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Evaluation of the effect of the cyanopropyl radical on the interaction of the methylene group with silicone stationary phases

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ABSTRACT

Values of the solute–polymer interaction parameter of *n*-alkanes and polar substances between 90 and 200°C were obtained on two packed columns (OV-101 and OV-105). Experiments carried out with a capillary column confirmed that with non-polar solute–polymer systems the values of both the specific retention volumes and the thermodynamic parameters derived from them are equivalent to those obtained with packed columns. The results showed that *n*-alkanes mix better with OV-101 and polar substances are better solvents of OV-105. The differences are small, however. Partial molar enthalpies and free energies of solution and mixing were calculated. The contribution of the methylene group of the *n*-alkanes to the thermodynamic parameters of solution was evaluated. The effect of cyanopropyl group substitution on the contribution of the methylene group to the partial molar free energy of solution of *n*-alkanes was found to be roughly linear with the cyanoalkyl group content, decreasing as the polarity of the polymer increases. The solubility parameter of the stationary phase increases only slightly when a 5% substitution of cyanopropyl groups is introduced in the polymer.

INTRODUCTION

The cyanoalkylsilicones form one of the most interesting families of stationary phases in gas chromatography (GC). Their selectivity varies with the cyanoalkyl group content of the polymer, which ranges from 5 to 100% substitution [1]. They have been considered as "preferred stationary phases" by Stark *et al.* [2] and Sandra *et al.* [3]. The presence of the cyano group in their structure confers on them certain characteristics which make them particularly suitable for some chromatographic separations. GC is a useful technique in the study of solute–polymer and polymer–polymer interactions [4], as shown by the increasing number of publications in the field. The technique is normally called inverse gas chromatography (IGC) because interest is focused on the stationary phase rather than on the solutes being eluted. In this sense, the results offer information on the expected behaviour of the solutes when they are used as solvents of the stationary phase, and conclusions may be drawn regarding the behaviour of other substances of the same or a similar chemical type, and the behaviour of mixtures of the liquids used as stationary phases. Many polymers have been studied by IGC, but data

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on cyanoalkylsilicones are scarce [5]. In this paper, two stationary phases, OV-101, polydimethylsiloxane, and OV-105, polymethylcyanopropylsiloxane, 5% substitution, are compared. Results reported for other cyanopropylsilicones are taken into account in the discussion section. Our interest was focused on an evaluation of the cyanopropyl group and its effect on the chromatographic behaviour of the polymer, on the study of the interaction of the methylene group of the *n*-alkanes with the polymers and on the effect of the cyanopropyl group on that interaction. The study might also allow a prediction of the degree of miscibility of each polymer with other stationary phases of different chemical types. The latter point would help in the understanding of the problem of modification of the selectivity of chromatographic columns by making use of mixtures of stationary phases.

EXPERIMENTAL

For packed columns the stationary phases were deposited on Chromosorb W AW DMCS (80–100 mesh) in the usual way, using methylene chloride (OV-101) or acetone (OV-105) as solvents. A Stainless-steel tube (1/8 in. O.D.) was employed. Other characteristics of the columns were as follows: OV-101, stationary phase loading 14.8% (w/w) and length 3 m; OV-105, loading 16.6% (w/w) and length 2 m. Stationary phase percentages were determined by an extraction method [6]. A capillary column was prepared with OV-101 by the static method described by Grob [7] on borosilicate glass silanized with hexamethyldisilazane and without any immobilization. The characteristics of the column were I.D. 0.2475 mm, length 21.42 m, weight of stationary phase in the column $5.647 \cdot 10^{-3}$ g and film thickness 0.34 μm. The density of OV-101 was measured by a pycnometric procedure and that of OV-105 was taken from the literature [8]. The gas chromatographs used were a Shimazdu R1A and a Perkin-Elmer Sigma 2 (packed columns) and a Hewlett-Packard 5890 (capillary column). Temperatures were checked with the help of a thermocouple placed close to the column, and head pressures were measured with precision manometers (packed columns) or a presure transducer (capillary column). Chromatograms were carried out between 90 and 200°C. Sample injection was always of the order of 0.1 μl (splitting ratio 1:20 in the capillary column). The high percentage of stationary phase in the packed columns ensured that the contribution of adsorption phenomena to the retention of solutes was negligible.

DATA REDUCTION

Specific retention volumes were calculated in the usual manner, using a mathematical dead time method [9] to correct retention times.

