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SOLUBILITY PARAMETERS OF GAS CHROMATOGRAPHIC MIXED STATIONARY PHASES

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SUMMARY

Gas chromatography was used to measure activity coefficients, Ω^∞ , partial molar free energies of mixing, $\Delta\bar{G}_1^\infty$, Flory–Huggins interaction parameters, χ^∞ , and its enthalpic and entropic contributions, of a number of solutes on five single and fourteen mixed stationary phases at 120°C. Solubility parameters of the stationary phases, δ_2 , were deduced by the method of DiPaola-Baranyi and Guillet for the different solute–stationary phase combinations. The polymer–polymer interaction parameter, $\chi'_{2,3}$, was also calculated for the various mixed systems.

INTRODUCTION

One of the problems with which the chromatographer is faced is to find a column with an appropriate selectivity for separating the components of the mixture to be analysed. Basically there are three procedures that can be used to modify the selectivity of the chromatographic column if no commercial stationary phase that can perform the separation is available: to synthesize new stationary phases with functional groups capable of producing the desired effect, to use columns coupled in series or to use mixtures of stationary phases in the same chromatographic column. Mixed stationary phases are particularly useful in connection with work with open-tubular columns, bearing in mind that there are few stationary phases with the necessary characteristics of stability, wettability, etc., which are needed if a long-lasting and efficient column is to be obtained. Some workers think that mixed stationary phase behaviour might easily be predicted from the characteristics of the liquids that are mixed^{1–5}. Others, however consider that there is great uncertainty in this matter^{1,6–12}. In our opinion, any attempt to predict the chromatographic behaviour of mixed stationary phases must be based on a good knowledge of their thermodynamic properties.

The most popular stationary phases in gas chromatography (GC) are polymers of high molecular weight, often unknown. Thermodynamic characterization of

polymers is possible with the use of GC¹³ and has been greatly facilitated after the work of Patterson *et al.*¹⁴, who showed that this characterization is possible with the molecular weight of the polymer being ignored. Many papers based on these ideas have been published^{15–22}. One such important thermodynamic parameter is the solubility parameter of the stationary phase. Many physical properties are related to this parameter, and it is a general impression that its knowledge may lead to approximate estimates of the chromatographic behaviour of mixed stationary phases.

In this work, solubility parameters at 120°C were calculated for three sets of stationary phases using partial molar free energies of mixing following the procedure described by Price *et al.*²⁰. The Flory–Huggins interaction parameter χ^∞ was also calculated, as together with its enthalpic and entropic contributions, χ_H^∞ and χ_S^∞ . The polymer–polymer interaction parameter $\chi_{2,3}$ was evaluated for different mixed stationary phases.

EXPERIMENTAL

The apparatus, stationary phases, columns and chromatographic procedures have been described previously¹². The same mixtures of OV-101–OV-25, OV-101–Carbowax 20M and OV-225–SP-2340 were used.

RESULTS AND DISCUSSION

Activity coefficients

Activity coefficients at infinite dilution based on the weight fraction, Ω_1^∞ , were calculated^{14,20} using the equation

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

which has the advantage of ignoring the molecular weight of the polymer. In this equation, a_1 and w_1 are the activity and weight fraction of the solute in the polymer, respectively, and M_1 , P_1^0 , B_{11} , V_1^0 and V_g^0 are the molecular weight, saturated vapour pressure, second virial coefficient, molar volume and specific retention volume of the solute at the column temperature T , respectively.

Vapour pressures were deduced using Antoine coefficients from various sources^{23,24}. The second virial coefficients of *n*-nonane, *n*-decane and *n*-dodecane were calculated by the procedure of O'Connell and Prausnitz²⁵; for other solutes, values were extrapolated from literature values corresponding to other temperatures²⁶. Densities at 393 K were calculated according to the pertinent equation²⁷. No data were found for six of the ten solutes used by McReynolds to characterize stationary phases²⁸. Molar volumes were calculated from molecular weight and density values. Molar enthalpies of vaporization were deduced from data published at various temperatures^{7,23,29,30}. Values at 393 K are shown in Table I.

Activity coefficients of the various solutes in the different stationary phases (single and mixed) found according to eqn. 1 are shown in Table II.

TABLE I
PHYSICAL PROPERTIES OF SOLUTES AT 393 K

| <i>Solute</i> | P_1^0 (Torr) | $-B_{11}$ (l mol ⁻¹) | ρ_1 (g ml ⁻¹) | V_1^0 (ml mol ⁻¹) | ΔH_v (cal mol ⁻¹) | δ_1 [(cal ml ⁻¹) ^{1/2}] |
|-----------------------|-------------------|-------------------------------------|-----------------------------------|------------------------------------|--|---|
| <i>n</i> -Hexane | 2984.49 | 0.895 | 0.5450 | 158.13 | 6125 | 5.81 |
| <i>n</i> -Heptane | 1373.88 | 1.285 | 0.5924 | 169.16 | 7263 | 6.19 |
| <i>n</i> -Octane | 647.74 | 1.785 | 0.6170 | 185.14 | 8327 | 6.38 |
| <i>n</i> -Nonane | 310.89 | 2.439 | 0.6368 | 201.43 | 9465 | 6.57 |
| <i>n</i> -Decane | 151.27 | 3.106 | 0.6536 | 217.70 | 10610 | 6.72 |
| <i>n</i> -Undecane | 74.34 | 3.935 | 0.6660 | 234.71 | 11750 | 6.84 |
| <i>n</i> -Dodecane | 36.89 | 5.102 | 0.6761 | 251.96 | 12650 | 6.86 |
| <i>n</i> -Tridecane | 18.25 | 6.362 | 0.6861 | 268.72 | 13750 | 6.95 |
| <i>n</i> -Tetradecane | 9.17 | | 0.6940 | 285.88 | 14800 | 7.00 |
| <i>n</i> -Pentadecane | 4.59 | | 0.6988 | 303.98 | 16010 | 7.08 |
| Benzene | 2249.31 | 0.74 | 0.7681 | 101.71 | 6950 | 7.79 |
| 1-Butanol | 823.27 | 1.055 | 0.7354 | 100.79 | 10255 | 9.69 |
| 2-Pentanone | 1259.22 | 1.29 | 0.7043 | 122.30 | 7720 | 7.53 |
| Pyridine | 870.96 | 0.97 | 0.8873 | 89.15 | 8323 | 9.21 |

The solute-polymer interaction parameter

The Flory-Huggins solute-polymer interaction parameter may be calculated from activity coefficients^{14,20,*}. In the case of pure solvents the equation is

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

where ρ_1 and ρ_2 are the densities of the solute (1) and the polymer (2) and V_1^0 and V_2^0 the corresponding molar volumes. When the polymer is in fact a mixture of two polymers (mixed stationary phases) the equation becomes^{15,31,32}

$$\chi_{1,(2,3)}^\infty = \ln \Omega_1^\infty + \ln \frac{\rho_1}{\rho_m} - \left(1 - \frac{V_1^0}{V_2^0}\right) \varphi_2 - \left(1 - \frac{V_1^0}{V_3^0}\right) \varphi_3 \quad (3)$$

where ρ_m is the density of the mixture of polymers, V_2^0 and V_3^0 are the molar volumes of the two polymers and φ_2 and φ_3 the corresponding volume fractions in the mixture. As V_2^0 and V_3^0 are much larger than V_1^0 , the use of both equations is greatly simplified.

