INVESTIGATION OF HPLC PACKINGS BY LIQUID MIXTURE ADSORPTION

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Summary

The adsorption isotherms of methanol (1) — benzene (2) and benzene (1) — n-heptane (2) mixtures on four different HPLC silica gel were recorded to determine the types of the liquid mixture adsorption isotherms. Based on the experimental results, qualitative statements could be made regarding the relationship between chromatographic and mixture adsorption properties.

In high-pressure liquid chromatographic practice, liquid mixtures consisting of two or more components are used as eluents.

This paper summarizes the first results of a program aiming to find relationship between the empirically established optimum compositions of binary eluents used in high-pressure liquid chromatography [1] and the character of the adsorption isotherms of the packing—liquid mixture system.

The binary eluents used in various ratios according to the literature are listed in Table 1.

Table 1

Binary eluents frequently used in chromatography [1]

Component (1)	(2)	x_1									
Benzene	pentane	0.07	0.08	0.16	0.21	0.30	0.44	0.46	0.68	0.70	0.90
Ethyl ether	pentane	0.03	0.08	0.16	0.20	0.26	0.37	0.40	0.55	0.71	
		0.72	0.90								
Chloroform	pentane	0.05	0.12	0.20	0.21	0.46	0.49	0.63	0.74	0.83	0.97
Dichloromethane	pentane	0.05	0.09	0.12	0.19	0.22	0.26	0.34	0.47	0.52	
		0.53	0.76	0.79	0.91	0.94					
Acetone	pentane	0.04	0.09	0.10	0.15	0.24	0.29	0.40	0.47	0.52	
		0.67	0.81	0.84	0.89	0.97					
Acetone	benzene	0.04	0.08	0.11	0.22	0.30	0.42	0.66	0.70	0.94	
Isopropanol	benzene	0.05	0.08	0.14	0.24	0.44	0.78				
Methanol	benzene	0.09	0.17	0.33	0.64						
Butanol	hexane	0.07	0.16	0.31							

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Experimental

Among the possible techniques to record mixture adsorption isotherms the batchwise multisample method was chosen [2]. Measurement conditions are summarized in Table 2. The contact time required for the equilibrium was determined by preliminary kinetic tests. Concentration changes were followed by measuring refraction index changes with a thermostated double-prism immersion refractometer. Absolute solvents were used in the experiments. The refractive index differences of the liquid pairs used are listed in Table 3. In selecting the liquid pairs, two points were considered. On the one hand, we

Table 2

Experimental conditions

$m_S/m_L \approx 1:5$
$t \approx 25\ °C$
$1\ h < \tau_q < 4\ h$
$\sigma_{n_D} = \pm 2 \cdot 10^{-5}$

where m_S is the mass of the adsorbent,
     m_L is the mass of the liquid phase
     τ_q is the time required for equilibrium being established
     σ_{n_D} is the standard deviation of the refractive index measurements

Table 3

Refractive index differences

Component		Δn_D^{25}
(1)	(2)	
Methanol	Benzene	0.1699
Benzene	n-Heptane	0.1135

Table 4

Manufacturer's data on the chromatographic packings

Adsorbent	Average particle diam. μm	Pore diam.* nm	Characteristics of the adsorbent
LiChrosorb Si 60	10	6	neutral silica gel
LiChrosorb Si 100	10	10	
LiChrosorb RP-2	10		silica gel chemically modified with dimethyldichlorosilane, resistant to hydrolysis
LiChrosorb DIOL	10		Modified silica gel with vicinal hydroxyl groups at the hydrocarbon chain ends; resistant to hydrolysis

   * Isotope molecule exchange studies performed with marked ethanol [3] indicated rapid exchange, i.e. half-time of exchange was found to be less than 10 s.

chose solvents characteristic for the binary eluents in current use in chromatographic practice. On the other hand, it was important that composition changes should be followed rapidly (one isotherm needs the determination of at least 30 points) and with satisfactory sensitivity with the routine analytical techniques at our disposition. Two paths were followed in preparing the adsorbents: they were heated for 48 hours at 110 °C in a vacuum oven; for solvent mixtures with alcohol, heating was preceded by extraction with alcohol. Extraction was continued, till the refractive index of the extracting agent became constant (24–32 hrs). The adsorbents used were products of MERCK; their properties as supplied by the manufacturer's catalogue are listed in Table 4.

