Adsorption characteristics evaluation of R134A and R404A on different adsorbents

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In order to design adsorption employed cooling or refrigeration system, it is inevitably required the knowledge of the adsorption isotherms and the isosteric adsorption heat for the assorted adsorbent/adsorbate pair. The physical adsorption phenomena occurs mainly within the pores and on the surface of the adsorbent. Since, the characteristics of each adsorbent-adsorbate pair is different than others. The knowledge of adsorption characteristics with the variation of temperature and pressure is necessary for the evaluation. However, these data are usually unavailable from the manufacturers of adsorbents. The objective of this study is to evaluate adsorption characteristics of R134A (HFC-134A) and R404A (HFC-404A) on different adsorbents experimentally by a constant volume variable pressure method at different adsorption temperatures ranging from 20 to 50 C and for pressures up to 5 bar. The forms of the isotherms obtained from the experimental measurements are similar in all cases and comparable to those reported in the literature for commercially available different adsorbents. Adsorption parameters are evaluated from the isotherms using the Dubinin-Astakhov (DA) equation. The concentration dependence of the isosteric enthalpies of adsorption is extracted from the obtained data. Further, the enthalpy of adsorption data are extracted, and correlations are provided for the different specimens investigated. These data are essential for the design of a thermally driven adsorption chiller employed the assorted pair.

Keywords: adsorbent, adsorbate, adsorption cooling, R134A, R404A

INTRODUCTION

Adsorption refrigeration and cooling research has attracted attention in view of the pressing need for combating ozone depletion and global warming [1, 2]. The main heat sources for adsorption systems are waste heat and solar energy. Physical adsorption working pairs are usually preferred when solar energy is the heat source [3]. It provides an alternative to conventional vapor compressor refrigeration, because the systems based on adsorption can be driven by low grade heat sources such as solar energy and industrial waste heat. In addition, they have minimal moving parts. In contrast to vapor absorption cycles, adsorption cycles dispense with the heat exchangers [4]. The properties of adsorbent/adsorbate pairs as well as the operating conditions have significant effects on the system performance [5]. 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 [6]. Meanwhile, on the refrigerant field considerable motivation already exists to use natural and/or ozone friendly refrigerants. If the need is to use refrigerants that result in system pressures above atmospheric pressures, that are also non-flammable, non-toxic and ozone friendly, the choice narrows down to partly halogenated hydro fluorocarbon refrigerants such as R134A (tetrafluoroetan

CF_3CH_2F) and R404A (CHF_2CF_3 / CH_3CF_3 / CF_3CH_2F) which is near a zeotropic blend of HFC-125/HFC-143A/HFC-134A. R134A is the one of the very well-known and widely used refrigerants in both domestic and commercial medium and high temperature refrigeration, residential and vehicle air conditioning as well as several industrial applications. A number of HFC refrigerant blends are also composed by the use of R134A. R404A is an HFC blend that is also employed a wide range of low and medium temperature refrigeration applications. R404A is a quite common refrigerant used in commercial refrigeration applications such as those used in the both chilled and frozen food refrigeration. Although, the Ozone Depletion Potential (ODP) of R404A and R134A is zero, the Global Warming Potential (GWP) of R404A and R134A are high and medium level with the value of 3943 and 1300, respectively. However, the safety classifications of R404A and R134A according to the ASHRAE Standard 34 are in the lowest rank (A1) to the hazard involved in their use [7].

Thus, R134A and R404A based adsorption refrigeration cycles provide a very well 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. [8,9].

Isosteric heat of adsorption is traditionally expressed as a function of concentration due to its dependence on temperature is relatively weaker

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[10,11,12]. For adsorption of fluids below their thermodynamic critical point, its magnitude is larger than the heat of vaporization of the adsorbate, which has a strong temperature dependence [12]. As a result, the difference between the two is a property of relevance in the design of adsorption refrigeration systems.

It is a matter of regret that adsorption data are unavailable from the manufacturers of adsorbents. The characteristics of a new adsorbent like a kind of silica gel or activated alumina may show differently than the known ones. 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.

From the above mentioned perspectives, the present paper reports an experimental study to obtain isotherm data for commercially available activated carbon (AC), silica gel (SG) and activated alumina (AA). Adsorption isotherms of R134A and R404A on the different materials were measured over a temperature range of 20–50 °C and pressures up to 5 bar using constant volume variable pressure (CVVP) method. Moreover, the isosteric heat of adsorption data is extracted from the data of the present experiments.

