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SINGLE-COMPONENT AND BINARY ADSORPTION EQUILIBRIUM OF 1,2 DICHLOROETHANE AND 1,2 DICHLOROPROPANE ON ACTIVATED CARBON

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Abstract

The adsorption equilibrium data were measured for two single-component systems: 1,2 dichloroethane (DCE) – activated carbon Supersorbon HS-4 and 1,2 dichloroproprane (DCP) - activated carbon Supersorbon HS-4 at temperatures of 20, 40, 60, 80, 100, and 120°C. The experimental data of adsorption equilibrium were correlated by some equations of adsorption isotherms. The best results were given using the Sips equation.

Equilibrium points of binary adsorption of the mixture of 1,2 DCE – 1,2 DCP were measured at a temperature of 303 K and a pressure of 10.1 kPa on the same activated carbon. The equilibrium data have been predicted using the extended Langmuir model, the ideal adsorbed solution theory (IAST) model, the FASTIAS method and the modified Sips equation. It was concluded that the modified Sips equation gives the best fit of the experiment. The IAST and FASTIAS models can predict the experimental data for our system at the used conditions with a reasonably good accuracy.

Key words: adsorption equilibrium, 1,2 dichloroethane, 1,2 dichloropropane, activated carbon

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Introduction

The aim of this contribution is to present and discuss the measured and calculated equilibrium data of pure components 1,2 dichloroethane (DCE) and 1,2 dichloropropane (DCP) on activated carbon Supersorbon HS-4 and of the mixture of DCE and DCP on activated carbon Supersorbon HS-4.

The single-component adsorption equilibrium in a gas phase is a three variables function [a=f(p,T)], while at the adsorption of two components from gas phase one has to know the values of five variables [a_1=f(p_1, p_2, T) and a_2=f(p_1, p_2, T)] for each equilibrium point. It is obvious that the essential effort in the theory of mixture adsorption equilibrium is to predict the mixture adsorption equilibrium from pure component data.

Theoretical

Single-component adsorption equilibrium

In this contribution the following equations describing the surface adsorption were used for the correlation of a single-component adsorption equilibrium data:

The Langmuir equation of adsorption isotherm based on localized adsorption in a monolayer has the following form:

$$\theta = \frac{a}{a_m} = \frac{bp}{1+bp} \tag{1}$$

Sips formulated a three-parameters equation as a combination of Langmuir and Freundlich equation. This equation describes well not only the adsorption equilibrium of hydrocarbons on activated carbons but it is also often used in modeling of bioprocesses. It can be written as:

$$\theta = \frac{a}{a_m} = \frac{(bp)^{1/n}}{1 + (bp)^{1/n}} \tag{2}$$

O'Brien and Myers[1] derived an equation accepting heterogeneity of adsorption surfaces in the members of central moments of adsorption energy distribution. The Langmuir isotherm was the base of this expression. The authors published the following equation:

$$\theta = \frac{a}{a_m} = \left[\frac{\eta}{1+\eta} + \frac{\sigma^2 \eta (1-\eta)}{2(1+\eta)^3} \right] \tag{3}$$

where η represents the pressure with dimension of unity:

$$\eta = bp \tag{4}$$

The first term in the bracket of Eq. (3) represents the Langmuir equation and the second term expresses the correction of adsorbent heterogeneity effects. σ^2 is the variance of adsorption energy distribution.

Another type of adsorption mechanism is described by the theory of micropore filling. At known behavior of the adsorbed phase one can judge the validity of the Polanyi's theory from the sets of isothermal data through the characteristic curve $A = f(V)$, where $A = RT\ln(P^*/p)$ represents the adsorption potential. The principle of the potential theory consists of postulating that at all temperatures a single curve (the characteristic curve) corresponds to the adsorbent - adsorbate system. According to this theory one can recalculate the isothermal equilibrium data of the adsorptive to another temperature:

$$V_1 = V_2; \qquad [RT \ln(P^*/p)]_1 = [RT \ln(P^*/p)]_2 \tag{5}$$

where the index 1 corresponds to the data at temperature T_1, and the index 2 to the data at temperature T_2.

