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THE CORRELATION BETWEEN THE PHYSICAL PROPERTIES AND STRUCTURE OF ALCOHOLS AND THEIR GAS CHROMATOGRAPHIC BEHAVIOUR ON POLAR AND NON-POLAR STATIONARY PHASES

II. BRANCHED-CHAIN ALCOHOLS

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SUMMARY

Branched-chain alcohols with from one to eight carbon atoms have been analysed by gas chromatography using thermal conductivity and flame-ionization detectors. The specific retention volumes, V_g, and the retention indices relative to normal alcohols were determined for all the compounds, and the effects of the branching and of the position of the hydroxyl groups have been investigated. Boiling points, vapour pressures, molecular volumes were correlated with the measured retention values. The activity coefficients at infinite dilution and the normalized activity coefficients were calculated, and their influence on the separation is discussed. The results are compared with the behaviour of branched-chain halogenoalkanes on polar and non-polar stationary phases.

INTRODUCTION

We have previously examined[1] the gas chromatographic (GC) behaviour of straight-chain primary and secondary alcohols on non-polar (squalane) and polar (Carbowax) columns, and the dependence of the retention values on physical properties. We have also compared this behaviour with that of linear halogenoalkanes[2].

This paper reports the effect of the position of the hydroxyl and methyl groups on the retention volume of some branched-chain alcohols, and compares this with the influence of halogen atom position[3]. The results are correlated with boiling points, vapour pressures and molecular volumes.

MATERIALS AND METHODS

The alcohols analysed are listed in Table I, together with their main physical constants. Straight-chain primary alcohols and linear alkanes were also analysed for comparison. The analyses were carried out at 100° with a Varian Aerograph Model 1520 gas chromatograph with proportional temperature control.

TABLE I

PHYSICAL CONSTANTS OF ANALYSED BRANCHED-CHAIN ALCOHOLS

Alcohol	*T_b (°C) at 760 Torr**	*Density at 20° (g/cm^3)*	*Molecular volume, V_m (cm^3)*
2-Methyl-1-propanol	108.4	0.8011	92.52
2-Methyl-2-propanol	82.2	0.7887	93.98
2-Methyl-1-butanol	128	0.8193	107.59
3-Methyl-1-butanol	128.5	0.8092	108.93
2-Methyl-2-butanol	102	0.8059	109.38
3-Methyl-2-butanol	114	0.819	107.63
2,2-Dimethyl-1-propanol	114	0.812	108.56
2-Methyl-1-pentanol	148	0.8263	123.66
3-Methyl-1-pentanol	152.5	0.8242	123.97
4-Methyl-1-pentanol	151.6	0.8131	125.67
2-Methyl-2-pentanol	120.5	0.8350	122.37
3-Methyl-2-pentanol	134.3	0.8307	123.00
4-Methyl-2-pentanol	133	0.8075	126.54
2-Methyl-3-pentanol	126.7	0.8243	123.96
3-Methyl-3-pentanol	122.4	0.8286	123.32
2,2-Dimethyl-1-butanol	136.7	0.8283	123.36
3,3-Dimethyl-2-butanol	120.4	0.844	121.07
2,3-Dimethyl-2-butanol	118.4	0.8236	124.06
2-Ethyl-1-butanol	146.3	0.8326	122.72
2-Methyl-1-hexanol	164	0.8313	139.79
2-Methyl-2-hexanol	143	0.8119	143.13

* Taken from ref. 7.

Both thermal conductivity (TCD) and flame-ionization (FID) detectors were used. Pure helium was used as carrier gas. Methods for readout of temperature, flow-rate, inlet and outlet pressure have been previously described[1].

Stainless-steel columns, 3 m × 1/8 in., filled with 20% w/w of liquid phase on dimethylchlorosilane-treated Chromosorb W, 60–80 mesh, screened before and after impregnation, were used.

Some analyses were also performed on a glass column, and no significant difference was found between the two sets of retention volumes.

