg} = -R \frac{\partial (\ln p_s)}{\partial (1/T)} \] (8)
where \( p_s \) is the saturation pressure.

The standard procedure for evaluation of isosteric heat of adsorption is to plot the isosters on \( \ln p \) versus \( 1/T \) plane. Normally, a constancy of slope is observed at temperatures well over the critical point of the adsorbate. As a result the classical treatment of isosteric heat of adsorption being shown as a function of relative uptake is a good approximation for adsorbent–adsorbate combinations which broadly follow the Dubinin’s isotherms [15]. However, the gas phase of the adsorbent is not ideal, during an adsorbate molecule uptake to the assorted adsorbent is affected by the pressure and temperature changes. Therefore, the heat of adsorption may be calculated by using the following Eq.9 as suggested by El-Sharkawy et al.[14].
\[ Q_{ads} = h_{fg} + (E)[\ln(C_0 v_0/C v_a)]^{1/n} + (ET\Omega / n)[\ln(C_0 v_0/C v_a)]^{(1-n)/n} \] (9)

Table 2. Properties and parameters of the adsorbate R134A [17].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>CH₂FCF₃</td>
</tr>
<tr>
<td>Molecular Weight (MW)</td>
<td>102.03 kg/kmol</td>
</tr>
<tr>
<td>Gas constant (R)</td>
<td>0.08149 kJ/kg K</td>
</tr>
<tr>
<td>Boiling Point at 101 [kPa] (T_b)</td>
<td>247.08 K</td>
</tr>
<tr>
<td>Critical Temperature (T_c)</td>
<td>374.21 K</td>
</tr>
<tr>
<td>Critical Pressure (P_c)</td>
<td>4059.3 kPa</td>
</tr>
<tr>
<td>Critical Density</td>
<td>511.9 kg/m³</td>
</tr>
<tr>
<td>Ozone Depletion Potential (ODP)</td>
<td>0</td>
</tr>
<tr>
<td>b</td>
<td>0.0009390</td>
</tr>
<tr>
<td>( v_b ) (m³/kg)</td>
<td>0.0007260</td>
</tr>
<tr>
<td>( v_0 ) (m³/kg)</td>
<td>0.0007657</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>0.002018</td>
</tr>
</tbody>
</table>

4. Results and Discussions

The experimental data was used to evaluate the adsorption parameters for the silica gel-R134a pair. Derived objection function is optimized by the use of a homemade code based on a genetic algorithm. Table 3 shows that computed values of the adsorption parameters (\( W_0, C_0, E \) and \( n \)) for the silica gel-R134a pair used in the present study.
Table 3. Computed constants of the Dubinin–Astakhov (D–A) equation (Eq. 1) for the silica gel-R134a pair used in the present study.

<table>
<thead>
<tr>
<th>$W_0$ (m$^3$/kg)</th>
<th>$C_0$ (kg/kg)</th>
<th>$E$ (kJ/kg)</th>
<th>$n$</th>
<th>Cor.Const.: $R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0003629</td>
<td>0.474</td>
<td>5120.9</td>
<td>1.034</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Comparison of the experimental and the computed adsorption isotherms of R-134a on silica gel is given in Fig. 2. It can be observed from the Fig. 2 that the measured data and the data obtained from D–A equation (Eq. 1) with the parameters given in Table 3 are in a very good agreement. Eqs. 1 to 9 were used to evaluate isosters and isosteric heat of adsorption for the adsorption of R-134a on silica gel as shown Fig. 3 and 4. It can be seen from the Fig. 4 that the isosteric heat of adsorption reduces with rising adsorbed mass of R-134a. Moreover, the temperature have important effect on isosteric heat, for all specific adsorbed mass values the isosteric heat of adsorption have a maximum value at the lowest temperature of 273 K. This can be explained as that the refrigerant molecules first penetrate into narrow gaps of silica gel, causing a stronger interaction between refrigerant molecules and silica gel. This results a higher value of isosteric heat of adsorption at lower concentrations. When the narrow gaps is completely filled with the R-134a molecules, larger pores were gradually accommodated by the adsorbate. The adsorption affinity becomes weaker in larger gaps. As a result of this phenomena, a monotonic decrease appears in isosteric heat of adsorption with the rising adsorbate uptake values.

Fig. 2. Comparison of the experimental and the computed adsorption isotherms of R134a on silica gel.
5. Conclusions

The aim of this study is to evaluate adsorption characteristics of R134a on a commercially available silica gel. An experimental study was performed to obtain isotherm data, which is not available in the current literature, during an adsorption process of R-134a on the silica gel over a temperature range from 293.15 to 320.15 K and pressure up to 500 kPa using constant volume variable pressure (CVVP) method. The obtained isotherm data were used to determine the constants of the Dubinin-Astakhov (D-A) equation for the silica gel and R134a pair by the use of a homemade optimization code. Then, adsorption parameters and the isosteric enthalpy of adsorption were evaluated using the D-A equation for the specimen investigated. Comparison between the correlated results and the experimental data shows very good agreement. It is found that the maximum adsorption capacity (C_d) of the silica gel-R134a pair is 0.47 [kg R134a per kg silica gel]. It is observed that the adsorption capacity per kg of adsorbate at the constant temperature increases rapidly with rising pressure during the adsorption process. It is also observed that higher values of adsorption capacity appear at the lower values of adsorbent temperature. It is shown that the value of the heat of adsorption is always quite higher than the vaporization enthalpy of the adsorbent. The isosteric heat of adsorption varied with the temperature and the adsorbed concentration. The value of the adsorption heat decreases with increasing temperature and increasing adsorbed concentration. The ratios of the isosteric heat of adsorption to the vaporization enthalpy at the same conditions are 1.75, 1.5, 1.38, 1.3 and 1.2 for the specific adsorbed mass of R134a as 0.1, 0.2, 0.4, 0.6 and 0.8, respectively. The presented results can be used on the design of an adsorption based cooling cycle system in which a silica gel-R134a pair is employed.

Acknowledgements

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Nomenclature

\( b \)  
van der Waals volume

\( C \)  
specific adsorbed mass of adsorption (kg of adsorbate per kg of adsorbent) [kg/kg]

\( E \)  
characteristic energy of the assorted adsorbent/adsorbate pair [kJ/kg]

\( h_{fg} \)  
heat of vaporization [kJ/kg]

\( \nu \)  
specific volume [m³/kg]

\( \nu_a \)  
the specific volume of the adsorbed phase [m³/kg]

\( \nu_b \)  
the saturated liquid specific volume at the normal boiling point [m³/kg]

\( n \)  
exponential constant

\( p \)  
pressure [kPa]

\( p_s \)  
saturation pressure [kPa]

\( R \)  
gas constant [kJ/kg K]

\( Q_{ads} \)  
isosteric adsorption heat

\( T \)  
temperature [K]

\( W \)  
specific volume of adsorption (volume of adsorbate per kg of adsorbent) [m³/kg]

Greek letters

Ω  
Constant defined in Eq.4.

Subscripts

\( a \)  
adsorbed phase

\( ads \)  
adsorption

\( b \)  
boiling points

\( c \)  
critical points

\( CC \)  
Clausius-Clapeyron relation

\( o \)  
value at T=273.15 K

\( s \)  
saturation

References


