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STUDY OF THE ADSORPTION EFFECTS AT THE SURFACE OF POLY-(ETHYLENE GLYCOL)-COATED COLUMN PACKINGS

D. F. FRITZ, ARAKSI SAHIL* and E. sz. KOVÁTS

Laboratoire de Chimie Technique de l'École Polytechnique Fédérale de Lausanne, 1015 Lausanne (Switzerland)

SUMMARY

Gas chromatographic data for a series of solutes on a purified dimethoxypoly-(ethylene glycol) are presented. The retention volumes were measured on columns prepared with two supports, one wettable and the other partially wettable by the stationary phase, at four temperatures and on four column packings with different loadings. The data permitted the evaluation of equilibrium parameters characterizing solute absorption in the stationary phase and solute adsorption at the different interfaces in the column. An attempt to interpret the results is described.

INTRODUCTION

The "relative adsorption" of solutes at liquid-solid and liquid-gas interfaces can best be studied with solvents of intermediate polarity which allow the simultaneous determination of solution and adsorption data with reasonable precision. Data at high solute dilution ("ideal dilution") can be obtained relatively easily in the dynamic measuring system of the gas chromatographic column if information is available on the surface areas of the different interfaces (support-liquid-gas) in the column. To circumvent the experimental determination of the actual surface areas, the model proposed by Martin¹ assumes that the surface area of the supported liquid in the column is equal to that of the support. As pointed out by Serpinet², this model presumes complete wettability and cannot be applied to partially wetted supports. The formation of a uniform film implies that a support with a high surface energy was used. Unfortunately, in this case adsorption at the liquid-solid interface cannot be excluded. Supports of low surface energy will be only partially wetted by a polar liquid. An extension of the model of Martin, proposed³ for the case of partial wetting, assumes that the sum of the surface areas, that of the liquid and of the non-wetted part of the support, equals the surface area of the support. Certainly, this approximation is not nearly as good as that for the case of complete wettability, but, it will allow the evalua-

* Partially from the Doctoral Thesis of A.S

tion of gas chromatographic data. We propose, therefore, to use eqn. 1, derived elsewhere³, for the interpretation of the data presented in this paper:

$$V_{g,j} = V_{g,j}^0 \{1 - \alpha [Y_j^{(\lambda\gamma)} + Y_j^{(\lambda\sigma)}] \zeta / \mathcal{R}T\} + (1 - \alpha) RT\zeta/k_j \quad (1)$$

where $V_{g,j}^0$ is the specific retention volume of the solute, j , in the absence of adsorption effects; α is the proportion of the surface covered by the stationary phase and $\zeta = \alpha_\sigma w_\sigma / w_\lambda$ (α_σ is the specific surface area of the support, w_σ and w_λ are the weights of the support, σ , and the stationary liquid, λ , respectively, in the column). The specific retention volume, $V_{g,j}^0$, accounts for solution phenomena. It permits the calculation of Henry's molal coefficient, $g_j (= RT/1000 V_{g,j}^0)$, which in turn is related to the difference of the standard chemical potential, $\Delta\mu_j^{(\lambda)}$, of the solute between the ideal dilute gas and liquid phases. The same is true, *mutatis mutandis*, for Henry's coefficient for the adsorption on the non-covered solid surface. The following equations express these coefficients in terms of the thermodynamic functions that characterize the dissolution and the adsorption equilibria:

$$RT \ln g_j = \Delta\mu_j^{(\lambda)} = \Delta H_j^{(\lambda)} - T\Delta S_j^{(\lambda)} + \Delta C_{P,j}^{(\lambda)} [T - T^\dagger - T \ln(T/T^\dagger)] \quad (2)$$

$$RT \ln k_j^{(\sigma)} = \Delta\mu_j^{(\sigma)} = \Delta H_j^{(\sigma)} - T\Delta S_j^{(\sigma)} + \Delta C_{P,j}^{(\sigma)} [T - T^\dagger - T \ln(T/T^\dagger)] \quad (3)$$

Thereby, $\Delta H_j^{(\beta)}$, $\Delta S_j^{(\beta)}$ and $\Delta C_{P,j}^{(\beta)}$ are the differences in the molar enthalpy, molar entropy and molar heat capacity of the solute (at constant pressure) between the ideal dilute gas phase and the phase $\beta (= \lambda \text{ or } \sigma)$.

The terms $Y_h^{(\lambda\beta)}$ account for interfacial adsorption and are related to the initial change of the interfacial tension, $\gamma^{(\lambda\beta)}$, with the solute concentration in the bulk, $m_j^{(\lambda)}$:

$$Y_j^{(\lambda\beta)} = \left[\frac{\partial \gamma^{(\lambda\beta)}}{m_j^{(\lambda)}} \right]_{T^\dagger} - \left[\frac{\partial s^{(\lambda\beta)}}{\partial m_j^{(\lambda)}} \right]_{T^\dagger} (T - T^\dagger); m_j^\lambda \rightarrow 0 \quad (4)$$

where T^\dagger is a chosen standard temperature, $s^{(\lambda\beta)}$ is the surface entropy either at the gas-liquid, $\lambda\gamma$ ($\beta = \gamma$), or at the liquid-solid, $\lambda\sigma$ ($\beta = \sigma$), interface.

In order to acquire data permitting the study of solution parameters in the bulk and adsorption data at the surface, firstly the polar liquid and the support had to be chosen. Dimethoxypoly(ethylene glycol) was considered to be a good model solvent for several reasons. First, poly(ethylene glycols) are prepared by polyaddition resulting in a polymer with a relatively narrow molecular weight distribution (Poisson-distributed degree of polymerization). Thus, such polymers are relatively well characterized and, especially those of high molecular weight, resemble monodisperse systems. Secondly, they can be considered to be of moderate polarity and thirdly, their thermal stability is excellent if contact with air is carefully avoided. Finally, a polymer "without end groups" can be prepared by methoxylation of the terminal hydroxyl groups (the synthesis of the methoxy derivative will be described in a forthcoming paper). We succeeded in transforming the end groups to a large extent with a procedure typically leaving less than 10^{-3} mol kg^{-1} of unreacted hydroxyl groups. An analytical

method, developed in our laboratory⁴, showed that the residual hydroxyl content in the polymer used in this investigation (molecular weight 2177 ± 27) was very low and amounted to $6.7 \cdot 10^{-4}$ ml kg^{-1} .

It would be desirable to have a polymer without end groups, as solution data on polymers with end groups cannot be interpreted unambiguously, especially when comparing polymers of different molecular weights. There will always be doubts as to whether a certain effect originates from the different end group concentrations or is caused by the different size of the polymer⁵⁻⁷. The general formula of the dimethoxy-(polyethylene glycols) is $\text{H} \{ \text{CH}_2\text{-O-CH}_2 \}_n \text{H}$. Consequently, it can be considered as a hydrogen-terminated poly-(2-oxapropane). This smallest and most neutral substituent will certainly minimize the end group effect but cannot eliminate it. The steric environment of the ether groups near the end is different from that inside the polymer chain.

It was intended to apply two different supports, one wettable (high surface energy) and the other non-wettable (low surface energy) by the polymer. The use of a support of high surface energy involves a certain risk. Eqn. 1 shows that the two terms responsible for the interfacial adsorption, $Y_f^{(\lambda\gamma)}$ and $Y_f^{(\lambda\sigma)}$, appear as a sum and there is no simple means of determining them separately. On high-energy supports, the liquid-solid interfacial energy, $\gamma^{(\lambda\sigma)}$, could also be high, and consequently the term $Y^{(\lambda\sigma)}$ might also make an important contribution. Non-treated silicas have wettable, high-energy surfaces. As poly(ethylene glycols) have repeatedly been proposed for their deactivation^{8,9}, one could hope that the use of a thermally deactivated silica, coupled with the special interaction of the basic ether groups of the polymer with the residual silanols at the surface, would result in an inactive interface. Therefore, Chromosorb G was chosen as the wettable support. An aliquot of this material, silanized in our laboratory by fixing on it a dense monomolecular trimethylsiloxy layer, was used as the partially wettable support.

With these materials, data were obtained that permit the evaluation of the parameters in eqn. 1 by assuming that the term responsible for the liquid-solid interfacial adsorption, $Y_f^{(\lambda\sigma)}$, is negligible.

EXPERIMENTAL

Materials

Solutes. The substances used as solutes were obtained from Fluka (Buchs, Switzerland) and were used without additional purification.

