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Interaction of methoxy- and methylenedioxyamphetamines with carbon and polymeric adsorbents in polar liquids

Research Article

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Abstract: Solid phase extraction (SPE) of methoxy- and methylenedioxyamphetamines from diluted aqueous solutions was investigated on carbon and polymeric adsorbents of different textures and chemical compositions. Those adsorbents were applied cartridges packed with three chemically modified carbons prepared from plum stones (initial A2PS, oxidized A2PS-O, and reduced A2PS-H) and commercially available adsorbents (polymeric LiChrolut EN, graphitized Hypercarb and Carboprep). Several factors influence the recovery rates of amphetamine derivatives such as the polarity of adsorbates (free energy of salvation), the specific surface area and surface composition of adsorbents, and the solvent characteristics. Different combinations of these factors affect the recovery rate (R1) for high- and low-surface area adsorbents. The minimal R1 values are observed for an amphetamine derivative at a maximal solvation effect and for a set of amphetamines adsorbed on graphitized carbons.

Keywords: *Amphetamines • Solid phase extraction • Carbon and polymeric adsorbents • Structural characteristics • Free energy of solvation*

1. Introduction

Amphetamine derivatives described as designer drugs are the most popular synthetically produced drugs of abuse in many European countries [1,2] at the beginning of XXI century. Recently, new metoxy- or thioamphetamines [3,4] have been proved to be very dangerous substances. Thus, the development of tailored analytical method for their analysis is of particular importantance to forensic laboratories.

An overview of earlier applications of solid phase extraction (SPE) in drugs analysis, including amphetamines, was presented by Frannke *et al.* at the end of nineties [5], when novel adsorbents and their packing formats had been introduced into analytical practice and applied successfully to different amphetamines. Amphetamine, methamphetamine and methylenedioxyamphetamines were extracted on disk cartridges containing mixed-mode modified silica [6] and on monolithic C-18 silica disk-packed spin column [7]. The columns prepared with monolithic C-18 bonded silica and packed into capillary column were applied successfully in the analysis of amphetamines [8]. Another new format of SPE columns used for determination of amphetamine and methamphetamine is pipette tip in which C-18 monolithic silica bed is

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fixed [9,10]. SPE using polar enhanced totally water-wettable SDVB resin as a very effective adsorbent was recently applied for simultaneous analysis of a variety of amphetamine related drugs [11]. The extraction of ring-substituted derivatives of 2,5-dimetoxyamphetamine and 2,5-dimetoxyphenylethylamine were studied on Bond Elut C-18 extraction columns packed with silica based adsorbent [12]. The recoveries were satisfactory; however, no correlation between adsorbate/adsorbent structures and the SPE effectiveness was presented.

In our previous work, we studied the SPE process of amphetamine and related N-alkyl substituted derivatives from diluted aqueous solutions using adsorbents with different textures and chemical compositions such as activated carbons prepared from plum stones, graphitized carbons (Hypercarb and Envicarb) and polymeric adsorbent (LiChrolut EN) [13]. It was found that the recovery rates of amphetamines increased nearly linearly with free energy of solvation due to better adsorption (and worse dissolution) of molecules with larger side non-polar groups from polar solution, and therefore smaller energy of desolvation of adsorbates. Reduction of carbon surface led to decrease in the recovery rates. Its minimal values were observed for amphetamines on graphitized carbons due to both lower adsorption and worse desorption (elution) in comparison with those for activated carbons [13]. However, no data concerning SPE of methoxyamphetamines and methylenedioxyamphetamines on carbon adsorbents have been yet reported. Therefore, the aim of this work was to comparatively investigate the adsorption–desorption of a variety of amphetamine derivatives (16 compounds) on previously applied carbon and polymeric adsorbents [13] (with exception of Envicarb replaced by Carboprep).