Values of the solute-polymer interaction parameters corresponding to the different solutes in the various stationary phases are presented in Table III. Comparing values of χ^∞ corresponding to *n*-alkanes with the corresponding values of the partition coefficients (K_R) for the same mixtures¹², it may be observed that even in the set of mixtures where values of K_R may be said to show a "quasi"-linear behaviour with mixture composition (OV-101-OV-25), the same type of behaviour may not be observed in the case of the χ^∞ values.

* There is a transcription error in eqn. 3 in ref. 20. The authors used the correct equation in their calculations.

TABLE II

ACTIVITY COEFFICIENTS AT 393 K ON DIFFERENT STATIONARY PHASES

Mixtures of OV-101-OV-25

| <i>Compound</i> | φ_{OV-101} | | | | | | | |
|--------------------|--------------------|--------------|--------------|--------------|--------------|--------------|--------------|----------|
| | <i>1</i> | <i>0.831</i> | <i>0.589</i> | <i>0.410</i> | <i>0.397</i> | <i>0.268</i> | <i>0.084</i> | <i>0</i> |
| <i>n</i> -Hexane | 4.70 | 5.18 | 6.30 | 7.70 | 7.70 | 8.40 | 10.90 | 11.57 |
| <i>n</i> -Heptane | 5.10 | 5.63 | 6.85 | 8.39 | 8.37 | 9.17 | 11.89 | 12.68 |
| <i>n</i> -Octane | 5.43 | 5.95 | 7.35 | 9.02 | 8.99 | 9.86 | 12.85 | 13.73 |
| <i>n</i> -Nonane | 5.76 | 6.32 | 7.78 | 9.54 | 9.56 | 10.52 | 13.71 | 14.68 |
| <i>n</i> -Decane | 6.05 | 6.67 | 8.20 | 10.11 | 10.12 | 11.17 | 14.54 | 15.75 |
| <i>n</i> -Undecane | 6.38 | 7.01 | 8.66 | 10.72 | 10.68 | 11.82 | 15.41 | 16.74 |
| <i>n</i> -Dodecane | 6.70 | 7.34 | 9.13 | 11.31 | 11.27 | 12.49 | 16.26 | 17.77 |
| Benzene | 4.69 | 4.62 | 4.63 | 4.74 | 4.85 | 4.82 | 5.02 | 4.85 |
| 1-Butanol | 14.62 | 14.48 | 15.48 | 16.06 | 16.65 | 16.64 | 18.09 | 17.14 |
| 2-Pentanone | 7.04 | 6.64 | 6.96 | 7.14 | 7.45 | 7.00 | 7.52 | 7.33 |
| Pyridine | 6.85 | 7.18 | 5.81 | 5.56 | 6.03 | 5.68 | 5.52 | 5.24 |

Mixtures of OV-101-Carbowax 20M

| <i>Compound</i> | φ_{OV-101} | | | | |
|--------------------|--------------------|--------------|--------------|--------------|----------|
| | <i>1</i> | <i>0.757</i> | <i>0.509</i> | <i>0.257</i> | <i>0</i> |
| <i>n</i> -Hexane | 4.70 | 6.54 | 9.61 | 14.95 | 25.77 |
| <i>n</i> -Heptane | 5.10 | 7.11 | 10.53 | 16.61 | 31.01 |
| <i>n</i> -Octane | 5.43 | 7.68 | 11.29 | 18.06 | 34.93 |
| <i>n</i> -Nonane | 5.76 | 8.18 | 12.15 | 19.57 | 40.09 |
| <i>n</i> -Decane | 6.05 | 8.68 | 13.02 | 21.08 | 45.48 |
| <i>n</i> -Undecane | 6.38 | 9.17 | 13.85 | 22.81 | 51.91 |
| <i>n</i> -Dodecane | 6.70 | 9.69 | 14.68 | 24.51 | 58.68 |
| Benzene | 4.69 | 5.54 | 5.69 | 6.05 | 5.58 |
| 1-Butanol | 14.62 | 12.94 | 9.74 | 7.83 | 6.54 |
| 2-Pentanone | 7.04 | 8.24 | 7.92 | 7.53 | 6.68 |

Mixtures of OV-225-SP-2340

| <i>Compound</i> | φ_{OV-225} | | | | | | |
|------------------------|--------------------|--------------|--------------|--------------|--------------|--------------|----------|
| | <i>1</i> | <i>0.781</i> | <i>0.508</i> | <i>0.363</i> | <i>0.327</i> | <i>0.103</i> | <i>0</i> |
| <i>n</i> -Hexane | 11.46 | 12.61 | 15.94 | 24.85 | 25.28 | 41.30 | 59.95 |
| <i>n</i> -Heptane | 13.03 | 14.35 | 18.45 | 29.06 | 29.29 | 50.10 | 74.39 |
| <i>n</i> -Octane | 14.52 | 15.99 | 21.22 | 33.46 | 33.96 | 60.11 | 91.68 |
| <i>n</i> -Nonane | 16.09 | 17.90 | 23.87 | 38.10 | 39.19 | 71.59 | 110.99 |
| <i>n</i> -Decane | 17.71 | 19.94 | 26.91 | 43.69 | 44.70 | 85.44 | 134.53 |
| <i>n</i> -Undecane | 19.51 | 21.87 | 30.08 | 48.99 | 50.87 | 100.69 | 162.91 |
| <i>n</i> -Dodecane | 21.37 | 24.09 | 33.67 | 55.88 | 57.81 | 117.12 | 196.58 |
| <i>n</i> -Tridecane | 23.56 | 26.69 | 37.89 | 63.51 | 65.77 | 140.88 | 237.91 |
| <i>n</i> -Tetradecane* | 25.71 | 29.24 | 42.29 | 71.50 | 74.42 | 166.16 | 285.56 |
| <i>n</i> -Pentadecane* | 28.53 | 32.59 | 47.87 | 81.77 | 85.51 | 198.80 | 346.19 |
| Benzene | 4.12 | 4.08 | 4.01 | 5.20 | 4.50 | 5.68 | 6.98 |
| 1-Butanol | 8.00 | 7.35 | 6.59 | 7.95 | 6.97 | 7.91 | 9.69 |
| 2-Pentanone | 4.23 | 4.18 | 4.10 | 6.19 | 4.57 | 6.60 | 8.22 |
| Pyridine | 3.72 | 3.37 | 3.02 | 3.80 | 3.18 | 3.58 | 4.37 |

* Values calculated without second virial coefficient correction.