When it is necessary to recalculate some equilibrium data to another temperature some equation based on the theory of micropore filling can be used. In this work the Dubinin –Astakhov equation was employed in the form

$$\theta = \frac{a}{a_o} = \frac{V}{V_o} = \exp\left[-\left(\frac{A}{E} \right)^n \right] \tag{6}$$

Multi-component adsorption equilibrium

Numerous models have been proposed for adsorption equilibria. The most important factor in selecting a model from an engineering standpoint is to have an accurate mathematical description over the entire range of process condition.

The Langmuir adsorption isotherm can be easily extended to a multi-component adsorption system by keeping all the assumptions made by this model in the treatment of pure component adsorption equilibria. In extending this model to a two-component system the adsorbed amount of a component *i* can be written as:

$$a_i = a_m \frac{b_i p_i}{1 + b_1 p_1 + b_2 p_2} \qquad i = 1,2 \tag{7}$$

For the extended Langmuir model to be thermodynamically correct it is required that the saturation capacities of all components should be the same. However, for physical adsorption of molecules of widely different sizes this assumption is unrealistic.

Similar to the Langmuir isotherm also the Sips equation can be extended for description of adsorption equilibrium of mixtures. For a binary mixture one can use the equation in the form:

$$a_i = a_m \frac{(b_i p_i)^{1/n}}{1 + (b_1 p_1)^{1/n} + (b_2 p_2)^{1/n}} \qquad i = 1,2 \tag{8}$$

Authors of [2] recommend to use the modified Sips model which can be written for a binary adsorption equilibrium as:

$$a_i = a_m \frac{b_i p_i (b_1 p_1 + b_2 p_2)^{(1/n-1)}}{1 + (b_1 p_1 + b_2 p_2)^{1/n}} \qquad i = 1,2 \tag{9}$$

Myers and Prausnitz[3] presented a technique for calculating the adsorption equilibria for components in a gaseous mixture, which is based on the concept analogous to Raoult's law – ideal adsorbed solution theory (IAST). This model does not require any mixture data and it is independent of the actual model of physical adsorption. It uses thermodynamic equations from vapour-liquid equilibria with volume replaced by surface area and pressure replaced by two-dimensional spreading pressure. Applying the IAST requires the calculation of an integral equation to obtain the spreading pressure:

$$\frac{\pi A}{RT} = \int_0^{P_i^o} \frac{a}{P} \mathrm{d}P \tag{10}$$

Most of the isotherm equations commonly used for describing the single-component data cannot be solved analytically for the spreading pressure. Therefore, the algorithm for the solution of the IAST equation requires numerical integration at each step of the iteration procedure.

O'Brien and Myers[4] proposed a procedure that allows fast computation of multi-component adsorption equilibria called FASTIAS. This method is based on the ideal adsorbed solution theory and the adsorbed amount of component *i* from a binary gas mixture can be calculated using the isotherm equation in the following form:

$$\theta_i = \frac{a_i}{a_m} = \left[\frac{\eta_i}{1+\eta_i} + \frac{\sigma_i^2 \eta_i (1-\eta_i)}{2(1+\eta_i)^3}\right] \qquad i = 1,2 \tag{11}$$

where: $$\eta_i = b_i p_i \tag{12}$$

Parameters η_i and σ_i are obtained for each component from experimental data using Eq. (3).

Experimental

The both used hydrocarbons, 1,2 dichloroethane (DCE) and 1,2 dichloropropane (DCP) were supplied by NCHZ Slovakia and their purity was higher than 99 %. The activated carbon Suspersorbon HS-4 of domestic provenance consisted of cylindrical particles with a diameter of 2-3 mm, a length of 5-6 mm, and a specific surface area of 917 m^2g^{-1}.

Equilibrium data of single component adsorption were measured in a glass gravimetric apparatus, which was described in more details in the paper of [5]. The measurements were conducted for both adsorption systems: DCE – AC Supersorbon HS-4 and DCP - AC Supersorbon HS-4 at temperatures of 20, 40, 60, 80, 100, and 120°C. The results are depicted in Fig.1A and 1B. These measurements were difficult due to instability of chlorinated hydrocarbons at higher temperatures.