Activity coefficients at infinite dilution based on weight fraction, Ω_1^∞, were calculated [10,11] according to the expression

$$\ln \Omega_1^\infty \equiv \ln\left(\frac{a_1}{w_1}\right) = \ln\left(\frac{273.15\,R}{P_1^0 V_g M_1}\right) - \frac{P_1^0}{RT}(B_{11} - V_1^0) \tag{1}$$

where a_1 and w_1 are the activity and weight fraction, respectively, of the solute in the polymer and M_1, P_1^0, B_{11} and V_1^0 are the molecular weight, saturated vapour pressure, second viral coefficient and molar volume respectively, of the solute at the column temperature T; R is the gas constant.

Vapour pressures were deduced using Antoine coefficients from various sources [12,13]. Second viral coefficients of n-alkanes were calculated by the method of O'Connell and Prausnitz [14]; for other substances, values were inter- or extrapolated from literature values corresponding to other temperatures [15]. Densities were calculated according to the pertinent equation [16,17]. Molar volumes were deduced from molecular weight and density values.

Flory–Huggins interaction parameters were calculated according to the expression [10,11,18]

$$\chi^{\infty} = \ln \Omega_1^{\infty} + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^0}{V_2^0}\right) \tag{2}$$

where ρ_1 and ρ_2 are the densities of the solute and the polymer, respectively, and V_1^0 and V_2^0 the corresponding molar volumes. Considering that $V_1^0 \ll V_2^0$, the ratio V_1^0/V_2^0 was taken as zero.

Partial molar enthalpies of solution, ΔH_s were deduced in each instance from experimental values, according to the expression

$$\Delta H_s = -R \cdot \frac{\partial(\ln V_g)}{\partial(1/T)} \tag{3}$$

Partial molar enthalpies of mixing of the solutes at infinite dilution, ΔH_m^{∞}, were calculated from

$$\Delta H_m^{\infty} = R \cdot \frac{\partial(\ln \Omega_1^{\infty})}{\partial(1/T)} \tag{4}$$

The partial molar enthalpy of vaporization of the solutes may be calculated [18] as the difference:

$$\Delta H_v = \Delta H_m^{\infty} - \Delta H_s \tag{5}$$

Solubility parameters of the solutes were deduced from the expression

$$\delta_1 = [(\Delta H_v - RT)/V_1^0]^{1/2} \tag{6}$$

Partial molar free energies of mixing were calculated from activity coefficients at infinite dilution [18,19]. Partial molar free energies of solution at infinite dilution were calculated from

$$\Delta G_s = -RT \ln(M_1 V_g/273.15R) \tag{7}$$

Solubility parameters of the stationary phases were deduced from the expression [5,11]

$$\frac{\delta_1^2}{RT} - \frac{\chi^{\infty}}{V_1^0} = \frac{2\delta_2}{RT} \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S^{\infty}}{V_1^0}\right) \tag{8}$$

where δ_2 is the solubility parameter of the polymer and χ_S^∞ is the entropic contribution to the interaction parameter χ^∞. On plotting the left-hand side term of eqn. 8 *versus* δ_1, a straight line was obtained, and from its slope the value of δ_2 was deduced.

A personal computer was used to run the FORTRAN programs necessary to obtain the values of the different parameters.

RESULTS AND DISCUSSION

Specific retention volumes

Table I gives the values of the specific retention volumes of the solutes on both stationary phases at various temperatures. The least mean squares (l.m.s.) method, applied to the straight line obtained by plotting ln V_g *versus* the inverse of the absolute temperature, gave in all instances correlation coefficients of 0.9998 or better. The

TABLE I

SPECIFIC RETENTION VOLUMES (V_g)

