

AN ABSTRACT OF THE THESIS OF

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Title: SOLUTE-SOLVENT INTERACTIONS IN GAS

CHROMATOGRAPHY

Abstract approved *Redacted for Privacy*  
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The study of solute-solvent interactions in gas chromatographic solutions is initially undertaken by means of the Rohrschneider Index System and the McReynold Index System. Quantitative isolations of various intermolecular forces by the retention index differences are proved to be unsuitable. However the polarity constants for a number of organic compounds are calculated based on McReynold's scheme for future reference.

Thermodynamic solution theories are applied to interpret solute activity coefficients in different mixture systems determined by gas chromatography. Accurate solute activity coefficient data are obtained from the literature.

The Flory-Huggins equation is used to estimate the excess partial molar entropy of mixing due to the difference in solute and solvent molecular sizes. The excess partial molar heats of mixing

due to dispersion interaction in nonpolar solute and nonpolar solvent systems are calculated by the Hildebrand-Scatchard equation. For the polar solute and nonpolar solvent systems and polar solute and polar solvent systems, the Hildebrand-Scatchard equation as modified by introducing other interaction parameters is employed so that interactions besides dispersion interaction are included.

Solubility parameters calculated by the internal pressure of pure components are shown to be more acceptable than those calculated by other means, namely, the heats of vaporization and the refractive indexes of the pure components. The excess partial molar heats of mixing are thus estimated by two sets of solubility parameters (Set I is based on the heats of vaporization and refractive indexes, and Set II is based on the internal pressures of the pure components). The Hildebrand-Scatchard equation is shown to be unable to predict accurate excess partial molar heats of mixing for nonpolar solute and nonpolar solvent systems where strong solute-solvent interactions and volume changes are expected. A binary coefficient is inserted into the Hildebrand-Scatchard equation to correct for failure of the geometrical mean assumption. The binary coefficients are found to be small and negative, decreasing with the solvent carbon atom number and the branching ratio of the solute component. Branched alkane solutes are found to have larger binary coefficients than the isomeric linear alkanes. The partial molar volumes of the solutes are also used

instead of the molar volumes in some mixture systems at higher temperatures to correct for the volume changes. These corrections are verified by the improved predictions of excess partial molar heat of mixing. The activity coefficients predicted by the combination of the Flory-Huggins equation and the Hildebrand-Scatchard equation are shown to have a 20% average deviation.

In polar solute and nonpolar solvent mixture systems, the modified Hildebrand-Scatchard equation is found to give good predictions for the excess partial molar heats of mixing. The induction interactions between solute and solvent molecules are shown to be significant. The solute activity coefficients are predicted within 10% relative deviation in all cases investigated.

The formation of hydrogen bonding and electron donor-acceptor interactions are indicated by the large negative specific interaction term,  $\Phi_h$ , in the modified Hildebrand-Scatchard equation for all polar solute and polar solvent mixture systems considered. No correlations are found between  $\Phi_h$  and the hydrogen bonding solubility parameters,  $\delta_h$ , of the solute and solvent components.

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# SOLUTE-SOLVENT INTERACTIONS IN GAS CHROMATOGRAPHY

## 1. INTRODUCTION

Gas-liquid chromatographic separation originates in the differential band migration of components. Therefore a concept of the physical and chemical contributions to the process of migration is fundamental to the understanding of gas-liquid chromatography.

The central item of gas-liquid chromatography is the chromatographic column into which liquid (stationary phase or solvent) coated solid-support is packed. A stream of inert gas (the carrier gas) passes continuously through the column and the solute (sample or mixture) to be separated is introduced in the form of vapor instantaneously at the beginning of the column nominally as an infinitely narrow band. The equilibrium distribution of the solute between the eluting inert gas and the solvent as the solute molecules migrated down the column is determined by the column performance and the efficiency of the solvent (34). The column performance is defined by the broadening factors<sup>1</sup>

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<sup>1</sup>Broadening factors:

- a. longitudinal and axial molecular diffusion of the vapor in the gas phase
- b. non-infinite rate of equilibration of the vapor with the solvent
- c. the geometry of the column packing
- d. non-linear isotherm.

and the column variables.<sup>2</sup> The random walk model describes statistical dispersion of the solute molecules in the band. The statistical broadening is therefore expressed as a variance and can be related with the plate height or the plate number (36). The famous van Deemter equation (9) provides a quantitative description of band dispersion contributed by the major broadening factors under the influence of various column variables.

The efficiency of the solvent determines the retention of the solute molecules which is characterized by the equilibrium distribution coefficient of the solvent. The chemical nature as well as the physical configuration of the solute and solvent molecules give rise to various forces of molecular interaction. Four solute-solvent interaction forces should be considered in a gas-liquid chromatographic column (30):

1. Dispersion, London, or non-polar, forces arising from the instantaneous dipoles of the two interacting species. This is the only source of attraction energy between two non-polar

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<sup>2</sup>Column variables:  
a. column length  
b. flow rate  
c. partition coefficient  
d. mass of stationary phase per unit length of the column  
e. pore volume per unit length of the column  
f. temperature  
g. type of carrier gas  
h. column diameter  
i. pressure drop across the column.

substances.

2. Induced dipole, or Debye, forces resulting from a permanent dipole in one molecule and the induced dipole in a neighboring molecule.
3. Orientation, or Keesom forces resulting from the interaction between two permanent dipoles.
4. Specific interaction forces, chemical bonding, complex formation between solutes and solvent molecules.

A general scheme for estimating chromatographic distribution would be of great value in achieving separation and in solute identification. A knowledge of the thermodynamic functions of distribution in a gas-liquid chromatographic solute-solvent system offers a starting basic approach.

The Hildebrand classical solubility parameter (24, 25) and regular solution theories provide a semi-quantitative estimation of interaction energies in binary mixture system (55). Since gas-liquid chromatographic technique has proven to give reliable activity coefficient data in binary mixture system (12), Hildebrand's theories are then applicable to study the molecular interaction energies in gas-liquid chromatographic solution systems.

Rohrschneider (49, 50, 51, 52, 53) has developed a scheme based on fundamental thermodynamic functions and Kovats' retention index (31) to classify all chromatographic solvents according to their various

types of interaction potentials. This scheme can also predict accurately the retention indexes of numerous chromatographic solute-solvent systems.

The applicability of gas-liquid chromatography is not restricted to the analytical field. It has potential possibilities for the determination of physical constants, for the investigation of thermodynamic solutions and for the study of normal and extractive distillation and extraction. The Rohrschneider constants system and one of the above applications viz. the determination of activity coefficient at infinite dilution will be discussed in this thesis.

## 2. THEORY

### Characterization in Retention Behavior

#### Retention Time and Retention Volume

The retention of a dissolved solute may be expressed by the time the solute takes to emerge from a gas-liquid chromatographic column. Since the solute is retarded by the solvent in the column, the lapse time between the emergence of the inert gas ( $t_A$ ) and the solute ( $t_R$ ) is the adjusted retention time ( $t'_R$ )

$$t'_R = t_R - t_A \quad [1]$$

or

$$t_R = t'_R + t_A \quad [1-a]$$

Equation [1-a] actually illustrates the fact that the retention time is the sum of the time spent by the solute in the gas-phase and the time during which the solute is sorbed by the solvent. In practical work, the use of retention times is most adequate. However the employment of retention volumes is necessary when chromatographic data should be connected to physico-chemical constants. The retention volume is the volume of the inert carrier gas which flows through the column during the retention time of the solute.

The net retention volume ( $V_N$ ) is expressed in Equation [2]:



$$V_N = t'_R F_c j \quad [2]$$

where

$F_c$  = the flow rate of the inert gas (cm/sec)

$j$  = the pressure drop correction across the column

It is also related to the partition coefficient,  $K$ , which is defined as

$$K = \frac{\text{amount of solute per volume of stationary phase}}{\text{amount of solute per volume of mobile phase}} \quad [3]$$

in the following way

$$V_N = KV_L = KW_s / \rho_s \quad [4]$$

where

$V_L$  = the volume occupied by the solvent (c. c.)

$W_s$  = the weight of the solvent present in the column (grams)

$\rho_s$  = the density of the stationary phase (grams/c. c.)

A more practical expression is the specific retention volume ( $V_g$ ) defined by Littlewood (34) as

$$V_g = \frac{\text{amount of solute per gram of solvent}}{\text{amount of solute per c. c. of gas phase at } 0^\circ\text{C}} \quad [5]$$

This quantity is equal to the net retention volume corrected to  $0^\circ\text{C}$  as reference per gram of liquid stationary phase in the column as shown by the following expression

$$V_g = (V_N/W_s)(273/T) \quad [6]$$

Retention Index (31, 32)

The retention index is a logarithmic, relative method of expressing retention. The logarithm of specific retention volume or the partition coefficient of a member of a homologous series is a linear function of its carbon atom number. Kovats (32) defined the index of a solute in a gas-liquid chromatographic column as

$$I = 100n + 100 \left[ \frac{\log_{10} V_{g(i)} - \log_{10} V_{g(n)}}{\log_{10} V_{g(n+1)} - \log_{10} V_{g(n)}} \right] \quad [7]$$

where

$I$  = retention index

$V_{g(i)}$  = specific retention volume of species of interest

$V_{g(n)}$  = specific retention volume of n-alkane emerged next before it

$V_{g(n+1)}$  = specific retention volume of n-alkane emerged next after it

$n$  = the number of carbon atoms in n-alkane of specific retention volume  $V_{g(n)}$

Therefore by definition the retention index of n-alkane of carbon number  $n$  is  $100n$  whatever the solvent is. The index system is

graphically shown in Figure 1, in which the logarithm of the retention volumes and the free energies of solution of the n-alkanes have been plotted against the number of carbon atoms (n) as well as the retention indices.

