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A classification of stationary liquids by infrared spectroscopy to evaluate the polarity was made using the solvent effect technique. The infrared C-Cl absorption frequency shift was measured for solutions of 1-chlorohexane dissolved in each stationary phase. These frequency shifts were correlated to the relative retention times of 1-octene/n-octane, trans-2-octene/n-octane and 1,7-octadiene/n-octane on the same stationary phases, through Ecknig's equation $\log r_{1,2} = E \overset{Ass}{}_{C\text{-}Cl} + F$. The correlation coefficients obtained for 1-octene and 1,7-octadiene presented good reliability considering that several conceptual and experimental assumptions had to be made. Measurements of relative retention times of homologous series of n-alkanes for each stationary phase were correlated to the number of carbon atoms and the slopes calculated by linear regression. The order obtained by this way was compared to the order obtained by the evaluation of polarity.

Classification of Stationary Liquids in Gas Chromatography by Infrared Spectrophotometry

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To my Colombian people, who suffer and strive for a future of justice, peace and freedom.

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I. INTRODUCTION

A. Introduction

The choice of the proper stationary phase is one of the most important decisions to be made in gas chromatography. Several hundred stationary phases have been described and are commercially available. Different catalogues can be obtained from suppliers, and have been used at times as a guide when selecting a stationary phase. But essentially, the selection has been empirical, although it is clear that the solute-stationary phase interactions play the most important role in the separation process.

Historically most of the discussions concerning selectivity have been done in terms of polar or non-polar stationary phases. A few other studies take into account some experimental data and phenomenological rules.

B. Classification of Stationary Phases

Polarity

In 1959 Rohrschneider (1) developed a simple model of polarity. He defined polarity as the difference between the logarithms of the retention ratios of butadiene and n-butane in a polar phase "p" and a non-polar one "u." Squalane was assigned to have polarity P = 0, and a polar phase (oxydipropionitrile) the polarity P = 100. The polarity

of any other stationary phase can be calculated by using the following expression

$$P_p = a\left(\log \frac{V_p^{\text{butadiene}}}{V_p^{\text{butane}}} - \log \frac{V_u^{\text{butadiene}}}{V_u^{\text{butane}}}\right) \qquad (1)$$

where a is a factor to adjust the scale to give P = 100 for oxydipropionitrile. For this experiment he used a = 144, $V_p^{\text{butadiene}}$ and V_p^{butane} are the retention volumes of butadiene and butane in polar "p" stationary phase and $V_u^{\text{butadiene}}$ and V_u^{butane} are the retention volumes of butadiene and butane in a non-polar "u" stationary phase.

Equation (1) was expressed in a more general way considering the polarity of a liquid phase with respect to a polar substance R_x and a non-polar one RH,

$$P_p = \log \frac{V_p^{R_x}}{V_p^{RH}} - \log \frac{V_u^{R_x}}{V_u^{RH}} \qquad (2)$$

With equation (2) the polarity scale is no longer in the range 0-100 because of the omission of a.

$$\text{As;} \quad \frac{V^{R_x}}{V^{RH}} = \frac{\gamma^{RH} P_o^{RH}}{\gamma^{R_x} P_o^{R_x}} \qquad (3)$$

Replacing (3) in (2)

$$P_p = \left(\log \frac{\gamma_p^{RH}}{\gamma_p^{Rx}} + \log \frac{P_o^{RH}}{P_o^{Rx}}\right) - \left(\log \frac{\gamma_u^{RH}}{\gamma_u^{Rx}} + \log \frac{P_o^{RH}}{P_o^{Rx}}\right) \quad (4)$$

rearranging

$$P_p = \log \frac{\gamma_p^{RH} \; \gamma_u^{Rx}}{\gamma_p^{Rx} \; \gamma_u^{RH}} \quad (5)$$

The polarity is directly related to the activity coefficients of the two substances and the two columns.

Rohrschneider (1) also considered polarity in terms of the retention index. He provided several empirical relationships that were generally regarded as polarity in the gas chromatographic sense. From the comparison of a polar column with a non-polar one (squalane) the retention index difference ΔI_p^{Rx} was derived.

$$\Delta I_p^{Rx} = \underline{a}^{Rx} \chi_p \quad (6)$$

where $\underline{a}$ is a factor that depends on the polarity of the solute and χ_p depends on the polarity of the liquid phase.

The thermodynamic meaning of the retention index difference, according to Rohrschneider (2) is

$$\Delta I^{Rx} = 100 \left(\frac{\Delta G_p^{Rx} - \Delta G_{po}^{Rx}}{\Delta G_p^{CH_2}}\right) \quad (7)$$

where ΔG_p^{Rx} is the free energy of solution for substance Rx in the liquid phase p, and ΔG_p^{Rx} is the free energy of solution for a paraffin. $\Delta G_p^{CH_2}$ is the free energy of solution for a methylene group in the polar phase. This approximation of polarity was used for experimental work where the polarities of several substances were calculated and reported in (2).

Polarity of Solvents

Reichardt (3) in a review paper has presented a summary of the empirical parameters for describing solvent polarities and their influence on spectra and reaction rates. Brownstein (4) combined both effects in one general equation.

$$\log\left(\frac{K_{solv}}{K_{EtOH}}\right) = S \cdot R \qquad (8)$$

Where K is the rate of reaction, an equilibrium constant, or a function of a spectral displacement. S is a constant that describes solvent polarity and R is another constant, characteristic of the sensitivity of a reaction toward the influence of solvent or polarity changes. This equation was used for several solvents and these results were compared with gas chromatographic polarities. Then it was found that a relation between solvent polarity and gas chromatographic polarities exists, but it was not strictly fulfilled.

C. Characterization of Gas Chromatographic Polarity

The method developed by Rohrschneider (1) was only an approximation and it was subject to considerable error. It was, however, the only

possible way to make an accurate prediction using a single parameter. This method of characterizing liquid phases was used by Maier and Karpathy (5) commercially to produce coupled gas chromatographic columns. They used Rohrschneider's finding that the combination of two stationary phases would result in a column of polarity intermediate between the two pure materials. So they investigated various methods of combining two different stationary phases.

Later, Chovin and Lebble (6) started with Rohrschneider's (1) polarity scales and they expanded the temperature from 30°C to a wider range. Also they took the retention ratio of any two consecutive paraffins rather than just the ratio of butadiene and butane, so it was independent of functional groups and therefore, a more general consideration.

Then, Chovin (7) determined the polarity of several new polar stationary phases using this more general equation.

$$P_c = (1/m) [\log (V^{n+1}/V^n) - a] \qquad (9)$$

where V^{n+1} and V^n are retention volumes of normal paraffins, with n and n + 1 carbon atoms respectively. The quantities a and m were introduced to obtain a polarity scale between squalane (0) and oxydipropionitrile (100).

Chovin based his equation on the assumption that the quantity (V^{n+1}/V^n) was independent of the number of carbon atoms. Rohrschneider (8) found that this is not strictly true. He observed Littlewood's (9) work and confirmed that the retention ratio of two neighboring paraffins

was dependent upon the number of carbon atoms, at least for carbon numbers below C_9. So Rohrschneider decided that Chovin's equation, even with a wider range of temperature, did not achieve any greater accuracy of prediction than his equation.

Based on the same behavior of liquid phase and paraffins initiated by Chovin and confirmed by Littlewood (9), Lazarre and Roumazeilles (10) derived another relationship

$$P_{L.R.} = T \log (V_p^{n+1} / V_p^n) = \alpha_p T \qquad (10)$$

where T is the absolute temperature of the column, and $P_{L.R.}$ is a constant that measures the polarity of the liquid phase. This equation did not consider non-polar columns. Also it was supposed to be independent of the temperature, but the thermodynamic relation of retention volume shows it can not be, since ΔG also depends on temperature.

$$\log V = 2.3\ \Delta G/RT \qquad (11)$$

Another misunderstanding of this approach to the definition of polarity is the lack of consideration of all types of interactions between the stationary phase and the sample.

Schomburg (11) suggested that the polarity of liquid phases should be defined by the expression

$$P = \Delta I^{benzene} - \Delta I^{cyclohexane} \qquad (12)$$

Schomburg determined the polarity of several stationary phases and found that the retention index difference of olefins increased linearly with increasing polarity.

Then, a more simple method for characterization of stationary phases was proposed by Rohrschneider (12). He suggested that the polarity of a stationary phase be characterized by the retention index difference of benzene. He obtained a linear relationship between the retention index difference of benzene and that of 2-ethylhexene. Rohrschneider considered the retention index difference of benzene at a given temperature as a precisely measurable quantity of general importance for liquid phase characterization.

Characterization of Liquid Phases by Several Polarity Factors

Rohrschneider (8) considered that the characterization of liquid phases by a single quantity would always be incomplete. In addition to the dispersion forces and the dipole interactions he decided to consider hydrogen bond formation and electron donor and acceptor interactions. Based on these interactions he designed several polarity factors to express the intermolecular energy of interaction ΔG_p which was composed of several additive terms whose sum determined the retention index

$$\Delta G_p^{Rx} = \Delta G_{po}^{Rx} + \Delta G_{p1}^{Rx} + \Delta G_{p2}^{Rx} + \ldots + \Delta G_{pu}^{Rx} \qquad (13)$$

From equation (6)

$$\Delta G_{pi}^{Rx} = a\, X_{pi}^{Rx} \qquad (14)$$

So the retention index difference will also be composed of several additive terms.

$$\Delta I_p^{Rx} = \Sigma(a^{Rx}x_p)_n \qquad (15)$$

where each term corresponds to a separate energy of interaction.

In his next publication, Rohrschneider (12) described the retention index differences as the product of three polarity factors

$$\Delta I = ax + by + cz \qquad (16)$$

where a, b, c are the polarity factors for three solutes (a, b and c) and x, y, z are the polarities of the three stationary phases.

He thought that from the data it was possible to predict the retention index differences. But in order to obtain the constants applying to the solutes and liquid phases respectively, he used an extensive and complicated trial and error calculation. Then he found that there were some other factors affecting the separation of some compounds, like alcohols and carbonyls that must be taken into consideration.

Finally, Rohrschneider (2) finished this paper with a characterization of liquid phases based on the additivity of intermolecular interaction energies. He took twenty-two liquid phases (see table IV in (8)) and five solutes, then calculated the polarity factors due to solutes and liquid phases, as follows

$$\Delta I = (a^{Rx}x_p) + (b^{Rx}y_p) + (c^{Rx}z_p) + (d^{Rx}U_p) + (e^{Rx}S_p) \qquad (17)$$

where x_p, y_p, z_p, U_p and S_p are liquid phase polarities for the polar liquid p and a^{Rx}, b^{Rx}, c^{Rx}, d^{Rx}, e^{Rx} are the polarities of benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine respectively.

Rohrschneider's polarity factors were a good approximation for the characterization of liquid phases, since he considered several possible interactions between the solute and the liquid phase. However, he did not achieve a suitable and specific technique to evaluate or measure the phenomena which are responsible for dipole-dipole interactions, hydrogen bonds between solvent and solute, and the hydrogen donor and acceptor interactions. He also did not clearly separate the different parameters of characterization according to the chemical and physical properties of solutes and liquid phases e.g. taking a pair of substances that may differ only in one factor such as dipole interaction so in that way evaluating it.

