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## USE OF LINEAR AND BRANCHED-CHAIN PARAFFINIC LIQUID PHASES AS NON-POLAR REFERENCE MATERIALS IN GAS CHROMATOGRAPHY

G. CASTELLO and G. D'AMATO

*Istituto di Chimica Industriale, Università di Genova, Corso Europa 30, I-16132 Genova (Italy)*

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### SUMMARY

The gas chromatographic analysis of linear and branched-chain hydrocarbons on squalane and *n*-triacontane columns was carried out under identical conditions in order to study the effect of branching of the liquid phase molecules on the selectivity towards the various homologous series. The results were compared with available literature data on squalane, *n*-triacontane, C<sub>87</sub>H<sub>176</sub> and polydimethylsilicones (SF 96).

It has been shown that branched paraffinic chains have a higher interaction with liquid phases that have a higher ratio of methyl groups to total carbon atoms, and this effect may impair the use of squalane as a non-polar reference material when the "polarity" of hydrocarbon or methylsilicone liquid phases must be determined.

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### INTRODUCTION

The choice of a liquid phase as a "non-polar" reference material in gas chromatography implies that it can interact with solutes by dispersion forces only, excluding hydrogen bonding, induction, orientation, etc.

Hydrocarbons are known to be the least polar liquid phases and are therefore used as reference materials. Linear alkanes of high molecular weight should be used, in order to avoid possible selectivity of branched-chain hydrocarbons towards methyl-containing solutes due to Van der Waals bonds formed between the methyl groups of the solute and of the solvent when their rotational frequencies correspond<sup>1</sup>.

The hypothetical liquid phase with a ratio of methyl groups to total carbon atoms of zero is obviously impossible to use as a reference material, but linear alkanes of high molecular weight have been tested as stationary phases<sup>2</sup>. Their melting points reduce their usefulness considerably at relatively low temperatures, whereas branched-chain alkanes can be used in a convenient, although restricted, temperature range.

Squalane (2,6,10,15,19,23-hexamethyltetracosane) has been widely used as the non-polar reference material in polarity scales for the characterization of the stationary phases used in gas chromatography<sup>3-8</sup>. The introduction of polymeric non-

polar liquid phases (*e.g.*, methylsilicones) with a wider useful temperature range did not affect the well established use of squalane as a non-polar standard solvent, although a suggestion has been made<sup>5</sup>.

A useful characteristic of squalane is its well defined chemical composition compared with the random composition of many polymeric liquid phases. Because the exact molecular weight is known, the determination of the activity coefficients at infinite dilution ( $\gamma^\infty$ ) for many substances can also be easily carried out. Notwithstanding this, for the accurate characterization of low-polarity liquid phases the use of squalane may not be the best choice. Squalane is a mixture of varying amounts of diastereoisomers that can interact in a slightly different way with the solutes, thus causing small variations in the retention values and a decrease in the column efficiency. Impurities may also be present in the commercial product, which therefore requires careful purification.

The main limitation to the use of squalane as the least polar reference material is the possibility that the high degree of branching of its molecule (with a  $\text{CH}_3/\text{C}$  ratio of 0.267) may be responsible for the selectivity of this phase towards molecules that contain branched hydrocarbon chains. This effect can be neglected when Rohrschneider or McReynolds constants are measured for highly polar phases, because the behaviour of these solvents is so different from that of a saturated hydrocarbon that the properties of squalane and of linear alkanes influence the results only very slightly, but this difference becomes important when low-polarity phases have to be characterized, and negative values of some constants are sometimes obtained. In this instance, squalane is not the optimal least polar solvent.

Van Kemenade and Groenedijk<sup>1</sup> found that for branched hydrocarbons squalane gives higher retention indices than octadecene-1, taken as a reference non-branched stationary phase, and ascribed this effect to the above-described methyl-methyl Van der Waals bonds. They concluded that the retention index increases with increasing methyl content of the solute and of the solvent, but some uncertainty remained owing to the differences in molecular weight and saturation between the liquid phases tested. A direct comparison of squalane with its linear isomer *n*-triacontane was therefore thought to be useful in order to confirm this effect.