TABLE III

SOLUTE-POLYMER INTERACTION PARAMETERS (χ^{∞}) AT 393 K*Mixtures of OV-101-OV-25*

| Compound | φ_{OV-101} | | | | | | | |
|--------------------|--------------------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 0.831 | 0.589 | 0.410 | 0.397 | 0.268 | 0.084 | 0 |
| <i>n</i> -Hexane | 0.044 | 0.102 | 0.248 | 0.412 | 0.409 | 0.471 | 0.696 | 0.741 |
| <i>n</i> -Heptane | 0.208 | 0.269 | 0.415 | 0.581 | 0.577 | 0.643 | 0.867 | 0.915 |
| <i>n</i> -Octane | 0.313 | 0.365 | 0.526 | 0.694 | 0.688 | 0.755 | 0.985 | 1.036 |
| <i>n</i> -Nonane | 0.401 | 0.458 | 0.614 | 0.782 | 0.781 | 0.852 | 1.082 | 1.134 |
| <i>n</i> -Decane | 0.477 | 0.538 | 0.693 | 0.866 | 0.864 | 0.938 | 1.167 | 1.231 |
| <i>n</i> -Undecane | 0.550 | 0.606 | 0.766 | 0.943 | 0.937 | 1.014 | 1.243 | 1.310 |
| <i>n</i> -Dodecane | 0.613 | 0.666 | 0.834 | 1.012 | 1.006 | 1.083 | 1.312 | 1.386 |
| Benzene | 0.385 | 0.332 | 0.282 | 0.269 | 0.290 | 0.258 | 0.263 | 0.214 |
| 1-Butanol | 1.478 | 1.430 | 1.446 | 1.446 | 1.480 | 1.454 | 1.503 | 1.433 |
| 2-Pentanone | 0.704 | 0.607 | 0.604 | 0.592 | 0.633 | 0.546 | 0.582 | 0.540 |
| Pyridine | 0.908 | 0.917 | 0.654 | 0.574 | 0.652 | 0.567 | 0.504 | 0.436 |

Mixtures of OV-101-Carbowax 20M

| Compound | φ_{OV-101} | | | | |
|--------------------|--------------------|-------|-------|-------|-------|
| | 1 | 0.757 | 0.509 | 0.257 | 0 |
| <i>n</i> -Hexane | 0.044 | 0.321 | 0.655 | 1.048 | 1.544 |
| <i>n</i> -Heptane | 0.208 | 0.487 | 0.829 | 1.237 | 1.813 |
| <i>n</i> -Octane | 0.312 | 0.606 | 0.940 | 1.361 | 1.973 |
| <i>n</i> -Nonane | 0.401 | 0.700 | 1.045 | 1.473 | 2.142 |
| <i>n</i> -Decane | 0.476 | 0.786 | 1.141 | 1.573 | 2.294 |
| <i>n</i> -Undecane | 0.550 | 0.860 | 1.221 | 1.671 | 2.445 |
| <i>n</i> -Dodecane | 0.613 | 0.930 | 1.294 | 1.758 | 2.583 |
| Benzene | 0.385 | 0.498 | 0.474 | 0.487 | 0.358 |
| 1-Butanol | 1.478 | 1.303 | 0.968 | 0.700 | 0.472 |
| 2-Pentanone | 0.704 | 0.809 | 0.718 | 0.618 | 0.451 |

Mixtures of OV-225-SP-2340

| Compound | φ_{OV-225} | | | | | | |
|------------------------|--------------------|-------|--------|-------|--------|-------|-------|
| | 1 | 0.781 | 0.508 | 0.363 | 0.327 | 0.103 | 0 |
| <i>n</i> -Hexane | 0.776 | 0.865 | 1.089 | 1.529 | 1.544 | 2.028 | 2.397 |
| <i>n</i> -Heptane | 0.988 | 1.077 | 1.319 | 1.769 | 1.775 | 2.304 | 2.696 |
| <i>n</i> -Octane | 1.137 | 1.226 | 1.499 | 1.950 | 1.964 | 2.527 | 2.946 |
| <i>n</i> -Nonane | 1.272 | 1.370 | 1.649 | 2.112 | 2.139 | 2.734 | 3.169 |
| <i>n</i> -Decane | 1.394 | 1.504 | 1.795 | 2.275 | 2.296 | 2.937 | 3.387 |
| <i>n</i> -Undecane | 1.509 | 1.615 | 1.925 | 2.408 | 2.444 | 3.120 | 3.597 |
| <i>n</i> -Dodecane | 1.615 | 1.727 | 2.053 | 2.555 | 2.587 | 3.286 | 3.800 |
| <i>n</i> -Tridecane | 1.727 | 1.844 | 2.186 | 2.697 | 2.731 | 3.485 | 4.006 |
| <i>n</i> -Tetradecane* | 1.826 | 1.947 | 2.307 | 2.827 | 2.866 | 3.662 | 4.200 |
| <i>n</i> -Pentadecane* | 1.937 | 2.063 | 2.438 | 2.968 | 3.012 | 3.848 | 4.399 |
| Benzene | 0.096 | 0.080 | 0.053 | 0.307 | 0.163 | 0.387 | 0.590 |
| 1-Butanol | 0.716 | 0.624 | 0.507 | 0.689 | 0.556 | 0.674 | 0.874 |
| 2-Pentanone | 0.035 | 0.016 | -0.013 | 0.395 | 0.089 | 0.451 | 0.666 |
| Pyridine | 0.137 | 0.031 | -0.086 | 0.139 | -0.040 | 0.069 | 0.265 |

* Values calculated without second virial coefficient correction.

The solubility parameter

According to the Hildebrand–Scatchard theory, the solubility parameter of a substance is defined as the square root of the cohesive energy density, defined as the ratio of the energy of vaporization to the molar volume, both at the same temperature:

$$\delta \equiv (\Delta E_v/V_1^0)^{\frac{1}{2}} \quad (4)$$

When two liquids are mixed the difference between the two solubility parameters (δ_1 and δ_2) is given²⁹ by the expression

$$\delta_1 - \delta_2 = (\Delta E_m/\varphi_1\varphi_2V_m)^{\frac{1}{2}} \quad (5)$$

where ΔE_m is the energy of mixing of the two liquids at constant volume, φ_1 and φ_2 are the volume fractions of the components and V_m is the average molar volume based on molar fraction. Solubility parameters have been useful in describing the thermodynamic properties of dilute solutions and have been shown to be related to a number of physical properties of polymers such as surface tension, wettability and glass transition temperature. Solubility parameters of substances at a given temperature T may be calculated with the expression

$$\delta_1 = \left(\frac{\Delta H_v - RT}{V_1^0} \right)^{\frac{1}{2}} \quad (6)$$

where ΔH_v is the molar enthalpy of vaporization of the substance at temperature T and R is the universal gas constant. In this way δ values at 120°C were calculated for the various solutes used in this work and are shown in the last column in Table I.