Stationary liquid. This was prepared from a poly(ethylene glycol) of nominal molecular weight 2000 (Fluka) purified as described elsewhere⁴. The molecular weight was calculated⁴ from the concentration of hydroxyl end groups in the polymer and amounted to 2149 ± 27 (average of six determinations). The method of methoxylation of this polymer will be described in a forthcoming paper. The molecular weight of the product, dimethoxypoly(ethylene glycol), was calculated to be $2149 + 28 = 2177 \pm 27$. The residual hydroxyl content was 6.7×10^{-4} mol kg^{-1} (average of six determinations).

Supports. Two kinds of support were used. One was the 200-250- μm diameter fraction of non-acid-washed Chromosorb G from Johns-Manville (Denver, Colo., U.S.A.) without any treatment [support N (non-silanized)]. Part of this fraction was first digested with 20% nitric acid at room temperature for 48 h, then washed with distilled water, dried at 110° and 15 torr and made to react with trimethylsilanol in

the presence of ammonia vapour at 100° for 24 h in three successive treatments [support S (silanized)]. The surface area of the support was calculated from the nitrogen isotherm by the standard BET method, using 16.2 Å² as the surface area occupied by one nitrogen molecule. The isotherms were determined with an automatic apparatus (Sorptomatic from Carlo Erba, Milan, Italy). The specific surface area of support N was $0.54 \pm 0.03 \text{ m}^2\text{g}^{-1}$ (average of three determinations). The same figure was assumed to be valid for support S.

Column packings. These were prepared by wetting an exact amount of support (20–40 g weighed with a precision of ± 0.01 g) with a methanolic solution of an exact amount of stationary phase (1–5 g weighed to ± 0.001 g) and evaporating the solvent at 70–80° under slightly reduced pressure in an argon atmosphere. Finally, the dry packing was kept at 10^{-3} torr at room temperature overnight. Contact with oxygen was carefully avoided when handling the prepared packing. Columns were filled under argon pressure; the prepared columns, if not used, were stored filled with high-purity argon and both ends closed airtight with a metal cap; the remaining column packings were stored under argon in sealed ampoules.

The weight of the packing in the column was calculated as the difference of the weight of the empty and packed columns (see Table I). After prolonged use a slight weight loss was always observed, which was attributed to the evaporation of last traces of methanol. The amount of the stationary liquid in the column was therefore calculated by taking into account this weight loss, as indicated in Table I.

Apparatus

The apparatus used for the determination of retention data was an assembly of a slightly modified Packard-Becker (Delft, The Netherlands) Model 419 chromatograph with accessory equipment for temperature and flow control. A substantial reduction in the temperature gradient was attained by inserting an additional box of aluminium into the column oven as described elsewhere¹⁰. For the measurement of the temperature gradient (see Fig. 1), a cube-shaped wire skeleton was built, slightly smaller than the dimensions of the oven (each edge 17.5 cm). A chromel wire was fixed on the

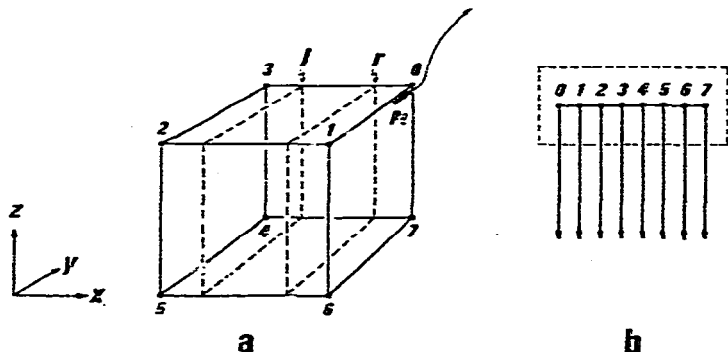


Fig. 1. Scheme of the disposition of measuring elements for the determination of the temperature and its gradient. Arrangement of the platinum resistance thermometer, Pt, and of the soldering points of the alumel (full line)–chromel (open line) thermocouple [shown in (b)] on the wire skeleton. The planes of the mean position of the left (l) and right (r) column are indicated by dashed lines. For details, see text.

skeleton and an alumel wire was soldered to it at each corner. The common reference point for the thermocouples 1-7 was the solder point zero. The temperature difference between 0 and 1-7 was measured with a microvoltmeter (digital voltmeter type Trendicator 400 A, with multipoint selector type 405-A; Doric Sci. Div., San Diego, Calif., U.S.A.). The absolute temperature was measured in position 0 with a platinum resistance thermometer (type DS-100-T5, Doric) which was calibrated by the Eidg. Amt für Mass und Gewichte (Berne, Switzerland) between 0° and 400° with a precision of $\pm 0.1^\circ$ for the absolute temperature.

Measurements

Flow-rate. The flow-rate was measured at the inlet of the column with a flow control and flow meter unit from Brooks Instrument Div. (Veenendaal, The Netherlands; flow control unit type 4251-IA-2DEO and a mass flow sensor type 5841-2).

The mass flow meter was calibrated to give a digital display of the volume flow-rate, \dot{V}_f , of the helium carrier gas at 760 torr and 0°. During a day, a more or less regular increase of 1% of the flow-rate was observed, as checked with a soap-film flow meter. Intermediate values for the day were calculated with the help of methane retention times, measured between every second chromatogram. The relative error of these corrected flow-rates used for calculations is estimated to be about $\pm 0.2\%$.

Column temperature. This was calculated as follows. The absolute temperature was read at position 0 (T_0) and the temperature differences (δT_i) were measured between this point and points 1-7 (the maximal temperature difference between two corners was typically 0.4°). A mean temperature was calculated for the left- and right-hand sides of the cube in the z - y plane using the following equations (see Fig. 1):

$$\overline{\delta T}_l = (\delta T_2 + \delta T_3 + \delta T_4 + \delta T_5)/4; \quad \overline{\delta T}_r = (\delta T_1 + \delta T_6 + \delta T_7)/4 \quad (5)$$

As the coils of the columns were parallel to the z - y plane (see Fig. 1a) and the centres of the columns were situated at 1/4 and 3/4 of the full distance along the x -axis, the average temperatures of the left-hand side (l) and right-hand side (r) columns are given as

$$T_{c,l} = T_0 + (3\overline{\delta T}_l + \overline{\delta T}_r)/4 \text{ and } T_{c,r} = T_0 + (\overline{\delta T}_l + 3\overline{\delta T}_r)/4 \quad (6)$$

Pressures. The inlet and outlet pressures necessary for calculating the mean column pressure were determined by considering the slight flow resistance of the injector tubing at the inlet and that of the detector at the outlet of the column. The inlet resistance (R_i) was determined at different temperatures and flow-rates by omitting the column and measuring the flow-rate after the injector (\dot{V}'):

$$R_i = \Delta P_i / \dot{V}' \quad (7)$$

To measure the outlet resistance (R_o), an empty column was placed in the apparatus and the total flow resistance was determined by measuring the flow-rate at the detector outlet, \dot{V}'' , giving

$$R_{tot} = R_i + R_o = (\Delta P_i + \Delta P_o) / \dot{V}'' \quad (8)$$

Both resistances, R_i and R_o , depended slightly on the temperature. However, the resulting correction was so small that a mean value was used in the calculations ($R_i = 0.10$ and $R_o = 0.03$ torr min ml⁻¹). With the packed column in the apparatus, the atmospheric pressure, P_a , and the pressure drop, $\Delta P'$, were measured (Ashcroft Digigauge from Dresser Industries, Stratford, Conn., U.S.A.) and the volumetric flow-rate was calculated at the inlet [$\dot{V}'_i(T_c)$] and at the outlet [$\dot{V}'_o(T_c)$] of the column for the given column temperature. The true pressure drop is then calculated as

$$\Delta P = \Delta P' - \dot{V}'_i(T_c)R_i - \dot{V}'_o(T_c)R_o \quad (9)$$

The true outlet and inlet pressures are then given by

$$P_o = P_a + \dot{V}'_o(T_c)R_o; \quad P_i = P_o + \Delta P \quad (10)$$

Gross retention times. These values (t_R) were determined as being the difference between the start and the peak maximum by using the Datachrom-2 evaluation system from Kratos-Instem (Stafford, Great Britain). For exact time measurements the original clock of the computer (type PDP-11-05 from Digital Equipment Corp., Maynard, Mass., U.S.A.) was replaced by a quartz frequency-controlled clock. The reproducibility of the time measurements was ± 0.2 sec. The long-range stability of the clock was such that it did not differ more than 1 sec day⁻¹ from real time (error less than 30 ppm). The dead time was determined as the gross retention time of methane and was subtracted from every determination. In this way a net retention time, t_N^* , was obtained.

