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## THERMODYNAMICS OF INTERACTIONS OF HEXENES WITH STATIONARY PHASES CONTAINING PdCl<sub>2</sub> AND AgNO<sub>3</sub> IN GAS CHROMATOGRAPHY

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### SUMMARY

Interactions of hexenes with PdCl<sub>2</sub>-N-methylacetamide and AgNO<sub>3</sub>-N-methylacetamide stationary phases in gas chromatography have been compared. The following were calculated for eight isomeric hexenes and 2-methylpentane: the values of some thermodynamic quantities of sorption, the temperature dependence of the activity coefficients, the excess quantities of sorption and the latent heats of evaporation. On the basis of the calculation of the differential molar free energies of the specific sorption, the contributions of both the complex formation and sorption in the solvent have been compared in relation to the specific interactions of the double bond in hexenes. In addition to the sorption effect in the solvent, the selectivity of the chromatographic separation is significantly affected by the stability constants of the individual complexes of hexenes with PdCl<sub>2</sub> or Ag<sup>+</sup>. These values are related to the thermodynamic quantities. These quantities express all the sorption effects and make it possible to provide an acceptable explanation of the selectivity of separation. Of the stationary phases used in this study, the system PdCl<sub>2</sub>-N-methylacetamide has been found to be the most selective for the separation of hexenes.

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### INTRODUCTION

Since 1955, when Bradford *et al.*<sup>1</sup> first reported the gas chromatographic separation of alkenes using stationary phases containing AgNO<sub>3</sub>, many papers have been published where the formation of a  $\pi$ -complex between a solute and a metal was utilized in order to separate the unsaturated compounds<sup>2</sup>. Most of the stationary phases described contained compounds of silver.

Recently, we have studied the separation of alkenes on stationary phases that

contain compounds of different metals, especially of those of the platinum group<sup>3</sup>. Successful separations of the hexene isomers were achieved with solutions of PdCl<sub>2</sub> in N-methylacetamide (NMA). This paper concerns the comparison of solute-solvent interactions and an attempt to evaluate them quantitatively by calculating some thermodynamic quantities. For this purpose, systems containing approximately the same molarity of the complex-forming compounds (10% of PdCl<sub>2</sub> in NMA and 9.6% of AgNO<sub>3</sub> in NMA) were used. The results showed that both PdCl<sub>2</sub> and AgNO<sub>3</sub> as solutions in NMA provide independent interactions with hexenes. It is clear, however, that there is no direct connection between the affinity of the hexenes for PdCl<sub>2</sub>-NMA and AgNO<sub>3</sub>-NMA and the boiling-points of the hydrocarbons, and that the elution order is completely different from that on pure NMA. Three main effects that affect the retention volumes can be recognized: (1) sorption in NMA, *i.e.*, the pure solvent selectivity separating essentially according to the boiling-points; (2) the formation of  $\pi$ -complexes of hexenes with PdCl<sub>2</sub> or Ag<sup>+</sup> taking place proportionally to the stability of the individual complexes; (3) the salting-out effect of the dissolved metal compound which is greater the weaker is the effect of the complex-forming reaction (it is greatest with 2-methylpentane).

By treating the retention data in this manner, the relationships among the thermodynamic quantities and the stability constants of the  $\pi$ -complexes of individual hexenes were investigated. These relationships can serve as a basis for elucidating the stationary phase selectivity during the chromatographic process. A further attempt was made to separate the sorption effects, especially that of the complex-forming reaction contributing to the total interaction of the double bond of an individual hexene with the stationary phase.

## EXPERIMENTAL

### *Apparatus*

An extensively modified<sup>4</sup> Chrom 2 chromatograph (Laboratorní přístroje, Prague) was used. The modification makes it possible to replace the build-in flame ionization detector with the katharometer as required. The measurements were performed within the temperature range 19–61°C, which was extended by means of the additional cooling device<sup>5</sup>. The column used was a 85 cm × 4 mm I.D. glass U-tube. The katharometer was used for measuring the retention data and the flame ionization detector for investigating the dependence of the retention volume on the amount of sample. Samples of C<sub>4</sub>–C<sub>6</sub> hydrocarbons were introduced with a 1-ml syringe as vapours, while the C<sub>7</sub> and C<sub>8</sub> hydrocarbons were injected with a 20- $\mu$ l microsyringe. The sample amount varied from 10<sup>-4</sup> to 10<sup>-3</sup> g. No concentration dependence of the retention data was observed in the range from 10<sup>-3</sup> to 10<sup>-7</sup> g of sample with any of the packings used.

### *Materials*

Anhydrous palladium dichloride was prepared from chloropalladic(II) acid, which was synthesized by dissolving palladium sponge (Kovohute, Vestec, near Prague) in *aqua regia*. The nitric acid was removed by repeated evaporation with HCl on a water-bath. The finely powdered evaporation residue was dried in a stream of dry chlorine<sup>6-8</sup> for several hours at 120°C. The purity of the resulting preparation

was checked gravimetrically. Silver nitrate (reagent grade, Kovohute) was recrystallized from redistilled water, dried at 110 °C and carefully re-melted. The alkenes used (Koch-Light Laboratories, Colnbrook, Great Britain) were of reagent grade. *n*-Butane, *n*-octane and 2-methylbutane (Fluka, Buchs, Switzerland), *n*-pentane and 2-methylhexane (Merck, Darmstadt, G.F.R.), *n*-hexane, 2-methylpentane and 2-methylheptane (Lachema, Brno) were all GC standards, and pure *n*-heptane (VEB Laborchemie, Apolda, G.D.R.) was used. *N*-Methylacetamide (b.p.  $96 \pm 1$  °C/13 torr, K and K Laboratories Inc., Plainview, U.S.A.) was redistilled under reduced pressure. Acetone (reagent grade, Lachema) was redistilled and dried over anhydrous potassium carbonate at its boiling-point.

Chromaton N, 0.25–0.43 mm (Lachema), was used as the support, and was washed with boiling 10% HCl. Nitrogen was used as the carrier gas at a flow-rate of 30–60 ml/min.