Decreasing amounts of the alcohols were injected in order to determine, by extrapolation, the retention time at zero concentration.

The specific retention volumes were calculated by the method of Littlewood *et al.*[4].

Squalane (Varian Aerograph, Walnut Creek, Calif., U.S.A.) and Carbowax 400, 1000 and 20M (Union Carbide, New York, N.Y., U.S.A.) were used as liquid phases. As the molecular weight of the liquid phase, M_L, has to be known in order for the activity coefficient at infinite dilution, γ^{∞}, to be calculated[5,6], squalane (M_L = 422.83) was used as non-polar liquid phase rather than silicon polymers.

The Carbowax 400 had $M_L = 425 \pm 3\%$, very close to that of squalane, as measured by a vapour pressure osmometer, Mechrolab Model 302, at 65°, with toluene as solvent. The precision and range of M_L of the Carbowax 1000 and 20M have been discussed previously[1]. The dispersion of molecular weights of these liquid phases was higher than that of Carbowax 400. Approximate M_L values (viscosimetric) of 1050 and 19500, respectively, were measured for the used products. Gel permeation chromatography at 120 p.s.i. on a 16-ft. Styragel column, with tetrahydrofuran as solvent, showed that, whereas Carbowax 1000 had a relatively narrow molecular weight distribution, the Carbowax 20M has a bimodal polydispersion.

Therefore, the γ^{∞} values were calculated on squalane and Carbowax 400 only, whereas the normalized activity coefficient[1], γ, was determined for other liquid phases.

The vapour pressure p_i°, of the solutes at the analysis temperature was calculated using the method reported by Hass and Newton[7]. The values of log p_i° are linearly correlated with the T_b values. The parameters of the equation $\log p_i^{\circ}\,(100^{\circ}) = a + bT_b$, calculated by the least-squares method, are: $a = 4.635$ and $b = -0.0175$ for linear and branched alcohols with from two to seven carbon atoms. The values of the parameters for various groups (1-alcohols, 2-alcohols, 3-alcohols, branched-chain alcohols) differ by less than $\pm 1\%$ for a and $\pm 2\%$ for b from the overall values.

RESULTS AND DISCUSSION

The specific retention volumes, V_g, at 100°, and the retention indices relative to linear 1-alcohols (I_{OH}) that permit direct comparison of the behaviour of branched compounds and primary straight-chain alcohols, are set out in Table II, which also includes some values reported by McReynolds[8].

TABLE II

SPECIFIC RETENTION VOLUME (V_g) AND RETENTION INDICES RELATIVE TO LINEAR 1-ALCOHOLS (I_{OH}) AT 100°

	Squalane		*Carbowax 400*		*Carbowax 1000*		*Carbowax 20M*	
	V_g	I_{OH}	V_g	I_{OH}	V_g	I_{OH}	V_g	I_{OH}
2-Methyl-1-propanol	27.64	369	103.7	343	88	347	72.5	349
2-Methyl-2-propanol	13.45	289	34.3	157	28.2	161	22.5	167
2-Methyl-1-butanol	68.5	474	203	453	175.2	455	145	460
3-Methyl-1-butanol	67	472	210.5	459	180.1	460	145.8	461
2-Methyl-2-butanol	37	402	64.6	264	53.9	270	45.3	275
3-Methyl-2-butanol	46.8	429	101.7	340	85.4	345	73.3	350
2,2-Dimethyl-1-propanol*	41.2	415	108	349	95.2	359	80.0	364
2-Methyl-1-pentanol	142	563	343	541	309	547	262.5	557
3-Methyl-1-pentanol	153	573	412	572	365	574	305.7	582
4-Methyl-1-pentanol	144	565	383	560	340	558	286.1	571
2-Methyl-2-pentanol	75	483	108	349	91.8	354	77.2	359
3-Methyl-2-pentanol	117	539	180	433.5	159	440	133.6	446.5
4-Methyl-2-pentanol	87	502	160	414	137	416	112.7	419
2-Methyl-3-pentanol	102	522	142.5	395	128	403	108.2	412
3-Methyl-3-pentanol	92	509	116	361	101	366	85	374
2,2-Dimethyl-1-butanol*	109	530	228	473	207	482	178.9	494
3,3-Dimethyl-2-butanol*	75.7	485.9	113	357	102	370	89.1	381
2,3-Dimethyl-2-butanol*	75.6	485.7	97	332	86	343	73.8	351
2-Ethyl-1-butanol*	153	573	356	548	316	551	262.6	557
2-Methyl-1-hexanol	288	655	579	631	556	645	474	655
2-Methyl-2-hexanol	166	583	180	434	162	443	131	444

