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THE INFLUENCE OF CARBON SURFACE OXIDATION ON THE ADSORPTION OF METHANOL AND ETHANOL

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Abstract

The influence of microporous carbon oxidation on thermodynamic properties of methanol and ethanol adsorbed at 308, 328, and 348 K was investigated. Adsorption mechanisms are suggested and the obtained results are compared with the presented previously for adsorption of methane and carbon tetrachloride on nonoxidised and oxidised microporous carbons.

Keywords: activated carbon, adsorption, ethanol, methanol, microporosity

Introduction

The adsorption on microporous carbon is still a subject of current investigations due mainly to the wide application of carbon materials. We reported previously some results on the influence of carbon surface oxidation on thermodynamic properties of adsorbed carbon tetrachloride [1, 2] and methane [3, 4]. The analysis of the temperature dependence of the adsorption isotherm and the enthalpy evolved together with the analysis of the integral molar entropy and the heat capacity of adsorbates made it possible to suggest the detailed adsorption mechanisms in micropores of unoxidised and oxidised carbons. We showed that for carbon tetrachloride adsorbed in the temperature range of 308–348 K the main differences in adsorption between the two carbons are caused by two changes: in pore geometry and in oxidised carbon surface chemism. The first of them results in a slight enhancement of the adsorption potential due to the narrowing of micropores, whilst the second plays the main role in adsorbate – adsorbate interactions. For this adsorbate carbon surface oxidation leads to the increase of adsorption, especially at higher coverages. This effect comes from the association of strong polarised (by surface oxides) CCl_4 molecules. For the methane molecule, with lower polarizability and smaller dimension than CCl_4,

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carbon surface oxidation leads to the decrease in adsorption. This effect originates from the changes in adsorption mechanism. The physicochemical properties of this adsorbate cause that in this case oxygen surface complexes block the pores with high adsorption energy, and the low polarizability of the methane molecule does not contribute to the generated adsorbate – adsorbate energy, as in the case of CCl_4, by interaction between induced dipoles. The detailed analysis of methane adsorption – desorption data leads also to the conclusion that at low coverages methane is irreversibly adsorbed in carbon ultramicropores, which are not very susceptible for nitric acid oxidation, and this is connected with slightly marked irreversible changes of carbon structure.

The main difference between methanol, ethanol, and the adsorbates mentioned above is the possibility of formation of hydrogen bonds in adsorbate – adsorbate as well as adsorbate – adsorbent interactions. In the present study we present the influence of both temperature and carbon surface oxidation on the mechanisms of methanol and ethanol adsorption.

Experimental

Adsorption isotherms and differential enthalpies of adsorption of methanol and ethanol at 308, 328 and 348 K on two microporous carbons (the unoxidised – called A and the oxidised – called B) were measured, using a Tian-Calvet iso-

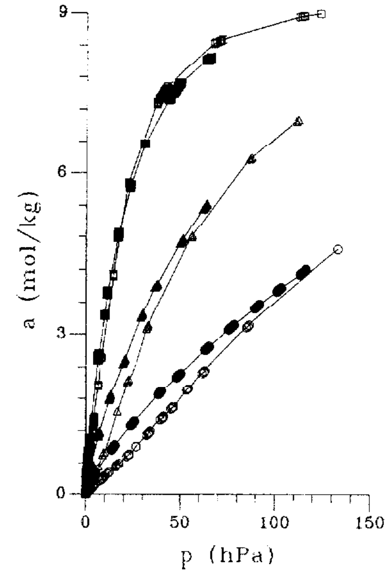

Fig. 1 Methanol adsorption isotherms at 308 K (squares), 328 K (triangles) and 348 K (circles). Open symbols – adsorption on carbon A; closed symbols – adsorption on carbon B

thermal microcalorimeter (with the accuracy of ±1.5 %). The detailed procedure of measurements, carbon preparation as well as carbon characteristics were given previously [1–8]. Adsorption isotherms of methanol are shown in Fig. 1. The adsorption isotherms of ethanol were published previously (3a Figs 3 and 4).

Results and discussion

The integral molar enthalpies of adsorption (Figs 2 and 5), integral molar entropies (Figs 3 and 6) and heat capacities (Fig. 4) of the two adsorbates were calculated numerically using the procedure proposed earlier [1–3].

