GAS CHROMATOGRAPHY OF INORGANIC VOLATILE CHLORIDES

A STUDY OF THEIR REACTIVITY TOWARDS CERTAIN COLUMN PACKING MATERIALS

G. PARISSAKIS, D. VRANTI-PISCOU AND J. KONTOYANNAKOS

Inorganic and Analytical Chemistry Laboratories, National Technical University of Athens, Athens (Greece)

(Received July 9th, 1970)

SUMMARY

The interaction of silicon tetrachloride, phosphorus oxychloride, phosphorus trichloride, tin tetrachloride, germanium tetrachloride, titanium tetrachloride, arsenic trichloride, carbon tetrachloride, antimony pentachloride and vanadium tetrachloride, upon the stationary phases: Kel-F oil 10, Apiezon L, Kel-F wax, Phasepak P, Silicone Rubber UC-W98, Silicone oil DC-550 and graphite was investigated.

With the exception of antimony pentachloride and vanadium tetrachloride, the chlorides tested showed no interaction with the above-mentioned phases.

INTRODUCTION

This investigation is a part of an extensive project, whose basic goal is to explore the application of GLC in the analysis of metals in alloys and oxides, based on the volatility of the corresponding metal chlorides.

The main problem in applying gas chromatography for the separation and eventually the quantitative determination of inorganic volatile chlorides is the choice of an appropriate liquid phase which does not react with these compounds. In the present work the overall stability of the following liquid phases: Kel-F oil 10, Kel-F wax, Apiezon L, Phasepak P, Silicone Rubber UC-W98, Silicone oil DC-550, and graphite against $SnCl_4$, $SiCl_4$, $GeCl_4$, VCl_4, $TiCl_4$, CCl_4, $POCl_3$, PCl_3, $AsCl_3$ and $SbCl_5$ is studied.

In general, reactivity may be a question of:

(a) interaction between solute and the liquid phase (sometimes due to the metallic tubing of the columns) resulting in the creation of interaction products;

(b) sorption of the solute on the solid support, or

(c) the way by which the solutes are dissolved in the liquid phase.

The term "reactivity" in this paper covers everything that causes the distortion or even disappearance of an expected peak.

The reactivity of inorganic volatile chlorides with respect to packing materials and, occasionally, the difficulty in determining the magnitude of this effect has often led to different opinions on the suitability of various substances that might be used as packing materials for the separation of inorganic chlorides.

For instance, FREISER[1] has reported the separation of $SnCl_4$ and $TiCl_4$ at $102°$ by using copper tubing packed with n-hexadecane coated Chromosorb. KELLER AND FREISER[2] and KELLER[3] have also studied the chromatographic behaviour of the above and of Nb(V) and Ta(V) chlorides in a column packed with squalane at a temperature of $200°$. They also investigated the phases, n-octadecane, silicone oil, paraffin wax and Apiezon grease at temperatures between $100°$ and $200°$, and they observed that both Apiezon grease and Silicone oil reacted with chlorides. HUTCHINSON[4], however, found that $AsCl_3$ could be separated from $SnCl_4$ using silicone oil on firebrick as the packing material with no apparent reaction.

WACHI[5] was unable to elute Sn(IV) and Ti(IV) chlorides at $125°$ and $FeCl_3$ at $325°$ using a stainless steel column packed with silicone grease or Apiezon M on ground C-22 Sil-O-Cel insulating brick, apparently owing to the reaction of the metal chlorides with the liquid phase and the walls of the column. TADMOR[6] also reported interaction between the chlorides and silicone wax, leading to several well-defined peaks.

Nevertheless, TADMOR[7] later proposed the separation of SCl_2, $PSCl_2$ and PCl_3 on Silicone oil DC-550 at $200°$ and ABE[8] described the qualitative separation of $SiHCl_3$, $SiCl_4$, BCl_3 and PCl_3 on various liquid phases, including silicone oil, on which he quantitatively separated $SiHCl_3$ from $SiCl_4$.

In another paper, TADMOR[9] studied the separation of $GeCl_4$, $SnCl_4$ and $AsCl_3$ and their interaction on a column packed with Sil-O-Cel C-22 insulating brick, either uncoated or coated with varying quantities of the liquid phase, by an isotopic exchange technique (hydrochloric acid labelled with ^{36}Cl). The chromatograms obtained with an uncoated support showed irregular peaks and imperfect separations. The incomplete recovery of the chlorides at the column's outlet was attributed to losses due to hydrolysis occurring within the column.