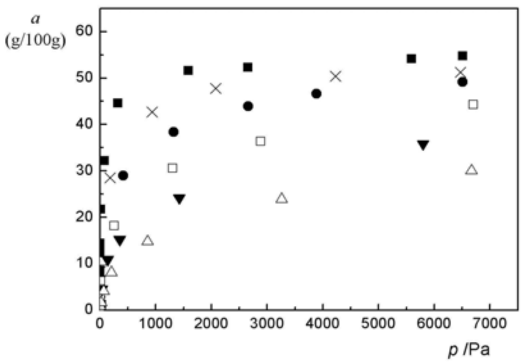

Fig.1A Experimental data of single component adsorption equilibrium of 1,2dichloroethane) on AC Supersorbon HS4:! 20°C, X 40°C, ● 60°C, ☐ 80°C, ▼ 100°C, ∆ 120°C

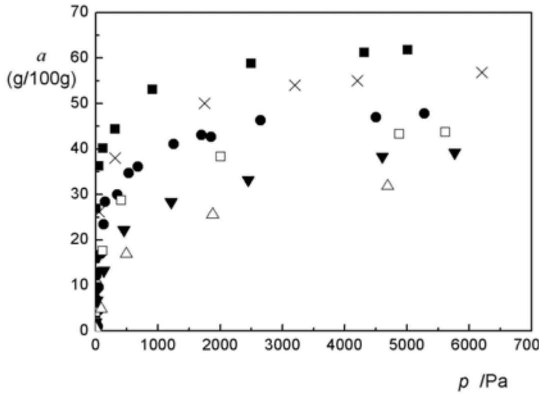

Fig.1B Experimental data of single component adsorption equilibrium of 1,2dichloropropane on AC Supersorbon HS4: ! 20°C, X 40°C, ● 60°C, ☐ 80°C, ▼ 100°C, ∆ 120°C

The measurements of binary adsorption isotherms were carried out using the volumetric apparatus presented in Figure 2 [6] . The measured volume of the apparatus was of 1.8 dm^3.