Recently, a synthetic branched-chain hydrocarbon (24,24-diethyl-19,26-dioctadecylheptatriacontane;  $\text{C}_{87}\text{H}_{176}$ ) that can be used over a wider range of temperatures than squalane was proposed as a non-polar reference material<sup>10</sup>. The  $\text{CH}_3/\text{C}$  ratio of this hydrocarbon (0.069) is very close to that for *n*-triacontane (0.067) and is much lower than that for squalane (0.267).

In this paper, a direct comparison of the behaviour of squalane and *n*-triacontane as liquid phases for the separation of alkanes is reported and the results are compared with the available literature data on squalane, linear alkanes,  $\text{C}_{87}\text{H}_{176}$  and polydimethylsilicones, in order to ascertain if the use of squalane instead of a linear alkane as a non-polar reference material can introduce appreciable errors in the characterization of non-polar liquid phases.

## EXPERIMENTAL

Several columns with the same length (3 m), I.D. (2.2 mm) and concentration of liquid phase (20%) on Chromosorb W AW (60–80 mesh) were prepared with

squalane (Sq) and *n*-triacontane (*n*-C<sub>30</sub>) as liquid phases. The stationary phases were prepared by using chloroform as a solvent and sieved with 60–80-mesh sieves.

The columns were filled with the same amount of stationary phase accurately weighed in order to permit the calculation of the specific retention volumes,  $V_g$  and conditioned overnight at 100° with a flow-rate of helium of 20 cm<sup>3</sup>/min. Various columns were prepared with each phase, in order to check the reproducibility of the retention data.

A dual-column gas chromatograph equipped with a thermal conductivity detector was used. The columns under test were connected in parallel. Helium (20 cm<sup>3</sup>/min) was used as the carrier gas. The pressures at the column inlets and outlets were monitored with a mercury manometer, in order to permit the calculation of the compressibility factor,  $J$ .

The temperatures of the columns and of the injectors were identical, were monitored by precision thermometers and maintained below 100°, the temperature limit for squalane. The lowest column temperature that can be used for the analysis depends on the melting point of *n*-C<sub>30</sub> (65.8°). A series of analyses of *n*-alkanes on the *n*-C<sub>30</sub> column from 40° to 70° (see Fig. 1, where the data for *n*-hexane are reported) showed a sharp increase in the retention times ( $t_R'$ ) between 64° and 65.8°. Above 66° the classical dependence of  $t_R'$  on temperature was observed.

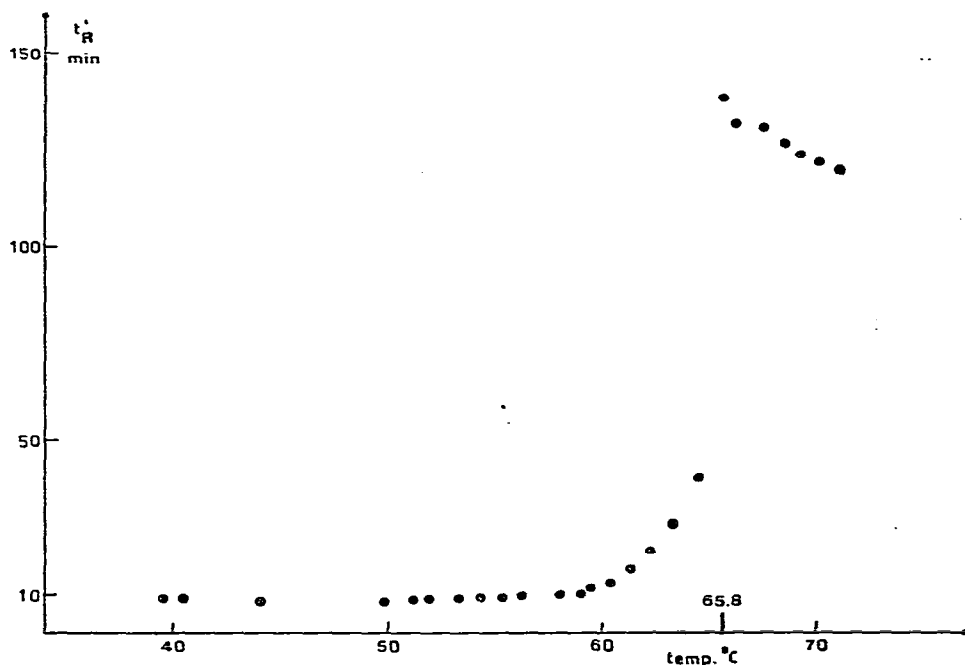


Fig. 1. Adjusted retention time ( $t_R'$ ) of *n*-hexane on *n*-triacontane (melting point) as a function of column temperature.

