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CALORIMETRIC INVESTIGATION OF THE ADSORPTION OF BINARY VAPOUR MIXTURES OF TETRAHYDROPYRROL WITH METHANOL AND CYCLOPENTANE ON THE HOMOGENEOUS SURFACE

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Abstract

Adsorption isotherms and differential heats of adsorption of tetrahydropyrrol (THP) and cyclopentane (CP), as well as THP and methanol mixtures (mole ratio 1:1, 1:2 and 1:4) on the graphitized carbon black Sterling MT surface were determined. The influence of dilution of [THP] on its ability to undergo homomolecular association was tested. Even 1:4 dilution of THP does not prevent its association. Methanol strongly interacts with THP in the mixed adsorbed layer forming heteromolecular associates.

Keywords: adsorption, calorimetry, mixtures

Introduction

Investigations on the adsorption of mixtures are based on experimental data of total adsorbed amounts and mole fractions of components in adsorbed and gaseous states [1–3]. These factors do not describe exactly this kind of adsorption processes.

This problem concerns in particular mixtures consisting of polar components which may strongly interact mutually. These intermolecular interactions may cause e.g. association of molecules (hydrogen bonds formation), variation in packing effects arising from the differences in the shape of the molecules or molecular deformation [4–7]. The calorimetric method is a powerful tool to investigate the mechanism of adsorption of binary mixtures.

Experimental

Adsorption isotherms, determined by volumetric method at 298 K. (Figs 1, 2) and differential heats of adsorption (measured calorimetrically) of the following vapour mixtures are investigated:

1) THP and CP-mixture I, II, III, mole ratio: 1:1, 1:2, 1:4, respectively.

2) THP and methanol-mixture 1,2,3, mole ratio: 1:1, 1:2, 1:4, respectively.

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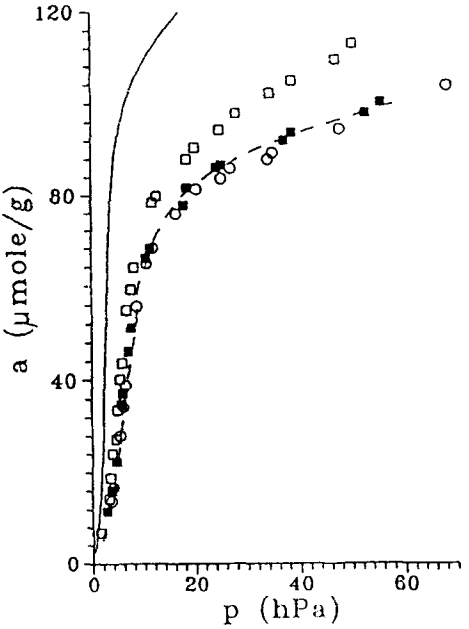

Fig. 1 Adsorption isotherms of THP (—), CP (– – –) and mixtures I(□), II(■) and III(o)

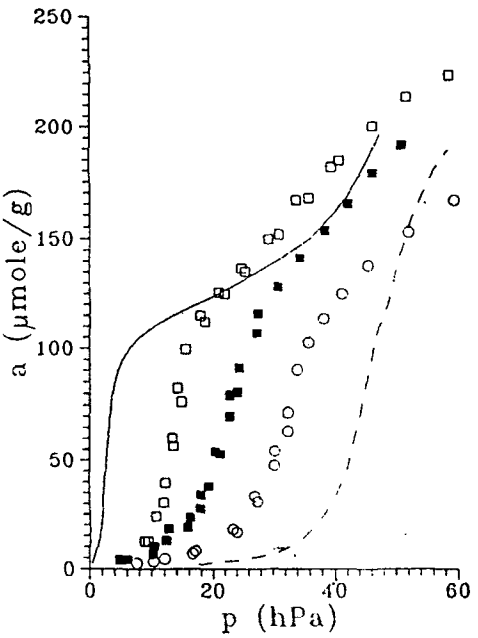

Fig. 2 Adsorption isotherms of THP (—), methanol (– – –) and mixtures 1(□), 2(■) and 3(o)