Polymers have very low vapour pressures and therefore it is not possible to calculate δ_2 directly using eqn. 6. However, Guillet¹³ has shown that gas–liquid chromatography is ideal for determining this parameter at a given temperature. Two methods²⁹ were used in this work to calculate values of δ_2 for the different mixtures of the three sets of stationary phases studied. One is based on the molar partial free energy of mixing, $\Delta \bar{G}_1^\infty$, and the other on the Flory–Huggins interaction parameter, χ^∞ . Assuming zero volume change on mixing, eqn. 5 may be written in terms of the partial molar heat of mixing ($\Delta \bar{H}_1^\infty$)²⁹:

$$\Delta \bar{H}_1^\infty = V_1^0 (\delta_1 - \delta_2)^2 \quad (7)$$

At constant pressure, it is the free energy and not the heat of mixing that is given directly by the solubility parameters^{29,33}, and eqn. 7 therefore becomes

$$\Delta \bar{G}_1^\infty = V_1^0 (\delta_1 - \delta_2)^2 \quad (8)$$

The partial molar free energy of mixing was evaluated²⁹ from the expression

$$\Delta \bar{G}_1 = RT \ln \Omega_1^\infty \quad (9)$$

TABLE IV

PARTIAL MOLAR FREE ENERGIES OF MIXING (ΔG_1^∞ , cal mol⁻¹) AT 393 K*Mixtures of OV-101-OV-25*

| Compound | φ_{OV-101} | | | | | | | |
|--------------------|--------------------|-------|-------|-------|-------|-------|-------|------|
| | 1 | 0.831 | 0.589 | 0.410 | 0.397 | 0.268 | 0.084 | 0 |
| <i>n</i> -Hexane | 1209 | 1284 | 1438 | 1595 | 1595 | 1663 | 1866 | 1913 |
| <i>n</i> -Heptane | 1273 | 1350 | 1503 | 1662 | 1660 | 1732 | 1934 | 1984 |
| <i>n</i> -Octane | 1323 | 1393 | 1558 | 1718 | 1716 | 1788 | 1995 | 2047 |
| <i>n</i> -Nonane | 1367 | 1441 | 1602 | 1762 | 1764 | 1839 | 2046 | 2099 |
| <i>n</i> -Decane | 1406 | 1483 | 1644 | 1807 | 1808 | 1885 | 2091 | 2154 |
| <i>n</i> -Undecane | 1448 | 1521 | 1686 | 1853 | 1850 | 1930 | 2137 | 2201 |
| <i>n</i> -Dodecane | 1486 | 1557 | 1728 | 1895 | 1892 | 1973 | 2179 | 2248 |
| Benzene | 1208 | 1196 | 1197 | 1215 | 1234 | 1228 | 1260 | 1234 |
| 1-Butanol | 2096 | 2088 | 2140 | 2169 | 2197 | 2197 | 2262 | 2220 |
| 2-Pentanone | 1525 | 1479 | 1516 | 1535 | 1569 | 1521 | 1576 | 1556 |
| Pyridine | 1504 | 1540 | 1375 | 1341 | 1404 | 1357 | 1335 | 1294 |

Mixtures of OV-101-Carbowax 20M

| Compound | φ_{OV-101} | | | | |
|--------------------|--------------------|-------|-------|-------|------|
| | 1 | 0.757 | 0.509 | 0.257 | 0 |
| <i>n</i> -Hexane | 1209 | 1467 | 1768 | 2113 | 2538 |
| <i>n</i> -Heptane | 1273 | 1532 | 1839 | 2195 | 2683 |
| <i>n</i> -Octane | 1322 | 1593 | 1894 | 2261 | 2776 |
| <i>n</i> -Nonane | 1367 | 1642 | 1951 | 2323 | 2884 |
| <i>n</i> -Decane | 1406 | 1689 | 2005 | 2382 | 2982 |
| <i>n</i> -Undecane | 1448 | 1732 | 2053 | 2443 | 3086 |
| <i>n</i> -Dodecane | 1486 | 1775 | 2099 | 2499 | 3181 |
| Benzene | 1208 | 1338 | 1358 | 1407 | 1344 |
| 1-Butanol | 2096 | 2000 | 1779 | 1608 | 1467 |
| 2-Pentanone | 1525 | 1648 | 1617 | 1577 | 1484 |

Mixtures of OV-225-SP-2340

| Compound | φ_{OV-225} | | | | | | |
|------------------------|--------------------|-------|-------|-------|-------|-------|------|
| | 1 | 0.781 | 0.508 | 0.363 | 0.327 | 0.103 | 0 |
| <i>n</i> -Hexane | 1906 | 1980 | 2163 | 2510 | 2523 | 2907 | 3198 |
| <i>n</i> -Heptane | 2006 | 2081 | 2277 | 2632 | 2638 | 3058 | 3367 |
| <i>n</i> -Octane | 2090 | 2166 | 2387 | 2742 | 2754 | 3200 | 3530 |
| <i>n</i> -Nonane | 2171 | 2254 | 2479 | 2844 | 2866 | 3337 | 3679 |
| <i>n</i> -Decane | 2246 | 2338 | 2572 | 2951 | 2969 | 3475 | 3830 |
| <i>n</i> -Undecane | 2321 | 2410 | 2659 | 3040 | 3070 | 3603 | 3979 |
| <i>n</i> -Dodecane | 2392 | 2486 | 2747 | 3143 | 3170 | 3721 | 4126 |
| <i>n</i> -Tridecane | 2469 | 2566 | 2840 | 3243 | 3270 | 3866 | 4275 |
| <i>n</i> -Tetradecane* | 2537 | 2637 | 2926 | 3336 | 3367 | 3995 | 4418 |
| <i>n</i> -Pentadecane* | 2618 | 2722 | 3022 | 3441 | 3476 | 4135 | 4568 |
| Benzene | 1106 | 1099 | 1085 | 1287 | 1176 | 1357 | 1518 |
| 1-Butanol | 1624 | 1558 | 1474 | 1620 | 1517 | 1615 | 1774 |
| 2-Pentanone | 1126 | 1117 | 1102 | 1424 | 1186 | 1475 | 1645 |
| Pyridine | 1025 | 948 | 864 | 1044 | 905 | 996 | 1152 |

* Values calculated without second virial coefficient correction.

Values of $\Delta\bar{G}_1^\infty$ for the different solutes and mixtures are presented in Table IV. Rearranging eqn. 8, values of $[\delta_1^2 - (\Delta\bar{G}_1^\infty/V_1^0)]$ may be plotted *versus* δ_1 . The slope of the straight line obtained is twice the solubility parameter of the polymer, δ_2 .

A second method, based on the procedure developed by Guillet and co-workers^{20,29}, was used to evaluate solubility parameters of the various stationary phases at 120°C. Combining the Flory treatment³⁴ with Hildebrand-Scatchard theory and bearing in mind that the interaction parameter has free energy characteristics with enthalpic (χ_H^∞) and entropic (χ_S^∞) contribution terms, the following expression may be written²⁰:

$$\chi^\infty = \frac{V_1^0 (\delta_1 - \delta_2)^2}{RT} + \chi_S^\infty \quad (10)$$

This equation may be rewritten as

$$\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V_1^0} = \frac{2\delta_2}{RT} \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S^\infty}{V_1^0} \right) \quad (11)$$

Representation of the term in the left-hand side of eqn. 11 *versus* δ_1 will yield a straight line whose slope will allow an estimation of δ_2 . Fig. 1 shows such plots for a few mixed stationary phases. In all instances (20 stationary phases) an excellent linear correlation was found (regression coefficients > 0.99). Values of the solubility parameter of the stationary phases at 120°C calculated according to eqns. 8 and 11 are given in Table V for the different mixtures investigated. The value obtained with eqn. 11 is slightly higher than that corresponding to eqn. 8 in all instances. Representation of the rearranged eqn. 8 allows the estimation of the solubility parameter of the stationary phase from the intercept of the straight line. The values so deduced are much closer to those obtained with eqn. 11. Comparing their results with literature values,