* Taken from ref. 8.

The dependence of log V_g on the number of carbon atoms, n, is shown in Fig. 1. Values for straight-chain alcohols[1] are included for comparison. The plots seem to follow the classical linear relationship, but the number of available members of the various homologous series of branched-chain alcohols does not permit the behaviour to be evaluated over a great range of n. As reported previously[1], linear compounds show a slight curvature, as Δ log V_g decreases with increasing n. The experimental scattering of the log V_g values is greater for branched compounds than for linear ones, but again Δ log V_g seems to decrease. As the observed curvature is very small, linear extrapolation of log V_g values will allow the V_g values of higher homologues to be calculated, at least for 2-methyl-1-alkanols and 2-methyl-2-alkanols, to a good approximation. In both polar and non-polar solvents, isobutanol and *tert.*-butanol have lower values of V_g than those extrapolated from higher terms.

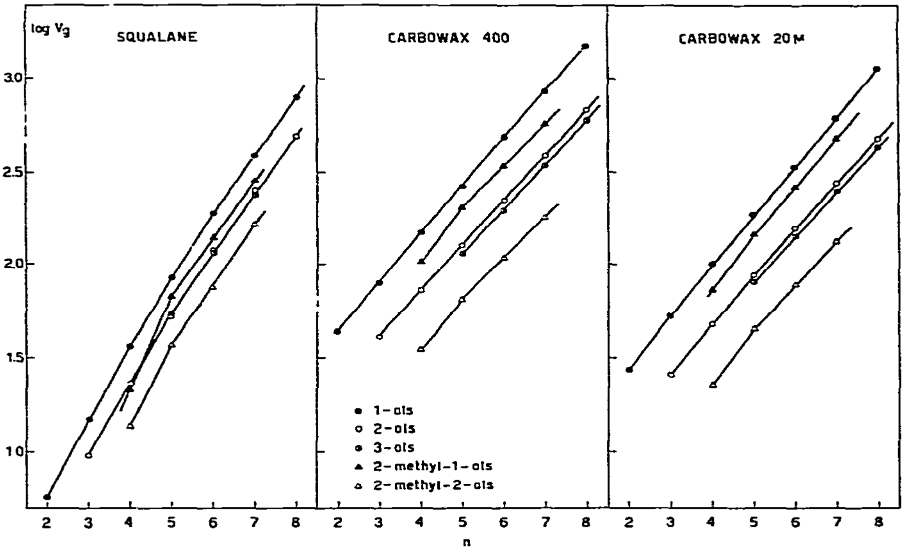

Fig. 1. Log V_g of linear and branched-chain alcohols as a function of the number of carbon atoms on squalane and Carbowax at 100°.

Polar phases allow a better separation of linear and branched-chain compounds, but the elution order is the same on Carbowax and squalane columns. By increasing the M_L of the Carbowax, the V_g values decrease, but the differences of log V_g between 1-alcohols and other alcohols remain about constant.