MATERIAL AND METHOD

The CVVP experimental setup comprises: (i) a charging tank with a volume of 3000 cc, (ii) an adsorption tank with a volume of 3000 cc, (iii) temperatures of the both the charging and adsorption tanks are controlled independently by the separate circulating water systems, (iv) a pressure transducer with an uncertainty of 0.15% of full scale and a pressure ranging from 0 to 1.6 MPa, (v) Pt 100 type thermometers with an uncertainty of 0.2% for temperature measurement, (vi) separate sensors with an uncertainty of 0.2% used with the adsorbent species for direct temperature measurement, (vii) a vacuum pump that achieves vacuum level of 0.5mbar, and (viii) a computer used to control the test system and record the data. The volume of both charging and adsorption tanks are inclusive of the volumes of related piping and valves.

Procedure

Prior to adsorption process, the specimen of the adsorbent is placed in an oven for 24 h to desorb any residual gas. The oven temperature is kept constant at 120°C. Before starting adsorption measurements the system was evacuated to take out any gases and moisture from the system using a vacuum pump to 0.5 mbar. The tanks were heated by using hot water circulation at 60°C during 6 h, while the vacuum process is still running. At the end of regeneration process, the test system is purged with helium gas and evacuated further to achieve low vacuum conditions. The evacuation and helium purging are continued several times to ensure that there is no residual gas left in the system. It is observed from the performed measurements that there is not any measurable interaction between the inert gas and the adsorbent. After evacuation, the charging cell is pressurized with the assorted refrigerant and left until it reaches an equilibrium state. During charging process, it is necessary to keep the charging pressure lower than the saturation pressure of the refrigerant to ensure no condensation is occurred. At this state the initial pressure and temperature in the charging cell are measured before adsorption. Once thermal equilibrium is achieved, the needle valve between the charging and adsorption tank is opened. The pressure and temperature in the adsorption tank are recorded to calculate the uptake of the assorted refrigerant by ensuring thermal equilibrium present. 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 5 bar.

Experimental study was performed by the use of commercially available adsorbents as activated carbon (AC), silica gel (SG) and activated alumina (AA) specimens. Phyiscal characteristics of the adsorbents used in the tests are presented in Table 1.

Table 1. Physical characteristics of the adsorbents used in the tests.

	Activated Carbon	Silica Gel	Activated Alumina
Size (mm)	0.6-2.6	2-5	1.4-2.8
Density (kg/m^3)	470	720	753
Micro Pore Specific Volume (cm^3/g)	0.472	0.276	0.166
Specific Surface Area (m^2/g)	949	556	350
Color	Black	Blue	White
Shape	Granulated	Spherical	Spherical

For each specimen with the known initial dry mass, experiments were performed at constant temperatures chosen as 20, 30 and 50 ºC for pressures up to 5 bar.

Assessment of overall uncertainty

There are some uncertainties associated with instrumentation, average adsorption cell temperature during adsorption and the void correction. Moreover, certain errors introduced due to the mathematical calculations. It is expected that the overall uncertainty will be within 3%.

ANALYTIC TREATMENT

The starting point for this analysis is the use of Dubinin–Astakhov (D–A) model of adsorption isotherm in the following form [8,9]:

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

with

$$W = Cv_a \quad \text{and} \quad W_0 = C_0 v_0 \qquad (2)$$

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 denotes the specific mass of adsorption (kg of adsorbate per unit mass of adsorbent), and v_a is the specific volume of the adsorbed phase, which is given by

$$v_a = v_b \exp(\Omega(T - T_b)) \qquad (3)$$

where

$$\Omega = \ln(b/v_b)/ (T_c - T_b) \qquad (4)$$

The quantity b denotes the van der Waals volume, v_b is the saturated liquid specific volume at the normal boiling point [11,12,13]. 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 = 0. Table 2 shows the properties and parameters of the adsorbates used in the present experimental study. Eq. (1) can be rewritten as follows:

$$\ln p = \ln p_s - E/(RT)[ln(C_0 v_0/Cv_a)]^{1/n} \qquad (5)$$

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

$$\frac{\partial \ln p}{\partial (1/T)} = \frac{\partial \ln p_s}{\partial (1/T)} - \left(\frac{E}{R}\right)[ln(C_0 v_0/Cv_a)]^{\frac{1}{n}}$$

$$-(ET\Omega/(nR))[ln(C_0 v_0/Cv_a)]^{((1-n))/n} \qquad (6)$$

Isosteric heat of adsorption is defined by the Clausius–Clapeyron relation at constant consantrations as

$$Q_{ads}|_{CC} = -R(\partial \ln p)/\partial (1/T) \qquad (7)$$

and for the heat of vaporization defined as

$$h_{fg} = -R(\partial \ln p_s)/\partial (1/T) \qquad (8)$$

Substituting Eq.7 and 8 into Eq.6, the following equation for the heat of adsorption can be derived.

