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Near-critical adsorption of CO_2 on 13X zeolite and N_2O on silica gel: lack of evidence of critical phenomena

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Abstract The excess adsorption of CO_2 on 13X zeolite and of N_2O on silica gel has been studied at high pressure using a magnetic suspension balance, i.e. a gravimetric method. Recently, a detailed study on the density distribution in the measuring cell of the magnetic suspension balance showed that a proper approach to thermostatting the unit should be used in order to obtain reliable and accurate excess adsorption measurements. This is particularly important in the vicinity of the critical point of the fluid, where the density is strongly dependent on pressure and temperature. In the past, several effects were observed in our laboratory when measuring near-critical adsorption on 13X zeolite and on silica gel, namely critical adsorption and critical depletion. In the present study, these effects have been checked using the balance in the new thermostatting configuration, and the conclusion can be drawn that the accuracy of the measurement is not sufficient to prove that they indeed occur. More accurate adsorption data for the two systems have been measured and reported.

Keywords Supercritical adsorption · Gravimetric method · Carbon dioxide · Nitrous oxide · 13X zeolite · Silica gel

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Abbreviations

n^{ex}	Molar excess adsorption per adsorbent mass [mmol/g]
T	Temperature [K]
P	Pressure [bar]
ρ	Density [g/cm^3]

Subscripts and superscripts

b	Bulk
B	Basket
c	Critical
ex	Excess
r	Reduced
Sk	Sinker

1 Introduction

The measurement and description of supercritical adsorption isotherms represent a scientific and technical challenge. The most common approaches used to measure adsorption are the volumetric and the gravimetric methods. For both techniques, the truly measurable quantity is the excess adsorbed amount n^{ex}, which can be used to fully describe the thermodynamic adsorption equilibria (Sircar 1985, 1999, 2001). The shape of supercritical excess adsorption isotherm plotted against the density of the bulk phase is typically characterized by a maximum with a subsequent decrease of the excess adsorption when the density is further increased. The position and shape of the maximum are determined, among other factors, by the pore size distribution of the adsorbent (Di Giovanni et al. 2001b; Hocker et al. 2003). This behavior has been reported by many authors when

measuring isotherms at temperatures well above the critical temperature of the fluid (Specovius and Findenegg 1980; Di Giovanni et al. 2001a; Ottiger et al. 2006). However, when approaching near-critical conditions from above, i.e. decreasing the temperature to values slightly above the critical temperature, the isotherm shape exhibits interesting features. In the past, mainly two types of behavior have been reported, which are characterized by positive or negative "bumps" in the excess adsorbed amounts at densities close to the critical density. These phenomena have been called critical adsorption and critical depletion, respectively. They have also been observed in our laboratory, using a Rubotherm magnetic suspension balance: critical adsorption for CO_2 on 13X zeolite (Hocker et al. 2003) and critical depletion for N_2O on silica gel (Rajendran et al. 2002). Similar features for other systems have been reported also by other researchers, making use of different experimental techniques. Critical adsorption was observed when measuring the adsorption of CO_2 on activated carbon near its critical temperature, namely at 305 K, using a volumetric technique (Chen et al. 1997). Anomalous peaks at near-critical conditions have been reported also for the adsorption of CO_2 on activated carbon and on NaY zeolite measured with a flow gravimetric apparatus (Humayun and Tomasko 2000; Gao et al. 2004). With a volumetric apparatus, critical depletion for SF_6 on graphitized carbon black (Thommes et al. 1994) and on two controlled pore glasses, namely CPG-350 (Thommes et al. 1995) and CPG-100 (Machin 1999), was measured.

The experimentally obtained near-critical adsorption isotherms have been subject to different theoretical explanations. Critical adsorption has a strong theoretical basis (Fisher and de Gennes 1978) and has been successfully modeled for the system CO_2 on 13X zeolite, where the appearance of positive bumps at near critical conditions was explained by the presence of the meso- and macropores and the occurrence of critical adsorption (Hocker et al. 2003). A lattice model failed to describe the criticality of the isotherms for a microporous NaY zeolite (Gao et al. 2004). A convincing physical explanation is however still missing for the phenomenon of critical depletion. Although initially some theoretical arguments appeared to be able to explain it (Thommes et al. 1995; Schoen and Thommes 1995; Schoen et al. 1997), it was shown later that the behavior of the simulation results was due to a simulation artifact (Wilding and Schoen 1999). As far as critical depletion is concerned, the situation is not satisfactory: there is experimental evidence, including our own data for N_2O adsorption on silica gel, but a theoretical justification of critical depletion is still missing, in spite of many efforts.