The significance of this system is that a substance (RX) having retention indices equivalent to a certain fraction number of n-paraffin of carbon atoms  $N_u$  and  $N_p$  in a non-polar and a polar column respectively would simultaneously emerge from the partition columns with the equivalent n-paraffins. The substance will have the same partition coefficient as well as the same free energy solution as the equivalent n-alkanes.

### Thermodynamics of Solutions

The classical thermodynamic solution theories have been studied and applied to gas-liquid chromatographic solute-solvent solution systems (34, 37). The thermodynamic treatment enables relations to be derived among partition coefficient, activity coefficient and measurable properties of solute and solvent. The ideal solution theory provides a foundation to understand normal gas-liquid chromatographic solutions. However this theory is frequently unable to account for the intricate behavior of this type of solution. Since regular solution theory has been applied quite successfully to solve many polymer-solvent systems (5), a better description of the thermodynamic

properties of gas-liquid chromatographic solutions may be achieved by the same theory.

### Properties of Ideal Solutions

A solution is said to be ideal if the chemical potential of every component is a linear function of the logarithm of its mole fraction according to the relation

$$\mu_i = \mu_i^0 + RT \ln x_i \quad [8]$$

where

$\mu_i$  = chemical potential of the  $i$  species

$\mu_i^0$  = chemical potential of the  $i$  species when  $x_i = 1$

$x_i$  = mole fraction of the  $i$  species

There are only a limited number of solutions which are ideal over the whole composition range. These solutions are sometimes called perfect solutions. In general, Equation [8] applies only to a given region of composition in many solutions and will approach closer and closer to ideality the more dilute they become in all but one of their components.

If the solute vapor is in equilibrium with the solute at a given temperature and pressure, the chemical potentials in both phases are equal. According to Equation [8] the chemical potentials of the solute are

$$\mu_2^l = \mu_2^0 + RT \ln x_2 \quad [9]$$

$$\mu_2^g = \mu_2^+ + RT \ln P_2 \quad [10]$$

where the subscript 1 and 2 refers to the solvent and the solute component respectively.

$\mu_2^l$  = chemical potential of the solute in solution

$\mu_2^g$  = chemical potential of the solute in gas phase

$\mu_2^0$  = a constant, chemical potential of the solute when  $x_2 = 1$

$\mu_2^+$  = a constant, chemical potential of the solute in gas phase  
when  $P_2 = 1$  atmosphere

At equilibrium,

$$\mu_2^l = \mu_2^g \quad [11]$$

Therefore,

$$\mu_2^0 + RT \ln x_2 = \mu_2^+ + RT \ln P_2 \quad [12]$$

and after rearranging Equation [12]

$$P_2/x_2 = k_2 \quad [13]$$

when

$$k_2 = \exp(\mu_2^0 - \mu_2^+ / RT)$$

$k_2$  is a constant only if the solution is perfect or  $x_2 \rightarrow 1$ ; thus  $k_2$  is equal to the true vapor pressure of the solute. This is the definition of Raoult's Law as illustrated by curve a in Figure 2.

Otherwise Equation [13] merely asserts a proportionality constant between  $P_2$  and  $x_2$ , and is the same as Henry's Law constant as shown in curve b.

The physical meaning of an ideal or perfect solution is that the molecular species of both the solute and the solvent are nearly alike in their attractive forces, molecular volumes, shapes and sizes. Upon mixing, they mix randomly, produce no heat and result in no change of the total volume of the solution. The thermodynamic functions of these phenomena are,

$$\Delta H_{(\text{ideal})}^M = 0 \quad [14]$$

$$\Delta V^M = 0 \quad [15]$$

$$\frac{\Delta S_{(\text{ideal})}^M}{R} = - \sum_i n_i \ln x_i \quad [16]$$

or in terms of the partial molar quantities of the solute

$$\Delta \bar{S}_2^M = -R \ln x_2 \quad [17]$$

$$\Delta \mu_2^M = R \ln x_2 \quad [18]$$

where

$\Delta H_{\text{ideal}}^{\text{M}}$  = heat of mixing per mole of ideal mixture

$\Delta V^{\text{M}}$  = change of total volume upon mixing

$\Delta S_{\text{ideal}}^{\text{M}}$  = entropy of mixing per mole of ideal mixture

$\Delta \bar{S}_2^{\text{M}}$  = partial molar entropy of mixing of the solute

### Properties of Non-Ideal Solutions

Gas-liquid chromatographic solutions in which a volatile solute is mixed with a non-volatile solvent are usually not even approximately ideal. These solutions show either a positive or negative deviation from the Raoult's Law curve as shown by curves c and d in Figure 2. The departure from ideality is expressed quantitatively by the activity coefficient  $\gamma$  of the solute. If the concentration of the solute is infinitely small, which is usually the case in gas-liquid chromatographic solution, the activity coefficient at infinite dilution for the solute  $\gamma_2^{\infty}$  is just the ratio of the slopes of curves a and b. Assuming the solute vapor is ideal, the vapor pressure of the solute above a non-ideal solution is given by

$$P_2 = \gamma_2 x_2 P_2^0 \quad [19]$$

The partition coefficient may be related to the activity coefficient at infinite dilution by the expression

$$K_2 = RT \rho_2 / M_1 \gamma_2 P_2^0 \quad [20]$$

Combining Equations [5], [6] and [20], the specific retention volume is given by

$$V_g = 273R / M_1 \gamma_2 P_2^0 \quad [21]$$

If the vapor phase is non-ideal, vapor pressure of the pure solute ( $P_2^0$ ) must be replaced by its fugacity,  $f_2$ , and therefore,

$$V_g = 273R / M_1 \gamma_2 f_2 \quad [22]$$

In the case of non-ideal solutions, the molecular species have unlike attractive forces; each molecule experiences a different environment compared to others. Upon mixing the molecules are no longer randomly distributed, and the heat of mixing has a finite value. The total free energy of mixing per mole of mixture is thus given by

$$\Delta F_T^M = \sum_i x_i RT \ln a_i \quad [23]$$

where

$\Delta F_T^M$  = total free energy of mixing per mole of mixture

$$a_i = \text{activity coefficient} = P_i / P_i^0 \quad [24]$$

Substituting Equation [19] into [23] yields



$$\Delta F_T^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad [25]$$

The first term on the right hand side of Equation [25] is actually the ideal free energy of mixing, while the second term is the excess due to the non-ideal behavior of the solution. Thus the total free energy of mixing can also be written as

$$\Delta F_T^M = \Delta F_{(\text{ideal})}^M + \Delta F_{(\text{nonideal})}^M \quad [26]$$

It is necessary to define a set of thermodynamic excess functions which can be regarded as the excess properties of the non-ideal solution over that of the ideal solution. These functions were first used by Scatchard (54) and are written as the following:

$$\Delta F^E = \Delta F_{(\text{nonideal})}^M = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad [27]$$

$$\Delta H^E = \Delta H_{(\text{nonideal})}^M = \Delta H_T^M \quad [28]$$

$$\Delta S^E = \Delta S_{(\text{nonideal})}^E = \Delta S_T^M - \Delta S_{(\text{ideal})}^M \quad [29]$$

Since  $\Delta F = \Delta H - T\Delta S$ , Equation [26] can be re-written as

$$\Delta F_{(\text{nonideal})}^M = \Delta F^E = \Delta H_T^M - T\Delta S_T^M - \Delta H_{(\text{ideal})}^M + T\Delta S_{(\text{ideal})}^M \quad [30]$$

After substituting Equation [14] onto Equation [30]

$$\Delta F^E = (H^E - T(\Delta S_T^M - \Delta S_{\text{ideal}}^M)) = \Delta H^E - T\Delta S^E \quad [31]$$

The partial molar excess free energy with respect to the solute is

given by

$$\Delta \bar{F}_2^E = RT \ln \gamma_2 \quad [32]$$

### Properties of Nonideal Athermal Solutions

The ideal solution theory assumes that all molecular species have the same shape, size and molecular volume. The mixing process takes place at constant temperature and pressure without change in energy or volume. However Guggenheim (17, 47) pointed out that solutions formed with no heat of mixing or change in volume do not necessarily have an ideal entropy of mixing. This type of solution is called non-ideal athermal. The entropy of mixing of a non-ideal athermal solution is usually less than the ideal solution.

$$\Delta S_{\text{nonideal athermal}}^M < \Delta S_{\text{ideal}}^M \quad [33]$$

A solution of unequal size molecules is a non-ideal athermal solution. Flory-Huggins (13, 28) derived an equation to evaluate the statistical athermal contribution to the entropy of mixing by assuming a quasi-crystalline lattice model for a solution. The excess entropy of mixing per mole of mixture is expressed as a function of the molar volumes of the molecular species.

$$\Delta S^E = -R(x_1 \ln \phi_1 + x_2 \ln \phi_2) \quad [34]$$

or in terms of partial molar quantity of the solute in an infinitely dilute solution (14)

$$\Delta \bar{S}_2^E = -R \left( \ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1} \right) \quad [35]$$

where

$\phi$  = volume fraction

$V$  = molar volume

Equations [34] and [35] have been applied successfully in the studies of polymer solutions (25, 57) as a correction for the size difference between the polymer molecules and the small compact solvent molecules.