Stationary phase	Solute	Temperature (K)						
		363.15	383.15	403.15	423.15	453.15	473.15	
OV-101	*n*-Hexane	26.2	16.5	10.9	7.5	4.5	3.3	
	n-Heptane	53.3	31.7	19.9	13.0	7.4	5.3	
	n-Octane	108.2	59.4	34.4	21.0	10.7	7.2	
	n-Nonane	219.2	111.7	60.6	34.4	16.5	10.5	
	n-Decane	372.7	188.4	100.4	56.7	25.2	17.0	
	n-Undecane	732.6	348.0	174.7	93.1	38.7	24.9	
	n-Dodecane	1484.2	657.3	309.2	155.3	59.4	36.7	
	Benzene	39.4	24.5	16.0	10.7	6.5	4.8	
	Toluene	82.0	47.2	28.8	18.1	10.1	7.0	
	2-Pentanone	42.3	26.0	16.5	10.9	6.2	4.5	
	Ethyl acetate	25.1	16.0	10.6	7.2	4.4	3.2	
	Pyridine	65.2	38.6	24.1	15.6	8.9	6.3	
	n-Butanol	36.5	22.0	14.0	9.4	5.4	3.9	
	1-Octanol	517.1	255.0	132.6	72.9	31.8	20.8	
	Dimethylaniline	615.9	306.1	160.4	88.8	39.1	25.8	
		372.9	383.35	393.55	403.6	413.5	453.15	473.15
OV-105	*n*-Hexane	19.3	15.1	12.7	10.4	8.6	4.6	3.4
	n-Heptane	36.5	27.5	22.3	17.8	14.2	6.8	4.9
	n-Octane	69.3	50.6	39.9	30.9	23.9	10.4	7.2
	n-Nonane	131.0	92.8	70.6	53.0	40.0	15.7	10.4
	n-Decane	248.2	169.7	125.4	91.1	67.1	24.0	15.1
	n-Undecane	469.9	310.7	222.2	156.7	112.0	36.2	21.7
	n-Dodecane	888.0	566.1	392.2	269.5	186.2	54.6	31.4
	Benzene	33.0	25.7	21.0	17.2	14.0	7.2	5.3
	2-Pentanone	35.0	30.9	24.8	19.8	15.8	7.5	5.4
	Pyridine	61.7	47.4	36.8	29.6	23.6	11.0	7.8
	n-Butanol	33.0	26.7	21.6	17.0	13.6	6.5	4.6

experimental values of the specific retention volumes of the *n*-alkanes with 7–12 carbon atoms, obtained on the OV-101 capillary column at 120°C, when compared with the corresponding values calculated for the packed column with the same stationary phase at the same temperature, as deduced from the l.m.s. equation (no experimental values available at that temperature), gave absolute errors with an average value of 1.87%, with the highest difference corresponding to *n*-decane (4.1%). This indicates that the adsorption phenomena in the packed column, if any, are negligible, and confirms the finding of Korol *et al.* [20] in the sense that for non-polar stationary phases and solutes, retention data obtained on packed and capillary columns are interchangeable.

Interaction parameters

Table II lists the corresponding solute–polymer interaction parameters (χ^∞). The variation of the interaction parameters with temperature may best be observed from Figs. 1–4. The curves show the parabolic dependence of χ^∞ on temperature

TABLE II

SOLUTE–POLYMER INTERACTION PARAMETERS (χ^∞)

Stationary phase	Solute	Temperature (K)						
		363.15	383.15	403.15	423.15	453.15	473.15	
OV-101	*n*-Hexane	0.17	0.08	−0.01	−0.10	−0.19	−0.26	
	n-Heptane	0.25	0.16	0.07	0.02	−0.12	−0.20	
	n-Octane	0.32	0.25	0.19	0.14	0.09	0.04	
	n-Nonane	0.37	0.30	0.26	0.23	0.19	0.17	
	n-Decane	0.59	0.46	0.37	0.31	0.28	0.17	
	n-Undecane	0.66	0.52	0.44	0.38	0.35	0.26	
	n-Dodecane	0.70	0.56	0.47	0.42	0.41	0.33	
	Benzene	0.51	0.42	0.33	0.27	0.14	0.10	
	Toluene	0.55	0.47	0.41	0.37	0.27	0.24	
	2-Pentanone	0.93	0.79	0.67	0.58	0.48	0.41	
	Ethyl acetate	0.73	0.59	0.48	0.39	0.30	0.27	
	Pyridine	1.23	1.11	1.00	0.92	0.79	0.74	
	n-Butanol	1.99	1.67	1.40	1.18	0.91	0.77	
	1-Octanol	1.98	1.59	1.31	1.11	0.93	0.79	
	Dimethylaniline	−0.80	−0.82	−0.80	−0.78	−0.69	−0.71	
		372.9	383.35	393.55	403.6	413.5	453.15	473.15
OV-105	*n*-Hexane	0.21	0.17	0.09	0.05	0.01	−0.16	−0.23
	n-Heptane	0.34	0.31	0.24	0.20	0.18	0.02	−0.04
	n-Octane	0.44	0.42	0.35	0.31	0.30	0.16	0.11
	n-Nonane	0.53	0.50	0.43	0.40	0.39	0.28	0.25
	n-Decane	0.61	0.58	0.51	0.48	0.47	0.38	0.35
	n-Undecane	0.67	0.65	0.58	0.56	0.55	0.47	0.46
	n-Dodecane	0.73	0.71	0.65	0.62	0.62	0.55	0.55
	Benzene	0.42	0.38	0.33	0.28	0.26	0.11	0.06
	2-Pentanone	0.67	0.67	0.55	0.50	0.47	0.33	0.29
	Pyridine	0.98	0.91	0.87	0.81	0.78	0.64	0.59
	n-Butanol	1.62	1.48	1.32	1.21	1.12	0.78	0.66