WILKE et al.[10] has reported on the determination of the purity of the tetrachlorides of silicon, tin and titanium by gas–liquid chromatography. They used nitrobenzene, silicone oil or Apiezon N on a diatomaceous support at $100°$. They found that well resolved individual peaks for $SiCl_4$ and $TiCl_4$ could only be obtained by preinjecting a sufficient quantity of $TiCl_4$.

SIE et al.[11] in a study of the gas chromatographic separation of inorganic chlorides observed the appearance of a peak, attributed to hydrochloric acid, in a sample of gaseous chlorine after its contact with silicone grease.

In the present work the interaction between silicon tetrachloride, germanium tetrachloride, carbon tetrachloride, tin tetrachloride, titanium tetrachloride, arsenic trichloride, phosphorus trichloride, phosphorus oxychloride, vanadium tetrachloride and antimony pentachloride and the liquid phases Kel-F oil 10, Kel-F wax, Silicone oil DC-550, Silicone rubber UC-W98 and Apiezon L and Phasepak P is studied.

Study of the interaction between solutes and packing materials

Conclusions regarding the interaction between chlorides and liquid phases may be drawn from: (a) observation of the chromatograms obtained, (b) the changes, if any, occurring in the packing material after the experiments, and (c) the log V_g/log $p°$ ratio.

The first thing to examine in studying the chromatograms is the stability of the base line and its eventual deviation from zero. The chromatograms can then be studied to ascertain the presence or absence of artifact peaks or the non appearance of expected peaks. One can then go on to observe the symmetry of the peaks, looking for tailing or skewing, so as to draw conclusions regarding the linearity of the partition isotherm.

As regards the appearance of the packing material at the end of a series of experiments, one should note any change that may have occurred in its colour or weight, or any other alteration. Possible retention of some of the solutes can be ascertained by checking whether there is any difference in the weight of the column before and after any long series of experiments. Finally, one can obtain indications as to whether or not the solutes are ideally dissolved in the liquid phase, without any change of their molecular structure, by examining the plot of log V_g versus log p^0, which should be a straight line with a slope equal to unity.

EXPERIMENTAL

Materials

Chlorides were obtained from commercial sources with the exception of germanium tetrachloride and vanadium tetrachloride which were prepared by chlorination of the corresponding metals. They were all purified by isothermal distillation and kept under absolutely anhydrous conditions.

Packing materials
(1) Kel-F oil 10, 10% w/w, on Celite 545
(2) Apiezon L, 10% w/w, on 45–60 mesh Chromosorb R
(3) Kel-F wax, 10% w/w, on Celite 545
(4) Phasepak P, 30–60 mesh
(5) Silicone rubber UC-W98, 10% w/w, on Diatoport S 80–100 mesh
(6) Silicone oil DC-550, 10% w/w on Celite 545
(7) Graphite purified Erg. B 6, 5% w/w, on glass beads 50–140 mesh

Operating conditions

Apparatus. A Hewlett-Packard chromatograph, Type 700, equipped with a Gow-Mac thermal conductivity detector with four W filaments was used. The instrument was modified in order to keep the oven temperature constant within $\pm$ 0.1°. From time to time the detector was washed with acetone in order to prevent alteration of response owing to deposits of hydrolysis or reaction products.

Columns. Glass coils of 183 cm length and an inside diameter equal to 4 mm were used. The columns were conditioned overnight at the maximum recommended temperature. The effluent end of the column was not connected to the detector during the conditioning period. All the columns were packed under anhydrous vacuum conditions by inserting a pyrex glass wool at one end of the column, applying vacuum to that end and adding the packing material at the other end of the column. Columns were vibrated and the vacuum continued until the packing material did not settle any further. Column oven temperatures used were at maximum ca. 30° below the maximum recommended temperature limit at isothermal conditions. The injection

port temperature was maintained at 50° above oven temperature, and that of detector was maintained equal to that of the oven.

Nitrogen, dried by passing through an activated molecular sieve and a phosphorus pentoxide trap, was used as the carrier gas at flow rates of between 10 and 100 ml/min so that the minimum height of a theoretical plate was obtained.

The column temperature was 60–190°. Bridge current T.C. detector was 150 mA.

