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## RETENTION VOLUME IN HIGH-PRESSURE GAS CHROMATOGRAPHY

### III. SQUALANE-TETRACHLOROMETHANE, ISOCTANE, TOLUENE-NITROGEN, HYDROGEN, CARBON DIOXIDE SYSTEMS

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#### SUMMARY

The specific retention volumes of tetrachloromethane, isooctane and toluene were measured on squalane at 50 and 75 °C with nitrogen and hydrogen as carrier gases at pressures of 10–100 atm and with carbon dioxide at pressures of 10–50 atm. Exact corrections of the data for the gas-phase non-ideality and liquid-phase compressibility effects were carried out, thus making it possible to distinguish and characterize unequivocally the role of the solubility of the carrier gas in the sorbent phase. The results show that the pseudo-binary model fails in a more refined interpretation of gas chromatographic retention data.

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#### INTRODUCTION

In a previous paper<sup>1</sup>, specific retention volumes measured for tetrachloromethane, isooctane and toluene on Apiezon K with nitrogen, hydrogen and carbon dioxide as carrier gases at 50 and 75 °C and at mean column pressures of 10–100 atm for nitrogen and hydrogen and 5–50 atm for carbon dioxide were processed according to the pseudo-binary model<sup>2</sup>. In accordance with this model, neglecting the solubility of the carrier gas in the stationary phase resulted in an effect as if the partial molar volumes of the solutes in the stationary phase acquired different values for each of the carrier gases employed. The differences in these effective partial molar volumes were especially marked with isooctane. However, the effect of the solubility of the carrier gas on the specific retention volume, which has been specified by eqn. 1 in the previous paper<sup>1</sup>, can be distinguished and treated separately only if the true partial molar volumes of the solutes in the stationary phase are known. The partial molar volumes of the components of a solution are experimentally accessible most readily from the dependence of the density of the solution on its composition. However, owing to their high viscosity, solutions that contain Apiezon K as a major component are not very amenable to the precise measurement of density. Therefore, we carried out analogous chromatographic measurements on squalane as the stationary phase, the solutes, carrier gases and experimental conditions being the same as those used

with Apiezon K. The partial molar volumes of the individual solutes in squalane were determined from the independently measured dependences of the densities of binary solute-squalane solutions on the molar fraction of the solute.

## EXPERIMENTAL

The specific retention volumes were measured on the instrument used in our earlier measurements with Apiezon K<sup>1</sup>, with some slight alterations in the design of the manostat. The transistor relays operating the solenoid valve were omitted and the solenoid coil was connected directly into the collection circuit of a power transistor. In addition, the pneumatic controlling section of the manostat was thermostatted at 50 °C in order to provide better long-term stability of the pressure.

The measurement of the density of the solute-squalane solutions was carried out pycnometrically at 50 and 75 °C. The concentrations of the solutes were approximately 1, 3, 5 and 10% (w/w). The results obtained were expressed as the dependences of the molar volume of the mixture on the molar fraction of the solute,  $x_1$ , and processed by the method of intercepts<sup>3</sup>; the limiting tangent at  $x_1 \rightarrow 0$  was determined by the least-squares method and the intercept cut by this tangent on the coordinate of molar volumes at  $x_1 = 1$  gave an estimate of the partial molar volume of the solute at infinite dilution in the mixture.

## RESULTS AND DISCUSSION

The procedure for processing the measured retention data was described in detail in our previous paper<sup>1</sup>. The specific retention volumes expressed at a reference temperature of 373 K,  $V_g^{373}$ , as measured for the solutes studied at different mean column pressures up to 100 atm and at column temperatures of 50 and 75 °C, are summarized in Table I. As shown in Figs. 1–3, the plots of  $\log V_g^{373}$  against the column pressure for the individual solutes on squalane display courses very similar to those obtained for analogous situations with Apiezon K as the stationary phase<sup>1</sup>.

