Grand canonical Monte Carlo simulation of ternary noble gas mixture (Ne (blue), Kr (pink), Xe (green)) adsorption on single wall carbon nanotubes.

Molecular Simulation of Adsorption and Separation of Pure Noble Gases and Noble Gas Mixtures on Single Wall Carbon Nanotubes

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ABSTRACT

Grand Canonical Monte Carlo simulations were performed to systematically study the adsorption and separation of noble gases on single wall carbon nanotube (SWCNT) bundles. Pure noble gases, as well as binary and ternary mixtures, were simulated in carbon nanotube systems under various conditions. Adsorption data was collected at 100 K and 300 K over a wide range of pressures. Carbon nanotube bundles present distinct adsorption capacities towards different noble gases. In particular, larger and heavier noble gases are easier to be adsorbed at low pressure, while lighter atoms with smaller sizes can be better stored at high pressure. For noble gas mixtures with equal molar loadings, selective adsorption was observed and the selectivity inverted at different pressure ranges according to the choice of mixtures. Furthermore, the influence of loading proportion of the components on the adsorption behavior was investigated by varying the loading partial pressure in binary mixtures from 1% to 99%. The results suggest gas-CNT interactions dominate the adsorption selectivity at low loading conditions, whereas the entropic effect plays a more important role at high loadings.

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1. Introduction

Single wall carbon nanotubes (SWCNTs) have attracted intense research interest.^{1,2} Excellent mechanical, electrical, thermal and structural properties enabled by their pristine tubular structure have been discovered with these materials.^{3,4} Particularly, the large specific surface area and high pore volume of carbon nanotubes qualify them for potential applications as adsorbents in many applications including gas storage,⁵ environmental contamination removal,⁶ and separation membranes⁷. Multiwall nanotubes have also been proposed as gas separation tools^{8,9}.

The application of gas separation and adsorption for mixtures of noble gases is highly important and has been studied to some extent in the literature. However, studies over the complete range of noble gases and large pressure ranges are still missing. The adsorption properties of single wall carbon nanotubes have been widely studied for a variety of adsorbate molecules, such as nitrogen,¹⁰ hydrogen,¹¹ carbon dioxide,¹² and methane¹³. Noble gases with their monatomic simple spherical structures, fit many adsorption models and have been widely utilized for porous materials characterizations. Experimental adsorption data has been collected for helium,¹⁴ argon,¹⁵ krypton,¹³ and xenon¹⁶ in different single wall carbon nanotube systems.

Molecular modelling including molecular dynamics (MD) and Monte Carlo (MC) has also been applied for noble gas adsorption on CNTs. Atomistic simulations can help understand the detailed adsorption process including dynamic and thermal properties. For the study of noble gas adsorption on single wall carbon nanotubes, Simonyan et al. performed grand canonical Monte Carlo (GCMC) simulations of Xenon adsorption on single wall carbon nanotubes at Xe critical temperature.¹⁷ Jalili and Majidi simulated the

adsorption processes of Xe and Kr on SWCNTs by MD and found adsorption primarily on the inside surfaces of CNTs.¹⁸ Besides pure noble gas adsorption, Foroutan and Nasrabadi used MD to model binary and ternary noble gas mixtures (Ar - Kr - Xe) for adsorption on SWCNT arrays and found selective adsorption.^{19,20} Nojini et al. predicted the adsorption and separation of helium/argon mixtures by single SWCNTs with GCMC.²¹

Mixed gas adsorption on SWCNTs has also been simulated for nitrogen/oxygen,²² methane/ethane,²³ and carbon dioxide/methane²⁴ mixtures. Selective adsorption was observed in all cases. Most studies focus on the adsorption of equal molar gas loadings. The influence of component loading proportions on adsorption is still not well understood.

In addition to the studies on gas adsorption, the influence of SWCNTs packing structures has been investigated. Jiang and Stanley compared nitrogen adsorption on infinite periodic CNT bundles and finite bundles with external surface.²⁵ The effect of the ends of nanotubes on the bundle was simulated by Calbi and Riccardo.²⁶ LaBrosse and Johnson compared the adsorption on carbon nanotube bundles with defect and nondefect interstitial channels.^{27,28}

However, very few experimental or computational studies have focused on the selective adsorption and subsequent potential for separation of noble gas mixtures, which is meaningful for the physical separation and storage of radioactive nuclear reaction waste gases, in which the chemically inert noble gases are major components.²⁹ Although the previous work has shown much of the basic interaction modes between nanotubes and gases previous work has not yet systematically studied the adsorption and separation of the whole series of noble gases and particularly many-component mixtures in SWCNTs.