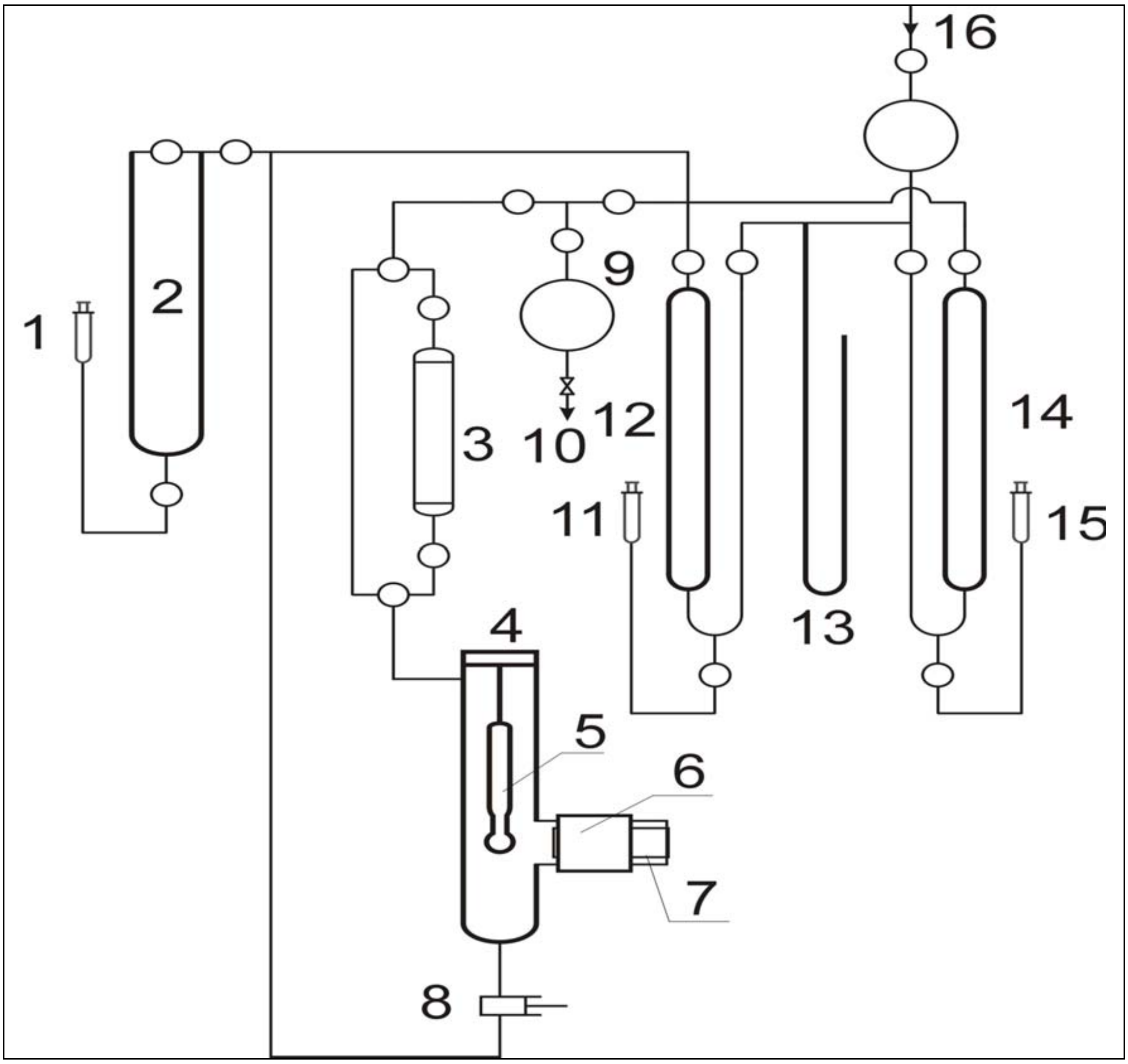

Fig.2. Volumetric circulation apparatus for binary adsorption equilibrium measurement

1,11,15	quicksilver reservoirs	7	iron core
2, 13	U-manometers	8	pump
3	adsorber	9	flask with known volume
4	sample offtake	10	to an air pump
5	sample ampoule	12, 14	burettes
6	induction coil	16	nitrogen input

Binary equilibrium experiments were performed in a mixture with nitrogen as a carrier gas at a temperature of 303 K and a pressure of adsorptives 10.1 kPa. The obtained data were transformed to the form x_1 and y_1 and are shown in Table I.

Tab.I. Binary equilibrium data calculated from experimental data at 303 K

Adsorptive pressure *p* [Pa]	y_1	x_1
10 066	0.530	0.382
10 133	0.195	0.142
11 733	0.775	0.651

Results and discussion

Experimental points of adsorption equilibrium of DCE on AC Supersorbon HS-4, and DCP on AC Supersorbon HS-4 were correlated by the equations of Langmuir, Sips and O'Brien Myers with the aim to obtain the basis for a mixture isotherm calculations. Tables II, III and IV show the results of calculation - parameters for pure component adsorption together with their errors.

Tab.II. Results of correlation using Langmuir equation

	DCE		DCP	
Temperature/(°C)	a_m /(mol.kg^{-1})	b /(Pa^{-1})	a_m /(mol.kg^{-1})	b /(Pa^{-1})
20	5.1 ± 0.2	0.06± 0.01	4.8 ± 0.2	0.14 ± 0.05
40	5.1 ± 0.2	0.007 ±0.001	4.7 ± 0.2	0.024 ± 0.009
60	5.0 ± 0.2	0.0032 ± 0.0008	4.1 ± 0.2	0.008 ± 0.001
80	4.1 ± 0.2	0.003 ± 0,001	3.9 ± 0.1	0.0053 ± 0.0008
100	3.7 ± 0.2	0.0020 ± 0.0004	3.5 ± 0.1	0.0032 ± 0.0007
120	3.2 ± 0.2	0.0012 ± 0.0002	3.07 ± 0.08	0.0018 ± 0.0002
30	5.3 ± 0.2	0.020 ± 0.004	4.9± 0. 4	0.06 ± 0.01