### Properties of Regular Solutions

The term regular solution which refers to a special kind of non-ideal solution was first proposed in 1929 by Hildebrand (20). The regular solution theory applies to all solution whose molecules are randomly mixed by thermal agitation, regardless of their difference in interaction forces, and their disparity in size, and thus possess nearly ideal entropy of mixing due to maximum randomness just as in an ideal solution. In other words, there would be no change in randomness and therefore of entropy in transferring one component from the solution to an ideal solution of the same composition, i. e. ,

$$\Delta S_{(\text{regular})}^{\text{E}} = \Delta S_{(\text{ideal})}^{\text{M}} - \Delta S_{(\text{regular})}^{\text{M}} = 0 \quad [36]$$

and the total volume is unchanged.

According to Equation [31], the excess free energy of mixing per mole of a regular solution is

$$\Delta F_{(\text{regular})}^{\text{E}} = \Delta H_{(\text{regular})}^{\text{E}} - T\Delta S_{(\text{regular})}^{\text{E}} \quad [37]$$

therefore

$$\Delta H_{(\text{regular})}^{\text{M}} = \Delta E_{(\text{regular})}^{\text{M}} = \Delta F_{(\text{regular})}^{\text{E}} = \Delta H_{(\text{regular})}^{\text{E}} \quad [38]$$

The heat of mixing determines solely the deviation from ideal solution and thus the activity coefficient  $\gamma_2^\infty$  of the solute.

### The Concept of Solubility Parameter

The activity coefficient, which solely accounts for the nonideal behavior of a regular solution, can be directly determined by the heat of mixing. The Hildebrand-Scatchard equation (23, 24, 42) for the excess heat of mixing per mole of mixture is

$$\Delta H^{\text{E}} = (x_1 V_1 + x_2 V_2) \phi_1 \phi_2 A_{12} \quad [39]$$

where

$$A_{12} = C_{11} + C_{22} - 2C_{12} \quad [40]$$

$C_{11}$  and  $C_{22}$  are the cohesive energy densities in the pure components;  $C_{12}$  is the corresponding energy density for the interaction between unlike species.

The interaction between unlike species can be expressed in terms of the cohesive energies of the pure components by means of the geometric mean assumption that

$$C_{12} = (C_{11}C_{22})^{1/2} \quad [41]$$

Therefore, Equation [39] becomes

$$\Delta H^E = (x_1V_1 + x_2V_2)\phi_1\phi_2(C_{11}^{1/2} - C_{22}^{1/2})^2 \quad [42]$$

for pure components,

$$C_{11} = -E_1/V_1 \quad \text{and} \quad C_{22} = -E_2/V_2 \quad [43]$$

where  $E$  = intermolecular potential energy.

Hildebrand, together with Westwater et al. (21, 61) have shown that over a small range of volume the intermolecular potential energy density can be expressed as

$$-\frac{E}{V} = \frac{1}{n} \left( \frac{\partial E}{\partial V} \right)_T = \frac{\Delta E^V}{V} \quad [44]$$

where  $\Delta E^V$  = energy of vaporization

Hildebrand has calculated the  $n$  value for a number of liquids by using Equation [44] and shown that  $n$  is in fact not far from unity. In order to re-evaluate the intermolecular potential energy for the pure species, accurate measurement of  $(\partial E/\partial V)_T$  is necessary. Pure thermodynamics yields the equation:

$$P = -\left(\frac{\partial E}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T \quad [45]$$

where  $P$  is the external pressure. Since  $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ , Equation [45] can be transformed into what has been called the thermodynamic equation of state:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad [46]$$

For normal liquids below their boiling point,  $P$  is entirely negligible in comparison with  $T(\partial P/\partial T)_V$ , so

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

Determination of the increase in pressure with temperature at constant volume may be achieved by means of the coefficient of thermal expansion  $\alpha$  and the compressibility factor  $\beta$ . Because of the unreliable nature of most compressibility data, the intermolecular potential energy density has been evaluated by the energy of

vaporization

$$-\frac{E}{V} = \frac{\Delta E^V}{V} \quad [47]$$

Hildebrand referred to the term  $E^V/V$  as a measure of the "internal pressure" of a liquid and named the value of  $(\Delta E^V/V)^{1/2}$  "solubility parameter" ( $\delta$ ). Therefore

$$C^{1/2} = \left(\frac{\Delta E^V}{V}\right)^{1/2} = \delta \quad [48]$$

Substituting Equation [48] into Equation [42], the excess heat of mixing per mole of mixture becomes

$$\Delta H^E = (x_1 V_1 + x_2 V_2) \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad [49]$$

### Gas-Liquid Chromatographic Solutions

#### Regular Solution Approach

In practice, all gas-liquid chromatographic solutions are by no means ideal. Most of these solutions show either a negative or a positive deviation from ideal solution theory which is mainly due to the presence of strong intermolecular interactions, namely, dispersion, induction, dipole orientation, hydrogen bonding and other specific interactions. To the first approximation, the regular solution theory can be applied to study these solutions (38). Therefore the excess

free energy of mixing per mole of non-polar mixture is, according to Equations [38] and [49]

$$\Delta F^E = (x_1 V_1 + x_2 V_2) \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad [50]$$

However Equation [50] cannot fully describe the real picture in gas-liquid chromatographic solution (40) due to the fact that the entropy of mixing is always less than the ideal case. In other words

$$\Delta S^M < -R(x_1 \ln x_1 + x_2 \ln x_2) \quad [51]$$

and

$$\Delta F^E \neq \Delta H^E \quad [52]$$

A correction term should be added to Equation [50] to take account of the molecular volume difference between the solvent and solute molecules. It is always the case in gas-liquid chromatographic solutions that the solvent molecules are substantially larger than the solute molecules. The entropy of mixing of a nonideal athermal solution which accounts for the size difference in molecular species provides a logical correction for Equation [50]; thus the excess free energy per mole of mixture becomes

$$\Delta F^E = RT(x_1 \ln \phi_1 + x_2 \ln \phi_2) + (x_1 V_1 + x_2 V_2) \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad [53]$$



Since the solute concentration is almost infinitely dilute in gas-liquid chromatographic solutions, the partial molar excess free energy of the solute component is

$$\Delta \bar{F}_2^E = RT \left( \ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1} \right) + V_2 (\delta_1 - \delta_2)^2 \quad [54]$$

Substituting Equation [54] into [32] yields

$$\ln \gamma_2^\infty = \ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1} + \frac{V_2}{RT} (\delta_1 - \delta_2)^2 \quad [55]$$

In view of Equation [55], Ashworth and Everett (3) suggested that the deviations from Raoult's Law exhibited by mixtures containing molecules of unequal size can be expressed as the sum of two contributions to the logarithm of the activity coefficient  $\gamma_2^\infty$  at infinite dilution.

$$\ln \gamma_2^\infty = \ln \gamma_2^s + \ln \gamma_2^e \quad [56]$$

where  $\gamma_2^s$  is associated with the statistical effect due to the size difference and  $\gamma_2^e$  is associated with the interaction energies between various molecules. Therefore

$$\ln \gamma_2^e = \frac{V_2}{RT} (\delta_1 - \delta_2)^2 \quad [56-a]$$

$$\ln \gamma_2^s = \ln \frac{V_1}{V_2} + 1 - \frac{V_1}{V_2} \quad [56-b]$$

### Solubility Parameters for Organic Compounds

The excess free energy of a mixture may also be expressed in the following way (51) if interactions other than dispersion force is involved.

$$\Delta F_T^E = \Delta F_s^E + \Delta F_d^E + \Delta F_{in}^E + \Delta F_o^E + \Delta F_h^E \quad [57]$$

where the subscripts refer to different interactions due to

s = unequal size entropy effect

d = dispersion interactions

in = induction interactions

o = dipole orientation

h = hydrogen bonding

The first two terms in Equation [57] are expressed by Equation [54]. In view of the Hildebrand-Scatchard equation for heat of mixing, solubility parameters for other interactions are necessary besides the  $\delta$  value for dispersion. R. F. Weimer and J. M. Prausnitz (60) separated the  $\delta$  value of polar molecule calculated from heat of vaporization into two solubility parameters by the homomorph method

$$\delta = (\delta_d^2 + \delta_o^2)^{1/2} \quad [58]$$

where

$\delta_d$  = solubility parameter for dispersion

$\delta_o$  = solubility parameter for dipole

C.M. Hansen and K. Skaarup (18) further separated the  $\delta$  value into three parts in which the solubility parameter for hydrogen bonding is included. The H-bonding solubility parameter was evaluated under the assumption that each OH-O bonding is approximately 5000 cal/mole (45). The cohesive energy density for hydrogen bonding can thus be calculated by

$$\delta_h = \left( \frac{5000N}{V_m} \right)^{1/2} \quad [59]$$

where

$N$  = the number of H-bonding groups

$V_m$  = the total volume of the solution

With these solubility parameters, Equation [55] for a polar-polar mixture becomes

$$\ln \gamma_2^\infty = \ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1} + \frac{V_2}{RT} [(\delta_{d_1} - \delta_{d_2})^2 + (\delta_{o_1} - \delta_{o_2})^2 + 2\Phi_{in} + 2\Phi_h] \quad [60]$$

where

$\Phi_{in}$  = a function of  $\delta_d$  and  $\delta_o$  for the induction interaction