In the recent years, gravimetric experiments using magnetic suspension balances have been increasingly used for adsorption equilibrium measurements (Dreisbach and Lösch 2000). Though gravimetric systems offer good accuracy (accuracy < 0.1 mg) even at high pressures, significant loss on accuracy can arise when they are operated at conditions near the critical point of the fluid. This has been highlighted in a recent study, where it was shown that for a Rubotherm magnetic suspension balance, among the different thermostatting configurations, there is one that allows for the best accuracy in carrying out excess adsorption measurements (Pini et al. 2006). For the case of near-critical adsorption of CO_2 on a F400 activated carbon it was in fact shown that bumps or even a behavior similar to critical depletion could be observed because of an inhomogeneous density distribution in the measuring cell when the non-optimal thermostatting configurations are adopted. Using the optimal thermostatting configuration instead, a homogeneous density distribution was obtained and only small deviations from the expected linear behavior of the excess adsorption isotherm near the critical point were reported. The conclusion of that study was that none of the critical phenomena were observed in the studied system and that at conditions too close to the critical point the experimental error of this measuring technique makes it impossible to attribute physical meaning to the small deviations observed. In the light of these important findings, we have repeated the measurements of adsorption of CO_2 on 13X zeolite (Hocker et al. 2003) and of N_2O on silica gel (Rajendran et al. 2002), using the same Rubotherm magnetic suspension balance and the optimal thermostatting configuration. In this work we report these results, and discuss them carefully in terms of critical adsorption and critical depletion.

2 Experimental section

2.1 Materials

Zeolite 13X pellets (Z10-02, lot number 16296) were obtained from Chemie Uetikon AG (Zurich, Switzerland). The adsorbent was regenerated at 300 °C under nitrogen for 12 hours before being used for the experiments. Silica gel (Kieselgel 60, 0.063–0.20 mm, Batch #1.07734.1000) was obtained from Merck KGaA (Darmstadt, Germany). The adsorbent was dried at 150 °C in a vacuum oven for 3 days before using it in the experiments. The gases used in this study were obtained from Pangas AG (Luzern, Switzerland), namely CO_2 (99.995% purity), N_2O (99.0% purity) and He (99.999% purity). The critical properties of the adsorbates are as follows: $T_c(\mathrm{He}) = 5.26$ K, $P_c(\mathrm{He}) = 2.26 \times 10^5$ Pa, $\rho_c(\mathrm{He}) = 69.3$ kg/m^3, $T_c(\mathrm{CO_2}) = 304.1$ K, $P_c(\mathrm{CO_2}) = 73.7 \times 10^5$ Pa, $\rho_c(\mathrm{CO_2}) = 467.6$ kg/m^3, $T_c(\mathrm{N_2O}) = 309.6$ K, $P_c(\mathrm{N_2O}) = 72.2 \times 10^5$ Pa, $\rho_c(\mathrm{N_2O}) = 453.2$ kg/m^3.

2.2 Set-up

To measure the excess adsorbed amounts, a Rubotherm magnetic suspension balance was used, which can be operated at pressures and temperatures up to 450 bar and 250 °C, respectively. The balance is kept at a constant temperature with two heating jackets (one for the suspension coupling and one for the measuring cell), and the temperature is measured with a calibrated thermocouple with an accuracy of 0.1 °C. Moreover, thanks to a titanium sinker (whose volume has been independently calibrated) the fluid phase density inside the measuring cell can be measured directly. The details of the balance and of its measuring principle can be found elsewhere (Dreisbach and Lösch 2000; Di Giovanni et al. 2001a; Rajendran et al. 2002). Special attention should be paid to the fact that the unit has been thermostatted using the configuration called PU (Parallel Up) in a previous work (Pini et al. 2006). This is different from and better than the PD (Parallel Down) configuration that was adopted in earlier studies on the same systems (Hocker et al. 2003; Rajendran et al. 2002).