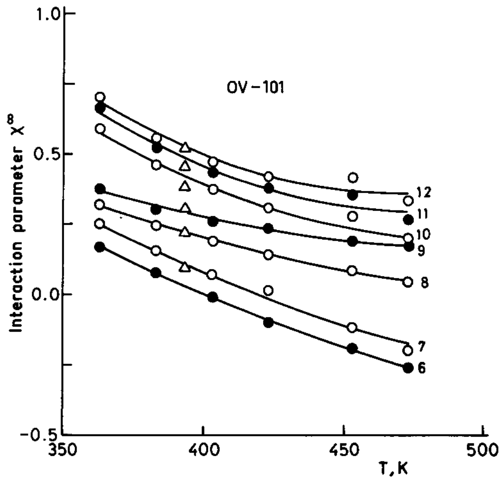

Fig. 1. Interaction parameters of the *n*-alkanes in OV-101. The numbers on the right represent the number of carbon atoms in the *n*-alkane. △, Values obtained from experiments on the capillary column.

predicted by theory [21–23]. They show, in all instances except for dimethylaniline, that as the temperature increases in the range studied, the systems leave the upper critical solution temperature (UCST), therefore increasing the solubility of the solute in the polymer (the curves tend to reach lower values of χ^{∞}). The UCST is a temperature below which complete miscibility of solute and polymer does not occur. It is important to realize that the concentration conditions met in IGC, where infinite dilution is the norm, are far from those where the critical conditions are satisfied (high concentration). However, the trends of the curves do indicate whether solubility increases or decreases. With dimethylaniline in OV-101 (Fig. 2), the temperature range

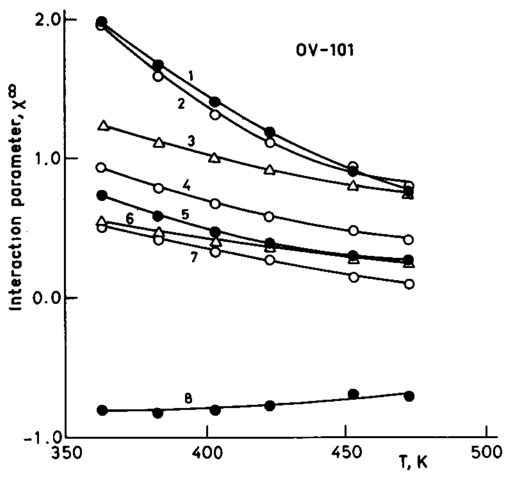

Fig. 2. Interaction parameters in OV-101. Substances: 1 = *n*-butanol; 2 = 1-octanol; 3 = pyridine; 4 = 2-pentanone; 5 = ethyl acetate; 6 = toluene; 7 = benzene; 8 = dimethylaniline.

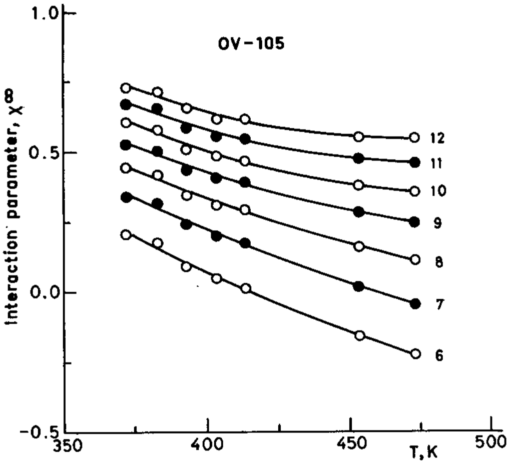

Fig. 3. Interaction parameters of the *n*-alkanes in OV-105. The numbers on the right represent the number of carbon atoms in the *n*-alkane.

considered is close to the zone of maximum solubility, the trend of the curve indicating that, as the temperature increases, the system is approaching its lower critical solution temperature (LCST), above which phase separation should occur under conditions of high solute concentration.

