

Thermodynamic characterization of Superox 20M by inverse gas chromatography

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ABSTRACT

Inverse gas chromatographic experiments carried out between 80 and 140°C were used to characterize Superox 20M deposited on glass capillary columns, using 28 substances belonging to five different chemical types. No absorption in the gas–liquid interphase was observed except in three cases corresponding to the highest molecular masses. The thermodynamic parameters of solution and mixing and the Flory–Huggins solute–stationary phase interaction parameter were measured. The dependences of all magnitudes on temperature and chain length were also calculated, and conclusions on the relationship between their values and the chromatographic behaviour of the solutes in the stationary phase were drawn. The solubility parameter of Superox 20M was measured between 80 and 140°C and was found to have a linear dependence on temperature. Values at 50, 64 and 280°C were deduced.

INTRODUCTION

Poly(ethylene oxide)s are among the most popular stationary phases for gas chromatography (GC). They have been used for years in the analysis of all kind of oxygenated compounds, and they are probably the most widely used polar stationary phases today. Carbowaxes and Superoxes are both poly(ethylene oxide)s, the latter, with higher molecular mass and without catalytic residues, having been prepared with capillary columns in mind. This type of polymer has been considered as “preferred stationary phases” [1,2]. The effect of immobilization on the phase transition of Superox 20M and therefore on the minimum allowed operating temperature (MAOT) has already been studied [3]. We report here a study of Superox 20M, at temperatures above its melting point, using

capillary columns, involving the thermodynamic characterization of the polymer and its interactions with certain chemical functions, based on the chromatographic behaviour of various substances belonging to five different families.

Inverse gas chromatography (IGC), introduced in 1967 by Kiselev [4] and later developed in theory and methods mainly by Smidsrod and Guillet [5], is the term applied to a technique which uses GC as it is normally known by analysts, but with the interest focused on the substance which is used as the stationary phase in the chromatographic column. With this aim, selected solutes are injected into the chromatograph and information on the thermodynamic parameters of the solute–stationary phase system is deduced from the chromatographic retention parameters measured. The term “inverse” refers to the fact that, in conventional analytical GC, the type of sample to be analysed determines the selection of the most convenient stationary phase, whereas in IGC studies, the solutes are chosen so that the appropriate information on the stationary phase may be obtained.

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EXPERIMENTAL

Three glass capillary columns (drawn from borosilicate glass in a Shimadzu GBM-1B machine) with Superox 20M (Alltech, Deerfield, IL, USA) as stationary phase were prepared by the procedure described previously [3]: column tube deactivated from Carbowax 20M (Hewlett-Packard) and no immobilization of the polymer. The dimensions of the three columns are given in Table I.

The samples used were ethylbenzene from Aldrich (Gillingham, Dorset, UK), 2-heptanone, 2-octanone and 1-hexanol from Aldrich Chemie (Steinheim, Germany), 1-butanol and 2-pentanone from BDH (Poole, UK), *n*-heptane, *n*-octane, benzene and 1-pentanol from Carlo Erba (Milan, Italy), *n*-decane, *n*-dodecane, 2-pentanone, methyl formate, methyl acetate, methyl hexanoate, methyl heptanoate and methyl octanoate from Fluka (Buchs, Switzerland), acetone, *n*-hexane and propylbenzene from Merck-Schuchard (Germany), toluene from Merck (Darmstadt, Germany), propanol, from Probus (Barcelona, Spain), methanol from Riedel-de Haën (Seelze, Germany), *n*-nonane and *n*-undecane from Sigma (St. Louis, MO, USA), methyl butyrate from UCB (Brussels, Belgium) and pentylbenzene, synthesized in the laboratories of the Institute of General Organic Chemistry, CSIC (Madrid, Spain).

Two gas chromatographs (Hewlett-Packard HP-5890A) with flame ionization detectors and capillary column injectors, were modified to measure the carrier gas head pressure by means of pressure transducers (WIKA Tronic 891.13.500, Alexander Wiegand GmbH, Klingenberg, Germany). Atmospheric pressure was

TABLE I
DIMENSIONS OF THE THREE CAPILLARY COLUMNS

Parameter	Column		
	1	2	3
Length (m)	22.46	24.88	24.88
Inner diameter (mm)	0.259	0.287	0.287
Film thickness (μm)	0.275	0.151	0.351

checked with a mercury barometer (precision 0.2 mmHg; 1 mmHg = 133.322 Pa). The density of Superox 20M at different temperatures was measured with a pycnometric procedure. Chromatograms were measured at 80, 100, 120 and 140°C.