In further processing, the data were corrected for the non-ideality of the gaseous phase and the compressibility of the liquid phase by employing the equation<sup>1</sup>

$$\ln \frac{z_2}{z_2^{T_r}} V_g^{T_r} - \left( \frac{2B_{12}}{z_2} - \bar{V}_i^L \right) \frac{\bar{P}}{RT} = \ln \frac{RT_r}{M_3 H_1^{P_r}} \quad (1)$$

where  $z_2$  and  $z_2^{T_r}$  are the compressibility coefficients of the carrier gas at the temperature of measurement (column temperature),  $T$ , and a reference temperature  $T_r$ ,  $V_g^{T_r}$  is the specific retention volume as measured at the temperature  $T$  and expressed at the reference temperature  $T_r$ ,  $B_{12}$  is the second cross-virial coefficient of the solute vapour and the carrier gas,  $\bar{V}_i^L$  is the partial molar volume of solute in the liquid phase,  $\bar{P}$  is the absolute mean column pressure,  $M_3$  is the molecular weight of pure (without dissolved carrier gas) liquid sorbent,  $H_1^{P_r}$  is the Henry's law constant of the solute in the actual liquid sorbent at a reference pressure  $P_r$  and  $R$  is the perfect gas constant. The logarithmed expression on the right-hand side of eqn. 1 represents the specific retention volume corrected for the non-ideal effects in the gaseous phase and the compressibility of the liquid phase, expressed at a temperature  $T_r$ . For the sake of brevity, this ex-

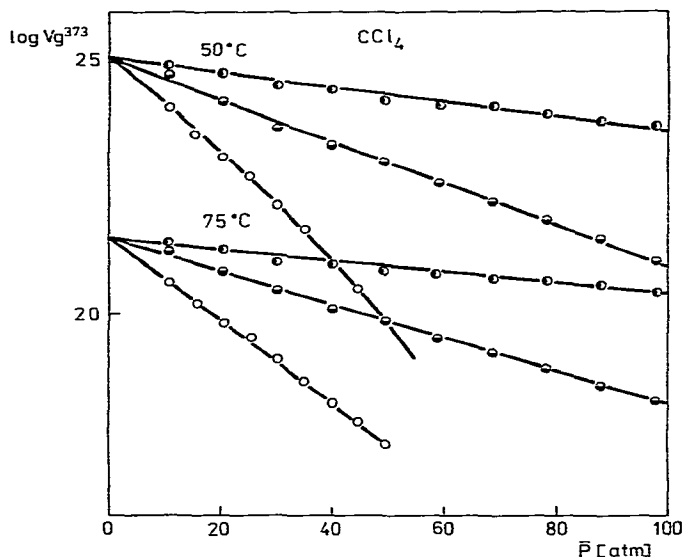


Fig. 1. Plot of  $\log V_g^{373}$  of tetrachloromethane on squalane at 50 and 75 °C against the column mean pressure with hydrogen (●), nitrogen (◐) and carbon dioxide (○) as carrier gases.

pression will subsequently be denoted by  $V_g^{\theta T_r}$ . The data on the cross-virial coefficients were taken from the paper by Prausnitz and Benson<sup>4</sup>.

The data on the density of the binary solute-squalane mixtures are summarized in Table II. The partial molar volumes of the individual solutes at infinite dilution in squalane,  $\bar{V}_i^L$ , and the molar volumes of the liquid solutes alone,  $V_i^L$ , at 50 and 75 °C

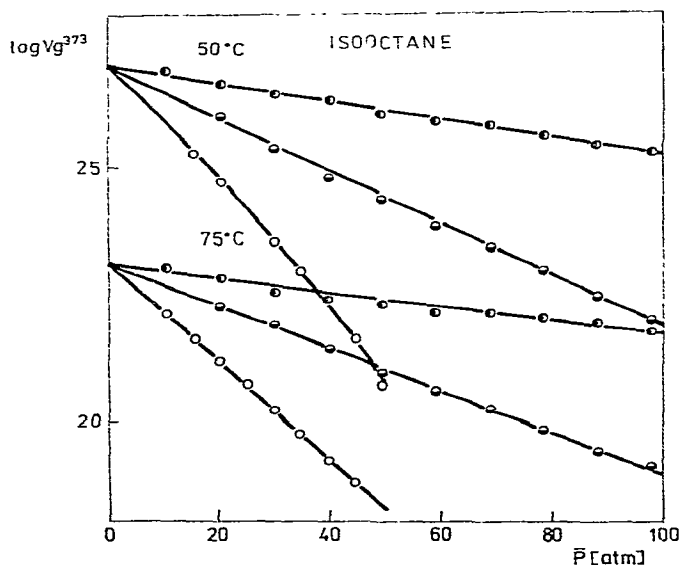


Fig. 2. Plot of  $\log V_g^{373}$  of iso-octane on squalane at 50 and 75 °C against the column mean pressure with hydrogen (●), nitrogen (◐) and carbon dioxide (○) as carrier gases.