Chromatographic data. Measurements were made on the substances listed in Table II at near 70°, 90°, 110° and 130° on the eight columns listed in Table I. The net retention volume, V_N^* , was calculated with the flow-rate corrections assuming that the helium carrier gas is an ideal gas:

$$V_N^* = t_N^* \dot{V}'_f(T_c/273.15) (760/P_o) J_3^2 \quad (11)$$

TABLE I

COLUMN PACKING CHARACTERISTICS

Percentages, p , are given as weight of stationary liquid/total weight of the packing. The columns were coiled Pyrex tubes (coil diameter 15.5 cm) of I.D. 0.4 cm. Column lengths were 330 cm except for nominal loading 33%, where the length was 230 cm.

Support	Percentage of liquid		Weight of packing in the column		Weight of liquid in the column $w_1 = p_1 w_{tot} / 100$ (g)
	Nominal, p_1 (%)	As prepared, p_2 (%)	Filled in, w'_{tot} (g)	After use, w_{tot} (g)	
N	4	4.001	24.44	24.40	0.976
	11	11.110	29.55	29.46	3.273
	20	20.002	34.96	34.93	6.987
	33	33.33	21.24	21.22	7.073
S	4	4.003	24.07	24.05	0.963
	11	11.111	27.59	27.51	3.057
	20	20.001	34.43	34.36	6.872
	33	33.33	19.56	19.55	6.516

where t_N^* is the net retention time by assuming that methane is a non-retained substance and \dot{V}_f is the mass flow-rate expressed in volume flow-rate at 0° and 760 torr. The determination of the column temperature, T_c , was explained above. The correction factor, $J_2^2 = (3/2)[(P_1/P_0)^2 - 1]/[(P_1/P_0)^3 - 1]$, was calculated with the aid of the corrected inlet and outlet pressures, P_1 and P_0 . After an initial evaluation of the specific retention volumes, V_N^*/w_λ , the specific retention volume of methane could be estimated from the regularity of the thermodynamic data for the n -alkanes. It was nearly independent of the temperature in the experimental range and amounted to about 0.3 ml g⁻¹. The specific retention volume of a given substance was then calculated by assuming that methane was not adsorbed at the surface of the liquid:

$$V_g = (V_N^*/w_\lambda) + V_g(\text{methane}) \approx V_g^* + 0.3 \quad (12)$$

Note that these specific retention volumes are according to the general nomenclature, V_g^T values measured at the column temperature.

Specific retention volumes. The experimental specific retention volumes are not given explicitly in this paper (a table of individual values can be supplied by the authors on request). The data on columns with a 33% nominal loading were systematically higher and were omitted from the calculation of the data in Table II. The data on all other columns were evaluated on the basis of eqn. 1 by the following scheme:

(i) First for each given substance j , on each given column, i , the dependence of $y_{j,i} = RT \ln V_g(j/i)$ on temperature was expressed as

$$y_{i,j} = a_{i,j} + b_{i,j}T + c_{i,j}T^2 \quad (13)$$

by fitting the experimental values by the method of least squares. The first derivative was then used to correct the experimental values of y for small temperature deviations from the desired values (70°, 90°, 110° and 130°). The largest deviation to account for was 0.6°. The corrected y values were transformed into specific retention volumes, which were now considered as experimental data determined at exactly 70°, 90°, 110° and 130°.

(ii) Eqn. 1 was fitted to the corrected experimental values of columns N by a numerical iterative regression calculation.

(iii) With the aid of regression coefficients the specific retention volumes were re-calculated and the difference, $\delta = V_g(\text{regr}) - V_g(\text{exp})$, was used to determine the relative error at every point:

$$\delta_{\text{rel}} = \delta/V_g(\text{regr}) \quad (14)$$

From these data, the variance of the specific retention volume can be calculated for each substance as

$$V[V_g(j/i)] = \sum_{\text{rel } i,j} \delta_{i,j}^2 / (N_{i,j} - \nu) = \sigma_{\text{rel}}^2 \quad (15)$$

where N is the number of experimental points and ν the number of parameters ($\nu = 5$). The regression coefficients are summarized in Table II.

TABLE II
EXPERIMENTAL RESULTS CALCULATED FROM SPECIFIC RETENTION VOLUMES ON DIMETHOXYPOLY(ETHYLENE GLYCOL)
OF MOLECULAR WEIGHT 2177 ± 27