#### *Preparation of the stationary phases and the column packing*

The stationary phases containing either PdCl<sub>2</sub> or AgNO<sub>3</sub> were prepared by a similar procedure. Amounts corresponding to 10% of PdCl<sub>2</sub> or 9.6% of AgNO<sub>3</sub> in NMA were dissolved in melted NMA. The mixture was stirred vigorously for about 4 h at 30 °C, excluding humidity, and was then left overnight. All operations were performed in the dark. The packings were prepared in the usual manner by dissolving the stationary phases in dried acetone and slurring with the support, and contained 20% of the stationary phase. The packed columns were conditioned for 12 h at 30 °C with a flow of carrier gas.

Retention data of all of the compounds investigated were expressed relative to *trans*-4-methylpentene as the standard at all temperatures used. Specific retention volumes ( $V_g$ ) were calculated for this hydrocarbon.

## RESULTS

The  $V_g$  values of the C<sub>6</sub> hydrocarbons measured on the stationary phases in question at 30 °C are given in Tables I and II. Values of log  $V_g$  corresponding to the individual compounds were plotted *versus* the reciprocal of the absolute temperature in the ranges 19–58 °C and 19–61 °C for PdCl<sub>2</sub> and AgNO<sub>3</sub>, respectively (see Figs. 1 and 2). From the slopes, the values of the differential molar sorption enthalpies,  $\Delta H_S$ , were calculated<sup>9</sup>, and the results are given in Tables I and II. The differential molar free energies of sorption,  $\Delta G_S$ , were calculated from the  $V_g$  values at 30 °C according to the equation<sup>10</sup>

$$\Delta G_S = -2.303RT \log(V_g \rho_L) \quad (1)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature of the column and  $\rho_L$  is the density of the stationary phase determined by the pycnometric method. By evaluating  $\Delta G_S$  and  $\Delta H_S$ , the differential molar entropy of sorption,  $\Delta S_S$ , can be calculated. The values of these quantities for the hydrocarbons investigated are given in Tables I and II.

The plots of log  $V_g$  against the boiling-points of the sorbed hydrocarbons (taken from the literature<sup>11,12</sup>) permitted the calculation of the total free energy of

TABLE I  
 SPECIFIC RETENTION VOLUMES ( $V_g$ ), DIFFERENTIAL MOLAR ENTHALPIES ( $\Delta H_s$ ), FREE ENERGIES ( $\Delta G_s$ ) AND ENTROPIES ( $\Delta S_s$ ) OF SORPTION, DIFFERENTIAL MOLAR FREE ENERGIES OF THE SPECIFIC INTERACTIONS ( $\Delta G_{sp}$ ) OF THE SORBATE-SORBENT (10% PdCl<sub>2</sub> IN NMA) SYSTEM AT 30 °C AND EFFECTIVE STABILITY CONSTANTS (K) AT 30 °C

Quantity	2-Methyl- pentane	4-Methyl- 1-pentene	cis- 4-Methyl- 2-pentene	trans-4- Methyl- 2-pentene	2-Methyl- 1-pentene	1-Hexene	2-Ethyl- 1-butene	trans- 2-Hexene	cis- 2-Hexene
Boiling-point (°C) <sub>11</sub>	60.3	53.9	56.3	58.6	60.7	63.5	64.7	67.9	68.4
$V_g^*$	0.58	1.43	1.70	1.00	1.09	2.29	1.22	1.53	2.34
$-\Delta H_s$ (kcal mole <sup>-1</sup> )	6.28	8.13	8.73	7.12	6.86	8.70	6.96	7.55	8.64
$-\Delta G_s$ (kcal mole <sup>-1</sup> )	2.24	2.79	2.89	2.57	2.62	3.07	2.69	2.83	3.08
$-\Delta S_s$ (cal mole <sup>-1</sup> K <sup>-1</sup> )	13.3	17.6	19.3	15.0	14.0	18.6	14.1	15.1	18.3
$-\Delta G_{sp, PdCl_2+NMA}$ (kcal mole <sup>-1</sup> ) (a)	—	0.66	0.71	0.35	0.38	0.73	0.37	0.41	0.65
$-\Delta G_{sp, NMA}$ (kcal mole <sup>-1</sup> ) (b)	—	0.26	0.24	0.22	0.34	0.25	0.33	0.25	0.28
$-\Delta G_{sp, PdCl_2}$ (kcal mole <sup>-1</sup> ) (a-b)	—	0.40	0.47	0.13	0.04	0.48	0.04	0.16	0.37
(a-b)/a (%)	—	60.6	66.2	37.1	10.5	65.7	10.8	39.0	56.9
K <sup>3</sup> (l mole <sup>-1</sup> )	—	1.5	1.8	0.38	0.14	1.9	0.13	0.49	1.3

\* Relative to *trans*-4-methyl-2-pentene, for which  $V_g=68.4$  ml.

TABLE II

SPECIFIC RETENTION VOLUMES ( $V_g$ ), DIFFERENTIAL MOLAR ENTHALPIES ( $\Delta H_s$ ), FREE ENERGIES ( $\Delta G_s$ ) AND ENTROPIES ( $\Delta S_s$ ) OF SORPTION, DIFFERENTIAL MOLAR FREE ENERGIES OF THE SPECIFIC INTERACTIONS ( $\Delta G_{sp}$ ) OF THE SORBATE-SORBENT (9.6%  $\text{AgNO}_3$  IN NMA) SYSTEM AT 30 °C AND EFFECTIVE STABILITY CONSTANTS ( $K$ ) AT 30 °C

