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Isosteric heats of adsorption extracted from experiments of ethanol and HFC 134a on carbon based adsorbents

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Abstract

The purpose of this paper is to provide empirical correlations for isosteric heats of adsorption on carbon based adsorbents for two refrigerants namely ethanol and HFC 134a. A non-dimensional correlation which partitions the contributions of the concentration and temperature dependence is proposed. The correlation is tested out against data obtained from experimental isotherms of ethanol adsorption on activated carbon fibers [ACF (A-20) and ACF (A-15)] and HFC 134a on two specimens of activated carbon powders and one specimen of carbon granules. It is expected that the suggested correlation will be useful for designers of adsorption chillers where indenting heat inventories fulcrums on the magnitude of isosteric heat of adsorption.

Keywords: Activated carbon; Activated carbon fiber; Adsorption; Isosteric heat of adsorption

1. Introduction

The isosteric heat of adsorption is a specific combined property of an adsorbent–adsorbate combination. It is a major contributor to the heating inventories of adsorption refrigeration and gas storage systems and also cooling requirements of adsorption heat pumps. It has a pronounced effect on internal temperature raise of adsorption beds. Adsorption refrigeration research has attracted attention in view of the pressing need for combating ozone depletion and global warming. It provides an alternative to conventional vapor compressor refrigeration, because the former 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 vapour absorption cycles, adsorption cycles dispense with the heat exchangers. In industry, considerable waste heat is available at temperatures of the order of 100 °C, which can be effectively utilized for driving an adsorption refrigeration unit. On the refrigerant field considerable impetus already exists to use natural and ozone friendly refrigerants. Though, water has been the favorite natural refrigerant, its use is limited to refrigeration above about 5 °C [1,2]. Methanol has been used before [3,4], but reservations exist on its toxicity. Ethanol as refrigerant can be one of the promising candidates in adsorption cooling systems due to its environmental friendliness, non-toxicity and having relatively high vapor pressure even at low temperature levels [5–8]. Yet, this refrigerant needs sub-atmospheric pressures during operation which is laden with problem of ingress of ambient air. 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 HFC 134a. Thus, ethanol and HFC 134a based adsorption refrigeration cycles provide a perfect match for the current aspirations and expectations from adsorption cooling systems. Among adsorbents activated carbons (both fibers and powders)

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Nomenclature

a	experimental parameter used in Eq. (14)
b	experimental parameter used in Eq. (14)
c	specific mass of adsorption (kg/kg)
c_0	maximum specific heat of adsorption (kg/kg)
E	parameter describes the isotherm in Eq. (1)
n	exponential parameter describes the isotherm in Eq. (1)
P	pressure (kPa)
P_s	saturation pressure (kPa)
R	gas constant (kJ/kg K)
T	temperature (K)
T_c	critical temperature (K)
T_b	boiling temperature (K)
T/T_c	reduced temperature (–)
v_a	specific volume of the adsorbed phase (m^3/kg)
v_b	the saturated liquid specific volume at the normal boiling point (m^3/kg)
W	volume of adsorbate per kg of adsorbent (m^3/kg)
W_0	maximum volume of adsorbate per kg of adsorbent (m^3/kg)

Subscripts

a	adsorbed phase
b	boiling point
c	critical
s	saturation
0	maximum

have a clear edge as they can be made with large micropore volumes and high surface areas. With the availability of highly microporous activated carbon fibers and powders with micropore volumes >1 cm^3/g, very compact adsorption chillers can be constructed. The design of these refrigeration systems requires data on isotherms for sizing the compressors and the heats of adsorption for indenting heating inventories. Banker et al. [9] have shown that the latter is a major component and its proper estimation is paramount to the performance of the cycle.

Isosteric heat of adsorption is traditionally expressed as a function of concentration due to its dependence on temperature is relatively weaker [10,11]. 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. As a result, the difference between the two is a property of relevance in the design of adsorption refrigeration systems.

From the above mentioned perspectives, the present paper attempts to provide a correlation for this important property which is conveniently segregated in to concentration and temperature dependent contributions. This approach is justified through experimental data on two adsorbates (ethanol and HFC 134a) and five specimens of carbon based adsorbents.