I	SUPPORT S (100° C)				SUPPORT N (100° C)				SUPPORT S (100° C)						
	ΔH_i^{\ddagger} cal. mol ⁻¹	ΔS_i^{\ddagger} cal. deg ⁻¹ mol ⁻¹	$\frac{\partial \ln V_i^{\ddagger}}{\partial \ln m_i}$ deg ⁻¹	$\sigma_{ii}(M)$	$\frac{\partial \ln V_i^{\ddagger}}{\partial \ln m_i}$ deg ⁻¹	$\sigma_{ii}(M)$	$\frac{\partial \ln V_i^{\ddagger}}{\partial \ln m_i}$ deg ⁻¹	$\sigma_{ii}(M)$	$\frac{\partial \ln V_i^{\ddagger}}{\partial \ln m_i}$ deg ⁻¹	$\sigma_{ii}(M)$	ΔH_i^{\ddagger} cal. mol ⁻¹	ΔS_i^{\ddagger} cal. deg ⁻¹ mol ⁻¹	$\sigma_{ii}(M)$		
1. PENTANE	-8936	-14.64	6.27	-89.12	-0.09	2.0(12)	300.0	0.00	0.00	0.30	2.94	0.02	-81.19	9(16)	
2. HEXANE	-8811	-15.71	6.76	-89.18	-0.21	1.8(12)	659.0	0.00	0.00	0.30	2.97	0.04	-39.91	6(16)	
3. HEPTANE	-8734	-16.72	11.10	-82.3	-0.29	0.9(12)	789.0	0.00	0.00	0.30	2.71	-0.07	-40.08	4(16)	
4. OCTANE	-8708	-17.05	11.83	-89.18	-0.24	0.9(12)	809.0	0.00	0.00	0.30	2.97	-0.10	-49.76	4(16)	
5. NONANE	-8722	-16.00	14.951	-81.3	-0.44	-0.1(12)	595.0	0.00	0.00	0.08	3.23	-0.14	-58.97	5(16)	
6. DECANE	-8823	-17.02	19.25	-87.0	-0.28	0.1(12)	1009.0	0.00	0.00	0.00	3.95	-0.28	-1.218	1(16)	
7. UNDECANE	-8833	-18.02	17.75	-74.2	-0.28	1.0(12)	1169.0	0.00	0.00	0.00	3.92	-0.22	-1.4953	-0.022	4(16)
8. DODECANE	-8804	-22.12	23.73	-81.2	-0.73	1.0(12)	1189.0	0.00	0.00	0.00	4.25	-0.22	-1.9322	-0.022	4(16)
9. 1-PENTENE	-8903	-15.90	6.1	-31.0	0.3	1.2(12)	587.2	-0.95	0.06	0.8	1.99	0.05	-37.86	5(7(16))	
10. 1-HEXENE	-8305	-16.94	11.83	-31.0	0.9	1.2(12)	659.0	-0.95	0.06	0.8	1.72	0.00	-5.682	2(7(16))	
11. 1-HEPTENE	-8676	-17.22	9.58	-37.2	-0.19	0.9(12)	783.0	-1.12	-0.06	0.3	1.95	-0.05	-0.023	-0.00	3(16)
12. 1-OCTENE	-8878	-16.23	14.83	-81.0	-0.27	1.0(12)	846.0	-0.95	-0.06	0.3	2.17	-0.09	-1.8778	-0.00	3(16)
13. 1-NONENE	-7735	-19.52	10.80	-84.9	-0.26	0.9(12)	949.3	-2.26	-0.07	0.08	2.39	-0.09	-1.2107	-0.00	3(16)
14. 1-DECENE	-8855	-20.95	11.40	-20.5	-0.37	1.0(12)	1059.6	-2.22	-1.01	0.0	2.68	-0.12	-1.3451	-0.00	3(16)
15. 1-UNDECENE	-8612	-22.12	23.40	-51.0	-0.17	1.0(12)	1159.3	-1.27	-1.29	0.2	2.77	0.0	-0.120	-0.00	3(16)
16. 1-PENTENE	-7344	-16.56	7.65	-17.0	0.0	1.3(12)	722.4	-3.39	-1.80	1.5	0.8	0.07	-5.836	2(7(16))	
17. 1-HEXENE	-8011	-16.37	6.05	-10.7	0.3	0.9(12)	825.3	-2.32	-2.00	1.5	1.01	0.04	-0.041	1(16)	
18. 1-HEPTENE	-8024	-20.52	9.08	-29.4	0.3	0.9(12)	959.2	-3.06	-2.10	2.0	1.11	0.04	-0.950	1(16)	
19. 1-OCTENE	-8812	-21.35	12.21	-21.9	-0.85	0.9(12)	1030.9	-2.79	-2.42	2.2	1.19	0.0	-1.4695	-0.00	1(16)
20. 1-NONENE	-9044	-22.03	19.25	-21.3	0.9	0.9(10)	1133.9	-3.43	-2.76	3.1	1.22	0.0	-3.091	1(3(16))	
21. CYCLOHEXANE	-9501	-15.98	11.02	-29.7	0.2	0.9(12)	759.4	2.96	-1.24	1.2	1.57	0.05	-6.922	4(8(7))	
22. CYCLOHEXANE	-9707	-17.33	11.21	-29.5	0.1	0.9(12)	909.3	4.09	-0.83	1.7	1.00	0.04	-5.951	4(8(7))	
23. CYCLOHEXANE	-7803	-16.10	14.69	-30.3	-0.06	0.9(12)	1091.1	5.27	-2.05	2.1	1.63	0.01	-6.693	3(16)	
24. TRANS-HYDRODANE	-8213	-10.68	3.22	-31.2	-0.85	1.0(10)	1189.9	5.56	-2.10	2.2	1.00	0.01	-2.049	3(7(7))	
25. CIS-HYDRODANE	-7312	-19.23	12.75	-11.3	-0.14	0.9(12)	956.5	2.69	-2.75	1.0	0.2	0.04	-1.7140	2(2(16))	
26. BENZENE	-8111	-19.17	12.06	-14.0	-0.12	0.9(12)	1057.6	2.97	-2.02	1.6	0.7	0.04	-6.673	4(8(7))	
27. TOLUENE	-8743	-20.00	13.34	-16.3	-0.12	1.0(10)	1153.6	3.42	-3.12	1.7	0.9	0.04	-1.4093	3(16)	
28. ETHYLENE	-8111	-17.34	6.50	-15.0	0.2	1.0(12)	755.0	0.00	2.02	1.1	0.0	0.0	-0.0013	2(8(16))	
29. 1-PROPYLENE	-8014	-16.11	10.61	-17.6	-0.03	0.9(12)	854.0	0.56	2.12	1.2	0.95	0.0	-0.9568	-0.017	2(8(16))
30. 1-BUTYLENE	-7840	-15.08	12.95	-19.9	-0.06	0.9(12)	916.7	0.70	-2.28	1.5	1.00	0.01	-1.5410	-0.00	3(16)
31. 1-PENTYLENE	-8449	-20.05	13.24	-22.7	-0.12	0.9(12)	1039.6	0.93	-2.47	1.0	1.23	-0.03	-1.6220	-0.00	3(16)
32. 1-HYDRODANE	-9397	-21.33	20.02	-23.6	-0.10	1.0(12)	1159.3	0.67	-2.68	2.1	1.40	-0.01	-1.4601	-0.019	2(16)
33. PROPYLENE	-8139	-17.47	6.77	-10.7	0.3	0.9(12)	775.0	1.70	-2.28	1.1	0.7	0.01	-2.007	1(8(16))	
34. 1-BROMOPROPANE	-8830	-17.92	9.16	-13.0	0.1	1.1(12)	879.0	1.36	-2.39	1.4	0.75	0.02	-0.664	4(8(7))	
35. 1-BROMOBUTANE	-7894	-16.77	11.68	-16.7	0.1	1.0(12)	965.8	1.60	-2.40	1.3	0.91	0.01	-0.7799	4(8(7))	
36. 1-BROMOPENTANE	-8271	-16.76	13.99	-19.1	-0.02	0.9(12)	1088.5	1.80	-2.68	2.3	1.04	0.0	-0.9307	4(8(7))	
37. 1-BROMOHHEXANE	-9173	-20.76	17.66	-23.9	-0.69	1.1(12)	1166.9	2.39	-2.79	2.0	1.1	-0.01	-1.6223	2(2(16))	
38. CYANETHANE	-8209	-16.06	11.25	-12.2	0.6	0.9(12)	1031.6	-0.47	-3.22	1.7	1.0	0.03	-1.0408	-0.00	2(16)
39. CYANOPENTANE	-8368	-20.72	13.47	-21.1	0.9	0.9(12)	1091.9	1.13	-3.09	2.3	0.9	0.03	-1.1363	3(14(16))	
40. 1-CYANOPROPANE	-8808	-20.12	15.47	-21.1	0.2	0.9(12)	1194.7	1.50	-3.93	2.5	1.4	0.02	-1.0382	-1(7(7))	
41. 1-CYANOPENTANE	-8932	-20.41	20.22	-14.8	-0.03	0.9(12)	1186.2	-1.30	-3.93	2.1	1.3	-0.01	-1.4924	1(6(16))	
42. NITROETHANE	-8501	-21.51	18.24	-25.8	-0.07	0.7(12)	1134.5	1.27	-3.72	1.3	1.2	-0.03	-1.1765	4(8(7))	
43. 1-NITROPROPANE	-9707	-21.65	17.70	-7.0	-0.04	0.9(12)	1209.3	1.11	-3.66	2.1	1.35	-0.01	-4.4092	2(8(16))	