2. Experimental Procedure

2.1. Materials

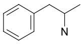
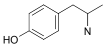
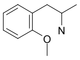
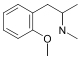
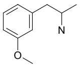
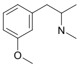
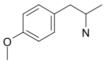
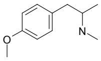
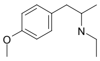
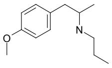
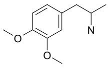
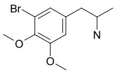
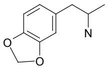
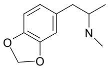
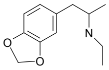
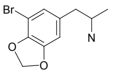
Commercial activated carbon A2PS (HPSD, Hajnówka, Poland) prepared from plum stones carbonized at 823–873 K, activated at 1173–1273 K, and demineralized using a technique described previously [14] was utilized as the starting material. The preparation of the oxidized carbon adsorbent (A2PS-O) and the carbon adsorbent with a lower content of oxygen-containing surface functionalities (reduced by hydrogen, A2PS-H) was described in detail previously [13]. Three commercial SPE adsorbents such as graphitized carbons Hypercarb (ThermoHypersil, UK), Carboprep (Restek, USA) and polymeric LiChrolut EN (Merck) were used as reference materials to compare with the A2PS carbons. The preparation of the SPE cartridges and the suppliers of HPLC grade solvents were detailed earlier [13].

In this work, 16 psychotropic substances were divided into three groups: (I) amphetamine and hydroxyamphetamine, (II) metoxyamphetamines (10 samples) and (III) methylenedioxyamphetamines (4 samples) were studied (Table 1). Amphetamine sulfate and hydrochlorides of 3,4-methylenedioxyamphetamine, 3,4-methylenedioxymethamphetamine and 3,4-methylenedioxyethylamphetamine were analytical standards (Sigma, USA), whereas other methoxyamphetamines were synthesized at the forensic laboratory of Internal Security Agency (Warsaw, Poland). 4-Methoxyamphetamine was synthesized using the Leuckart method [15] and 4-hydroxyamphetamine was prepared by treatment of 4-methoxyamphetamine in boiling hydrobromic acid. 4-Methoxy-N-methylamphetamine, 4-methoxy-N-ethylamphetamine and 4-methoxy-N-propylamphetamine were prepared by reductive amination of phenylpropan-2-one analogue [16]. 2-Methoxyamphetamine, 2-metoxy-N-methylamphetamine, 3-methoxyamphetamine, 3-methoxy-N-methylamphetamine and 3,4-dimethoxyamphetamine were prepared using the corresponding arylacetones [17]. 5-Bromo-3,4-dimetoxyamphetamine and 5-bromo-3,4-methylenedioxyamphetamine were prepared using 3,4-dimetoxyamphetamine and 3,4-methylenedioxyamphetamine reacting with bromine in acetic acid. The molecular structure and the purity of obtained compounds in the form of hydrochlorides or free bases were confirmed by spectroscopic (^{1}H NMR, TPD-MS, FTIR) and chromatographic (GC, HPLC) methods.

2.2. SPE procedure

The SPE experiments were performed as previously reported [13]. Standard stock solutions of amphetamines at concentration of 5 mg/mL (as free bases) were prepared in water/acetonitrile (1/1) mixtures and stored at 275 K for a week. For the recovery studies, samples of 100-mL water alkalized with 5 mL of ammonia solution (pH ≈ 10) were prepared daily and spiked with the described standard solution to get a concentration of 50 μg mL^{-1}. Prepared cartridges were washed with 5 mL of dimethylformamide (DMFA) and conditioned by 20 mL of water before experiments. The amphetamine samples were percolated through cartridges at a flow rate of 5 mL min^{-1} using a vacuum manifold. The effluents obtained from each cartridge were collected for further studies. The residual water was removed from cartridges by nitrogen aspiration for 10 min, and subsequent elution was performed using 5 mL of DMFA

Table 1. Structures, molecular data, applied abbreviations and numbers of amphetamine derivatives.