Adsorption of methanol

In Fig. 1 it is seen that at low coverages the adsorption isotherms of methanol on carbon A are concave (this effect is usually observed during adsorption of polar molecules on hydrophobic solids [9, 10]). The enthalpy of adsorption of methanol (Fig. 2) on this carbon is larger by about 20–30 kJ mol^{-1} than observed for methane. This difference is in the range of energies characteristic to hydrogen bonding [11]. The enthalpies of adsorption at 308 and 328 K, after the increase at low coverages, are significantly decreasing in the adsorption range of 3–4 mol kg^{-1}. This effect is accompanied by the increase in integral molar entropy (Fig. 3) and decrease in the heat capacity of the adsorbate (Fig. 4). The temperature dependence of the adsorbate entropy shows that at 348 K the methanol molecules penetrate the micropores inaccessible at lower temperatures.

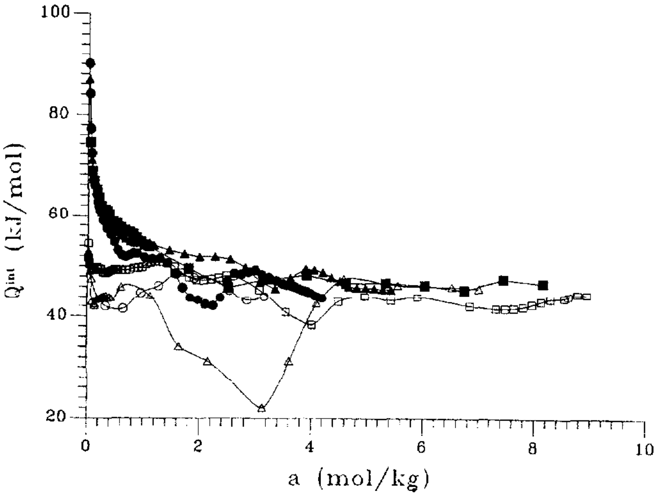

Fig. 2 Integral molar enthalpies of adsorption of methanol on carbon A and carbon B. Symbols as on Fig. 1

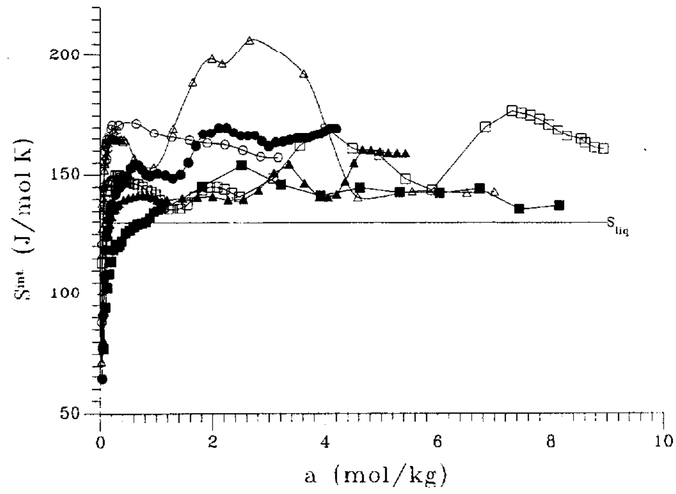

Fig 3 Integral molar entropies of methanol adsorbed on carbon A and carbon B. Symbols as on Fig. 1. Solid horizontal line – molar entropy of liquid methanol at 308 K

The presented data allow to suggest that in carbon A micropores, at low coverages, methanol association occurs and the multiplicity of associates increases with the degree of micropore filling. The analysis of the adsorbate entropy suggests that the stability of associates, created in carbon A micropores, markedly decreases with temperature (for example enthalpy of adsorption of methanol at 328 K and a=3 mol kg^{-1} is practically equal to that for methane). It is interesting to admit that for two areas of the heat capacity increase (similar maxima were observed for alcohols on graphitized carbon black and for water adsorbed in micropores of some zeolites [12]) above the value characteristic for liquid methanol (a=0.6 and 2.8 mol kg^{-1}), the volumes of micropores filled with quasi-liquid adsorbate are close to those determined from the potential theory of adsorption [5]; and this confirms the proposed adsorption mechanism.

Carbon surface oxidation leads to an increase in enthalpy of adsorption (by about 20 kJ mol^{-1}) and lower mobility of adsorbed methanol molecules. The comparison of enthalpy of adsorption values on the two carbons leads to the conclusion that each methanol molecule creates (on the average) two hydrogen bonds with surface oxygen groups. The strong adsorbate – adsorbent interactions bring about substantiate deformations of methanol electron structure and the primary adsorbed molecules create new adsorption centers for molecules adsorbed at higher coverages.