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4 E.g. in nuclear fuel reprocessing mixtures of the whole range of noble gases are present at
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6 the same time and need to be controlled.³⁰ CNTs have the potential to help manage these
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8 gas products but a better understanding of nanotube gas interaction in many-component
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10 mixtures is needed to employ CNTs as separation tools in these systems. This will be
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12 addressed here.
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17 In the present work, grand canonical Monte Carlo was used to investigate the adsorption
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19 of the whole series of noble gases on periodic uniform single-walled carbon nanotube
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21 bundles under various circumstances. Adsorption isotherms of pure noble gases, as well
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23 as binary and ternary noble gas mixtures, were determined by simulations at both low
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25 (100 K) and room temperatures (300 K). In addition, different loading proportions in
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27 binary mixtures were simulated to illustrate their influence on the adsorption behavior of
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29 the single wall carbon nanotube system.
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33 34 35 **2. Simulation model and methods** 36 37

38 Carbon nanotubes have been observed experimentally to exist in bundles.³¹ The
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40 simulation model in this study includes 9 hexagonally packed open-end single-walled
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42 carbon nanotubes (SWCNTs) corresponding to the van der Waals interactions preferred
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44 alignment,²⁵ as shown in Fig. 1. All SWCNTs are of the (10, 10) armchair type with a
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46 diameter of 13.56 Å, as these are the experimentally most abundant ones.^{16,32} The
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48 influence of SWCNT chirality on gas adsorption was not considered here as the influence
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50 of SWCNT chirality on hydrogen adsorption and diffusion has been determined earlier by
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52 both, ab initio and molecular mechanics simulations.^{33,34} These studies showed that the
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54 adsorption of hydrogen is not affected by the chirality of the nanotubes. For noble gases,
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56 with monatomic spherical shape, we expect the influence of the CNT chirality on the
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adsorption to be negligible. The length of the nanotubes (and correspondingly the system size in the axial direction as we use infinitely long nanotubes) was 49.2 Å (20 unit cells). Periodic boundary conditions were applied in all three directions to simulate the intrinsic nanotube bundles without considering packing defects and the influence of the ends and external surfaces.

Fig. 1 - Carbon nanotube bundle simulation model

All nanotubes were treated as completely rigid without intramolecular vibrations which is considered to have only slight influence on the adsorption.²² The C-C bond length was 1.42 Å and the inter-nanotube distance was 3.2 Å, as observed in experiments corresponding to the van der Waals gap between nanotubes.^{31,35} Noble gas atoms were treated as spherical monatomic molecules with only van der Waals potentials modeled by a Lennard-Jones 12-6 potential

$$\phi_{ij} = 4\epsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$$

where r denotes the pair distance between atom i and j ; ϵ_{ij} and σ_{ij} represent the depth of the potential energy well and the intermolecular collision diameter, respectively. Lennard-Jones (L-J) parameters for carbon and gases were taken from literature (cf. Table. 1)^{36,37} where k_B is the Boltzmann constant. Lorentz-Berthelot mixing rules were used for unequal atoms:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2.$$

The L-J potential cutoff distance was 20.0 Å.

Table 1 - Lennard-Jones parameters of carbon and noble gases

Element	ε/k_B (K)	σ (Å)
C	28.2	3.4
He	10.2	2.56
Ne	35.6	2.75
Ar	120	3.40
Kr	171	3.60
Xe	221	4.10

Potential energy distributions of each noble gas atom across the radial direction of an isolated (10, 10) SWCNT are plotted in Figure. 2. The vertical lines in the figure indicate the CNT walls with $x = 0$ denoting the center of the CNT. For all noble gases, the depths of potential energy wells inside the CNTs are deeper than the ones outside the tubes, which are attributed to confinement effect induced by the carbon nanotube curvature structures. Moreover, the gas atoms in larger sizes with stronger carbon-gas potentials show deeper potential energy wells than the smaller ones both inside and outside the nanotube.

Fig. 2 - Potential energy distribution of noble gases across the radial direction of an isolated SWCNT.