No.	Compound	Abbreviation	Molecular formula	W[a]	μ[b] (D)	Structure
1.	Amphetamine	A	$C_9H_{13}N$	135.21	1.86	
2.	p-hydroxyamphetamine	4-OHA	$C_9H_{13}NO$	151.21	2.41	
3.	2-metoxyamphetamine	2-MA	$C_{10}H_{15}NO$	165.24	1.68	
4.	2-metoxy-N-methylamphetamine	2-MMA	$C_{11}H_{17}NO$	179.26	1.44	
5.	3-metoxyamphetamine	3-MA	$C_{10}H_{15}NO$	165.24	1.35	
6.	3-metoxy-N-methylamphetamine	3-MMA	$C_{11}H_{17}NO$	179.26	2.67	
7.	4-metoxyamphetamine	4-MA	$C_{10}H_{15}NO$	165.24	1.79	
8.	4-metoxy-N-methylamphetamine	4-MMA	$C_{11}H_{17}NO$	179.26	1.67	
9.	4-metoxy-N-ethylamphetamine	4-MEA	$C_{12}H_{19}NO$	193.29	1.69	
10.	4-metoxy-N-propylamphetamine	4-MPA	$C_{13}H_{21}NO$	207.32	1.66	
11.	3,4-dimetoxyamphetamine	3,4-DMA	$C_{11}H_{17}NO_2$	195.26	2.48	
12.	5-bromo-3,4-dimetoxyamphetamine	5-Br,3,4-DMA	$C_{11}H_{16}BrNO_2$	274.16	5.35	
13.	3,4-methylenedioxyamphetamine	MDA	$C_{10}H_{13}NO_2$	179.22	6.16	
14.	3,4-methylenedioxymethamphetamine	MDMA	$C_{11}H_{15}NO_2$	193.25	5.81	
15.	3,4-methylenedioxyethylamphetamine	MDEA	$C_{12}H_{17}NO_2$	207.27	5.77	
16.	5-bromo-3,4-methylenedioxyamphetamine	5-BrMDA	$C_{10}H_{12}BrNO_2$	258.11	6.60	

[a] *molecular weight (W)*
[b] *dipole moment (μ, HF/6-31G(d,p))*

in a 10 mL graduated flask. Water was added to obtain the final eluate volume of 10 mL. The consecutive SPE experiments allow evaluating the efficiency of the adsorption and the elution separately. The effluents obtained from the amphetamine adsorption on the previously studied adsorbents were collected and then passed through a cartridge containing polymeric packing LiChrolut EN (100 mg in 3 mL tube). Then the elution was performed according to the procedure described above.

2.3. Chromatography

The HPLC method used for quantitative analysis of metoxy- and methylenedioxyamphetamines in effluents and extracts was described elsewhere [13]. The SPE recovery rates were calculated using peak areas and ephedrine or β-phenylethylamine was used as an internal standard. The calibration curves for the studied substances were obtained by linear regression over the 30–850 μg mL^{-1} range with six experimental points (correlation coefficient 0.98–0.99). The RSD for the peak areas of five injections was <3%. The average values of the recovery rates were evaluated from five SPE measurements at the RSD of 4–7%.