Quantity	2-Methyl- pentane	4-Methyl- 1-pentene	cis-4- Methyl- 2-pentene	trans- 4-Methyl- 2-pentene	2-Methyl- 1-pentene	1-Hexene	2-Ethyl- 1-butene	trans- 2-Hexene	cis- 2-Hexene
Boiling-point (°C) <sup>11</sup>	60.3	53.9	56.3	58.6	60.7	63.5	64.7	67.9	68.4
$V_g^*$	0.63	1.10	1.17	1.00	1.45	1.70	1.77	1.41	1.89
$-\Delta H_s$ (kcal mole <sup>-1</sup> )	6.18	6.96	7.18	6.80	7.19	7.59	7.66	7.10	7.62
$-\Delta G_s$ (kcal mole <sup>-1</sup> )	2.27	2.61	2.64	2.55	2.77	2.87	2.89	2.76	2.93
$-\Delta S_s$ (cal mole <sup>-1</sup> K <sup>-1</sup> )	12.9	14.3	15.0	14.0	14.6	15.6	15.7	14.3	15.5
$-\Delta G_{sp, \text{AgNO}_3 + \text{NMA}}$ (kcal mole <sup>-1</sup> ) (a)	—	0.45	0.44	0.30	0.50	0.51	0.55	0.32	0.47
$-\Delta G_{sp, \text{NMA}}$ (kcal mole <sup>-1</sup> ) (b)	—	0.26	0.24	0.22	0.34	0.25	0.33	0.25	0.28
$-\Delta G_{sp, \text{AgNO}_3}$ (kcal mole <sup>-1</sup> ) (a-b)	—	0.19	0.20	0.08	0.16	0.26	0.22	0.07	0.19
(a-b)/a (%)	—	42.2	45.5	26.7	32.0	51.0	40.0	21.9	40.4
$K^3$ (l mole <sup>-1</sup> )	—	0.62	0.66	0.24	0.50	0.86	0.72	0.20	0.62

\* Relative to *trans*-4-methyl-2-pentene, for which  $V_g = 66.2$  ml.

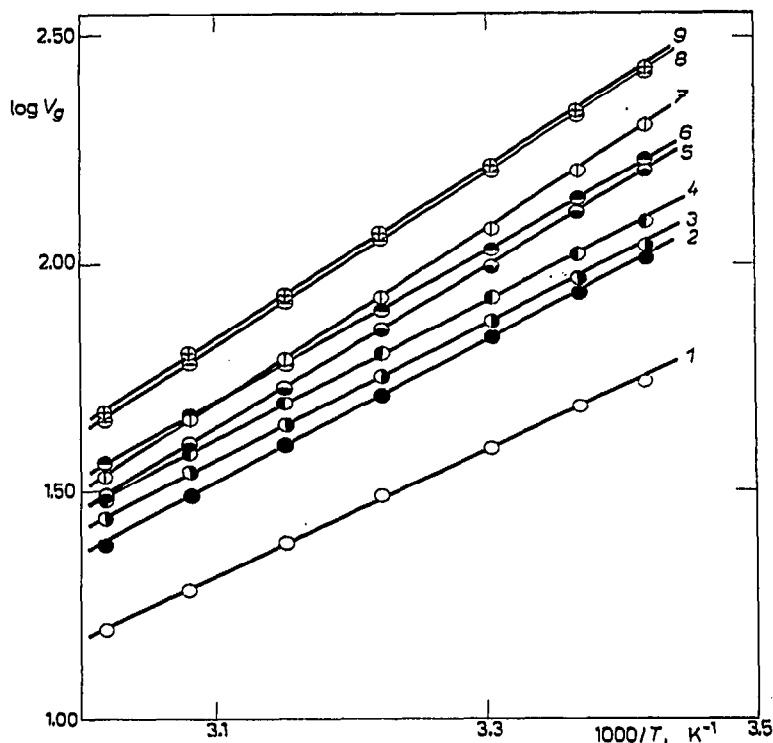


Fig. 1. Plots of  $\log V_g$  against  $1/T$  for the elution of hexenes and 2-methylpentane from 10%  $\text{PdCl}_2$  in NMA. 1=2-Methylpentane; 2=*trans*-4-methyl-2-pentene; 3=2-methyl-1-pentene; 4=2-ethyl-1-butene; 5=4-methyl-1-pentene; 6=*trans*-2-hexene; 7=*cis*-4-methyl-2-pentene; 8=1-hexene; 9=*cis*-2-hexene.

the specific interactions of sorption,  $\Delta G_{\text{sp}}$ , of hexenes in the  $\text{PdCl}_2$ -NMA and  $\text{AgNO}_3$ -NMA systems on the basis of the following equation derived by Brookman and Sawyer<sup>13</sup>:

$$\Delta G_{\text{sp}} = -2.303RT \log(V_{g_{X_i}}/V_{g_{A}}) = -2.303RTD_i \quad (2)$$

where  $V_{g_A}$  represents  $V_g$  in the homologous series of *n*-alkanes,  $V_{g_{X_i}}$  represents  $V_g$  in other homologous series, and  $D_i$  is the vertical distance between the lines corresponding to the total interaction of sorption on the one hand and that of non-specific interactions on the other. In calculating the  $\Delta G_{\text{sp}}$  value that would correspond to the interactions of sorption of the double bond, the effect of the hydrocarbon chain-branching on the interaction of compounds with the stationary phases cannot be neglected. Therefore, the plots of  $\log V_g$  against boiling-points include the lines for non-specific interactions both for the homologous series of *n*-alkanes and for that of 2-methylalkanes. By measuring the vertical distance between any point belonging to a certain hexene and one of the non-specific interaction lines, the  $D_i$  values were obtained. For *n*-alkenes and 2-methylalkenes (as well as for 2-ethyl-1-butene), the