2.3 Experimental procedure

After regeneration, about 3 g of the adsorbent were weighed and placed in the sample basket, which was then attached to the suspension coupling. In order to prevent moisture uptake, special care was taken to transfer the adsorbents into the measuring cell quickly. The cell was closed; vacuum was applied at 150 °C and the weight of the sorbent material plus all the metal parts was measured. As a second step, measurements with helium were performed, in order to measure the volume of all the solid parts that is needed to calculate the buoyancy correction. The detailed procedure for these measurements, which takes into account adsorption of helium on the adsorbent as well as thermal expansion of the solid parts inside the measuring cell, is described elsewhere (Rajendran et al. 2002; Hocker et al. 2003). Finally, the cell was again evacuated and the desired adsorbate was introduced. All the isotherms were measured in the desorption mode, i.e. starting from the highest pressure and reducing it stepwise. However, for each system investigated some points were repeated at increasing pressure and no significant difference has been observed.

3 Experimental results

In this section the results of the adsorption experiments of CO_2 on 13X zeolite and of N_2O on silica gel are presented. For each system a complete set of data covering a wide temperature range is shown. These consist of isotherms measured using the balance in the new thermostatting configuration (mainly near-critical isotherms) together with some data that were previously published, namely the isotherms measured far enough from the critical point where we have shown that the measurements are not sensitive to the chosen thermostatting configuration (Pini et al. 2006).

3.1 Nitrous oxide on silica gel

The excess adsorption isotherms of N_2O on silica gel are reported in Fig. 1 as a function of the reduced density ρ^b/ρ_c, i.e. the bulk density divided by the critical density of the fluid, for seven different temperatures. The isotherms at 36.9 °C, 38.4 °C and 38.9 °C (solid lines) have been newly

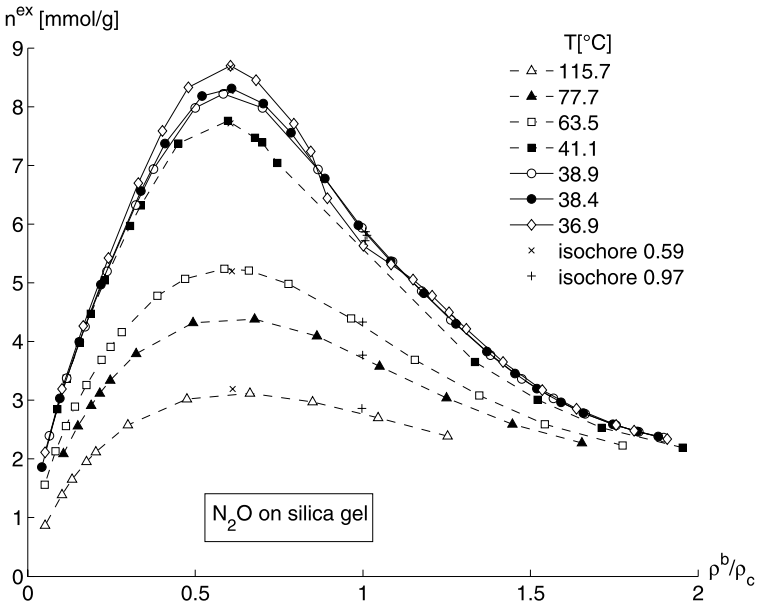

Fig. 1 Excess adsorption isotherms of N_2O on silica gel as a function of the reduced density ρ^b/ρ_c measured at different temperatures. The *symbols* × and + represent the isochoric runs. The *symbols* represent the experimental data while the *lines* are drawn to guide the eye. Isotherms with the *solid lines* were measured in the present study, whereas those with the *dashed lines* are the ones reported earlier (Rajendran et al. 2002)

Table 1 Experimental excess adsorption data of N_2O on silica gel

T [K]	ρ [g/L]	n^{ex} [mmol/g]	T [K]	ρ [g/L]	n^{ex} [mmol/g]
310.0	865.0	2.34		490.7	5.37
	819.8	2.48		447.2	5.98
	795.5	2.58		401.7	6.78
	742.0	2.85		355.9	7.55
	695.9	3.17		318.4	8.05
	642.9	3.65		275.9	8.31
	592.9	4.22		235.9	8.18
	569.9	4.50		185.8	7.37
	546.8	4.78		153.1	6.57
	521.0	5.05		99.2	4.97
	491.4	5.31		69.7	3.99
	453.9	5.63		43.8	3.03
	405.5	6.44		19.4	1.86
	383.0	7.24	312.1	859.8	2.37
	360.0	7.71		826.1	2.46
	308.7	8.45		795.5	2.57
	274.5	8.70		754.0	2.77
	217.4	8.33		711.0	3.03
	182.3	7.58		668.1	3.36
	149.9	6.70		625.6	3.77
	109.5	5.43		572.5	4.37
	75.3	4.26		532.8	4.86
	46.6	3.19		493.1	5.36
	23.5	2.11		452.0	5.94
311.6	852.6	2.38		392.4	6.93
	824.3	2.47		317.8	7.98
	791.2	2.59		264.5	8.22
	751.5	2.78		226.4	7.98
	721.3	2.96		170.3	6.94
	688.7	3.20		146.3	6.32
	658.7	3.45		107.5	5.20
	620.7	3.83		77.7	4.25
	578.8	4.30		52.8	3.38
	535.5	4.82		29.4	2.39