2.4. Nitrogen adsorption

Low-temperature nitrogen adsorption–desorption isotherms (77.35 K) were recorded using a Micromeritics ASAP 2010 or 2405N adsorption analyzer. The specific surface area of adsorbents (Table 2, S_{BET}) was calculated according to the standard BET method [18]. The total pore volume (V_p) was evaluated by converting the volume of nitrogen adsorbed at $p/p_0 \approx 0.98$–0.99 (p and p_0 denote the equilibrium pressure and the saturation pressure of nitrogen at 77.4 K, respectively) to the volume of liquid nitrogen per gram of the adsorbent. The pore size distribution (PSD) functions f(x) (differential $f_V(x) \sim dV_p/dx$ and $f_S(x) \sim dS/dx$, where x is the pore half-width or radius) were calculated using Density Functional Theory, DFT [19]. To calculate the density of a gaseous adsorbate (nitrogen) at a given pressure p, the generalized Bender equation [20] was applied. The nitrogen desorption data were utilized to compute the f(x) functions using the model of cylindrical pores for LiChrolut EN and slit-shaped pores for carbon adsorbents and the modified regularization procedure CONTIN [21] under nonnegativity condition ($f(x) \geq 0$ at any x) with a fixed regularization parameter $\alpha = 0.01$. For estimation of the deviation of the pore shape from the model of cylindrical or slit-shaped pores the value $\Delta w_{sl(cyl)} = S_{BET}/S_{sum} - 1$ (where $S_{sum} = \int f_S(x)dx$) was used. The PSD functions were recalculated to the incremental PSD functions (IPSD)

$$\Phi_{V,S}(x_i) = 0.5(f_{V,S}(x_i) + f_{V,S}(x_i))(x_i - x_{i-1})V_p \,/ \int_{x_{\min}}^{x_{\max}} \Phi_{V,S}(x)dx \quad (1)$$

2.5. FTIR spectroscopy

The transmission FTIR spectra of three carbon adsorbents, Hypercarb and LiChrolut EN were analyzed previously [13]. The FTIR spectrum of Carboprep was recorded using a FTIR 1725x (Perkin–Elmer, USA) spectrophotometer over the 4000–400 cm^{-1} range. Sample (0.083 wt%) was stirred with dry KBr (Merck, spectroscopy grade) and then pressed to form an appropriate tablet.

2.6. Quantum chemical calculations

The geometry of amphetamines was optimized using HF/6-31G(d,p) with the GAMESS (Firefly program package, version 7.1G) [22] and Gaussian 03 [23] program suits. The free energy of solvation, ΔG_s (estimated at room temperature), and other parameters of amphetamine molecules dissolved in water, acetonitrile, and DMFA (assuming infinite dilution) were calculated using the IEFPCM method with the B3LYP/6-31G(d,p) basis set and the HF/6-31G(d,p) geometry (Gaussian 03) [23].

3. Results and Discussion

The A2PS adsorbents are rather microporous than mesoporous [13,24-26], LiCholut EN [27] possesses mainly narrow mesopores but Hypercarb and Carboprep have broader mesopores and smaller S_{BET} and V_p values than other adsorbents (Table 2, Fig. 1). The surfaces of A2PS carbons and polymeric adsorbent are relatively rough because the deviation of the model of slit-shaped (carbons) and cylindrical (LiChrolut EN) pores corresponds to 13-28%. The negative Δw_{sl} values for graphitized carbons are due to the presence of open surfaces (graphite planes) in macropores which are incompletely filled by nitrogen at $p/p_0 \rightarrow 1$. This circumstance corresponds to higher accessibility of the graphitized carbon surfaces for adsorbates than that for other adsorbents. Notice that oxidation (A2PS-O) or reduction (A2PS-H) of the A2PS surface weakly affects the structural characteristics of the adsorbents (Table 2, Fig. 1); however, micro- and mesoporosity of A2PS-O and A2PS-H are slightly greater than that of the initial carbon, but the changes in the pore volume are considerably smaller.

As a whole, an increase in the specific surface area with the same or similar structural and adsorption characteristics causes better recovery rates [13,24-

Table 2. The S_{BET} and V_p values and structural characteristics of adsorbents calculated using the DFT method with the model of slit-shaped (carbons) or cylindrical (LiChrolut EN) pores