$$Q_{ads} = h_{fg} + (E)[ln(C_0 v_0/Cv_a)]^{1/n}$$

$$+(ET\Omega/n)[ln(C_0 v_0/Cv_a)]^{((1-n))/n} \qquad (9)$$

Table 2. Properties and parameters of the adsorbates.

	R134A	**R404A**
Molecular Weight (MW)	102.03	97.60
Boiling Point at 1 atm (T_b)	-26.06 °C	-46.45 °C
Critical Temperature (T_c)	101.08 °C	72.07 °C
Critical Pressure (P_c)	4059 kPa	3729 kPa
Critical Density	515.3 kg/m^3	484.5 kg/m^3
b	0.0009390	0.0009857
v_b (m^3/kg)	0.0007260	0.0007655
v_0 (m^3/kg)	0.0007657	0.0008445
Ω	0.002018	0.002125

The standard procedure for evaluation of isosteric heat of adsorption as described by Eq.7, 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 [14, 15]. Due to non-ideality of the gas phase, during an adsorbate molecule uptake to the assorted adsorbent is affected by the pressure and temperature changes [5, 8]. In order to consider the effect of pressure and temperature changes, heat of adsorption can be calculated by using the Eq.9.

RESULTS AND DISCUSSIONS

The experimental data was used to evaluate the adsorption parameters for the activated carbon (AC)-R134A, silica gel (SG)-R134A, activated alumina (AA)-R134A, activated carbon (AC)-R404A, silica gel (SG)-R404A pairs. By the use of Eqs. 1-4, an objection function can be derived as follow:

$$F = \sum_{i=1}^{N}\left[C_i - \frac{C_0 v_0}{v_a}\exp\left\{-\left[\frac{RT_i}{E} \ln\left(\frac{p_s}{p_i}\right)\right]^n\right\}\right]^2 \qquad (10)$$

Where N is the number of data sets, C_i, p_i and T_i are known variables obtained from the

experimental measurements. C_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, C_0, E and n) for the AC-R134A, SG-R134A, AA-R134A, AC-R404A and SG-R404A pairs.

Table 3. Computed adsorption parameters of the different adsorbent-adsorbate pairs.

Pairs	W_0 (m³/kg)	C_0 (kg/kg)	E (kJ/kmol)	n
AC-R134A	0.3728×10^{-3}	0.487	8874.9	1.725
SG-R134A	0.3629×10^{-3}	0.474	5120.9	1.034
AA-R134A	0.2412×10^{-3}	0.315	5509.4	1.318
AC-R404A	0.3379×10^{-3}	0.400	11090	1.734
SG-R404A	0.3268×10^{-3}	0.387	6130.7	1.300

Comparison of the experimental and the computed isotherms of the adsorbent-adsorbate pairs at 20 °C are given in Fig.1. It can be seen from the Fig.1 that the measured results and the computed data obtained from D-A equation (Eq.1) with the parameters given in Table 2 are in a very good agreement.
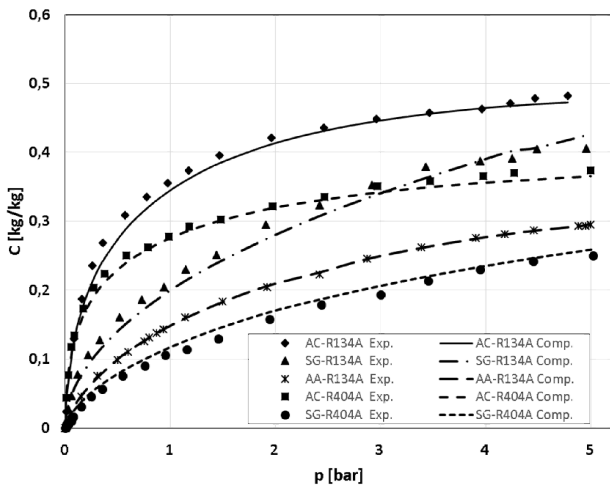