measured using the balance in the new thermostatting configuration, whereas the isotherms at the other temperatures (dashed lines) correspond to the published data (Rajendran et al. 2002). For the sake of completeness, the new experimental data are reported also in Table 1. The shape of the dashed isotherms is characterized by a maximum and a subsequent decreasing part with increasing fluid phase density. Closer to the critical temperature, it can be observed that after reaching the maximum also the two isotherms measured at 38.4 °C and 38.9 °C fall smoothly with increasing density, in contrast with the sharp decrease observed in our previous study at similar temperatures near the critical point. In that case, the isotherms were crossing those measured at a higher temperature (Rajendran et al. 2002). In the present study this crossover phenomenon still appears, although in a much less pronounced way, for the isotherm measured at 36.9 °C, i.e. at a temperature which is only 0.4 °C above the critical temperature of nitrous oxide (the reduced temperature is 1.001) and in the reduced density range $0.8 \leq \rho^b/\rho_c \leq 1.2$, i.e. at conditions very close to the bulk critical point. It is worth noting, that an error estimation of the measuring technique leads to errors that are so small that the corresponding error bars would be hardly visible.

Isochoric runs have also been carried out at two different reduced densities ρ^b/ρ_c, namely 0.59 and 0.97, in order to confirm the accuracy of the published experimental results at higher temperatures, i.e. at conditions which are far away from the critical point. In Fig. 1 it can be observed that the data obtained through isochoric measurements agree well with both the published data (dashed lines) and the new results from the isothermal runs (solid lines). The data measured in the isochoric runs are also plotted against the temperature in Fig. 2. Here, as expected the excess adsorbed amount increases as the critical temperature T_c is approached. This increase is weaker at larger densities, since, when approaching the critical temperature, the excess adsorption isotherms get more closely spaced.

3.2 Carbon dioxide on 13X zeolite

The excess adsorption isotherms of CO_2 on 13X Zeolite are shown in Fig. 3. Again, the dashed lines correspond to the already published isotherms measured at temperatures far enough from the critical temperature T_c. The solid lines ($T = 49.3$ °C, 35.0 °C, 31.7 °C, 31.4 °C) were measured using the balance in the new thermostatting configuration and the corresponding data are reported also in Table 2. After a sharp rise, each isotherm reaches a maximum and falls off with a further increase in the bulk density. In the descending part, however, the two isotherms at the lowest temperatures exhibit a different behavior from the others. Instead of following the linear decrease, the isotherms measured at 31.7 °C and at 31.4 °C (the reduced temperatures being 1.002 and 1.001, respectively) exhibit a characteristic positive "bump" in the reduced density range $0.5 < \rho^b/\rho_c < 1$. Right after the bumps two isotherms exhibit also a slight cross over. In particular, the isotherms measured at 31.4 °C and at 31.7 °C cross the isotherm measured at 35.0 °C, i.e. at a higher temperature.

In order to confirm the reliability of those isotherms measured at higher temperatures, which have been published, also for this system isochoric runs have been performed. In particular, two reduced density values have been chosen, namely $\rho^b/\rho_c = 0.2$ and 0.7, which correspond to the position of the isotherms' maximum and of the bumps, respectively. The measurements obtained in the isochoric runs are