TABLE I  
EXPERIMENTAL  $V_{\theta}^{373}$  VALUES

$P$ ( <i>atm</i> )	$V_{\theta}^{373}$ ( <i>ml/g</i> )	$CCl_4-N_2$		$CCl_4-H_2$		<i>Isooctane-N<sub>2</sub></i>		<i>Isooctane-H<sub>2</sub></i>		<i>Toluene-N<sub>2</sub></i>		<i>Toluene-H<sub>2</sub></i>		$CCl_4-CO_2$		<i>Isooctane-CO<sub>2</sub></i>		<i>Toluene-CO<sub>2</sub></i>	
		50 °C	75 °C	50 °C	75 °C	50 °C	75 °C	50 °C	75 °C	50 °C	75 °C	50 °C	75 °C	50 °C	75 °C	50 °C	75 °C	50 °C	75 °C
		10.6	301	133	310	139	310	462	190	485	201	861	330	895	348	260	116	392	162
15.5														228	105	336	144	580	242
20.3	266	121	300	134	300	398	169	465	192	749	296	860	333	204	96.4	295	130	506	216
25.2														186	89.5	262	119	445	197
30.0	235	112	286	127	344	344	152	441	181	654	268	818	315	164	81.1	226	105	380	172
34.8														147	73.7	198	94.2	329	154
39.7	216	103	282	124	308	308	138	429	175	587	245	799	305	125	66.5	164	83.6	271	136
44.5														113	61.2	144	75.5	236	122
49.3	199	95.0	268	122	276	276	124	404	170	536	224	752	298	97.0	54.0	120	65.3	196	106
54.2																			
59.0	180	89.6	262	120	244	244	115	391	166	480	209	729	291						
68.7	166	83.7	260	118	220	220	105	385	163	436	193	720	285						
78.3	153	77.5	249	117	198	198	95.7	367	161	396	177	689	283						
88.0	140	72.0	241	115	177	177	87.3	351	156	358	162	665	274						
97.7	128	67.5	237	111	158	158	81.2	341	150	323	151	647	265						

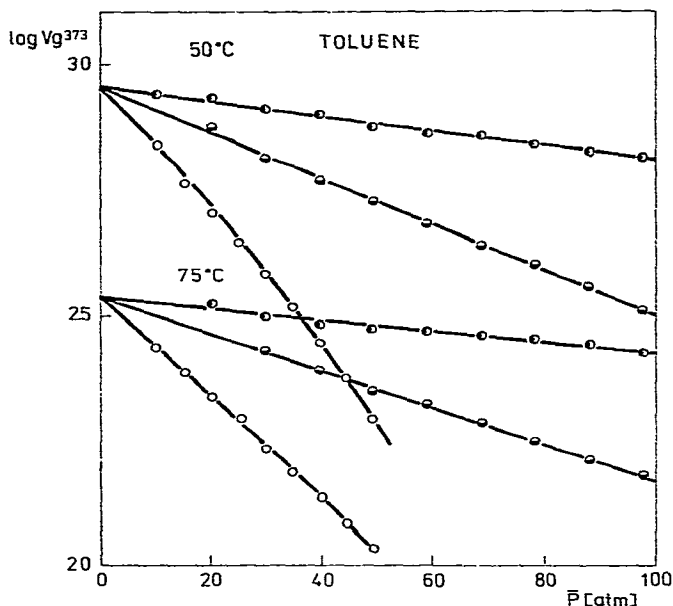


Fig. 3. Plot of  $\log V_g^{373}$  of toluene on squalane at 50 and 75 °C against the column mean pressure with hydrogen (●), nitrogen (◐) and carbon dioxide (○) as carrier gases.

are given in Table III. A comparison of the corresponding partial molar and molar volumes shows that the properties of the solutions studied approach closely those of an ideal solution.