Processing of the experimental results

The surface excess isotherms were calculated from the experimental data by Eq. (1); they were then analyzed corresponding to the isotherm classification by Schay and Nagy [2].

$$n_1^{\sigma(n)} = \frac{N}{m}(x_{1,0} - x_1) \tag{1}$$

where N is the number of mols of the mixture, m is the mass of the adsorbent, $x_{1,0}$ and x_1 are the initial and equilibrium concentrations, resp., of the liquid bulk phase.

Further differentiation of the systems is possible by the relationships $\frac{x_1 x_2}{n_1^{\sigma(n)}}$ vs. x_1 for isotherms of type I and II, and $\frac{x_1(x_{1,a} - x_1)}{n_1^{\sigma(n)}}$ vs. x_1 for isotherms of type III and IV. For transition type isotherms, the representation $\frac{n_1^{\sigma(n)}}{x_2} = f(x_1)$ is proposed in the literature [2], among others to decide the question $\beta \lessgtr 1$. The analytical shapes of these functions are given in Eqs (2) to (5):

$$n_1^{\sigma(n)} = n^s(x_1^s - x_1) = n^s x_1^s - n^s x_1 = n_1^s - n^s x_1 \tag{2}$$

$$\frac{n_1^{\sigma(n)}}{x_2} = n_1^s - n_2^s \frac{x_1}{x_2} \tag{3}$$

$$\frac{x_1 x_2}{n_1^{\sigma(n)}} = \frac{1}{n_1^s}\left(\frac{\beta}{\alpha - 1} + \frac{\alpha - \beta}{\alpha - 1}x_1\right) = \frac{1}{n_1^s}\left(\frac{1}{\alpha - 1} + x_1\right) \tag{4}$$

$$\frac{x_1(x_{1,a} - x_1)}{n_1^{\sigma(n)}} = \frac{-x_1^2}{n_1^{\sigma(n)} - a} = \frac{x_1}{a + b} \tag{5}$$

where $\alpha = \dfrac{x_1^s}{x_2^s} \cdot \dfrac{x_2}{x_1}$ is the separation factor; $\beta = \dfrac{a_2}{a_1}$ is the ratio of the space

requirement of the molecules of the liquids; $x_{1,a}$, for type III isotherms, is the intersection point of the straight (extrapolated) portion of the isotherm with the x_1 axis, the "apparent" azeotropic composition, and for type IV isotherm it is the true concentration of the adsorption azeotrope.

Discussion of the results

Our experimental results are presented in Figures 1–12. These isotherms can be classified into types I to IV.

The exact physical interpretation of the isotherm classification by Schay and Nagy is well known from the literature on adsorption [2]; for this reason,

$*-*\ \dfrac{n_1^{\sigma(n)}}{x_2}$ $\odot-\odot\ \dfrac{x_1 x_2}{n_1^{\sigma(n)}}$