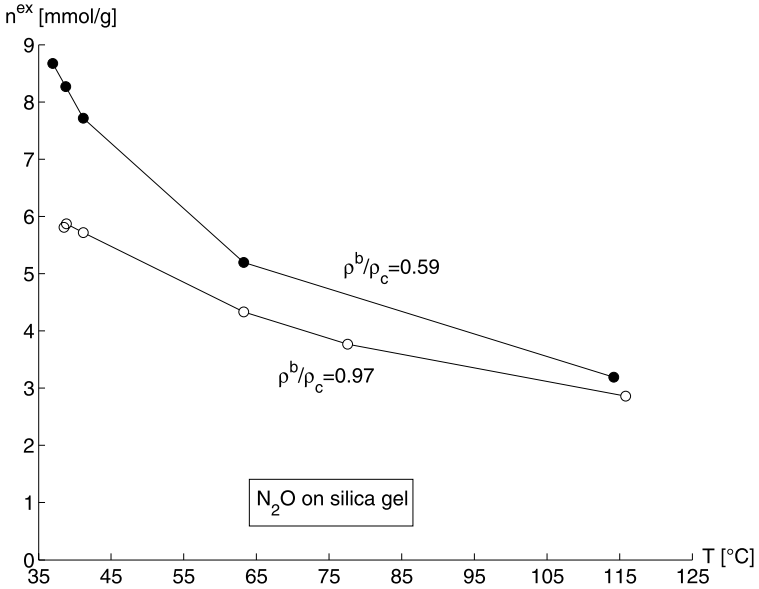

Fig. 2 Excess adsorption isochores of N_2O on silica gel as a function of the temperature T measured at two different reduced densities ρ^b/ρ_c: 0.59 and 0.97

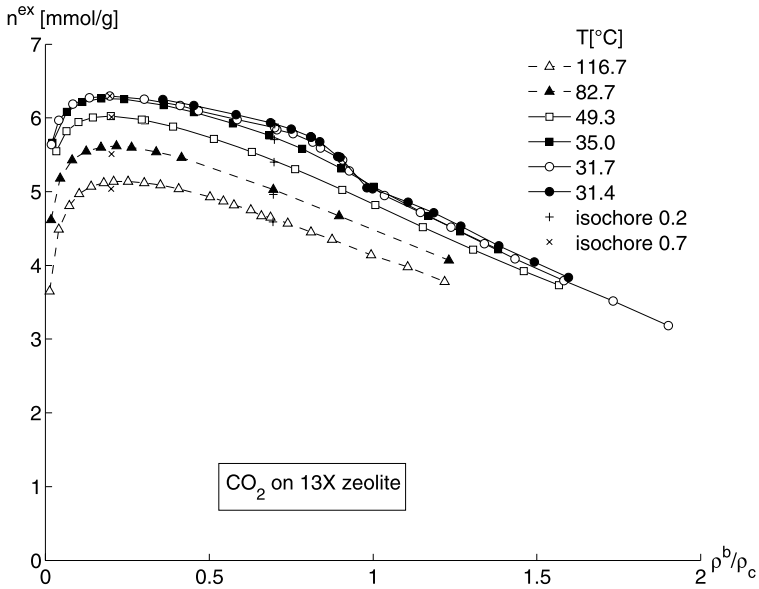

Fig. 3 Excess adsorption isotherms of CO_2 on 13X zeolite as a function of the reduced density ρ^b/ρ_c measured at different temperatures. The *symbols* $\times$ and $+$ represent the isochoric runs. The *symbols* represent the experimental data while the *lines* are drawn to guide the eye. Isotherms with the *solid lines* were measured in the present study, whereas those with the *dashed lines* are the ones reported earlier (Hocker et al. 2003)

plotted together with the isotherms in Fig. 3 against reduced density and in Fig. 4 against temperature. From Fig. 3, it can be observed that the isochoric points are in good agreement with the newly measured isotherms and also with the isotherm measured at 116.7 °C and at 82.7 °C, i.e. the previously published data. In Fig. 4 the excess adsorbed amount increases with decreasing temperature, as expected. Moreover, the two isochores run parallel to each other with the exception of the temperatures close to T_c, where the isochore measured at $\rho^b/\rho_c = 0.7$ shows a larger increase in the excess adsorbed amount with decreasing temperature. This larger increase corresponds in fact to the observed bump in the isotherms.