The system that was used to calculate Rohrschneider's polarity factors was complicated and involved a knowledge of statistics and matrix algebra by the analyst.

In 1970, McReynolds (13) published a paper that attacked the same problem of liquid phase characterization in gas chromatography. He used Rohrschneider's (2) approach to calaculate the retention indices of 68 compounds (including the 33 used by Rohrschneider) in 25 liquid phases. After he obtained these data, he computed by regression analysis the retention indices of an appropriate combination of solutes in certain stationary phases that could be used to predict retention indices of other compounds on the same stationary phases. The best

solutes that he found to characterize liquid phases were: benzene, butanol, 2-pentanone, nitropropane, pyridine, 2-methyl-2 pentanol, 1-iodobutane, 2-octene, 1-4 dioxane and cis-hydrindane. McReynolds determined ΔI values for about 200 stationary phases using the above ten compounds as solutes and squalane as reference. He also published two other parameters; (see table I, (13)) b which is the slope of the straight line obtained when the logarithms of the net retention times of the n-alkanes are plotted as a function of the number of carbon atoms; and r the ratio of the net retention times of adjacent n-alkanes. To calculate this value he used the square root of the ratio of the net retention times of dodecane and decane. He obtained all his data at $120^{o}C$.

Finally, McReynolds emphasized that the main purpose of his work "...was not to present a large number of liquid phases for use, but rather to show the similarity of many liquid phases now in use..." Indeed this is quite important since there has been a notorious proliferation of commercial stationary phases, that according to McReynolds' publication, have similar properties with different brand names.

The polarity scale published by McReynolds was an experimental application of Rohrschneider's approach. It has been a great contribution to several chromatographers who are concerned about the characterization of stationary phases. After other attempts to classify stationary phases by the use of various parameters, Burns and Hawkes (14) developed a model of classification that collected and expanded upon some of the earlier attempts. They used the relative retention times to set scales of polarity, hydrogen bond effects and dispersion

interactions. They defined every one of the parameters using different theoretical and experimental considerations. The dispersion interactions were related to the refractive index using the relation derived by Keller and Karger (15);

$$\delta_d = 30.7\ (n^2 - 1)/(n^2 + 2) \qquad (18)$$

where δ_d is the dispersive solubility parameter in $(cal/ml)^{\frac{1}{2}}$ and $\underline{n}$ is the refractive index. Then, they obtained experimental data and calculated the retention time of benzene relative to $\underline{n}$-heptane on a series of stationary phases which possessed only dispersion interactions. After considerations about retention increments (ΔI), molar volume (V) and energy of interaction (E), they obtained the following expression

$$\log\ (t'_{benzene}/t'_{C7}) = (\delta^2_{d,st.ph} - 9.4\delta_{d,st.ph})\ 59/2.3RT \qquad (19)$$

where t' is the corrected retention time and $\delta_{d,st.ph}$ is the dispersive solubility parameter of the stationary phase.

A plot of $\log\ (t'_{benzene}/t_{C7})$ against $(\delta^2_d - 9.4\delta_d)$ should be linear and have a slope equal to 5.9/2.3RT for T equal absolute temperature (used 120°C) and R is the constant of gases in (cal/mol °K). This expected quantity should be 0.033. They obtained a straight line but the plot failed to yield the predicted slope. Many reasons were discussed for the cause of the deviation from the theoretical slope. The most probable answer was that the deviation was caused by a combination of effects. Regardless, they calculated δ_d values for

several stationary phases by using the refractive index. Polarity interactions were considered the most important chemical properties of a stationary phase that may be used as a means of classification.

Burns and Hawkes combined the dispersion and dipole interactions for solutes for which acid-base interactions were insignificant. After considering the energy of solution as the sum of dispersion and dipole interactions and manipulation of some equations dealing with the relative retention of benzene and heptane, they obtained an expression for polarity as follows

$$P = 10 \log(t'_{benzene}/t'_{\underline{n}\text{-heptane}}) - 6.4 - (\delta_d^x - 4.7\, x\delta_d)\ 590/2.3RT \quad (20)$$

where $\underline{x}$ is the deviation from the theoretical dispersion value. Using this expression Burns and Hawkes tabulated a polarity scale (see table I in (14)). Acidity and basicity indices were also reported. They consider the ability of a hydroxyl group to form hydrogen bonds with the stationary phase as an important separation mechanism when sample components have similar dipoles and dispersion potentials. So they studied both Bronsted basicity and Lewis and Bronsted acidity.

Using McReynolds data (13, 16) they used $\underline{n}$-butanol to evaluate the relative retention and after a search they found that ethyl acrylate matched $\underline{n}$-butanol in its dipole and dispersion potential. The ratio $t'_{BuOH}/t'_{Et.acr.}$ on non-polar stationary phases should preferably have been unity but it was not, so they figured out a correction of 0.1 as follows

$$H = 10[\ 0.1 + \log(t'_{BuOH}/t'_{Et.acr.})] \quad (21)$$

where H is the Bronsted acidity in arbitrary units.

Few stationary phases commonly show acidity but Burns and Hawkes found that Lewis acidity can be conveniently evaluated from the retention of pyridine. However, they did not find a matching substance with sufficient available data to offset both the dipole of pyridine and its dispersion potential. Using estimated empirical coefficients, they derived the following formula for the acidity index A

$$A = 5 [\log (t'_{py}/t'_{benz}) - P/22 - 0.13] \quad (22)$$

Burns and Hawkes' approach even though it had various problems and limitations, has been shown to be correct in its general way of classification. Most of the problems they encountered could be resolved with the use of better experimental techniques to evaluate the various parameters used in this approach. The dispersion indices could be obtained in an experimental way. Acidity, basicity and polarity can follow this above procedure and if better-matched pairs of solutes were used, more reliable results could be expected. They could also be determined spectroscopically so the literature limitation will no longer be a problem.

The basic problem in Burns and Hawkes' classification was that they used data from other researchers, so that really well-matched pairs of substances could not be found. However, their work has provided direction and encouragement to this present work.

In 1978 Snyder (17) described a scheme for the classification of common solvents according to their "polarity" or chromatographic

strength. The solvents were classified by their relative ability to engage in hydrogen bonding or dipole interactions. Dispersion interactions in solutions of polar solvents were considered to play an unimportant role in contributing to solvent selectivity. On this basis, and taking Rohrschneider's (18) experimental study into account, Snyder calculated values of polarity (P) and selectivity factors (x_i) for common solvents that could be used as stationary phases. Further, he found that these various solvents could be grouped into eight selectivity classes (e.g. I, II, III, ..., VIII) for easier selection of solvents of significantly differing selectivity. As he pointed out, the major validation of his classification scheme was provided by the observation that solvents of similar functionality were grouped into the same selectivity class, as would be expected on a theoretical basis.

Snyder's scheme for the classification of stationary phases has made a great contribution to this subject, since he considered that the relative importance of dipole and hydrogen bonding interactions were determined by the functional groups within molecules rather than by overall molecular structures. This is quite important since some of the commonly used stationary phases are polymers that do not have known molecular weights or sizes.

He also considered the case when two or more functional groups were present in the same stationary phase molecule. When this happens the more polar group would dominate the selective characteristics of the solvent. This phenomenon was understood on the basis of intermolecular electronic effects.

The method of classification designed by Snyder is more general than those of the previous investigators since he studied both liquid and gas chromatographic solvents. This system is still complex and its use requires some background in statistics and matrix algebra by the analyst. Also the analyst must use chemical intuition to judge the significance of the numbers and use them to choose a stationary phase; such judgment comes only with experience.

This present approach to the classification of stationary phases tries to be empirical rather than theoretical and will correlate spectroscopic and chromatographic techniques. In general, it follows Burns and Hawkes' (14) approach but it is more specific and essentially experimental.

It is desirable to complete a table of indices of basicity, acidity, polarity and dispersion interaction potential for several stationary phases, to assist analysts in choosing a stationary phase for a particular use. The stationary phases that are going to be studied come from the list of preferred stationary phases which was compiled by the Hawkes' committee (19).

The polarity was determined from the infrared frequency shift of the absorbance band of C-Cl bond, from 1-chlorohexane dissolved in every stationary phase, using squalane as a reference phase. This frequency shift is linearly related, as shown by Ecknig (20), to the logarithm of the relative retention time of an alkene referred to the corresponding alkane. Unfortunately it is not possible to differentiate between a permanent or induced dipole, so the polarity measurement might include a contribution from induction.

II. THEORY

A. Classification of Stationary Phases by Infrared Spectroscopy

The retention ratio of volatile substances (1, 2) depends, according to Herington (21), on their vapor pressures in the pure state (P^o) and on the activity coefficient (γ^o) of the substances in the stationary phase. γ^o can be related from the properties of sample and stationary phase ($\gamma^o_{2,3}, \gamma^o_{2,3}$)

$$\frac{V_1}{V_2} = \frac{P^o_2 \gamma^o_{2,3}}{P^o_1 \gamma^o_{1,3}} \qquad (1)$$

In order to establish a selective order of stationary liquids or to estimate or precalculate retention times, one must consider the most important forces that exist between the sample and stationary liquid. These forces can be described by the activity coefficients.

To express the intermolecular forces in solutions of non electrolytes, Ecknig (20) took a simple model of chemical addition potential μ_i^E of sample i and expressed it as

$$\mu_i^E = RT \ln \gamma^o \qquad (2)$$

The chemical addition potential consists of different types of intermolecular forces which play the most important role in the interaction between sample and stationary liquid. According to Keulemans

(22) these forces are:

(a) Forces between permanent dipoles of solute and solvent.

(b) Forces between permanent dipole either of solute or solvent and the induced dipole of the other.

(c) Non-polar forces between solute and solvent molecules.

In the same order they have been designated by the terms: orientation (Keesom) forces, induction (Debye) forces and dispersion (London) forces. The van der Waals forces are the sum of these three:

(a) If μ_A and μ_S are the permanent dipoles of solute and solvent molecules respectively, and $\underline{r}$ the distance between these dipoles, the polar axis being the line between their centers, Keesom, by applying Boltzmann statistics, derived the following expression for the average potential energy between two dipoles.

$$\overline{\varepsilon_a} = - \frac{2\mu_A^2 \mu_S^2}{3r^6 kt} \qquad (3)$$

It is important to note that, with increasing temperature, the attraction energy caused by the forces of orientation decreases, and at very high temperature, when all the orientations are equally probable, tends to become zero.

(b) The interaction energy resulting from the attraction between a permanent dipole and moments induced by this dipole is expressed by the Debye formula

$$\overline{\varepsilon_b} = - \frac{I}{r^6} \left(\alpha_s \mu_A^2 + \alpha_A \mu_S^2\right) \qquad (4)$$

the permanent dipole $_A$ produces a field strength $F \sim \mu_A / r^3$. This field produces an induced dipole $\mu_i = \alpha F$, where α is the polarizability of the relative molecule. The energy $\varepsilon = -\frac{1}{2}\alpha F^2$ is then proportional to $-\frac{1}{2} \frac{\alpha \mu i^2}{r^6}$. It is important to note here that the induced energy is independent of temperature.