DATA REDUCTION

Specific retention volumes (V_g) were calculated in the usual manner [6]. Activity coefficients at infinite dilution based on mass fraction, Ω_1^∞ , were calculated according to the expression of Guillet and co-workers [7,8]. Vapour pressures were deduced using Antoine coefficients from various sources [9,10]. Second virial coefficients of *n*-alkanes were calculated by the method of O'Connell and Prausnitz [11]; for other substances, values were inter- or extrapolated from literature values corresponding to other temperatures [12]. Densities of the solutes were calculated according to the pertinent equation [13,14]. Molar volumes were deduced from molecular mass and density values.

Flory-Huggins interaction parameters, $\chi_{1,2}^\infty$ were calculated from the known expression [7,8,15]. Partial molar enthalpies of solution, ΔH_s , mixing, ΔH_m , and vaporization, ΔH_v , were deduced in each instance from experimental results [16]. Partial molar free energies of mixing were calculated from activity coefficients at infinite dilution [15]. Partial molar free energies of solution at infinite dilution were calculated from experimental values of V_g [15].

Solubility parameters of the solutes were deduced from the known expression, using the experimentally determined enthalpies of vaporization. Solubility parameters of the polymers used as stationary phases were deduced from a plot based on the expression of Price *et al.* [8]. The FORTRAN programs necessary to obtain the values of the different parameters were run on a personal computer.

The equations used for these calculations are given in the Appendix.

RESULTS AND DISCUSSION

Plots of V_g versus the inverse of the volume of the stationary phase in the column show that the values are equivalent, indicating no adsorption

of the solutes at any temperature (*i.e.*, the values are independent of the stationary phase loading) except for *n*-dodecane, *n*-pentylbenzene and methyl octanoate, which presented slightly lower values of V_g at higher loadings. In these three cases, the V_g values were corrected to infinite film thickness. All other figures presented here correspond to the experimental values obtained on the column made with the thickest film (column 3). Plots of values of $\log V_g$ versus $1/T$ showed correlation coefficients of 0.9999 or better in the three columns for all the solutes tested.

Solute-polymer interaction parameters ($\chi_{1,2}^\infty$)

The value of the Flory-Huggins solute-stationary phase interaction parameter, $\chi_{1,2}^\infty$, may be considered as an indicator of the behaviour of the solute as a solvent of the stationary phase, high values corresponding to substances that behave as poor solvents. Experimental values are given in Table II. Values of $\chi_{1,2}^\infty$ deduced from IGC experiments are averages of all possible interactions encountered in the solute-stationary phase system. It is clear that *n*-alkanes show values of $\chi_{1,2}^\infty$ that are much higher than those corresponding to other solutes. Therefore, it may be deduced that alkanes are poor solvents of Superox 20M, whereas alcohols, aromatics, esters and ketones may be considered as good solvents. Table II also shows that for any given homologous series, the solubility decreases with increasing chain length, as would be expected from the values obtained in the case of the *n*-alkanes.

The dependence of $\chi_{1,2}^\infty$ on temperature may be observed from examination of Table II. In some instances the points seem to fit a linear correlation, whereas in others the points describe a second-degree curve. As an example, Fig. 1 shows this dependence for *n*-alkanes and ketones and the fact that the values of $\chi_{1,2}^\infty$ decrease with increasing temperature. For all solutes tested, miscibility with the stationary phase increases with increasing temperature, indicating that solutes are leaving their upper critical solution temperature (UCST) [17,18], below which phase separation should occur in high-concentration solutions. The Flory-Huggins interaction param-

TABLE II
SOLUTE-POLYMER INTERACTION PARAMETER, $\chi_{1,2}^\infty$, AT DIFFERENT TEMPERATURES

Solute	Temperature (K)			
	353	373	393	413
<i>n</i> -Hexane	1.32	1.09	0.91	0.72
<i>n</i> -Heptane	1.50	1.28	1.11	0.93
<i>n</i> -Octane	1.67	1.45	1.28	1.09
<i>n</i> -Nonane	1.82	1.59	1.44	1.23
<i>n</i> -Decane	1.97	1.72	1.56	1.35
<i>n</i> -Undecane	2.11	1.86	1.68	1.47
<i>n</i> -Dodecane	2.26	2.00	1.80	1.59
Benzene	-0.22	-0.28	-0.29	-0.34
Toluene	-0.04	-0.10	-0.11	-0.17
Ethylbenzene	0.14	0.07	0.07	0.02
<i>n</i> -Propylbenzene	0.29	0.22	0.20	0.15
<i>n</i> -Pentylbenzene	0.64	0.51	0.44	0.36
Methyl formate	-0.03	-0.08	0.01	-0.15
Methyl acetate	-0.07	-0.16	-0.18	-0.27
Methyl butyrate	0.10	0.05	0.04	-0.04
Methyl hexanoate	0.33	0.31	0.31	0.28
Methyl heptanoate	0.39	0.29	0.25	0.19
Methyl octanoate	0.50	0.37	0.30	0.23
2-Butanone	0.08	0.00	-0.05	-0.12
2-Pentanone	0.15	0.07	0.02	-0.07
2-Heptanone	0.32	0.24	0.20	0.12
2-Octanone	0.77	0.58	0.45	0.30
Methanol	0.42	0.27	0.12	-0.03
Ethanol	0.36	0.23	0.14	-0.04
<i>n</i> -Propanol	0.22	0.10	0.01	-0.14
<i>n</i> -Butanol	0.19	0.05	0.02	-0.16
<i>n</i> -Pentanol	0.11	0.01	-0.03	-0.11
<i>n</i> -Hexanol	0.18	0.04	0.00	-0.09