2. Analytic treatment

The starting point for this analysis is the use of Dubinin–Astakhov (D–A) model of adsorption isotherm in the following form [10]:

$$W = W_0 \exp[-\{RT \ln(p_s/p)/E\}^n] \quad (1)$$

with $W = cv_a$ (2)

and $W_0 = c_0 v_0$ (3)

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

$$v_a = v_b \exp[\Omega(T - T_b)] \quad (4)$$

where $\Omega = \ln(b/v_b)/(T_c - T_b)$ (5)

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. (4) at $T = 0$. When $n = 2$, Eq. (1) becomes the Dubinin–Radushkevich (D–R) equation and $n = 1$ gives the classical Dubinin equation. Eq. (1) can be rewritten as follows:

$$\ln p = \ln p_s - E/(RT)[\ln(c_0 v_0/cv_a)]^{1/n} \quad (6)$$

Differentiating Eq. (6) with respect to $1/T$ and noting that v_a is also a function of temperature, one can get the following equation:

$$\partial \ln p/\partial(1/T) = \partial \ln p_s/\partial(1/T) - E/R[\ln(c_0 v_0)/cv_a]^{1/n} - ET\Omega[\ln(c_0 v_0)/cv_a]^{(1-n)/n}/(nR) \quad (7)$$

Eq. (7) can be compared to that developed by Do [12]. Substituting for isosteric heat of adsorption which is defined by the Clausius–Clapeyron relation as

$$h_{st} = -R\partial \ln p/\partial(1/T) \quad (8)$$

and for the heat of vaporization defined as

$$h_{fg} = -R\partial \ln p_s/\partial(1/T) \quad (9)$$

one can get

$$h_{st} = h_{fg} + E[\ln(c_0 v_0)/(c v_a)]^{1/n} + ET\Omega[\ln(c_0 v_0)/(c v_a)]^{(1-n)/n}/n \tag{10}$$

when $n = 1$, the above equation reduces to

$$(h_{st} - h_{fg})/E = \ln(c_0/c) + \ln(v_0/v_b) + T_b\Omega \tag{11}$$

indicating that the isosteric heat of adsorption is not a function of temperature.

The standard procedure for evaluation of isosteric heat of adsorption is to plot the isosters on ln p *vs.* $1/T$ plane. Normally, a constancy of slope is observed at temperatures well over the critical point of the adsorbate and this does not warrant bringing in the temperature dependence. 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 [11].

There is an analogy with the heat of vaporization which shows constancy at low temperatures based on which Antoine's vapour pressure equation is derived in conjunction with the assumption of negligibility of liquid phase specific volume in comparison to the vapour phase one. As the temperature increases, this assumption is no longer valid and one has a temperature dependence of the heat of vaporization.

At low uptakes occurring at high temperatures, adsorbed phase specific volume is no longer negligible compared to bulk gas phase specific volume. This is particularly true for uptakes by high surface area activated carbonaceous adsorbents for polar fluids such as ethanol and HFC 134a. As shown in Fig. 1, the left hand side of Eq. (11) will be a function of temperature as well. In this figure, the isosteric heats of adsorption are plotted against the temperature at a typical concentration of 0.45 kg/kg of ACF (A-20) and ACF (A-15) for adsorption of ethanol. For HFC 134a, the concentrations chosen are 1.2, 0.4 and 0.25 kg/kg for Maxsorb II, Fluka and Chemviron, respectively. Large pressure and temperature swings brought about by homogeneous micropore sights (indicated by a value of $n > 1$) make it pertinent to bring in the temperature dependence of isosteric heat of adsorption. For example when $n = 2$, which is the case with ethanol adsorption on activated carbon fibers [13], Eq. (10) reduces to

$$(h_{st} - h_{fg})/E = [\ln(c_0 v_0)/(c v_a)]^{1/2} + T\Omega/[2\{\ln(c_0 v_0)/(c v_a)\}^{1/2}] \tag{12}$$

Now, both terms on the right hand side of Eq. (12) are functions of temperature and concentration.

3. Proposed correlation

What we propose is that the temperature and concentration contributions can be segregated such that

$$(h_{st} - h_{fg})/E = [\ln(c_0/c)]^{1/n} + f(T) \tag{13}$$

This proposal is impelled by the observation that a plot of $h_{st} - h_{fg}/E$ *vs.* $[\ln(c_0/c)]^{1/n}$ is only a function of temperature irrespective of the concentration (Figs. 2a–2e). The function $f(T)$ is formalized through experimental isotherm data for ethanol on two activated carbon fiber samples (ACF A-20 and ACF A-15) [13] and for HFC 134a on two specimens of activated carbon powders (Maxsorb-II and Fluka) and one specimen of granules (Chemviron) [10]. Further, it is observed that the second term on the right hand side of Eq. (13) is only a function of the adsorbate and independent of the specimen of the adsorbent. It is fortuitous that, the terms on the right hand side depict a behavior analogous to those on the left hand side, namely the isosteric heat of adsorption being adsorbent–adsorbate combination dependent and the heat of vaporization being only adsorbate dependent. After considering several least squares fits, it is found that the following simple form fits the experimental data the best.