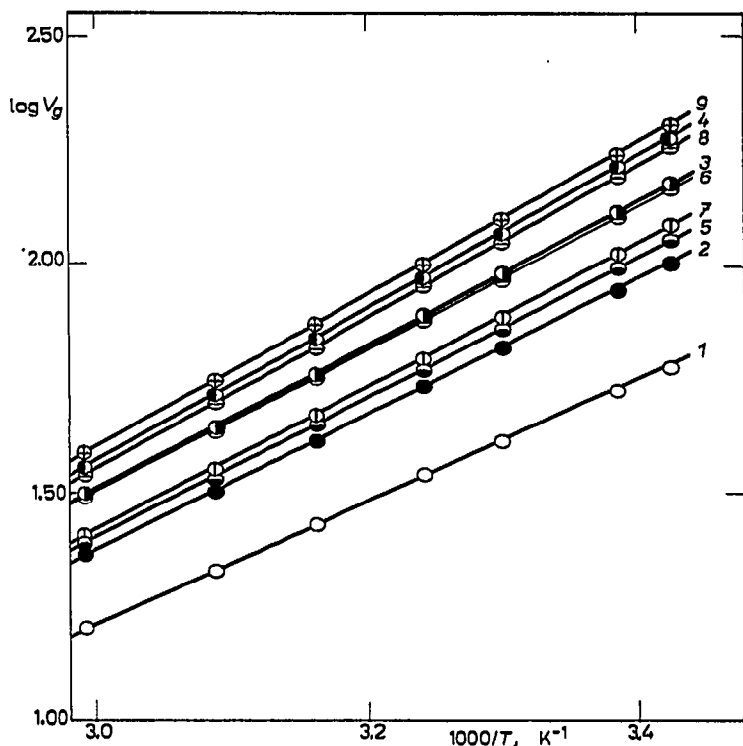


Fig. 2. Plots of  $\log V_D$  against  $1/T$  for the elution of hexenes and 2-methylpentane from 9.6%  $\text{AgNO}_3$  in NMA. For key see Fig. 1.

lines for homologous series of  $n$ -alkanes and 2-methylalkanes, respectively, were used as the referential line.

In order to isolate the various contributions to the total value of the specific interactions of double bonds, the above method was also applied to the calculation of  $\Delta G_{sp}$ , for pure NMA. The contribution of  $\text{PdCl}_2$  or  $\text{AgNO}_3$  to the interactions of the stationary phase with the double bond of an individual hexene is expressed as the difference of the  $\Delta G_{sp}$  values for the system  $\text{PdCl}_2$ -NMA and pure NMA or for the system  $\text{AgNO}_3$ -NMA and pure NMA.

The plots of  $\log V_D$  against boiling-points of hexenes, homologous series of  $n$ -alkanes and 2-methylalkanes at 30 °C are illustrated in Figs. 3 and 4 for the systems  $\text{PdCl}_2$ -NMA and  $\text{AgNO}_3$ -NMA, respectively. For the sake of comparison, both plots include data corresponding to pure NMA. The  $\Delta G_{sp}$  values calculated for the system  $\text{PdCl}_2$ -NMA and pure NMA are summarized in Table I. Similar data concerning the system  $\text{AgNO}_3$ -NMA and pure NMA are given in Table II. The stability constants of hexene- $\text{PdCl}_2$  and  $\text{Ag}^+$  complexes are also listed in Tables I and II.

From the specific retention volumes, the activity coefficients,  $\gamma^\circ$ , of the hydrocarbons were calculated<sup>14</sup> for both of the systems investigated. The molecular weights of the stationary phases were considered to be the mean molecular weights of the solutions, the vapour pressures of the hydrocarbons were calculated from the Antoine

TABLE III  
TEMPERATURE DEPENDENCE OF ACTIVITY COEFFICIENTS ( $\gamma^0$ ) OF SORBATES

Temperature (°C)	2-Methyl- pentane	4-Methyl- 1-pentene	cis- 4-Methyl- 2-pentene	trans- 4-Methyl- 2-pentene	2-Methyl- 1-pentene	1-Hexene	2-Ethyl- 1-butene	trans- 2-Hexene	cis- 2-Hexene
<i>System of 10% PdCl<sub>2</sub> in NMA</i>									
19.2	22.3	6.0	5.4	11.4	11.8	5.2	12.0	10.0	6.4
23.6	21.1	6.2	5.6	11.2	11.5	5.4	11.7	10.1	6.6
29.5	20.1	6.4	6.0	11.0	11.2	5.7	11.3	10.1	6.8
37.1	19.4	6.6	6.3	10.9	11.0	5.8	11.1	10.0	7.0
44.1	19.0	6.9	6.7	10.9	10.9	6.3	11.0	10.0	7.3
51.4	18.7	7.2	7.0	11.0	10.7	6.6	10.9	10.1	7.5
58.2	18.3	7.5	7.5	11.2	10.8	7.0	10.9	10.2	8.1
<i>System of 9.6% AgNO<sub>3</sub> in NMA</i>									
18.8	21.3	8.8	9.1	12.0	8.9	8.0	8.1	11.8	8.8
22.2	20.6	8.7	9.2	11.8	8.8	8.0	8.0	11.8	8.9
29.9	19.4	8.8	9.2	11.4	8.7	8.0	8.1	11.5	8.9
35.4	18.7	8.8	9.2	11.3	8.7	8.0	8.1	11.4	8.9
43.1	18.0	8.8	9.2	11.1	8.8	8.2	8.3	11.2	8.9
50.7	17.5	8.9	9.3	11.1	8.8	8.3	8.3	11.2	9.0
61.1	16.6	8.7	9.3	10.8	8.7	8.4	8.5	11.0	9.0