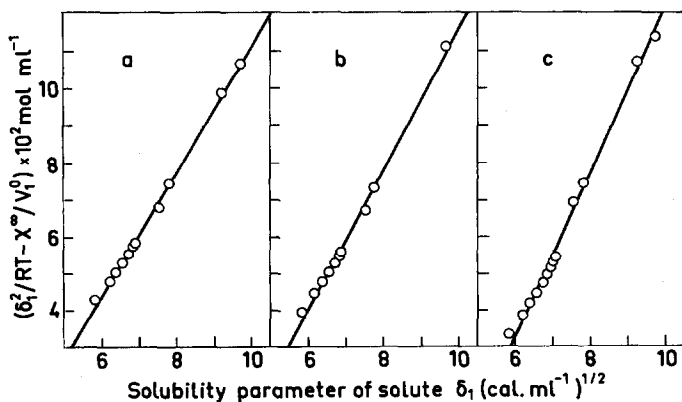


Fig. 1. Estimation of solubility parameter (δ_2) of mixed stationary phases from χ (eqn. 11). (a) OV-101/OV-25 = 0.831:0.169; (b) OV-101/Carbowax 20M = 0.509:0.491; (c) OV-225/SP-2340 = 0.363:0.637.

DiPaola-Baranyi and Guillet²⁹ arrived at the conclusion that in their case the procedure based on χ gave better results. In the present instance there are no reported values to compare at 120°C, so we cannot say that one of the methods is better than the other. In any event, the values are sufficiently close to each other to make us think that the values are not far from correct.

Fig. 2 shows the variation of the solubility parameter δ_2 of the various stationary phases in the three systems studied, as deduced with the help of eqn. 11. For curves a and b the values corresponding to a volume fraction of 1 (polymer OV-101 in both instances) are slightly different because the number of solutes used to calculate it is not the same (see Tables III and IV). The general shape of the curves resembles that of the partition coefficients of *n*-alkanes corresponding to the same mixed systems^{1,2}. Except perhaps for curve a, it may be said that solubility parameters of mixtures of polymers may not be deduced as a linear combination of those corresponding to the pure components.

Enthalpic and entropic contributions to the solute-polymer interaction parameter

Once the solubility parameter of the stationary phase has been found, eqn. 10 may be used to calculate the enthalpic and entropic contributions to the solute-polymer interaction parameter ($\chi^\infty = \chi_H^\infty + \chi_S^\infty$). χ_S^∞ can also be found from the intercept of the straight line defined by eqn. 11. Table VI presents the values obtained for χ_H^∞ for the various solutes on the different stationary phases. The values of χ_S^∞ deduced from the representation of eqn. 11 (Fig. 1) are given in Table VII. The value of χ_S^∞ obtained by difference between the values shown in Tables III and VI is generally higher than that obtained from eqn. 11 (Table VII). As an example, Table VIII shows the differences corresponding to one mixed stationary phase (OV-101/OV-25 = 0.397/0.603). All three systems of mixed stationary phases show similar

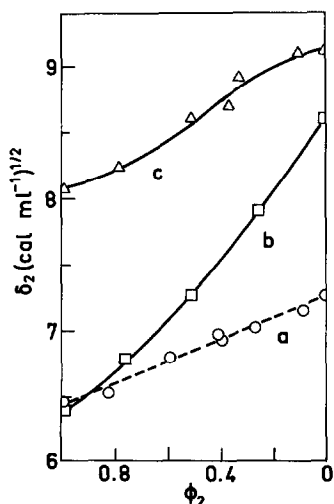


Fig. 2. Variation of the solubility parameter δ_2 (eqn. 11) of the stationary phase with mixture composition. (a) OV-101-OV-25; (b) OV-101-Carbowax 20M; (c) OV-225-SP-2340. ϕ_2 represents the volume fraction of the first polymer in each instance.

TABLE V
 SOLUBILITY PARAMETERS OF STATIONARY PHASES, δ_2 [(cal mol⁻¹)^{1/2}], AT 393 K

| <i>Mixtures of OV-101-OV-25</i> | | | | | | | | | |
|--|--------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|--|
| Equation | φ_{OV-101} | | | | | | | | |
| | 1 | 0.831 | 0.589 | 0.410 | 0.397 | 0.268 | 0.084 | 0 | |
| Eqn. 8 (ΔG_1^{∞}) | | 5.92 ± 0.19 | 6.21 ± 0.18 | 6.35 ± 0.18 | 6.28 ± 0.18 | 6.39 ± 0.18 | 6.53 ± 0.20 | 6.65 ± 0.19 | |
| Eqn. 11 (χ_1^{∞}) | | 6.46 ± 0.12 | 6.54 ± 0.10 | 6.97 ± 0.16 | 6.90 ± 0.15 | 7.02 ± 0.16 | 7.19 ± 0.19 | 7.32 ± 0.21 | |
| <i>Mixtures of OV-101-Carbowax 20M</i> | | | | | | | | | |
| Equation | φ_{OV-101} | | | | | | | | |
| | 1 | 0.757 | 0.509 | 0.257 | 0 | | | | |
| Eqn. 8 (ΔG_1^{∞}) | | 5.85 ± 0.24 | 6.16 ± 0.26 | 6.73 ± 0.23 | 7.29 ± 0.20 | 7.99 ± 0.09 | | | |
| Eqn. 11 (χ_1^{∞}) | | 6.37 ± 0.14 | 6.72 ± 0.16 | 7.32 ± 0.17 | 7.90 ± 0.18 | 8.63 ± 0.27 | | | |
| <i>Mixtures of OV-225-SP-2340</i> | | | | | | | | | |
| Equation | φ_{OV-225} | | | | | | | | |
| | 1 | 0.781 | 0.508 | 0.363 | 0.327 | 0.103 | 0 | | |
| Eqn. 8 (ΔG_1^{∞}) | | 7.40 ± 0.11 | 7.59 ± 0.11 | 7.93 ± 0.12 | 8.19 ± 0.13 | 8.41 ± 0.13 | 8.43 ± 0.13 | | |
| Eqn. 11 (χ_1^{∞}) | | 8.10 ± 0.23 | 8.30 ± 0.25 | 8.64 ± 0.29 | 8.91 ± 0.30 | 9.13 ± 0.30 | 9.15 ± 0.29 | | |

