ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理
Chinese Physics B

Competitive and synergistic adsorption of binary volatile organic compound mixtures on activated carbon

Jing Zhu(祝静), Hong-Lei Zhan(詹洪磊), Kun Zhao(赵昆), Xin-Yang Miao(苗昕扬), Qiong Zhou(周琼), Wen-Zheng Yue(岳文正)

Citation: Chin. Phys. B . 2019, 28(2): 020204. **doi:** 10.1088/1674-1056/28/2/020204
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Broadband microwave absorption properties of polyurethane foam absorber optimized by sandwiched cross-shaped metamaterial

Long-Hui He(贺龙辉), Lian-Wen Deng(邓联文), Heng Luo(罗衡), Jun He(贺君), Yu-Han Li(李宇涵), Yun-Chao Xu(徐运超), Sheng-Xiang Huang(黄生祥)

Chin. Phys. B . 2018, 27(12): 127801. **doi:** 10.1088/1674-1056/27/12/127801

Linear and nonlinear optical analysis on semiorganic $_L$-proline cadmium chloride single crystal

Mohd Anis, M I Baig, S S Hussaini, M D Shirsat, Mohd Shkir, H A Ghramh

Chin. Phys. B . 2018, 27(4): 047801. **doi:** 10.1088/1674-1056/27/4/047801

Terahertz-dependent identification of simulated hole shapes in oil—gas reservoirs

Ri-Ma Bao(宝日玛), Hong-Lei Zhan(詹洪磊), Xin-Yang Miao(苗昕扬), Kun Zhao(赵昆), Cheng-Jing Feng(冯程静), Chen Dong(董晨), Yi-Zhang Li(李羿璋), Li-Zhi Xiao(肖立志)

Chin. Phys. B . 2016, 25(10): 100204. **doi:** 10.1088/1674-1056/25/10/100204

Optoelectronic and thermoelectric properties of Zintl YLi_3X_2(X=Sb, Bi) compounds through modified Becke—Johnson potential

T Seddik, G Uğur, R Khenata, Ş Uğur, F Soyalp, G Murtaza, D P Rai, A Bouhemadou, S Bin Omran

Chin. Phys. B . 2016, 25(10): 107801. **doi:** 10.1088/1674-1056/25/10/107801

Broadband, polarization-insensitive, and wide-angle microwave absorber based on resistive film

Dan-Dan Bu(布丹丹), Chun-Sheng Yue(岳春生), Guang-Qiu Zhang(张广求), Yong-Tao Hu(胡永涛), Sheng Dong(董胜)

Chin. Phys. B . 2016, 25(6): 067802. **doi:** 10.1088/1674-1056/25/6/067802

Competitive and synergistic adsorption of binary volatile organic compound mixtures on activated carbon*

Jing Zhu(祝静)[1,2], Hong-Lei Zhan(詹洪磊)[2,4,†], Kun Zhao(赵昆)[2,3], Xin-Yang Miao(苗昕扬)[1,4], Qiong Zhou(周琼)[4], and Wen-Zheng Yue(岳文正)[1]

[1] *State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing* 102249, *China*
[2] *Beijing Key Laboratory of Optical Detection Technology for Oil and Gas, China University of Petroleum, Beijing* 102249, *China*
[3] *Petroleum and Chemical Industry Federation Key Laboratory of Oil and Gas Terahertz Spectroscopy and Photoelectric Detection, China University of Petroleum, Beijing* 102249, *China*
[4] *Department of Material Science and Engineering, China University of Petroleum, Beijing* 102249, *China*

(Received 26 July 2018; revised manuscript received 12 October 2018; published online 10 January 2019)

The adsorption of four substances and their binary mixture is investigated via the terahertz time domain spectroscopy (THz-TDS). The selected unary compound (ethanol, acetone, ethyl acetate, and n-propyl acetate) and binary mixture (solution 1 is composed of ethanol and acetone, and solution 2 is composed of ethyl acetate and n-propyl acetate) exhibit different adsorption behaviors with varied polarities. In comparison with single component, solution 1 shows shorter adsorption equilibrium time, faster adsorption rate, and stronger adsorption capacity, which conform to a synergistic adsorption mechanism, while the competitive behavior is attributed to the slower adsorption in solution 2. In addition, the pseudo-second-order equation with terahertz parameter is used to assess the rate of binary component organics. The present results indicate a further understanding of multicomponent adsorption mechanisms.