$$f(T) = a(T/T_c)^b \tag{14}$$

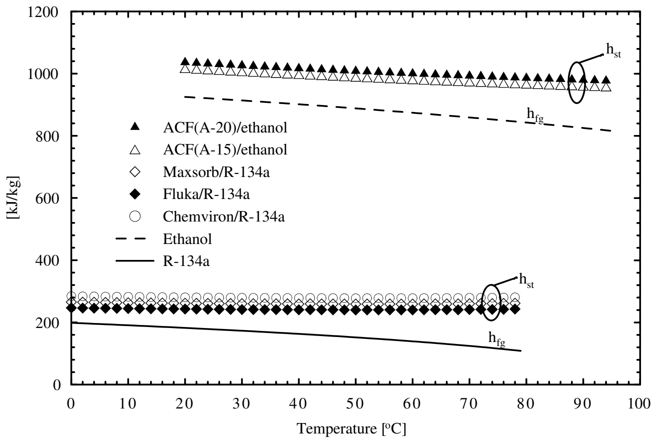

Fig. 1. Temperature effect on isosteric heats of adsorption for various carbon based adsorbents/refrigerants pairs.

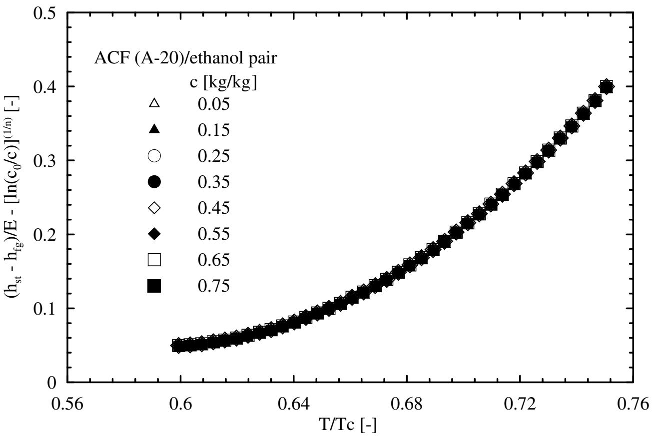

Fig. 2a. Plot of $(h_{st} - h_{fg})/E - [\ln(c_0/c)]^{1/n}$ vs. $\left(\frac{T}{T_c}\right)$ at different concentrations for ACF (A-20)/ethanol pair.

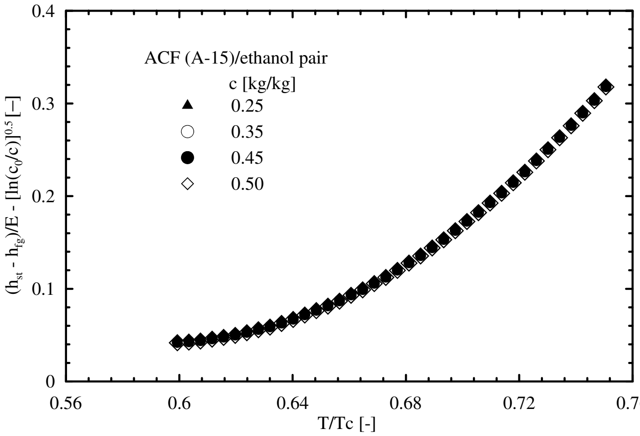

Fig. 2b. Plot of $(h_{st} - h_{fg})/E - [\ln(c_0/c)]^{1/n}$ *vs.* $\left(\frac{T}{T_c}\right)$ at different concentrations for ACF (A-15)/ethanol pair.

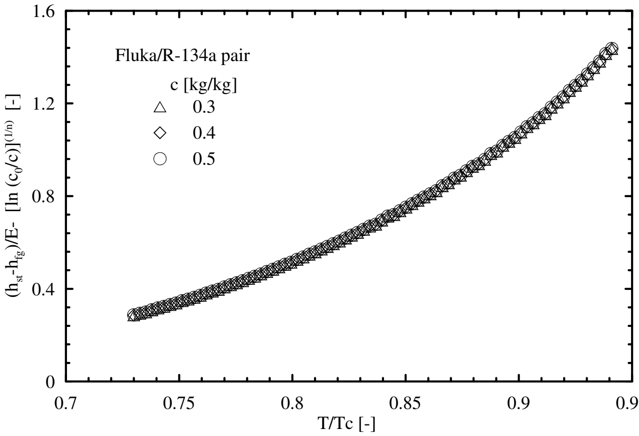

Fig. 2d. Plot of $(h_{st} - h_{fg})/E - [\ln(c_0/c)]^{1/n}$ *vs.* $\left(\frac{T}{T_c}\right)$ at different concentrations for Fluka/H-134a pair.