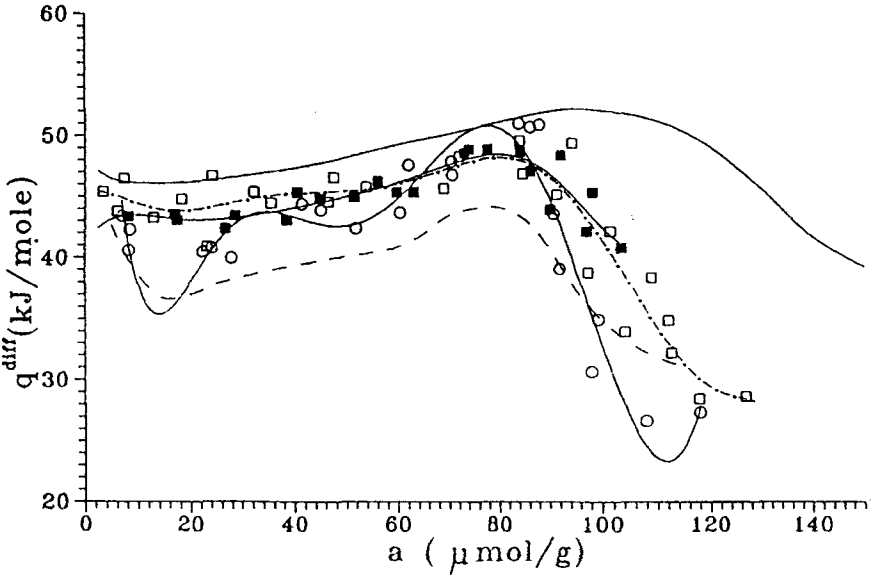

Fig. 3 Differential heats of adsorption of THP (—), CP (- - -) and mixtures: I(□), II(■) and III(o)