$\blacksquare-\blacksquare\ n_1^{\sigma(n)}$ $\triangle-\triangle\ \dfrac{x_1(x_{1,a}-x_1)}{n_1^{\sigma(n)}}$
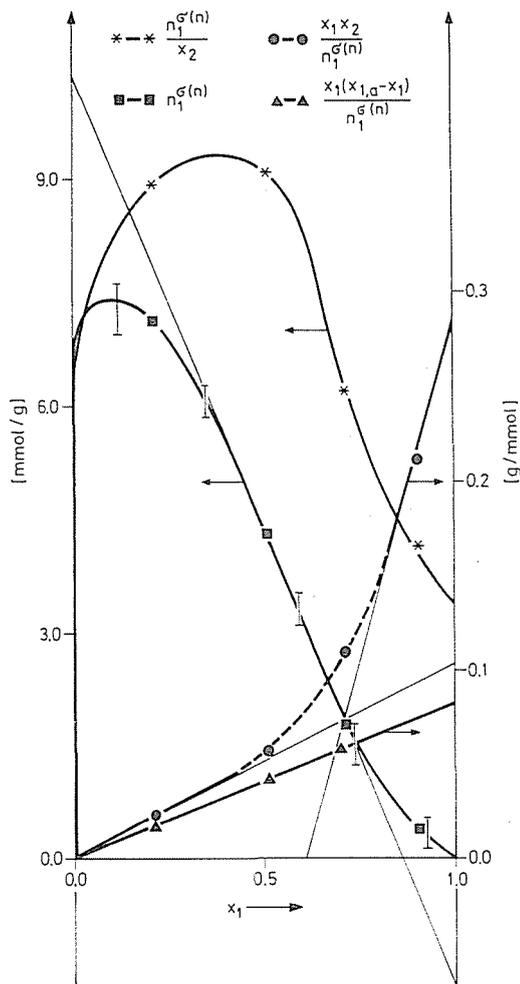
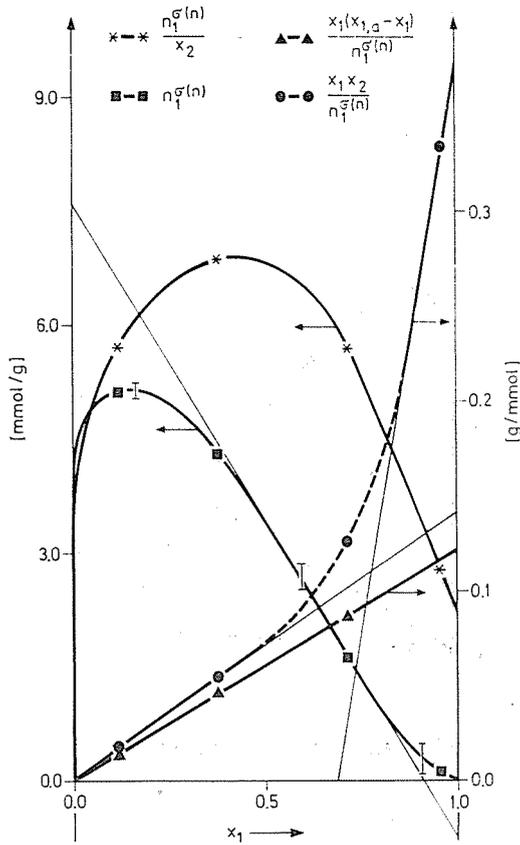*Fig. 1.* Methanol (1) and benzene (2) mixtures on LiChrosorb Si 60

Fig. 2. Methanol (1) and benzene (2) mixtures on extracted LiChrosorb Si 60

only the most important characteristics shall be briefly pointed out here.

Type I: component (1) is adsorbed preferentially over the total concentration range. However, no magnitudinal differences exist between the concentrations of the interfacial layer and the bulk phase.

Type II: above a defined concentration value, in a first approach only component (1) will be adsorbed in the interfacial layer, while the concentration of the bulk phase may vary within relatively wide limits.

Type III: above a defined concentration value, in a first approach the composition of the interfacial layer may be considered constant; at $x_1 \rightarrow 1$ values the composition of the interfacial layer approaches that of the bulk phase.