The recorder used was a Kipp and Zonen, Type Micrograph BD2, 1 mV. The chart speed was 1 in. per min.

Injected volume of the sample was from 0.5 μl up to 10 μl injected with a Hamilton 701N syringe.

RESULTS AND DISCUSSION

Base line

In most of the chromatograms obtained the base line was stable and no deviation from zero was observed. However when $SbCl_5$ and VCl_4 were chromatographed a continuous displacement of the base line from its initial level appeared.

Artifact peaks

The $SiCl_4$, $AsCl_3$, $SnCl_4$, PCl_3, $POCl_3$ and CCl_4 behaved normally with all packing materials giving a single peak. In contrast to this, $SbCl_5$, VCl_4 and $TiCl_4$ showed abnormal behaviour. Thus, $SbCl_5$ when it was chromatographed with Apiezon L decomposed, yielding only one peak attributable to Cl_2. On silicone oil, a large number of well resolved unidentified peaks were obtained, while Phasepak P also gave a large number of peaks one of which was Cl_2. With graphite only one very distorted peak appeared. With Kel-F wax four peaks resulted, one of which was identified as Cl_2; while on Kel-F oil 10 no peak at all appeared, and the conclusion was drawn that the solute was completely retained by the liquid phase.

VCl_4, on silicone oil gave rise to two peaks. One of VCl_4, the second of $VOCl_3$. With Kel-F wax and Kel-F oil only a single but very distorted peak resulted.

$TiCl_4$ was completely retained by Apiezon L.

Due to their pronounced reactivity no further experiments were conducted with $SbCl_5$ and VCl_4. Graphite was used to overcome difficulties rising from the reactivity of these two compounds, upon the other liquid phases, but without complete success.

Symmetry of the peaks

Asymmetry of a peak may be due to one of two causes, according to the resulting shape. It may be the result of sorption on the solid support, which produces tailing, or may be attributed to a non-linear partition isotherm corresponding to a deviation from Raoult's law, i.e. variation of the partition coefficient with the concentration of the substance in the liquid phase. This results in skewing of the entire peak.

Tailing. Some small amount of tailing was observed in all experiments. This was clearly due to the fact that the solid supports being used were not silanised with the exception of Diatoport S. Of the packing materials studied, Kel-F wax on Celite gave the most symmetrical peaks with negligible tailing. There was a minimal amount of tailing on Phasepak P and on the liquid phase Silicone rubber on Diatoport S. The

two liquid phases Silicone oil and Kel-F oil on Celite only gave a very small amount of tailing though rather more was shown by Apiezon L, also on Celite.

Skewing. The peaks obtained using the stationary phase, Phasepak P and the liquid phases Apiezon L, Silicone rubber and Silicone oil on Celite showed no skewing except as noted.

With Kel-F oil 10 and Kel-F wax backward skewing of the peaks was observed in some cases, indicating a positive deviation from Raoult's law and a consequent increase of the partition coefficient in the gas and liquid phases due to an increase in the concentration of the chromatographed substance. More precisely Kel-F wax produced slight skewing of the $TiCl_4$ peak at a temperature of 100°.

Kel-F oil produced a pronounced skewing of the $TiCl_4$ peak and slight skewing of $SnCl_4$, $POCl_3$, $AsCl_3$ and CCl_4 peaks at 60°. Silicone oil resulted in a slight but quite noticeable skewing of the $POCl_3$, $AsCl_3$ and $TiCl_4$ peaks, only at 100°. This skewing appears when the sample size is relatively large, *e.g.* more than 2.5 μl of $POCl_3$ or $TiCl_4$. It was noticed that skewing is more pronounced when other chlorides have already been passed through the column. For instance, in the case of $AsCl_3$ with silicone oil at 150° it was observed that an injection of a 17 μl sample in a column that had not been used before for any other substances gave no skewing, whereas in a column through which $SnCl_4$, $SiCl_4$ and PCl_3 have been passed, the peaks started to skew as soon as the sample of $AsCl_3$ exceeded 2.5 μl.

Change of colour or weight of the packing material

No change in the colour of the listed packing materials was observed in all experiments, except in the case of titanium chloride, which caused darkening of the Apiezon L. Furthermore, after a great number of experiments no increase or decrease in the weight of the columns, could be observed. The check on the liquid phase was carried out by emptying the column, extracting the packing material with absolute ether, and weighing the residue. In a few cases there was a slight decrease in the weight when the column had been kept under working conditions for a long period at a relatively high temperature: this was clearly due to partial bleeding of the liquid phase.