From the values in Table II, it may be deduced that the best solvents for the polymers are the alkanes and aniline (low values of χ^∞), whereas alcohols are clearly bad solvents, especially at low temperatures. The carbonyl compounds may be considered as medium solvents. The expected behaviour of aromatic compounds as solvents of OV-101 and OV-105 is not clear. Whereas benzene and toluene show low values of χ^∞ (good solvents), pyridine presents values of the interaction parameter that are closer to those of the alcohols, indicating poorer solubility.

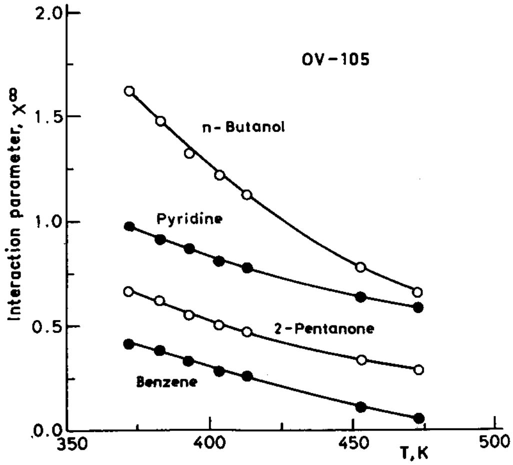

Fig. 4. Interaction parameters in OV-105.

On comparing the values of the interaction parameter of those solutes that were run on both polymers (Table II), we find that *n*-alkanes are more soluble in polydimethylsiloxane than they are in polymethylcyanopropylsiloxane. On the other hand, polar solutes mix better with the polymer OV-105, because the cyano group, with a high electronic attraction and dipolar moment, interacts with π electron-containing substances, increasing their solubility in the stationary phase, thus producing higher values of V_g and consequently lower values of Ω_1^∞ (eqn. 1). This results in lower values of χ^∞ (eqn. 2).

Values of the interaction parameters of a few *n*-alkanes, deduced from experimental measurements carried out in the capillary column at 120°C, were compared with those calculated for the packed column OV-101 for the same temperature. The results are included in Fig. 1. Again, it is shown that the values deduced from experiments with capillary columns are comparable to those obtained with packed columns.

Partial molar enthalpies and free energies

Table III presents the results obtained for the partial molar enthalpies of solution and mixing (eqns. 3 and 4) on both stationary phases. The values of ΔH_m for the *n*-alkanes are lower in both polymers than those corresponding to more polar solutes, the difference being highest with alcohols. An exception is dimethylaniline, as observed when considering interaction parameters. Comparing values for the same solutes, it might be said that *n*-alkanes are not as good solvents and the polar substances are slightly better solvents of OV-105 than they are of the polymer OV-101. The cyanopropyl content of OV-105 is low, so it is not surprising that the values of ΔH_s

TABLE III

PARTIAL MOLAR ENTHALPIES OF SOLUTION AND MIXING (kcal mol^{-1})

Errors based on a 95% confidence limit.

Solute	OV-101		OV-105	
	ΔH_s	ΔH_m	ΔH_s	ΔH_m
n-Hexane	−6.40 ± 0.05	0.88 ± 0.11	−6.01 ± 0.11	1.30 ± 0.12
n-Heptane	−7.16 ± 0.06	0.99 ± 0.06	−7.02 ± 0.11	1.10 ± 0.12
n-Octane	−8.42 ± 0.06	0.53 ± 0.16	−7.91 ± 0.12	1.01 ± 0.15
n-Nonane	−9.43 ± 0.05	0.41 ± 0.17	−8.85 ± 0.10	0.94 ± 0.14
n-Decane	−9.69 ± 0.25	1.03 ± 0.34	−9.78 ± 0.10	0.89 ± 0.18
n-Undecane	−10.60 ± 0.23	1.02 ± 0.37	−10.73 ± 0.12	0.81 ± 0.21
n-Dodecane	−11.59 ± 0.26	0.95 ± 0.45	−11.67 ± 0.11	0.74 ± 0.22
Benzene	−6.55 ± 0.08	1.02 ± 0.11	−6.39 ± 0.07	1.17 ± 0.09
Toluene	−7.63 ± 0.07	0.82 ± 0.08	–	–
2-Pentanone	−7.01 ± 0.10	1.29 ± 0.26	−7.06 ± 0.08	1.20 ± 0.17
Ethyl acetate	−6.38 ± 0.05	1.55 ± 0.16	–	–
Pyridine	−7.25 ± 0.04	1.47 ± 0.12	−7.23 ± 0.05	1.46 ± 0.10
n-Butanol	−6.93 ± 0.03	3.69 ± 0.34	−7.07 ± 0.10	3.45 ± 0.25
1-Octanol	−10.06 ± 0.21	3.51 ± 0.85	–	–
Dimethylaniline	−9.94 ± 0.21	−0.45 ± 0.29	–	–