Adsorbent	S_{BET} (m^2 g^{-1})	S_{mic} (m^2 g^{-1})	S_{mes} (m^2 g^{-1})	V_p (cm^3 g^{-1})	V_{mic} (cm^3 g^{-1})	V_{mes} (cm^3 g^{-1})	V_{mac} (cm^3 g^{-1})	$\Delta w_{sl(cyl)}$
A2PS	1054	960	94	0.72	0.51	0.20	0.01	0.130
A2PS-O	1162	1053	291	0.71	0.50	0.20	0.01	0.278
A2PS-H	1201	1093	108	0.73	0.52	0.20	0.01	0.272
LiChrolut EN	1512	272	1240	0.83	0.07	0.76	0.0	0.197
Hypercarb	93	37	55	0.62	0.04	0.55	0.55	-0.385
Carborep	130	58	72	0.49	0.05	0.43	0.01	-0.333

Notes. S_{mic}, S_{mes}, and S_{mac} *are the specific surface areas of micro-, meso-, and macropores;*
V_p *is the sum of* V_{mic}, V_{mes}, *and* V_{mac} *volumes of micro-, meso-, and macropores;*
$\Delta w_{sl(cyl)}$ *is the deviation of the pore shape from the slit (cylindrical) shape.*

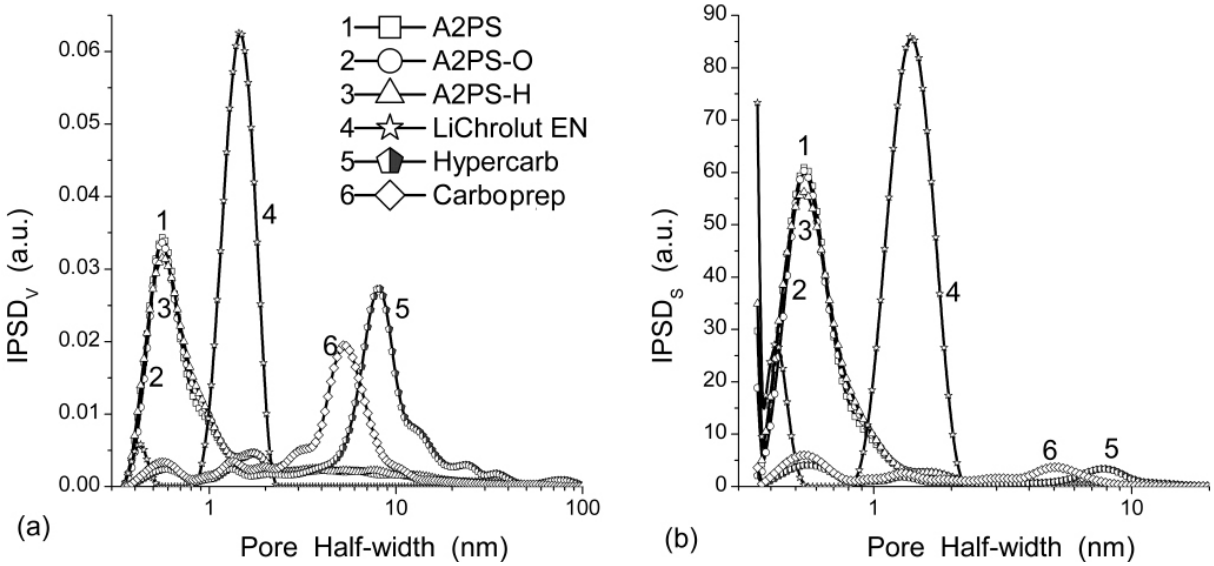


Figure 1. Pore size distributions with respect to (a) pore volume and (b) specific surface area calculated using the DFT method with the models of slit-shaped (carbons) and cylindrical (LiChrolut EN) pores.

26]. Changes in the surface structure, accessibility of pores for molecules of both adsorbates and solvents can strongly affect the recovery rates. The chemical structure of adsorbents used in this study was described in details previously [13,24-27] with the exception of Carboprep. Therefore, this adsorbent is analyzed here in detail.