(c) The potential energy between nonpolar molecules has been derived by London (23). For a better understanding of the dispersion or London forces it is useful to consider a nonpolar molecule as a rapidly varying dipole producing an electric field. This electric field will act upon the polarizability of the other molecule and produce an induced dipole in phase with the first. The attraction energy was derived by London as:

$$\bar{\varepsilon}_c = - \frac{3\alpha_A \alpha_s}{2r^6} \cdot \frac{h\nu_{oA} \times h\nu_{os}}{h\nu_{oA} + h\nu_{os}} \qquad (5)$$

Where ν_o refers to the characteristic frequency of a molecule corresponding to its zero point energy.

The contribution of each of these three constituents to the total van der Waals forces may be estimated from those of some pure substances. The expressions for $\bar{\varepsilon}_a$, $\bar{\varepsilon}_b$ and $\bar{\varepsilon}_c$ will apply to similar as well as to dissimilar molecules.

All these interactions are contained in the activity coefficients (γ). The precalculation of (γ) in gas chromatographic systems implies the knowledge of several physical constants that are not simple to evaluate. Martire (24) derived an expression, relating the activity

coefficient of a solute in a dilute solution to dispersion and orientation forces and physical constants of the solute and stationary phase. He used this technique successfully to predict relative volatilities. He also successfully predicted retention times when column operating conditions were known. However, the case was a simple one involving a monomeric stationary phase (N,N-dimethyl-formamide) and hydrocarbon solutes. Stationary liquids used in gas chromatography are sometimes complex molecules for which it is difficult to find some of the physical constants such as dipole moment, polarizability, dielectric constant, refractive index, molar volume, molecular weight etc. required by Martire's system. It is also difficult to formulate a mathematical relationship of general validity between these constants and the activity coefficients. In contrast, Ecknig (20) determined the intermolecular forces responsible for the separation process in a manner independent of gas chromatography. This appeared very promising in practice, since the solvent effect observed in infrared spectroscopy offered itself as a suitable method of measurement.

B. Infrared Spectroscopy and Solvent Effect

The solvent effect in the measurement of spectroscopic parameters, has been studied by numerous investigators. Hallam (25) has studied some theories of solvent shifts in infrared spectroscopy for polar and non-polar solvents. The spectroscopic investigations have shown that the absorption frequencies of dissolved substances depend to a large extent on the properties of the solvent. In

general the characteristic frequency of the polar group of a sample decreases with increasing polarity of the solvent. According to the work of Bellamy and Williams (26) the dominant factors in producing frequency changes, even in relatively nonpolar sovents, are the local association effects between the polar groups of the solute and solvent. In another publication, Bellamy, Hallam and William (27) also found that the solvent effects are purely local, and that some other specific properties of the solvent such as dielectric constant, refractive index etc. play little or no part in determining the size of the frequency shifts in solution. Later Bellamy and Hallam (28) reconfirmed their results. This time, their approach to the study of solvent effect was through inter and intramolecular bonding.

Ecknig (20) ascribed all the interactions to association forces. As early as 1937 Badger and Bauer (29) studied the character of the OH absorption in the case of intermolecular hydrogen bonds, and intramolecular association. They found an approximate proportionality between the energy of the hydrogen bond, and the shift of the OH vibrational frequency. So they concluded that the frequency shifts are a semiquantitative measure of the bond energies.

Josien (30) studied solvent effects and the intermolecular associations between solvents and some functional groups of solutes by infrared spectroscopy. She also calculated enthalpies of formation of the resultant molecular complexes. These enthalpies of formation were compared to the infrared frequency shifts to obtain a proportionality relationship.

This part is ascribed to dispersion forces. By comparison, Ecknig observed that, in the system sample-stationary liquid, gas chromatographic data will express the sum of all intermolecular forces, while infrared spectroscopic data expresses only a representative part of the effective polar forces. However, the effective polar forces are very important in gas chromatography, because the separation of substances with similar boiling points can essentially be brought about by polar effects.

C. Calculations of the Infrared Frequency Shift

The solvent effect can be observed as a shift of absorption frequencies. With the use of a reference solvent, a quantitative treatment can be set up. The absorption frequency (ν_i), for a polar functional group of a solute dissolved in a nonpolar stationary liquid (squalane) is used as a reference frequency. This frequency corrects for the self association of the polar group of the solute, because the self association could also shift the frequency.

The difference between this reference frequency (ν_i squalane) and the absorption frequency of the polar functional group from some solute dissolved in a polar stationary liquid (ν_i stationary liquid), provides the shift $\Delta\nu_i^{Ass}$.

$$\Delta\nu_i^{Ass} = (\nu_{i(\text{squalane})} - \nu_{i(\text{stationary liquid})}) \ (\text{cm}^{-1}) \qquad (7)$$

The choice of squalane as the reference stationary liquid was made because of the fact that many authors (1, 6, 8, 13, 14) have assigned a polarity of zero to this hydrocarbon on their polarity scales.

D. Relationship Between Chromatographic Retention Data and Infrared Frequency Shifts

A relationship between chromatographic retention volumes and infrared spectroscopic frequency shifts is obtained by a thermodynamic consideration of the causes of a gas chromatographic separation, and consideration of the attainable and nonattainable part of the infrared measurements. Therefore Ecknig (20) found that the nonattainable part (dispersion forces) which occurs between alkyl groups of the solute and the stationary liquid, may be eliminated in a first approximation when the retention volume (V_i) of a substance with a polar group (i) is measured relative to a retention volume (V_{st}) of a nonpolar substance in the same stationary liquid. From equation (1) after logarithmic calculation and expansion with RT, the following equation was obtained.

$$RT\ell n\, V_{i,st} = RT(\ell nP^{o}_{st} - \ell nP^{o}_{i}) + RT(\ell n\gamma^{o}_{st} - \ell n\gamma^{o}_{i}) \qquad (8)$$

The indices i and st denote the polar chromatographic sample, and the reference respectively. The first term of equation (8), the vapor pressure ratio, is a constant for a specific pair of substances, at a definite temperature. It is expressed as (a). The second term

can be obtained from equation (2) and will be the difference of the chemical addition potential. So equation (8) is transformed into:

$$RT\ell n\ V_{i,st} = a + \mu^{E}_{st} - \mu^{E}_{i} \qquad (9)$$

As was considered before, individual structural groups of the test molecule, provided characteristic contributions to the intermolecular interaction. Therefore the chemical addition potential can be divided into two parts.

$$\mu^{E} = \mu^{Ass} + \mu^{D} \qquad (10)$$

Where μ^{A} represents the association forces between polar groups from the sample and the stationary liquid, and corresponds to the infrared spectroscopic measurements and μ^{D} represents the dispersion forces between the hydrocarbon residue of the sample and the stationary liquid. The association part (μ^{Ass}) for the nonpolar reference substance is considered to be equal to zero by definition, so equation (9) is transformed into:

$$RT\ell nV_{i,st} = A + \mu^{D}_{st} - \mu^{D}_{i} - \mu^{Ass}_{i} \qquad (11)$$

The dispersion forces μ^{D}_{st} and μ^{D}_{i} are still difficult to compensate for completely. However, Ecknig (20) assumed in his first approximation that the difference ($\mu^{D}_{st} - \mu^{D}_{i}$) within a series of stationary liquids remains constant, because the gas chromatographic sample and reference have the same molecular size. For this case the dispersion forces should change approximately in the same amount from one stationary

liquid to another. Using this assumption the dispersion parts of the chemical potential (equation (11)) can be incorporated into the constant (A) and equation (11) reduces to:

$$RT\ell nV_{i,st} = A - \mu_i^{Ass} \tag{12}$$

The chemical potential μ_i^{Ass} can be expressed by thermodynamics according to Moore (31) as the free energy per mole

$$\mu_i^{Ass} = H^{Ass} - T \cdot S_i^{Ass} \tag{13}$$

The chemical potential depends on enthalpy of association, entropy of association, and also on temperature.

However, the test molecule should contain only one polar group, and the same substance should be used for all the stationary liquids in study. Ecknig could therefore assume constant entropy. He also stated that temperature should remain constant. Taking into account all these considerations, equation (13) can be changed to

$$\mu_i^{Ass} = H_i^{Ass} + C \tag{14}$$

where

$$C = -T \cdot S_i^{Ass} \tag{15}$$

combining equations (12) and (14) and introducing relationship (6) derived by Josien (29), the following expression was obtained

$$RT\ell nV_{i,st} = \sim (A - C + \Delta\nu_i^{Ass}) \tag{16}$$

Then Ecknig introduced a proportionality factor that he called (E). After he rearranged the constants into one term (F) and transformed natural logarithms into common logarithms, he obtained the final expression.

$$\log V_{i,st} = E \cdot \Delta\nu_i^{Ass} + F \qquad (17)$$

This equation is valid only at constant temperature. In practice, it is possible to express the left term of this equation, relative retention volumes, as relative retention times. They are synonymous, according to Rohrschneider (8). Ecknig (20) tested this relationship experimentally and found it to be reliable.

III. EXPERIMENTAL WORK

A. Infrared Spectroscopy

Choice of Solute

The stationary phases were used as solvents in the investigation of the solvent effect. The solute was chosen from Ecknig's (20) work. He used different solutes to study the polarity of different functional groups such as; acetone, propionaldehyde, methyl acetate for C=O bonds; methanol and ethanol for OH bonds; and propyl chloride and butyl chloride for C-Cl bonds. He also studied benzene as a solute to determine the polarity of several stationary phases. After observing Ecknig's results it was found that the C-Cl absorption frequency presented an approximately linear relationship when it was plotted against the logarithm of relative retention volume. It is also important to note that the C-Cl functional group is not very common in the stationary phase molecules; so it was hoped that there would not be many interferences in this region of the infrared spectrum. Considering the above reasons, butyl chloride was the first choice as a solute for the preparations of the solutions for the IR measurements. After the solutions were prepared and the infrared spectra taken, the C-Cl absorption band did not appear. Since butylchloride is volatile (boiling point 78.5 C^{o}(31)) it was found that it would evaporate from the solution in a very short time. To solve this problem, 1-chloro-hexane, which is not very volatile (boiling point 134^{o}C (32)) was substituted for the butyl chloride.

The infrared spectrum of 1-chlorohexane was studied first in order to see if the reagent was really free of water. It was found that it was wet, so it had to be distilled before it could be used. This procedure was very important since the polarity contribution from the water could change the results appreciably, concerning the polarity of the stationary phases.

The solutions should be very fresh because the vapor pressure of 1-chlorohexane is high and it can easily be lost from the solution.

Choice of Instrument

A PERKIN-ELMER 180 double beam infrared spectrometer was used for all the infrared measurements. This instrument provided sufficient sensitivity for the weak C-Cl absorption band. A scale expansion function was also available on the instrument, so that the relatively small frequency shifts (5-10 cm^{-1}) could be measured with a precision of ± 0.3 cm^{-1}. The double beam capacity of the instrument was also used with the pure liquid stationary phase in the reference compartment.

Choice of Cells

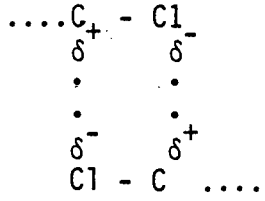
Because the solute that was already chosen is a liquid, the infrared cells should be for liquids. NaCl windows would have less absorption but it was found that KBr was soluble in some of the stationary phases.