Grand Canonical Monte Carlo (GCMC)^{38,39} with fixed chemical potential (μ), volume (V), and temperature (T) was chosen for this study. In GCMC, the SWCNT bundle is considered in contact with an infinite gas reservoir which is not explicitly modeled. Gas particles are exchanged between the reservoir and the nanotube bundle. The pressure is defined through the chemical potential in the reservoir, which is constant and connected to the chemical potential by an equation of state. Equilibration in the system is reached when the chemical potential and the temperature of the gases inside and outside the SWCNTs are equal. Temperature is controlled by the acceptance criterion of GCMC as that ensures the μVT ensemble. All simulations were performed with the open source MCCCSTowhee code⁴⁰ to understand the noble gas adsorption behavior in single-walled carbon nanotube bundles. The chemical potential applied for each adsorption simulation represents the μ value of the corresponding bulk gas phase. Separated isothermal-isobaric

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4 simulations with only gas molecules were utilized to simulate the gas reservoir to
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6 calculate the chemical potentials by the Widom insertion method.⁴¹
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10 Monte Carlo moves of insertion/deletion, and displacement moves were applied on gas
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12 adsorbents in the simulations in every case with the possibilities of 0.5, 0.4, and 0.1,
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14 respectively. The intermolecular exchange moves were applied additionally in multiple
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16 components mixtures. All Monte Carlo simulations were performed for 2×10^7 steps,
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18 where the first 10^7 MC steps were applied to equilibrate the system and the second 10^7
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20 MC steps were for data collection.
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25 **3. Results and Discussion**

26 **3.1. Pure noble gas adsorption**

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28 The adsorption was characterized by the absolute adsorption, which counts the total
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30 number of gas molecules in the CNT system expressed as adsorbed gas/carbon.
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32 Adsorption isotherms were plotted semi-logarithmically over a wide range of pressures.
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39 Adsorption isotherms for pure noble gases are presented in Fig. 3. At 300 K (Fig. 3a),
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41 very weak adsorption was observed below 0.0001 MPa. With increasing pressure, Xenon
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43 which has the strongest interaction with the CNT adsorbs first, followed by Kr, Ar, Ne,
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45 He in order of decreasing molecular weight and size, which also corresponds to the
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47 strength of potential energy between the gas molecules and the CNTs. However, if the
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49 pressure keeps rising, the heavier and larger noble gases reach saturation which means
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51 the finite space in the CNT system is fully occupied by the gas atoms and the adsorption
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53 does not increase much further with pressure. The larger atoms show a relative small
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55 maximum adsorption. Smaller and lighter molecules, like He and Ne, were not
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4 significantly adsorbed until high pressure, but can be stored in much higher amounts in
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6 the CNTs, since the smaller size atoms can be more effectively packed in the pores to
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8 reduce the local pressure at high loadings.
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11 At 100 K, the adsorption of all gases started at much lower pressures and varied very
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13 quickly with pressure. The thermal energy at 100 K is much lower than at 300 K, so that
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15 the energy compensation of the total potential energy is lower. Xenon greatly loaded the
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17 bundle at extremely low pressure, while Helium is barely adsorbed at pressure as high as
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19 0.1 MPa, since Xenon has very strong van der Waals interaction with the carbon surface,
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21 so the SWCNT system has strong energetic potential to adsorb Xenon to reduce the total
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23 energy of the system. Also, at 100 K, the condensation pressure of Xenon is very low.
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25 Xenon atoms keep accumulating on the SWCNT surface, and eventually trigger the
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27 capillary condensation, which means Xenon condenses and saturates the whole inner
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29 nanotube space. For Helium, the gas – carbon interaction is very weak. Comparing to
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31 Xenon, the adsorption amount of Helium is very low. This also explains why the slopes
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33 of the adsorption isotherms of Xenon and Helium do not change much over the selected
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35 pressure range. In general it is the entropy (Packing) - energy interplay which leads to
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37 this. At 100 K, the overall adsorption sequence is the same as in the 300 K case, which
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39 agrees with the potential energy distribution mapping.
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Fig. 3 - Adsorption isotherms of individual type of noble gas adsorbed in the SWCNT bundle: (a) 300 K; (b) 100 K

Simulation snapshots were taken viewing along the axial direction of each pure noble gas adsorption simulation in the CNT system at 300 K at 1 MPa and 100 MPa to present the lightly and highly occupied systems (Figure 4). The boundaries of the simulation box are the blue lines. The green rings denote the nanotubes. For the small Helium and Neon atoms, adsorption can take place both within the nanotubes and in the interstitial space

between nanotubes. Ar, Kr and Xe do not fit in the inter-nanotube channels in the selected pressure range, since the van der Waals radii exceed the limit of the interstitials. Taking a particular look at the adsorption behavior in the inner tube space, He and Ne can be randomly stored in the nanotubes, while Ar and Kr formed an adsorption ring and a center rod, and Xe forms a single adsorption ring only. The results coincide well with the prediction of a previous study⁴² and explain the differences in maximum adsorption of different noble gases in the isotherms (Fig 3).