Keywords: competitive adsorption, synergistic adsorption, oil–gas reservoirs, terahertz time domain spectroscopy (THz-TDS)

PACS: 02.70.Rr, 78.20.Ci, 78.30.Jw **DOI:** 10.1088/1674-1056/28/2/020204

1. Introduction

Volatile organic compounds (VOCs) are highly toxic and lethal to humans and cause serious environmental problems, such as greenhouse effects, photochemical smog, and stratospheric ozone depletion.[1] In recent years, great efforts have been made to develop efficient VOC abatement techniques, such as catalysis oxidation, condensation, biological degradation, absorption, and adsorption. Among these methods, activated carbon adsorption is recognized as one of the most economic and effective techniques for the treatment of VOCs.[2]

Multiple components are involved in active carbon adsorption. As a conventionally used adsorbent, active carbon has extremely complex surface chemistries, resulting in a wide variety of binding sites that are available to solutes. The diverse functional groups on the surface of adsorbents have a tremendous impact on the adsorption behavior.[3] Furthermore, the driving forces between adsorbents and adsorbate are diverse, such as chemisorption, hydrophobic interaction, hydrogen bonding, electrostatic interaction, and complexation.[4] The adsorption process can be controlled or influenced by various simultaneous interactions.[5,6] Therefore, an in-depth understanding of adsorption mechanisms is important and many studies have been devoted to multicomponent adsorption.[3,7,8]

Various characterization methods have been used to detect the adsorption of VOCs, such as calorimetric measurement,[9] thermal conductivity detection (TCD),[10] temperature-programmed desorption (TPD),[11] quartz crystal microbalance (QCM),[12] and gravimetric and optical methods.[13] Single crystal adsorption calorimetry (SCAC) measures adsorption energies for high vapor-pressure substances and metal atoms on clean single crystal surfaces. A calibrated TCD is used to determine the quantity of reactant molecules taken up by active sites. QCM, which only requires a small amount of absorbent, offers short response times and allows for detection of mass changes.

The terahertz (THz) wave bridges the gap between microwave and infrared,[14–18] which can evaluate adsorption process regarding intermolecular and intramolecular modes because the THz spectrum is sensitive to fluctuations in the dipole moment of organic compounds.[19–23] In this study, the adsorption process of four substances and two binary mixtures is studied by terahertz time domain spectroscopy (THz-TDS). Compared with that of single component, the adsorption mechanism of binary organics has been analyzed using terahertz parameters. In addition, dynamic models play an important role in evaluating the adsorption rate and predicting the mechanism of adsorption, and the pseudo-second-order equation with terahertz parameter is used to assess the adsorption

*Project supported by the National Natural Science Foundation of China (Grant No. 11574401), the Science Foundation of China University of Petroleum, Beijing (Grant Nos. 2462017YJRC029 and yjs2017019), and the Beijing Natural Science Foundation, China (Grant No. 1184016).

†Corresponding author. E-mail: zhanhl@cup.edu.cn

© 2019 Chinese Physical Society and IOP Publishing Ltd

rate of binary organic systems.

2. Experimental methods

Solvents from Aladdin included ethanol, acetone, ethyl acetate, and n-propyl acetate (purity $> 99.5\%$). Solution 1 was prepared by combining equal volumes of ethanol and acetone, and solution 2 was prepared by mixing equal volumes of ethyl acetate and n-propyl acetate. To investigate the influence of polarity on the adsorption process, the compounds and mixtures were divided into two groups. The first group included ethanol, acetone, and solution 1, and the second group contained ethyl acetate, n-propyl acetate, and solution 2. Activated carbon is mainly composed of carbon, hydrogen, and oxygen elements. In our case, active carbon fiber cloth (ACFC) was used to perform the adsorption experiment. Polypropylene (PP) slices were used to seal the ACFC with 20 μL of chemical reagent on the middle of the ACFC. The adsorption behaviors of single and binary organic systems onto ACFC were measured by a typical THz-TDS set-up at room temperature.[21] Time span of measure, sampling time interval, and sampling point were about 45 min, 38 second, and 70, respectively. The experimental data was accurate to five decimal places.