Plot of log V_g versus log p^0

According to the relationship, $\ln V_g = - a \ln p^0 + C$, derived by HOARE AND PURNELL[12,13] the coefficient a is equal to the ratio of the heat of solution to the heat of vaporisation and is approximately unity in the case of liquid phases of similar polarity to the chromatographed substances. Consequently the plot of $\ln V_g$ *vs.* $\ln p^0$ is linear, with a slope of $a = 1$. Values of a greater or smaller than unity reflect deviations from ideal solution behaviour and are a measure of solute interaction with the liquid phase. Figs. 1–4 show the plot of log V_g *vs.* log p^0 for the systems studied.

On the liquid phase Kel-F oil 10 (Figs. 1 and 2) for the PCl_3 and $TiCl_4$ the plot of log V_g *versus* log p^0 is a straight line with a slope equal to unity or with a minimal deviation therefrom. Consequently ideal solution behaviour in this liquid phase can be deduced. In the case of $AsCl_3$, $SnCl_4$ and $GeCl_4$ the resulting plot is linear with a slope deviating 0–5° from unity, up to the value of log p^0 corresponding to a temperature of 70°. Beyond this the slope declines suddenly and this probably indicates that above this temperature these compounds cease to have ideal solution behaviour and interaction of the chlorides with the liquid phase takes place.
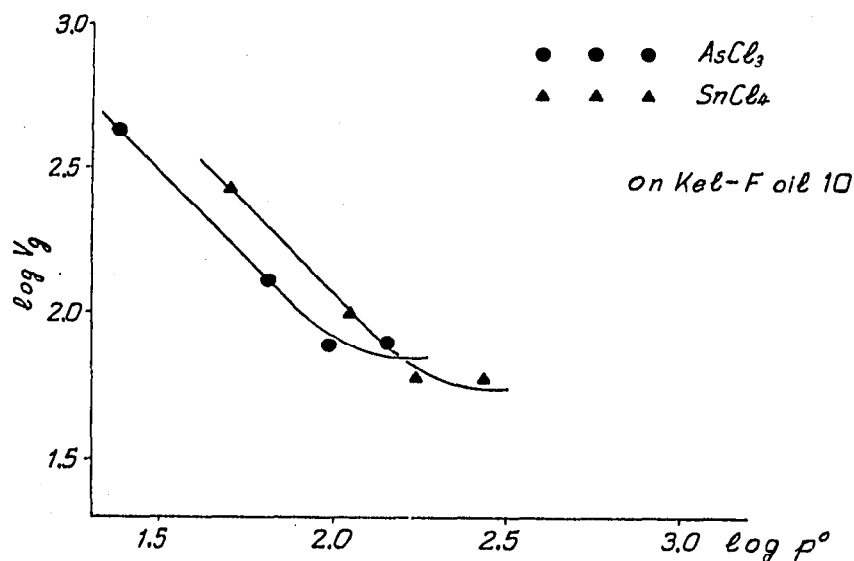
Fig. 1. Specific retention volume–vapour pressure plots for certain chlorides. Packing material: Kel-F oil 10, 10% w/w, on Celite 545.

Figs. 3 and 4 show the log V_g–log p^0 plots for the other phases. With only one exception these phases give plots that are linear, with a deviation from unity fluctuating between +8° and —7°.

On the liquid phases silicone oil and Kel-F wax (Fig. 3) AsCl$_3$ shows considerable deviation, while SnCl$_4$ gives a linear plot that barely deviates from unity. POCl$_3$ and TiCl$_4$ on Kel-F wax show no deviation at all.