The structure–retention correlations may be expressed quantitatively through the γ^{∞} values. The calculation of the activity coefficients at infinite dilution by the eqn. 1, reported by Purnell[5] and Brown[6],

$$\gamma^{\infty} = \frac{273\,R}{p_l^{\circ} M_L V_g} \tag{1}$$

requires knowledge of the true molecular weight of the solvent, M_L. As mentioned above, M_L values are available for squalane and Carbowax 400 only (within ±3%

for Carbowax 400), and therefore the γ^{∞} values can be calculated. These values are reported in Table III. It must be noted that the true values for Carbowax 400 may be *ca.* 3% higher or lower, depending on the M_L of liquid phase, but that the reported values are comparable, as they have been determined on the same column. Similarly, the values of γ^{∞} on both squalane and Carbowax 400 are comparable with the γ^{∞} of straight-chain alcohols previously reported[1].

TABLE III

VALUES OF γ^{∞} AND γ FOR SQUALANE ($M_L = 422.83$), CARBOWAX 400 ($M_L = 425 \pm 3\%$), CARBOWAX 1000 AND 20M

Alcohol	γ^{∞}		γ			
	Squalane	*Carbowax 400*	*Squalane*	*Carbowax 400*	*Carbowax 1000*	*Carbowax 20M*
2-Methyl-1-propanol	2.64	0.70	15.07	4.01	4.67	5.74
2-Methyl-2-propanol	2.03	0.79	11.59	4.54	5.53	6.92
2-Methyl-1-butanol	2.28	0.765	10.94	3.69	4.28	5.17
3-Methyl-1-butanol	2.39	0.755	11.45	3.64	4.26	5.26
2-Methyl-2-butanol	1.55	0.88	7.42	4.25	5.09	6.06
3-Methyl-2-butanol	1.93	0.89	9.28	4.27	5.09	5.93
2,2-Dimethyl-1-propanol	2.20	0.83	10.54	4.02	4.56	5.43
2-Methyl-1-pentanol	2.47	1.016	10.21	4.226	4.69	5.52
3-Methyl-1-pentanol	2.75	1.017	11.39	4.23	4.77	5.70
4-Methyl-1-pentanol	2.81	1.05	11.63	4,37	4.92	5.85
2-Methyl-2-pentanol	1.55	1.073	6.43	4.46	5.25	6.24
3-Methyl-2-pentanol	1.72	1.11	7.11	4.62	5.23	6.23
4-Methyl-2-pentanol	2.19	1.19	9.09	4.94	5.77	7.02
2-Methyl-3-pentanol	1.45	1.04	6.02	4.31	4.80	5.68
3-Methyl-3-pentanol	1.36	1.075	5.64	4.47	5.14	6.10
2,2-Dimethyl-1-butanol	2.03	0.97	8.41	4.02	4.43	5.12
3,3-Dimethyl-2-butanol	1.53	1.02	6.35	4.25	4.71	5.40
2,3-Dimethyl-2-butanol	1.42	1.10	5.88	4.58	5.17	6.02
2-Ethyl-1-butanol	2.13	0.91	8.83	3.79	4.27	5.14
2-Methyl-1-hexanol	2.35	1.16	8.54	4.25	4.42	5.19
2-Methyl-2-hexanol	1.72	1.58	6.25	5.76	6.40	7.92

Moreover, the values of the normalized activity coefficient γ, calculated for Carbowax 400, 1000 and 20 M using eqn. 2

$$\gamma = \frac{273\,R}{p_l^0 M_l V_g} \tag{2}$$

and the values of the interaction coefficient $C = 1/\gamma$ are comparable with the corresponding values for straight-chain alcohols.

The behaviour of γ and γ^{∞} as a function of the molecular structure is very similar. As an example, Fig. 2 shows γ and γ^{∞} values for 2-methyl- and 3-methyl-*X*-butanols on various grades of Carbowax. The increase in γ shows that the solute–solvent interaction decreases with increasing grade of the Carbowax depending on the hydrogen bonding, and is therefore correlated with the ratio O/OH of internal ether linkages to terminal hydroxyl groups in the solvent molecule, as discussed previously[1].

