AN EXPERIMENTAL STUDY ON ADSORPTION CHARACTERISTICS OF R134A AND R404A ONTO SILICAGEL ADSORBENTS

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ABSTRACT
The objective of this study is to evaluate adsorption characteristics of R134a and R404a on commercially available silica gel samples. A constant volume variable pressure method at different adsorption temperatures ranging from 293 to 323 K and for pressures up to 500 kPa is used in the experimental measurements. Three different type of commercially available silica gel samples were chosen as adsorbent. The isotherms obtained from the experimental measurements were presented. Adsorption parameters were evaluated from the isotherms in order to obtain correlations in the form of the Dubinin-Astakhov (DA) equation. The pressure and temperature dependence of the isosteric enthalpies of adsorption is computed with the evaluation of the measured data and the derived equations. Further, the enthalpy of adsorption data were extracted, and correlations are provided for adsorbent-adsorbate pairs obtained from the combinations of the three different silica gel specimens and two refrigerants.

INTRODUCTION
Among the thermally driven refrigeration systems, adsorption systems, which can be powered by relatively low temperature renewable energy and waste heat resources, are of great interest and considerable research and development studies have been performed by numerous researchers in recent decades [1, 2]. The main heat sources for adsorption cooling/refrigeration systems are industrial waste heat and solar energy. The systems in which the physical adsorption working pairs employed are usually preferred when solar energy is used as the heat source [3-6]. The physical adsorption process of the gas occurs mainly within the pores and surface of the solid adsorbent [7]. The adsorbed amount and concentration of refrigerant in the pores are strongly dependent on pressure and temperature variations as well as the operating conditions of the system [8]. The design of an adsorption refrigeration system requires the knowledge of adsorption characteristics of the employed adsorbent-adsorbate pair when the temperature and pressure are varying.

The isosteric heat of adsorption is a specific combined property of an adsorbent/adsorbate combination. The equilibrium adsorption properties at several adsorbent temperatures and adsorption chamber adsorbate pressures were studied for a wide range of pairs [9-11].

Silica gel belongs to low temperature working adsorbent, which can be driven by heat source with the temperature lower than 90 °C [2, 12]. The silica gel is a type of amorphous synthetic silica. Each kind of silica gel has only one type of pore, which usually is confined in narrow channels. The pore diameters of common silica gel are 2, 3 nm (A type) and 0.7 nm (B type), and the specific surface area is about 100–1000 m²/g [12, 13].

Meanwhile, a considerable motivation already exists to employ environment and/or ozone friendly working fluids in the refrigeration systems. If the cooling system is desired to work above atmospheric pressures by the use of a non-corrosive, non-toxic, non-flammable and environment friendly working fluids, the selection options of the working fluids reduce to partly halogenated hydro fluorocarbon refrigerants such as R134a (tetrafluoroetan CF₃CH₂F) and R404a (CHF₂CF₃ / CH₃CF₃ / CF₃CH₂F) which is near a zeotropic blend of HFC-125/HFC-143a/HFC-134a. Therefore, adsorption refrigeration systems with the refrigerants R134a and R404a used as working fluid almost satisfy the aspirations and expectations mentioned above.

The design of adsorption refrigeration systems requires the data of isotherms and the heats of adsorption for the calculation and analysis [14, 15]. Detailed literature review on adsorption working pairs for refrigeration is given by references [1, 10].

Isosteric heat of adsorption has been commonly given as a function of adsorbate relative uptake ratio due to its temperature dependence is relatively weaker [16]. However, there is a strong temperature dependence on the adsorption of adsorbate fluids at the temperatures smaller than the adsorbate fluid’s thermodynamic critical point temperature. The magnitude of isosteric heat of adsorption is considerably larger than the heat of vaporization of the adsorbate at that region [17]. Therefore, the variation of the isosteric heat of adsorption for the adsorbent-adsorbate pairs used in the system must be provided for the proper design of adsorption refrigeration/cooling systems.

The adsorption characteristics of each adsorbent-adsorbate pair is usually quite different than the known ones. In addition to that, the manufacturers of adsorbents do not mostly provide the adsorption data for each adsorbent-adsorbate pair. In order to design adsorption based cooling cycle it is inevitable to evaluate
adsorption isotherms of the assorted adsorbent/adsorbate pair as well as the isosteric heat of adsorption.

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 the refrigerants R134a and R404a as adsorbate fluid on the silica gel as adsorbent solid. From this mentioned perspective, the present paper presents an experimental study to obtain the characteristics of the adsorption processes for the adsorbate fluids of R134a and R404a on the commercially available silica gels employed as the adsorbent solid. The presented results and correlations can be used on the design of an adsorption based cooling cycle systems in which a silica gel – R134a or a silica gel – R404a pair is employed.