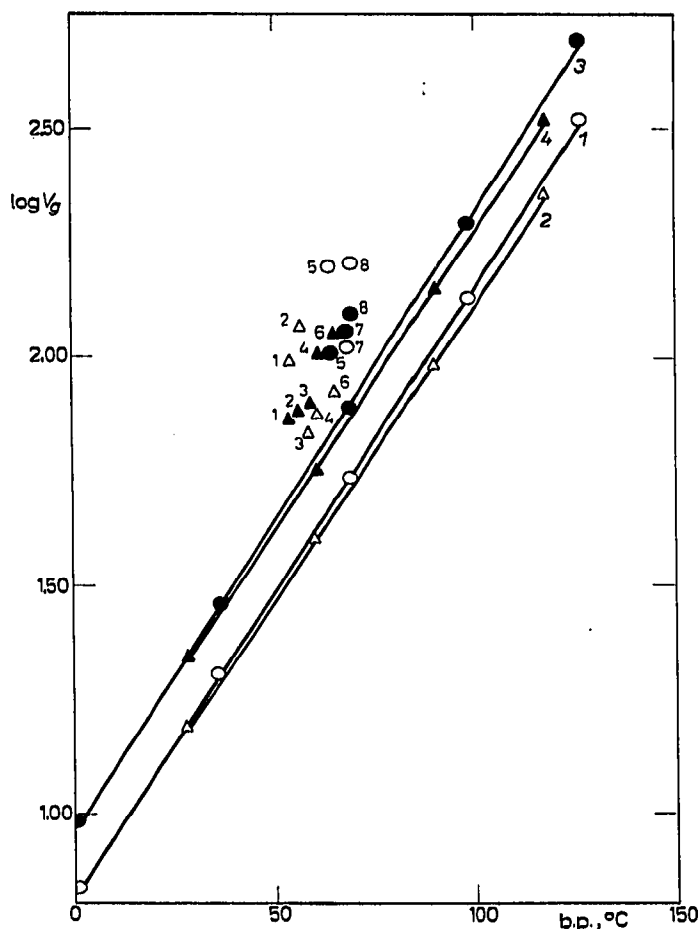


Fig. 3. Plots of  $\log V_D$  (at  $30^\circ\text{C}$ ) against the boiling-points of hydrocarbons eluted from NMA and from 10%  $\text{PdCl}_2$  in NMA. Points on lines 1 and 2 refer to *n*-alkanes and 2-methylalkanes, respectively, on  $\text{PdCl}_2$ -NMA; points on lines 3 and 4 refer to *n*-alkanes and 2-methylalkanes, respectively, on NMA. Numbered points:  $\circ$ , *n*-alkenes and  $\Delta$ , 2-methylalkenes on  $\text{PdCl}_2$ -NMA;  $\bullet$ , *n*-alkenes and  $\blacktriangle$ , 2-methylalkenes on NMA. 1=4-Methyl-1-pentene; 2=*cis*-4-methyl-2-pentene; 3=*trans*-4-methyl-2-pentene; 4=2-methyl-1-pentene; 5=1-hexene; 6=2-ethyl-1-butene; 7=*trans*-2-hexene; 8=*cis*-2-hexene.

equation, and the values of the  $A$ ,  $B$  and  $C$  constants were taken from the literature<sup>11</sup>. The temperature dependences of  $\gamma^\circ$  are listed in Table III.

Activity coefficients were used for calculating the partial molar excess free energy of sorption,  $\Delta G_M$ , according to the equation

$$\Delta G_M = 2.303RT \log \gamma^\circ \quad (3)$$

The plots of  $\Delta G_M$  versus  $T$  for hexenes and 2-methylpentane on  $\text{PdCl}_2$ -NMA and  $\text{AgNO}_3$ -NMA are illustrated in Figs. 5 and 6.

TABLE IV  
 PARTIAL MOLAR EXCESS ENTROPIES ( $\Delta S_M$ ) AND ENTHALPIES ( $\Delta H_M$ ), DIFFERENTIAL MOLAR HEATS OF SORPTION ( $\Delta H_S$ )  
 AND HEATS OF EVAPORATION ( $\Delta H_V$ ) OF SORBATES

Quantity	2-Methyl- pentane	4-Methyl- 1-pentene	cis- 4-Methyl- 2-pentene	trans- 4-Methyl- 2-pentene	2-Methyl- 1-pentene	2-Methyl- 1-pentene	1-Hexene	2-Ethyl- 1-butene	trans- 2-Hexene	cis- 2-Hexene
System of 10% PdCl <sub>2</sub> in NMA (37.1 °C)										
$-\Delta S_M$ (cal mole <sup>-1</sup> K <sup>-1</sup> )	2.70	7.22	8.89	4.64	3.17	8.26	3.36	4.75	7.33	
$\Delta H_M$ (kcal mole <sup>-1</sup> )	+0.99	-1.07	-1.63	+0.03	+0.50	-1.47	+0.44	-0.05	-1.07	
$-\Delta H_S$ (kcal mole <sup>-1</sup> )	6.28	8.13	8.73	7.12	6.86	8.70	6.96	7.55	8.64	
$\Delta H_V$ (kcal mole <sup>-1</sup> )*	7.27	7.06	7.10	7.15	7.36	7.23	7.40	7.50	7.57	
$\Delta H_V$ (kcal mole <sup>-1</sup> )**	6.98	6.81	6.90	6.99	7.07	7.17	7.22	7.34	7.38	
System of 9.6% AgNO <sub>3</sub> in NMA (35.4 °C)										
$-\Delta S_M$ (cal mole <sup>-1</sup> K <sup>-1</sup> )	2.18	4.32	4.80	3.42	4.08	4.91	4.97	3.82	4.63	
$\Delta H_M$ (kcal mole <sup>-1</sup> )	+1.13	-0.01	-0.12	+0.43	+0.07	-0.24	-0.25	+0.31	-0.09	
$-\Delta H_S$ (kcal mole <sup>-1</sup> )	6.18	6.96	7.18	6.80	7.19	7.59	7.66	7.10	7.62	
$\Delta H_V$ (kcal mole <sup>-1</sup> )*	7.31	6.95	7.06	7.23	7.26	7.35	7.41	7.41	7.53	
$\Delta H_V$ (kcal mole <sup>-1</sup> )**	7.00	6.83	6.92	7.01	7.09	7.19	7.25	7.37	7.41	

\* Calculated from the chromatographic data.

\*\* Calculated from the data found in the literature<sup>11</sup>.