In order to improve precision it was necessary that the path length of the cells was constant. It was also necessary to have matching cells; for sample and blank when it was necessary to do compensation of absorption. The choice made to fill those requirements

was to use matching precision cells. Even then it was not possible to use precision cells for some solutions because they were very viscous and difficult to handle; for these cases it was necessary to use the regular separable type of cells.

Choice of Concentration

The concentration of the solutions should be as low as possible in order to avoid self association of the solute. 1-chlorohexane can associate as follows;



This association produces a polar environment which will cause a frequency shift. To correct for this solute-solute association the concentration must be kept very low. The ideal concentration would be infinite dilution.

Solutions of different concentrations of 1-chlorohexane in each stationary phase were prepared. 0.1 M solutions were in general too dilute for measurement. Concentrations up to 1.0 M were tried and 0.25 M was found to be sufficient for most cases. For the stationary phases that absorb too much light, it was necessary to use a higher concentration of 1-chlorohexane. The solutions of 1-chlorohexane in each stationary phase were prepared by weight rather than volume because the solvents were very viscous and accurate volumes were very difficult to measure.

Standardization

A comprehensive check of the overall spectrometer performance was made using polystyrene film as the reference. For the specific frequency region between 600 and 700 cm^{-1}, the 698.9 cm^{-1} peak from polystyrene was used as the reference, because the reference should be as close as possible to the absorption band under study. This 698.9 cm^{-1} peak is very intense. When using the absorption and frequency expansions necessary to obtain good accuracy with the solution, this polystyrene peak was off scale. To solve this problem a thinner film of polystyrene was prepared by taking a little piece from a film and dissolving it in toluene. A couple of drops were placed on a clean and polished NaCl plate. The thinner film worked well for the expansion conditions.

Later it was observed that the infrared spectrometer that was used (PE 180) changes grating and filter at certain frequency (33). This change produces a pause in the scanning and hence a variation in the calibration. It is important that the reference band and the C-Cl band under study have frequencies which are on the same grating and have the same filter.

An alternate method of frequency calibration was to use an absorption frequency of carbon dioxide. The closest absorption band for atmospheric CO_2 was reported by the D.M.S. (34) to be at 667.4 cm^{-1}. This absorption band can be easily obtained by operating the instrument in the single beam mode. All of the infrared spectra were calibrated with either polystyrene or carbon dioxide; either method is acceptable.

Solid and Semi-Solid Stationary Phases: Extrapolation from Solutions

Some of the stationary phases used in this experiment were either solid or semi-solid. The technique used to study the polarity of the stationary phases, was the solvent effect (24). This means that the stationary phases are supposed to be the solvents.

However, because of the solid or semi-solid nature of some of the stationary phases, other solvents were necessary. The ideal solvent should have the same functional groups as the stationary phase under study.

Mixtures with different proportions of solvent and stationary were prepared, with a constant concentration of 1-chlorohexane in every mixture. The frequency shift ($\Delta\nu$) was measured for each solution. Plotting the frequency shift ($\Delta\nu$) against the percent composition of solvent and stationary phase yields a straight line with a minimum slope (the experimental proof of this will be given later in this chapter).

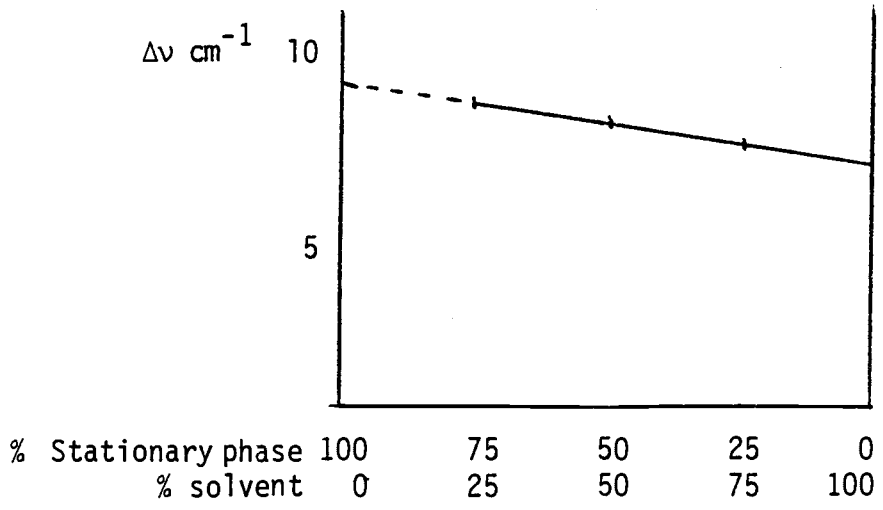


Figure 1. Extrapolation technique to measure the frequency shift ($\Delta\nu$) for solid and semi-solid stationary phases.

The similarity between solvent and stationary phase is responsible for the linearity and the low slope of the line. By extrapolating to 100 percent stationary phase it was possible to obtain the frequency shift of the C-Cl bond due to the polar effect of the stationary phase.

Infrared Procedure

First, the stationary phases used as solvents were carefully studied, taking the full infrared spectrum in order to observe if they contain some water and also to see if they present some absorption that could interfere with the C-Cl absorption frequency (600-700 cm^{-1}). When the stationary phases were wet, the water was removed using molecular sieves. If the stationary phases presented some absorption at this frequency (600-700 cm^{-1}), either the use of a blank or compensating techniques were used. The compensating techniques suggested by Potts (35) were used in cases that the spectra were difficult to interpret because of overlapping or when the solvent absorbs too much light that the baseline goes down to 10 to 20 percent of transmittance.

After these properties of the stationary phase were known, then solutions of 1-chlorohexane in each stationary phase were prepared. The infrared spectrum was taken with the fresh solution. Sometimes it was necessary to prepare more solutions with a higher concentration (0.10-1.00 M). For highly viscous stationary phases, the solutions were heated a little in order to make the injection of sample into the infrared cell easier. Solution was scanned at least three times

and every time the wavelength reference was scanned too. The measurement of the C-Cl frequency bond was done with a large expansion in order to decrease the uncertainty.

B. GAS CHROMATOGRAPHY

Choice of Solutes

It was necessary to correlate the relative retention times of gas chromatographic solutes to the infrared frequency shifts. According to Ecknig's equation (17; Chapter 2) these two parameters should maintain a linear relationship under the conditions proposed in the assumptions made in the theory section. The retention times of chromatographic solutes should be measured relative to a reference substance for each stationary phase. The reference substance should be similar to the solute in every way except for the presence of a polar group in the solute. Ecknig (20) used the same solutes for both infrared and chromatographic determinations. In the present work it was decided to have different solutes for the two techniques.

The decision was made to use an alkene as the solute and the corresponding alkane as the reference. Any separation between the hydrocarbons would be caused by the interaction of a polar group of the stationary phase under study with an induced dipole in the olefin group. Three different solutes (1-octene, trans-2-octene, and 1,7 octadiene) were studied with octane as the reference.

Instrumentation

A gas chromatograph PERKIN-ELMER model 3920 was used. This is a versatile laboratory instrument. It can be used either as a single-column or dual-column instrument, which was very convenient in this work. Its oven (36) is designated for precise control of column temperature. It also includes a heated interface to ensure that there is no sample condensation in the injection system. The chromatograph was equipped with a flame ionization detector in which an air-hydrogen flame is used to ionize sample components in the column effluent. An electrode above the flame collects the resulting electrons and applies the ionization current to the input of an electrometer amplifier. Because of the air-hydrogen flame of the detector, it was not possible to use air to obtain the unretained time. Therefore, methane was used for that purpose.

Helium was the carrier gas and hypodermic syringe was used for injection.

Choice of Solid Support

The main emphasis of this study in gas chromatography is to observe the interactions between stationary phase and solute, and to establish a polarity relationship for the staionary phases. It is important to use a solid support that will produce very low adsorption.

Adsorption by the solid support might distort the retention pattern and may alter predicted separations and retention ratios due to the characteristics of stationary phases.

As stated by Hawkes (37), the glass bead surface is small so only a small amount of liquid can be supported (commonly up to 0.5 percent of the weight of the beads). The small surface area also has the advantage that the glass surface will cause little adsorption of the sample.

For these reasons, glass bead support was used. The smaller the size of the beads, the smaller are the spaces between the beads and, therefore, the lower is the zone dispersion or plate height. This suggests that the beads must be as small as possible. But smaller beads need a high pressure to force the mobile phase through the packing and also have a greater ratio of surface area to column volume and consequent risk of adsorption. In this work the main concern is not efficiency but resolution, so that moderately large beads could be used. Therefore the glass beads that were used were 60 to 80 mesh.

Construction of Columns

The material for the gas chromatographic columns that were used, according to Hawkes (38) should have the following characteristics;

1. It should not catalytically decompose the sample.
2. It should not absorb the sample.
3. It should be capable of being packed with an efficient packing structure.
4. It should be pliable enough to be coiled after packing.
5. It should be easily installed.

Stainless steel was decided to be the most satisfactory material with the above conditions. The columns were constructed of the same length (6 feet). The stainless steel should be washed first. The procedure to clean them was;

1. Rinsing with chloroform.
2. Rinsing with methanol.
3. Washing out with water.
4. Washing out with HNO_3, 6N.
5. Rinse with plenty of water.
6. Rinsing with methanol again.
7. Dry it with nitrogen, helium or air.

Packing of the columns was done observing certain rules that are provided by Supina (39).

1. Assure uniform distribution of phase.
2. Avoid breakage of support particles.
3. Avoid use of highly volatile solvents.
4. Minimize oxidation or loss of packing.

The packing procedure used was the evaporative method suggested by Supina (40).

At first the volume of the column was calculated and then it was considered that only 62 percent of this volume was occupied by the glass beads. Knowing the approximate density of glass beads (2.98 g/ml) it was able to figure out the weight of glass beads needed to pack the column. The amount of stationary phase needed to coat the glass beads was 0.5 percent of the glass bead weight. The stationary phase was

dissolved completely in the volatile solvent such as acetone, chloroform or methanol. If there was any residue remaining it was filtered off. The glass beads were then poured slowly into the solution of stationary phase, followed by mixing and stirring continually while heating on a hot plate until the solvent was almost completely evaporated.

This evaporative method was very useful because the solutions of some stationary phases were very viscous and difficult to handle by other techniques. Then the columns were packed using a combined technique of both vibration and bouncing.

Procedure

Each column was conditioned by heating it in the oven by the gas chromatograph at a temperature higher than the highest temperature at which the stationary phase under study was to be used while passing helium through the column. This conditioning was done for two hours.

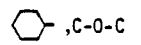
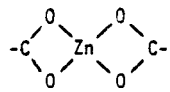
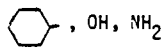
A mixture of homologous series of hydrocarbons was run first, using methane gas to measure the unretained time. The retention time of each hydrocarbon was measured. The logarithms of the retention times of the n-hydrocarbons were plotted against the number of carbon atoms for each stationary phase. The homologous n-alkanes produced straight lines, and the slopes and intercepts are reported in Table VI.

Mixtures of chromatographic solutes and the reference were prepared in a proportion of about 70 percent of solute and 30 percent of the reference. The lower percentage of the reference substance

was used because it was expected that it would be retained less than the solute in a polar stationary phase. The individual retention of each solute and reference substance were also measured at least three times. For some of the most complex stationary phases the relative retention times were measured at several temperatures looking for an explanation of unexpected retention times that were obtained.