eter, $\chi_{1,2}^\infty$, has the physical meaning of a residual free energy [19] with a parabolic dependence on temperature between two values corresponding to the UCST and to the lower critical solution temperature (LCST) above which, again, phase separation takes place. The minimum of the curve corresponds to the region of maximum solubility. The trend of the values of $\chi_{1,2}^\infty$ indicates that all solutes will reach their maximum solubility in the stationary phase at temperatures above 140°C. Experiments with IGC are carried out under concentration conditions that are far from those where the critical conditions are satisfied (high solute concentration), but the shape of the curves is a good indication of the

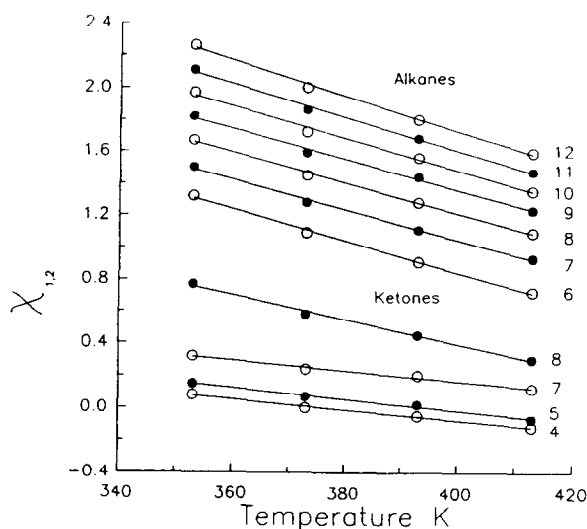


Fig. 1. Dependence of the value of the solute-polymer interaction parameter, $\chi_{1,2}^\infty$, on temperature on Superox 20M for *n*-alkanes and ketones. The figures on the right represent the number of carbon atoms in the solute molecule.

temperature zone of the system in the corresponding solute-polymer solution diagram.

The dependence of the value of $\chi_{1,2}^\infty$ on the chain length of a homologous series may best be observed from Fig. 2. *n*-Alkanes, aromatics and

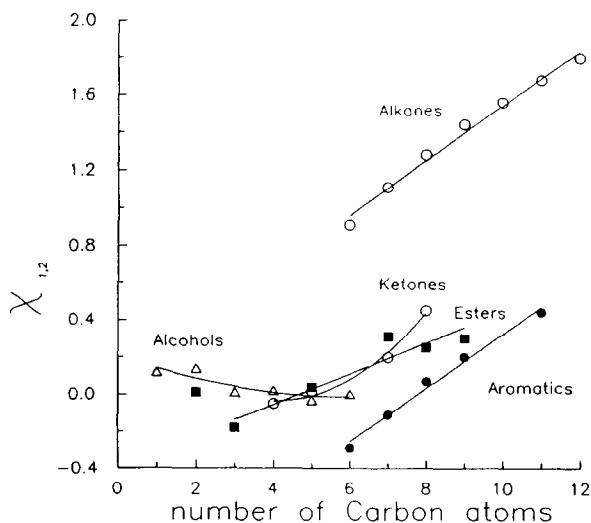


Fig. 2. Variation of the value of the solute-polymer interaction parameter, $\chi_{1,2}^\infty$, with chain length for each homologous series.

esters show a linear dependence of solubility on chain length, if methyl formate is excluded. The slope of the lines (the contribution of the methylene group to the value of $\chi_{1,2}^\infty$) is a measure of the deterioration of solubility due to the addition of one methylene group to the chain. This contribution is similar with *n*-alkanes and aromatic hydrocarbons, and smaller with methyl esters, indicating that the contribution of the methylene group to $\chi_{1,2}^\infty$ depends on the “active” radical attached to the hydrocarbon chain in the homologous series. In all these cases the solubility deteriorates with the addition of methylene groups, as expected.