reported in Table III are similar in both polymers for all the solutes considered, polar and apolar.

Discussion on the solution parameters ΔG_s, ΔH_s and $T\Delta S$

The values of the partial molar free energies of mixing are given in Table IV. The thermodynamic parameters of solution, ΔG_s, ΔH_s and $T\Delta S$, were calculated for the *n*-alkanes on both stationary phases. The process of solution implies the transfer of solute molecules from the gas to the liquid phase. The solute–polymer interaction is closely related to this process, and therefore the enthalpy of solution will also depend on the interaction. Fig. 5 presents results obtained at 200°C for the different parameters *versus* the number of carbon atoms of the *n*-alkane in OV-105. The lines corresponding to the polymer OV-101 are similar. The slope of the lines represents the contribution of the methylene group to the corresponding parameter. Values are

TABLE IV

PARTIAL MOLAR FREE ENERGIES OF MIXING, ΔG_m (kcal mol^{-1})

Stationary phase	Solute	Temperature (K)						
		363.15	383.15	403.15	423.15	453.15	473.15	
OV-101	*n*-Hexane	1.16	1.17	1.18	1.19	1.23	1.25	
	n-Heptane	1.19	1.20	1.20	1.22	1.24	1.25	
	n-Octane	1.21	1.23	1.26	1.30	1.37	1.42	
	n-Nonane	1.23	1.26	1.29	1.34	1.42	1.48	
	n-Decane	1.37	1.36	1.36	1.38	1.47	1.44	
	n-Undecane	1.41	1.39	1.40	1.42	1.51	1.50	
	n-Dodecane	1.43	1.40	1.41	1.44	1.54	1.54	
	Benzene	1.19	1.20	1.20	1.23	1.22	1.25	
	Toluene	1.22	1.23	1.25	1.28	1.31	1.34	
	2-Pentanone	1.56	1.54	1.55	1.56	1.61	1.63	
	Ethyl acetate	1.34	1.31	1.29	1.28	1.27	1.27	
	Pyridine	1.62	1.62	1.62	1.63	1.64	1.67	
	n-Butanol	2.30	2.19	2.09	2.01	1.92	1.88	
	1-Octanol	2.28	2.11	2.00	1.93	1.92	1.87	
	Dimethylaniline	0.16	0.16	0.19	0.22	0.32	0.32	
		372.9	383.35	393.55	403.6	413.5	453.15	473.15
OV-105	*n*-Hexane	1.22	1.24	1.21	1.21	1.22	1.21	1.22
	n-Heptane	1.28	1.30	1.28	1.29	1.30	1.32	1.34
	n-Octane	1.33	1.35	1.33	1.34	1.36	1.39	1.42
	n-Nonane	1.37	1.39	1.38	1.39	1.41	1.45	1.49
	n-Decane	1.42	1.43	1.42	1.43	1.45	1.51	1.56
	n-Undecane	1.45	1.48	1.46	1.47	1.50	1.57	1.62
	n-Dodecane	1.48	1.51	1.50	1.51	1.54	1.62	1.69
	Benzene	1.15	1.16	1.14	1.14	1.15	1.14	1.15
	2-Pentanone	1.40	1.41	1.39	1.39	1.40	1.42	1.46
	Pyridine	1.46	1.46	1.44	1.44	1.45	1.45	1.46
	n-Butanol	2.09	2.04	1.97	1.93	1.90	1.76	1.71