45 ACETONITRILE	-6922	-19.03	17.20	-5.6	.05	64(12)	824.7	-1.69	-2.69	.14	.10	.03	-66.06	-63.53	.1(13)
46 ACETONITRILE	-7558	-19.74	16.31	-9.0	.07	9(112)	893.7	-2.94	-2.94	.13	.09	.05	-194.23	-64.67	.7(19)
47 3-ACETOPROPANE	-8255	-20.43	16.33	-11.3	.07	7(112)	974.9	-2.10	-2.77	.24	.09	.03	-634.0	-82.57	3.1(19)
48 3-ACETOPROPANE	-9050	-21.43	17.49	-13.0	.03	8(110)	1075.2	-1.10	-2.99	.25	.09	.03	-107.02	-93.17	.7(19)
49 3-ACETOPENTANE	-9979	-22.54	20.78	-17.3	-.01	1(17.5)	1176.5	-1.44	-3.17	.23	.09	.02	-127.23	-96.94	.6(14)
50 ETHANOL	-7834	-20.69	16.90	-10.3	.01	1.1(112)	662.5	-3.14	-2.52	.13	.06	.02	-125.42	-96.45	.5(17)
51 ETHANOL	-8036	-20.95	16.35	-8.2	.06	6(112)	903.4	-4.91	-2.72	.13	.05	.02	-181.44	-74.54	6.3(17)
52 1-PROPANOL	-8938	-21.95	16.03	-7.4	-.10	7(112)	1103.9	-4.70	-3.12	.17	.04	.04	-192.61	-65.20	4.4(6)
53 1-BUTANOL	-9816	-23.02	20.10	-7.7	-.07	9(110)	1113.7	-4.29	-3.50	.21	.03	.03	-200.02	-79.90	.5(15)
54 2-PROPANOL	-8092	-21.03	16.03	-9.3	-.09	7(112)	691.0	-5.23	-2.64	.11	.00	.04	-164.32	-69.50	2.1(18)
55 2-BUTANOL	-8868	-21.05	16.51	-9.0	-.07	6(112)	995.0	-4.76	-2.95	.16	.05	.03	-173.9	-71.16	3.1(6)
56 2-PENTANOL	-9635	-22.02	18.05	-11.9	-.00	7(112)	1091.0	-4.55	-3.16	.21	.05	.03	-187.73	-73.91	3.1(6)
57 2-HEXANOL	-10549	-24.06	26.36	-14.3	-.13	6(19)	1200.0	-4.25	-3.41	.13	.09	.04	-190.45	-73.26	.1(4)
58 2-ETHYLPROPANOL-(2)	-7957	-21.75	14.91	-13.0	-.01	1.3(112)	665.5	-5.74	-2.39	.15	.00	.01	-222.87	-66.63	.0(7)
59 2-ETHYLPROPANOL-(1)	-8752	-21.00	20.12	-12.0	-.00	6(112)	985.3	-4.60	-2.80	.21	.05	.01	-185.24	-64.85	.6(16)
60 2-ETHYLPROPANOL-(2)	-9584	-22.69	19.45	-14.3	-.03	6(112)	1076.1	-4.72	-2.97	.21	.00	.00	-190.52	-75.09	.2(15)
61 2-PROPANONE	-8775	-19.42	7.64	-8.8	.11	9(112)	814.6	-1.00	-2.50	.17	.07	.07	-75.00	-65.34	.2(8)
62 2-BUTANONE	-7419	-19.00	10.61	-8.0	.04	7(112)	903.7	-3.59	-2.70	.17	.00	.03	-92.05	-50.36	3.1(8)
63 2-PENTANONE	-7959	-19.60	12.31	-10.1	-.01	1(112)	904.0	-.07	-2.69	.13	.09	.01	-120.44	-60.61	2.1(7)
64 2-HEXANONE	-8639	-20.40	13.09	-11.9	-.13	1(10)	1087.0	.82	-3.13	.15	.05	.06	-183.34	-73.33	3.1(5)
65 2-HEPTANONE	-9032	-21.09	13.76	-8.0	.16	6(11)	1109.2	.42	-3.67	.12	.09	.10	-140.60	-63.30	3.2(4)
66 DIETHYL ETHER	-9006	-16.03	13.39	-22.6	.15	1.0(112)	617.0	-.32	-1.40	.00	1.19	.05	-151.12	-60.93	.4(7)
67 DIETHYL ETHER	-8446	-16.00	12.20	-32.4	-.08	9(112)	773.3	-.30	-1.16	.03	1.71	.01	-94.95	-51.36	.2(7)
68 DIETHYL ETHER	-9030	-19.97	12.00	-40.4	-.14	1.1(112)	970.0	-1.05	-1.27	.13	2.16	.02	-129.91	-57.72	3.1(6)
69 DIETHYL ETHER	-9660	-22.09	17.22	-46.6	-.22	9(110)	1153.1	-1.64	-1.62	.19	2.51	.03	-201.10	-76.43	3.4(7)
70 1,2-DIMETHOXY ETHANE	-7659	-19.57	12.23	-8.2	-.14	7(112)	920.6	.83	-2.80	.00	.45	.05	-180.95	-75.00	.3(4)
71 DICHLOROMETHANE	-7056	-20.05	12.60	-4.5	-.17	9(112)	922.7	-2.35	-3.00	.04	.25	.09	-304.75	-111.56	.6(14)
72 TRICHLOROMETHANE	-8664	-23.12	17.55	-9.2	-.00	1.0(112)	1016.5	-2.59	-3.04	.21	.51	.01	-160.21	-70.36	3.1(7)
73 TETRACHLOROMETHANE	-7140	-16.51	15.56	-14.2	.04	1.0(112)	690.2	.46	-2.30	.17	.77	.04	-211.29	-65.77	3.6(14)
74 FLUOROBENZENE	-8090	-19.01	13.05	-10.3	.05	9(112)	937.5	-.04	-2.92	.23	.57	.04	-103.07	-53.06	.4(8)
75 CHLOROBENZENE	-8673	-21.42	20.04	-8.4	.13	1.0(19)	1225.0	2.65	-3.62	.31	.67	.09	-72.12	-63.45	.5(14)
76 PYROLYNE	-9032	-20.25	4.87	-7.3	.02	6(19)	1177.9	3.85	-3.71	.23	.41	.02	-63.79	-64.15	2.2(6)
77 TETRAHYDROFURANE	-8718	-17.95	10.59	-10.4	-.04	6(112)	875.0	2.34	-2.55	.11	.96	.01	-149.70	-65.04	4.4(8)
78 Dioxane	-8546	-19.69	14.46	-3.9	-.00	3(112)	1067.4	2.00	-3.13	.10	.32	.04	-132.60	-60.11	2.1(4)
79 THIOPHENE	-8063	-19.12	16.05	-6.4	-.06	5(112)	1033.2	1.99	-3.14	.10	.46	.02	-124.43	-56.44	.1(5)

Supports N (non-treated) and S (silylated) and columns are described in Table I. Results calculated from data measured on columns of nominal loading 4, 11 and 20%. Symbols: the standard thermodynamic quantities are given for a temperature of 100°C (373.15°K). ΔH_{ij}^0 , ΔS_{ij}^0 and $\Delta C_{p,ij}^0$: difference in the standard molar enthalpy, entropy and heat capacity of the solute between gas and bulk liquid phases. λ , $(\partial \rho_{ij}^{(g)}) / (\partial m)_{100}$ and $(\partial \rho_{ij}^{(l)}) / (\partial m)_{100}$: change in the surface energy and of the surface entropy of the liquid surface with the concentration of the solute at $m_j = 0$ (m is the molality of the solute in the liquid). I^0 : retention index without adsorption; $\partial I^0 / \partial T$ is its temperature dependence. α : specific surface area of the stationary liquid in the column ($m^2 g^{-1}$). I^0 : a hypothetical retention index calculated with hypothetical non-adsorbed *n*-alkanes but with adsorbed solutes. ΔH_{ij}^0 and ΔS_{ij}^0 : standard molar enthalpies and entropies for the adsorption on the uncovered silylated support. σ_{rel} : relative standard deviation of a single measurement around the regression surface. N: number of determinations.

(iv) For the evaluation of data on support S, first the value of the proportion of the surface wetted by the stationary phase, α , was estimated as explained in Results and Discussion. By using solution and adsorption data on the totally wetted support N and the value of α , two new coefficients were calculated accounting for the adsorption on the non-wetted surface of support S (see Table II). For the calculation of the standard deviation it was supposed that the number of parameters is two ($\nu = 2$) and the other parameters (determined on support N) have no error.

The results expressed by the regression coefficients are given in Table II. In order to illustrate the general trend on the different columns at different temperatures, the average of the specific retention volumes of all substances was calculated. The results are summarized in Table III. To illustrate the orders of magnitude and to facilitate conversion of retention indices into specific retention volumes, such data were calculated for *n*-alkanes for every 0.5 carbon number and for every 5° step in temperature. The results are given in Table IV.

TABLE III

AVERAGE SPECIFIC RETENTION VOLUMES, \bar{V}_s (ml g⁻¹), AS A FUNCTION OF THE TEMPERATURE AND THE NOMINAL LOADING OF THE PACKING

Data calculated with omission of all substances that were not determined at all temperatures and on all columns (the numbers refer to *j* in Table II): 8, 15, 20, 24, 25, 28, 33–38, 42–44, 48, 49, 53, 57, 64, 65, 69, 75 and 76.

Support	Loading (%)	Temperature (°C)				Average over-all temperatures
		70	90	110	130	
Non-treated (N)	4	161.45	84.86	49.29	30.82	81.61
	11	151.00	80.59	46.29	29.67	76.89
	20	147.55	78.91	46.36	29.03	75.46
	33	148.87	79.64	46.28	29.26	76.01
Silanized (S)	4	157.15	82.98	47.92	29.85	79.25
	11	150.03	79.85	46.26	29.20	76.34
	20	145.80	77.68	45.44	28.69	74.40
	33	145.98	78.10	45.62	28.86	74.64

Calculations. All the necessary calculations were made using a Control Data Computer (Model Cyber 7326) at the École Polytechnique Fédérale de Lausanne. The programs were written in Fortran and the various regression coefficients were determined by the least-squares method, using the routine CARLIN of the numerical analysis library POLYFTN, developed in the Department of Mathematics (under the responsibility of Prof. J. Descloux).

RESULTS AND DISCUSSION

For the evaluation of the data on the wettable support, N, it was assumed that the stationary phase forms a uniform film. In this instance the parameter α can be set equal to unity and the last term in eqn. 1 reduces to $z\epsilon_0$. Fig. 2 shows that the average overall specific retention volumes vary linearly as a function of ζ , with the exception of the highly loaded column (33% nominal), which systematically gave too high results.

We have no reasonable explanation for this phenomenon. Actually, one would expect the opposite effect, because assuming that at high loading the pores of the support are filled by the stationary liquid the liquid surface should therefore be lower than assumed in the model. For this reason all data on this column will not be considered further.

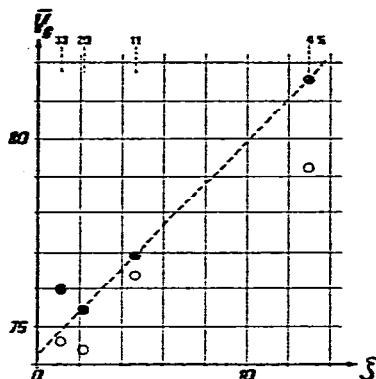


Fig. 2. Average specific retention volumes on columns with non-treated support (N; full symbols) and on columns with silanized support (S; open symbols). For the calculation of the average, only solutes with complete set of data were considered (see Table III).