3. Results and discussion

The selected THz-TDS spectra of ACFC with ethanol, acetone, solution 1, ethyl acetate, n-propyl acetate, and solution 2 are displayed in Figs. 1(a)–1(f). The time-dependent signal peak amplitudes (E_{P}) of ethanol, acetone, solution 1, n-propyl acetate, ethyl acetate, and solution 2 are $E_{\mathrm{P11}}(t)$, $E_{\mathrm{P12}}(t)$, $E_{\mathrm{PS1}}(t)$, $E_{\mathrm{P21}}(t)$, $E_{\mathrm{P22}}(t)$, and $E_{\mathrm{PS2}}(t)$, respectively. Their values at t equal 0.10159 V, 0.07577 V, 0.09494 V, 0.09443 V, 0.07469 V, and 0.08307 V, respectively. Due to the mixing of two components, the magnitude of THz waveforms of solution 1 and solution 2 is compromised between that of their components.

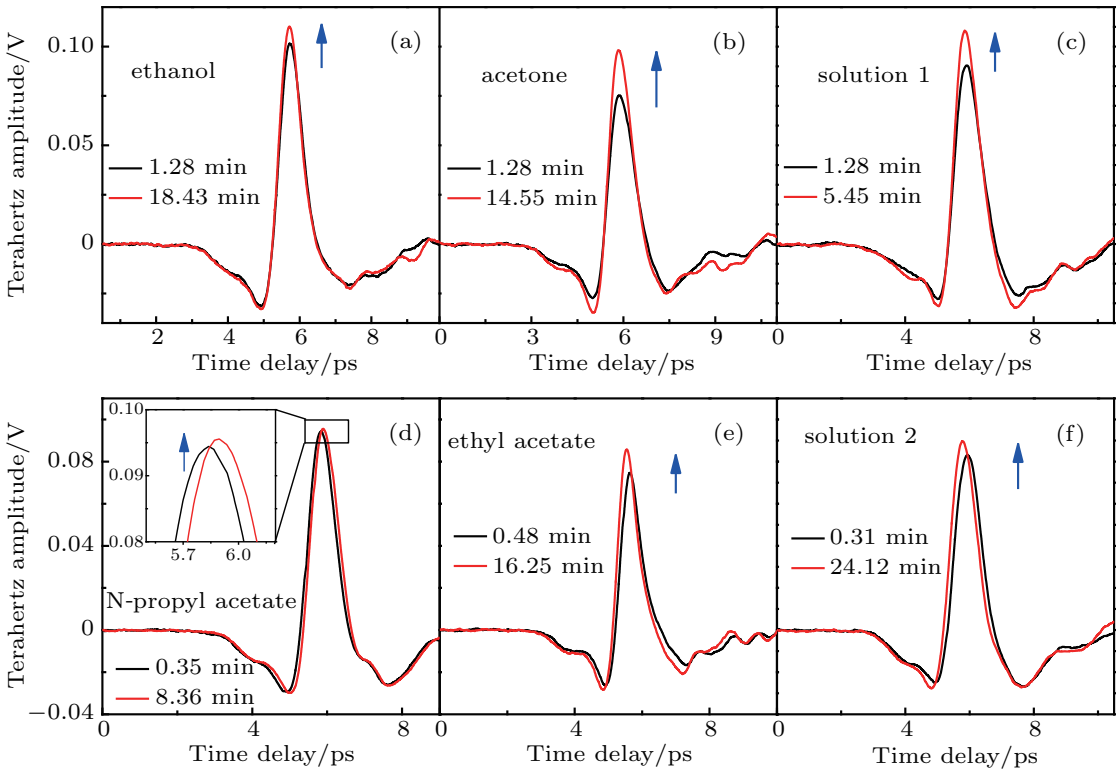


Fig. 1. The THz-TDS spectra of selected ACFC with (a) ethanol at 1.28 min and 18.43 min, (b) acetone at 1.28 min and 14.55 min, (c) solution 1 at 1.28 min and 5.45 min, (d) n-propyl acetate at 0.35 min and 8.36 min, (e) ethyl acetate at 0.48 min and 16.25 min, and (f) solution 2 at 0.31 min and 24.12 min.