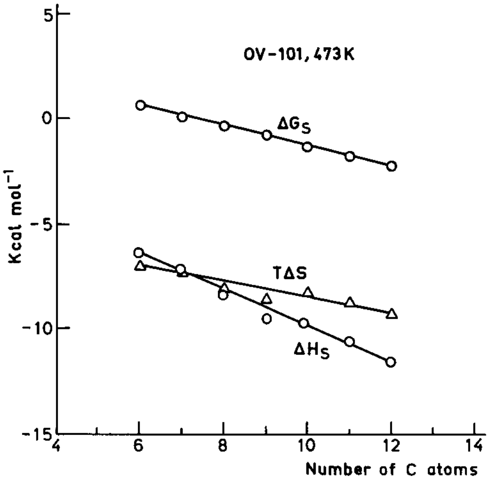

Fig. 5. Thermodynamic parameters of solution of the *n*-alkanes in OV-105 at 473.15 K.

presented in Table V. The difference between the values obtained for the two stationary phases for the slopes of the lines corresponding to ΔH_s (0.07 kcal mol^{-1}) may be attributed to the effect of the 5% substitution of methyl groups by cyanopropyl groups in the polymer, indicating that the solution of the methylene group in the OV-105 polymer is slightly more exothermic. The contribution of the methylene group to the interaction parameter χ^{∞} at 200°C may be deduced from Table II as *ca.* 0.10 for OV-101 and 0.13 for OV-105. The lower value found for OV-101 is indicative of the fact that in this stationary phase, the solubility of *n*-alkanes of longer chain length is more similar to the solubility of those of lower molecular weight than it is in the polymer OV-105, where the solubility decreases more rapidly with increasing chain length. On the other hand, the variation with temperature of the contribution of the CH_2 group to χ^{∞}, as deduced from Table II, is small in both instances, but smaller for OV-101, indicating less deterioration of solubility of the *n*-alkanes with temperature in this instance.

Results obtained on additional stationary phases, and not only those corresponding to the two polymers so far considered, have been taken into account for the purpose of the following discussion on the partial molar free energy of solution. This discussion is concerned with the effect of the presence of the cyanopropyl group in the polymers, and this should be deduced from data obtained on cyanoalkylsilicones.

TABLE V

CONTRIBUTIONS OF THE METHYLENE GROUP TO ΔG_s, ΔH_s AND $T\Delta S$ (kcal mol^{-1}) AT 473.15 K

Errors based on a 95% confidence limit.

Stationary phase	ΔG_s	ΔH_s	$T\Delta S$
OV-101	−0.483 ± 0.017	−0.868 ± 0.082	−0.385 ± 0.097
OV-105	−0.452 ± 0.012	−0.938 ± 0.011	−0.487 ± 0.017

TABLE VI

COMPOSITION OF SILICONE STATIONARY PHASES

Stationary phase	Group substitution (%)		
	Methyl	Phenyl	Cyanopropyl
Methylphenylsilicones			
OV-101	100	0	0
OV-3	90	10	0
OV-7	80	20	0
OV-11	65	35	0
OV-17	50	50	0
OV-22	35	65	0
OV-25	25	75	0
Cyanopropylsilicones			
OV-105	95	0	5
SP-2300	0	50	50
SP-2310	0	25	75
SP-2330	0	5	95
SP-2340	0	0	100

However, some of the commercially available stationary phases containing this group also contain the phenyl group, so the effect of the latter must also be considered. The percentage substitutions of the various groups in the polymers are presented in Table VI.

Using V_g data for *n*-alkanes at 120°C [24], values of the partial molar free energy of solution were calculated for the methylphenylsilicones listed in Table VI. For each stationary phase, ΔG_s was plotted *versus* the number of carbon atoms in the *n*-alkane. In all instances, the correlation coefficients obtained were 0.9997 or higher. The slopes of these straight lines represent, in each instance, the contribution of the methylene group of the *n*-alkanes to the partial molar free energy of solution [$\Delta G_s(CH_2)$] of those substances in the polymer at that temperature. A representation of the slope of the straight lines just mentioned *versus* percentage substitution of the phenyl group is presented in Fig. 6. It can be seen that, taking OV-101 as a reference, the value of $\Delta G_s(CH_2)$ decreases as the phenyl group content increases (-10.6 cal mol^{-1} at *ca.* 30% substitution), and later increases ($+1.4$ cal mol^{-1} at *ca.* 60% substitution; $+15.5$ cal mol^{-1} at 75% substitution). We found that the points fit a parabola very well. The equation is

$$\Delta G_s(CH_2)_{MPS} = 0.0125\,x^2 - 0.7273\,x - 548 \qquad (9)$$

where MPS refers to methylphenylsilicones, x represents the percentage substitution of phenyl groups in the silicone and the result is given in cal mol^{-1} (sum of squares of residuals = 2.5). Although the effect of the phenyl group on $\Delta G_s(CH_2)$ is not uniform, it is in any case small.