Type IV: within a defined concentration range, adsorption of component (1) is positive, and subsequently that of component (2) is positive. In an
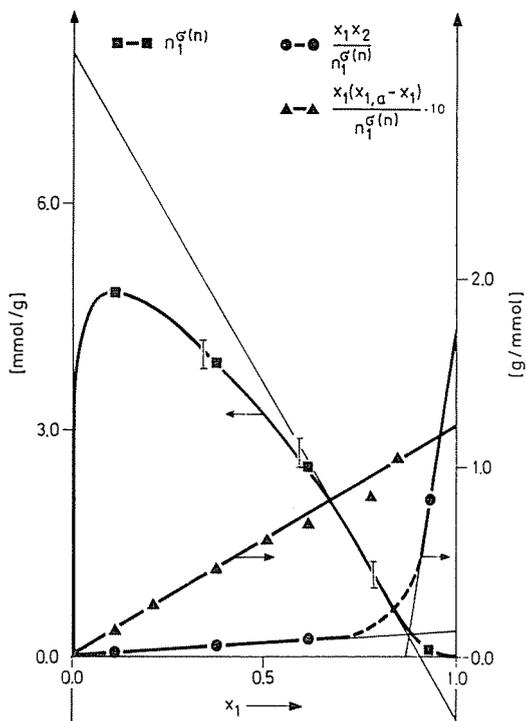
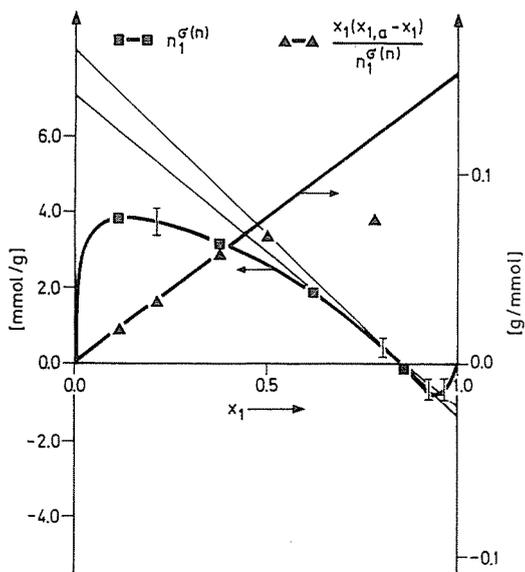*Fig. 3.* Methanol (1) and benzene (2) mixtures on LiChrosorb Si 100

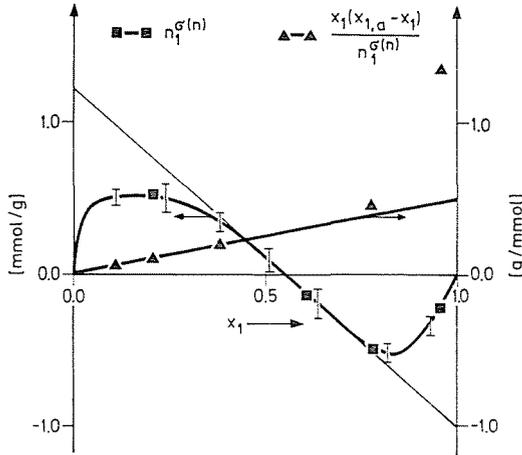*Fig. 4.* Methanol (1) and benzene (2) mixtures on extracted LiChrosorb Si 100

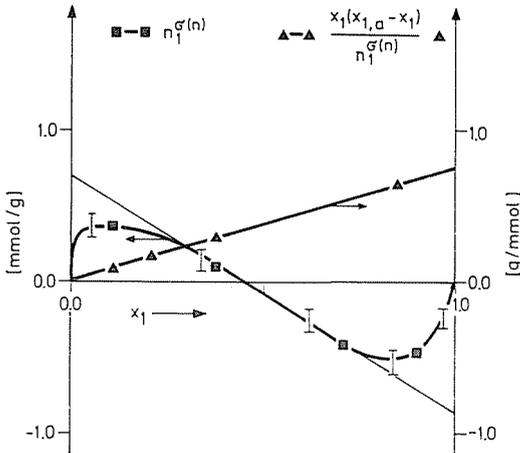*Fig. 5.* Methanol (1) and benzene (2) mixtures on LiChrosorb RP-2

Fig. 6. Methanol (1) and benzene (2) mixtures on extracted LiChrosorb RP-2

intermediate concentration range, in a first approach, the composition of the interfacial layer is constant, while the composition of the bulk phase changes continuously.

Let us start from the chromatographic experience that retention of the components to be separated can be affected by varying the composition of binary eluents. Comparing this with the physical sense of the individual isotherm types, the following qualitative statements can be made.