Fig.1. Comparison of the experimental and the computed isotherms of R134A and R404A on different adsorbents at 20 °C

The shapes of the isotherms obtained from the experimental data were similar in all cases and comparable to those reported in the literature for commercially available different adsorbents [3, 5,6,11,12]. Then, Eq.5 and Eq.9 with the parameters provided in Table 3 were used to evaluate isosters and isosteric heat of adsorption of the adsorbent-adsorbate pairs. Fig.2 shows the

isosters of adsorption of R134A and R404A on activated carbon, silica gel and activated alumina for $C/C_0 = 0.6$ It can be seen from the Fig.2 that the variation of ln(p) with 1/T presents linear variation for each adsorbent-adsorbate pairs. It is interesting to see that the isosters of the adsorbates of R134A and R404A with activated carbon is overlap each other, while the slopes of the lines are different for each adsorbent-adsorbate pairs.
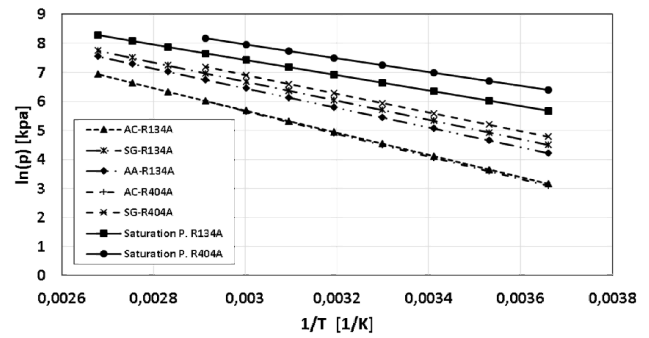

Fig.2. Obtained isosters of adsorption of R134A and R404A on activated carbon, silica gel and activated alumina for $C/C_0 = 0.6$
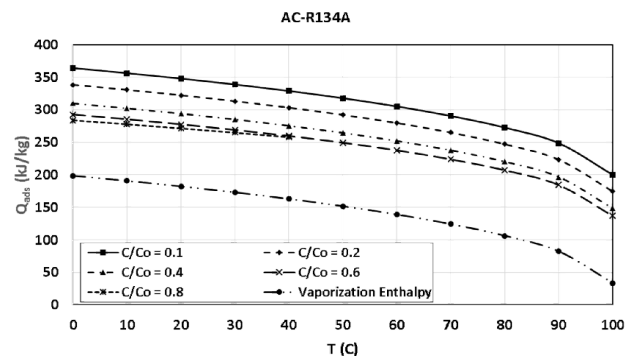