Tab.III. Results of correlation using Sips equation

	DCE			DCP		
	a_m (mol.kg^{-1})	b /(Pa^{-1})	n	a_m (mol.kg^{-1})	b /(Pa^{-1})	n
20	6.0±0.1	0.022±0.003	2.0±0.08	6.2±0.3	0.021±0.08	2.5±0.2
40	6.1±0.2	0.005±0.001	1.9±0.1	6.0±0.4	0.005±0.002	2.5±0.2
60	6.0	0.0025±0.0001	1.88±0.04	5.8±0.6	0.002±0.001	2.3±0.2
80	6.0	9x10^{-4}±6x10^{-5}	1.84±0.06	4.7±0.2	0.0025± 5x10^{-4}	1.9±0.1
100	5.8±0.6	4x10^{-4}±1x10^{-4}	1.8±0.17.6	4	0.0019±1x10^{-4}	1.78±0.09
120	5.4±0.6	2.2x10^{-4} ± 9x10^{-5}	1.7±0.1	3.3±0.2	0.0015±3x10^{-4}	1.1±0.1
30	5,84±0.04	0.0117±4x10^{-4}	1.72±0.06	5.56.±0.05	0.0182±0.0007	1.99±0.09

Tab.IV. Results of correlation using O’Brian Myers equation

	DCE			DCP		
	a_m (mol.kg^{-1})	b /(Pa^{-1})	σ	a_m (mol.kg^{-1})	b /(Pa^{-1})	σ
20	5.43±0.08	0.042±0.004	1.86±0.09	5.2±0.1	0.06±0.01	2.1±0.2
40	5.33±0.06	0.015±0.001	2.06±0.07	4,97±0.1	0.022±0.004	2.1±0.2
60	5.24±0.07	0.0074±0.0005	2.12±0.06	4.2±0.2	0.015±0.002	2.1±0.1
80	4.6±0.2	0.0033±0.0008	1.7±0.2	3.9±0.1	0.017±0.002	2.3±0.2
100	4.3±0.5	0.0013 ±0.0006	1.3±0.3	4	0.0021 ± 7x10^{-4}	1.5±0.5
120	3.8±0.8	0.0008±0.0005	1.1±0.4	4.3±0.1	6.2x10^{-4} ± 5x10^{-5}	1.49±0.04
30	5.4±0.1	0.020±0.002	1.7±0.1	5.12±0.05	0.020±0.004	1.5

From Tabs. II and III one can see that all the parameters of Langmuir and Sips equation decrease with increasing temperature with acceptance of parameters errors. A decrease of parameter a_m can be accepted with respect to a decrease of adsorption capacity with increasing temperature. Parameter b is also a function of temperature therefore it’s decreasing trend is logical. Likewise it is also in Tab. IV but the variation of parameter σ with temperature is not definite. It should be noted that the experiments at lower temperatures could testify more because the measurements were completed at a higher value of the relative pressure p/P*. Sips and O’Brien-Myers equations correlate the experimental data better than the Langmuir isotherm. This is documented in the Figs. 3A and B. There are experimental points at 20°C and correlations using all the three equations. The Langmuir equation is quite suitable to describe the adsorption equilibrium only at a lower adsorbent loading for both adsorption systems. A similar course of adsorption isotherm lines can be seen also at the other temperatures.

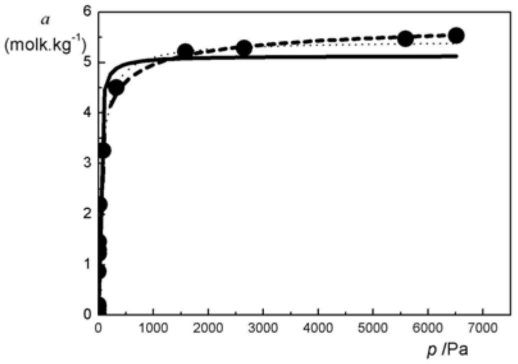

Fig.3A Correlation of DCE at 20°C: ! experimental data, thick solid line – Langmuir equation, thick dash line - Sips equation, thin dot line – O'Brien-Myers equation

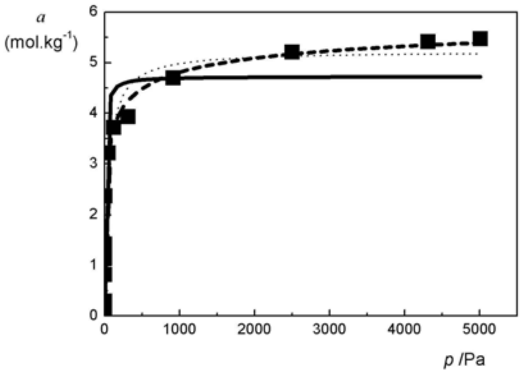

Fig.3B Correlation of DCP at 20°C: experimental data, thick solid line – Langmuir equation, thick dash line - Sips equation, thin dot line – O'Brien-Myers equation