(i) If the isotherm is of the type I, the compositions of the interfacial layer and the bulk phase are both responsible for the change of the retention factor.
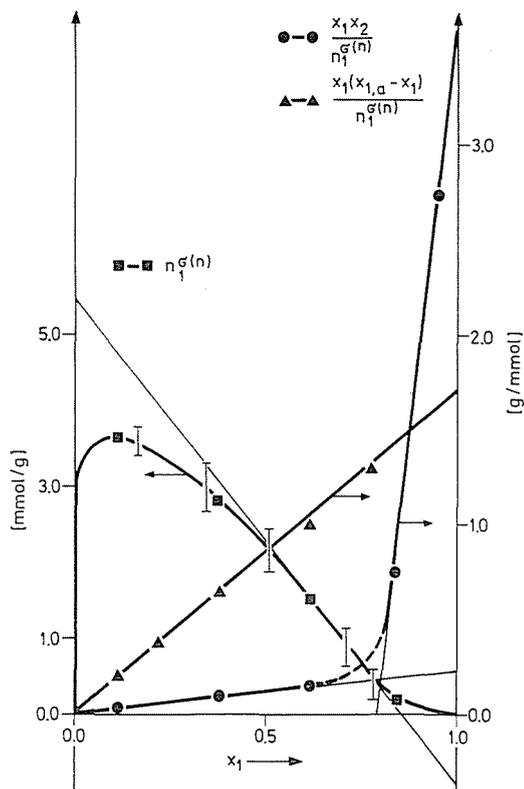
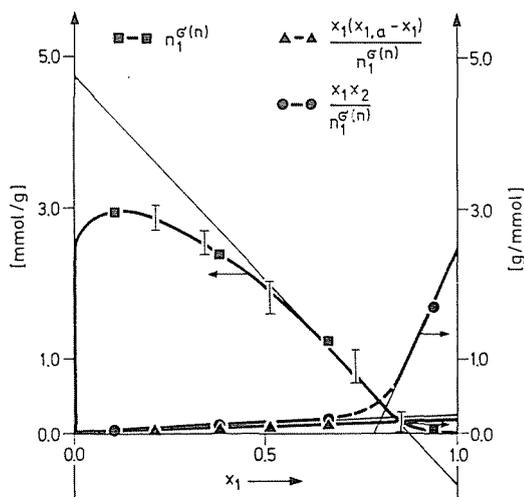*Fig. 7.* Methanol (1) and benzene (2) mixtures on LiChrosorb DIOL

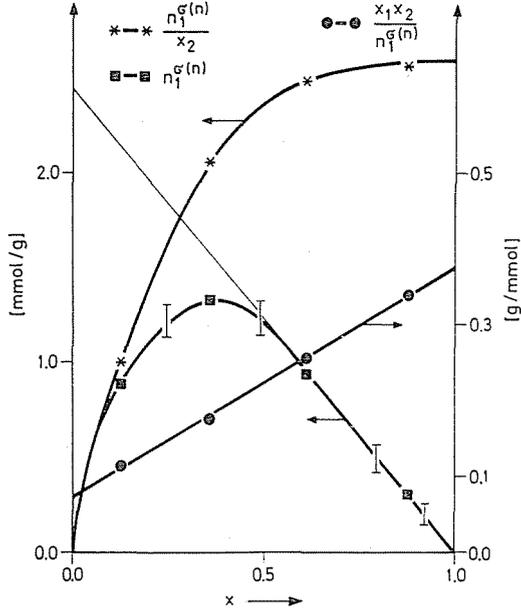*Fig. 8.* Methanol (1) and benzene (2) mixtures on extracted LiChrosorb DIOL

Fig. 9. Benzene (1) and n-heptane (2) mixtures on LiChrosorb Si 60
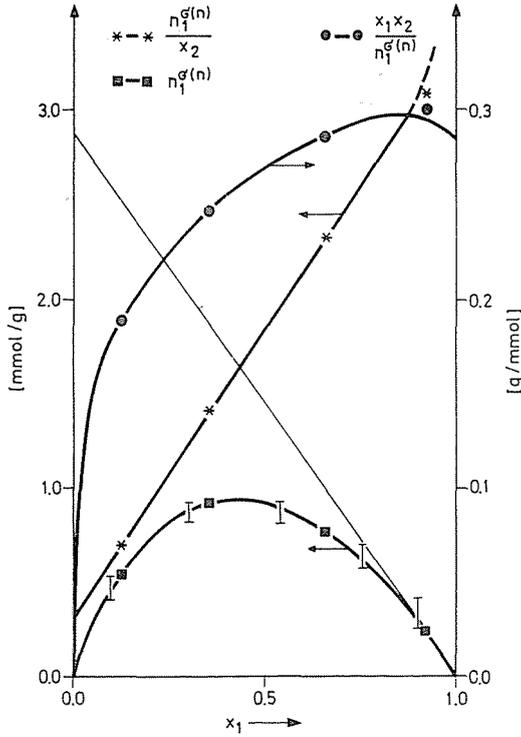