The effect of the addition of a methylene group to the chain of alcohols and ketones is not as uniform. In the former, there seems to be a maximum in solubility round *n*-butanol or *n*-pentanol, indicating that for these chain lengths stronger specific interactions are produced between the alcohols and Superox 20M. Alcohols should interact fairly strongly with this stationary phase, but their strong autoassociation competes with the association with Superox 20M, making them poorer solvents of the polymer than expected. This is particularly important in the case of the smaller molecules, producing the peculiar behaviour observed. When ketones are considered, solubility deteriorates with increase in chain length, but the deterioration (in terms of the change in the value of $\chi_{1,2}^\infty$ per methylene group) seems to increase with increasing chain length, as may be deduced from the rate at which the values of $\chi_{1,2}^\infty$ change.

Thermodynamic parameters of mixing

Partial molar enthalpies and free energies of mixing are given in Table III. Ideal solutions should have values of the partial molar enthalpy of mixing of zero. The value of ΔH_m is a measure of the departure of the system from ideality. It can be seen that the solute-polymer systems considered here show parallelism between the values of $\chi_{1,2}^\infty$ and those of ΔH_m : low values of the interaction parameter correspond to less non-ideal solutions. Once again, alcohols depart from the general rule.

Values of the partial molar free energy of mixing show a good correlation with the corre-

TABLE III
PARTIAL MOLAR ENTHALPY AND FREE ENERGY
OF MIXING

Solutcs	ΔH_m (kcal mol ⁻¹)	ΔG_m (kcal mol ⁻¹)			
		353 K	373 K	393 K	413 K
<i>n</i> -Hexane	2.52	2.07	2.03	2.02	1.99
<i>n</i> -Heptane	2.48	2.17	2.13	2.13	2.11
<i>n</i> -Octane	2.56	2.26	2.23	2.23	2.20
<i>n</i> -Nonane	2.61	2.35	2.31	2.33	2.29
<i>n</i> -Decane	2.74	2.43	2.39	2.41	2.37
<i>n</i> -Undecane	2.92	2.53	2.48	2.48	2.45
<i>n</i> -Dodecane	3.12	2.62	2.57	2.56	2.53
Benzene	0.31	0.78	0.79	0.84	0.85
Toluene	0.41	0.90	0.92	0.97	0.98
Ethylbenzene	0.37	1.03	1.05	1.11	1.13
<i>n</i> -Propylbenzene	0.55	1.14	1.15	1.21	1.23
<i>n</i> -Pentylbenzene	1.23	1.39	1.37	1.39	1.41
Methyl formate	-0.09	0.86	0.89	1.03	0.99
Methyl acetate	0.50	0.85	0.85	0.90	0.90
Methyl butyrate	0.35	0.99	1.02	1.08	1.09
Methyl hexanoate	-0.04	1.16	1.22	1.30	1.36
Methyl heptanoate	0.71	1.21	1.21	1.26	1.29
Methyl octanoate	1.08	1.29	1.27	1.30	1.32
2-Butanone	0.67	1.05	1.07	1.10	1.11
2-Pentanone	0.77	1.10	1.11	1.15	1.15
2-Heptanone	0.73	1.20	1.22	1.26	1.27
2-Octanone	2.11	1.51	1.46	1.45	1.41
Methanol	1.87	1.30	1.27	1.24	1.20
Ethanol	1.58	1.26	1.24	1.25	1.19
<i>n</i> -Propanol	1.51	1.15	1.12	1.11	1.08
<i>n</i> -Butanol	1.38	1.11	1.08	1.09	1.05
<i>n</i> -Pentanol	0.87	1.05	1.04	1.07	1.08
<i>n</i> -Hexanol	1.15	1.09	1.06	1.09	1.07

sponding values of $\chi_{1,2}^\infty$, at all temperatures. The straight lines (not shown) obtained by plotting $\chi_{1,2}^\infty$ versus ΔG_m , at any temperature, including all 28 solutes, have correlation coefficients of 0.99 or better, and the four lines corresponding to 80, 100, 120 and 140°C, are almost indistinguishable when plotted on the same graph. There is, however, a small relative increase in the values of ΔG_m with increase in temperature (the four lines have slopes which increase slightly with temperature) owing to the contribution of the entropic term to the value of the partial molar free energy of mixing. Nevertheless, if all 112 values are included in one plot (28 solutes,

four temperatures), a straight line with a correlation coefficient of 0.975 may be drawn, indicating how small the effect of temperature on ΔG_m is. The contribution of the entropic term to ΔG_m produces the following effect: if we take any solute and compare the plot of $\chi_{1,2}^\infty$ versus T with the corresponding plot of ΔG_m versus T (using the units of Tables II and III), we find that at any given temperature, the slope of the curve of the interaction parameter is lower than that of the curve of ΔG_m versus T at the same temperature. For this reason, Tables II and III show examples of solute–polymer systems where both magnitudes decrease from 80 to 140°C (*n*-alkanes, alcohols, 2-octanone) and others, with smaller changes in the value of $\chi_{1,2}^\infty$, in which the partial molar free energy of mixing does not change or increases by about 0.1 kcal/mol (1 cal. = 4.14 J) or less. The former instances correspond to systems with a partial molar enthalpy of mixing of, say, 1.5 kcal/mol or higher, whereas the latter present smaller values.