TABLE I

Change of the C-Cl frequency under the influence of stationary liquids.

No.	Stationary Phase	Functional Group	Density d_4^{20} (g/ml)	C-Cl Frequency (cm^{-1})	± σ	Δν (cm^{-1})
1	Squalane	C-H	0.8115 (32)	653.72 655.60 655.72 655.10 654.30 654.40 654.10 Ave. 654.71	0.66	0.00
2	Tetrahydroxyethyl-ethylenediamine (THEED)	OH, NH_2	1.13 (a)	(b)		1.80
3	Polypropylene Glycol	OH, C-O-	1.0030 (32)	652.10 652.00 652.10 651.60 Ave. 651.95	0.21	2.76
4	Poly-m-phenyl Ether	 ,C-O-C	1.22 (a)	651.25 651.25 651.20 651.25 651.22 Ave. 651.23	0.02	3.48
5	Zinc Stearate			650.90 651.00 651.20 Ave. 651.03	0.13	3.68
6	Kel-F oil No. 10	C-F, C-Cl	1.97 (a)	648.90 649.40 648.90 648.90 Ave. 649.03	0.22	5.68
7	Phenldiethanolamine Succinate	 , OH, NH_2		(b)		7.50
8	Carbowax 400	OH, C-O-	1.125 (32)	(b)		8.60
9	β,β'-oxydipropionitrile	C≡N, C-O-C	1.043 (32)	644.80 644.80 644.02 Ave. 644.54	0.37	10.17
10	N,N-Bis(2-cyanoethyl)-formamide	C≡N, C=O, C-N	1.15 (a)	643.90 644.50 644.00 644.30 644.00 Ave. 644.14	0.23	10.57

a) Measured in the laboratory.

b) The frequency shift was taken by extrapolation.

TABLE II

Infrared shifts for 0.25 M solutions of 1-chlorohexane in mixtures of phenyldiethanolamine succinate and acetone.

Phenyldiethanolamine Succinate (percentage)	Acetone Percentage	C-Cl Frequency (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\pm \sigma$
25	75	647.22 647.40 647.50	7.49 7.31 7.21 Ave. 7.34	0.10
50	50	647.40 647.30 647.50	7.31 7.41 7.21 Ave. 7.31	0.070
60	40	647.05 647.10 647.40	7.66 7.61 7.31 Ave. 7.53	0.14

Linear Regression Calculation

$$\Delta\nu = mA + \Delta\nu_o$$

$\Delta\nu_o$ = intercept = 7.622

m = slope = -0.004154

correlation coefficient = -0.62770

TABLE III

Infrared shifts for 0.50 M solutions of 1-chlorohexane in mixtures of Tetrahydroxyethylethylenediamine and methanol.

THEED Percentage	Methanol Percentage	C-Cl Frequency (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\pm \sigma$
25	75	653.10	1.61	
		652.45	2.26	
		652.90	1.81	
			Ave. 1.89	0.24
50	50	652.60	2.11	
		653.20	1.51	
		653.40	1.31	
		653.40	1.31	
			Ave. 1.56	0.28
75	25	653.15	1.56	
		652.45	2.26	
		652.45	2.26	
			Ave. 2.03	0.31

Linear Regression Calculation

$\Delta\nu_n = mA + \Delta\nu_o$

$\Delta\nu_o$ = incercept = 1.97

m = slope = -0.0028

correlation coefficient = -0.290076

TABLE IV

Frequency shifts for 0.25 M solutions of 1-chlorohexane in mixtures of Carbowax 400 and Triethylene glycol.

Carbowax 400 Percentage	Triethylene glycol Percentage	C-Cl frequency (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\pm \sigma$
50	50	646.10	8.61	
		645.80	8.91	
			Ave. 8.76	0.15
62.5	37.5	644.90	9.81	
		644.80	9.91	
		644.70	10.01	
			Ave. 9.91	0.07
75	25	646.50	8.21	
		646.60	8.31	
		646.20	8.51	
			Ave. 8.34	0.11
85.5	12.5	645.20	9.51	
		645.60	9.11	
		645.70	9.01	
			Ave. 9.21	0.20
100	0.0	645.40	9.31	
		645.60	9.11	
		645.20	9.51	
		645.20	9.21	
			Ave. 9.28	0.12

Linear Regression Calculation

$\Delta\nu = mA + \Delta\nu_o$

$\Delta\nu$ = intercept = 9.168

m = slope = -0.00272

correlation coefficient = -0.09110

TABLE V

Gas Chromatographic Results

Relative retention times of n-alkanes in each stationary phase.

Stationary Phase	Carbon Number		Relative Retention Time
Squalane	6		1.00
	7		4.20
	8		10.97
	9		29.21
	10		75.95
Polypropylene glycol	6		1.00
	7		2.28
	8		5.00
	9		11.50
	10		24.77
Poly-m-phenyl ether	6		1.00
	7		2.21
	8		4.88
	9		10.66
	10		23.20
Kel-F oil No. 10	6	1.00	---
	7	2.16	1.00
	8	4.77	2.23
	9	10.30	4.73
	10	22.12	10.28
	11	---	22.06
Phenyldiethanolamine succinate	10	1.00	1.00
	11	4.73	4.55
	12	9.72	9.54
	13	21.20	20.43

TABLE V Continued

Stationary Phase	Carbon Number	Relative Retention Time
β,β' oxydipropionitrile	8	1.00
	9	2.018
	10	4.123
	11	8.189
	12	19.298
Tetrahydroxyethylethylene diamine	10	1.00
	11	3.69
	12	7.13
	13	13.79
N,N-Bis(2-cyanoethyl) formamide	10	1.00
	11	1.667
	12	3.170
	13	6.140
	14	12.450
Carbowax 400	7	1.00
	8	1.87
	9	3.46
	10	6.50
	11	12.09
Zn Stearate	8	1.00
	9	1.86
	10	3.33
	11	6.143
	12	11.86

TABLE VI

Regression constants for n-alkanes. log t_s = A + B (carbon number).

No.	Stationary Phase	Correlation Coefficient	Slope (B)	Intercept (A)	Temperature (°C)
1	Squalane	0.99612	0.4597	-2.6770	50
2	Polypropylene glycol	0.99993	0.3489	-1.9678	75
3	Poly-m-phenyl ether	0.99999	0.3414	-2.0462	75
4	Kel-F oil No. 10	0.99998 0.99996	0.3369 0.3352	-2.0210 -2.3410	75
5	Phenyldiethanolamine succinate	0.99991 0.99999	0.3306 0.3272	-3.3026 -3.3026	75
6	β,β'oxydipropionitrile	0.99971	0.3209	-2.5790	50
7	THEED	0.99999	0.2849	-2.8502	75
8	N-N-Bis(2-cyanoethyl)-formamide	0.99839	0.2756	-2.7860	75
9	Carbowax 400	0.99999	0.2705	-1.8933	75
10	Zn Stearate	0.99980	0.26669	-2.13604	130

TABLE VII

Relative retention times of 1-octene, trans-2-octene and 1,7-octadiene using n-octane as the reference.

No.	Stationary Phase	(cm^{-1})	r $\frac{\text{1-octene}}{\text{n-octane}}$	±	r $\frac{\text{trans-2-octene}}{\text{n-octane}}$	±	r $\frac{\text{1,7-octadiene}}{\text{n-octane}}$	±
1	Squalane	0.00	0.860 0.829 0.790 Ave. 0.823	0.029	0.987 0.966 0.971 Ave. 0.975	0.0896	0.736 0.732 Ave. 0.734	0.0020
2	Polypropylene Glycol	2.76	1.07 1.07 1.14 Ave. 1.093	0.033	1.007 1.290 1.210 Ave. 1.169	0.119	1.20 1.14 1.19 Ave. 1.176	0.026
3	Poly-m-phenyl Ether	3.48	1.20 1.19 1.00 Ave. 1.13	0.092	1.390 1.395 1.370 Ave. 1.385	0.0108	1.38 1.37 1.36 Ave. 1.37	0.0082
4	Zinc Stearate	3.68	1.019 0.990 1.005 Ave. 1.005	0.012	0.970 1.004 0.991 Ave. 0.989	0.0140	0.880 0.880 0.880 Ave. 0.880	0.0
5	Kel-F oil No. 10	5.68	0.940 1.030 1.000 Ave. 0.990	0.037	1.290 1.00 1.00 Ave. 1.097	0.136	1.06 1.00 1.00 Ave. 1.02	0.028
6	Phenyldiethanolamine Succinate	7.62	1.360 1.450 1.060 Ave. 1.290	0.17	1.14 1.14 1.00 Ave. 1.094	0.066	1.55 1.45 1.45 Ave. 1.483	0.047
7	Carbowax 400	9.28	1.44 1.42 1.38 1.39 1.42 1.33 Ave. 1.397	0.036	1.71 1.54 1.74 1.56 1.44 1.62 Ave. 1.602	0.102	2.07 2.01 2.09 2.02 Ave. 2.05	0.034
8	β,β'oxydipropionitrile	10.17	1.66 1.66 Ave. 1.66	0.00	1.44 1.55 1.53 Ave. 1.51	0.048	2.04 2.10 2.03 Ave. 2.06	0.031
9	N,N-Bis(2-cyanoethyl)-formamide	10.57	1.92 1.96 Ave. 1.94	0.020	1.00 1.00 1.00 Ave. 1.00	0.00	2.23 2.68 2.80 Ave. 2.57	0.245

Note: Tetrahydroxyethyldiamine (THEED) was not included because the data obtained were not reliable.

TABLE VIII

Retention data on Zinc stearate at different temperatures (cm. of chart).

Temperature (C°)	110	130	150
methane	8.20	8.60	8.68
n-octane	11.73	11.18	10.70
1, 7-octadiene	11.20	10.88	10.52
n-octane	11.72	11.22	10.78
1, 7-octadine	11.37	10.95	10.59
methane	8.40	8.64	8.70
methane	8.50	8.64	8.70
trans-2-octene	11.90	11.18	10.85
methane	8.55	8.62	8.65
trans-2-octene	11.90	11.23	10.78
methane	8.48	8.65	8.70
1-octene	11.55	11.30	10.60
methane	8.50	8.75	8.65
1-octene	11.60	11.32	10.60
$r \frac{\text{1-octene}}{\text{n-octane}}$	0.87 0.88	1.019 0.990	0.950 0.922
$r \frac{\text{trans-2-octene}}{\text{n-octane}}$	0.97 0.95	0.977 1.004	1.034 1.044
$r \frac{\text{1:7 - octadiene}}{\text{n-octane}}$	0.85 0.901	0.88 0.88	0.893 0.917