In Fig. 2, average 1 and average 2 are calculated by $E_{\mathrm{PA1}}(t) = [E_{\mathrm{P11}}(t) + E_{\mathrm{P12}}(t)]/2$ and $E_{\mathrm{PA2}}(t) = [E_{\mathrm{P21}}(t) + E_{\mathrm{P22}}(t)]/2$, indicating the properties of two components. As shown in Fig. 2 (a), the $E_{\mathrm{PS1}}(t)$ is much higher than $E_{\mathrm{PA1}}(t)$, showing that the absorption of solution 1 is influenced by the interaction between ethanol and acetone in the THz range. This phenomenon is mainly caused by the solvent effect, which is common in multi-components organics. In solution 1, ethanol interacts with the C=O function of acetone via hydrogen bonding. Han and Kim's calculations showed that the formation of such a complex changed the charge densities of the carbonyl carbon and one methyl hydrogen atom.[24] However, in solution 2, the solvent effects are less obvious because ethyl acetate and n-propyl acetate are both dipolar aprotic solvents. Therefore, $E_{\mathrm{PA2}}(t)$ approximates that of solution 2 (Fig. 2(b)).

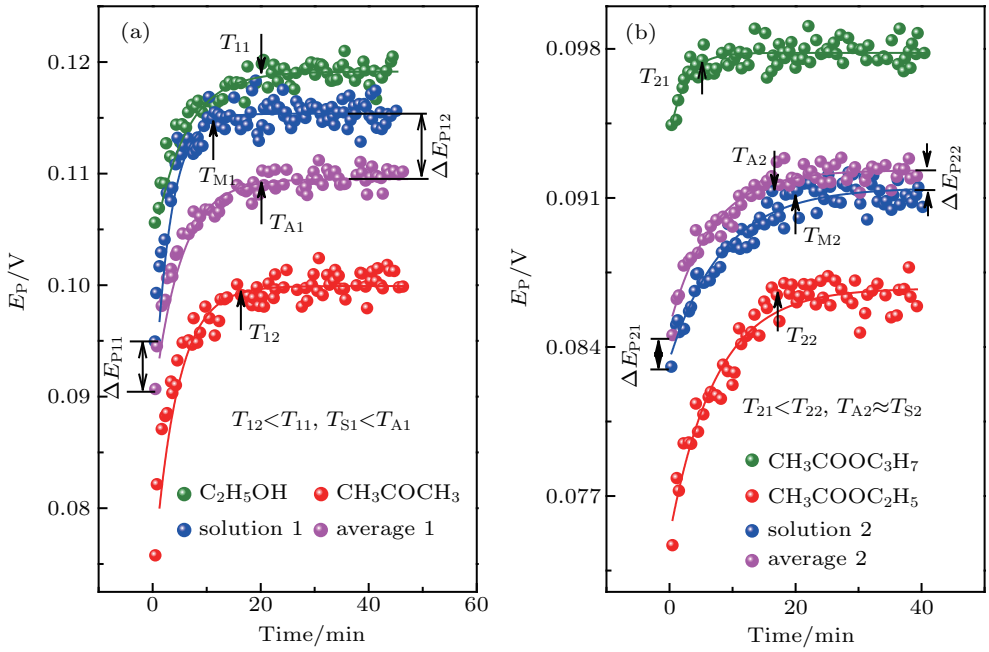


Fig. 2. (a) The time-dependent E_P of ACFC with ethanol, acetone, solution 1, and average 1. (b) The time-dependent E_P of ACFC with n-propyl acetate, ethyl acetate, solution 2, and average 2.

As shown in Fig. 2, the E_P of VOCs increases with time and attains a maximum value at the equilibration time (T). Thereafter, it reaches a constant value, which indicates that VOC adsorption on activated carbon is saturated. T is found to be around 20 min, but the adsorption experiment runs for 40 min, for practical reasons. As depicted in Fig. 2, the T values of adsorption of ethanol, average 1, solution 1, acetone, n-propyl acetate, average 2, solution 2, and ethyl acetate (T_{11}, T_{A1}, T_{S1}, T_{12}, T_{21}, T_{A2}, T_{S2}, and T_{22}) are 20.01 min, 20.07 min, 11.02 min, 16.42 min, 5.19 min, 17.05 min, 20.26 min, and 16.25 min, respectively. $E_{P11}(T_{11})$, $E_{PA1}(T_{A1})$, $E_{PS1}(T_{S1})$, $E_{P12}(T_{12})$, $E_{P21}(T_{21})$, $E_{PA2}(T_{A2})$, $E_{PS2}(T_{S2})$, and $E_{P22}(T_{22})$ are equal to 0.11925 V, 0.10945 V, 0.11537 V, 0.09992 V, 0.09781 V, 0.09228 V, 0.09135 V, and 0.08662 V, respectively.