NOMENCLATURE

- \( b \) [m\(^3\)] the van der Waals volume
- \( E \) [kJ/\( \text{kg} \)] characteristic energy of adsorption pair
- \( h_\text{v} \) [kJ/\( \text{kg} \)] vaporization enthalpy
- \( MW \) [\( \text{kg/\text{kmol}} \)] molecular weight of refrigerant
- \( ODP \) [-] ozone depletion potential
- \( p \) [kPa] pressure
- \( R \) [kJ/kgK] gas constant
- \( SGW \) [-] white silicagel
- \( SGB \) [-] blue silicagel
- \( SGO \) [-] brown silicagel
- \( T \) [K] temperature
- \( v_a \) [m\(^3\)/kg] adsorbed phase specific volume
- \( v_\text{s} \) [m\(^3\)/kg] saturated liquid specific volume at the normal boiling temperature
- \( n \) [-] exponential constant
- \( X \) [kg/kg] adsorption uptake per kg of adsorbent
- \( X_0 \) [kg/kg] maximum adsorption uptake per kg of adsorbent
- \( \Delta H_{\text{ads}} \) [kJ/kg] isosteric adsorption heat

| Subscripts | \( a \) | adsorbed phase | \( b \) | boiling point | \( c \) | critical point | \( CC \) | constant concentration | \( ads \) | adsorption | \( f_g \) | phase change from liquid to gas form | \( \text{max} \) | maximum | \( s \) | saturation | \( 0 \) | maximum |

MATERIAL AND METHODS

The constant volume variable pressure (CVVP) method 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 0.003 m\(^3\). The volumes of the tanks are inclusive of the related valves and piping volumes. 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 which have a pressure measurement range from 0 to 1.6 MPa with an uncertainty of 0.15% of full scale. 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.

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. 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 using 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. During this process, it is observed that there is not any measurable interaction between the inert gas (helium) and the adsorbent in the tank. After the final evacuation process, the charging tank is fill up with the assorted adsorbate fluid and left until a thermodynamic equilibrium state is obtained.

| Table 1. Physical characteristics of the adsorbents used in the tests. |
|-------------------|-------|------|------|
| Silicagel | SGW | SGB | SGO |
| Chemical Composition | SiO\(_2\).n(H\(_2\)O) | SiO\(_2\).n(H\(_2\)O).CoCl\(_2\) | SiO\(_2\).Al\(_2\)O\(_3\) |
| SiO\(_2\) content | 99.7% | 99% | 97% |
| Diameter (mm) | 2.5 | 2.5 | 2.5 |
| Density (kg/m\(^3\)) | 720 | 720 | 801 |
| Micro Pore Volume (cm\(^3\)/g) | 0.343 | 0.276 | 0.4 |
| Specific Surface Area (m\(^2\)/g) | 693 | 556 | 750 |
| Pore Diameter (Å) | 17.4 | 17.8 | 17.8 |
| Shape | Spherical | Spherical | Spherical |
| Colour | White | Blue | Brown |

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 the each charging step until the high pressure 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.

For each specimen with the known initial dry mass, experiments to obtain the adsorbed mass of the adsorbate fluid were performed at constant temperatures chosen at the range of 293 to 323 K for pressures from 0 to about 500 kPa.

The devices and instruments used in the experimental measurements have some uncertainties as given above. These effect the accuracy of the obtained data during adsorption process. In addition to that some errors occur during the mathematical calculations and the evaluations of the data. It is predicted that the overall uncertainty of the results given in this study is within 3%. Experimental results are presented with error bars as seen in Figs. 1 to 3.

MATHEMATICAL MODELLING

It is become a common approach that the use of Dubinin–Astakhov (D–A) model for the calculation of the adsorbate uptake value on the adsorbent as a function of temperature and pressure in the adsorption bed [18, 19]. Dubinin–Astakhov (D–A) model for the calculation of the adsorbate uptake value on the adsorbent as a function of temperature and pressure was not changed indicating that the adsorption process was continued until the temperature and isothermal conditions in the adsorption tank. The isothermal energy of the assorted adsorbent-adsorbate pair which may be evaluated from the experimental measurements. It is known that the Clausius–Clapeyron relation can be used to define the isosteric heat of adsorption and the heat of vaporization as given in Eq.(6) and Eq.(7), respectively.

Table 2 shows the properties and parameters of the adsorbate used in the present experimental study.

Table 2. Properties and parameters of the adsorbates [20].