The data on columns with 4, 11 and 20% nominal loadings, determined at 70°, 90°, 110° and 130°, were used to calculate all regression coefficients in one run as under Experimental (see Table II). It is important to note that it was necessary to use all of the terms in eqn. 2, including the last term accounting for the temperature dependence of the molar enthalpy and entropy of dissolution. This term was highly significant, and further, interacted strongly with the term describing the interfacial adsorption in the regression calculations. The values derived for the difference in molar heat capacity, $\Delta C_{P,J}^{(2)}$, appeared to be reasonable and showed obvious regularities: for instance, they increased regularly in homologous series. The residual variance around the regression surface corresponded in general to relative errors of about $\pm 2\%$ for a single determination (95% significance level), the values being higher for solutes with low retention volumes.

Fig. 2 shows that the average retention volumes on columns prepared with the silanized support, S, were systematically lower than those on columns N. Consequently, it could be concluded that, as a general rule, adsorption on the uncovered surface was much lower than that at the liquid interfaces. Because of this, a direct evaluation of the adsorption parameters was not possible. Therefore, the following procedure was applied. Firstly, one of the columns S (20%) was extracted with hot methanol overnight. The surface of the resulting support should be similar to the non-wetted part of the column packings, both surfaces having been in contact with a solution of the stationary phase. With this extracted support in a column, retention volumes were determined at 100° for those solutes which showed the largest interfacial adsorption in previous experiments and the parameter $k_j^{(\sigma)}$ was calculated for each solute. All parameters in eqn. 1 were now known and the value of α could be calculated

TABLE IV
SPECIFIC RETENTION VOLUMES OF NON-ADSORBED *n*-ALKANES CALCULATED WITH THE REGRESSION COEFFICIENTS LISTED
IN TABLE II

Hypothetical *n*-alkanes with half carbon numbers are also listed in order to facilitate interpolation and conversion of retention indices, I° , to specific retention volumes. Experimental values are limited to within the marked frames. Retention volumes marked in every second row serve to illustrate the effect of the adsorption. They are given for a column containing 1 g of stationary phase having a surface area of 5 m² (with the support N actually used this would correspond to a loading of 9.7%).

Z	T	70	75	80	85	90	95	100	105	110	115	120	125	130
4.0	2.912	2.759	2.619	2.492	2.377	2.271	2.174	2.085	2.003	1.926	1.859	1.795	1.735	1.678
	1.233	1.237	1.239	1.240	1.241	1.242	1.243	1.244	1.245	1.246	1.247	1.248	1.249	1.250
4.5	4.165	3.910	3.678	3.471	3.293	3.141	2.995	2.854	2.683	2.504	2.454	2.393	2.301	2.201
	1.376	1.385	1.390	1.395	1.398	1.400	1.402	1.404	1.406	1.408	1.410	1.412	1.414	1.416
5.0	5.358	5.091	4.840	4.608	4.394	4.203	4.017	3.795	3.593	3.400	3.248	3.085	2.945	2.800
	1.553	1.558	1.560	1.562	1.564	1.566	1.568	1.570	1.572	1.574	1.576	1.578	1.580	1.582
5.5	6.521	6.251	5.997	5.758	5.533	5.322	5.124	4.931	4.742	4.557	4.386	4.228	4.083	3.937
	1.816	1.821	1.824	1.827	1.830	1.833	1.836	1.839	1.842	1.845	1.848	1.851	1.854	1.857
6.0	7.659	7.387	7.131	6.890	6.663	6.450	6.250	6.062	5.885	5.718	5.561	5.413	5.274	5.144
	2.020	2.025	2.030	2.035	2.040	2.045	2.050	2.055	2.060	2.065	2.070	2.075	2.080	2.085
6.5	8.775	8.501	8.242	7.997	7.765	7.546	7.339	7.144	6.960	6.787	6.624	6.471	6.327	6.192
	2.235	2.240	2.245	2.250	2.255	2.260	2.265	2.270	2.275	2.280	2.285	2.290	2.295	2.300
7.0	9.873	9.600	9.347	9.104	8.871	8.648	8.435	8.233	8.041	7.859	7.686	7.523	7.369	7.224
	2.445	2.450	2.455	2.460	2.465	2.470	2.475	2.480	2.485	2.490	2.495	2.500	2.505	2.510
7.5	10.958	10.685	10.431	10.187	9.952	9.726	9.509	9.301	9.102	8.912	8.730	8.557	8.393	8.238
	2.655	2.660	2.665	2.670	2.675	2.680	2.685	2.690	2.695	2.700	2.705	2.710	2.715	2.720
8.0	12.031	11.758	11.503	11.257	11.020	10.791	10.570	10.357	10.152	9.955	9.766	9.584	9.409	9.241
	2.865	2.870	2.875	2.880	2.885	2.890	2.895	2.900	2.905	2.910	2.915	2.920	2.925	2.930
8.5	13.092	12.819	12.573	12.335	12.105	11.883	11.669	11.462	11.262	11.069	10.882	10.701	10.526	10.357
	3.075	3.080	3.085	3.090	3.095	3.100	3.105	3.110	3.115	3.120	3.125	3.130	3.135	3.140
9.0	14.141	13.868	13.622	13.384	13.153	12.929	12.712	12.501	12.296	12.097	11.904	11.717	11.535	11.358
	3.285	3.290	3.295	3.300	3.305	3.310	3.315	3.320	3.325	3.330	3.335	3.340	3.345	3.350
9.5	15.178	14.905	14.659	14.421	14.189	13.963	13.743	13.529	13.321	13.119	12.922	12.730	12.543	12.361
	3.495	3.500	3.505	3.510	3.515	3.520	3.525	3.530	3.535	3.540	3.545	3.550	3.555	3.560
10.0	16.203	15.930	15.684	15.446	15.214	14.987	14.765	14.548	14.336	14.129	13.926	13.728	13.534	13.345
	3.705	3.710	3.715	3.720	3.725	3.730	3.735	3.740	3.745	3.750	3.755	3.760	3.765	3.770
10.5	17.217	16.944	16.708	16.479	16.255	16.035	15.819	15.607	15.399	15.195	14.995	14.799	14.607	14.419
	3.915	3.920	3.925	3.930	3.935	3.940	3.945	3.950	3.955	3.960	3.965	3.970	3.975	3.980
11.0	18.220	17.947	17.711	17.481	17.256	17.035	16.818	16.605	16.396	16.191	15.989	15.791	15.597	15.407
	4.125	4.130	4.135	4.140	4.145	4.150	4.155	4.160	4.165	4.170	4.175	4.180	4.185	4.190
11.5	19.213	18.940	18.704	18.474	18.248	18.026	17.808	17.593	17.381	17.172	16.966	16.763	16.563	16.366
	4.335	4.340	4.345	4.350	4.355	4.360	4.365	4.370	4.375	4.380	4.385	4.390	4.395	4.400
12.0	20.196	19.923	19.687	19.457	19.231	19.008	18.789	18.573	18.360	18.150	17.942	17.737	17.534	17.333
	4.545	4.550	4.555	4.560	4.565	4.570	4.575	4.580	4.585	4.590	4.595	4.600	4.605	4.610
12.5	21.169	20.896	20.660	20.429	20.202	19.978	19.757	19.539	19.323	19.110	18.900	18.692	18.486	18.282
	4.755	4.760	4.765	4.770	4.775	4.780	4.785	4.790	4.795	4.800	4.805	4.810	4.815	4.820
13.0	22.132	21.859	21.623	21.392	21.164	20.939	20.716	20.495	20.276	20.059	19.844	19.631	19.420	19.211
	4.965	4.970	4.975	4.980	4.985	4.990	4.995	5.000	5.005	5.010	5.015	5.020	5.025	5.030

for these substances. On columns S of nominal loadings 20 and 33% the calculation gave inconsistent results with values of α ranging from -1 to $+1$; these were identified as being artefacts due to random experimental errors and data on these columns were excluded from the following evaluations. Experimental values of α , listed in Table V, for the columns of nominal loadings 4 and 11%, should be independent of the solute and therefore their average was used in the following calculations. By assuming that the values of all parameters determined on columns S remain valid and using the value of α estimated as described, the only unknown term in eqn. 1 is that which is responsible for the liquid-solid adsorption. For the evaluation of this term the corresponding enthalpy, $\Delta H_f^{(s)}$, and entropy, $\Delta S_f^{(s)}$, were assumed to be constant in the experimental range. Consequently, the last term in eqn. 3 was taken to be zero. With these assumptions, the parameters $\Delta H_f^{(s)}$ and $\Delta S_f^{(s)}$ were evaluated for each substance by using data on columns S of 4 and 11% loading (see Table II).