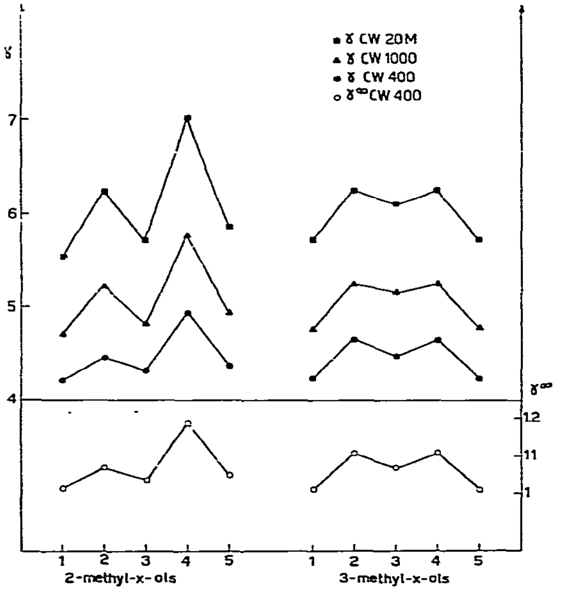

Fig. 2. Values of γ and γ^{∞} (where available) of methyl alkanes on various polar phases.

A linear dependence of log V_g of branched alcohols as a function of log O/OH was observed, similar to the behaviour of straight-chain alcohols.

The effect of chain branching and of the position of the OH group on the solute–solvent interaction is shown in Fig. 3, where the interaction coefficients C for methylbutanes and methylpentanes, calculated on squalane, Carbowax 400 and

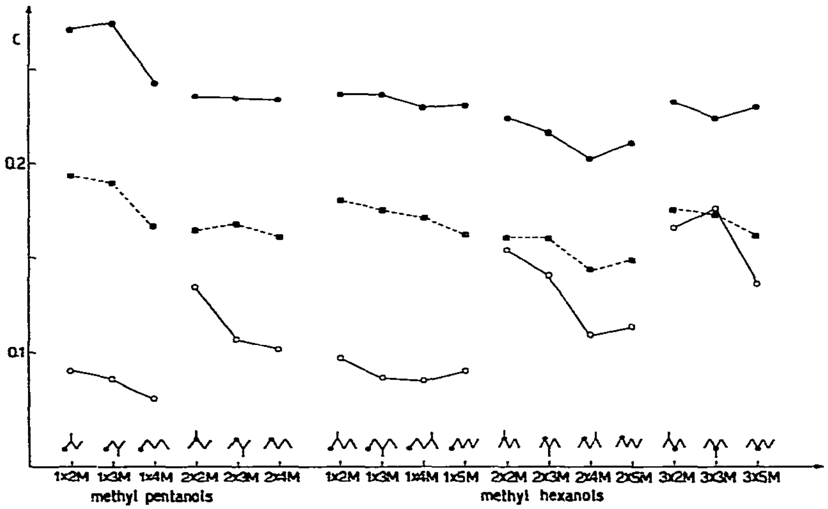

Fig. 3. Values of the interaction coefficient C (see text) on squalane (○), Carbowax 400 (●) and Carbowax 20M (■) at 100° for methylalcohols (× = position of OH group).

Carbowax 20 M, are reported. The values of C are higher on Carbowax columns, but a small variation is seen as a function of the branching and of the position of the OH group.

In contrast, the C values on squalane largely increase when, in an isomeric series, the OH group moves from the end to the centre of the chain, and when the number of methyl groups increases due to branching and to the "internal" position of the substituent. The 2-methyl compounds generally have higher C values.