Trying to obtain the isotherm at 30°C, which was not experimentally measured, the theory of volume filling of micropores was used. All experimental data were converted to the form *A*=f(*V*) and they are depicted in Figs. 4A and 4B. It was found out, that characteristic curves for both adsorption systems do exist. Thus, the experimental data were fitted using the Dubinin-Astakhov equation and the obtained parameters are shown in Table V.

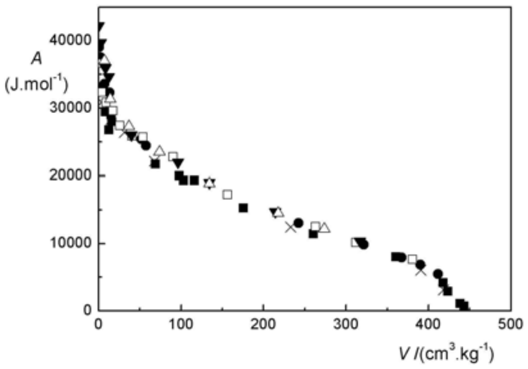

Fig.4A Characteristic curve for the system DCE - AC Supersorbon HS-4

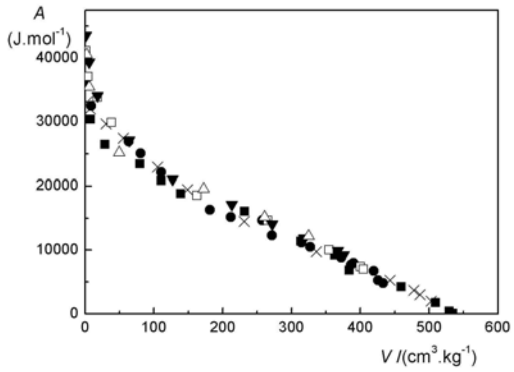

Fig.4B Characteristic curve for the system DCP - AC Supersorbon HS-4

Table V. Parameters of the Dubinin-Astakhov equation for the whole experimental data set

	DCE	DCP
V_o /(cm^3 .kg)	448 ± 3	506 ± 6
E /(J.mol^{-1})	16 700 ± 133	17 250 ± 220
n	2	2

Using parameters from Tab.V the points of the isotherms of DCE and DCP on AC Supersorbon HS-4 at 30°C were obtained. These points were correlated by the Langmuir, Sips and O'Brien-Myers equations. The obtained values of parameters are in the last line of the Tables II, III and IV. It could be expected that the values of parameters at 30 °C would lie between the values corresponding to parameters at 20 and 40 °C, i. e. that the trend of particular parameters would be maintained. The existing differences may be related to the fact that Dubinin Astakhov equation does not describe the experiment precisely enough.

The parameters obtained at 30°C were used in the calculation of the mixture adsorption isotherms.

Using equation (7) and (9) the courses of Langmuir and Sips adsorption isotherms for the used binary system were calculated. The adsorptives 1,2 DCE and 1,2 DCP are not very different therefore the average values of a_{mi} and n_i parameters were taken into account. The results are depicted together with the others in Fig. 5.

Application of the IAS theory is described in details in [3] or [7]. Using the numerical integration of Eq. (10) the dependencies $\pi_1=f(P_1^o)$ and $\pi_2=f(P_2^o)$ have been found from the points of single-component adsorption isotherms at 30°C. P_i^o are the single-component pressures. For the unambiguous definition of the system in the state of thermodynamic equilibrium the third independent variable – spreading pressure π is chosen in addition to the equilibrium pressure and temperature. The values of pure component equilibrium pressures P_1^o and P_2^o are found out for the chosen spreading pressure and then, mole fractions of components in the adsorbate and the gas phase can be calculated:

$$x_1 = \frac{P - P_2^o}{P_1^o - P_2^o} \quad \text{and} \quad y_1 = \frac{P_1^o x_1}{P}$$

The choice of the spreading pressure value is connected with the pressure of the system. The choice of π_1 and π_2 makes sense only by the validity of $P_1^o \geq P \geq P_2^o$. Mole fractions values x and y were evaluated from acquired equilibrium data.