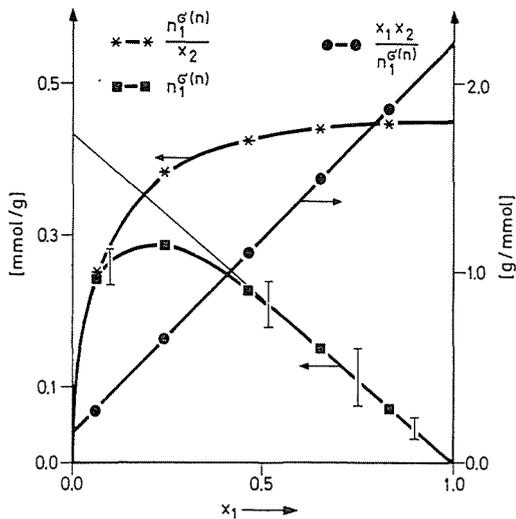*Fig. 10.* Benzene (1) and n-heptane (2) mixtures on LiChrosorb Si 100

Fig. 11. Benzene (1) and n-heptane (2) mixtures on LiChrosorb RP-2
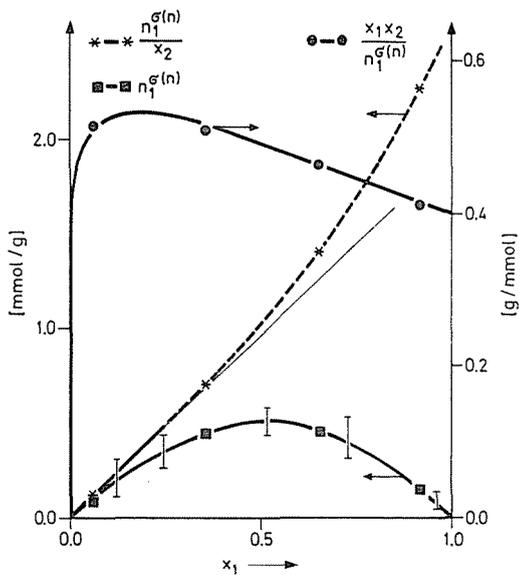

Fig. 12. Benzene (1) and n-heptane (2) mixtures on LiChrosorb DIOL

(ii) If the isotherm is of type II to IV, and the concentration change of the bulk phase is within the linear portion of the representation $n_1^{\sigma(n)}$ vs. x_1, the retention factor is practically not affected by the composition of the interfacial layer, i.e. changes can be caused exclusively by the bulk phase. For the non-linear portion of types II and III the statement in (i) is valid, while for type IV in the range $x_1 \to 1$, the reversal of the sign of adsorption may cause the change in the retention factor.

Table 5

Characteristic data of representations for mixtures of methanol (1) and benzene (2)

Adsorbent	Type of isotherm	(a)		(b)	(c)	(d)
		n_1^s	n_2^s	$\dfrac{1}{tg\,\delta_1}$	$\dfrac{1}{tg\,\delta_2}$	$\dfrac{1}{tg\,\delta'}$
				mmol/g		
LiChrosorb Si 60	III	10.35	1.65	9.52	1.34	11.90
LiChrosorb Si 60 extracted	III	7.55	0.70	7.04	0.81	8.20
LiChrosorb Si 100	III	8.00	0.75	7.14	0.08	8.20
LiChrosorb Si 100 extracted	IV	7.00...	1.20...	–	–	6.49
		8.20	1.40			
LiChrosorb RP-2	IV	1.22	1.02	–	–	2.00
LiChrosorb RP-2 extracted	IV	0.70	0.87	–	–	1.33
LiChrosorb DIOL	III	5.50	1.00	4.17	0.06	5.88
LiChrosorb DIOL extracted	III	4.75	0.7	4.00	0.09	5.00

(a) By extrapolation, from the representation $n_1^{\sigma(n)}$ vs. x_1

(b) reciprocal initial slope of the representation $\dfrac{x_1 x_2}{n_1^{\sigma(n)}}$ vs. x_1