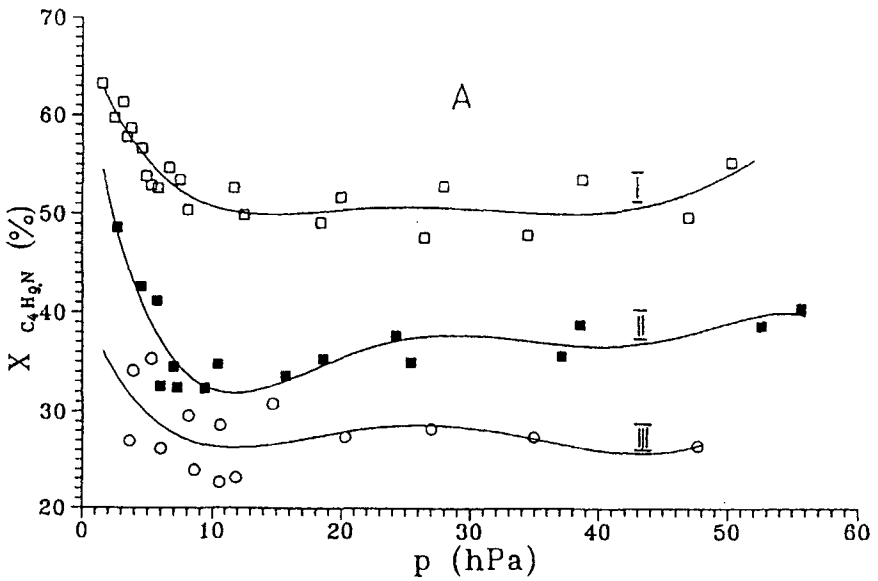

Fig. 4A Percentage mole fractions of THP in the adsorbed layer

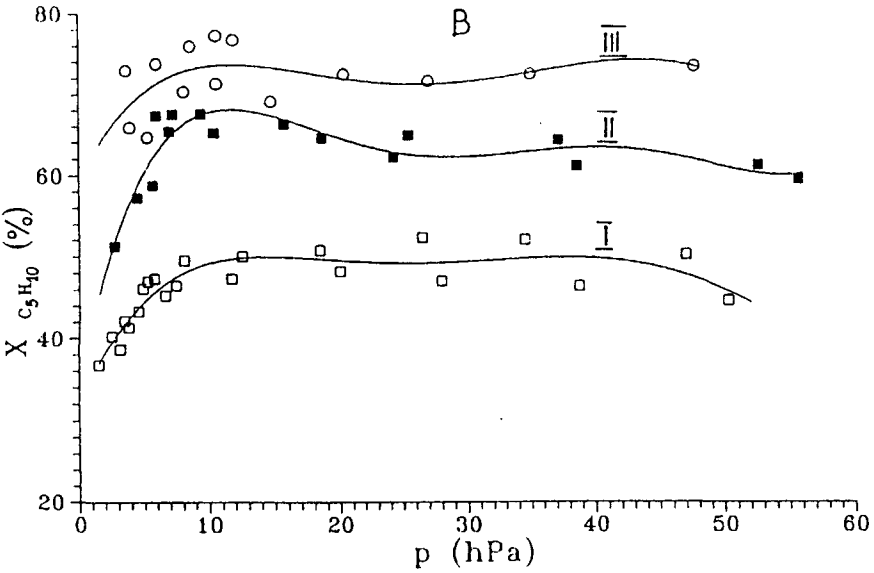

Fig. 4B Percentage mole fractions of CP in the adsorbed layer

The specific surface area of the Sterling MT graphitized carbon black was 20.2 m^2/g. The equilibrium composition of the gaseous phase was measured using IR spectroscopy.

Results and discussion

THP and CP have similar molecular diameters but different dipole moments ($\mu_{CP}=0.0$, $\mu_{THP}=1.59$ D). Moreover, THP molecules may interact mutually forming associates. Association of molecules brings about higher values of THP adsorption heat than of CP (Fig. 3).

From Figs 3 and 4 it is evident that the dilution of THP with CP in molar ratio 1:1 (mixture I) and 1:2 (mixture II) does not prevent association of THP molecules. The mechanism of adsorption of mixture III is quite different. Single molecules of THP are adsorbed at low equilibrium pressure. With increasing coverage THP – CP interactions occur. We have suggested previously [5] this kind of interactions, connected with the deformation of CP structure.

It is well known that pure amines do not form strong internal hydrogen bonds but they easily interact with e.g. water, forming stable associates. This effect is well seen in presented investigations. Heat of adsorption of mixtures 1–3 has slightly higher values than of pure components (Fig. 5). In spite of considerable differences in the size of adsorbed molecules the composition of adsorbed layer is close to the composition of the initial mixtures 1 and 2 (except the initial coverage) – Fig. 6.

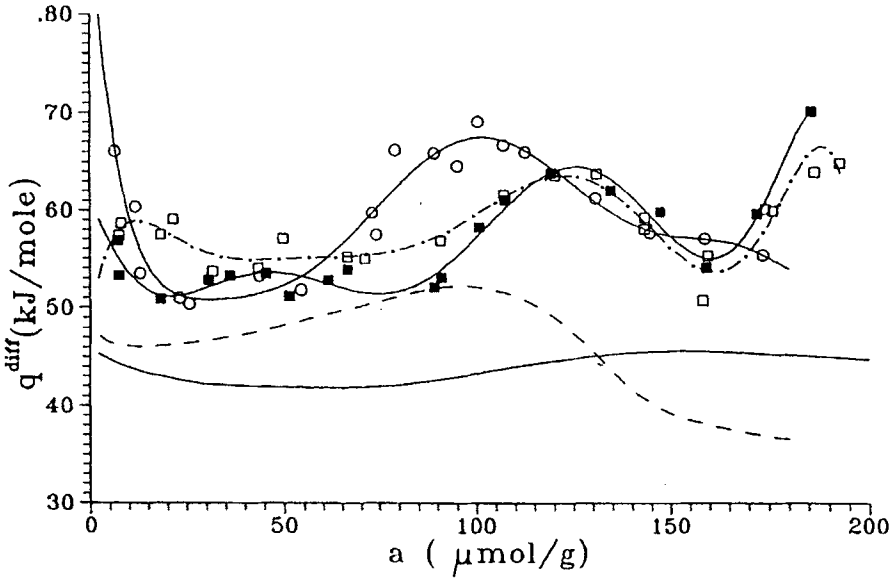

Fig. 5 Differential heats of adsorption of THP (—), methanol (– – –) and mixtures: 1(□), 2(■) and 3(o)