The IAS theory is basically independent from the form of the pure-component isotherm. Eq. (3) can be solved analytically for the spreading pressure according to Eq. (10). According to the procedure described in [4] one obtains a set of non-linear algebraic equations with the solution of the vector (η_1, η_2). From this set one may obtain the results P_i^o, x_i and a_m.

The results of binary adsorption equilibrium 1,2DCE-1,2DCP on the AC Supersorbon HS-4 obtained by all the methods used and from the experiment at 30°C and 10.1 kPa are depicted in Fig.5. It can be seen, that the modified Sips equation gives the best results. The IAST procedure and FASTIAS method work reasonably well. The extended Langmuir equation gives the worst fit of the mixture experimental data.

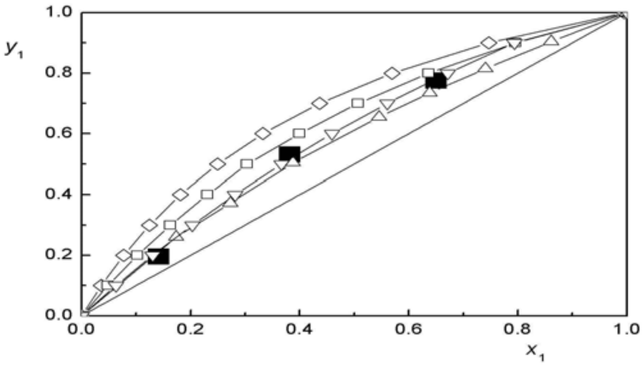

Fig.5. Prediction of binary adsorption equilibrium of 1,2DCE - 1,2DCP on AC Supersorbon HS-4 at 30°C and 10,1 kPa obtained by various methods: ■ experiment, M the extended Langmuir model, X Sips model, □ FASTIAS procedure, 8 IAST

Conclusions

The measured single-component adsorption equilibrium data of 1,2 DCE and 1,2 DCP on AC Supersorbon HS-4 were fitted by the known equations of adsorption isotherm. The Sips equation gives the best results.

From the existence of the characteristic curves one can judge that also the mechanism of volume filing of micropores can be used for the description of adsorption equilibrium of our two adsorption systems. On the basis of this fact the Dubinin-Astakhov equation was applied. Thus, the values of the adsorption isotherm at 30 °C (which was not measured experimentally) were obtained.

By comparing the experimental points of adsorption equilibrium of 1,2DCE –1,2DCP mixture at a temperature of 30 °C and a pressure of 10.1 kPa with calculated values one can come to the following conclusions:

The best description of the measured points was obtained using the modified Sips equation. For prediction of the binary mixture adsorption equilibrium of our adsorption system also the model of ideal adsorbed solution theory and FASTIAS model give the reasonably good results. It was found out that the extended Langmuir equation provides the less accurate results.

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Symbols

a	adsorbed amount	mol.kg^{-1}
a_m	adsorbed amount at monolayer	mol.kg^{-1}
a_i^o	adsorbed amount of a pure component i	mol.kg^{-1}
A	adsorption potential	J.mol^{-1}
b	parameter of Eqs.(1), (2), (4), (7), (8), (9), (12)	Pa^{-1}
E	characteristic energy	J.mol^{-1}
n	parameter of Eqs. (2), (6), (8), (9), (11)	-
p	adsorption pressure	Pa
P^*	saturated vapour pressure	Pa
P_i^o	pressure of a single component *i*	Pa
R	gas constant	J.mol^{-1}.K^{-1}
t	parameter in the Eq. 2	-
T	temperature	K
V	adsorbate volume	cm^3.kg^{-1}
V_o	micropore saturation volume	cm^3.kg^{-1}
x	mole fraction in the adsorbed phase	-
y	mole fraction in the gas phase	-
η	parameter defined by Eq.(4)	-
θ	fractional surface coverage	-
	spreading pressure	Pa.m
σ	parameter of Eq. (3)	-

Superscripts

^{o}	a pure component property

Subscript

i=1,2	components , i=1 – DCE, i=2-DCP

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