Fig. 4 - Snapshots of pure noble gas adsorption on CNT bundles at: (I) 300 K, 1 MPa: (a) He; (b) Ne; (c) Ar; (d) Kr; (e) Xe; (II) 300 K 100 MPa: (f) He; (g) Ne; (h) Ar; (i) Kr; (j) Xe

3.2. Binary mixtures adsorption

To investigate the selective adsorption performance of CNT bundles towards noble gases, binary noble gas mixtures with equal molar loadings of two components were simulated in the CNT system. Figure 5 shows the adsorption isotherms of Kr - Xe mixtures at 300 K and 100 K, and the corresponding selectivity defined as:

$$S_{xy} = \frac{x_i y_j}{x_j y_i}$$

where i, j denotes the atom types; x, y stands for the mole fractions of gas phase and adsorbed phase, respectively.

At 300 K adsorption of both components presented no significant difference at very low pressure (< 0.001 MPa) with Xe slightly more stored in the CNT bundle than Kr (Figure 5 (a, b)). By increasing pressure, Xe adsorption increased rapidly and reached the maximum near 2 MPa at about 0.45 gas atom/carbon atom coverage, then adsorption of Xe dropped as it became replaced by Kr. The selectivity of Kr/Xe was inverted around 200 MPa. The inversion is believed to correspond to the balance of gas – carbon potential strength and the entropy (packing). In particular, for Xe – Kr binary adsorption, at low

pressures, the gas loading in the system is low, Xe atoms with stronger interaction with the SWCNTs can be more strongly adsorbed. When the pressure increases, the nanotube pores are close to fully occupied, and then the size effect dominates the adsorption process. Over the whole pressure range, the total adsorption increased quickly when Xenon started to be adsorbed and slowed down after the maximum Xe adsorption was reached. The total adsorption kept raising with pressure. Figure 5 (c, d) represents the data at 100 K. Xenon was strongly selectively adsorbed at low pressure and dropped with higher pressure, while Kr storage kept increasing. The equal adsorption was reached at 2×10^{-6} MPa. At higher pressure, adsorption consistently preferred Kr, while the total adsorption increased slowly by pressure.

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Fig. 5 - Adsorption of Kr - Xe binary noble gas mixture: (a) adsorption isotherm at 300 K; (b) selectivity at 300 K; (c) adsorption isotherm at 100 K; (d) selectivity at 100 K

The adsorption isotherms of another binary noble gas mixture (He - Ar) are presented in Figure 6. At 300 K Ar was more adsorbed at relatively low pressure compared to He. At higher pressure the adsorption of He raised quickly while increase rate of Ar slowed down. From the trend of adsorption, the selectivity inversion is expected at higher pressure beyond the selected pressure range. However, when at very high pressures the Monte Carlo insertion performance greatly drops which prevents effective adsorption simulations. Figure 6b represents the He - Ar adsorption at 100 K. The isotherms at low temperature show that Ar dominates the total adsorption with no He being considerably adsorbed over the full pressure range. Similar to the Kr - Xe mixture, the larger size component of the binary mixture was more adsorbed at low pressures and is expected to be more adsorbed while Ar atoms are crowded out at higher pressure.

(a)

(b)

Fig. 6 - Adsorption isotherms of He - Ar binary noble gas mixture: (a) 300 K; (b) 100 K

3.3. Ternary mixture adsorption

To further study the selective adsorption capability of CNTs on noble gas mixtures, a ternary noble gas mixture with equal loading of Ne, Kr, and Xe was investigated. Adsorption isotherms were again measured at 300 K and 100 K (Figure 7). At 300 K, Xe dominated the total adsorption at low pressure. By increasing pressure, Xe was replaced by Kr and Ne. The adsorption amounts of Xe, Kr and Ne were closed to equal at 300 MPa. At very high pressure, Ne adsorption grew rapidly and became the majority adsorbed. Over the whole pressure range, the total adsorption increased with more smaller and lighter atoms. At 300 K, the selective adsorption changed from Xe to Kr at 10^{-6} MPa and kept steady, while Ne was not significantly adsorbed over the simulated pressure range. By adjusting pressure and temperature the adsorption selectivity on CNTs can be controlled to effectively remove a specific component from a multi-component noble gas mixture.