$\Phi_h$  = hydrogen bonding interaction

### Rohrschneider Index System

Rohrschneider (51) proposed that the retention index difference of a polar compound between a polar and a nonpolar stationary phase column is assumed to be the sum of the excess free energies contributed by various molecular interactions

$$\Delta I^{RX} = I_p^{RX} - I_u^{RX} = \frac{100(\Delta F_p^{RX} - \Delta F_u^{n_u})}{\Delta F_p^{CH_2}} \quad [61]$$

where

$I_p$  = retention index of compound RX in a polar stationary phase column

$I_u$  = retention index of compound RX in a nonpolar stationary phase column (squalane)

$\Delta F_p^{RX}$  = free energy of solution of RX in a polar phase (P)

$\Delta F_u^{n_u}$  = free energy of solution of a paraffin with  $n_u$  carbon atoms in the same column where the n-paraffin  $n_u$  has the same retention index on the non-polar liquid phase as RX (see Figure 2)

$\Delta F_p^{CH_2}$  = free energy of solution of a methylene group

or

$$\Delta I^{RX} = 100 \sum \Delta F_{i(p)}^{RX} / \Delta F_{(p)}^{CH_2} \quad [62]$$

where  $i = \text{ith}$  type of molecular interactions.

If a compound shows a certain type of interaction strongly due to a particular functional group in its molecule, the free energy of solution is mainly dominated by the interaction. Therefore it is possible to characterize a chromatographic liquid phase by means of the  $\Delta I$  values of a few reference compounds with each having an unique interaction with the stationary phase. Assuming that the intensity of the interaction is proportional to a substance-specific factor and to another factor characteristic of liquid phase. This assumption is supported by the Debye formula, where the interaction energy between two dipoles corresponds to the product of the squares of their dipole moment. Pullin and Werner (48) also observed that the strength of the frequency shift of the OH absorption band of alcohols is proportional to the product of the H-donor and the H-acceptor strength. Rohrschneider also proposed an empirical formula relating the  $\Delta I$  value of a compound in a stationary phase, with the characteristic constants of the stationary phase and Rohrschneider Constants for that compound.

$$\Delta I_{\text{P}}^{\text{RX}} = ax + by + cz + \dots \quad [63]$$

where

$$x, y, z, \dots = \frac{I(\text{reference in polar phase}) - I(\text{reference in squalane})}{100}$$

$a, b, c, \dots =$  Rohrschneider constants for compound RX

The Rohrschneider constants for compound  $RX$  can be evaluated by means of a least-square fitting method to Equation [63] provided that  $\Delta I_p$  values are known in five or more stationary phases. If the constants of the compound and the stationary phase are known, accurate  $\Delta I_p^{RX}$  value can be predicted in any stationary phase within experimental error.

### 3. DISCUSSION

#### The Choice of Experimental Data

All solute activity coefficients in gas-liquid chromatographic solution systems are basically calculated by Equation [21] which relates the solute activity coefficient with the specific retention volume. Although several groups (12, 15) have proven favorably with thermodynamic information obtained from gas-liquid chromatographic measurements, some vital assumptions, explicit and implicit, underlying the Equation [21] must be considered in order to evaluate the validity of the data (40). The following are the basic assumptions.

- a. The gas-liquid chromatographic solution must obey Henry's Law.
- b. The solute concentration must be infinitely dilute in the liquid phase.
- c. The column must be isothermal and there is no pressure drop across the column.
- d. Equilibrium is maintained between the vapor and the liquid at all points in the column.
- e. There is no adsorption of solute on the solid support.
- f. There is no adsorption of the solute at gas-liquid interface.
- g. The liquid phase behaves as a bulk partitioning liquid.

h. Interactions such as solute-solute, solute-carrier gas and carrier gas-carrier gas should be absent in the vapor phase.

Assumptions (a) and (b) are usually met in experimental work by injecting the smallest sample sizes into the column in order to prevent the over-loading effect. The peak retention times or retention volumes should be extrapolated to zero sample size.

In modern instrumentation accurate column temperature and pressure control can be easily achieved to fulfill assumption (c). Assuming that the packing is uniform throughout the column and the inlet and outlet pressures are controlled and measured accurately, the compressibility factor can be calculated and then applied to correct the retention volume to zero pressure drop.

The agreement of static equilibrium data with the "dynamic" equilibrium data in gas-liquid chromatographic solutions provide a final proof of the validity of assumption (d). Instantaneous equilibrium may be assumed at all points in the column because the diffusion rate of the solute in both the gas phases are extremely rapid (15).

To ascertain no solute adsorption upon the solid support is present, active sites on the solid support can be removed by acid washing or silanizing the support. Evered and Pollard (12) suggested that the tailing or skewness of the solute peak indicates adsorption. If the total packing material contains at least 15% by weight of liquid phase, adsorption effect should be absent.



Assumptions (f) and (g) are frequently major drawbacks to the application of gas-liquid chromatographic data to thermodynamic equations. Martire (37, 38) observed that the solute elution order in polar phases changes with the weight ratio of liquid phase to solid support and with the surface area of the covered support. He attributed this to the gas-liquid interface adsorption. When the liquid is spread upon the solid support, the surface to volume ratio is high and any difference in concentration between the bulk and the surface might be significant. Only if the solute concentration is uniform throughout the liquid, the stationary phase can then be regarded as possessing the properties of the bulk liquid. The cause for excess solute at surface of the liquid phase may be attributed to high insolubility of solute molecules which brings about large values for the activity coefficient. This frequently occurs in the use of a very polar stationary.

Finally, assumption (h) implies that the vapor phase is ideal above the solution. If helium is used as carried gas, this assumption has shown to be valid. However the nonideality of the vapor phase can be significant in many cases.

In view of the critical assumptions mentioned above, extensive literature research has been done in order to find gas-liquid chromatographic activity coefficient data available for the present studies. Gas-liquid chromatographic data published after 1960 are considered.

D.E. Matire and L. Z. Pollara (41) collected a large number of activity coefficient data for branched and linear alkanes, and halo-alkanes in various types of solvents. However, data in squalane column are unreliable. D.H. Desty and W.T. Swanton (10) made an effort to correct gas-phase imperfection in calculating the solute activity coefficient in squalane at 20° C, these data are the only reliable source to study intermolecular forces between non-polar solute in squalane at low temperature. Cruickshank et al. (8), Hicks and Young (19), Young (62), and Tewari et al. (58) published extensive data on branched and linear alkanes in C<sub>16</sub> to C<sub>36</sub> n-alkane solvents. These data were proven to agree with data obtained by accurate static method. In comparing these data from different sources, the agreement is quite acceptable. Tewari et al. (59) has also published activity coefficient data of a few chloro-alkanes in n-alkane solvent, these data may be used to study intermolecular forces in polar-nonpolar solution systems. All activity coefficient data used in our present studies are listed with their sources in Table 1. Solutes selected for the present studies are indicated by numbers from 1 to 21. The nomenclatures of these solutes are listed in Appendix I.

#### Estimation of Molar Volumes

Molar volumes of all organic compounds at 20° C are obtained

from the American Petroleum Institute tables of physical properties of hydrocarbons (2). Molar volumes at higher temperatures for n-alkanes have to be estimated from Bondi and Simki method (6) which bases upon a modified law of corresponding states. These calculated values yield less than 2 percent relative error. The molar volumes of these compounds are presented in Table 2.

### Solubility Parameters

#### Non-Polar Organic Molecules

##### Evaluation of Solubility Parameters from Heats of

Vaporization. The solubility parameter of any organic compound is calculated by Equation [48]

$$\delta = \left( \frac{\Delta E^V}{V} \right)^{1/2} \quad [48]$$

where  $\delta$  is the solubility parameter,  $\Delta E^V$ , the total energy of vaporization,  $V$ , the molar volume. Both  $\Delta E^V$  and  $V$  are temperature dependent, so it is necessary to calculate  $\delta$  for each temperature needed. Since  $\Delta E = \Delta H - P\Delta V$ , assuming  $\Delta V = V_g$  where  $V_g$  is the volume of the gas-vapor,  $\delta$  may be expressed as

$$\delta = \left( \frac{\Delta H^V - RT}{V} \right)^{1/2} \quad [64]$$

where  $\Delta H^V$  is the enthalpy of vaporization at temperature  $T$ .

The enthalpy of vaporization can be determined calorimetrically at any desired temperature well below normal boiling point. If accurate enthalpy of vaporization is known the  $\delta$  value can be calculated. Often, however, no calorimetric measurements are available for a particular temperature. The enthalpy of vaporization must be estimated from the temperature dependence of the vapor pressure by means of the Antoine equation (58):

$$\Delta H^V = 2.303RB\left(\frac{t+273.2}{t+C}\right)^2 \quad [65]$$

where  $B$  and  $C$  are the Antoine constants defined within a certain temperature range. The Antoine constants are available in literature (2). The solubility parameters of n-alkanes ranging from  $C_5$  to  $C_{36}$  at various temperatures have been calculated by the author by Equations [64] and [65] and listed in Table 3.