The theoretical plate number ( $n$ ) was similar for the two phases above 66°, with a mean value of about 2000 for *n*-hexane on *n*-C<sub>30</sub>, and a slightly lower value for squalane. Below 66°, the values of  $n$  for *n*-C<sub>30</sub> columns decreased sharply, owing

to the solidification of the hydrocarbon. Values between 170 and 200 were found on  $n\text{-C}_{30}$  in the range 25–66°.

Pure hydrocarbons with six to eight carbon atoms were used as samples. The retention indices were calculated by comparison with  $n$ -pentane,  $n$ -hexane,  $n$ -heptane and  $n$ -octane, added to each sample mixture. Several branched-chain hydrocarbons were included in the mixture when preliminary tests had ensured that complete resolution of the peaks could be obtained.

The samples (0.2–0.5  $\mu\text{l}$ ) were injected by means of a microsyringe directly into the columns, the inlets of which were very close to the silicone rubber septa.

The adjusted retention times,  $t'_R$ , were measured by injecting 1  $\mu\text{l}$  of air with the sample. The specific retention volumes,  $V_g$ , and the retention indices,  $I$ , were calculated by using classical equations<sup>11,12</sup>.

The activity coefficients at infinite dilution,  $\gamma^\infty$ , (refs. 12 and 13) and the normalized activity coefficients,  $\gamma$ , (ref. 14), were used to compare the behaviour of the various columns tested,  $\gamma$  being used when the molecular weight of the solvent was unknown (as in the case of polymeric liquid phases), thus rendering impossible the calculation of  $\gamma^\infty$ . The values of  $\gamma^\infty$  and  $\gamma$  were calculated by using the equations

$$\gamma^\infty = \frac{273 R}{P_i^0 M_L V_g}$$

and

$$\gamma = \frac{273 R}{P_i^0 M_i V_g} = \gamma^\infty \cdot \frac{M_L}{M_i}$$

where  $P_i^0$  is the saturation vapour pressure of the solute at the temperature of the analysis,  $M_L$  is the molecular weight of the solvent (422.83 for squalane and  $n\text{-C}_{30}$  and 1222.37 for  $\text{C}_{87}\text{H}_{176}$ ) and  $M_i$  is the molecular weight of the solute. When linear and branched-chain solutes with the same  $M_i$  are involved, the ratio of the  $\gamma$  values on a given liquid phase corresponds to the ratio of the  $\gamma^\infty$  values and therefore solvents with known or unknown  $M_L$  can be compared with respect to their selectivity towards branched chain compounds.

$P_i^0$ , which is purely a solute property, has an effect on the partition coefficients and relative volatilities. Its values were calculated by using an Antoine-type equation:

$$\text{Log } P^0 = A - B/(C + t)$$

where  $t^\circ\text{C}$  is the temperature and  $A$ ,  $B$  and  $C$  are constants taken from A.P.I. Tables<sup>15</sup>. It was previously shown<sup>16</sup> that this equation gives the best approximation in the temperature interval of interest.

Rohrschneider constants were also determined on both squalane and  $n\text{-C}_{30}$  columns by injecting the basic test substances (ethanol, nitromethane, methyl ethyl ketone, benzene and pyridine) in mixtures with  $n$ -alkanes.

## RESULTS

Table I shows the experimental specific retention volumes,  $V_g$ , on squalane and  $n\text{-C}_{30}$  at 70° and 80° for the  $n$ -alkanes used as reference materials for the

TABLE I

EXPERIMENTAL SPECIFIC RETENTION VOLUMES,  $V_g$ , OF *n*-ALKANES ON SQUALANE AND *n*-C<sub>30</sub> COLUMNSLiquid phase loading, 20%; column, 3 m × 2.2 mm I.D.; carrier gas, helium (20 cm<sup>3</sup>/min).