The presence of O-containing surface functionalities at A2PS adsorbents was shown previously [13] using Boehm titration method and FTIR spectroscopy. Carbonyl groups in the form of carboxyls and lactones were found at the surfaces of the initial and oxidized carbons. Additionally, the presence of cyclic ethers was suggested. Reduction of A2PS by hydrogen led to a significant decrease in the intensity (up to full disappearance) of all the bands of O-containing functionalities, and according to the Boehm titration results, concentration of basic groups increased [13].

The O-containing groups were practically absent at the Hypercarb and Envicarb surface [13]. The FTIR spectrum of Carboprep (Fig. 2) shows bands related to the stretching vibrations of C−H (2918, 2850, and 1454 cm^{-1}), aromatic CC (1630 cm^{-1}), C−O (1306 and 1110 cm^{-1}), and surface O−H groups and/or adsorbed water (3436 cm^{-1}). The FTIR spectra of Carboprep (Fig. 2), Hypercarb, and Envicarb [13] show substantial similarity; however, there is certain difference in a band at 1110 cm^{-1} related to O-containing functionalities which is more intensive for Carboprep (Fig. 2) than for Hypercarb or Envicarb [13]. Consequently, Carboprep is characterized by a slightly larger amount of the O-containing groups than Hypercarb or Envicarb. This can affect the recovery rates of amphetamines from polar solvents because of changes in the effects of solvation/desolvation of the adsorbent surfaces [13,24-27].

The recovery rates (R_1) of amphetamine, hydroxyamphetamine, metoxy- and methylenedioxyaphetamines adsorbed on carbons A2PS, A2PS-O, A2PS-H and reference adsorbents from the aqueous solution (alkalized with ammonia to pH 10

Table 3. Recovery rates R_1 and R_{av}[a] [%] of amphetamine derivatives on studied adsorbents.

Adsorbent	R_{av}	Compound number[b] 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
A2PS	81	72	0	74	87	85	93	79	85	91	93	73	69	82	81	80	63
A2PS-O	86	72	8	80	88	86	96	82	87	92	97	78	83	83	94	92	76
A2PS-H	77	56	3	70	86	80	91	65	80	90	95	72	68	75	80	79	64
Average[c]	81																
LiChrolut EN	90	81	2	90	97	88	90	83	92	92	96	94	87	85	95	94	83
Hypercarb	46	0	0	49	79	14	37	1	2	16	63	94	99	2	63	77	98
Carboprep	59	1	0	82	94	38	64	4	9	48	91	94	98	6	75	90	94
Average[d]	53																

[a] *average recovery calculated for single adsorbent without data for 4-OHA;*
[b] *compounds numbers as in Table 1;.*
[c] *average recovery calculated from R_{av} for A2PS adsorbents;*
[d] *average recovery calculated from R_{av} for graphitized adsorbents.*

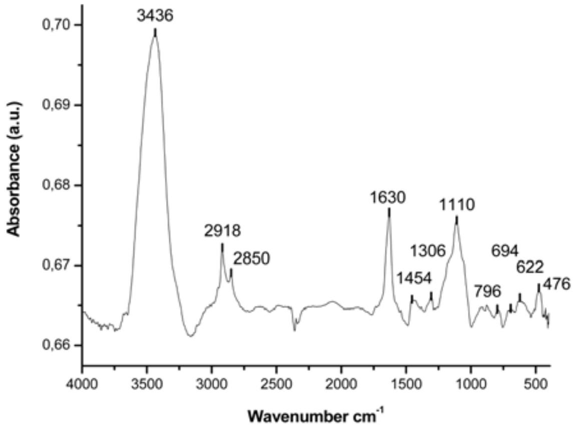


Figure 2. FTIR spectrum of Carboprep.