This effect is clearly seen while considering the heat capacity of methanol adsorbed on the two carbons. At the initial stage, the heat capacity lower on carbon B is a result of the weakening of the adsorbate – adsorbate interactions which is an effect of the creation of hydrogen bonds with surface oxides. For the methanol

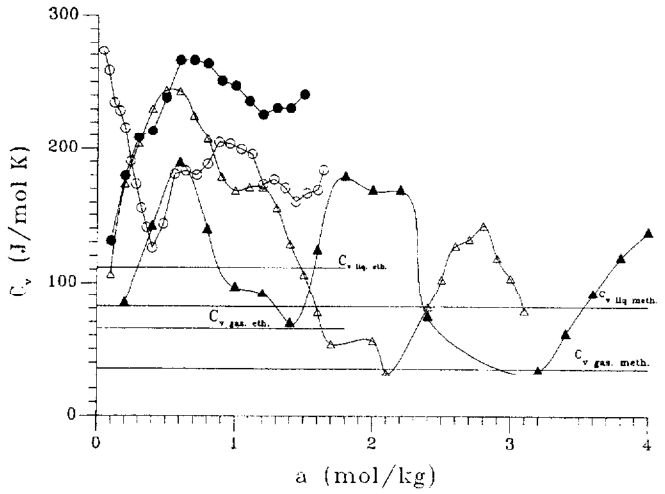

Fig. 4 Integral molar heat capacities of methanol (triangles) and ethanol (circles) adsorbed on carbon A and carbon B. Open symbols – adsorption on carbon A; closed symbols – adsorption on carbon B. Solid horizontal lines – molar enthalpy capacities of gaseous and liquid adsorbates at 308 K

heat capacity on carbon B a new maximum is observed, and the increase in the heat capacity starts at the adsorption value characteristic for concentration of surface functional groups.

The comparison of adsorption isotherms (Fig. 1) indicates that carbon surface oxidation increases methanol adsorption only at low coverages, because at higher coverages the decrease in entropy predominates (it is well known that the adsorption isotherm is the measure of the affinity between adsorbate and adsorbent and both the enthalpy and the entropy contribute to this affinity).

Adsorption of ethanol

The integral molar enthalpy of adsorption (Fig. 5) and entropy (Fig. 6) of ethanol on carbon A at 308 K are nearly constant, except the area of very low coverages. The comparison of methane and ethanol enthalpy of adsorption values leads, as in the case of methanol adsorption, to the conclusion that the hydrogen bonds are created in carbon A micropores. On the heat capacity plot (Fig. 4) (as well as on the enthalpy of adsorption one) the characteristic decrease down to the adsorption value equal to the concentration of surface Lewis basic centers is observed [6]. The absence of such a decrease during methanol adsorption allows to make a conclusion of higher acidity of ethanol, and not methanol, in carbon micropores (the same situation is observed in the gaseous state [13]). The heat capacity of the adsorbed ethanol lower, than in the case of methanol, leads to the conclusion of lower stability of created hydrogen bonds. This suggests nearly the same adsorption mechanism as for methanol on this carbon. The main difference is caused by the smaller polarity of the ethanol molecule, which leads to the lower mobility of this molecule in carbon micropores.

At all investigated temperatures the oxidised carbon is a better ethanol adsorbent than the unoxidised one; however, the differences decrease as the tem-

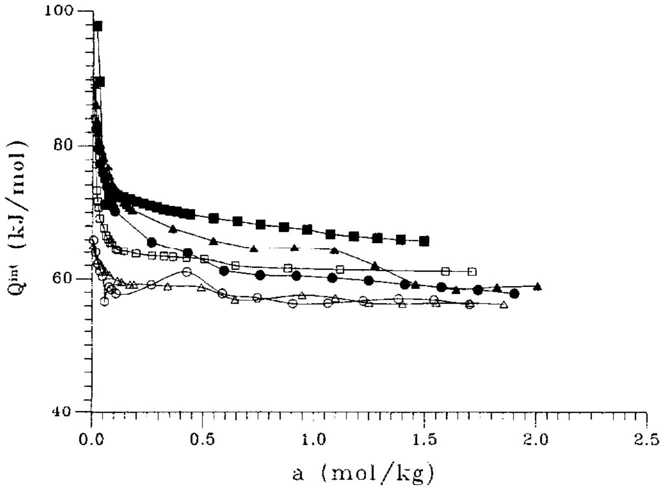

Fig. 5 Integral molar enthalpies of adsorption of methanol on carbon A and carbon B. Symbols as on Fig. 1