<i>n</i> -Alkane	<i>Squalane</i>		<i>n</i> -C <sub>30</sub>	
	70°	80°	70°	80°
<i>n</i> -Pentane	26.1	20.3	26.5	20.8
<i>n</i> -Hexane	63.9	48.1	65.1	49.6
<i>n</i> -Heptane	153.3	117.2	156.2	116.4
<i>n</i> -Octane	372.8	280.6	380.7	268.3

calculation of the retention indices. The plots of the log  $V_g$  in the range of carbon numbers considered are linear for both liquid phases (regression coefficient  $r > 0.9999$ ).

Table II shows the retention indices of the Rohrschneider test substances on squalane and *n*-C<sub>30</sub> and the corresponding values of the Rohrschneider phase-specific constants for *n*-C<sub>30</sub>. Negative values are obtained, indicating the higher "polarity" of squalane compared with *n*-C<sub>30</sub> if the Rohrschneider scale of polarity is used. The use of squalane as the least polar reference term is therefore questionable.

TABLE II

RETENTION INDICES OF THE ROHRSCHEIDER TEST SUBSTANCES AT 80° ON SQUALANE AND *n*-C<sub>30</sub> (MEAN OF 10 RUNS) AND CORRESPONDING VALUES OF THE PHASE-SPECIFIC CONSTANTS

Compound	Retention index		Rohrschneider constants for <i>n</i> -C <sub>30</sub>	
	<i>Squalane</i>	<i>n</i> -C <sub>30</sub>	Symbol	Value
Benzene	651.6	650.6	<i>x</i>	-0.02
Ethanol	354.2	347.0	<i>y</i>	-0.07
Methyl ethyl ketone	557.0	542.6	<i>z</i>	-0.14
Nitromethane	496.0	459.0	<i>u</i>	-0.37
Pyridine	751.4	735.0	<i>s</i>	-0.16

It should be noted that the greatest negative value is obtained for the constant *u*, probably owing to the effect of the methyl group of the test substance (nitromethane) on the solute-solvent interactions.

Table III (first four columns of results) shows the retention indices ( $I_{S_q}$  and  $I_{n-C_{30}}$ ) of branched-chain alkanes. The fifth and sixth columns show the greatest differences observed between the  $I_{S_q}$  values obtained at 70° and 80° on the various squalane columns tested ( $\Delta_{\max} I_{S_q}$ ); absolute values are reported. The  $\Delta_{\max} I_{n-C_{30}}$  values were smaller. The last five columns show the differences between the values of  $I_{S_q}$  and  $I_{n-C_{30}}$  of the first four columns of results and the values reported in the literature ( $I_x$ ) at the same temperature<sup>2,17-19</sup>. References 18 and 19 do not report decimal values for  $I_{S_q}$ , and therefore the differences in the eighth, ninth and tenth columns are approximate. Values of  $I_x$  for *n*-C<sub>30</sub> were calculated from the reported values<sup>2</sup> of  $V_g$ .

TABLE III

RETENTION INDICES ON SQUALANE ( $I_{Sq}$ ) AND  $\mu$ -C<sub>30</sub> ( $I_{\mu-C_{30}}$ ) COLUMNS, WITH LARGEST DATA FLUCTUATION ( $I_{max}$ ) AND DIFFERENCE FROM LITERATURE DATA ( $I_x$ )