Thermodynamic parameters of solution

The values of ΔH_s and ΔG_s deduced for the different solute–Superox 20M pairs are given in Table IV. The fact that the values now do not follow too closely the tendencies found earlier is because the process of solution implies the transfer of molecules from the gas to the liquid phase, so both processes of condensation and mixing take place and, therefore, the thermodynamic parameters of vaporization must be taken into account (see Appendix). Fig. 3 shows the dependence of ΔH_s and ΔG_s on the number of carbon atoms of the molecule for each homologous series at 100°C. The plots are similar at other temperatures. Plots of $T\Delta S_s$ (not shown) obtained by difference (see Appendix) are equally straight.

The values of the slopes of the lines are presented in Table V. The correlation coefficients were 0.997 or better for ΔH_s and ΔG_s and 0.98 or better for $T\Delta S_s$. The slopes represent, in each instance, the contribution of the methylene group of that homologous series to the corresponding thermodynamic parameter. Accepting the additivity principle, we could consider that the value obtained for *n*-alkanes is the “genuine”

TABLE IV
THERMODYNAMIC PARAMETERS OF SOLUTION

Solute	ΔH_s (kcal mol ⁻¹)	ΔG_s (kcal mol ⁻¹)			
		353 K	373 K	393 K	413 K
<i>n</i> -Hexane	-4.86	-0.27	-0.02	0.25	0.51
<i>n</i> -Heptane	-5.77	-0.83	-0.56	-0.26	0.01
<i>n</i> -Octane	-6.56	-1.37	-1.08	-0.77	-0.49
<i>n</i> -Nonane	-7.45	-1.90	-1.60	-1.25	-0.97
<i>n</i> -Decane	-8.29	-2.43	-2.11	-1.75	-1.45
<i>n</i> -Undecane	-9.10	-2.95	-2.60	-2.23	-1.91
<i>n</i> -Dodecane	-9.95	-3.46	-3.08	-2.70	-2.36
Benzene	-7.38	-1.81	-1.51	-1.18	-0.88
Toluene	-8.13	-2.37	-2.05	-1.70	-1.40
Ethylbenzene	-8.80	-2.84	-2.52	-2.16	-1.84
<i>n</i> -Propylbenzene	-9.42	-3.28	-2.95	-2.57	-2.25
<i>n</i> -Pentylbenzene	-10.68	-4.25	-3.89	-3.51	-3.16
Methyl formate	-6.37	-0.73	-0.44	-0.03	0.19
Methyl acetate	-7.02	-1.20	-0.88	-0.52	-0.22
Methyl butyrate	-8.13	-2.15	-1.81	-1.44	-1.14
Methyl hexanoate	-9.70	-3.22	-2.85	-2.46	-2.12
Methyl heptanoate	-10.37	-3.71	-3.34	-2.95	-2.59
Methyl octanoate	-11.22	-4.23	-3.84	-3.43	-3.04
2-Butanone	-7.23	-1.52	-1.20	-0.86	-0.55
2-Pentanone	-7.79	-1.99	-1.67	-1.32	-1.02
2-Heptanone	-9.39	-3.09	-2.74	-2.36	-2.03
2-Octanone	-10.08	-3.60	-3.25	-2.86	-2.51
Methanol	-7.23	-0.87	-0.51	-0.14	0.21
Ethanol	-8.12	-1.28	-0.89	-0.47	-0.13
<i>n</i> -Propanol	-8.92	-1.94	-1.54	-1.13	-0.76
<i>n</i> -Butanol	-9.76	-2.57	-2.16	-1.73	-1.36
<i>n</i> -Pentanol	-10.60	-3.18	-2.75	-2.31	-1.93
<i>n</i> -Hexanol	-11.54	-3.76	-3.32	-2.85	-2.45

contribution of the methylene group to the parameter, as only methylene groups are present in the molecule. In all other instances, we must admit that the “polar” group at the end of the hydrocarbon chain (phenyl, methyl ester, acetyl or hydroxyl) has an effect on the nearby methylene groups, modifying their contribution to the thermodynamic parameters. This effect is “measured” in a way by the difference between the slopes of the lines corresponding to that homologous series and the *n*-alkanes. It may be observed that the effect diminishes in the order aromatics > esters > ketones > alcohols.