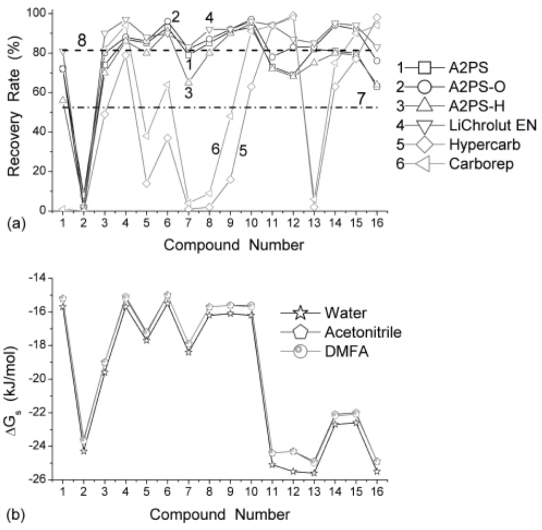


Figure 3. (a) Recovery rates for different adsorbents and different amphetamine derivatives; and average recovery for A2PS-i (line 7) and for graphitized carbons (line 8); (b) free energy of solvation of amphetamine derivatives in (1) water, (2) acetonitrile and (3) DMFA calculated using IEFPCM/B3LYP/6-31G(d,p) (compound numbers are shown in Table 1).

and containing 0.5 vol% of acetonitrile) and desorbed in dimethylformamide are shown in Table 3 and Fig. 3a.

It follows from the individual recoveries and their average values for the particular adsorbents that the most effective beds for extraction of studied amphetamines from the aqueous solutions are activated carbons and polymeric LiChrolut EN. The results acquired for A2PS-i are quite consistent since average recoveries ranged from 77 to 86% (average value 81%). The R_1 values for LiChrolut EN are slightly higher since the average result reaches 90%. Graphitized carbons (especially Hypercarb) give worse results (average 53%). On the other hand the recoveries achieved on Carboprep for some amphetamines (A, 2-MA, 2-MMA, 4-MPA, 3,4-DMA, 5-Br-3,4-DMA, MDEA and 5-Br-MDA) are close to the values obtained for LiChrolut EN. For some of them (3,4-DMA, 5-Br-3,4-DMA and 5-Br-MDA) the recoveries for Carboprep and Hypercarb are equal or higher than that for the polymeric adsorbent. The recoveries of 4-OHA for all studied adsorbents are lower than 10% because of its high hydrophilicity (Fig. 3b) that consequently leads to a great value of the desolvation energy of this compound. Taking into consideration results shown in Table 3 and Fig. 3a it is possible to divide the studied adsorbents into two groups: (I) LiChrolut EN and A2PS-i and (II) graphitized carbons.

In contrast to discussed results, the previous data obtained from N-substituted amphetamines [13] suggested three groups of adsorbents: (i) LiChrolut EN, A2PS and A2PS-O, (ii) A2PS-H, and (iii) graphitized carbons Hypercarb and Envicarb. The highest recoveries (> 90%) were obtained for the first group while for A2PS-H the average recovery was 71%. The results for graphitized adsorbents were ranged from 0 to 80% (average value ≈35%). The recovery rates of amphetamines increased systematically with the length of the alkyl chain attached to the amino group for the adsorption onto graphitized adsorbents and A2PS-H. In the present work a similar effect can also be found for homologues of 4-MA and MDA, *e.g.* the recoveries increase systematically for series 4-MA, 4-MMA,

Table 4. Residual recovery rates of amphetamine derivatives R_2 [%] obtained on LiChrolut EN for the effluents collected after adsorption step (no data for R_2 means 0%) and summarized recoveries $R_\Sigma = R_1{}^a + R_2$ [%].