TABLE V

ESTIMATION OF THE PARAMETER α IN EQN. 1 FOR COLUMNS OF NOMINAL LOADING 4 AND 11% WITH THE AID OF ALKANES AND ALKENES

For explanation, see text. Data on columns of nominal loading 20 and 30% gave inconsistent results.

Solute	Loading (%)	
	4	11
Heptane	0.42	0.64
Octane	0.38	0.65
Nonane	0.30	0.57
Decane	0.27	0.59
Undecane	0.27	0.55
Dodecane	0.27	0.62
Heptene	0.25	0.34
Octene	0.23	0.36
Nonene	0.22	0.39
Decene	0.24	0.43
Undecene	0.28	0.36
Average	0.28	0.50

We shall not discuss solution parameters here as they will be compared in forthcoming papers to data on hydroxyl-terminated poly(ethylene glycols) and dimethoxypoly(ethylene glycols) of different molecular weights. However, we shall make a few remarks on the retention indices listed in Table II.

Berezkin¹¹ showed that, to a first approximation, retention indices depend linearly on the variable $\zeta = a_\sigma w_\sigma / w_\lambda$. They also depend almost linearly on temperature. Consequently, by using the coefficients listed in Table II, retention indices can be estimated with good precision for any column if the specific surface area of the liquid-gas interface $a_{\lambda\gamma} (= A_{\lambda\gamma} / w_\lambda \approx \zeta)$ are known, by the use of eqn. 16:

$$I_T = I_T^0 + (T - T^\dagger) \frac{\partial I}{\partial T} + a_{\lambda\gamma} \cdot \frac{\partial I}{\partial a_{\lambda\gamma}} + (T - T^\dagger) a_{\lambda\gamma} \cdot \frac{\partial^2 I}{\partial a_{\lambda\gamma} \partial T} \tag{16}$$

where I_T^0 is the retention index at temperature T without any adsorption effects and T^\dagger is a chosen standard temperature (here $T^\dagger = 100^\circ$).

It is now interesting to note that in homologous series the value of I^0 increases by almost 100 i.u. for each additional methylene group in the molecule, as has been stated earlier as a general rule¹². Actually, it was described in the literature that this rule fails on polar stationary phases¹³.

Obviously, this rule fails if retention indices are examined on a column where interfacial adsorption contributes seriously to the retention, *n*-alkane standards being retained more strongly than polar solutes by adsorption. From the results, we conclude that the methylene increment in a slightly adsorbed homologous series on a column without adsorption amounts to 100 i.u. but decreases more or less linearly with increasing importance of the interfacial adsorption. On the basis of this observation, an exploratory test may be proposed for judging the importance of the interfacial adsorption on a given column. By determining the retention indices of a few supposedly slightly adsorbed homologous series on columns of low loading, a strong deviation of the increment below 100 will indicate strong adsorption of the *n*-alkanes.

Let us now put forward the question of whether precise retention indices can be determined on polar stationary phases by the use of another homologous series, as a secondary standard, as was proposed in the literature¹⁴⁻¹⁶. To discuss this question, hypothetical retention indices, I' , are listed in Table II. They were calculated as if the *n*-alkanes would not be adsorbed at all, thus artificially creating a series of non-adsorbed standards. It is now observed that the retention indices, I' , of the "real" *n*-alkanes are strongly influenced by the column loading. At the same time the variation of I' of the polar solutes is strongly attenuated but, with a very few exceptions, remains noticeable. It can be concluded that by using secondary, slightly adsorbed standards, the effect of adsorption can be accounted for a very few similar substances but that this method does not permit the determination of precise retention indices.

The contribution of the adsorption on the uncovered part of the silanized support is very low, in the order of 0.1% of the total retention. Therefore, the estimated parameters $\Delta H_j^{(\sigma)}$ and $\Delta S_j^{(\sigma)}$ should only be taken as approximate values despite the fact that the relative error would suggest a better accuracy (see Table II). It is observed that the adsorption enthalpies are too high for such an adsorption and they do not always show the expected regularities, e.g., in homologous series. The two parameters combined allow the calculation of the standard chemical potential differences, $\Delta\mu_j^{(\sigma)}$, the value of which, of course, is of better quality. Actually, in the calculation the other two parameters were determined from the temperature dependence of this function. It can be assumed that the surface of a silanized support is more or less apolar in nature and that the intervening adsorption forces are dispersion forces. Such forces are well characterized by retention indices on a non-polar stationary phase, I^A , such as a saturated hydrocarbon, $C_{37}H_{176}$.

Therefore, in Fig. 3 the values of $\Delta\mu_j^{(\sigma)}$ (100°) are plotted as a function of retention indices, I^A . It is observed that polar solutes, especially those with basic substituents, are adsorbed more strongly than slightly polar solutes. They might form a loose complex with the trimethylsiloxy substituents at the surface by a very weak σ (d,p) additive bond such as for instance, in the case of nitriles, $\equiv \bar{S}i - \overset{+}{N} \equiv C - R$.

The thermodynamic interpretation of the interfacial adsorption is given in eqn. 4. As was mentioned in the Introduction, there is no simple means of measuring separately the terms allowing for the adsorption at the gas-liquid and gas-solid inter-

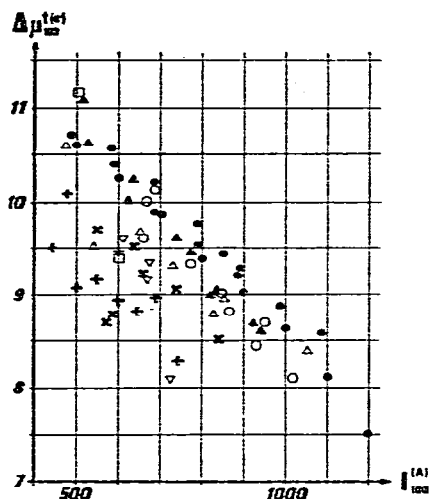


Fig. 3. Standard chemical potential difference, $\Delta\mu_{100}^{(\sigma)}$, characterizing the adsorption on the non-covered surface of columns S at 100° (silanized support) plotted as a function of the retention indices $I_{100}^{(A)}$. The stationary phase A is a branched alkane, $C_{37}H_{176}$. Solute symbols (the numbers refer to j in Table II): ●, alkanes, alkenes and alkynes (1–20); ○, cyclic and bicyclic compounds (21–28, 74,75); ▲, chloro- and bromoalkanes (29–38); ×, cyano-, nitro- and acetoxyalkanes (39–49); +, alcohols (50–60); △, ketones and ethers (61–70); □, chloromethanes (71–73); ▽, others (76–79).

faces, and the evaluation of the data gives the sum of both terms. Therefore, before any attempt is made to correlate the measured sum with solute properties, a decision has to be made concerning the relative importance of the individual contributions. Data given by Martin¹⁷ and Martire¹⁸ suggest that even on liquids of medium polarity the liquid-gas term predominates. Therefore, for the following comparison with the model of Defay and Prigogine¹⁹ we assumed that the measured values, listed in Table II, are due exclusively to liquid-gas adsorption. In ref. 3, the equation given by Defay and Prigogine for the surface tension of non-athermal binary mixtures of molecules of different size was adapted to the ideal dilute case. Considering the small molecules as solutes, as is the case in gas chromatography, we obtain

$$\left[\frac{\partial \gamma}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0} = \frac{M_\lambda \mathcal{R} T}{1000 r_\lambda \omega_j} \left\{ 1 - \exp \left[\left(\gamma_\lambda - \gamma_j + \frac{q_j \beta}{\omega_j} \right) \frac{\omega_j}{\mathcal{R} T} \right] \right\} \quad (17)$$

where m_j is the molal concentration of the solute, j , in the polymeric solvent, λ ; γ_λ and γ_j are the surface tensions of the solution, pure solvent and solute, respectively; and ω_j is the molar surface area of a monolayer of the substance identified by the subscript. The solvent molecule is considered to be a chain composed of r_λ segments. The size of the unit segment changes with the solute; its volume is set equal to that of the solute molecule. An essential feature of the underlying "parallel layer model" for the derivation of eqn. 17 is that a solute molecule is assumed to exhibit a certain "configurational enthalpy", q_j , inside the solvent, due to the solute being surrounded by a certain number of interacting segments of the solvent. The number of surrounding segments will be lower for solutes at the surface: the proportion of the coordination

number lost is β . The estimation of most parameters in eqn. 17 is straightforward. For the remaining parameters, different methods of approximations and methods of evaluation were proposed elsewhere³ which will not be repeated here in detail. In the following we describe the application of these methods in order to correlate our experimental values, $Y_j^{(\lambda)}$, with solute properties.