Provided that the pseudo-binary model is valid, the values of  $\ln V_g^{\theta T_r}$  calculated by eqn. 1 should be independent of the type and pressure of carrier gas. In Figs. 4–6 the values of  $\ln V_g^{\theta T_r}$  at  $T_r = 373$  K obtained for the individual solutes and carrier gases are plotted against the mean column pressure. The corresponding correlation

TABLE II

DENSITY OF SOLUTE-SQUALANE MODEL SOLUTIONS AT 50 AND 75 °C

Solute	Concentration (wt.%)	$d_{50}$	$d_{75}$
CCl <sub>4</sub>	1.413	0.7957	0.7803
	2.842	0.8024	0.7867
	6.124	0.8155	0.7990
	10.277	0.8326	0.8146
Isooctane	1.098	0.7896	0.7726
	3.039	0.7889	0.7717
	5.934	0.7849	0.7689
	9.928	0.7796	0.7634
Toluene	0.932	0.7932	0.7778
	3.079	0.7955	0.7795
	6.512	0.7965	0.7804
	10.148	0.7982	0.7813

TABLE III

MOLAR VOLUMES ( $V_l^L$ ) AND PARTIAL MOLAR VOLUMES AT INFINITE DILUTION IN SQUALANE ( $\bar{V}_l^L$ ) OF  $\text{CCl}_4$ , ISOCTANE AND TOLUENE AT 50 AND 75 °C

Solute	$V_{l,75}^L$	$V_{l,50}^L$	$\bar{V}_{l,75}^L$	$\bar{V}_{l,50}^L$
$\text{CCl}_4$	100.2	103.5	94.4	95.4
Isooctane	171.3	176.9	159.4	160.9
Toluene	109.8	113.0	102.5	104.2

equations are summarized in Table IV. A slight dependence of  $\ln V_g^{\theta T_r}$  on pressure can be observed with both toluene and tetrachloromethane, but the precision of the data is not sufficient for quantitative conclusions to be drawn.

The systems with isooctane deserve special mention. Whereas with the systems isooctane–nitrogen–squalane and isooctane–hydrogen–squalane is it not possible to prove unequivocally a pressure dependence of  $\ln V_g^{\theta T_r}$  within the limits of precision of our data, with the system isooctane–carbon dioxide–squalane the  $\ln V_g^{\theta T_r}$  values show a marked linear increase with increasing pressure. This behaviour, which was found for a system alkane–carbon dioxide–non-polar stationary liquid in our earlier work<sup>1</sup>, indicates that the pseudo-binary model fails in a more refined interpretation of retention data.

The dependence of retention data corrected in the above way for non-ideality of the gaseous phase and compressibility of the liquid phase is caused by an increase in the overall amount and a change in the composition of the stationary phase due to the solubility of carrier gas in it. Under the given conditions, the composition of the stationary phase (stationary liquid proper plus dissolved carrier gas) is obviously

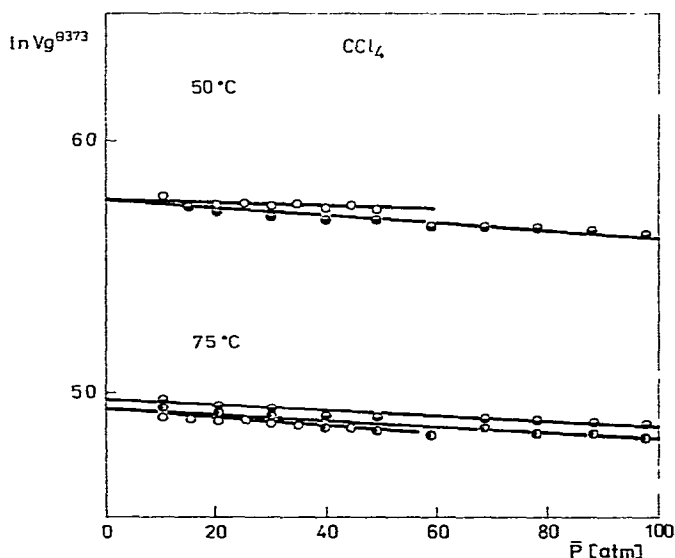


Fig. 4. Dependence of  $\ln V_g^{0.9373}$  on the column mean pressure for tetrachloromethane on squalane at 50 and 75 °C. Carrier gas: ●, hydrogen; ●, nitrogen; ○, carbon dioxide.