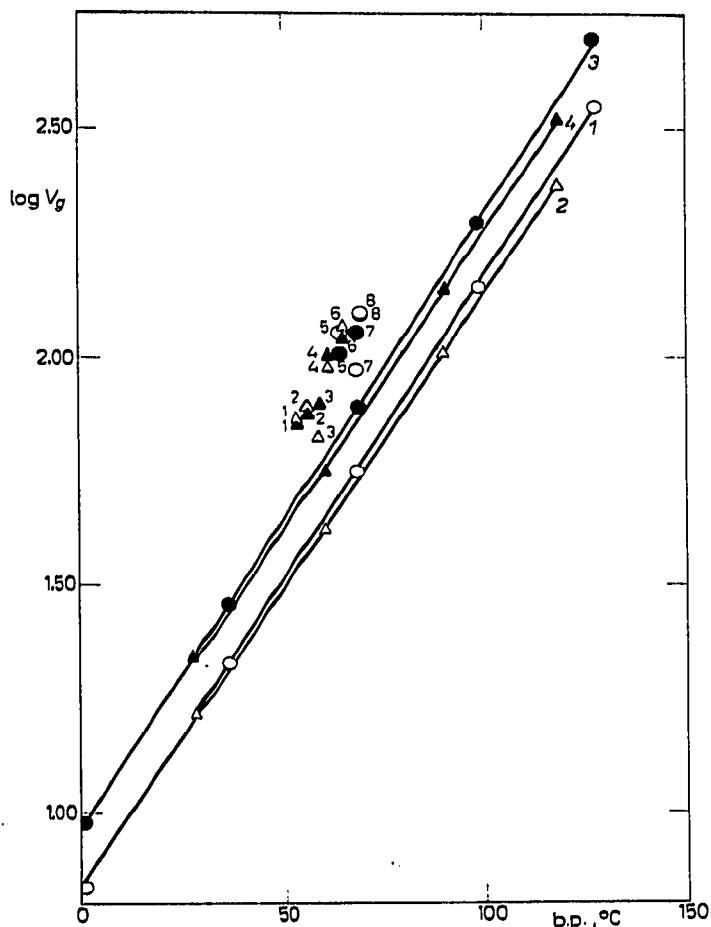


Fig. 4. Plots of  $\log V_{\theta}$  (at 30 °C) against the boiling-points of hydrocarbons eluted from NMA and from 9.6%  $\text{AgNO}_3$  in NMA. Points on lines 1 and 2 refer to *n*-alkanes and 2-methylalkanes, respectively, on  $\text{AgNO}_3$ -NMA; points on lines 3 and 4 refer to *n*-alkanes and 2-methylalkanes, respectively, on NMA. Numbered points:  $\circ$ , *n*-alkenes and  $\Delta$ , 2-methylalkenes on  $\text{AgNO}_3$ -NMA;  $\bullet$ , *n*-alkenes and  $\blacktriangle$ , 2-methylalkenes on NMA. For key see Fig. 3.

From these plots and the equation

$$\frac{\partial \Delta G_M}{\partial T} = -\Delta S_M \quad (4)$$

the values of the partial molar excess entropy of sorption were calculated for the mean value of the temperature range used. Then,  $\Delta G_M$  and  $\Delta S_M$  were used for calculating the partial molar excess enthalpy of sorption,  $\Delta H_M$ . The results are given in Table IV.

Finally, the latent heats of evaporation,  $\Delta H_V$ , of the hydrocarbons were obtained from  $\Delta H_M$  and  $\Delta H_S$  using the equation

$$\Delta H_V = \Delta H_M - \Delta H_S \quad (5)$$

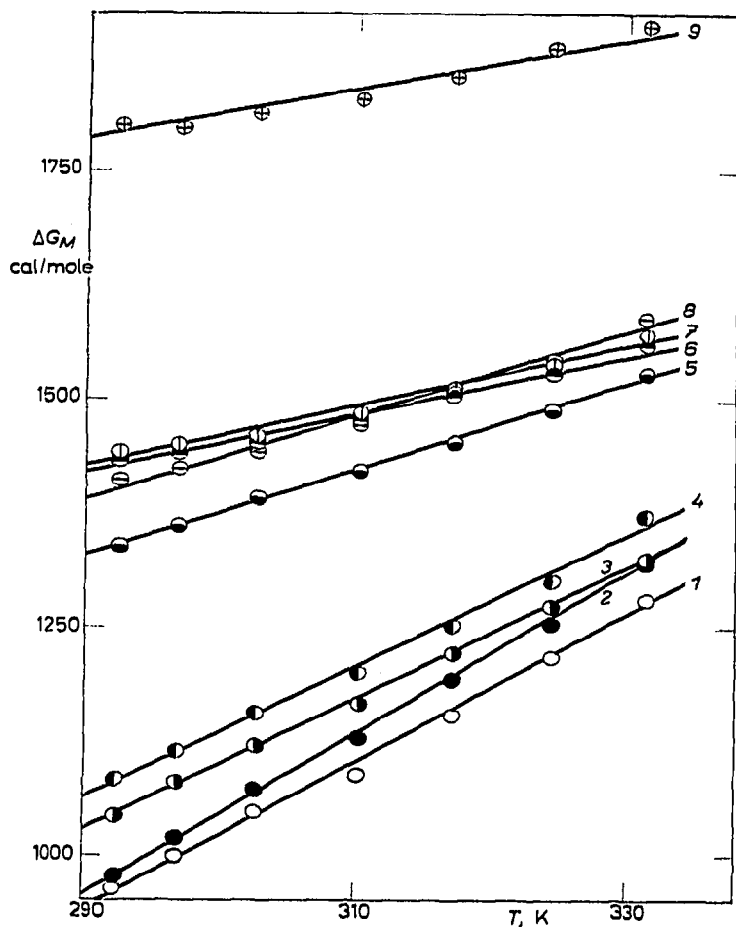


Fig. 5. Plots of  $\Delta G_M$  against  $T$  for hydrocarbons eluted from 10%  $\text{PdCl}_2$  in NMA. 1 = 1-Hexene; 2 = *cis*-4-methyl-2-pentene; 3 = 4-methyl-1-pentene; 4 = *cis*-2-hexene; 5 = *trans*-2-hexene; 6 = 2-methyl-1-pentene; 7 = 2-ethyl-1-butene; 8 = *trans*-4-methyl-2-pentene; 9 = 2-methylpentane.