TABLE VI

ENTHALPIC CONTRIBUTIONS (χ_{H}^{∞}) TO THE SOLUTE-POLYMER INTERACTION PARAMETERS AT 393 K*Mixtures of OV-101-OV-25*

| Compound | φ_{OV-101} | | | | | | | |
|--------------------|--------------------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 0.831 | 0.589 | 0.410 | 0.397 | 0.268 | 0.084 | 0 |
| <i>n</i> -Hexane | 0.085 | 0.107 | 0.197 | 0.272 | 0.238 | 0.296 | 0.385 | 0.461 |
| <i>n</i> -Heptane | 0.016 | 0.027 | 0.081 | 0.133 | 0.109 | 0.151 | 0.218 | 0.279 |
| <i>n</i> -Octane | 0.001 | 0.006 | 0.041 | 0.082 | 0.063 | 0.097 | 0.155 | 0.209 |
| <i>n</i> -Nonane | 0.003 | 0.000 | 0.014 | 0.043 | 0.028 | 0.054 | 0.101 | 0.148 |
| <i>n</i> -Decane | 0.019 | 0.009 | 0.002 | 0.018 | 0.009 | 0.026 | 0.063 | 0.102 |
| <i>n</i> -Undecane | 0.042 | 0.026 | 0.000 | 0.006 | 0.001 | 0.011 | 0.038 | 0.071 |
| <i>n</i> -Dodecane | 0.052 | 0.033 | 0.001 | 0.004 | 0.000 | 0.008 | 0.035 | 0.068 |
| Benzene | 0.229 | 0.202 | 0.127 | 0.087 | 0.103 | 0.076 | 0.046 | 0.028 |
| 1-Butanol | 1.349 | 1.283 | 1.081 | 0.956 | 1.009 | 0.921 | 0.807 | 0.726 |
| 2-Pentanone | 0.180 | 0.154 | 0.084 | 0.049 | 0.063 | 0.041 | 0.018 | 0.007 |
| Pyridine | 0.858 | 0.809 | 0.659 | 0.568 | 0.606 | 0.542 | 0.461 | 0.404 |

Mixtures of OV-101-Carbowax 20M

| Compound | φ_{OV-101} | | | | |
|--------------------|--------------------|-------|-------|-------|-------|
| | 1 | 0.757 | 0.509 | 0.257 | 0 |
| <i>n</i> -Hexane | 0.063 | 0.165 | 0.456 | 0.880 | 1.605 |
| <i>n</i> -Heptane | 0.007 | 0.060 | 0.275 | 0.633 | 1.290 |
| <i>n</i> -Octane | 0.000 | 0.026 | 0.205 | 0.543 | 1.194 |
| <i>n</i> -Nonane | 0.010 | 0.006 | 0.145 | 0.458 | 1.098 |
| <i>n</i> -Decane | 0.034 | 0.000 | 0.099 | 0.388 | 1.017 |
| <i>n</i> -Undecane | 0.065 | 0.004 | 0.069 | 0.339 | 0.966 |
| <i>n</i> -Dodecane | 0.078 | 0.007 | 0.066 | 0.346 | 1.007 |
| Benzene | 0.261 | 0.150 | 0.029 | 0.002 | 0.092 |
| 1-Butanol | 1.424 | 1.145 | 0.731 | 0.416 | 0.146 |
| 2-Pentanone | 0.211 | 0.104 | 0.007 | 0.021 | 0.189 |

Mixtures of OV-225-SP-2340

| Compound | φ_{OV-225} | | | | | | |
|------------------------|--------------------|-------|-------|-------|-------|-------|-------|
| | 1 | 0.781 | 0.508 | 0.363 | 0.327 | 0.103 | 0 |
| <i>n</i> -Hexane | 1.058 | 1.246 | 1.614 | 1.641 | 1.937 | 2.221 | 2.249 |
| <i>n</i> -Heptane | 0.791 | 0.960 | 1.298 | 1.324 | 1.600 | 1.869 | 1.895 |
| <i>n</i> -Octane | 0.698 | 0.865 | 1.202 | 1.228 | 1.507 | 1.781 | 1.808 |
| <i>n</i> -Nonane | 0.607 | 0.771 | 1.106 | 1.132 | 1.413 | 1.690 | 1.717 |
| <i>n</i> -Decane | 0.532 | 0.692 | 1.025 | 1.051 | 1.334 | 1.615 | 1.643 |
| <i>n</i> -Undecane | 0.480 | 0.639 | 0.975 | 1.001 | 1.288 | 1.576 | 1.604 |
| <i>n</i> -Dodecane | 0.494 | 0.662 | 1.016 | 1.044 | 1.348 | 1.653 | 1.683 |
| <i>n</i> -Tridecane | 0.458 | 0.625 | 0.983 | 1.011 | 1.321 | 1.634 | 1.664 |
| <i>n</i> -Tetradecane* | 0.441 | 0.612 | 0.978 | 1.007 | 1.328 | 1.651 | 1.683 |
| <i>n</i> -Pentadecane* | 0.407 | 0.577 | 0.947 | 0.976 | 1.302 | 1.634 | 1.666 |
| Benzene | 0.013 | 0.034 | 0.094 | 0.099 | 0.163 | 0.233 | 0.240 |
| 1-Butanol | 0.328 | 0.253 | 0.144 | 0.138 | 0.080 | 0.042 | 0.039 |
| 2-Pentanone | 0.051 | 0.091 | 0.191 | 0.200 | 0.296 | 0.398 | 0.408 |
| Pyridine | 0.139 | 0.094 | 0.037 | 0.034 | 0.010 | 0.001 | 0.000 |

* Values calculated without second virial coefficient correction.

TABLE VII

ENTROPIC CONTRIBUTION (χ_s^∞) TO THE SOLUTE-POLYMER INTERACTION PARAMETERS CALCULATED FROM EQN. 11*Mixtures of OV-101-OV-25*

| Compound | φ_{OV-101} | | | | | | | |
|--------------------|--------------------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 0.831 | 0.589 | 0.410 | 0.397 | 0.268 | 0.084 | 0 |
| <i>n</i> -Hexane | 0.268 | 0.297 | 0.388 | 0.483 | 0.497 | 0.514 | 0.640 | 0.635 |
| <i>n</i> -Heptane | 0.287 | 0.318 | 0.415 | 0.516 | 0.532 | 0.550 | 0.685 | 0.679 |
| <i>n</i> -Octane | 0.314 | 0.348 | 0.454 | 0.565 | 0.582 | 0.602 | 0.750 | 0.743 |
| <i>n</i> -Nonane | 0.342 | 0.379 | 0.494 | 0.615 | 0.633 | 0.655 | 0.816 | 0.809 |
| <i>n</i> -Decane | 0.370 | 0.409 | 0.534 | 0.664 | 0.684 | 0.708 | 0.882 | 0.874 |
| <i>n</i> -Undecane | 0.398 | 0.441 | 0.576 | 0.716 | 0.738 | 0.763 | 0.951 | 0.942 |
| <i>n</i> -Dodecane | 0.428 | 0.474 | 0.618 | 0.769 | 0.792 | 0.819 | 1.021 | 1.012 |
| Benzene | 0.173 | 0.191 | 0.249 | 0.310 | 0.320 | 0.331 | 0.412 | 0.408 |
| 1-Butanol | 0.171 | 0.190 | 0.247 | 0.308 | 0.317 | 0.328 | 0.408 | 0.405 |
| 2-Pentanone | 0.208 | 0.230 | 0.300 | 0.373 | 0.384 | 0.397 | 0.495 | 0.491 |
| Pyridine | 0.151 | 0.167 | 0.218 | 0.272 | 0.280 | 0.289 | 0.361 | 0.357 |