With the stationary phase Phasepak P (Fig. 3) deviations of +4° and —17° are given by SnCl$_4$ and AsCl$_3$, respectively.
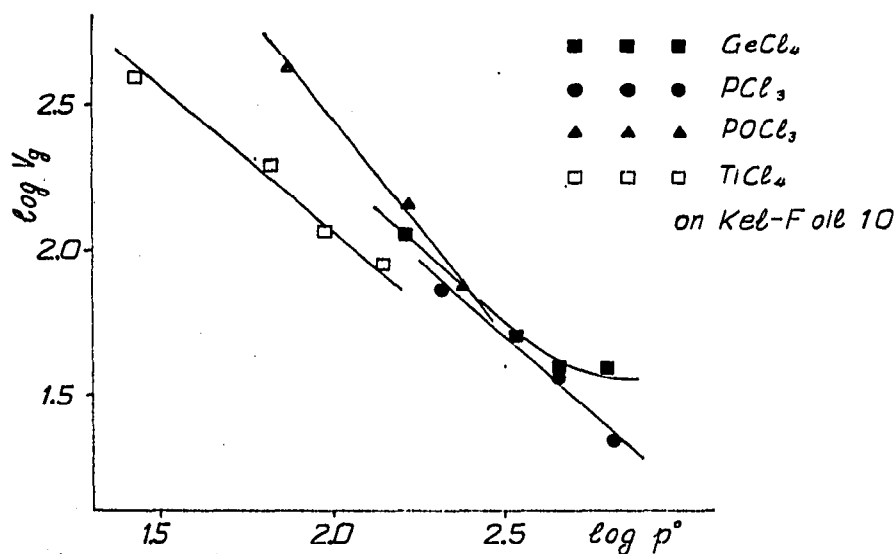

Fig. 2. Specific retention volume–vapour pressure plots for certain chlorides. Packing material: Kel-F oil 10, 10% w/w, on Celite 545.
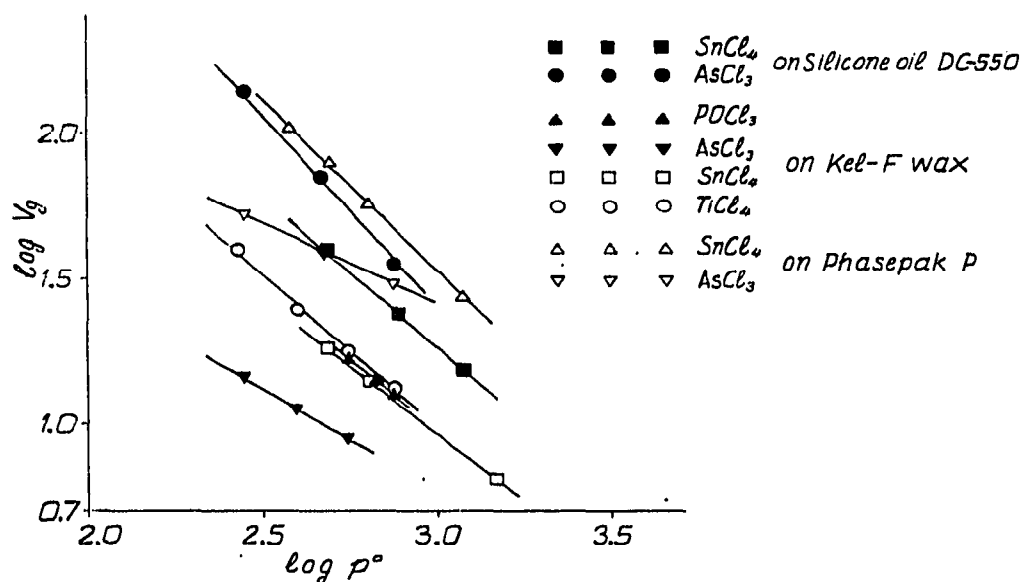
Fig. 3. Specific retention volume–vapour pressure plots for certain chlorides. Packing materials: (a) Silicone oil DC-550, 10% w/w, on Celite 545, (b) Kel-F wax, 10%, on Celite 545 and (c) Phasepak P 30–60 mesh.

With the liquid phases silicone rubber and Apiezon L (Fig. 4) the linear plots given by $AsCl_3$ and $SnCl_4$ show a slight deviation from unity, while for $POCl_3$ the slope of the plot log V_g vs. log p^0 is equal to unity.