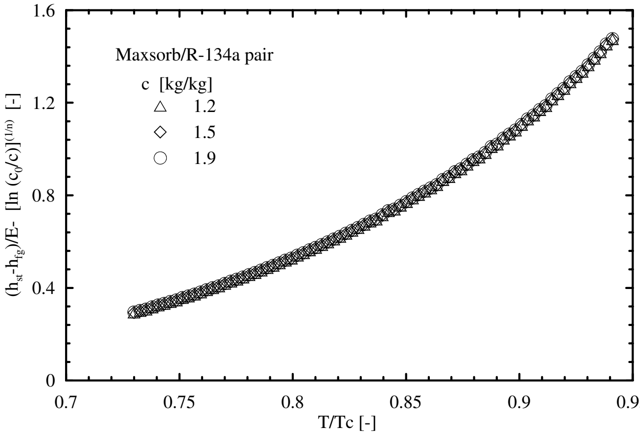

Fig. 2c. Plot of $(h_{st} - h_{fg})/E - [\ln(c_0/c)]^{1/n}$ *vs.* $\left(\frac{T}{T_c}\right)$ at different concentrations for Maxsorb II/HFC-134a pair.

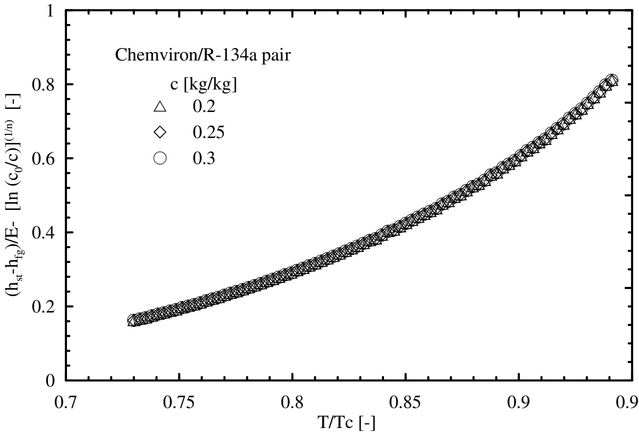

Fig. 2e. Plot of $(h_{st} - h_{fg})/E - [\ln(c_0/c)]^{1/n}$ *vs.* $\left(\frac{T}{T_c}\right)$ at different concentrations for Chemviron/H-134a pair.

4. Verification of the correlation

In order to obtain best fits, the raw data from the two sources of experimental isotherms [10,13] are processed rather than using the correlations given in those papers. The relevant constants and the parameters are shown in Tables 1 and 2.

Fig. 3a–e shows plot of deviations between the Eq. (13) and the data those are obtained from Eq. (8) using the experimental isotherms for ACF (A-20)/ethanol, ACF (A-15)/ethanol, Maxsorb II/HFC 134a, Fluka/HFC 134a and Chemviron/HFC 134a, respectively. It is seen that the deviations are minimal for all five assorted adsorbent/

Table 1
Thermophysical and experimental constants of the refrigerants

Adsorbent	Ethanol	R 134a
T_c (K)	489.15	374.21
$(a \times E)$ (kJ/kg)	927	156
b	9.75	6.25

Table 2
Adsorption parameters of the adsorbent/adsorbate pairs

Adsorbent	Adsorbate	n	a	c_0 (kg/kg)	E (kJ/kg)	Coefficient of determination r^2	Concentration range (kg/kg)	Reduced temperature range (–)
ACF(A-20)	Ethanol	2	6.717	0.797	138	0.999	0.05–0.75	0.6–0.75
ACF(A-15)	Ethanol	2	5.297	0.570	175	0.973	0.25–0.5	0.6–0.75
Maxsorb II	HFC 134a	1.3	2.136	2.058	73	0.994	1.2–1.9	0.73–0.94
Fluka	HFC 134a	0.9	2.079	0.592	75	0.987	0.3 –0.5	0.73–0.94
Chemviron	HFC 134a	1.45	1.173	0.354	133	0.96	0.2–0.3	0.73–0.94