Compound	$I_{Sq}$		$I_{\mu-C_{30}}$		$I_{max}$ ( $I_{Sq}$ ) (abs. values)		$I_{Sq} - I_x$ (ref. 17), 70°		$I_{Sq} - I_x$ (ref. 18), 80°		$I_{Sq} - I_x$ (ref. 19), 80°		$I_{\mu-C_{30}} - I_x$ (ref. 19), 80°	
	70°	80°	70°	80°	70°	80°								
2-Methylpentane	570.3	570.5	599.0	570.3	0.2	0.5	0.3	1.3	-0.5	0.5	0	0	0	
3-Methylpentane	584.7	585.6	584.6	584.8	0.5	0.6	-0.4	-1.3	-0.4	0.6	0	0	0	
2,2-Dimethylbutane	538.1	540.1	536.7	537.6	0.3	0.2	0.4	-0.9	1.1	1.1	0.3	0.3	0.3	
2,3-Dimethylbutane	569.2	569.6	568.2	568.2	0.4	0.5	0.1	-0.2	0.6	0.6	-0.2	-0.2	-0.2	
2-Methylhexane	668.5	667.7	666.3	666.2	0.5	0.8	1.5	0.5	0.3	0.7	0.2	0.2	0.2	
3-Methylhexane	676.8	677.0	676.3	676.9	0.4	0.6	-0.1	-0.2	-1	0	0.3	0.3	0.3	
3-Ethylpentane	688.0	688.2	686.4	686.5	0.5	0.3	0.8	1.0	-1	-1	0.6	0.6	0.6	
2,2-Dimethylpentane	627.4	627.9	624.8	626.2	0.7	0.7	0.4	1.4	1.4	1.9	0.6	0.6	0.6	
2,3-Dimethylpentane	673.5	674.4	672.8	672.9	0.2	0.3	0.1	0.5	1.4	2.4	-0.4	-0.4	-0.4	
2,4-Dimethylpentane	631.5	631.3	628.7	628.8	0.4	0.5	1.0	1.5	1.3	1.3	0.2	0.2	0.2	
3,3-Dimethylpentane	662.1	662.8	660.6	661.9	0.6	0.2	0.6	1.1	1.3	0.8	0.2	0.2	0.2	
2,2,3-Trimethylbutane	643.2	644.6	640.7	642.0	0.6	0.4	0.6	1.2	1.6	1.6	-0.4	-0.4	-0.4	
2-Methylheptane	765.5	765.5	764.3	764.3	0.3	0.3				0.5	0.2	0.2	0.2	
3-Methylheptane	772.6	772.6	772.4	772.4	0.1	0.1			-1.4	-0.4	0.2	0.2	0.2	
4-Methylheptane	766.9	766.9	767.6	767.6	0.1	0.1			-1.1	-1.1	0.5	0.5	0.5	
3-Ethylhexane	773.5	773.5	772.9	772.9	0	0				-1.5	0.5	0.5	0.5	
2,2-Dimethylhexane	720.9	720.9	717.9	717.9	1.0	1.0				-1.3	0.7	0.7	0.7	
2,3-Dimethylhexane	762.0	762.0	761.3	761.3	0.5	0.5				-1.0	0.7	0.7	0.7	
2,4-Dimethylhexane	733.1	733.1	731.5	731.5	0.4	0.4				-0.9	0.7	0.7	0.7	
2,5-Dimethylhexane	729.7	729.7	727.7	727.7	0.4	0.4			0.7	0.7	0.7	0.7	0.7	
3,3-Dimethylhexane	746.2	746.2	745.7	745.7	0.3	0.3				-0.8	0.7	0.7	0.7	
3,4-Dimethylhexane	774.1	774.1	773.1	773.1	0.4	0.4				-0.8	0.1	0.1	0.1	
2-Methyl-3-ethylpentane	764.2	764.2	763.1	763.1	0.5	0.5				0.2	0.2	0.2	0.2	
3-Methyl-3-ethylpentane	779.6	779.6	779.9	779.9	0.2	0.2				-0.4	0.2	0.2	0.2	
2,2,3-Trimethylpentane	742.3	742.3	741.0	741.0	0.7	0.7				0.3	0.3	0.3	0.3	
2,2,4-Trimethylpentane	693.7	693.7	690.7	690.7	0.3	0.3			-0.3	-0.3	-0.4	-0.4	-0.4	
2,3,3-Trimethylpentane	765.3	765.3	765.0	765.0	0.3	0.3				0.2	0.2	0.2	0.2	
2,3,4-Trimethylpentane	756.4	756.4	754.6	754.6	0.5	0.5				-1.6	0.2	0.2	0.2	
2,2,3,3-Tetramethylbutane	773.0	773.0	771.0	771.0	0.4	0.4				0	0	0	0	

Whereas the differences between the  $I$  values on the same liquid phase are very small and random, greater positive differences are observed between the values of  $I_{\text{Sq}}$  and  $I_{n\text{-C}_{30}}$  reported in the first four columns.

When the chain branching of the solute increases, the retention indices on squalane increase in comparison with the values on  $n\text{-C}_{30}$ .