A study of the relationship between the chro-

matographic behaviour of the solutes and the thermodynamic parameters is summarized in Table VI for five substances of similar boiling point. The number of carbon atoms of the hypothetical *n*-alkane (6.35 carbon atoms) was deduced from a plot of the boiling points of *n*-alkanes versus the number of carbon atoms. The other figures in Table VI for that hydrocarbon were deduced by interpolation, using values from Tables II, III and IV.

The hydrocarbon has a retention index that is considerably lower than those of the other substances in Table VI. It may also be observed that the thermodynamic parameters of solution and

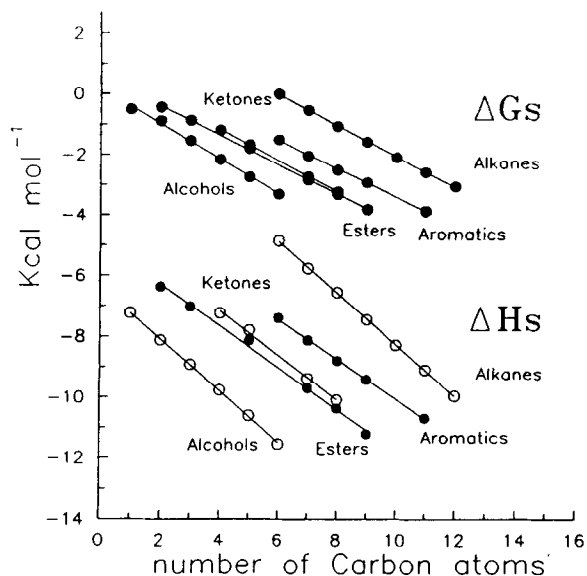


Fig. 3. Dependence of the values of ΔH_s and ΔG_s on the number of carbon atoms in the molecule at 100°C.

TABLE V

SLOPES OF THE PLOTS OF THE THERMODYNAMIC PARAMETERS OF SOLUTION *VERSUS* THE NUMBER OF CARBON ATOMS OF THE ALKYL CHAIN [$s(X)$], AT 100°C, AND DIFFERENCE FROM THE SLOPE OF THE PLOT CORRESPONDING TO *n*-ALKANES [$\Delta s(X)$] (kcal mol⁻¹)

Compounds	$s(\Delta H_s)$	$\Delta s(\Delta H_s)$	$s(\Delta G_s)$	$\Delta s(\Delta G_s)$	$s(T\Delta S_s)$	$\Delta s(T\Delta S_s)$
<i>n</i> -Alkanes	-0.85	—	-0.55	—	-0.33	—
Aromatics	-0.65	0.20	-0.47	0.08	-0.18	0.15
Esters	-0.69	0.16	-0.49	0.06	-0.20	0.14
Ketones	-0.73	0.12	-0.52	0.03	-0.21	0.12
<i>n</i> -Alkanols	-0.85	-0.01	-0.58	-0.03	-0.27	0.06

TABLE VI

DATA FOR FIVE SELECTED SOLUTES AT 373 K

Parameter	<i>n</i> -C _{6,35}	Benzene	2-Butanone	Methyl acetate	Ethanol
Boiling point (°C)	79.6	80.0	79.6	77.1	78.5
Retention index	635	966	907	828	912
ΔH_s (kcal mol ⁻¹)	-5.18	-7.38	-7.23	-7.02	-8.12
ΔH_m (kcal mol ⁻¹)	2.50	0.31	0.67	0.50	1.58
ΔH_v (kcal mol ⁻¹)	7.68	7.69	7.90	7.52	9.70
ΔG_s (kcal mol ⁻¹)	-0.21	-1.51	-1.20	-0.88	-0.89
$\chi_{1,2}^*$	1.16	-0.28	0.00	-0.16	0.23

mixing and the solute–polymer interaction parameter ($\chi_{1,2}^\infty$) are also higher (or less negative) than in any of the other instances. Benzene, 2-butanone and methyl acetate have retention indices that follow the opposite tendency of the thermodynamic parameters and the values of $\chi_{1,2}^\infty$ (the lower the values, the higher is the retention index). Ethanol, however, seems to be an exception. The low value of the enthalpy of solution (the lowest in Table VI) would make us expect a higher retention index for this substance. However, the enthalpy of mixing, the partial molar free energy of solution and the interaction parameter $\chi_{1,2}^\infty$ show that ethanol does not mix with Superox 20M as easily as the other three compounds, probably owing to the high degree of autosolvation that alcohols present (observe also the higher enthalpy of vaporization of ethanol), and therefore its retention volume (and hence the retention index) are

lower than expected. Plots of retention index (from Table VI) versus ΔH_s , ΔH_m , ΔG_s or $\chi_{1,2}^\infty$ show that the best fit is obtained with retention index vs. ΔG_s plots. However, all the thermodynamic parameters listed in Table VI have some effect on the value of the retention index.