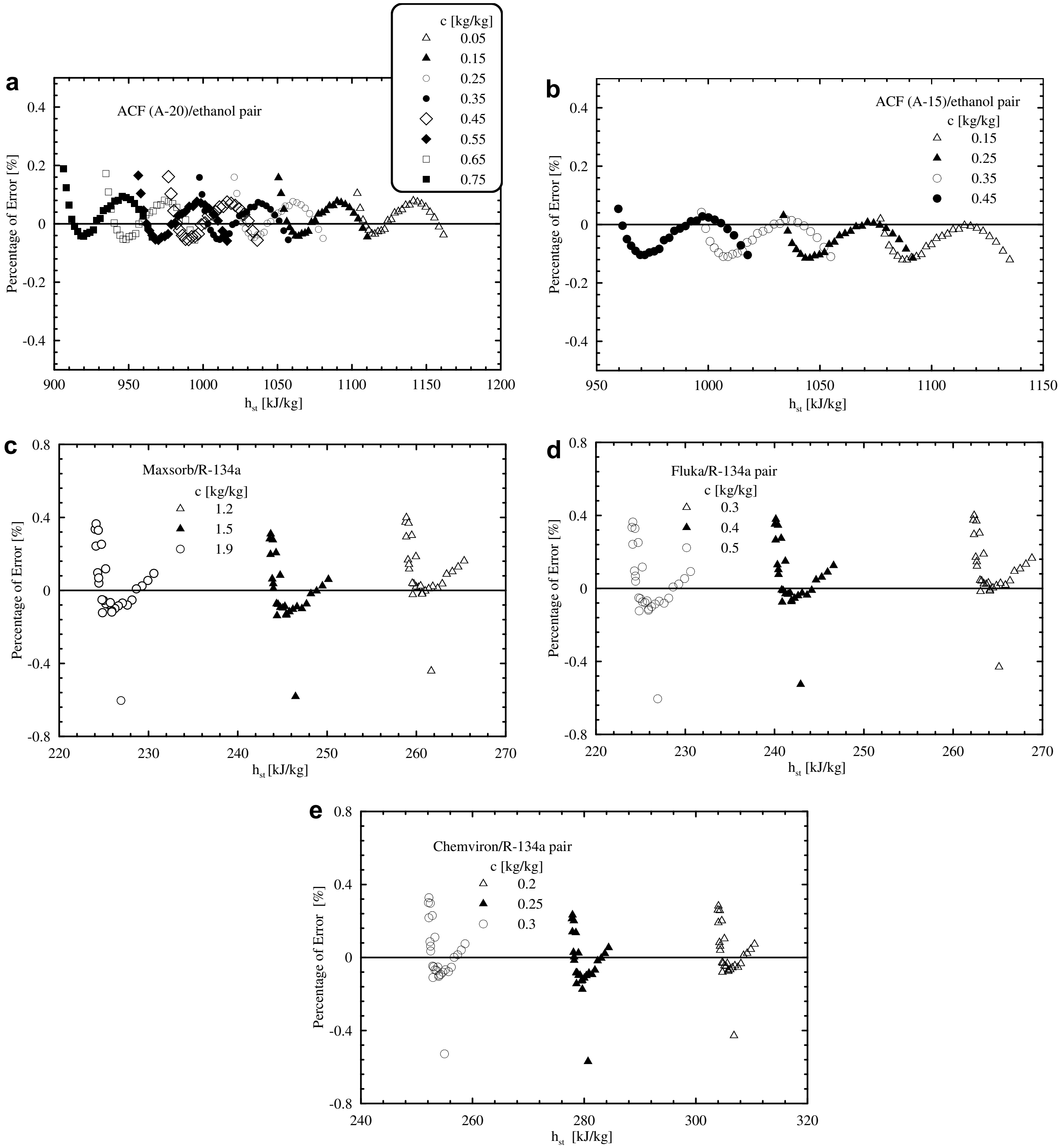

Fig. 3a–e. Deviation plots for difference between heats of adsorption and vaporization estimated by using the proposed method and those obtained from experimental isotherms. (a) ACF (A-20) + ethanol; (b) ACF (A-15) + ethanol; (c) MaxsorbII + HFC 134a; (d) Fluka + HFC 134a; (e) Chemviron + HFC 134a.

refrigerant pairs over a wide range of concentrations and temperatures confirming the validity of the proposal.

5. Conclusions

It is shown that the concentration and temperature contributions to differences between isosteric heat of adsorption and heat of vaporization can be segregated. A non-dimensional correlation for this property is proposed and validated from the experimental isotherm data for ethanol on two types of activated carbon fibers, and HFC 134a on two specimens of activated carbon powders and one specimen of carbon granules.

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