3.3 Near-critical isotherms

In this section, the isotherms measured at conditions close to the critical temperature are described in more detail, in order to analyze their peculiar behavior. For both systems, i.e. N_2O on silica gel and CO_2 on 13X zeolite, the accuracy of the measured isotherms is discussed using the data obtained from experiments carried out without adsorbent in the sample basket (empty runs). If the balance is operated without adsorbent, the density of the fluid can be measured at two different positions in the measuring cell, namely at the basket and at the sinker position; on the contrary, when the basket is filled with an adsorbent, the density is measured at the sinker position only (Pini et al. 2006;

Table 2 Experimental excess adsorption data of CO_2 on 13X zeolite

T [K]	ρ [g/L]	n^{ex} [mmol/g]	T [K]	ρ [g/L]	n^{ex} [mmol/g]
304.5	746.8	3.83		91.4	6.30
	697.9	4.05		62.7	6.27
	647.1	4.27		38.9	6.19
	592.7	4.53		18.9	5.97
	554.3	4.71		8.5	5.64
	517.4	4.86	308.1	646.0	4.22
	466.8	5.04		591.8	4.46
	458.8	5.05		546.5	4.67
	420.6	5.47		468.4	5.06
	416.9	5.48		422.2	5.31
	391.3	5.68		366.2	5.58
	379.6	5.74		319.7	5.76
	378.6	5.74		267.6	5.93
	350.6	5.85		211.6	6.08
	321.3	5.93		168.7	6.17
	271.9	6.05		112.3	6.25
	211.8	6.17		79.6	6.26
	167.5	6.25		52.3	6.22
304.8	889.3	3.18		30.2	6.08
	810.5	3.52		9.9	5.66
	740.2	3.79	322.4	733.0	3.73
	670.2	4.09		682.7	3.92
	626.4	4.29		610.3	4.21
	578.7	4.52		538.7	4.52
	535.1	4.72		470.7	4.82
	484.1	4.95		423.7	5.02
	433.6	5.28		356.5	5.30
	424.0	5.43		294.7	5.54
	392.4	5.59		240.6	5.72
	381.6	5.67		182.0	5.88
	353.2	5.79		141.8	5.97
	330.3	5.84		137.5	5.98
	327.1	5.87		93.1	6.02
	273.2	5.98		67.7	6.01
	218.3	6.10		47.1	5.94
	192.4	6.17		29.8	5.82
	141.0	6.25		15.1	5.55

Dreisbach and Lösch 2000). Ideally, the density should be homogeneous throughout the measuring cell, i.e. the density measured at the sinker position (ρ^b_{Sk}) should be equal to the density measured at the basket position (ρ^b_B). This condition ensures an accurate measurement of the excess adsorbed amount. On the contrary, if the density is not homogeneous and the two measured densities are different, the measured excess adsorption will be affected by an error related to the density difference, i.e. $\Delta\rho = \rho^b_{Sk} - \rho^b_B$. This latter situation arises especially when measuring adsorption isotherms at conditions very close to the critical point, where very small changes in the temperature lead to significant differences in density. In a previous work we have shown how data from the empty runs can be used to analyze the measured excess adsorption isotherms in terms of accuracy (Pini et al. 2006).

Let us consider the two set of measurements obtained for N_2O and CO_2 at 36.9 °C and 31.4 °C, respectively, by operating the balance without adsorbent. These two temperatures correspond to the same reduced temperature, i.e. $T_r = T/T_c = 1.001$. The density difference $\Delta\rho$ obtained from the experiments without adsorbent for N_2O and CO_2 is plotted against the reduced density ρ^b/ρ_c in Fig. 5 and Fig. 6, respectively. Based on these results, the reduced density range covered in the experiments (0 to 2) can be divided into three regions: Region 1, for $\rho^b/\rho_c \leq 0.8$, where $\Delta\rho$ is almost zero; Region 2, for $0.8 < \rho^b/\rho_c < 1.2$, where $\Delta\rho$ vs. ρ^b/ρ_c is not zero but shows a peak at $\rho^b/\rho_c = 1$; and finally Region 3, for $\rho^b/\rho_c \geq 1.2$, where $\Delta\rho$ is again zero. When measuring isotherms very close to the critical temperature, the homogeneity of the density in the measuring cell in Region 1 and 3 ensures accurate measurement of the excess adsorption, whereas in Region 2 this is precluded by the non-zero value of $\Delta\rho$ (Pini et al. 2006). This observation leads to the conclusion that the technique we are using is not appropriate to study and quantify controversial phenomena such as critical depletion and critical adsorption. As a consequence, we have to withdraw our statements about these two phenomena that were made in previous publications, and that were based on the assumption that our measurements were very accurate also near the critical point (Rajendran et al. 2002; Hocker et al. 2003).

In Fig. 5, beside the density difference $\Delta\rho$ obtained from the experiments without adsorbent discussed above, the raw excess adsorption data measured at 36.9 °C are shown together with those obtained by using the corrected density from the empty run for the system N_2O-silica gel. Moreover, as a comparison, another isotherm is plotted, which has been measured at a higher temperature, where the conditions for an accurate adsorption measurement are met. The corresponding diagram for the system CO_2-13X zeolite is shown in Fig. 6.