Mixtures of OV-101-Carbowax 20M

| Compound | φ_{OV-101} | | | | |
|--------------------|--------------------|-------|-------|-------|-------|
| | 1 | 0.757 | 0.509 | 0.257 | 0 |
| <i>n</i> -Hexane | 0.264 | 0.502 | 0.634 | 0.684 | 0.609 |
| <i>n</i> -Heptane | 0.283 | 0.538 | 0.678 | 0.732 | 0.652 |
| <i>n</i> -Octane | 0.309 | 0.588 | 0.742 | 0.801 | 0.713 |
| <i>n</i> -Nonane | 0.336 | 0.640 | 0.807 | 0.872 | 0.776 |
| <i>n</i> -Decane | 0.364 | 0.692 | 0.873 | 0.942 | 0.839 |
| <i>n</i> -Undecane | 0.392 | 0.746 | 0.941 | 1.016 | 0.904 |
| <i>n</i> -Dodecane | 0.421 | 0.801 | 1.010 | 1.091 | 0.971 |
| Benzene | 0.170 | 0.323 | 0.408 | 0.440 | 0.392 |
| 1-Butanol | 0.168 | 0.320 | 0.404 | 0.436 | 0.388 |
| 2-Pentanone | 0.204 | 0.389 | 0.490 | 0.529 | 0.471 |

Mixtures of OV-225-SP-2340

| Compound | φ_{OV-225} | | | | | | |
|------------------------|--------------------|-------|-------|-------|-------|-------|-------|
| | 1 | 0.781 | 0.508 | 0.363 | 0.327 | 0.103 | 0 |
| <i>n</i> -Hexane | 0.418 | 0.364 | 0.305 | 0.653 | 0.425 | 0.676 | 0.985 |
| <i>n</i> -Heptane | 0.447 | 0.390 | 0.326 | 0.698 | 0.454 | 0.724 | 1.055 |
| <i>n</i> -Octane | 0.489 | 0.426 | 0.357 | 0.764 | 0.497 | 0.792 | 1.154 |
| <i>n</i> -Nonane | 0.532 | 0.464 | 0.388 | 0.831 | 0.541 | 0.862 | 1.255 |
| <i>n</i> -Decane | 0.575 | 0.501 | 0.420 | 0.899 | 0.585 | 0.931 | 1.357 |
| <i>n</i> -Undecane | 0.620 | 0.540 | 0.452 | 0.969 | 0.630 | 1.004 | 1.463 |
| <i>n</i> -Dodecane | 0.665 | 0.580 | 0.486 | 1.040 | 0.677 | 1.078 | 1.571 |
| <i>n</i> -Tridecane | 0.710 | 0.619 | 0.518 | 1.109 | 0.722 | 1.149 | 1.675 |
| <i>n</i> -Tetradecane* | 0.755 | 0.658 | 0.551 | 1.180 | 0.768 | 1.223 | 1.782 |
| <i>n</i> -Pentadecane* | 0.803 | 0.700 | 0.586 | 1.255 | 0.816 | 1.300 | 1.895 |
| Benzene | 0.269 | 0.234 | 0.196 | 0.420 | 0.273 | 0.435 | 0.634 |
| 1-Butanol | 0.266 | 0.232 | 0.194 | 0.416 | 0.271 | 0.431 | 0.628 |
| 2-Pentanone | 0.323 | 0.282 | 0.236 | 0.505 | 0.328 | 0.523 | 0.762 |
| Pyridine | 0.235 | 0.205 | 0.172 | 0.367 | 0.239 | 0.381 | 0.555 |

* Values calculated without second virial coefficient correction.

TABLE VIII

ENTROPIC CONTRIBUTION TO THE SOLUTE-POLYMER INTERACTION PARAMETER FOUND WITH EQNS. 10 AND 11 FOR OV-101/OV-25 = 0.397:0.603

| Solute | χ_H^∞ | χ_S^∞ | |
|--------------------|-----------------|-----------------|---------|
| | | Eqn. 10 | Eqn. 11 |
| <i>n</i> -Hexane | 0.238 | 0.171 | 0.497 |
| <i>n</i> -Heptane | 0.109 | 0.468 | 0.532 |
| <i>n</i> -Octane | 0.063 | 0.626 | 0.582 |
| <i>n</i> -Nonane | 0.028 | 0.753 | 0.633 |
| <i>n</i> -Decane | 0.009 | 0.855 | 0.684 |
| <i>n</i> -Undecane | 0.001 | 0.936 | 0.738 |
| <i>n</i> -Dodecane | 0.0004 | 1.006 | 0.792 |
| Benzene | 0.103 | 0.187 | 0.320 |
| 1-Butanol | 1.009 | 0.472 | 0.317 |
| 2-Pentanone | 0.063 | 0.570 | 0.384 |
| Pyridine | 0.606 | 0.046 | 0.280 |

differences between the values found for χ_S^∞ by the two procedures. Perhaps values derived from the intercept of eqn. 11 (Table VII) are less reliable than those found from eqn. 10. The reason might be that the range of values of solubility parameters of solutes, δ_1 , used is small (5.8–9.7) and extrapolation to $\delta_1 = 0$ is not very precise.

As predicted by Flory³⁵, it may be found that $\chi_H^\infty < \chi_S^\infty$ with values of χ_H^∞ that are small for solutes and polymers of similar chemical structure (values of the solubility parameters of the same order). From the results shown in Table VI it may be observed that, as expected, χ_H^∞ values for *n*-alkanes in OV-101 are rather small, increasing as the mixed stationary phase becomes more and more polar (the proportion of the polar component increases in the mixed stationary phase). On polar polymers, polar substances show small values of the enthalpic contribution to the interaction parameter (benzene in OV-225 or OV-25; pyridine in SP-2340). When the "polarities" of the solute and polymer are dissimilar, the value of the enthalpic contribution becomes more important. Thus it may be observed that χ_H^∞ values are larger than χ_S^∞ values for the polar solutes in apolar stationary phases or *n*-alkanes in systems such as that of the cyanosilicones. In all instances of solute-polymer similarity, χ_S^∞ should be more important than χ_H^∞ , and the contrary should be expected in instances of dissimilarity. The values of δ_1 and δ_2 may give an idea of the relative values of χ_H^∞ and χ_S^∞ . However, the prediction of the value of the solute-polymer interaction parameter, χ^∞ , does not seem possible from a knowledge of the two solubility parameters.