The cohesive energy density (c. e. d.) which is defined as

$$\delta^2 = \left(\frac{\Delta H^V - RT}{V}\right) = \text{c. e. d.} \quad [66]$$

should be linearly related to the reciprocal of  $N$ , the number of carbon atoms of a homolog (1). In Figures 3, curve a, the cohesive energy densities of the n-alkanes at  $20^\circ\text{C}$  calculated by Equations [65] and [66]

are plotted against  $1/N$ . The unusual behavior of the calculated cohesive energy density of the n-alkanes is mainly due to two reasons. Firstly, Equation [64] assumes that the vapor phase of the n-alkane which is in equilibrium with the liquid is ideal. This may be true for low carbon number alkanes (e.g.,  $C < 10$ ), however when carbon number is larger than ten, the vapor phase may no longer be ideal. Therefore a correction factor should be inserted into Equation [65] to correct for the imperfect vapor phase. Secondly, the Antoine constants in Equation [65] are defined within a limited range of temperatures. Hoy (27) reported that the use of these constants outside the range of temperature specified results in erroneous estimation of the heat of vaporization. This effect is illustrated in Figure 4.

The Antoine constants for all alkanes below decane are defined at temperatures below  $60^{\circ}\text{C}$  (11), while other alkanes are defined at temperatures above  $60^{\circ}\text{C}$ . In the present studies, the temperature range of interest is between  $20^{\circ}\text{C}$ - $76^{\circ}\text{C}$  which is far lower than the temperature range specified for the higher alkanes. New sets of Antoine constants are necessary for accurate estimation of heat of vaporization at the desired temperatures. Unfortunately, these new sets of Antoine constants are not always available.

G. Allen (1) have published cohesive energy density data at  $20^{\circ}\text{C}$  of n-alkanes which have been corrected for imperfect vapor phase behavior. These data are shown in Figure 3, curve b. The curve is

linear and the lower alkane values agree quite well with the calculated results. The higher alkane region shows that these two factors exhibit a significant influence on the calculation of heat of vaporization by Equation [65].

In Figure 5, the temperature dependence of the solubility parameter of n-heptane and n-hexadecane further confirm this conclusion. Curves a and b are heptane data obtained from Antoine equation and accurate heat of vaporization data from Bagley et al. (4), which have been corrected for gas phase imperfection, respectively, agree well within experimental error at low temperature range. It is simply due to the fact that Antoine constants are well defined and the vapor phase for lower alkanes are approximately ideal. At high temperature region, curve b slightly deviates from curve a. This is probably caused by gas phase imperfection. However, this is not true for the case of n-hexadecane. Solubility parameters of n-hexadecane estimated from the index of refraction method<sup>3</sup> and Antoine equation are plotted against temperature as shown by curves e and f respectively. Antoine constants are not defined at low temperature region for n-hexadecane so that curve f has a large deviation from curve e. At high temperature, curves e and f are well correlated due to the fact that Antoine constants become applicable while the temperature

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<sup>3</sup>The estimation of solubility parameter by index of refraction which yields fairly agreeable results with those estimated from accurate heat of vaporization data will be discussed in the next section.

is still not high enough to cause serious gas-phase imperfection.

Evaluation of Solubility Parameters from Indexes of Refraction.

Scatchard (54), Lawson et al. (33) and Keller et al. (29) have noted that the solubility parameter is proportional to the Lorentz-Lorenz function.

$$\delta = c(n^2 - 1)/(n^2 + 2) \quad [67]$$

where

$n$  = the refractive index

$c$  = 30.7 at 20° C

Solubility parameters for n-alkanes have been calculated by the author by means of Equation [67]. The corresponding cohesive energy densities are thus plotted against  $1/N$  in Figure 3, curve c. The curve is also linear. In considering the empirical nature in estimating the solubility parameters by Equation [67], the agreement between curves b and c may be considered to be satisfactory. Actually Equation [67] is valuable as a means of obtaining values of solubility parameters for which alternative methods are at present unsatisfactory. Equation [67] can also be used to calculate solubility parameters at temperatures other than 20° C by assuming that constant  $c$  is approximately independent of temperature. Since the refractive index is related to the molar refraction  $R$  by

$$R = \left( \frac{n^2 - 1}{n^2 + 2} \right) \left( \frac{M}{d} \right) \quad [68]$$

where

M = molecular weight

d = density

R is, to a first approximation, independent of temperature or physical state, and it provides an approximate measure of the actual total volume (without free space) of the molecules in one gram mole (7). Therefore, the Lorentz-Lorenz function is related to the molar volume as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{R}{V} \quad [69]$$

For a very large number of compounds, R is approximately additive for the bonds present in the molecule. The atomic group or structural contributions to R have been published by Vogel (7). Therefore, Equation [69] can yield the Lorentz-Lorenz function at any temperature desired provided that the molar volume is known. Substituting Equation [69] into [67], the solubility parameter at any temperature can be calculated. In Table 4, the  $\delta$  values for heptane calculated by Equations [68] and [69] are compared with Bagley's (4) data.

The agreement between these data affirms the use of Equation [68] for calculations of solubility parameter at different temperatures.



Solubility parameters of n-alkanes at various temperatures based on Equation [68] are listed in Table 5. The results for n-heptane and n-hexadecane are plotted against temperature are shown in Figure 5, curves c and e.

#### Evaluation of Solubility Parameter from Direct Measurements

of Internal Pressure. The simplification of Equation [45] by assigning

$$\frac{1}{n} \left( \frac{\partial E}{\partial V} \right)_T = \frac{\Delta E^V}{V} \quad \text{might be acceptable for qualitative calculations but}$$

for quantitative calculations problems may arise. Nonpolar organic molecules in the liquid state can be regarded as having a quasi-lattice structure. There will be a zero point energy,  $E_Z^L$ , of the molecule in the quasi-lattice site as in the solid case where  $E_Z^L$  is the energy measured from zero vibrational level to infinite separation of molecular species. There will also be internal and external modes of motions. The internal modes of motion are due to interatomic vibrations and rotations. The external modes of motions are due to the rotation, kinetic and potential energies of the molecule as a whole.

Therefore the total liquid state energy  $E_T^L$  is

$$E_T^L = E_Z^L + E_{in}^L + E_{ex}^L \quad [70]$$

In the gas state, the total energy  $E_T^G$  is

$$E_T^G = E_p^G + E_{in}^G + E_{ex}^G \quad [71]$$

where

$E_p^G$  = interaction energy of gaseous molecule. This energy is equal to zero if the gas is assumed to be ideal

$E_{in}^G$  = internal modes energy

$E_{ex}^G$  = external modes energy

The external modes of motion in both phases can be further divided into translational, rotational and vibrational motions. The translational motion of the molecules in the liquid state can be assumed to be zero. For nonpolar molecules the internal molecular energy is the same in the liquid and the gas states. The energy of vaporization,  $\Delta E^V$ , is then given by the difference between the gas state and the liquid state energies.

$$\Delta E^V = E_T^G - E_T^L \quad [72]$$

$$\Delta E^V = E_p^G - E_Z^L + E_{ex}^G - E_{ex}^L \quad [73]$$

Assuming the gas phase is ideal, Equation [73] becomes

$$\Delta E^V = -E_Z^L + E_{ex}^G - E_{ex}^L \quad [74]$$

Dividing Equation [74] by the molar volume of the liquid at a fixed temperature yields

$$\frac{\Delta E^V}{V} = \frac{-E^L}{Z} - \frac{1}{V} (E_{ex}^L - E_{ex}^G) \quad [75]$$

According to the equipartition principle in classical thermodynamics, the term  $(E_{ex}^G - E_{ex}^L)$  is just a function of  $RT/2$ . Therefore,

$$\frac{\Delta E^V}{V} = -\frac{E^L}{Z} - \frac{\Delta n}{2V} (RT) \quad [76]$$

where  $\Delta n$  = the change in effective number of classical degrees of external freedom in going from the gas to liquid states.

If the solubility parameter refers to the magnitude of the non-polar dispersion forces, Equation [76] becomes

$$\left(\frac{-E^L}{Z}\right) = \frac{\Delta E^V}{V} + \frac{\Delta n}{V} RT = \delta'^2 \quad [77]$$

where  $\delta'$  is the solubility parameter calculated by  $-E^L/Z$ . Bagley et al. (4) reported that the internal pressure of a liquid is

$$P_i = \left(\frac{\partial E^L}{\partial V}\right)_T = \left(\frac{\partial E^L}{\partial Z}\right)_T \quad [78]$$

because the external and internal motions are independent of volume. Assuming that the volume change is small and the zero point energy behaves similar to the intermolecular potential,  $E^L/Z$  can be expressed as

$$E_Z^L = - \frac{a(T)}{V} \quad [79]$$

where  $a(T)$  may be a function of temperature. Then

$$P_i = \frac{a(T)}{V^2}$$

and therefore

$$-E_Z^L = P_i V \quad [80]$$

Substituting Equation [80] into [75] yields

$$P_i = \delta'^2 = \frac{\Delta E^V}{V} + \frac{\Delta n}{V} RT \quad [81]$$

Comparing this new definition of the square of the solubility parameter or the cohesive energy density with the one Hildebrand proposed which is  $\delta^2 = E^V/V$ , there is a difference of  $(\Delta n/V)RT$ . This difference is significant when the solubility parameters are used to calculate the excess heat of mixing according to Equation [49]

$$\Delta H^E = (x_1 V_1 + x_2 V_2) \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad [49]$$

A 1% error in estimating the solubility parameters in Equation [49] has led to an approximately 15% error in  $\Delta H^E$ . The error is significant in doing quantitative work like the calculations of activity coefficients.