(c) reciprocal final slope of the representation in (b)

(d) reciprocal slope of the linear portion of the representation $\dfrac{x_1(x_{1,a} - x_1)}{n_1^{\sigma(n)}}$ vs. x_1

Table 6

Characteristic data of representations for mixtures of benzene (1) and n-heptane (2)

Adsorbent	Type of isotherm	(a)	(b)	(c)	
		n_1^s	$\dfrac{1}{tg\,\delta_1}$	$n_1^{\sigma(n)}/x_2$	$(x_1 \to 1)$
			mmol/g		
LiChrosorb Si 60	II	2.44	3.33	2.58	
LiChrosorb Si 100	I–II	2.68	3.29	3.0	
LiChrosorb RP-2	II	0.435	0.49	0.45	
LiChrosorb DIOL	I	–	2.11	?	

(a) By extrapolation, from the representation $n_1^{(n)}$ vs. x_1

(b) reciprocal initial slope of the representation $\dfrac{x_1 x_2}{n_1^{\sigma(n)}}$ vs. x_1

Table 7

Specific surface area values (m^2/g) for LiChrosorb Si 60 determined by various methods

Method of determination	Methanol (1) and benzene (2)		Benzene (1) and n-heptane (2)
	Non-extracted adsorbent	Extracted adsorbent	
A	1275	834	447
B	1021	738	609
C	—	—	472
D	1119	771	—
E	231		231
F	500		500

Table 8

Specific surface area values (m^2/g) for LiChrosorb Si 100 determined by various methods

Method of determination	Methanol (1) and benzene (2)		Benzene (1) and n-heptane (2)
	Non-extracted adsorbent	Extracted adsorbent	
A	889	878...820	527
B	679	—	602
C	—	—	549
D	771	610	—
E	261		261
F	300		300

Table 9

Specific surface area values (m^2/g) for LiChrosorb RP-2 determined by various methods

Method of determination	Methanol (1) and benzene (2)		Benzene (1) and n-heptane (2)
	Non-extracted adsorbent	Extracted adsorbent	
A	301	225	80
B	—	—	90
C	—	—	82
D	188	125	—
E	229		229
F	350		350

Table 10

Specific surface area values (m^2/g) for LiChrosorb DIOL determined by various methods

Method of determination	Methanol (1) and benzene (2)		Benzene (1) and n-heptane (2)
	Non-extracted adsorbent	Extracted adsorbent	
A	700	575	—
B	398	384	384
C	—	—	?
D	553	470	—
E	189		189
F	250		250

In Tables 5 and 6 the types and basic characteristics for specific surface area determination of the adsorption isotherms shown in the figures are summarized, based on the methods known from the literature [2].

The values of the specific surface areas determined by different methods are listed in Table 7. The extrapolation method by Schay and Nagy is marked by A; according to this method, $a_s = n_1^s a_1 + n_2^s a_2$, where the molar surface requirements are 94 m^2/mmol for methanol, 183 m^2/mmol for benzene and 256 m^2/mmol for n-heptane. In method B the slopes of the initial and final portion, resp., of the representation $\dfrac{x_1 x_2}{n_1^{\sigma(n)}}$ vs. x_1 are utilized to calculate specific surface area by the relationship $a_s = \left(\dfrac{1}{\text{tg } \delta_1} + \dfrac{1}{\text{tg } \delta_2} \right) a_1$. In method C specific surface area is obtained by the expression $a_s = a_1 \left(\lim\limits_{x_1 \to 1} \dfrac{n_1^{\sigma(n)}}{x_1} \right)$. According to method D one calculates with the expression $a_s = \dfrac{1}{\text{tg } \delta'} a_1$ utilizing the slope of the linear portion of the representation $\dfrac{x_1 (x_{1,a} - x_1)}{n_1^{\sigma(n)}}$ vs. x_1. Methods E and F yield the BET surface area. In method E nitrogen gas was used with a sorptometer (dynamic technique); the results were evaluated by using the two-parameter BET equation. The values marked by F are those reported by MERCK; in the catalogue, however, neither the adsorptive nor the manner of evaluating the results are referred to. A possible explanation of the differences significant in some cases will need further experiments and theoretical considerations.

References

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