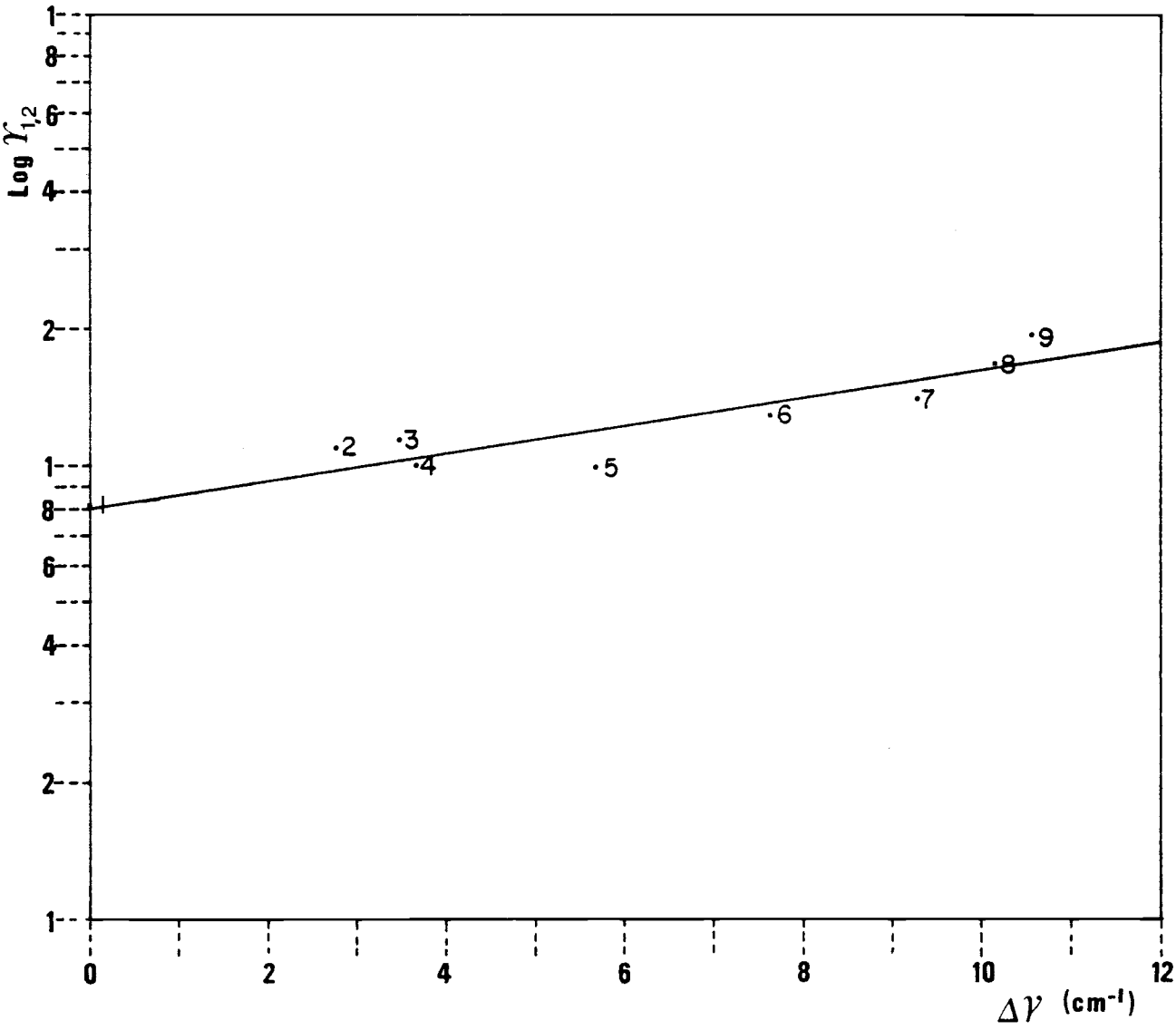


Figure 2. Logarithm of the relative retention times of 1-octene/n-octane ($\log r_{1,2}$) versus the C-Cl infrared frequency shift $\Delta\nu(cm^{-1})$

1-Squalane, 2-Polypropylene glycol, 3-Poly-m-phenyl ether
4-Zinc stearate, 5-Kel-F-oil, 6-Phenyldiethanolamine succinate
7-Carbowax 400, 8-β,β' oxydipropionitrile, 9 - N,N-Bis (2-cyanoethyl) formamide.

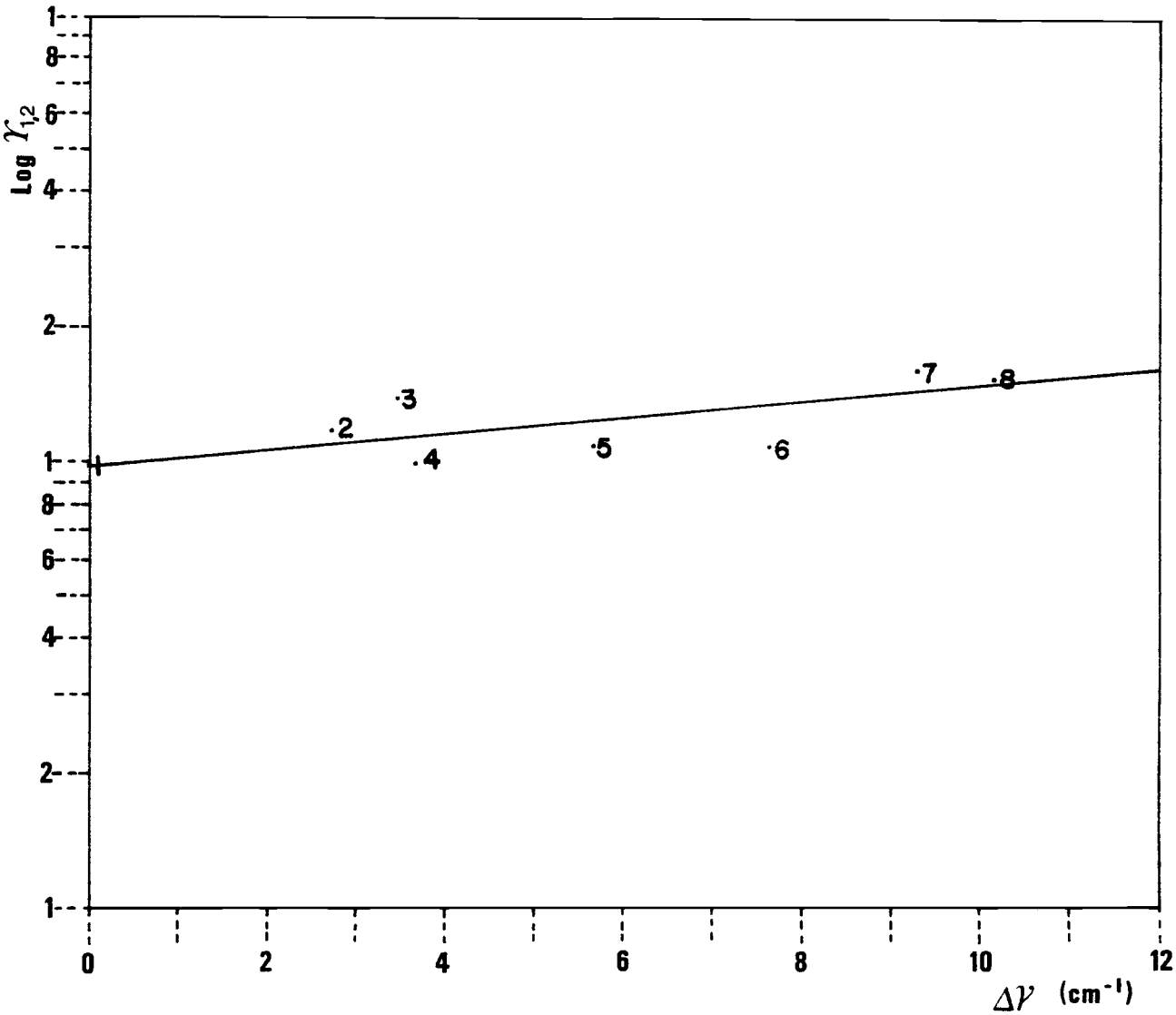


Figure 3a. Logarithm of the relative retention times of trans-2-octene/n-octane (log $r_{1,2}$) versus the C-Cl infrared frequency shift $\Delta\nu$ (cm^{-1}) , excluding stationary phase No. 9. 1-Squalane, 2-Polypropylene glycol, 3-Poly-m-phenyl ether 4-Zinc stearate, 5-Kel-F-oil, 6-Phenyldiethanolamine succinate 7-Carbowax 400, 8-β,β' oxydipropionitrile, 9-N,N-Bis (2-cyanoethyl) formamide.

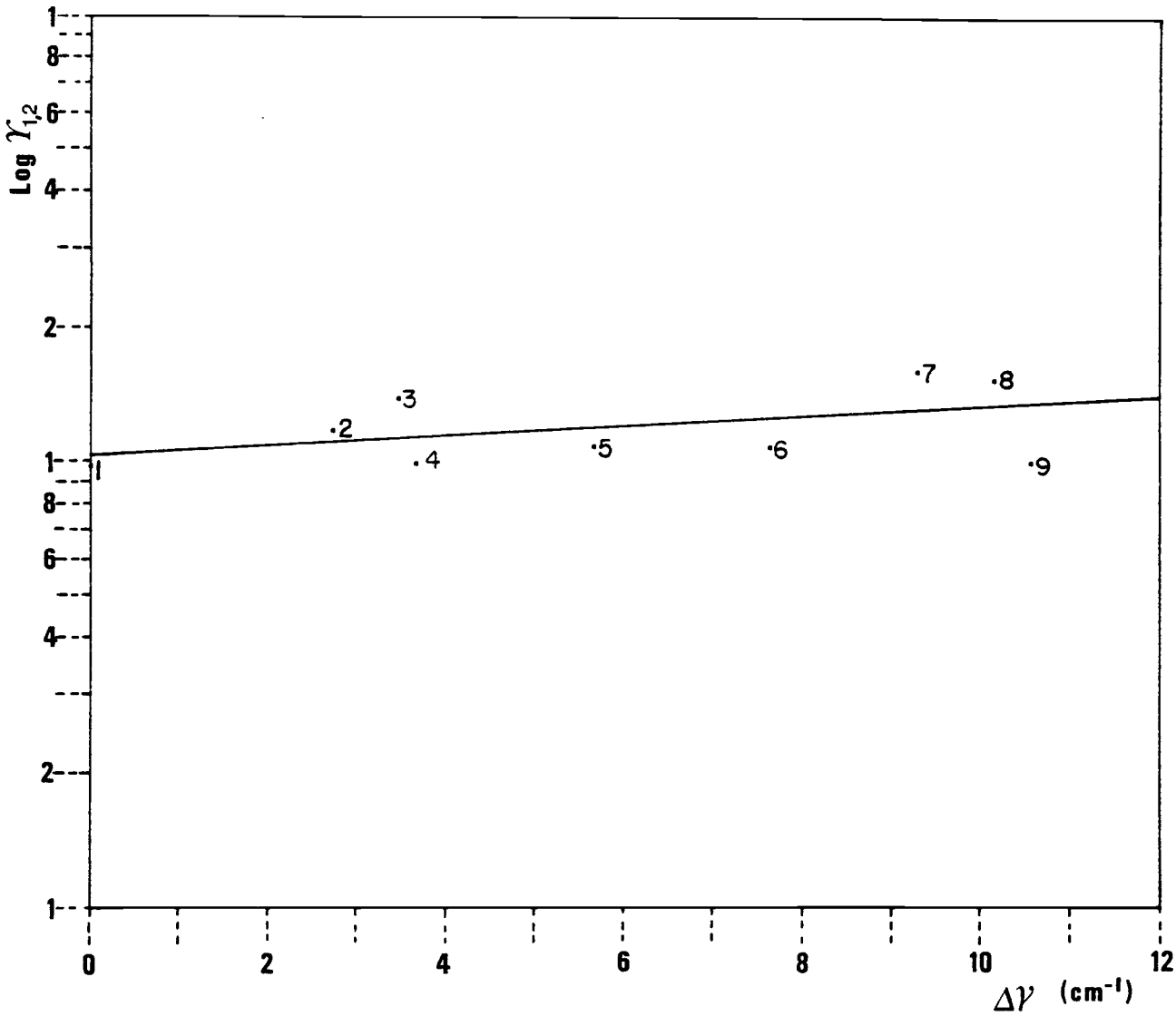


Figure 3b. Logarithm of the relative retention times of trans-2-octene/n-octane (log $r_{1,2}$) versus the C-Cl infrared frequency shift $\Delta\nu$ (cm^{-1}).