Solubility parameters of Superox 20M

The results obtained allow the calculation of the solubility parameter of Superox 20M at the experimental temperatures, as explained in the Appendix. The values are presented in Table VII. There seems to be a linear dependence of δ_2 on the absolute temperature, according to the equation

$$\delta_2 = 11.025 - 0.003T \text{ (cal}^{1/2} \text{ cm}^{-3/2}\text{)}$$

with a correlation coefficient of 0.993. The linear dependence of the solubility parameter of polymers (δ_2) on temperature has been observed in the past [20–22]. If linearity holds for lower temperatures, we may deduce that the value of the solubility parameter of Superox 20M at 64°C (the minimum allowed operating temperature (MAOT) of non-immobilized Superox 20M [3]) should be $10.02 \text{ cal}^{1/2} \text{ cm}^{-3/2}$, and the value at 50°C (the MAOT for immobilized Superox 20M) should be $10.06 \text{ cal}^{1/2} \text{ cm}^{-3/2}$. Extrapolation to room temperature is not allowed owing to the existence of a transition temperature, below which the stationary phase solidifies. If extrapolation is carried out to higher temperatures, the value corresponding to 280°C (the maximum operating temperature for Superox 20M) will be $9.37 \text{ cal}^{1/2} \text{ cm}^{-3/2}$. Solubility parameters of both the stationary phase and the solutes to be separated will probably play an important role in the

TABLE VII
SOLUBILITY PARAMETERS OF SUPEROX 20M

Temperature (K)	δ_2 [(cal cm ⁻³) ^{1/2}]
353	9.956
373	9.900
393	9.820
413	9.780

prediction of the chromatographic performance of the system considered, and also in the prediction of the behaviour of mixed stationary phases (prepared by mixing two or more standard stationary phases).

CONCLUSIONS

It has been shown that both the thermodynamic and the interaction parameters measured by IGC for a number of solutes with respect to a particular stationary phase are indicative of the chromatographic behaviour that may be expected from the solute–stationary phase system.

SYMBOLS

a_1	activity of the solute in the stationary phase
B_{11}	second virial coefficient of the solute at the column temperature T
F_0	carrier gas flow-rate, as measured at the column outlet, at ambient temperature (T_0) and atmospheric pressure (p_0)
j	James and Martin's correction factor
M_1	molecular mass of the solute
p_0	pressure of the carrier gas in the flow meter, normally atmospheric pressure
P_1^0	saturated vapour pressure of the solute at the column temperature T
p_w	vapour pressure of the water at the flow meter temperature (T_0)
R	gas constant
T_0	absolute temperature of the carrier gas in the flow meter
T	absolute temperature of the column
t'_R	adjusted retention time of the solute
V_1^0, V_2^0	molar volumes of the solute and the stationary phase at the column temperature. The ratio V_1^0/V_2^0 has been taken as 0
V_g	the specific retention volume of the solute
w_1	mass fraction of the solute in the polymer
w_2	mass of the stationary phase in the column

Greek letters

- δ_1, δ_2 solubility parameters of the solute (δ_1) and the stationary phase (δ_2)
 ρ_1, ρ_2 densities of the solute and the polymer
 $\chi_{1,2}^\infty$ Flory–Huggins solute–polymer interaction parameter
 χ_s^∞ entropic component of the Flory–Huggins solute–polymer interaction parameter
 Ω_1^∞ activity coefficient of the solute at infinite dilution, based on mass fraction.

Subscripts

Subscript 1 refers to the solute and 2 to the stationary phase.

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APPENDIX

Specific retention volumes:

$$V_g = \frac{F_{0j}}{w_2} \cdot t'_R \cdot \frac{273.15}{T_0} \cdot \frac{(p_0 - p_w)}{p_0} \quad (\text{A1})$$

Activity coefficients at infinite dilution:

$$\ln \Omega_1^\infty \equiv \ln \left(\frac{a_1}{w_1} \right) = \ln \left[\frac{273.15R}{P_1^0 V_g M_1} - \frac{P_1^0}{RT} (B_{11} - V_1^0) \right] \quad (\text{A2})$$

Partial molar enthalpy of solution:

$$\Delta H_s = -R \cdot \frac{\partial(\ln V_g)}{\partial(1/T)} \quad (\text{A3})$$

Partial molar enthalpy of mixing of the solute at infinite dilution:

$$\Delta H_m^\infty = R \cdot \frac{\partial(\ln \Omega_1^\infty)}{\partial(1/T)} \quad (\text{A4})$$