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Unit</th>
<th>R134a</th>
<th>R404a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (MW)</td>
<td>kg/kmol</td>
<td>102.03</td>
<td>97.60</td>
</tr>
<tr>
<td>Boiling Point at 1 atm (Tb) K</td>
<td>247.09</td>
<td>226.70</td>
<td></td>
</tr>
<tr>
<td>Critical Temperature (Tc) K</td>
<td>374.23</td>
<td>345.22</td>
<td></td>
</tr>
<tr>
<td>Gas constant (R) kJ/kg K</td>
<td>0.08149</td>
<td>0.08519</td>
<td></td>
</tr>
<tr>
<td>Critical Pressure (pc) kPa</td>
<td>4059</td>
<td>3729</td>
<td></td>
</tr>
<tr>
<td>Critical Density</td>
<td>kg/m$^3$</td>
<td>515.3</td>
<td>484.5</td>
</tr>
<tr>
<td>b</td>
<td>m$^3$</td>
<td>0.0009390</td>
<td>0.0009857</td>
</tr>
<tr>
<td>va</td>
<td>m$^3$/kg</td>
<td>0.0007260</td>
<td>0.0007655</td>
</tr>
<tr>
<td>v0</td>
<td>m$^3$/kg</td>
<td>0.0007657</td>
<td>0.0008445</td>
</tr>
<tr>
<td>$\Omega$</td>
<td></td>
<td>0.002018</td>
<td>0.002125</td>
</tr>
</tbody>
</table>

Ozone Depletion Potential (ODP)

0

Eq. (1) may be easily converted to the form as follows:

\[
\ln p = \ln p_s - E/(RT)[\ln(X_0 v_0/X v_a)]^{1/n}
\]

Considering $\ln p$ as a variable in Eq. (5), it can be differentiated with respect to $1/T$ for the isosteric conditions (i.e. $X$ is constant). It should be noted that $v_0$ is also a function of temperature as given in Eq.(3). The resulting equation can be obtained as follow:

\[
\frac{\partial \ln p}{\partial (1/T)} = \frac{\partial \ln p_s}{\partial (1/T)} - \frac{E}{R}[\ln(X_0 v_0/X v_a)]^{1-n} - \frac{RT}{nR}[\ln(X_0 v_0/X v_a)]^{(n-1)/n}
\]

It is known that the Clausius–Clapeyron relation can be used to define the isosteric heat of adsorption and the heat of vaporization as given in Eq.(7) and Eq.(8), respectively.

\[
\Delta H_{ads/CC} = -R(\partial \ln p_s/\partial (1/T))
\]

\[
h_{fg} = -R(\partial \ln p_s/\partial (1/T))
\]

where $p_s$ is the saturation pressure.

It is a common procedure to plot the isosters on $ln p$ versus $1/T$ plane by using the Eq.(7) for the evaluation of isosteric heat of adsorption. It is normally observed that the isosters show a linear variation with a constant slope at temperatures lower than the critical point temperature of the refrigerant. By the use of this common evaluation procedure, it has been shown that isosteric heat of adsorption can be approximated as a function of relative adsorption uptake for adsorbent-adsorbate pair combinations which broadly follow the Dubinin’s isotherms [19]. However, the gas phase of the adsorbent is not ideal, during the adsorption of the adsorbate molecules onto 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.[18].
\[ \Delta H_{ads} = h_f g + (E)[\ln(X_0 v_0 / X v_0)]^{1/n} + (E \Omega / n)[\ln(X_0 v_0 / X v_0)]^{(1-n)/n} \]  

(9)

RESULTS AND DISCUSSIONS

The experimental data was used to evaluate the adsorption parameters for the adsorbent-adsorbate pairs. By the use of Eqs. 1-4, an objection function can be derived as follow:

\[ F = \sum_{i=1}^{N} \left[ X_i - \frac{X_0 n_e}{v_e} \exp \left\{ -\frac{RT \ln \left( \frac{T}{T_e} \right)^n \right\} \right]^2 \]  

(10)

Where N is the number of data sets, \(X_i, p_i, T_e\) are known variables obtained from the experimental measurements. \(X_0, E\) and \(n\) are unknown constants. To obtain the unknown parameters, the objection function must be minimized. 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 (\(W_0, X_0, E\) and \(n\)) for the adsorbent-adsorbate pairs used in this study.

Table 3. Computed constants of the Dubinin–Astakhov (D–A) equation (Eq.1) for the adsorbent-adsorbate pairs used in the present study.