The mean values of the  $I_{\text{Sq}} - I_{n\text{-C}_{30}}$  values, calculated for hydrocarbons with the same  $\text{CH}_3/\text{C}$  ratio, increase with increasing  $\text{CH}_3/\text{C}$  ratio. A strictly linear correlation is not observed, owing to the effects of other properties (boiling point, molecular volume, etc.) on the retention times. The observed values of  $I_{\text{Sq}} - I_{n\text{-C}_{30}}$  are greater than the differences between the  $I_{\text{Sq}}$  values obtained with different squalane columns or given in the literature, showing that the effect of the branching of both solutes and solvents on  $I$  is greater than the statistical variations due to the column preparation and analysis conditions.

Table IV gives the values of the  $p_i^0$  at  $80^\circ$ , activity coefficients ( $\gamma^x$ ) and the ratios between the activity coefficients of branched-chain and the corresponding linear alkane isomers ( $\gamma_b^x/\gamma_n^x$ ) on squalane,  $n\text{-C}_{30}$  and  $\text{C}_{87}\text{H}_{176}$ .

The values of  $\gamma_b/\gamma_n$  on the SF 96 columns, calculated from previously published values of the normalized activity coefficient<sup>16</sup>, are also shown and, as discussed above, are identical with the  $\gamma_b^x/\gamma_n^x$  ratios that cannot be calculated directly for this polydimethylsilicone liquid phase, the exact molecular weight ( $M_L$ ) of which is unknown.

Smaller values of  $\gamma_b^x/\gamma_n^x$  on different liquid phases indicate higher degree of interaction of the branched-chain compounds in comparison with the linear compounds. This effect is clearly shown by the values in Table IV for hexanes and heptanes, the  $\gamma_b^x/\gamma_n^x$  ratios of which decrease with increasing methyl content of the liquid phase, available values on  $\text{C}_{87}\text{H}_{176}$  (calculated from ref. 10) being closer to the values on  $n\text{-C}_{30}$  than those on squalane and the  $\gamma_b/\gamma_n$  values on SF 96 being the lowest, thus showing the highest selectivity of this phase for branched-chain compounds.

Values of  $\gamma_b^x/\gamma_n^x$  calculated from available literature data<sup>2</sup> for  $n\text{-C}_{30}$  are very close to those obtained from our experimental data. The order  $(\gamma_b^x/\gamma_n^x)_{n\text{-C}_{30}} > (\gamma_b^x/\gamma_n^x)_{\text{C}_{87}\text{H}_{176}} > (\gamma_b^x/\gamma_n^x)_{\text{Sq}} > (\gamma_b/\gamma_n)_{\text{SF 96}}$  is not followed by octanes except for the values on SF 96, which are the lowest. Uncertainty in the values of  $V_q$  for compounds strongly retained at low temperatures may be responsible for the observed discrepancies. In any event, the highest retention of branched-chain solutes on branched-chain solvents is confirmed by the available experimental data.

The differences between retention indices taken from various sources show that hydrocarbons with retention indices that differ by less than 1–2 units cannot be identified exactly on the basis of their tabulated or calculated retention indices only, as they are influenced by variations in the performance of the columns.

On the other hand, the order of elution is the same on all of the squalane and  $n\text{-C}_{30}$  columns tested and in the literature (except for the co-eluting compounds 2-methylheptane and 2,3,3-trimethylpentane, and 3-ethylhexane and 3,4-dimethylhexane). Therefore, the identification of a peak in a group of closely eluting hydrocarbons on a non-polar (hydrocarbon or methylsilicone type) phase can be based on  $I_{\text{Sq}}$  values taken from the literature when one of the peaks has been positively identified by the addition of a standard sample.

TABLE IV

VALUES OF  $P_1^0$ , ACTIVITY COEFFICIENTS AND THEIR RATIOS ON VARIOUS LIQUID PHASES WITH INCREASING METHYL CONTENTIn  $\gamma_b^x$  and  $\gamma_n^x$  the subscripts  $b$  and  $n$  refer to branched-chain and linear isomers, respectively.