Some remarks are worth making which are valid for both systems. On the one hand, the results of the isotherms measured at a temperature very close to the critical point seem to suggest the presence of critical depletion and critical adsorption, respectively. This conclusion would also be supported by the very small correction on the measured excess adsorbed amount obtained by the use of the corrected density from the empty run (corrected data in the figures). In fact, the corrected data overlap with the raw data in Region 1 and 3 and only a small difference can be seen between the two sets of data in Region 2. Estimating the error associated to the measuring technique yields values that are so small

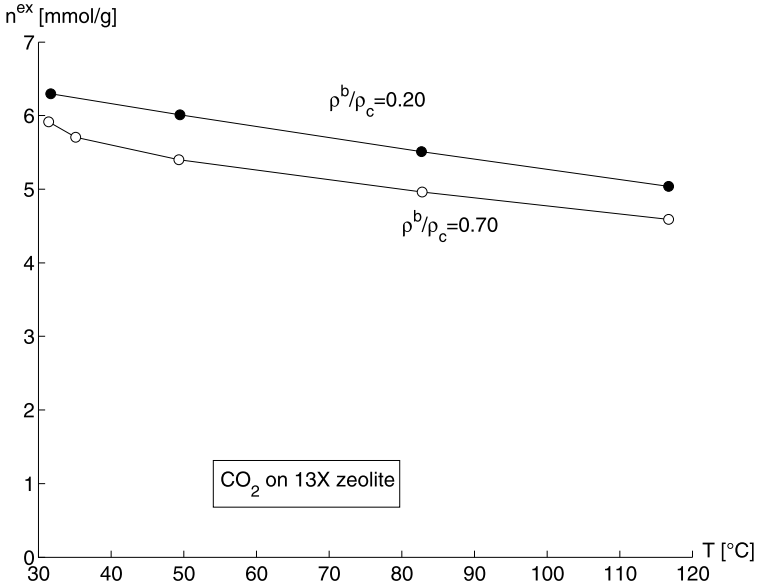

Fig. 4 Excess adsorption isochores of CO_2 on 13X zeolite as a function of the temperature T measured at two different reduced densities ρ^b/ρ_c: 0.2 and 0.7

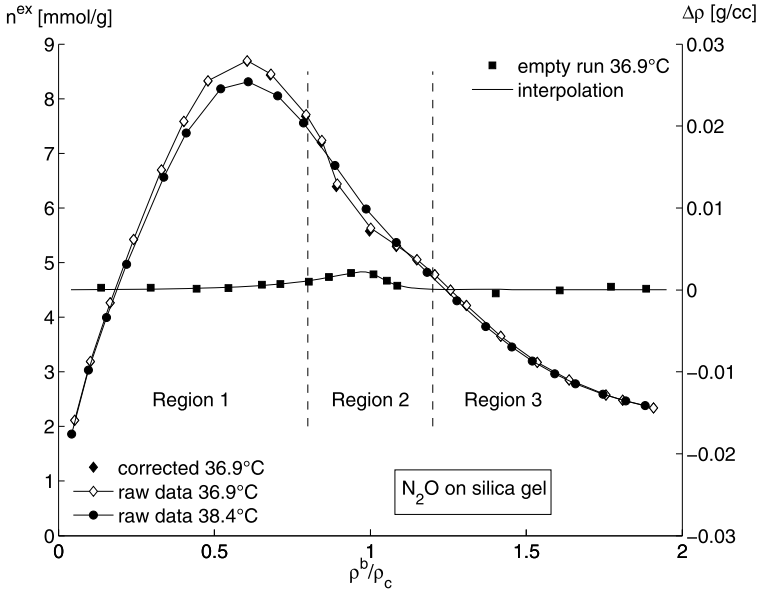

Fig. 5 Excess adsorption isotherms of N_2O on silica gel (*left y-axis*) as a function of the reduced density ρ^b/ρ_c measured at two different temperatures. Density difference $\Delta\rho$ obtained from the empty runs (*right y-axis*) as a function of the reduced density ρ^b/ρ_c. The *symbols* (■) represent the experimental data while the *line* is an interpolation used for the correction of the raw data