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(b)

Fig. 7 - Adsorption isotherms of ternary gas mixture consisting with Ne, Kr, Xe, at (a) 300 K; (b) 100 K

3.4. Adsorption with different loading proportions

Our study was extended to different loading proportions. Binary gas mixtures of He - Ne and Kr - Xe were simulated with molar loading ratios of 1%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 99%. All these simulations were performed at 0.1 MPa.

Figure 8a represent the isotherm of He - Ne at 100 K. The small size He – Ne mixture shows a nearly linear selective adsorption in the CNT bundle. With increasing Ne loading, the total adsorption increased rapidly with the adsorption of Ne, while He adsorption decreased. The adsorption selectivity right corresponds to the loading proportions under the unsaturated conditions.

In Figure 8(b, c), the isotherms of Kr - Xe mixture in large atom sizes showed distinct trends at different loadings. At 150 K, Kr adsorption dominated over the most proportion range, and eventually the adsorption selectivity converted to Xe at 90% Xe loading. The system was close to be fully loaded and the total loading was near steady when Kr dominated, and then dropped rapidly after the selectivity inverted. At 300 K, the adsorption preference switched at very low Xe loading (around 7%). With increasing Xe loading, more Xe atoms were adsorbed, while Kr was close to be fully replaced. The total adsorption did not vary much with increasing Xe loading after the inversion. We see that when the system is fully loaded at very low temperature, the dominating factor for selectivity is entropy, which prefers to pack more atoms in the finite space. At high temperature, the selective adsorption is mainly governed by the component with stronger gas-CNT potential energy. The larger Xe atoms with stronger intermolecular potential with the CNTs are more preferred to be adsorbed over Kr.

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(c)

Fig. 8 - Adsorption isotherms of binary gas mixtures with different loading proportions: (a) He - Ne, at 100 K, 0.1 MPa; (b) Kr - Xe, at 150 K, 0.1 MPa; (c) Kr - Xe, at 300 K, 0.1 MPa

4. Conclusions

The adsorption and separation of the whole series of noble gases on regular single wall carbon nanotube bundles was investigated for the first time. SWCNTs presented different adsorption capacities towards each pure noble gas. In particular, Xenon, which has the strongest energetic interaction with CNTs, was the easiest to be adsorbed at low pressure, but was stored the least at saturation. For noble gas molecules of smaller sizes, the adsorption became harder at low pressure because of the weaker gas - CNT interactions, but presented increasing saturation adsorption capacities. In general energetic interactions favor larger (heavier) gases whereas entropic packing effects lead to a higher adsorption capacity of smaller capacity. In addition, the interstitial space between the CNTs were only occupied by the small He and Ne atoms. Ar, Kr and Xe could not be stored in the channels in the selected pressure range.

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4 For binary and ternary noble gas mixtures, selective adsorption was observed at different
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6 pressure ranges. The selectivity corresponded well to the potential energy distribution in
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8 connection with packing arguments. At both 100 K and 300 K, the gas components in
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10 larger molecular sizes were selectively adsorbed at low pressure and then partially
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12 replaced by other components at high pressure where packing effects become more
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14 prevalent.
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19 Furthermore, the influence of mixture loading proportions on adsorption was investigated.
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21 At 100 K and 0.1 MPa, adsorption of He - Ne was below saturation and showed strong
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23 preference for Ne, which has the stronger interaction with the CNTs. Meanwhile, at 150
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25 K and 300K, 0.1 MPa, Kr - Xe adsorption selectivity varied and eventually inverted from
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27 Kr to Xe, where the inversion loading proportion decreased with increasing temperature.
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29 The results indicated that adsorption selectivity is mainly determined by the gas-CNT
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31 potential strength in sub-saturation conditions, whereas the entropy effect plays a more
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33 important role in fully loaded circumstances.
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39 The present work proved the dependences of SWCNTs adsorption behavior on pressure
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41 and temperature, and investigated the dominant factor in noble gas selective adsorption.
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43 The simulation results show that at low loading the adsorption is dominated by the
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45 strength of gas – carbon intermolecular potential; at high loading the size effect is more
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47 important where small molecules are preferred to be packed in the pores to reduce the
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49 local pressure. It suggests the potential to utilize carbon nanotubes to effectively adsorb
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51 and separate noble gases and their mixtures. For further study, the simulation work will
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53 be extended to more complex SWCNT bundle systems with considering the effects of
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55 nanotube size distribution, packing defects, etc.
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