The internal pressure of a liquid can be calculated by Equation [82]

$$\left(\frac{\partial E}{\partial V}\right)_T = P_i = T\gamma - P \quad [82]$$

where  $\gamma = \left(\frac{\partial P}{\partial T}\right)_V$  and  $P =$  external pressure.  $\gamma$ , the thermal pressure coefficient can be measured experimentally. Orwoll et al. (43), with their accurate data on the thermal pressure coefficients of n-alkanes over a wide range of temperatures and at zero pressure in conjunction with selected data from literature produced equations of state relating the thermal pressure coefficient with polynomials in powers of temperature for a few alkanes ( $n\text{-C}_6\text{H}_{14}$ ,  $n\text{-C}_8\text{H}_{18}$ ,  $n\text{-C}_{16}\text{H}_{34}$ ,  $n\text{-C}_{22}\text{H}_{46}$  and  $n\text{-C}_{36}\text{H}_{74}$ ). These equations are listed in Table 6.

Values of  $\gamma$  computed from these equations deviate no more than 1% from experimental determined values. Internal pressures of n-alkanes at various temperatures have been evaluated for this thesis by means of Equation [82] and Equations in Table 6. The results and those published by Allen et al. (1) are shown in Table 7. The internal pressures of n-alkanes at 20°C are linearly related to the reciprocal of the carbon atom numbers as shown in Figure 3, curve d. The temperature dependence of  $\delta'$  for  $\text{C}_7$  and  $\text{C}_{16}$  are plotted in Figure 5, curves d and g. The internal pressures of n-alkanes other than those listed in Table 8 can be achieved by linear interpolation of an

internal pressure versus  $1/N$  plot at a desired temperature.

Comparison of Methods for the Evaluation of Solubility Parameters. The solubility parameters at 20°C of n-alkanes computed by the four methods discussed above are tabulated in Table 8 for purpose of comparison. The values calculated by using the internal pressures are consistently higher than those calculated by using the other three methods due to the factor  $(\Delta n/V)RT$  difference except those n-alkanes in column A. As the carbon atom number increases, the differences in solubility parameters increase gradually. This is probably due to the increase in number of vibrational modes in the liquid states introduced by the segmental character of the molecular motion which is known to occur from viscosity and diffusion studies. Bagley et al. (4) claimed that solubility parameters should be calculated by accurate internal pressure measurements for quantitative studies due to the fact that the internal and external motions of the molecules contribute a significant effect. Table 9 illustrates the magnitude of the factor  $(\Delta n/V)RT$  by comparing the internal pressure and the heat of vaporization of heptane.

Although this discovery has shaken the use of old solubility parameters in any quantitative work, yet they still provide meaningful information to many practical qualitative studies, such as the choice of solvent in polymer and coating industry which is mainly based on the Hildebrand solubility parameter concept. Internal pressure data for

organic molecules are scarce, therefore accurate heat of vaporization data can serve to approximate meaningful solubility parameters.

Sometimes even accurate heat of vaporization data are unavailable, the index of refraction method shows promising results in the evaluation of "true" solubility parameters for both long and short chain n-alkanes with a standard deviation of  $\pm 0.4$  units in  $\delta$  value as shown in Table 8, column C. In Figure 6, the  $\delta^2$  values of n-alkanes at  $40^\circ\text{C}$  and  $60^\circ\text{C}$  estimated by both the internal pressure method and the refractive index method are plotted against  $1/N$ .

The internal pressure curve slightly deviates from the straight line at low  $1/N$  values. However at present, the extrapolated lines are used and the internal pressure obtained agrees with the calculated results within a  $\pm 3\%$  relative error. The internal pressure data obtained by extrapolation is noted with an asterisk in Table 7.

The curves in Figure 6 appear to be parallel. An empirical equation has been obtained by least square fitting the Lorentz-Lorenz function of n-alkanes with their corresponding experimental internal pressures.

The least square equation obtained is

$$P_i = 0.499 + 30.41 \left( \frac{n^2 - 1}{n^2 + 2} \right) \quad [83]$$

and the correlation coefficient is 0.9986. The uncertainty of the  $P_i$  values obtained is  $\pm 3\%$ .  $P_i$  and  $\delta'$  values of some of the short chain

branched n-alkanes are calculated at 76°C by Equation [83] and are listed in Table 7.

Polar Organic Molecules. The total liquid state energy is

$$E_T^L = E_Z^L + E_p^L + E_{hb}^L + E_{in}^L + E_{ex}^L \quad [84]$$

where

$E_p^L$  = energy associated with polar interaction

$E_{hb}^L$  = energy associated with hydrogen bonding

For the vapor in equilibrium with the liquid, the total vapor state energy is (assuming ideal vapor and taking  $E_Z^G = E_p^G = E_{hb}^G = 0$ ).

$$E_T^G = E_{in}^G + E_{ex}^G \quad [85]$$

Then, the energy of vaporization is

$$\Delta E^V = -E_Z^L - E_p^L + \Delta E_r \quad [86]$$

where  $\Delta E_r = (E_{in}^G - E_{in}^L) + \frac{\Delta nRT}{2} - E_{hb}^L$

This residual energy term  $\Delta E_r$  depends only on temperature at pressure near atmospheric.

The internal pressure measurement which is volume dependent will thus include the contribution of both polar and nonpolar energies (4), so that



$$P_i = -(E_Z^L + E_P^L)/V \quad [87]$$

Consequently the residual energy is

$$\Delta E_r = (\Delta E^V - P_i V) \quad [88]$$

According to Equation [88] there are two solubility parameters to be defined:

$$P_i = \delta_V^2 \quad [89]$$

and

$$\delta_V^2 = \delta_d^2 + \delta_p^2 \quad [90]$$

The volume dependent solubility parameter ( $\delta_V$ ) can be evaluated by accurate internal pressure data. By means of the homomorph method  $\delta_d$  and  $\delta_p$  can be separated from  $\delta_V$  (60).  $\delta_r$  results directly from  $(\Delta E^V/V - P_i)$  which is designated to the solubility parameter for hydrogen bonding  $\delta_h$ . Hensen (18) has published a large amount of data on  $\delta_d$ ,  $\delta_p$  and  $\delta_h$  for many organic compounds. Due to the limited scope of the present study, only five chlorinated hydrocarbons and a polar solvent, di-n-butyl phthalate are involved and their corresponding solubility parameters at 20°C obtained from Hensen (18) are shown in Table 10.

The Prediction of Solute Activity Coefficients in Gas-Liquid  
Chromatographic Solutions

Nonpolar Paraffinic Solutes in Nonpolar Paraffinic  
Stationary Phases

Paraffinic stationary-liquid phases have been widely used for boiling-point type gas-liquid chromatographic separations. In these solution systems, the molecular interactions between non-polar solute and an alkane stationary phase are predominantly due to dispersion forces alone. Also in solution systems with large solvent and small solute molecules, the size effect term should play an important role as the interaction parameters (solubility parameters) in determining the magnitude of the solute activity coefficients. These systems should provide a good test on both the Hildebrand regular solution theory and the Flory-Huggins theory.

The activity coefficient data to be considered have been tabulated in Table 1. There are actually three types of solute-solvent mixture systems described by these activity coefficient data. Namely, mixtures of linear molecules, mixtures of linear and branched molecules and mixtures of branched molecules.

The solution forces in all solute-solvent systems listed in Table 1 give rise to activity coefficients which are much less than unity largely due to the fact that the molecular volume difference between the solute and the solvent is significant. Probably the hydrocarbon

solutes are oriented so as to lie as parallel as possible to the solvent molecules with maximum interaction between the methyl groups.

Small and flexible molecules will be better accommodated within the solvent lattice and thus will be retained longer than larger molecules and will consequently have smaller activity coefficients.

The Excess Partial Molar Entropy of Mixing. The excess partial entropy of mixing in all cases considered are calculated by the Flory-Huggins equation [56-b]. The results are listed in Table 11. In all cases  $\ln \gamma_2^s$  values are negative which is mainly due to the small molar volume ratio of the solute and the solvent. In other words, the larger size effect results in a more distorted solution, hence a larger excess partial molar entropy term and a lower activity coefficient. This effect can be illustrated by comparing the results of hexane and heptane in Tetracosane at 76°C. Heptane has a larger molar volume than hexane and the  $\ln \gamma_2^s$  values are -0.389 and -0.459 which is equivalent to the 0.777 and 0.918 entropy unit respectively. The same solutes experience larger disorderness (more positive excess partial molar entropy of mixing) in solvents such as Triacontane ( $C_{30}$ ) and Hexatriacontane ( $C_{36}$ ) because of the large molar volume of these solvents. The molar volume of the solute decreases when temperature changes from 76°C to 60°C and results in a more disordered solution; therefore the excess partial molar entropy of mixing is larger at lower temperature. (At 76°C, hexane has an

excess partial molar entropy of 0.918 e. u. in n-Tetracosane and at 60°C, 0.933 e. u.). Isomeric paraffin solutes also exhibit the same effect. Comparing the excess partial molar entropy of mixing of all isomeric heptanes in squalane at 20°C, the larger the molar volume the less positive the excess entropy value will be. The discrepancies of the Flory-Huggins expression are that the excess partial entropy of mixing is considered to be solely contributed by the volume difference between the solute and solvent and that the total volume of the mixture remains constant after mixing. This is not always true in many liquid mixtures. A positive heat of mixing in most n-alkane mixtures is reported with a decrease of the total volume and thus makes the excess partial molar entropy term larger than the value calculated by the Flory-Huggins expression. Furthermore, random distribution of the solute and the solvent species throughout the solution is also assumed. However, a non-zero excess heat of mixing must be attributed to a degree of preferential formation of stronger interacting species resulting in less randomness in the mixture. These factors affect the accuracy of estimating the excess partial molar entropy of mixing (or  $\ln \gamma_2^s$ ) if the excess partial molar entropy of mixing is considered separately. Hildebrand (24) remarked that even though these assumptions are important, yet the percentage correction for the entropy is small when the excess energy of mixing is small.