It has previously been reported that hydrophobic interactions and hydrogen bonding are important to VOC adsorption by activated carbon, and hydrophobic interaction was the predominant driving force.[22–25] The hydrophobicity of n-propyl acetate is greater than that of ethyl acetate. Compared with ethyl acetate, n-propyl acetate has a greater affinity for activated carbon, leading to shorter T. Similarly, ethanol is more polar and has a weaker affinity for activated carbon than acetone; thus, T_{12} is shorter than T_{11}.

Binary component adsorption has been investigated by analysis of the THz parameters of two mixtures. As shown in Fig. 2(a), the difference between $E_{PS1}(t)$ and $E_{PA1}(t)$ (ΔE_{P11}) is less than that between $E_{PS1}(T_{S1})$ and $E_{PA1}(T_{A1})$ (ΔE_{P12}). $E_{PS1}(T_{S1}) < E_{PA1}(T_{A1})$, which indicates that more organic molecules are adsorbed by active carbon in solution 1. Moreover, T_{S1} is shorter than T_{A1}, reflecting the fact that the adsorption rate of solution 1 is faster than average 1. Therefore, it can be concluded that the adsorption rate increases significantly by mixing ethanol and acetone. Stronger adsorption of solution 1 is observed compared to that of average 1. By forming hydrogen bonding, solvent effects lead to the synergetic adsorption.[21,22] As shown in Fig. 3(a), ethanol interacts with the C=O group in acetone via hydrogen bonding, which is adsorbed by activated carbon.

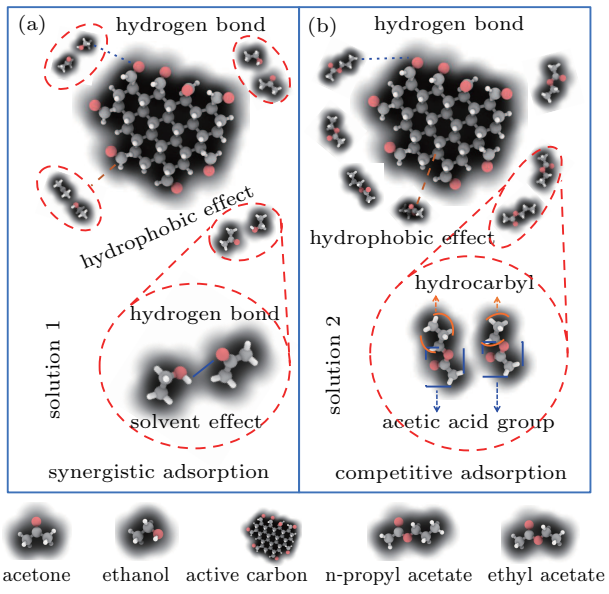


Fig. 3. The map of (a) synergistic and (b) competitive mechanisms of adsorption.

As can be seen in Fig. 2(b), $E_{PA2}(T_{A2})$ slightly exceeds $E_{PS2}(T_{S2})$. The difference between $E_{PS2}(t)$ and $E_{PA2}(t)$ (ΔE_{P21}) is approximately the same as the difference between

$E_{PS2}(T_{S2})$ and $E_{PA2}(T_{A2})$ (ΔE_{P22}), which suggests that the adsorption capacity is not influenced by mixing n-propyl acetate with ethyl acetate. However, T_{S2} is longer than T_{A2}, as shown in Fig. 2(b). The sketch of competitive adsorption mechanisms is shown in Fig. 3(b). Ethyl acetate and n-propyl acetate molecules compete in adsorption process to enter certain adsorption site. N-propyl acetate molecules have a stronger affinity to the activated carbon and can be adsorbed onto hydrophobic microdomains. Therefore, T_{S2} is limited by the adsorption rate of ethyl acetate.