Adsorbent		Compound number[b]															
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
A2PS	R_2	19	15				10					12	18	7	10	12	29
	R_Σ	91	89	87	85	93	89	85	91	93	0	85	87	89	91	92	92
A2PS-O	R_2	21	10				5					8	6	12			17
	R_Σ	93	90	88	86	96	87	87	92	97	8	86	89	95	94	92	93
A2PS-H	R_2	32	27		11		24	12				23	30	19	12	16	28
	R_Σ	88	97	86	91	91	89	92	90	95	3	95	98	94	92	95	92
LiChrolut EN	R_2	7					11				3						6
	R_Σ	88	90	97	88	90	94	92	92	96	5	94	87	85	95	94	89
Hypercarb	R_2	73	32	10	61	49	82	74	67	24				75	26	19	
	R_Σ	73	81	89	75	86	83	76	83	87	0	94	99	77	89	96	98
Carboprep	R_2	81	9		52	20	76	79	41					69	12		
	R_Σ	82	91	94	90	84	80	88	89	91	0	94	98	75	87	90	94

[a] *values of R_1 from Table 3;*
[b] *compounds numbers as in Table1.*

4-MEA, 4-MPA and MDA, MDMA, MDEA. This is clearly seen in Fig. 3a for graphitized adsorbents. The main reason for the increase in the recoveries for these sets is an increase in the adsorption rate that directly follows from a decrease in the residual recoveries (Table 4, R_2) obtained from the effluents collected after the first step of the SPE experiments. Additionally, results shown in Table 4 suggest that the position of the methoxy substitute at the benzene ring influences the SPE effectiveness of amphetamines. This substituent effect similar to the above described impact of alkyls attached to the amino group is evident only for graphitized adsorbents. The recoveries decrease gradually in series 2-MA, 3-MA, 4-MA and 2-MMA, 3-MMA, 4-MMA. At the same time the efficiency of the adsorption decreases and the quantity of not retained amphetamines in effluents considerably increases (Table 4, R_2).

Calculations of the free energy of solvation (Fig. 3b) and comparison of the ΔG_s values with the R_1 (Fig. 3a) and R_2 (Table 4) values reveal the influence of solvation/desolvation effects on the adsorption efficiency of amphetamines. This effect is especially clearly seen for 4-OHA with low ΔG_s values for all the used polar solvents (Fig. 3b, compound 2) and the minimal recovery rates for all adsorbents (Fig. 3a, and Table 4). Notice that a trend of the ΔG_s curve (Fig. 3b) is close to that of R_1 values (Fig. 3a) for more effective adsorbents of the first group (A2PS-i, LiChrolut EN). For graphitized adsorbents the trend of ΔG_s curve is different than that of R_1 values. This results from the hydrophobic (dispersive) interactions of amphetamine derivatives with these adsorbents and from their surface characteristic as well. Dispersive interactions are weaker than hydrogen bonds, which are the primary interactions of amphetamines with active carbons containing oxygen functionalities on their surface. Moreover applied graphitized adsorbents have much smaller specific surface area and broader pores than activated carbons A2PS-i or LiChrolut EN (Table 2, Fig. 1). Therefore, the trend of the recovery rate (R_1) for graphitized carbons corresponds to a stronger diminution of the R_1 values than the reduction of the ΔG_s values (Fig. 3, *e.g.* compounds 7, 8, and 13).

4. Conclusion

The surface functionalities of the carbon adsorbents with similar morphology have a relatively small impact on the recovery rates of amphetamines since close values are obtained for initial A2PS, oxidized A2PS-O and reduced A2PS-H adsorbents. Stronger effects of the specific surface area and the pore size distributions are observed for Carboprep and Hypercarb with low S_{BET} values. The recovery rates for lots of amphetamines are lower than that for the adsorbents with greater porosity (A2PS-i, LiChrolu EN). The solvation/desolvation effects for the studied derivatives play an important role because the minimal recovery rate is registered for 4-OHA, characterized by substantial solvation effects in all polar solvents used. This effect is much stronger than the influence of the porosity and surface chemistry on the R_1 value for 4-OHA. The effects of the structure of amphetamines are much stronger for graphitized adsorbents Hypercarb and Carboprep because of the enhancement of hydrophobic interactions and low specific surface area in comparison with activated carbons or LiChrolut EN.

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