1-Squalane, 2-Polypropylene glycol, 3-Poly-m-phenyl ether
4-Zinc stearate, 5-Kel-F-oil, 6-Phenyldiethanolamine succinate
7-Carbowax 400, 8-β,β' oxydipropionitrile, 9-N,N-Bis (2-cyanoethyl) formamide.

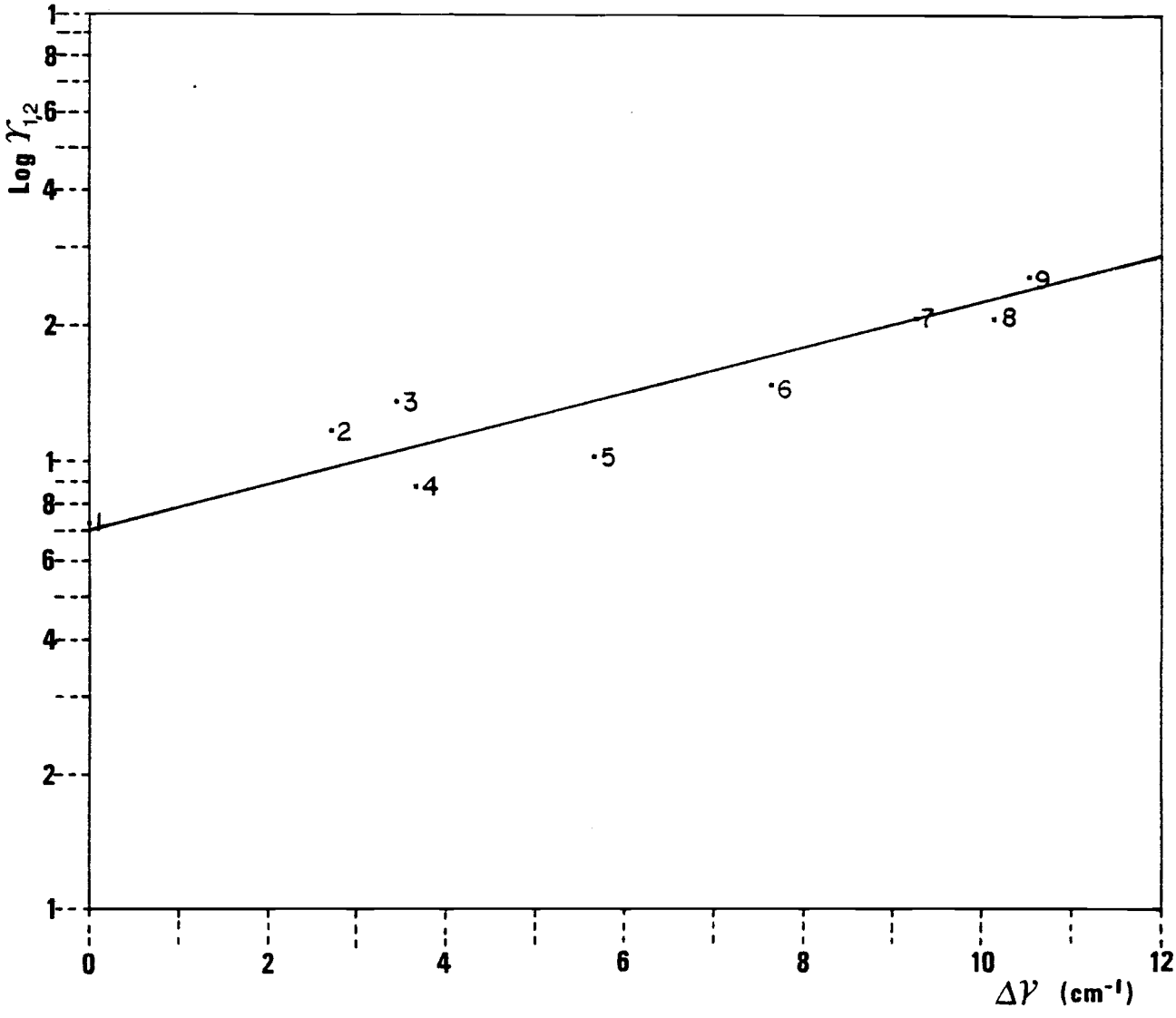


Figure 4. Logarithm of the relative retention times of 1,7-octadiene/n-octane (log $r_{1,2}$) versus the C-Cl frequency shift $\Delta\nu$ (cm^{-1}).

1-Squalane, 2-Polypropylene glycol, 3-Poly-m-phenyl ether
4-Zinc stearate, 5-Kel-F-oil, 6-Phenyldiethanolamine succinate
7-Carbowax 400, 8-β,β' oxydipropionitrile, 9-N,N-Bis (2-cyanoethyl) formamide.

TABLE IX

Correlations for log relative retention times against frequency shifts ($\Delta\nu$)

Correlation Constants	r $\frac{\text{1-octene}}{\text{n-octane}}$	r $\frac{\text{trans-2-octene}}{\text{n-octane}}$	r $\frac{\text{1,7 octadiene}}{\text{n-octane}}$
Correlation coefficient	0.8935	0.24445 0.69648*	0.9000
Slope (E)	0.08589	0.013668 0.047847*	0.15059
Intercept (F)	0.7506	1.08148 0.97242*	0.59173

*Stationary phase No. 9, not considered (referring to Figure 3a).

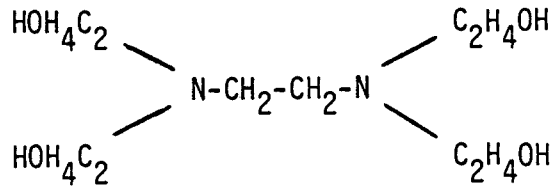
IV. DISCUSSION AND CONCLUSIONS

Table I first shows a survey of the stationary phases that were studied. It includes the structure of the functional groups that each stationary phase has in its molecule: this is useful as background in order to compare the magnitude of the infrared frequency shifts, to the expected polarity strength, by simple consideration of the possibility of association between the functional group of the infrared sample (1-chlorohexane) and the stationary phases. This table also shows the density of the liquid stationary phases. Some of them were not found in the literature and they were measured in the laboratory. The infrared frequency for the C-Cl band of 1-chlorohexane dissolved in each stationary phase is reported in different multiplicity because each solution has specific problems (that will be discussed later) that made their measurement distinctly different. The next column shows the standard deviation ($\pm\sigma$) in the measurement of each frequency, and the last column the average frequency shifts obtained. As was mentioned before, squalane was used as the reference stationary phase. That means that its average C-Cl frequency in squalane (654.71 cm^{-1}) was the reference. Each C-Cl frequency was subtracted from this value to obtain the frequency shifts ($\Delta\nu$). Tables II, III and IV, show the data obtained for THEED, phenyldiethanolamine succinate, and carbowax 400 respectively, by the extrapolation technique, used to measure the

C-Cl frequency shift for solids and for liquids too viscous to mount in the cells. 1-Chlorohexane was dissolved in mixtures of each stationary phase and a solvent and the resulting infrared shifts were extrapolated to the pure 100 percent stationary phase. Tables V and VI present the gas chromatographic retention times obtained for the homologous series of hydrocarbons, and the linear regression results applied for each stationary phase under study. Table VII shows the relative retention times of 1-octene, trans-2-octene and 1,7-octadiene with n-octane as the reference on each stationary phase. Table VIII is a complementary retention data on Zinc Stearate that confirm the results reported in Table VII.

A. Tetrahydroxyethylethylenediamine (THEED)

THEED is shown in Table I. In fact, THEED was a very difficult stationary phase to be used as solvent in the solvent effect technique used in infrared to measure the C-Cl frequency bond. When THEED was first scanned to study its infrared spectrum to be used as solvent it was found that it presents so much absorption that it blocked out the light completely even when using a very thin spacer between the NaCl plates of the infrared cell. This difficulty was due to the



Structure of THEED

complexity of infrared spectrum in the 700-600 cm^{-1} region. It could possibly be caused by the rocking and bending motions of the molecule's carbon skeleton. In order to correct for this intense absorption it was necessary to dilute the THEED with a suitable solvent. The dilution was made with methanol because it was one of the few compounds that is miscible with THEED.

Table II shows the results obtained in the extrapolation techniques used to measure the C-Cl frequency shift under the THEED effect. As it was stated in Chapter III, the plot was expected to be linear but the correlation coefficient shows that it was not. The results seemed to be completely random, maybe because methanol was not a good choice to do the dilution of the THEED. The presence of many hydroxyl groups can produce hydrogen bonding effect which can also shift the C-Cl frequency bond. It was also expected to have a minimum slope in the linear relationship between frequency shifts and the different mixtures of THEED and methanol. In fact it was very low, maybe because of the randomness of the data obtained. The intercept that was obtained (see Table II) represents the frequency shift ($\Delta\nu$) of the C-Cl band dissolved in THEED. This value was (1.97 cm^{-1}) related to the gas chromatographic retention data on THEED as stationary phase through Ecknig's (17; Ch. 2) relationship. The gas chromatographic retention data did not follow the pattern either: so this data was not reported in Table VII because it was not reliable. The principal problem was that the methane, which was used to measure the unretained time, was retained almost the same time as the sample and the reference, so that made it

difficult to figure out the relative retention time. Three different temperatures were used in the gas chromatographic measurements, (30^{o}, 50^{o} and 75^{o}C) using the three different gas chromatographic samples (1-octene, trans-2-octene, and 1,7-octadine and n-octane as the reference for all of them). In all cases the n-octane peak was too close to the unretained methane peak to give reliable retention ratios.

B. Zinc Stearate

The next anomalous result that was obtained, and is reported in Table I was the infrared data from the study of Zinc Stearate. First of all it is important to mention that it is a solid and it is soluble only in a few possible solvents. The one which is commonly reported (32) is benzene but because of the danger of working with this chemical, this possibility was neglected. But it was decided to try with toluene. Zinc stearate was slightly soluble in toluene and since it did not present any considerable infrared absorption at the frequency of interest (700-600 cm^{-1}), it was decided to use toluene to prepare the extrapolation technique to measure the C-Cl frequency shift. The difficulty came when it was found that the solubility of zinc stearate in toluene has a very low limit (1:8) so it was very difficult to prepare the mixtures to build up the extrapolation technique. Because of all those problems it was decided to estimate the C-Cl frequency shift in zinc stearate by assuming that it was equal to that given by a 1:8 solution of zinc stearate in toluene. With the use of an appropriate blank, the frequency was measured without problem. Of course, it has to be clear

that this C-Cl frequency measurement was an approximation, relying on the inertness of the toluene.