The pseudo-second order kinetic model is an adsorption reaction model that is proposed to describe adsorption kinetics. Based on the pseudo-second order kinetic model and the assumption of the proportional relationship between the adsorbed amount and E_P, an adsorption equation has been proposed to describe the adsorption kinetics of single-molecule VOC systems. In our case, the binary mixture data is fitted to the pseudo-second order kinetic model with terahertz parameters, and this enables us to predict the adsorption mechanism. The kinetic equations are given as follows:

$$t/E_P(t) = 1/(kE_{PE}^2) + t/E_{PE}, \tag{1}$$

where t is the time of adsorption, k is the adsorption rate constant, $E_P(t)$ is the E_P value of samples adsorbed onto active carbon at t, and E_{PE} is $E_P(t)$ at T. The linear positive correlation model between t/E_P and time t of the organic compounds is shown in Fig. 4. The correlation coefficients of the VOCs are greater than 0.9999, which suggests that the pseudo-second order kinetic model can not only describe the adsorption behavior of single component but can also describe the adsorption behavior of binary component.

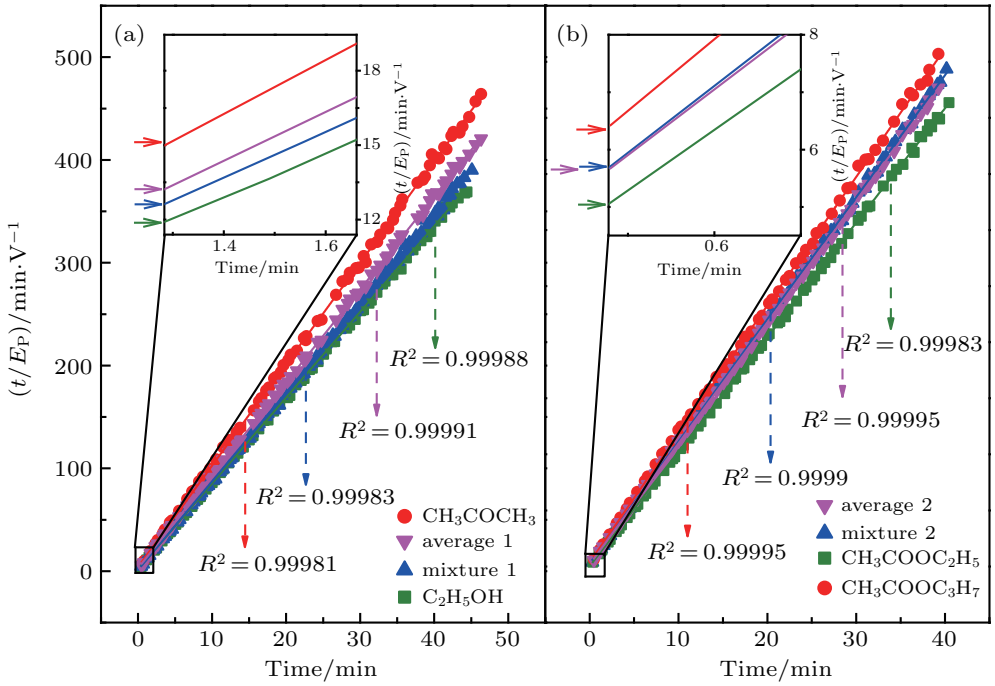


Fig. 4. (a) Graph that plots t/E_P as a function of the time difference t for adsorption of ethanol, average 1, solution 1, and acetone. (b) Graph that plots t/E_P as a function of the time difference t for adsorption of n-propyl acetate, average 2, solution 2, and ethyl acetate.

The calculated parameters for terahertz pseudo-second order model are shown in Table 1, and show high precision resulted from the great repeatability of the experimental data. The slope of the regressions decreases in the order of ethyl acetate > solution 2 > average 2 > n-propyl acetate > acetone > solution 1 > average 1 > ethanol. The results suggest that the order of E_{PE} calculated using the slope is roughly in accordance with that in Fig. 2. In addition, the intercept $d = 1/(kE_{PE}^2)$ indicates the adsorption rate. Based on $k = 1/(dE_{PE}^2)$, k increases in the order of ethanol < acetone < average 1 < solution 1 and solution 2 < ethyl acetate < average 2 < n-propyl acetate, which indicates the order of adsorption rates. The adsorption rate of solution 1 is faster than that of average 1 due to the synergetic stronger interaction between adsorbates and active carbon. In contrast, the adsorption rate of solution 2 is limited by that of ethyl acetate, due to competition with n-propyl acetate.

Table 1. Parameters for terahertz pseudo-second order kinetic model.