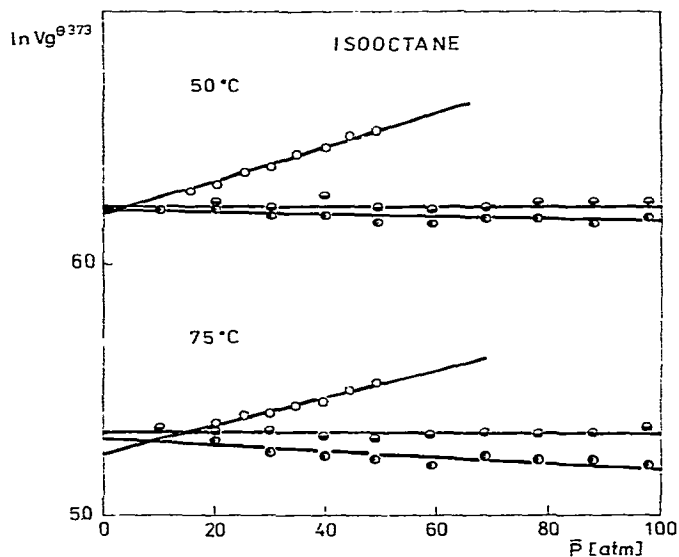


Fig. 5. Dependence of  $\ln V_g^{0.373}$  on the column mean pressure for isooctane on squalane at 50 and 75 °C. Carrier gas:  $\bullet$ , hydrogen;  $\ominus$ , nitrogen;  $\circ$ , carbon dioxide.

the same for all of the solutes investigated, so that the differences in the pressure dependences of  $\ln V_g^{0.373}$  are determined simply by the different sensitivities of the activity coefficients of the solutes to the varying composition of the liquid phase.

Figs. 4-6 and the correlation equations in Table IV can further be interpreted

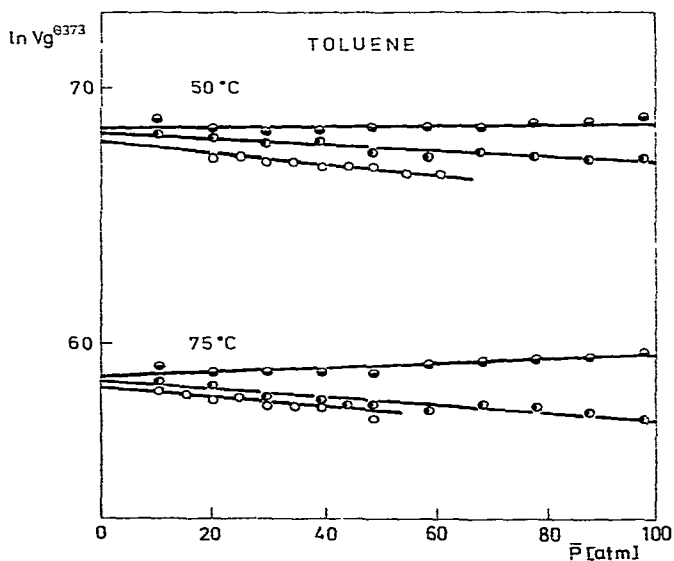


Fig. 6. Dependence of  $\ln V_g^{0.373}$  on the column mean pressure for toluene on squalane at 50 and 75 °C. Carrier gas:  $\bullet$ , hydrogen;  $\ominus$ , nitrogen;  $\circ$ , carbon dioxide.

TABLE IV

EQUATIONS OF THE CORRELATION OF  $\ln V_g^{0.373}$  WITH COLUMN MEAN PRESSURE ( $\bar{P}$ ) FOR  $\text{CCl}_4$ , ISOCTANE AND TOLUENE ON SQUALANE AT 50 AND 75 °CFor the meaning of  $V_g^{0.373}$ , see eqns. 1 and 2.

Carrier gas	Temperature (°C)	$\ln V_g^{0.373}$		
		$\text{CCl}_4$	Isooctane	Toluene
$\text{N}_2$	50	$5.7751 - 0.00168 \bar{P}$	$6.2254 - 0.00018 \bar{P}$	$6.8412 + 0.00013 \bar{P}$
	75	$4.9551 - 0.00101 \bar{P}$	$5.3298 - 0.00003 \bar{P}$	$5.8744 + 0.00074 \bar{P}$
$\text{H}_2$	50		$6.2144 - 0.00067 \bar{P}$	$6.8240 - 0.00119 \bar{P}$
	75	$4.9277 - 0.00128 \bar{P}$	$5.3018 - 0.00111 \bar{P}$	$5.8517 - 0.00168 \bar{P}$
$\text{CO}_2$	50	$5.7576 - 0.00055 \bar{P}$	$6.1919 + 0.00671 \bar{P}$	$6.7791 - 0.00209 \bar{P}$
	75	$4.9221 - 0.00160 \bar{P}$	$5.2426 + 0.00550 \bar{P}$	$5.8196 - 0.00127 \bar{P}$