A further solubility problem with zinc stearate, is the contamination with zinc oxide. Both zinc stearate and zinc oxide have been investigated by Roberts et al. (41) by infrared at different temperatures and they have found the presence of a liquid crystal state which disappeared at 127 to 132^{o}C. This fact produces some changes in the infrared spectrum and also in the gas chromatographic data because of the formation of liquid crystals, as shown by Roberts et al (41). The presence of these liquid crystals could change the separation in gas chromatography expected from the polarity of the stationary phase.

The additional retention data provided in Table VIII did not improve much the knowledge about this stationary phase because the gas chromatographic samples and the reference did not present serious steric differences, which is the main factor to separate samples in stationary phases forming liquid crystals. It may be that the greater rigidity of the olefin molecules provided sufficient steric difference to account for the data. Thus it is suggested to use m- and p-xylene to be separate on zinc stearate under its liquid crystal behavior.

C. Kel-F

Kel-F oil No. 10 was another peculiar stationary phase. The presence of C-F and C-Cl vibrations bonds, even though they are in low proportion, may distort the measurements of the C-Cl frequency shift. The absorption band from the solvent (Kel-F oil No. 10) was compensated

with the use of a proper blank and matched precision infrared cells. Even so, there is always the possibility of a non-complete compensation of the bands and it may result in an erroneous C-Cl frequency shift measurement.

The gas chromatographic retention data obtained, seems to be too low for the correspondent frequency shift according to Figures 2, 3, and 4. It is suggested to use several compensation techniques for the infrared frequency measurements. Such as increasing the resolution of the instrument, scanning several solutions of different concentrations and by comparison it may be able to see the differences in the absorption of the band.

D. Regression Constants for n-alkanes

Table VI, includes the gas chromatographic data obtained when homologous series of n-alkanes were run on each stationary phase. As Rohrschneider (42) has found experimentally, the representation of retention data in a logarithmic scale produced relatively simple relationships with the number of carbon atoms of the solute molecules; in this case n-alkanes were the solutes. The logarithm of the retention times as is shown in Table V were plotted against the number of carbon atoms for each stationary phase. The homologous n-alkanes produced straight lines as shown in Table VI by the correlation coefficients obtained after applying linear regression calculation. The slope of those lines were also calculated. According to Rohrschneider (42) the magnitude of these slopes represents a criterion to consider the

polarity of the stationary phase. As the slope increases, the retention times of the solutes also go up but the polarity of the stationary phase decreases at the same temperatures. As shown in Table VI, even though the temperature was not constant, the magnitude of the slope is increasing, in the same direction as the results in the Table VII are growing; with a few exceptions. The stationary phases that behaved differently in Tables VI and VII are: zinc stearate which was discussed as having specific problems such as the formation of liquid crystals at 127-132^{o} (this data was taken at 130^{o}C) and also could present electron donor and acceptor effects. THEED has difficulties in the measurement of the retention data. It also had complex infrared absorption producing anamalous results.

Carbowax 400 showed (Table VI) a higher polarity position by the regression data for n-alkanes than the polarity obtained by the use of Ecknig's equation (Table VII). This could be because Carbowax 400 presents hydrogen bonding effects, which will also prevent solution of n-alkanes and decrease the slope.

The numerical values of the slopes obtained from regression data (Table VI) were compared to the slopes reported by McReynolds (13) and it was found that they can not be expected to be equal because McReynolds used 120^{o}C and in the present work different temperatures were used (see Table VI) but the most commonly used was 75^{o}C. However, it was possible to compare the order of the slopes with other scales of polarity in a qualitative way.

E. Ecknig's Relationship

The logarithm of the relative retention times (log $r_{1,2}$) for 1-octene, trans-2-octene and 1,7-octadiene with n-octane as the reference, was plotted against the C-Cl frequency shift ($\Delta\nu$) as shown in Ecknig's equation (17; Ch. 2). The correlation constants obtained are shown in Table IX. The correlation coefficients obtained by linear regression were a little different for each gas chromatographic solute. In general, it has to be considered that there were deviations to the parameters that were initially discussed in the theory section.

Ecknig (20) stated that the temperature should be constant for the two experimental techniques that were involved in the use of Ecknig's equation (17; Ch. 2). This requirement is important because the temperature was involved in two ways in this relationship. First, equation (1; Ch. 2) was expanded with the gas constant (R) and the absolute temperature (T). The temperature-dependent term came at the end of Ecknig's equation (17; Ch. 2) and it was assumed to be constant. Second, when the association chemical potential was expressed thermodynamically, (equation (13; Ch. 2)) per mole it depended on temperature and it was assumed to be constant according to equation (15; Ch. 2). Therefore, temperature should be a very critical parameter. In the present work, it was found difficult to maintain the temperature constant because of specific physical properties of the stationary phases under study. For example, zinc stearate is a solid with a melting point of 120^{o}C, so the gas chromatographic determinations were done at

130°C, while the rest of stationary phases were done at 50° or 75°C. Conversely, β,β'-oxydipropionitrile could not be used at 130°C because it evaporates from the column at temperatures above 75°C.

It was intended to use as low a temperature as possible in order to agree with the infrared determinations (40°C). But most of this work was done during the summer when the room temperature might be that high so it was decided to use 75°C to obtain a stable temperature. In the infrared determinations there was no heated cell available so the work had to be performed at ambient temperature.

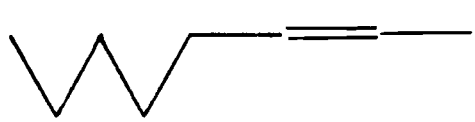
Another important assumption that Ecknig (20) made was that the entropy was the same for the solute and the non polar reference used in gas chromatography. Similarly in this case it was assumed that the entropy of the alkene used as solute and n-alkane used as reference were equal, so that they canceled out. This was expected since the size of solute and reference were almost the same. Littlewood suggested that the entropy of mixing could be assumed to be negligible compared to the magnitude of the enthalpy. However, other entropy effects in solution such as those involved in dipole-dipole interaction or hydrogen bonding may not be negligible and may well be different between octane and octene. Ecknig also assumed that the dipole interactions due to the reference alkane in gas chromatography were negligible. That might not be exactly true and it could produce the deviation of the results obtained in these experimental graphs (Figures 2, 3 and 4). In examining the results it also was found that one of the most important assumptions to ensure the validity of the relationship used in the present work,

was that the infrared frequency shift ($\Delta\nu$) was directly proportional to the enthapy of vaporization (30) of 1-chlorohexane (ΔH_{C-Cl}) in gas chromatography, and also to the enthalpy of an alkene (ΔH_{ene}) due to this dipole interaction. Josien (30) confirmed this relationship experimentally in the general sense, but still for the specific conditions used here it is not very clear if they could deviate.

According to the results plotted in Figures 2, 3 and 4, the three olefins behave differently from each other.

The use of 1-octene/n-octane seems to be a good approach for the study of stationary phases that are very polar. As shown in Figure 2, the stationary phase that deviated the most, excepting Kel-F (Stationary Phase No. 5), that presented the problems already mentioned, was N,N-Bis (2-cyanoethyl)formamide which resulted in the most polar.

In general, the results obtained in the gas chromatographic part using trans-2-octene do not correlate well with the infrared frequency shifts. The correlation coefficient was the lowest obtained (see table IX). The correlation coefficient was also reported excluding the N,N-Bis (2-cyanoethyl)formamide (Stationary Phase No. 9) data and it was improved considerably (Figure 3a). However, the distribution of the results from trans-2-octene looks random (see Figures 3a and 3b). This may be the result of the greater rigidity of the 2-olefin. It has the molecular structure



trans-2-octene

which makes it a poor match for the more flexible n-octane than the 1-octene, which has the less rigid structure

1-octene

The 1,7-octadiene/octane system worked out better for the most polar stationary phases but not very well for the stationary phases with lower polarity. The double bonds would give a very large enthalpy of interaction with the dipole-dipole interactions of those polar stationary phases making other complicating interactions less important, but with lower polarities the more rigid structure

1,7-octadiene

and greater capacity for dispersion interaction arising from the two double bonds would make it again a poor match for n-octane. The correlation coefficient was good also (see Table IX) even though the graph (Figure 4) still presents deviations but is better correlated.

Therefore, the 1-octene/n-octane gas chromatographic system appeared to be the most reliably linear with the infrared C-Cl frequency shift of 1-chlorohexane dissolved in the stationary phases and therefore the most satisfactory indicator for the classification of stationary phases. The trans-2-octene/n-octane did not appear to be a

a good choice; it was originally chosen because the relative retention of it on squalane was 1.00 but it was proved in this work that it is not that important because for the other two approaches their relative retentions on squalane was less than 1.0 but the correlation was better. The 1,7-octadiene/n-octane system appears to be a useful supplement to the 1-octene system for high polarities.

In conclusion, 1-octene/n-octane and 1,7-octadiene/n-octane gas chromatographic systems correlated with the infrared C-Cl frequency shift of 1-chlorohexane dissolved in the gas chromatographic stationary phases, with the degree of accuracy expected from Ecknig's previous work, with some improvements such as the use of a suitable reference, and the extension of the technique to solid and semi-solid stationary phases.

The use of the frequency shift as an indicator of dipole-dipole interaction of the solute (1-chlorohexane) with the stationary phase seemed to be reliable. There were certain difficulties, especially with the stationary phases that presented infrared absorption in the frequency region of interest (700-600 cm^{-1}) because in those cases the transmitted energy through the sample was very low. Therefore, it was necessary to decrease the amount of sample using a thinner spacer, but as there was also an upper limit of concentration of the solute that could be used to avoid self-association of the 1-chlorohexane, so the C-Cl absorption band was weak and difficult to identify. Otherwise, the infrared technique was simple and worked well.

The comparison of the order of classification of stationary phases obtained experimentally in this work (See Table VII) and the order established in the Phase Selectivity Table of Applied Laboratories (43) shows certain differences. But it has to be clear it should be like that because the classification presented in this work was just under one parameter of selectivity which is the polarity, and the Phase Selectivity Table (43) was calculated using Mc-Reynolds (13) approach, which combined all the possible interactions that can modify a Selectivity Table of stationary phases into a single number.

A complete classification of stationary phases should contain tables of indices of basicity, acidity and dispersion interaction. The author hopes that this attempt of classification of stationary phases under polarity will contribute to the complete classification proposed prior to the present work, which brought about all the encouragement and enthusiasm in this field.

F. Error Analysis

To analyze both the gas chromatography and infrared data, the Q test (45) was applied to one set of data in each technique and it was found that none of the values reported should be rejected. This provides considerable confidence in the data. Standard deviation (σ) was reported for each measurement and it was low.

My intuitive assessment of the uncertainty in the measurement of the frequency in infrared arising from the measurement of the chart using a ruler was ± 0.20 cm^{-1} while for gas chromatography was from ± 0.20 to ± 0.50 cm for the measurement of the retention times.

TABLE X

Polarity Scale

POLARITY	STATIONARY PHASES
↓	1-Squalane
	2-Polypropylene glycol
	3-Poly-m-phenyl ether
	4-Zinc Stearate
	5-Kel-F-oil
	6-Phenyldiethanolamine succinate
	7-Carbowax 400
	8-β,β' oxydipropionitrile
	9-N,N-Bis (2-cyanoethyl)formamide

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