The behaviour of alcohols and of halogenoalkanes cannot be compared on the basis of the γ^{∞} and γ values because the values of V_g are not available. In fact, the long conditioning at relatively high temperature needed to make the column clean enough for the use of electron capture detector results in a serious initial loss of weight of the liquid phase. Eqn. 3

$$V_g = \frac{273\, F_0 j t'_r}{WT} = K t'_r \tag{3}$$

(where F_0 is the flow-rate at the column outlet, corrected for the vapour pressure of water, j is the pressure gradient correction factor of Martin and James, t'_r is the corrected retention time, W is the weight (in grams) of liquid phase in the column, and T is the absolute temperature at which the gas flow was measured), cannot therefore be solved but, as V_g is proportional to t'_r, when the column is the same and the parameters T and W are constants, K is constant too.

Therefore, a parameter g, linearly proportional to γ and given by eqn. 4

$$g = \frac{273\, R}{p_l^{\circ} M_l t'_r} = \gamma\, K \tag{4}$$

can be calculated and compared with the γ values. When M_L is used in eqn. 4 instead of M_l, a g^{∞} value can also be calculated.

It is important to note that the comparison between g and γ (or g^{∞} and γ^{∞}) values can be made on a relative basis, *i.e.* one can compare the behaviour of a series of isomeric compounds, whereas the conversion of the absolute value of one of the cited parameters into another is only possible when the constant K is exactly known.

The use of g values for the relative comparison of the behaviour of different solute–solvent pairs could be extended to tabulated retention times taken from literature, as this is easier than the calculation of V_g and γ^{∞} values. It could also be applied to tabulated retention indices values if the t'_r of some terms in the reference series are known, in order to allow the back-calculation of the retention times.

Fig. 4 shows the behaviour of $1/g$ values for halogenoalkanes on polar (Carbowax 20M) and non-polar (Apiezon) columns. The data can be directly compared with the C values of alcohols in Fig. 3.

The behaviour of iodoalkanes is very similar on the two stationary phases. A near-constant ratio of 2.5 ± 0.15 is found between the g values on Carbowax 20M and Apiezon.

Pronounced interaction is again observed for the 2-methyl compounds, especially

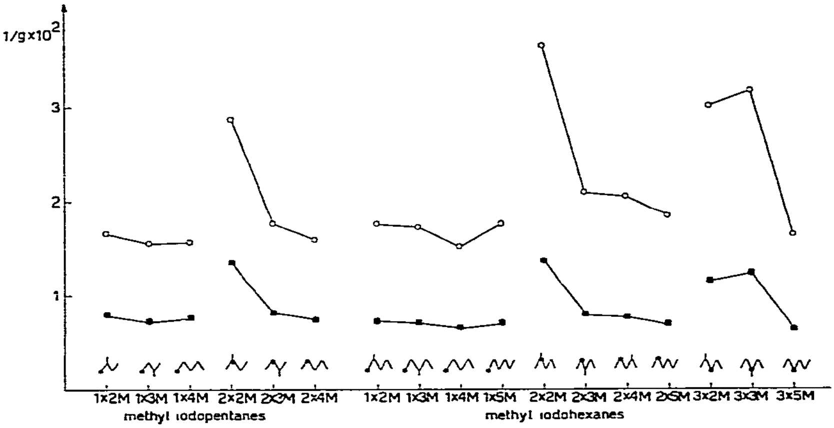

Fig. 4. Values of $1/g$ (see text) on Apiezon (○) and Carbowax 20M (■) at 100° for methyliodoalkanes (× = position of halogen).

when the halogen is on the same carbon atom as a methyl group (2-iodo-2-methyl, 3-iodo-3-methyl), as in the case of alcohols on squalane. Similar behaviour has been observed for the available bromo- and chloroalkanes.

A previous study of the behaviour of branched paraffins on non-polar phases showed that the interaction coefficient increases slightly from linear to 2-methyl to 3-methyl alkanes. Therefore Figs. 3 and 4 show that the effect of the substituent group (halogen or hydroxyl) overcomes the effect of the branching of the chain.