that the corresponding error bars would be hardly visible in the diagrams of Figs. 5 and 6. Moreover, the largest experimental errors would be obtained at high fluid phase densities of Region 3 and not in Region 2. On the other hand, the presence of a density gradient in the measuring cell and the correspondence between the $\Delta\rho$ peak measured near the critical density in the experiment without adsorbent and the anomalous behavior of the isotherms in the same reduced density range support the conclusion that the measurements in Region 2 may not be accurate, despite their precision and reproducibility. The correction introduced to take into account the density difference between the sinker and the basket allows us to apply a correct buoyancy force in the operating equation of the balance (Pini et al. 2006), but not to remove its effect on adsorption itself. Therefore, we can not rule out the possibility that the particular behavior of the isotherms at near critical conditions is indeed a consequence of small density gradients in the cell.

4 Conclusion

When measuring adsorption at conditions close to the critical point there are inherent difficulties that are essentially due to the very strong temperature dependence of density. Moreover, interpreting adsorption data is complicated by critical effects that may arise from long-range interactions in the confined space provided by the pore structure of the

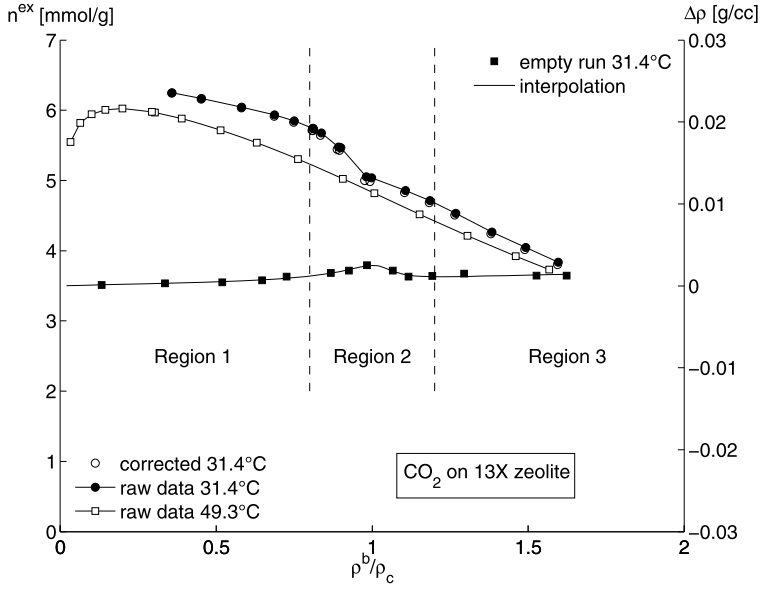

Fig. 6 Excess adsorption isotherms of CO_2 on 13X zeolite (*left y-axis*) as a function of the reduced density ρ^b/ρ_c measured at two different temperatures. Density difference $\Delta\rho$ obtained from the empty runs (*right y-axis*) as a function of the reduced density ρ^b/ρ_c. The *symbols* (■) represent the experimental data while the *line* is an interpolation used for the correction of the raw data

adsorbent. In this work we have used a magnetic suspension balance operated using an improved thermostatting configuration that guarantees higher accuracy than before, and we have repeated earlier measurements of supercritical adsorption isotherms of nitrous oxide on silica gel and of carbon dioxide on 13X zeolite. The improved accuracy is particularly evident for adsorption measurements very close to the critical point, where earlier we thought to have evidence of critical depletion for the former system and of critical adsorption for the latter.

The new measurements evidence two things. First, the earlier near-critical measurements were unfortunately not accurate enough and have to be discarded when compared to the newer measurements. Secondly, although the new measurements exhibit anomalies, these occur in a range of operating conditions so close to the critical point where also the current experimental configuration does not offer a sufficient level of accuracy. Therefore, these anomalies may be due either to critical adsorption effects or to density gradients in the measuring cell, which at conditions very close to the critical point have a much amplified effect.

Thus, the conclusions reached in this work can be summarized as follows. On the one hand, we need to withdraw our statement that earlier measurements provided experimental evidence of critical depletion (Rajendran et al. 2002) and of critical adsorption (Hocker et al. 2003). The new measurements prove that this evidence is not there, and that it should be sought using techniques different from what we have applied here. On the other hand, we believe that the adsorption practitioner can benefit of our results since they provide clear indications of the strengths of the gravimetric technique and of our gravimetric apparatus, which is quite popular in the adsorption community, when used properly, but also of its limits when used very close to the critical point.

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