CONCLUSIONS

It has been shown in this paper that a number of organic partitioning phases, under particular operation conditions, do not interact with inorganic volatile chlorides
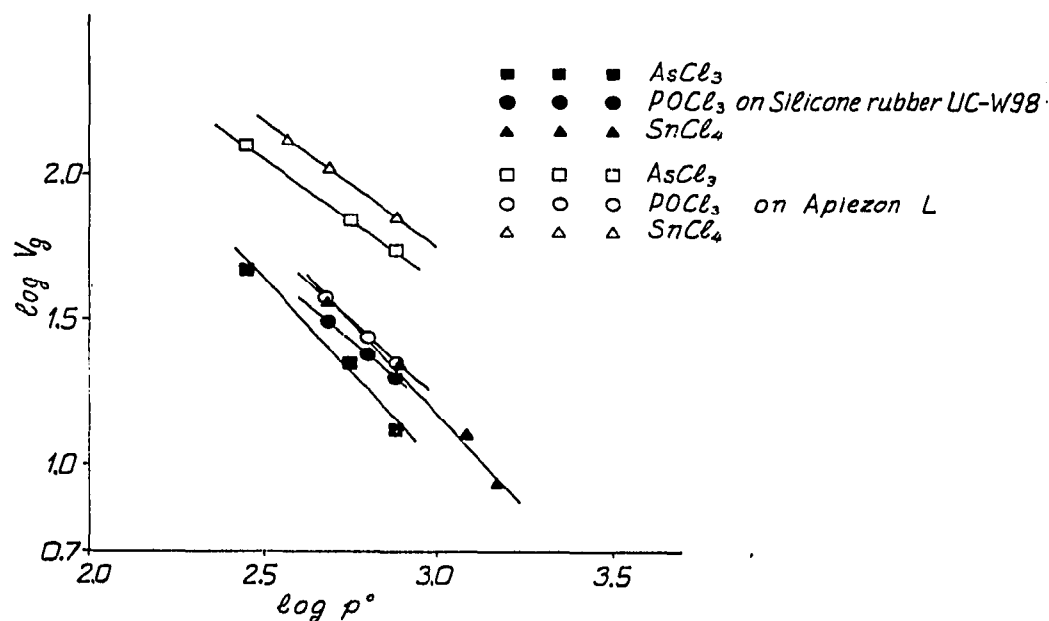

Fig. 4. Specific retention volume–vapour pressure plots for certain chlorides. Packing materials: (a) Silicone rubber UC-W98, 10% w/w, on Diatoport S and (b) Apiezon L, 10% w/w, on Celite 545.

and consequently they can be recommended for the quantitative separation and determination of these volatile compounds.

The absence of reactivity has been deduced from the fact that no artifact peaks appeared, the peaks were symmetrical with no skewing, so long as the columns were not overloaded, and had only slight tailing which was attributed to the non-silanisation of the solid support. In addition the plot of log V_g vs. log p^0 gave a straight line which is an indication of non reactivity between partitioning phase and solute.

Previously reported failures when using some of these phases for the same purpose can partially attributed to the fact that in the present work the experiments were done under anhydrous conditions and glass columns were used. CCl_4, $AsCl_3$ $SiCl_4$, $POCl_3$, PCl_3, $SnCl_4$, $GeCl_4$ and $TiCl_4$ behaved normally towards the partitioning phases tested. In contrast to these, $SbCl_5$ and VCl_4 reacted with almost all of them giving rise to a number of well resolved but unidentified peaks. The use of graphite as stationary phase was promising. Further experimental work is continuing on this system to see if better results may be achieved.

REFERENCES

1 H. Freiser, *Anal. Chem.*, 31 (1959) 1440.
2 R. A. Keller and H. Freiser, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworth, London, 1960, p. 301.
3 R. A. Keller, *J. Chromatog.*, 5 (1961) 225.
4 K. A. Hutchinson, *Ph.D. Dissertation, Wayne State University Dissertation Abs.*, 24 (1964) 4372.
5 F. M. Wachi, *Ph.D. Dissertation*, University of Illinois, Urhana, Ill., 1959.
6 J. Tadmor, *Res. Council Israel, Bull.*, IIA, No. 2 (1962) 144.
7 J. Tadmor, *J. Gas Chromatog.*, 3 (1965) 121.
8 Y. Abe, *Bunseki Kagaku*, 9 (1960) 795; *C.A.*, 35 (1961) 18421h.
9 J. Tadmor, *Anal. Chem.*, 36 (1964) 1565.
10 J. Wilke, A. Losse and H. Sackmann, *J. Chromatog.*, 18 (1965) 482.
11 S. T. Sie, J. P. A. Bleumer and G. W. A. Rijnders, *Separation Sci.*, 1 (1966) 41.
12 M. R. Hoare and J. H. Purnell, *Research*, 8 (1955) S 41.
13 M. R. Hoare and J. H. Purnell, *Trans. Faraday Soc.*, 52 (1956) 222.