The concept of χ_S^∞ is ambiguous and it probably indicates the importance of the interaction of the solute molecule with the polymer in the ordering of the system³⁶. It must be considered as a correction factor and probably should be further corrected to take into account pressure-volume effects²⁰:

$$\chi^\infty = \chi_H^\infty + \chi_S^\infty + \chi_{PV}^\infty \quad (12)$$

TABLE IX

POLYMER-POLYMER INTERACTION PARAMETER, $\chi'_{2,3}$, AT 393 K*Mixtures of OV-101-OV-25*

| <i>Compound</i> | φ_{OV-101} | | | | | |
|--------------------|--------------------|-------|-------|--------|--------|--------|
| | 0.831 | 0.589 | 0.410 | 0.397 | 0.268 | 0.084 |
| <i>n</i> -Hexane | 0.423 | 0.340 | 0.180 | 0.230 | 0.423 | -0.182 |
| <i>n</i> -Heptane | 0.417 | 0.348 | 0.184 | 0.243 | 0.425 | -0.146 |
| <i>n</i> -Octane | 0.495 | 0.348 | 0.189 | 0.254 | 0.444 | -0.131 |
| <i>n</i> -Nonane | 0.479 | 0.367 | 0.214 | 0.260 | 0.437 | -0.120 |
| <i>n</i> -Decane | 0.474 | 0.385 | 0.232 | 0.280 | 0.464 | 0.014 |
| <i>n</i> -Undecane | 0.517 | 0.398 | 0.229 | 0.298 | 0.474 | 0.042 |
| <i>n</i> -Dodecane | 0.548 | 0.399 | 0.234 | 0.304 | 0.486 | 0.110 |
| Benzene | 0.175 | 0.136 | 0.061 | -0.035 | 0.009 | -0.453 |
| 1-Butanol | 0.285 | 0.054 | 0.021 | -0.123 | -0.046 | -0.856 |
| 2-Pentanone | 0.489 | 0.133 | 0.062 | -0.117 | 0.196 | -0.358 |
| Pyridine | -0.637 | 0.247 | 0.226 | -0.122 | -0.024 | -0.371 |

Mixtures of OV-101-Carbowax 20M

| <i>Compound</i> | φ_{OV-101} | | |
|--------------------|--------------------|--------|--------|
| | 0.757 | 0.509 | 0.257 |
| <i>n</i> -Hexane | 0.476 | 0.503 | 0.582 |
| <i>n</i> -Heptane | 0.603 | 0.667 | 0.859 |
| <i>n</i> -Octane | 0.600 | 0.751 | 0.969 |
| <i>n</i> -Nonane | 0.675 | 0.845 | 1.163 |
| <i>n</i> -Decane | 0.718 | 0.914 | 1.330 |
| <i>n</i> -Undecane | 0.817 | 1.039 | 1.506 |
| <i>n</i> -Dodecane | 0.877 | 1.144 | 1.670 |
| Benzene | -0.651 | -0.409 | -0.636 |
| 1-Butanol | -0.378 | 0.063 | 0.159 |
| 2-Pentanone | -0.906 | -0.555 | -0.534 |

Mixtures of OV-225-SP-2340

| <i>Compound</i> | φ_{OV-225} | | | | |
|------------------------|--------------------|-------|-------|-------|-------|
| | 0.781 | 0.508 | 0.363 | 0.327 | 0.103 |
| <i>n</i> -Hexane | 1.559 | 1.939 | 1.212 | 1.466 | 2.189 |
| <i>n</i> -Heptane | 1.666 | 2.037 | 1.330 | 1.647 | 2.336 |
| <i>n</i> -Octane | 1.796 | 2.111 | 1.467 | 1.775 | 2.514 |
| <i>n</i> -Nonane | 1.851 | 2.225 | 1.593 | 1.862 | 2.593 |
| <i>n</i> -Decane | 1.905 | 2.319 | 1.681 | 1.995 | 2.654 |
| <i>n</i> -Undecane | 2.052 | 2.447 | 1.866 | 2.136 | 2.843 |
| <i>n</i> -Dodecane | 2.141 | 2.550 | 1.957 | 2.265 | 3.132 |
| <i>n</i> -Tridecane | 2.234 | 2.652 | 2.082 | 2.408 | 3.094 |
| <i>n</i> -Tetradecane* | 2.331 | 2.749 | 2.210 | 2.534 | 3.178 |
| <i>n</i> -Pentadecane* | 2.418 | 2.844 | 2.323 | 2.646 | 3.222 |
| Benzene | 0.729 | 1.146 | 0.449 | 1.207 | 1.646 |
| 1-Butanol | 0.744 | 1.151 | 0.555 | 1.214 | 1.990 |
| 2-Pentanone | 0.918 | 1.433 | 0.182 | 1.683 | 1.624 |
| Pyridine | 0.786 | 1.145 | 0.344 | 1.197 | 1.979 |

* Values calculated without second virial coefficient correction.

The polymer-polymer interaction parameter

The polymer-polymer interaction parameters have been presented previously¹² for the three systems studied here. The values, deduced according to Perry and Tiley⁷, are mean values for all *n*-alkanes and stationary phase compositions, including single stationary phases. The value corresponding to each solute on every mixed stationary phase may be deduced according to the expression^{15,16,37}

$$\chi_{1,(2,3)}^{\infty} = \chi_{1,2}^{\infty}\varphi_2 + \chi_{1,3}^{\infty}\varphi_3 - \chi'_{2,3}\varphi_2\varphi_3 \quad (13)$$

where all the symbols have the usual meanings and $\chi'_{2,3}$ is the polymer-polymer interaction parameter normalized for the size of the solute molecule ($\chi'_{2,3} = V_1^0\chi_{2,3}/V_2^0$). In this way, values of $\chi'_{2,3}$ are obtained for each probe and mixture composition. Table IX presents the results obtained. It may be observed that the value of $\chi'_{2,3}$ depends on both the solute and mixture composition. This effect has been observed in the past³⁷.

The dependence of the value of the polymer-polymer interaction parameter on the chemical structure of the solute is a common phenomenon, although not allowed by theory³². It has been interpreted as arising from the preferential interaction with one of the two types of polymer segments³⁸. Olabisi³⁹ attributed this to the non-random distribution of the solute in the stationary phase owing to its preferential affinity for one of the components. Selective solutes do not "sense" the three varieties of intramolecular contacts in the polymer mixture (A-A, A-B, B-B) in proportion to concentration. Instead, they detect a relatively low concentration of the chains for which they are non-solvents. This modifies the retention volume (and $\chi'_{2,3}$) values relative to those which would be obtained by a truly random mixing of the solute with the polymer³⁸. Less selective solvents, on the other hand, exhibit a more random "sampling" of the molecular environment of the stationary phase owing to the equal affinities they have for both. It is therefore expected that a better measure of the polymer-polymer interaction will be likely with less selective solvents. According to these ideas, solutes with different chemical structure should behave differently in a mixture of two "different" polymers, *i.e.*, polymers of very different "polarity". Accordingly, one type of solute may behave in such a way that they show a "linear behaviour with mixture composition" when specific retention volumes are considered, whereas other types of solutes might not show the same type of linear dependence on mixture composition, when the same mixture is considered in both instances.

TABLE X

MEAN VALUES OF $\chi'_{2,3}/V_1^0$ FOR *n*-ALKANES AT 393 K

| System | <i>a</i> * | <i>b</i> ** |
|---------------------|------------|-------------|
| OV-101-OV-25 | 1.59 | 1.42 |
| OV-101-Carbowax 20M | 4.39 | 4.33 |
| OV-225-SP-2340 | 9.02 | 9.79 |

* Values obtained according to Perry and Tiley^{7,12}.

** This work.

In order to compare the values of the polymer-polymer interaction parameter obtained in this paper based only on mixed stationary phases with those found previously for the same systems using both single and mixed stationary phases, we calculated the average value of $\chi'_{2,3}/V_1^0$ corresponding to all *n*-alkanes in all mixed stationary phases. The values are compared with those obtained previously¹² in Table X. The figures corresponding to each system are not exactly the same because in the present instance only mixed stationary phases could be considered.

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