These values are also included in Table IV. For the sake of comparison,  $\Delta H_V$  values at 25°C calculated from the literature<sup>11</sup> are also given.

## DISCUSSION

For the calculation of the thermodynamic quantities, it would be advantageous to measure the temperature dependence of the retention data over the widest temperature range possible, but unfortunately, the highest usable temperature is limited<sup>3</sup>. At temperatures above 50–60°C, the volatility of the solvent is considerable, the packings are liable to break down and the role of chemical reactions catalyzed by  $\text{PdCl}_2$ -NMA has to be considered. Contrary to this effect, the lower temperature limit is given by the melting-points of the stationary phases, near to which some irregularities can be observed on the straight lines of the plots of  $\log V_R$  against  $1/T$ . The lowest usable temperature for both packings was found to be 18°C.

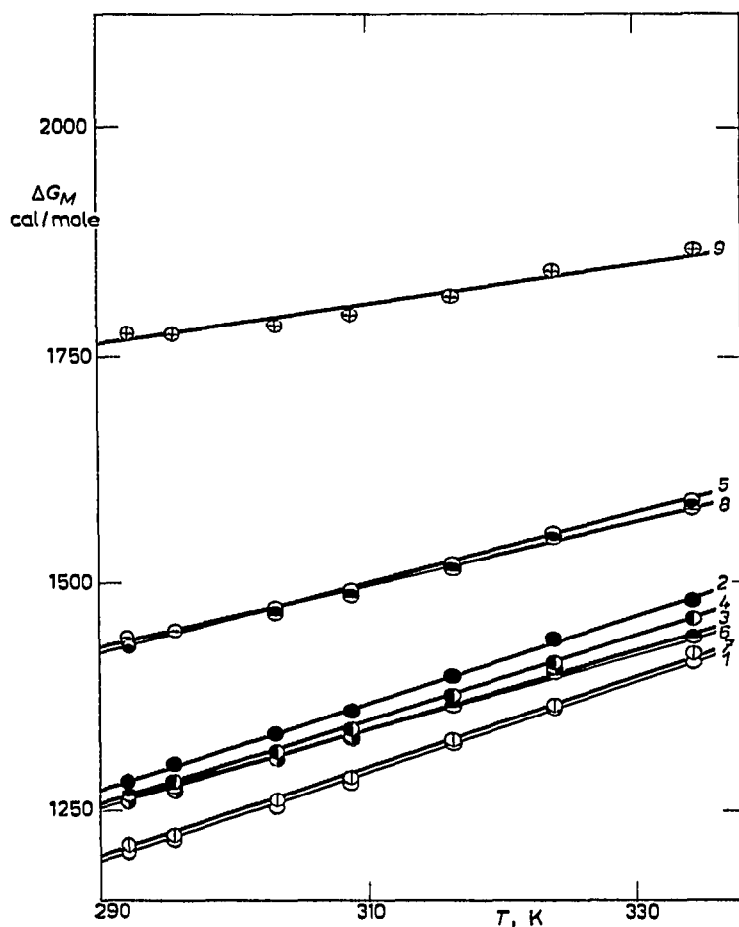


Fig. 6. Plots of  $\Delta G_M$  against  $T$  for hydrocarbons eluted from 9.6%  $\text{AgNO}_3$  in NMA. For key see Fig. 5.

The  $\Delta H_S$  values obtained from the above dependence were determined with an accuracy of not less than  $\pm 0.2$  kcal. These values represent the sum of interactions of the hydrocarbons investigated with the stationary phase, and involve both the fraction of the interaction with the solvent and that of the complex-forming reaction that is characterized by the magnitude of the stability constant,  $K$ , and has a significant effect on the total  $\Delta H_S$  value. It was found that 2-methylpentane, which cannot form complexes with any of the stationary phases used, possesses the lowest  $\Delta H_S$  value, while  $\Delta H_S$  is the highest for hydrocarbons that are able to form the most stable complexes. The relationship between the stability of the complex and the  $\Delta H_S$  values can be also observed with *cis*- and *trans*-isomers. Comparing  $\text{AgNO}_3$ -NMA and  $\text{PdCl}_2$ -NMA, a wider range of  $\Delta H_S$  values is evident for the latter and also the values for the individual hydrocarbons are higher. This fact is consistent with the higher selectivity of the  $\text{PdCl}_2$ -NMA. Similar relationships are also apparent for the  $\Delta G_S$  and  $\Delta S_S$  values. The  $\Delta S_S$  values obtained are subject to an error of not more than  $\pm 0.7$  cal mole $^{-1}$  K $^{-1}$  (Tables I and II).