The Excess Partial Molar Heat of Mixing. In the following

discussion, the "experimental" ( $h_{\text{ex}}^e$ ) and theoretical ( $h_t^e$ ) excess partial molar heats of mixing are defined as

$$\frac{h_{\text{ex}}^e}{RT} = \ln \gamma_{\text{ex}}^e = \ln \gamma_2^\infty - \ln \gamma_2^s \quad [91]$$

$$\frac{h_t^e}{RT} = \ln \gamma_t^e = \frac{V_2}{RT} (\delta_1 - \delta_2)^2 \quad [92]$$

The so-called "experimental" excess partial molar heat of mixing is actually the difference between the logarithm of activity coefficient obtained from experimental result such as those listed in Table 1 and  $\ln \gamma_2^s$  calculated by Flory-Huggins' expression. The results of these experimental excess partial molar heat of mixing are listed in terms of  $\ln \gamma_{\text{ex}}^e$  in Table 12. Since there are no accurate data on the excess partial molar heat of mixing in the solution systems considered, the "experimental" partial molar heat of mixing values are used to compare with the theoretical results calculated by Equation [92] even though the "experimental" values are subject to uncertainties. If all assumptions are valid for the estimation of excess partial molar entropy of mixing, a 1% error in the estimation of molar volumes will lead to approximately 5% relative error in  $\ln \gamma_2^s$ , and about 4% relative error in  $\ln \gamma_{\text{ex}}^e$ . The experimentally determined activity coefficients  $\gamma_2^\infty$  directly affect the reliability of  $\ln \gamma_{\text{ex}}^e$ . A 1% relative error in  $\gamma_2^\infty$  results in about 6% relative error in  $\ln \gamma_{\text{ex}}^e$ .

Fortunately, all activity coefficient data are reported to have better than 1% uncertainty. Considering all these sources of uncertainties and selecting the best data on activity coefficients, approximately a minimum of  $\pm 5\%$  error is expected in  $\ln \gamma_{\text{ex}}^{\text{e}}$ . A semi-quantitative comparison between the "experimental" and the theoretical excess partial molar heat of mixing will be presented in the following discussion.

The theoretical excess partial molar heats of mixing evaluated by the Hildebrand-Scatchard equation depend on the accuracy of the solubility parameters. A detailed discussion of the evaluation of solubility parameters has been given in the precedings. In view of the theoretical background and the results obtained from each method, two sets of solubility parameters are adopted for the evaluation of  $\ln \gamma_{\text{t}}^{\text{e}}$ . The first set (Set I) of solubility parameters are calculated by means of both the heat of vaporization and refractive index methods. According to previous discussion in solubility parameter, the heat of vaporization estimated by Antoine equation fails to provide reasonable solubility parameters for higher n-alkanes while the refractive index method yields good solubility parameters for higher n-alkanes. Therefore, the refractive index method is used to estimate  $\delta$  values for the higher alkanes and the heat of vaporization method for the lower alkanes. The second set (Set II) of solubility parameters are calculated directly from the internal pressures of the liquids.

$\ln \gamma_t^e$  calculated by Set I and Set II are listed in Tables 13 and 14, respectively. The observed theoretical  $\ln \gamma_t^e$  values generally are small and positive. These small positive excess partial molar heats of mixing cannot offset the large negative  $\ln \gamma_2^s$  term due to unequal size molecules resulting in a negative deviation from Raoult's Law. In comparing with the  $\ln \gamma_{ex}^e$  values, Set I gives better overall predictions to the  $\ln \gamma^e$  values. However this does not mean that solubility parameters calculated by heat of vaporization or index of refraction are superior or theoretically correct. These results are fortuitous in nature. In fact, the results in Set II are noteworthy. Strictly speaking, the solubility parameter of a liquid should be calculated by the internal pressure. Therefore, results in Set I can only serve for qualitative studies. Since results in Set II are based on a better theoretical foundation, they yield more meaningful information to the actual intermolecular energy in these solution systems.  $\ln \gamma_t^e$  results in Set II in all cases are very much larger than the  $\ln \gamma_{ex}^e$  values. Hildebrand (25) and Shinoda-Hildebrand (56) also discovered this anomalous behavior of paraffin mixtures which cannot be explained by the Hildebrand-Scatchard equation.

The Discrepancies of the Hildebrand-Scatchard Equation in Paraffinic Solutions. Geometric Mean Assumption: Shinoda (56) attributed the large  $\ln \gamma_t^e$  values predicted to the breakdown of the Hildebrand-Scatchard equation. The linear n-alkane molecules can fit

into a close-packing conformation to attain the maximum interaction such that the geometric mean approximation is no longer true, or in other words

$$C_{12} > (C_{11} C_{22})^{1/2}$$

and as a consequence  $\ln \gamma_t^e$  values become too large. This anomalous effect decreases as the molar volume of the n-alkane increases. For example, hexane has a  $\ln \gamma_{ex}^e$  value 0.228 in n-Tetracontane at 76°C, and  $\ln \gamma_t^e$  is 0.424, while nonane  $\ln \gamma_t^e$  value is 0.159 which is quite close to  $\ln \gamma_{ex}^e$  value of 0.140. This effect may be due to the fact that small molecules (small molar volume) can fit into the solvent lattice better than large molecules. Therefore, the smaller molecules attain a stronger interaction and thus causing  $C_{12}$  deviates further from the geometric approximation, while the larger molecules interact less effectively with the solvent molecules. As a consequence,  $C_{12} \approx (C_{11} C_{22})^{1/2}$ .

The failure of the geometric mean assumption can be compensated by an empirical adjustment of the  $(C_{11} C_{22})^{1/2}$  term. Instead of using the geometrical mean assumption for  $C_{12}$ , the following equation will be used

$$C_{12} = (1 - l_{12})(C_{11} C_{22})^{1/2} \quad [93]$$

where  $l_{12}$  is an empirical binary coefficient, small compared to



unity. Substituting into Equation [92], Equation [93] becomes

$$\ln \gamma_t^e = \frac{V_2}{RT} [(\delta_1 - \delta_2)^2 + 2\ell_{12} \delta_1 \delta_2] \quad [94]$$

Hildebrand (25) found that  $\ell_{12}$  in simple hydrocarbon mixtures are negative.  $\ell_{12}$  values have been calculated in all cases by the author and are listed in Table 15. The magnitude of the empirical binary parameters vary from zero to a small negative value (e. g.,  $-1.7 \times 10^{-2}$ ). It is obvious that a very small value in  $\ell_{12}$  will have a large effect on  $\ln \gamma_t^e$ . At present, unless accurate excess partial molar heat of mixing and  $\ln \gamma_{ex}^e$  were obtained,  $\ell_{12}$  can only be discussed qualitatively because both  $\ln \gamma_{ex}^e$  and  $\ln \gamma_t^e$  are subject to considerable uncertainty. In a relative scale a larger negative  $\ell_{12}$  value implies that  $C_{12}$  deviates farther from the geometrical mean assumption, whereas a smaller negative  $\ell_{12}$  value implies the opposite.

The branching ratio of a molecule which is defined as

$$r = \frac{\text{number of methyl groups}}{\text{total number of carbon atoms}} \quad [95]$$

are well correlated with  $\ell_{12}$ .