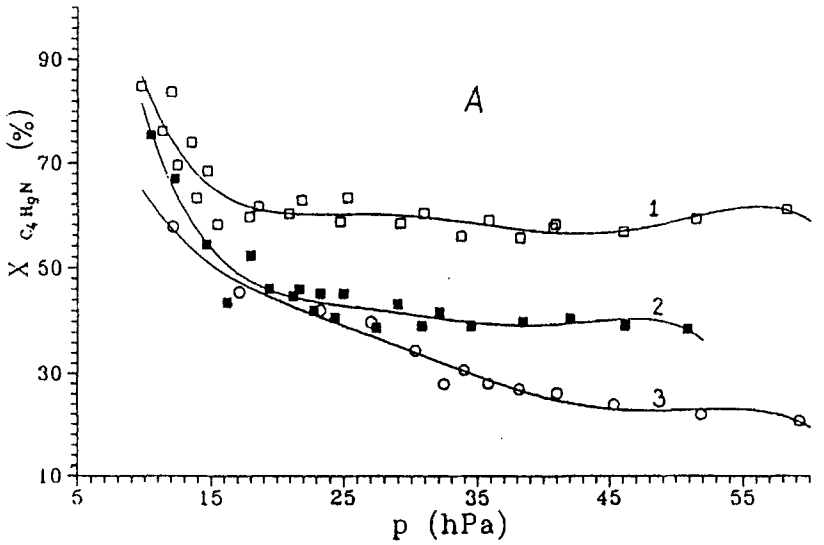

Fig. 6A Percentage mole fractions of THP

The character of changes in differential adsorption heat, as well as molar fraction of components of the methanol–THP mixtures in the adsorbed layer in-

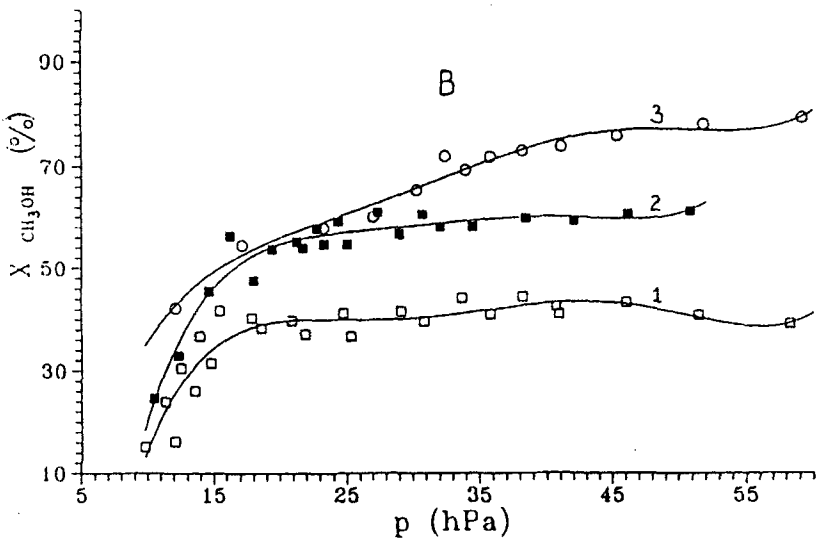

Fig. 6B Percentage mole fractions of methanol in the adsorbed layer

dicates that the process of monolayer formation can be presented by the following quasichemical reactions:

$$C_4H_8NH + NHC_4H_8 = C_4H_8NH - - - NHC_4H_8 + Q_1$$

$$CH_3OH + OHCH_3 = CH_3OH - - - OHCH_3 + Q_2$$

$$CH_3OH + NHC_4H_8 = CH_3OH - - - NHC_4H_8 + Q_3.$$

References

1 A. E. De Gance, Fl. Phase Equil., 78 (1992) 99.
2 E. Costa, G. Calleja, C. Marron, A. Jimenez and J. Pau, J. Chem. Eng. Data, 34 (1989) 156.
3 D. M. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley – Intersci. Publ., (1984).
4 H. Kowalczyk, Polish J. Chem., 65 (1991) 959.
5 H. Kowalczyk and K. Karpinski, J. Thermal Anal., 38 (1992) 2033.
6 G. A. Somorjai, J. Phys. Chem., 94 (1990) 1013.
7 R. Lazzaroni, A. Calderone, G. Lambin, J. P. Rabe and J. L. Bredas, Synth. Metals, 525 (1991) 41.

Zusammenfassung — An grafitierter Rußoberfläche wurden die Adsorptionsisothermen und die differentiellen Adsorptionswärmen von Tetrahydropyrrol (THP) und Cyclopentan (CP) sowie von THP/Methanol-Gemischen (Molverhältnis 1:1, 1:2 und 1:4) bestimmt. Der Einfluß des Verdünnens von THP auf seine Fähigkeit, homomolekulare Assoziationen einzugehen, wurde untersucht. Selbst eine Verdünnung von 1:4 kann die Assoziation von THP nicht verhindern. In der gemischten adsorbierten Schicht tritt Methanol mit THP in starke Wechselwirkungen, wobei heteromolekulare Assoziationen gebildet werden.