The same kind of representations of values of V_g for the *n*-alkanes in the cyanopropylsilicones in Table VI [25] plus the polymer OV-101 produced values of the dependence of $\Delta G_s(CH_2)$ on the cyanopropyl percentage substitution which are also

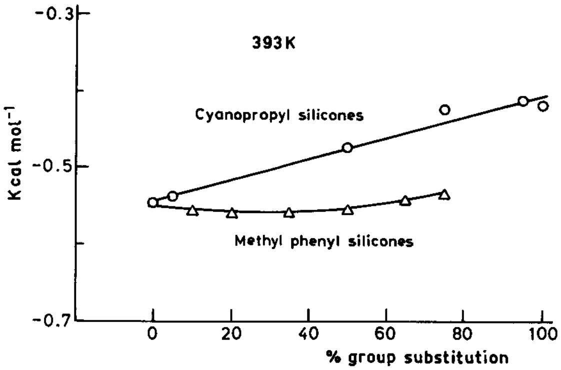

Fig. 6. Contribution of the methylene group of the n-alkanes to the partial molar free energy of solution [$\Delta G_s(CH_2)$] of the n-alkanes in methylphenyl- and cyanopropylsilicones with different contents of the active group.

shown in Fig. 6. The correlation coefficient obtained was 0.989, indicating that with cyanopropylmethylsilicones there is a linear dependence of the contribution of the methylene group to ΔG_s with the cyanopropyl group substitution of the polymer, given by the expression

$$\Delta G_s(CH_2)_{CPS} = 1.405x - 543 \tag{10}$$

where CPS refers to cyanopropylsilicones, x now represents the percentage of cyanopropyl substitution in the polymer and $\Delta G_s(CH_2)$ is given in cal mol^{-1}. In view of the low contribution of the phenyl group, eqn. 10 may be considered as a good approximation for the determination of the effect of cyanopropyl substitution in the polymer. The slope of the line (1.405 cal mol^{-1}) represents the contribution of the methylene group to the partial molar free energy of solution per unit cyanopropyl substitution (expressed as a percentage).

Fig. 6 shows that the value of $\Delta G_s(CH_2)$ increases (becomes less negative) with increasing cyanopropyl content of the polymer, indicating a decrease in the interaction of the methylene group with the polymers of higher cyanopropyl group content. This explains the high values of the solute–polymer interaction parameter of the n-alkanes, χ^{∞}, of between 2.4 and 3.8 for n-hexane to n-dodecane at 120°C, reported for the stationary phase SP-2340 (100% cyanopropyl) [5].

Solubility parameters of the stationary phases

GC has proved to be a good experimental technique to deduce values of solubility parameters of polymers [5,11,18,26–28]. In the case of the two stationary phases considered here, the straight lines obtained with the help of eqn. 2 produced values for δ_2 of 6.49 ± 0.04 (cal cm^{-3})$^{1/2}$ for OV-101 and 6.83 ± 0.04 (cal cm^{-3})$^{1/2}$ for OV-105. In neither instance was the dependence of δ_2 on temperature significant, with perhaps slightly lower values at higher temperatures. The value found for OV-101 agrees well with that reported by Roth [29] for polydimethylsiloxane [6.53 (cal cm^{-3})$^{1/2}$ at 90°C].

CONCLUSIONS

The introduction of a small proportion of cyanopropyl groups in the molecule of a dimethylsilicone stationary phase decreases the solubility of *n*-alkanes and improves that of polar compounds. At the same time, it increases the value of the solubility parameter of the polymer, although only slightly.

It has been confirmed that with non-polar solute–polymer systems, specific retention volumes, and therefore the thermodynamic parameters derived from them, may be obtained either from chromatograms carried out in packed or in capillary columns.

The values of the solute–polymer interaction parameters presented here suggest the behaviour that could be expected in the preparation of columns with mixed stationary phases. Polymers containing cyanoalkyl groups should not mix well with hydrocarbon-type stationary phases (hydrocarbons or silicones with alkyl groups), or with those of alcoholic type. They should mix better with polymers containing the phenyl group in their structure.

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