In order to discriminate between the contributions of the complex-forming reaction and sorption in the solvent to the total interaction of the hexene double bond, the method of Brookman and Sawyer<sup>13</sup> was used for evaluating the free energy of the specific interactions of sorption in the equilibrium systems of  $\text{PdCl}_2\text{-NMA}$  and  $\text{AgNO}_3\text{-NMA}$ . In order to eliminate the chain-branching effect in alkenes, the  $\Delta G_{\text{sp}}$  values were calculated from a comparison with compounds of the same molecular arrangement but differing only in the presence of the double bond. The  $\Delta G_{\text{sp}}$  values obtained by this means are adequate to the double bond of the hydrocarbon molecule, and they represent the sum of the free energies of the specific interactions of the double bond with the solvent and the complex-forming compound. As is evident from Tables I and II, the  $\Delta G_{\text{sp}}$  values corresponding to the total specific interaction of the double bond evaluated using Figs. 3 and 4 are generally lower than the  $\Delta G_S$  values for the sorption of a whole molecule. Similarly, the sorption enthalpy (Tables I and II) for the double bond interaction represents only a small fraction of  $\Delta H_S$ , as is apparent from a comparison of  $\Delta H_S$  values for the hexenes and 2-methylpentane. This indicates that the contribution corresponding to the total specific interaction of the double bond is only a small portion of the total interaction of the molecule with the stationary phase. In order to evaluate the magnitude of both contributions with respect to the total  $\Delta G_{\text{sp}}$  value, the  $\Delta G_{\text{sp}}$  values of hexenes on  $\text{PdCl}_2\text{-NMA}$  and  $\text{AgNO}_3\text{-NMA}$  were compared with the  $\Delta G_{\text{sp}}$  value taken on pure NMA. The  $\Delta G_{\text{sp}}$  value obtained in this way represents the formation of the  $\pi$ -complexes of the individual alkenes with  $\text{PdCl}_2$  and  $\text{Ag}^+$ . The results in Tables I and II are in good agreement with the stability constants,  $K$ , of the complexes (Tables I and II). With  $\text{PdCl}_2\text{-NMA}$ , the calculated total  $\Delta G_{\text{sp}}$  values are in most instances higher than those with  $\text{AgNO}_3\text{-NMA}$ , and therefore the  $\Delta G_{\text{sp}}$  values are also higher, corresponding to complex formation with  $\text{PdCl}_2$ . The only exceptions are 2-methyl-1-pentene and 2-ethyl-1-butene, the complexes of which with  $\text{PdCl}_2$  are of low stability. As for  $K$ , similar relationships are also valid for  $\Delta G_{\text{sp}}$  of  $\pi$ -complex-forming reactions between hexenes and the metal. The contribution of this reaction immediately becomes clear if it is expressed as a percentage, as given in Tables I and II. The values found with  $\text{PdCl}_2\text{-NMA}$  and  $\text{AgNO}_3\text{-NMA}$  were 10–66% and 22–51%, respectively. The wide range of  $\Delta G_{\text{sp}}$  values must result in a greater selectivity for the sorption of hexenes.

The temperature dependence of the activity coefficients (Table III) corresponds with the dependence of the retention volumes of the hydrocarbons (Figs. 1 and 2) in the given systems. The fact that the activity coefficients of all of the hydrocarbons are significantly greater than unity throughout the temperature range used can be ascribed to the salting-out effect. However, the  $\gamma^\circ$  values are generally lower (with the exception of 2-methylpentane) when compared with the activity coefficients in solutions where complex formation does not take place. The relationships can be seen between the stability constants of the individual hydrocarbons and their activity coefficients over the complete temperature range. In general, the  $\gamma^\circ$  values are lower and closer to unity the more stable are their complexes with  $\text{PdCl}_2$  or  $\text{Ag}^+$  and the more the complex-forming reaction contributes to the total interaction. Therefore, the highest  $\gamma^\circ$  values were found with 2-methylpentane and with hexenes that form complexes of low stability. With the hydrocarbons used, three types of changes in the activity coefficients with the temperature are observed. The  $\gamma^\circ$  values of 2-methylpentane are significantly

irreversibly related to the temperature. With hexenes that form less stable complexes, the  $\gamma^\circ$  values are either slightly decreased or remain virtually unchanged with temperature. However, the  $\gamma^\circ$  values are increased with hexenes that form more stable complexes. This result can be explained by the parallel decrease in both the salting-out effect and the stability of the complex, resulting in smaller differences among the activity coefficients and the lower selectivity of separation.

The above relationships can also be found between the  $\Delta G_M$  and  $K$  values. The temperature dependence of  $\Delta G_M$  (Figs. 5 and 6) shows that the above observation is approximately valid also when the  $\Delta G_M$  value is lower the more stable is the complex formed by a particular hydrocarbon. Three groups of compounds can be found that differ in the slopes of the plots of  $\Delta G_M$  versus  $T$ . The slope is steepest with hexenes that form more stable complexes, while it is flattest with 2-methylpentane. The tangents of these plots represent the  $\Delta S_M$  values (Table IV). Plots of  $\Delta G_M$  against  $T$  are not likely to be strictly linear because both  $\Delta H_V$  and  $\Delta H_M$  show a certain dependence upon temperature. For this reason,  $\Delta S_M$  values were correlated with the mean values over the temperature range used and  $\Delta H_M$  values were calculated for these temperatures (Table IV).

The  $\Delta H_M$  values were scattered on both sides of the zero value. Positive deviations were shown by hydrocarbons that interact weakly with the stationary phase and are predominantly affected by the salting-out effect. On the other hand, negative deviations were observed with hydrocarbons that are capable of forming fairly stable complexes, where the complex-forming effect more than compensates for the salting-out effect. Comparison of  $\Delta H_M$ ,  $\Delta H_S$  and  $\Delta H_V$  indicates that with the hydrocarbons that possess a negative  $\Delta H_M$  value, the value of  $-\Delta H_S$  is greater than  $\Delta H_V$  because the heat released during the formation of complexes is greater than the latent heat of condensation. On the other hand, the hydrocarbons with positive  $\Delta H_M$  values have  $-\Delta H_S$  values smaller than  $\Delta H_V$ . In this case, the positive deviation is caused by the salting-out effect, which prevents compounds from mixing. Some part of the latent heat of condensation is consumed in order to allow this operation to take place. The  $\Delta H_V$  values evaluated from the retention data are subject to an error of not more than  $\pm 0.3$  kcal mole<sup>-1</sup>. They are in good agreement with those calculated by means of the data found in the literature<sup>11</sup>. Small differences (about 3%) indicate that the chromatographic measurements were carried out with good accuracy.

## CONCLUSIONS

The thermodynamically based treatment of the retention data of hexenes measured on PdCl<sub>2</sub>-NMA or AgNO<sub>3</sub>-NMA throws some light on the nature of solute-solvent interactions in gas chromatographic separations. The thermodynamic quantities evaluated are unambiguously related to the stability of the complex of individual hexenes with PdCl<sub>2</sub> and Ag<sup>+</sup>. The differences between the stabilities of complexes determine the selectivity of the chromatographic separation, which was found to be greater with PdCl<sub>2</sub>-NMA. The evaluation of the differential molar free energy of specific interactions of sorption makes it possible to separate the contributions of the main sorption effects and to ascertain the fraction of the complex-forming reaction from the total sorption interaction of the double bond.

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