<table>
<thead>
<tr>
<th>Pairs</th>
<th>(W_0) (m³/kg)</th>
<th>(X_0) (kg/kg)</th>
<th>(E) (kJ/kg)</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGW-R134a</td>
<td>0.0004020</td>
<td>0.525</td>
<td>68.15</td>
<td>1.237</td>
</tr>
<tr>
<td>SGB-R134a</td>
<td>0.0003629</td>
<td>0.474</td>
<td>50.19</td>
<td>1.034</td>
</tr>
<tr>
<td>SGO-R134a</td>
<td>0.0004164</td>
<td>0.544</td>
<td>57.04</td>
<td>1.148</td>
</tr>
<tr>
<td>SGW-R404a</td>
<td>0.0003440</td>
<td>0.407</td>
<td>83.52</td>
<td>1.613</td>
</tr>
<tr>
<td>SGB-R404a</td>
<td>0.0003268</td>
<td>0.387</td>
<td>62.81</td>
<td>1.300</td>
</tr>
<tr>
<td>SGO-R404a</td>
<td>0.0003994</td>
<td>0.466</td>
<td>69.70</td>
<td>1.404</td>
</tr>
</tbody>
</table>

Figure 1 Comparison of the experimental and the computed isotherms of R134a and R404a on the white silica gel (SGW) at 20, 30 and 50 °C.

Figure 2 Comparison of the experimental and the computed isotherms of R134a and R404a on the blue silica gel (SGB) at 20, 30 and 50 °C.

Figure 3 Comparison of the experimental and the computed isotherms of R134a and R404a on the brown silica gel (SGO) at 20, 30 and 50 °C.

It can be seen from the Table 3 that the highest maximum adsorption uptake value (\(X_0 = 0.544\)) appears for the brown silica gel and R134a pair. Meanwhile, the lowest maximum adsorption uptake value (\(X_0 = 0.387\)) appears for the blue silica gel and R404a pair. In general, the maximum uptake values for R134a are higher than the one for R404a.
very good agreement. Brown silica gel has the highest uptake values (X) for both refrigerants R134a and R404a, whereas blue silica gel has the lowest. Comparing the adsorption uptake values of refrigerants R134a and R404a, it is observed that R134a is adsorbed more than R404a at the same conditions by all three types of the silica gels. From the isotherms given in Figs.1-3, it can also be seen that adsorption uptake value increases with rising pressure at the constant temperature. On the other hand, adsorption at lower temperature results higher adsorption uptake values for all the considered pairs.

Eqs. 1 to 9 were used to evaluate isosters and isosteric heat of adsorption for the adsorption of R134a and R404a on silica gels as shown Figs. 4 to 9. It can be seen from the Figs. 4-9 that the isosteric heat of adsorption reduces with rising adsorbed mass of refrigerant. 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 may be explained as that the refrigerant molecules first penetrate into smaller gaps of silica gel, causing a stronger interaction between fluid molecules and silica gel surfaces. This results a higher value of isosteric heat of adsorption at lower adsorption uptake values. When the smaller cavities are completely filled with the fluid molecules, larger cavities are gradually accommodated by the adsorbate molecules. The adsorption affinity becomes weaker in larger cavities. As a result of this phenomena, the magnitude of the isosteric adsorption heat gradually decreases with the increasing adsorption uptake values.
The aim of this study is to evaluate adsorption characteristics of R134a and R404a on a commercially available silica gels. Experimental measurements were performed using a constant volume variable pressure (CVVP) method to obtain isotherm data during the adsorption processes of R134a and R404a on the silica gel samples over a temperature range from 293.15 to 320.15 K and pressure up to 500 kPa. The obtained isotherm data were used to determine the constants of the Dubinin-Astakhov (D-A) equation for the adsorbent-adsorbate pairs. Then, adsorption parameters and the isosteric enthalpy of adsorption were evaluated using the D-A equation for the specimens investigated. Comparison between the correlated isotherm functions and the experimental data shows very good agreement. Among the pairs considered in this study, it is found that the maximum adsorption uptake capacity (X₀) of the brown silica gel-R134a pair is the highest (X₀= 0.544 [kg R134a per kg brown silica gel]). And the maximum adsorption uptake capacity (X₀) of the blue silica gel-R404a pair is the lowest (X₀= 0.387 [kg R404a per kg blue silica gel]). It is observed that the adsorption uptake (X) on the adsorbent at the constant temperature increases rapidly with rising pressure during the adsorption process. It is also shown 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. It is also shown that the temperature and the adsorbed uptake value have a significant effect on the isosteric heat of adsorption. The value of the adsorption heat significantly decreases with increasing temperature and adsorbed uptake ratio. The presented data and the correlations can be used on the design of an adsorption based cooling cycle system in which a silica gel-R134a or a silica gel-R404a pair is employed.

**CONCLUSION**

It can be seen from the Figs.4 to 9 that the adsorption heat values of refrigerant R134a are higher than the values of R404a. Meanwhile, it is observed that the adsorbent type is not significant effect on the isosteric adsorption heat value. For all the cases considered in this study, the isosteric adsorption heat is quite higher than the vaporization enthalpy.

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**REFERENCES**