by virtue of the relationships derived in Part I of this series<sup>2</sup>. Eqn. 26 in that paper<sup>2</sup> can be written in the form

$$\ln V_g^{0T_r} = \ln \frac{RT_r}{M_3 f_1^{0P_r}} \cdot \frac{1}{\gamma_1^{+P_r} (1 - x_2)} \quad (2)$$

where  $f_1^{0P_r}$  is the fugacity of the pure liquid solute at the temperature of measurement and a reference pressure  $P_r$ ,  $\gamma_1^{+P_r}$  is the Raoult's law activity coefficient of the solute in the actual liquid sorbent at the temperature of measurement and the reference pressure and  $x_2$  is the molar fraction of the carrier gas dissolved in the sorbent phase. From eqn. 2 we can readily obtain

$$\begin{aligned} \frac{d \ln V_g^{0T_r}}{d \bar{P}} &= \frac{d \ln V_g^{0T_r}}{dx_2} \cdot \frac{dx_2}{d \bar{P}} \\ &= \frac{1}{\gamma_2^{*P_r} H_2^{P_r}} \left( 1 - \frac{d \ln \gamma_2^{*P_r}}{d \ln \bar{P}} \right) \left( \frac{1}{1 - x_2} - \frac{d \ln \gamma_1^{+P_r}}{dx_2} \right) \end{aligned} \quad (3)$$

where  $H_2^{P_r}$  is the Henry's law constant of the carrier gas dissolved in the liquid sorbent at the temperature of measurement and the reference pressure  $P_r$ , and  $\gamma_2^{*P_r}$  is the corresponding Henry's law activity coefficient. A similar relation was recently quoted by Lauer<sup>5</sup>. Eqn. 3 defines the slope of the pressure function of  $\ln V_g^{0T_r}$  as shown by the plots in Figs. 4-6 and specified numerically by the equations in Table IV.

In order to carry out this last correction, it would be necessary to know the solubility of the carrier gas in the stationary liquid and the dependence of the activity coefficient of the solute on the concentration of the dissolved carrier gas.

## CONCLUSIONS

It follows from eqns. 1 and 2 that the gas chromatographic retention volume is generally a function of a number of second-order parameters which are difficult to



specify and to distinguish experimentally. These effects are of little importance in ordinary gas chromatographic measurements, but they become significant in measurements at higher pressures of the carrier gas and/or even at moderate pressures in high-precision measurements, especially when employing easily condensable carrier gases. In addition, the specific retention volume is also dependent on dynamic factors<sup>6</sup>. A complete correction for all of these non-ideal effects is very difficult.

This situation is unfavourable towards the possibility of both precise analytical processing and the exact physicochemical interpretation of retention data. It is evident that a perfect reproducibility of high-precision gas chromatographic retention data cannot be attained by standardizing merely the chromatographic sorbent; it would be necessary to standardize the entire chromatographic system in order to achieve this objective.

Eqns. 2 and 3 can be used to verify the finding<sup>7</sup>, curious at first sight, that the character of the dependence of retention indices on the type and pressure of the carrier gas depends on the type of stationary phase used.

#### REFERENCES

- 1 S. Wičar and J. Novák, *J. Chromatogr.*, 95 (1974) 13.
- 2 S. Wičar and J. Novák, *J. Chromatogr.*, 95 (1974) 1.
- 3 W. J. Moore, *Physical Chemistry*, Longmans, London, 5th ed., 1972, p. 234.
- 4 J. M. Prausnitz and P. R. Benson, *AIChEJ*, 5 (1959) 161.
- 5 H. H. Lauer, *Thesis*, University of Amsterdam, 1976.
- 6 S. Wičar, J. Novák and N. Ruseva-Rakshieva, *Anal. Chem.*, 43 (1971) 1945.
- 7 L. Soják, J. Janák and J. A. Rijks, *J. Chromatogr.*, 138 (1977) 119.