Fig.3. Obtained isosteric heat of adsorption of R134A on activated carbon

A careful inspection on the Fig.3 to Fig.7, it can be seen that the isosteric heat of adsorption decreases with increasing adsorbate uptake for all the cases. In addition, the temperature has more effect on isosteric heat, where the maximum value of isosteric heat obtained with low temperature at 0˚C. The adsorbate molecules first penetrate into narrow pores of adsorbent, where a stronger interaction between adsorbate and adsorbent exists. As a result of this a higher isosteric heat value of adsorption at lower loading occurs. After completely filling the smaller pores, adsorbate molecules are gradually accommodated in larger pores, in which the adsorption affinity becomes weaker. Therefore a monotonic decrease in isosteric heat of adsorption as a function of adsorbate uptake.
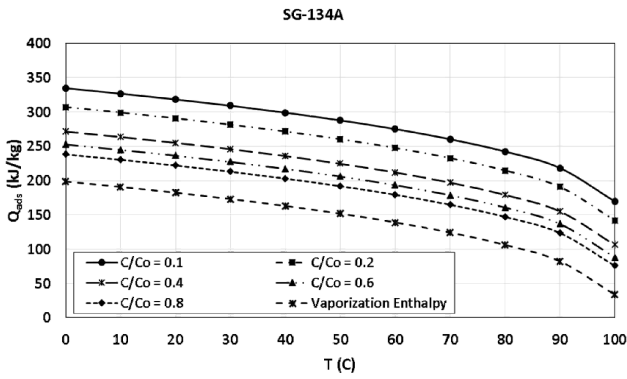
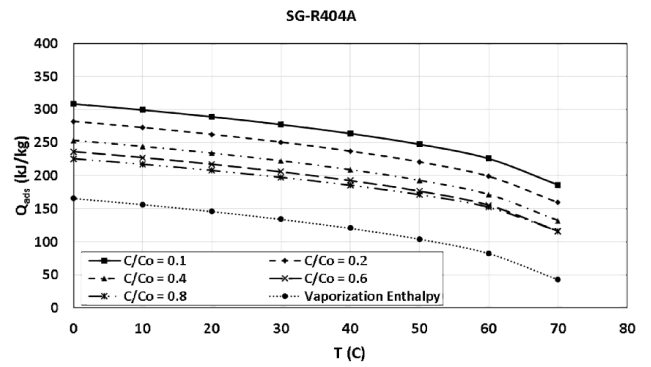**Fig.4.** Obtained isosteric heat of adsorption of R134A on silica gel
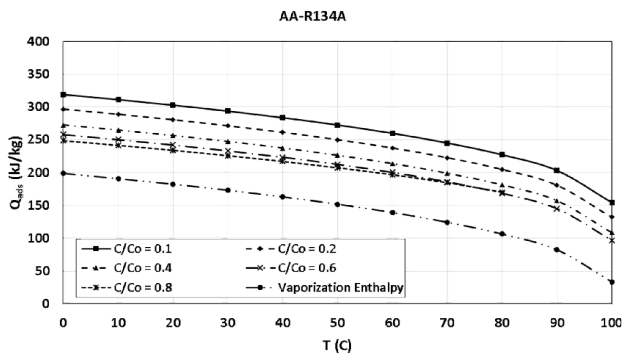

Fig.5. Obtained isosteric heat of adsorption of R134a on activated alumina

Comparing the magnitude of the isosteric adsorption heat, AC-R134A pair has the greatest one among the pairs tested in this study. Meanwhile, SG-R134A and AA-R134A pairs have the comparable magnitude of the isosteric adsorption heat. It is also observed that replacing R134A with R404A do not significant effect on the magnitude of the isosteric adsorption heat on the same adsorbent as seen Fig.4 and Fig.6 for AC, and also Fig.5 and Fig.7 for SG.

In addition to all, the magnitude of the heat of adsorption is greater than that of the enthalpy of vaporization of R134A and R404A in the all range of the experimental tests performed.
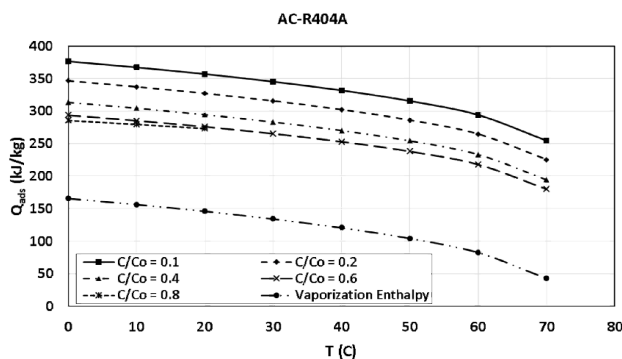

Fig.6. Obtained isosteric heat of adsorption of R404A on activated carbon

Fig.7. Obtained isosteric heat of adsorption of R404A on silica gel

CONCLUSIONS

In this study, the adsorption properties of R134A and R404A on commercially available specimens of activated carbon, silica gel and activated alumina for adsorption process has been experimentally studied. The measurements were performed over a temperature range from 20°C to 50°C and pressure up to 5 bar. The data were correlated with Dubinin-Astakhov (D-A) equation for corresponding adsorption process. Adsorption parameters were evaluated from the isotherms using the D-A equation. Further, the isosteric heat of adsorption were obtained, and correlation parameters were provided for the specimens investigated. Comparisons between the correlated results and the experimental data show very good agreement. It is observed that the adsorption capacity per kg of adsorbent increases rapidly with rising relative pressure at the starting period of the adsorption process. The maximum value of adsorption capacity decreases with the rising temperature of adsorbent . The isosteric heat of adsorption varied with the temperature and the maximum value of isosteric heat obtained at the lowest temperature. In addition, it is also observed that the magnitude of the heat of adsorption is higher than that the vaporization enthalpy of R134A and R404A in the range of experimental studies performed. This aspect is important for the design of thermal compressors in which the amount of coolant requirements to remove the heat of adsorption process have to be estimated.

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