In Method A in ref. 3, the parameter $r_\lambda \omega_j$ was equated to the molar surface area of the solvent, ω_λ , and was considered as an empirical parameter. Its estimation was based on the fact that 1,2-dimethoxyethane forms a nearly athermal solution in dimethoxypoly(ethylene glycol) [enthalpy of dissolution (see Table II), $\Delta H_j^{(\lambda)} = -7669 \text{ cal mol}^{-1}$; enthalpy of condensation of the pure substance, $\Delta^{\text{cond.}}H_j^0 = -7681 \text{ cal mol}^{-1}$ (ref. 20)]. Therefore, the excess enthalpy of mixing, identified as the configurational enthalpy, q_j , is zero. In this case eqn. 17 permits the calculation of the parameter ω_λ by using the experimental value for $Y_j^{(\lambda)}$, which is $-8.2 \text{ erg kg cm}^{-1} \text{ mol}^{-1}$. This gives $5.4 \cdot 10^{10} \text{ cm}^2 \text{ mol}^{-1}$ for the molar surface area of dimethoxypoly(ethylene glycol). It is interesting to compare this value with two simple estimates. Assuming that the solvent molecules have cubic (approximately spherical) shape, the surface area of the monomolecular layer is given by $\omega_\lambda = V_\lambda^{2/3} N^{1/3} = 1.4 \cdot 10^{10} \text{ cm}^2 \text{ mol}^{-1}$ (V_λ is the molar volume; N is Avogadro's number). By assuming that the molecules are cylinders with a diameter of 3.7 \AA , a similar estimation gives $7.2 \cdot 10^{10} \text{ cm}^2 \text{ mol}^{-1}$. The experimental value obtained with eqn. 17 is a reasonable intermediate between these extremes. Adopting now the intermediate value for ω_λ , the term $q_j \beta$ can be calculated for each solute, j , using the experimental values for Y_j listed in Table II.

In Method B in ref. 3, it was assumed that the molar surface could be estimated from the molar volume as $\omega_j = V_j^{2/3} N^{1/3}$. This permitted the calculation of the values of the term $q_j \beta$ with the aid of experimental data.

Having calculated the term $q_j \beta$ by the two methods A and B, an experimental estimate of the configurational enthalpy, q_j , was necessary in order to derive the value of β . In the following, two methods (a and b) are proposed for this estimation.

Method a

In Method a it was assumed that

$$q_j = \Delta H_j^{(\lambda)} - \Delta^{\text{cond.}}H_j^0 \quad (18)$$

Values of $\Delta H_j^{(\lambda)}$ were taken from Table II. The enthalpy of condensation of the pure substance, $\Delta^{\text{cond.}}H_j^0$, was calculated with the aid of the Antoine equation:

$$\ln p_j^0 = A_j - \frac{B_j}{T + C_j} \quad (19)$$

The constants A_j , B_j and C_j were taken from ref. 21.

Method b

In Method b, values of q_j are estimated by comparing gas chromatographic data measured on dimethoxypoly(ethylene glycol) with those measured on a non-polar standard. As a non-polar stationary phase the branched alkane $C_{27}H_{54}$ considered earlier¹⁰ was chosen, the molar volume of which is comparable to that of the

actual stationary phase. Details of this method are described elsewhere³ together with the estimation of the necessary numerical values of the constants. The configurational enthalpy is given by

$$q_j = RT \ln [V_o(j|A)/V_o(j|X)] - (V_j \delta \mu_x^{*+(X)} + C^o) \quad (20)$$

where X and A refer to the polar and to the non-polar stationary phases, respectively. The "specific polarity", $\delta \mu_x^{*+(X)}$ ($= -7.0 \text{ cal mol}^{-1}$), of the polar chain of the solvent molecule was estimated from data for segment-like molecules, such as dimethoxyethane. The constant C^o , which allows for the effect of the end groups, was assumed to be zero.

The experimental values of $q_j \beta$, calculated by Methods A and B, were now plotted as a function of the configurational enthalpies estimated by Methods a and b. The parameter β was obtained from the slope of this plot. Method A gave values of β that depended on the solute, j . The plot of values of $q_j \beta$ calculated by Method B versus configurational enthalpies estimated by Method a gave values for β ranging from 0.32 to 0.6 for solutes with important interfacial adsorption. By plotting the same values against q_j estimated by Method b the same solutes gave values of β between 0.35 and 0.40. A very strong dispersion was observed for slightly adsorbed solutes.

By accepting an average value of $\beta \approx 0.4$ obtained with Method B, the interfacial adsorption was now re-calculated by using eqn. 17 with configurational enthalpies estimated by Method a, giving values $Y_j^{(a)}$, and with those estimated by Method b, giving $Y_j^{(b)}$. Values of surface tensions were taken from ref. 22.

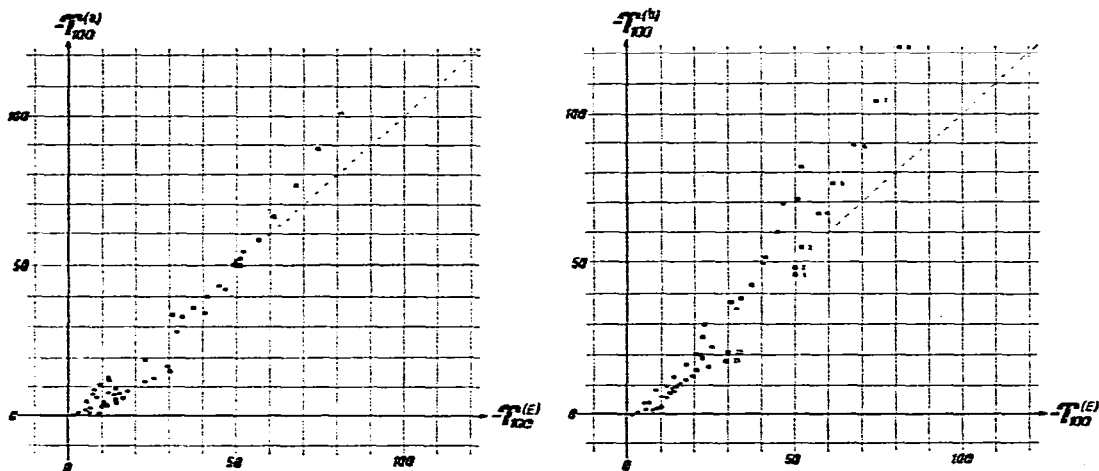


Fig. 4. The initial decreases [at $m_j^{(A)} = 0$] in the surface tension of the solution calculated by Method Ba (see text), $-Y_{100}^{(A)}$, plotted as a function of experimental values from Table II, $Y_{100}^{(E)} = \partial \gamma / \partial m_j^{(A)}$ at 100° . The parameter β was set equal to 0.4. No data for the following solutes: 16–20, 22, 24, 25, 31, 37, 38, 46, 49, 55, 57, 58, 69 and 77.

Fig. 5. The initial decrease [at $m_j^{(A)} = 0$] of the surface tension of the solution calculated by Method Bb (see text), $-Y_{100}^{(b)}$, plotted as a function of experimental values from Table II, $Y_{100}^{(E)} = \partial \gamma / \partial m_j^{(A)}$, at 100° . The parameter β was set equal to 0.4. No data for the following solutes: 16, 17, 22, 24, 25, 46, 55, 57, 58, 60 and 77.

In Figs. 4 and 5, these values of $Y_j^{(a)}$ and $Y_j^{(b)}$ are plotted as a function of the experimental values, $Y_j^{(E)}$, which are listed in Table II [$Y_j^{(E)} \equiv \partial\gamma^{(L\gamma)}/\partial m_j^{(L)}$]. The correlation is reasonable, especially considering the assumptions and approximations used in the derivation. Let us enumerate the points which seem to be the most problematic.

The configurational enthalpy estimated by Methods a and b gave a very poor correlation if plotted against each other. Nevertheless, the plots in Figs. 4 and 5 both give reasonable correlations, indicating that the calculated data for interfacial adsorption are not influenced seriously by the choice of q_j , especially for slightly adsorbed solutes. By using data determined on pure substances (Method a), the correlation seems to be improved.

It was assumed that the solid-liquid interfacial adsorption is negligible. This need not necessarily be true, especially for solutes capable of specific interactions with the solid surface.

The assumption that all molecules are spherical, which permitted the calculation of the molar surface areas from molar volumes, is also questionable.

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