Molar enthalpy of vaporization of the solutes:

$$\Delta H_v = \Delta H_m - \Delta H_s \quad (\text{A5})$$

Partial molar free energy of sorption:

$$\Delta G_s = -RT \ln (M_1 V_g / 273.15R) \quad (\text{A6})$$

Relationship between activity coefficients at infinite dilution and partial molar free energy of mixing:

$$\Delta G_m = RT \ln \Omega_1^\infty \quad (\text{A7})$$

Solubility parameters of the solutes (δ_1):

$$\delta_1 = [(\Delta H_v - RT)/V_1^0]^{1/2} \quad (\text{A8})$$

Flory–Huggins interaction parameter:

$$\chi_{1,2}^\infty = \ln \Omega_1^\infty + \ln \left(\frac{\rho_1}{\rho_2} \right) - \left(1 - \frac{V_1^0}{V_2^0} \right) \quad (\text{A9})$$

Solubility parameters of the polymer (δ_2): deduced from a plot of the right-hand side of eqn. A10 versus δ_1 :

$$\frac{\delta_1^2}{RT} - \frac{\chi_{1,2}^\infty}{V_1^0} = \frac{2\delta_2}{RT} \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_1^0} \right) \quad (\text{A10})$$

REFERENCES

- 1 T.J. Stark, P.A. Larson and R. Dandeneau, *J. Chromatogr.*, 279 (1983) 31.
- 2 P. Sandra, F. David, M. Proot, G. Diricks, M. Verstape and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 782.
- 3 E. Fernández-Sánchez, A. Fernández-Torres, J.A. García-Domínguez and M.D. Salvador-Moya, *J. Chromatogr.*, 556 (1991) 485.
- 4 A.V. Kiselev, *Adv. Chromatogr.*, 4 (1967) 113.
- 5 O. Smidsrod and J.E. Guillet, *Macromolecules*, 2 (1976) 272.
- 6 E. Fernández-Sánchez, A. Fernández-Torres, J.A. García-Domínguez, J. García-Muñoz, V. Menéndez, M.J. Molera and J.M. Santiuste, *J. Chromatogr.*, 410 (1987) 13.
- 7 D. Patterson, Y.B. Tewari, H.P. Schreiber and J.E. Guillet, *Macromolecules*, 4 (1971) 356.
- 8 G.J. Price, J.E. Guillet and J.H. Purnell, *J. Chromatogr.*, 369 (1986) 273.
- 9 R.C. Wilhoit and B.J. Zwolinski, *Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds*, Thermodynamics Research Centre, Texas A&M University, College Station, TX, 1971.
- 10 T. Boublík, V. Fried and E. Hála, *The Vapour Pressures of Pure Substances*, Elsevier, Amsterdam, 1975.
- 11 J.P. O'Connell and J.M. Pruasnitz, *Ind. Eng. Chem., Process Des. Dev.*, 6 (1976) 245.

- 12 J.H. Dymond and E.B. Smith, *The Virial Coefficients of Pure Gases and Mixtures. A Critical Compilation*, Clarendon Press, Oxford, 1980.
- 13 National Research Council of the USA, *International Critical Tables of Numerical Data. Physics, Chemistry and Technology*, Vol. III, McGraw-Hill, New York, 1928.
- 14 *TRC Thermodynamic Tables*, Thermodynamics Research Centre, Texas Engineering Experiment Station, Texas A & M University, College Station, TX.
- 15 G. DiPaola-Baranyi and J.G. Guillet, *Macromolecules*, 11 (1978) 228.
- 16 M.R. Becerra, E. Fernández-Sánchez, A. Fernández-Torres, J.A. García-Domínguez and J.M. Santiuste, *J. Chromatogr.*, 547 (1991) 269.
- 17 P.I. Freeman and J.S. Rowlinson, *Polymer*, 1 (1960) 20.
- 18 T. Bohossian, G. Charlet and G. Delmas, *Polymer*, 30 (1989) 1695.
- 19 J.I. Iribarren, M. Iriarte, C. Uriarte and J.J. Iruin, *J. Appl. Polym. Sci.*, 37 (1989) 3459.
- 20 M.J. Fernández-Berridi, G. Martín Guzmán, J.J. Iruin and M.E. Elorza, *Polymer*, 24 (1983) 417.
- 21 O. Humpa, J. Uhdeová and M. Roth, *Macromolecules*, 24 (1991) 2514.
- 22 M.R. Becerra, E. Fernández-Sánchez, A. Fernández-Torres, J.A. García-Domínguez and J.M. Santiuste, *Macromolecules*, 25 (1992) 4665.