	Ethanol	Average 1	Solution 1	Acetone	n-propyl acetate	Average 2	Solution 2	Ethyl acetate
$(1/kE_{PE}^2)$/min·V^{-1}	0.97854	0.301	0.645	0.829	0.0134	0.99112	1.422	1.93217
$(1/E_{PE})$/V^{-1}	8.3853	9.13325	8.66776	10.0008	10.2239	10.83658	10.9469	11.54468
k	71.85527	129.32	249.6015	120.64656	7800.6068	118.4836	84.27188	68.979249

4. Conclusions

In summary, the adsorption behavior of four components and their binary mixtures onto activated carbon has been discussed according to THz-TDS in this work. The adsorption of selected objects with different polarities follows different adsorption mechanisms according to terahertz parameters. Solution 1 shows shorter adsorption equilibrium time, faster adsorption rate, and stronger adsorption capacity because of the synergistic adsorption mechanism. In addition, solution 2 exhibits a competitive adsorption mechanism and the adsorption rate is limited by that of ethyl acetate. Moreover, the pseudo-second-order equation based on terahertz parameter has been used to assess the adsorption rate of binary VOCs. The correlation coefficients are greater than 0.9999, which indicates that the pseudo-second order kinetic model with THz parameter applies to binary systems. The results show that THz-TDS is promising for adsorption

References

[1] Zhang X, Gao B, Creamer A E, Cao C and Li Y 2017 *J. Hazard. Mater.* **338** 102
[2] Chuang C L, Chiang P C and Chang E E 2003 *Chemosphere* **53** 17
[3] Nesterov I, Shapiro A and Kontogeorgis G M 2015 *Ind. Eng. Chem. Res.* **54** 3039
[4] Maity N and Payne G F 1991 *Langmuir* **7** 1247
[5] Gu B, Schmitt J, Chen Z, Liang L and Mccarthy J F 1994 *Environ. Sci. Technol.* **28** 38
[6] Lin D and Xing B 2008 *Environ. Sci. Technol.* **42** 7254
[7] TovarG ómez R, Moreno-Virgen M D R and érez P 2015 *J. Chem. Eng. Res.* **93** 755
[8] Mohan D and Chander S 2001 *Colloid Surf. A* **177** 183
[9] Ihm H, Ajo H M and Gottfried J M 2004 *J. Phys. Chem. B* **108** 14627
[10] Luis C C, Hilda G B, Adriana F C, Hector D G G and Rogelio C G 2008 *Catal. Today* **133** 244
[11] Popescu M, Joly J P and Carré J 2003 *Carbon* **41** 739
[12] Bingen P, Wang G and Steinmetz N F 2008 *Anal. Chem.* **80** 8880
[13] Kao P, Patwardhan A and Allara D 2008 *Anal. Chem.* **80** 5930
[14] Zhan H L, Zhao K, Zhao H, Li Q, Zhu S M and Xiao L Z 2016 *J. Phys. D: Appl. Phys.* **49** 395101
[15] Zhan H L, Wu S X, Zhao K, Bao R M and Xiao L Z 2016 *J. Geophys. Eng.* **13** 768
[16] Jiang C, Zhao K, Zhao L J, Jin W J, Yang Y P and Chen S H 2014 *Energy Fuels* **28** 483
[17] Du L L, Zhao S F, Zhou X X and Zhao Z X 2015 *Chin. Phys. B* **24** 043203
[18] Zhang M, Yang Z G, Liu J S, Wang K J, Gong J L and Wang S L 2018 *Chin. Phys. B* **27** 060204
[19] Zhang J Q and Grischkowsky D 2004 *Opt. Lett.* **29** 1031
[20] Zhan H L, Wu S X, Bao R M, Zhao K, Xiao L Z, Ge L N and Shi H J 2015 *RSC Adv.* **5** 14389
[21] Yamaguchi A, Arafune H, Hotta K, Itoh T and Teramae N 2011 *Anal. Sci.* **27** 597
[22] Zhu J, Zhan H L and Miao X Y 2016 *Phys. Chem. Chem. Phys.* **18** 27175
[23] Zhu J, Zhan H L and Miao X Y 2017 *J. Phys. D: Appl. Phys.* **50** 235103
[24] Cha D K, Kloss A A and Tikanen A C 1999 *Phys. Chem. Chem. Phys.* **1** 4785
[25] Zhou X, Wei J and Liu K 2014 *Langmuir* **30** 13861