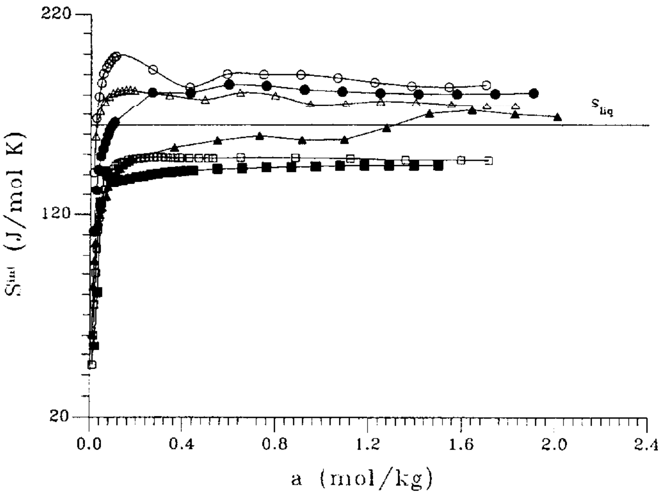

Fig. 6 Integral molar entropies of ethanol adsorbed on carbon A and carbon B. Symbols as on Fig. 1. Solid line – molar entropy of liquid ethanol at 308 K

perature increases. The differences in enthalpy of adsorption values on the both carbons are in the range of 6–25 kJ mol^{-1} at low coverages, and 2–5 kJ mol^{-1} at higher coverages. It means that, as in the case of methanol adsorption, an additional hydrogen bond is created (this effect was observed using IR spectroscopy for adsorption on carbon films [14]). However, in the case of ethanol, in contrast to methanol, the creation of an additional bond with carbon B surface groups is not accompanied by sharply outlined entropy decrease as it occurs in adsorption on carbon A. Moreover, the heat capacity on B type carbon is larger than on carbon A what is different from the adsorption of methanol. This leads to the conclusion that in the case of ethanol the competition between primary and secondary adsorption centers starts at very low coverages, and both are filled gradually. The proposed mechanism can be confirmed by the results of the investigations on the catalytic activity of carbon B [15]; during the catalytic process, the creation of transition states with positive charge on carbon atom of the ethanol molecule is suggested. The positively charged carbon atom creates the hydrogen bonding with the oxygen atom of another ethanol molecule. This effect explains the differences in adsorption behaviour of the two alcohols on carbon B because the stability of the created transition states should be similar to observed for carbo-cations.

The comparison with other adsorbates

The affinity of carbon A, at the all investigated temperatures, towards the investigated molecules decreases in the sentence: CCl_4, C_2H_5OH, CH_3OH, CH_4. The same sentence is observed for the enthalpy of adsorption on this carbon, and it means that adsorption on an unoxidised carbon is determined by the enthalpy (and not entropy) effect value.

On carbon B, at 308 and 328 K, the same sentence referring to adsorption isotherm and enthalpy of adsorption decrease are observed, however, the enthalpies of adsorption of carbon tetrachloride and ethanol are practically the same. This situation changes at the highest temperature, where the enthalpy of adsorption of CCl_4 predominates. This effect is a result of the decrease in the temperature stability of the hydrogen bonds of ethanol.

References

1 G. Rychlicki, A. P. Terzyk and G. S. Szymanski, Polish J. Chem., 67 (1993) 1121.
2 G. Rychlicki, A. P. Terzyk and J. Zawadzki, Polish J. Chem., 68 (1994) 557.
3 G. Rychlicki and A.P. Terzyk, J. Thermal Anal., 45 (1995) 1183, 3a) ibid. 961.
4 G. Rychlicki, A.P. Terzyk and J. Zawadzki, Polish J. Chem., 69 (1995) 1328.
5 G. Rychlicki, Rola Chemizmu Powierzchni Wegla w Procesach Adsorpcji i Katalizy (in Polish), UMK, Torun 1989.
6 J.K. Garbacz, G. Rychlicki and A. P. Terzyk, Adsorption Sci. Technol., 11 (1994) 15.

7 G. Rychlicki, A. P. Terzyk and J.P. Lukaszewicz, Coll. Surf., 96 (1995) 105.
8 A. P. Terzyk, Badanie Oddzialywan Miedzyczasteczkowych w Ukladzie: Adsorbat – Mikroporowaty Wegiel Aktywny – PhD Thesis (in Polish), UMK, Torun 1995.
9 R.C. Bansal, T. L. Dhami and J. Parkash, Carbon, 16 (1978) 389.
10 S. S. Barton and M. J. B. Evans, ibid., 22 (1984) 3.
11 R. McWeeny, Coulson's Valence, Oxford Univ. Press, 1979.
12 N. N. Avgul, A. V. Kiselev and D. P. Poshkus, Adsorpcja gazov i parov na odnorodnych poverhnostiah (in Russian), Chimija, Moskva, 1975.
13 J. Hine, Structural Efects on Equilibria in Organic Chemistry, Willey Intersci. Publ., New York, 1975.
14 J. Zawadzki, Polish J. Chem., 54 (1980) 1257.
15 G. S. Szymanski and G. Rychlicki, Carbon, 31 (1993) 247.