Compound	$P_1^0$ (torr) at 80°	$n\text{-C}_{30}$		$\text{C}_{87}\text{H}_{176}$		Squalane		SF-96, $\gamma_b/\gamma_n$
		$\gamma^x$	$\gamma_b^x/\gamma_n^x$	$\gamma^x$	$\gamma_b^x/\gamma_n^x$	$\gamma^x$	$\gamma_b^x/\gamma_n^x$	
<i>n</i> -Hexane	1068	0.760	1	0.232	1	0.784	1	1
2-Methylpentane	1366	0.769	1.012			0.790	1.008	0.986
3-Methylpentane	1250	0.739	0.973			0.758	0.967	0.955
2,2-Dimethylbutane	1819	0.767	1.010	0.235	1.012	0.771	0.984	0.919
2,3-Dimethylbutane	1448	0.739	0.972	0.223	0.961	0.751	0.958	0.936
<i>n</i> -Heptane	427.8	0.808	1	0.251	1	0.803	1	1
2-Methylhexane	558.3	0.826	1.023			0.820	1.021	0.970
3-Methylhexane	526.9	0.799	0.989			0.800	0.996	0.961
3-Ethylpentane	502.7	0.772	0.955			0.760	0.947	0.951
2,2-Dimethylpentane	778.3	0.834	1.032	0.258	1.029	0.839	1.044	0.912
2,3-Dimethylpentane	564.8	0.772	0.955	0.234	0.931	0.786	0.951	0.929
2,4-Dimethylpentane	748.4	0.848	1.050	0.263	1.048	0.846	1.054	0.944
3,3-Dimethylpentane	634.4	0.754	0.934			0.754	0.939	0.904
2,2,3-Trimethylbutane	740.8	0.766	0.948	0.232	0.926	0.759	0.946	0.889
<i>n</i> -Octane	175.0	0.857	1	0.271	1	0.820	1	1
2-Methylheptane	230.9	0.875	1.021			0.840	1.024	0.975
3-Methylheptane	221.7	0.852	0.994			0.822	1.002	0.954
4-Methylheptane	230.5	0.853	0.995			0.831	1.013	0.962
3-Ethylhexane	225.2	0.835	0.975			0.803	0.979	0.934
2,2-Dimethylhexane	331.8	0.898	1.047	0.283	1.043	0.864	1.054	0.929
2,3-Dimethylhexane	250.0	0.829	0.967	0.259	0.956	0.800	0.975	0.934
2,4-Dimethylhexane	305.0	0.872	1.017	0.275	1.014	0.843	1.028	0.922
2,5-Dimethylhexane	307.2	0.893	1.042			0.863	1.052	0.935
3,3-Dimethylhexane	284.5	0.830	0.968			0.807	0.984	0.899
3,4-Dimethylhexane	234.0	0.803	0.937	0.248	0.916	0.769	0.937	0.900
2-Methyl-3-ethylpentane	251.1	0.813	0.949			0.781	0.952	0.849
3-Methyl-3-ethylpentane	235.4	0.754	0.880			0.741	0.904	0.894
2,2,3-Trimethylpentane	306.4	0.801	0.935			0.775	0.945	0.871
2,2,4-Trimethylpentane	425.9	0.879	1.026	0.259	0.957	0.853	1.040	0.889
2,3,3-Trimethylpentane	264.4	0.760	0.887			0.735	0.896	0.892
2,3,4-Trimethylpentane	271.6	0.807	0.942	0.248	0.913	0.773	0.942	0.969
2,2,3,3-Tetramethylbutane	344.7	0.774	0.904			0.747	0.911	0.871

The differences observed between the behaviour of squalane and  $n\text{-C}_{30}$  are not so great as to invalidate the large amount of information available from work with squalane as the reference phase, but unacceptable scattering is found for less polar liquid phases, and efforts are needed to characterize these solvents with respect to an  $n$ -alkane or a less branched alkane than squalane.

The reported data show that the proposed  $\text{C}_{87}\text{H}_{176}$  stationary phase seems to have good characteristics for use as a non-polar reference material. Its  $\text{CH}_3/\text{C}$  ratio (0.069) is very low and the interaction between its methyl groups and those of the branched-chain solutes would be of the same order of magnitude as those found for  $n\text{-C}_{30}$ , while its useful temperature range is much greater than those of  $n\text{-C}_{30}$  and squalane. A direct comparison of the behaviour of this phase with squalane and linear alkanes would be useful for confirming the validity of its use as non-polar reference material.



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