In the case of halogenoalkanes the nature and position of the substituent seem to have the same effect on both retention and physical properties, as shown by the similar values of $I_{nh}/T_b \cdot V_m$ (where I_{nh} is the retention index with respect of the linear halogenoalkanes series, T_b is the boiling point in °K, and V_m the molecular volume) for compounds with the same skeleton and different position of the halogen atom on both polar and non-polar phases[3]. Moreover, the behaviour of $1/g$ closely follows that of the molecular volumes.

In the case of alcohols, the ratio $I_{OH}/T_b \cdot V_m$ calculated on polar phases shows larger fluctuations as a function of the position of hydroxyl group, as indicated in Table IV. This may be due to the different hindrance and shielding effects of the methyl groups when the OH is near the centre of the molecule.

No clear correspondence of the C values with the V_m values for alcohols has been observed.

The behaviour of branched alcohols on squalane cannot be explained on the basis of hydrogen bonding phenomena. It is possible that solute–support interactions, minimized by the silanization of the support but still present, overcome the solute–solvent interactions, but the strong relative variation of the C values may also be due to interaction of methyl groups of the solute with the eight methyl groups of the branched squalane[9].

As pointed out by Ettre[10], the presence of impurities in commercial squalane may significantly change the behaviour of this supposedly "non-polar" phase. Moreover, if non-polar interaction dispersion forces are involved, the choice of a branched hydrocarbon as the standard non-polar phase satisfies the requirements

TABLE IV

RATIOS $I_{OH}/T_b \cdot V_m$ FOR BRANCHED-CHAIN ALCOHOLS AT 100° (WITH VALUES FOR 1-ALCOHOLS FOR COMPARISON)

Alcohol	$I_{OH}/T_b \cdot V_m \cdot 10^{-3}$			
	Squalane	*Carbowax 400*	*Carbowax 1000*	*Carbowax 20M*
1-Butanol	11.18	11.18	11.18	11.18
2-Methyl-1-propanol	10.45	9.72	9.83	9.89
2-Methyl-2-propanol	8.65	4.70	4.82	5.00
1-Pentanol	11.23	11.23	11.23	11.23
2-Methyl-1-butanol	10.98	10.49	10.54	10.66
3-Methyl-1-butanol	10.79	10.49	10.51	10.54
2-Methyl-2-butanol	9.80	6.43	6.58	6.70
3-Methyl-2-butanol	10.29	8.16	8.28	8.40
2,2-Dimethyl-1-propanol	9.87	8.30	8.54	8.66
1-Hexanol	11.11	11.11	11.11	11.11
2-Methyl-1-pentanol	10.81	10.39	10.50	10.69
3-Methyl-1-pentanol	10.86	10.84	10.88	11.03
4-Methyl-1-pentanol	10.58	10.49	10.45	10.70
2-Methyl-2-pentanol	10.03	7.24	7.35	7.45
3-Methyl-2-pentanol	10.75	8.65	8.78	8.91
4-Methyl-2-pentanol	9.77	8.06	8.09	8.15
2-Methyl-3-pentanol	10.53	7.97	8.13	8.31
3-Methyl-3-pentanol	10.43	7.40	7.50	7.67
2,2-Dimethyl-1-butanol	10.48	9.35	9.53	9.77
3,3-Dimethyl-2-butanol	9.64	7.09	7.34	7.56
2,3-Dimethyl-2-butanol	9.43	6.45	6.66	6.81
2-Ethyl-1-butanol	11.13	10.65	10.70	10.82

concerning chemical definition, but may be misleading when methyl group interactions are concerned.

A proposed synthetic C_{87} hydrocarbon can fulfil the requirements for a non-polar reference phase for high temperatures, but its branching may still be too high[11].

Research is in progress aimed at evaluating the properties of other paraffins as standard non-polar phases, comparing the behaviour of solvents with various degrees of branching and ascertaining the importance of the purity of the liquid phase and of solute–support interaction.

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