In Figure 7, the branching ratios of the n-alkanes are plotted against  $\ell_{12}$  for four solvents (n-Tetracosane, n-Triacontane,

n-Dotriacontane and Hexatriacontane) at 76°C and two solvents (n-Tetracosane and n-Octadecane) at 50°C.  $\ell_{12}$  decreases as the carbon number of the solvent increases but fails to decrease further when the carbon number of the solvent reaches 30. All  $\ell_{12}$  data points for n-Triacontane, n-Dotriacontane and n-Hexatriacontane fall on the same curve. This is probably because of the similar environment a solute molecule experienced in these solvents. The temperature dependence of  $\ell_{12}$  is shown in Figure 8. In the case of n-Tetracosane, the curve displaces downward ( $\ell_{12}$  increasing) as the temperature decreases. This displacement of the curve with variation of temperature is not linear as shown by the curves at 60°C and 50°C. At low branching ratio region, the curves corresponding to different temperatures approach an asymptote. The squalane curve displaced in Figure 8 yields an interesting contrast between a mixture of linear solute and linear solvent and a mixture of linear solute and branched solvent. Assuming that the  $C_{36}$  (76°C) curve will behave similarly as the  $C_{24}$  and  $C_{18}$  curves, at 20°C, the  $C_{36}$  curve would probably lie very much below the squalane curve. The more negative  $\ell_{12}$  values in squalane implies a stronger interaction between molecular species. Comparing the actual structural difference between the two solvents, squalane, 2, 6, 10, 15, 19, 23-hexamethyl tetracosane, is a highly branched alkane while n-Hexatriacontane is a linear alkane, it is reasonable to speculate that squalane has more contact sites than

the linear n-Hexatriacontane so that molecules in squalane experience stronger interaction. Smaller molecules such as butane can just fit into the interstices of the squalane solvent molecules. As a consequence, the squalane curve exhibits a sharp rise with  $r > 0.4$ . Branched alkane molecules interact with squalane in a very confusing pattern. The data points of  $l_{12}$  of these branched alkanes do not fit into the general pattern displaced by the linear alkanes. All isomeric alkanes have higher branching ratios than their corresponding linear alkanes, however the  $l_{12}$  values of these isomeric alkanes are lower than values expected. This is simple because steric hindrance probably prevents the branched molecules from attaining stronger interaction with the solvent molecules. An effective branching ratio has been assigned to each of those branched alkanes with respect to their n-alkanes.

Constant Volume Mixing Assumption: One of the assumptions of the regular solution theory is that there is no volume change upon mixing. Orwoll and Flory (44) discovered that many of n-alkane mixtures show volume change. The excess volume is of the order -0.5 to -1.0 c. c. /mole. As temperature is raised, the volume change becomes increasingly negative and it is not surprising that the experimental heat of mixing decreases with increasing temperature. Flory has called this the "equation of state" effect; the short chain n-alkanes is at a high reduced temperature than the long chain solvent and

increasingly more expanded over its close-packed volume than either the solvent or the mixture.  $\ln \gamma_{ex}^e$  values follow the trend found by Orwoll and Flory, however  $\ln \gamma_t^e$  values estimated by the Hildebrand-Scatchard equation show the opposite trend.  $\ln \gamma_t^e$  values increased with the increase of temperature. These results are not unexpected because of the discrepancy of the theory.(47). This negative change of volume produces a large disparity between  $\Delta E_V^E$  and  $\Delta H_p^E$  especially at high temperatures. Therefore the energy of mixing calculated by the Hildebrand-Scatchard equation must be corrected for the volume change. In view of this argument the poor agreement between  $\ln \gamma_t^e$  and  $\ln \gamma_{ex}^e$  cannot be solely ascribed to the invalidity of the geometric mean. Moreover all mixture systems in this study are infinitely dilute with respect to the solute and the volume change is assumed to be small enough to cause insignificant errors.

Dissolution of Gaseous Solutes in Liquid Solvents: Usually gas chromatographic systems are operated above the boiling points of many organic compounds. These organic compounds exist essentially as vapor states rather than liquid states. Therefore, the use of liquid solubility parameters to estimate the heat of mixing is not appropriate, and at the same time the isothermal, isopiestic dissolution of a gas in a liquid is not a constant volume process. If two liquids are mixed it is usually accompanied by a change of enthalpy and entropy; however, for a gas dissolving in a liquid, there is, in addition, a large decrease

in volume. In order to apply regular solution theory (which assumes no volume change) it is necessary first to condense the gas to a liquid like volume or its partial molar volume in the liquid solvent.

Hildebrand and Gjaldbaek (22) proposed that solute partial molar volume should be used in the Hildebrand-Scatchard equation and the Flory-Huggins' equation when gaseous solute is dissolved in liquid. Equations [91] and [92] are thus modified by replacing the molar volume by the partial molar volume to improve the prediction of  $\ln \gamma_t^e$ . There is no accurate way to estimate the partial molar volume of the solute in a solution. An equation proposed by Watson (26) is adopted to estimate, with fair accuracy, the partial molar volume of solute.

$$\bar{V} = V_1 \omega_1 (5.7 + 3.0T/T_c) \quad [93]$$

where

$\bar{V}$  = partial molar volume of solute

$V_1 \omega_1$  = Watson's expansion factor

$T_c$  = critical temperature of the solute (2)

Those mixture systems with temperatures above the boiling points of the solutes have been studied.  $\bar{V}$ ,  $\ln \gamma_{ex}^s$ ,  $\ln \gamma_{ex}^e$ ,  $\ln \gamma_t^e$  and  $\gamma_2^\infty$  are calculated and given in Table 16. Comparing the  $\ln \gamma_{ex}^e$  and  $\ln \gamma_t^e$  values, a better agreement has been obtained. Because of the unreliable nature of the partial molar volume estimated, the results should not be analyzed with those obtained in Tables 14 and 15.

Prediction of Solute Activity Coefficients. The activity coefficient of a solute in a solution at infinite dilution is obtained by the summation of  $\ln \gamma_t^e$  and  $\ln \gamma_{ex}^s$  terms predicted by the Flory-Huggins and Hildebrand-Scatchard equations.

$$\ln \gamma_t^\infty = \ln \gamma_{ex}^s + \ln \gamma_t^e \quad [56]$$

This over simplified solution model probably introduce far more serious errors in the calculation of the heat and the entropy separately than that of the free energy or  $\ln \gamma_2^\infty$ . Scott (55) concluded that solubility parameter theory does in fact fit the free energy of mixing data in most binary systems of non-polar electrolytes.

The calculated results of the activity coefficients are given with their relative deviations in Tables 17 and 18. Again, activity coefficients with their  $\ln \gamma_t^e$  terms estimated by Set I solubility parameters yield smaller relative error than those estimated by Set II solubility parameters. However this should not be the criterion to conclude that the former is the better method. It is the latter that provide more meaningful results. In some cases, the relative deviations are larger than 20%. The causes of such large deviations which may be attributed to the breakdown of Hildebrand-Scatchard equation have already been discussed in detail previously. The employment of "partial molar volume" have shown significant improvement of the

prediction of activity coefficients as indicated in Table 16.

### Polar-Solutes in Non-Polar and Polar Stationary Phases

Polar-Solutes in Non-Polar Paraffinic Stationary Phases. The activity coefficients of polar-solutes in non-polar solvents can also be predicted by the combination of Flory-Huggins equation and Hildebrand-Scatchard equation. However the Hildebrand-Scatchard equation which solely accounts for dispersion interaction must be modified to suit the new situation where induction interaction is significant. The modified form is shown by Equation [60]

$$\ln \gamma_t^\infty = \ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1} + \frac{V_2}{RT} [(\delta_{d_1} - \delta_{d_2})^2 + \delta_{o_2}^2 + 2\Phi_{in} + 2\Phi_h] \quad [60]$$

The equation can also be broken down as before to

$$\ln \gamma_{ex}^s = \ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1} \quad [56-b]$$

$$\ln \gamma_t^e = \frac{V_2}{RT} [(\delta_{d_1} - \delta_{d_2})^2 + \delta_{o_2}^2 + 2\Phi_{in} + 2\Phi_h] \quad [94]$$

Blank et al. (5) reported the  $\Phi_{in}$  is function of the product of  $\delta_d$  and  $\delta_o$ . Keller et al. (29) introduced a solubility parameter  $\delta_{in}$  for induction interaction and expressed the  $\Phi_{in}$  function as

$$\Phi_{in} = \frac{2V_2}{RT} [\delta_{in_1} \delta_{d_1} + \delta_{in_2} \delta_{d_2} - \delta_{in_1} \delta_{d_2} - \delta_{in_2} \delta_{d_1}] \quad [95]$$

Since  $\Phi_{in}$  was reported to be related to  $\delta_d$  and  $\delta_o$ , all  $\delta_{in}$  in Equation [95] are replaced by  $\delta_o$ . Therefore, Equation [95]

becomes

$$\Phi_{in} = \frac{2V_2}{RT} [\delta_{o_1} \delta_{d_1} + \delta_{o_2} \delta_{d_2} - \delta_{o_1} \delta_{d_2} - \delta_{o_2} \delta_{d_1}] \quad [96]$$

For polar solute and nonpolar solvent mixtures, Equation [95] further simplified to

$$\Phi_{in} = \frac{2V_2}{RT} [\delta_{o_2} \delta_{d_2} - \delta_{d_1} \delta_{o_2}] \quad [97]$$

Due to the lacking of accurate data on the polar solubility parameters and solute activity coefficients of polar solutes in nonpolar solvents, two cases have been chosen for examination. With this limitation, the results can only serve for a test rather than a proof to the validity of theory. Tewari's (59) data on activity coefficients of halo-alkanes in Tetracosane, Triacontane and Hexatriacontane paraffinic solvents are used. "Simple" polar molecules like the halo-alkanes are expected to interact with the paraffinic solvent molecules without any complex interactions, such as hydrogen bonding and acid-base interactions, or in other words  $\Phi_h = 0$ .



$\ln \gamma_{\text{ex}}^s$ ,  $\ln \gamma_{\text{ex}}^e$ ,  $\Phi_d$  (dispersion interaction energy),  $\Phi_{\text{in}}$  (induction interaction energy),  $\ln \gamma_t^e$ ,  $\gamma_t^\infty$  and the relative deviations of the predictions of  $\gamma_t^\infty$  are all listed in Table 19. The prediction on  $\gamma_2^\infty$  is surprisingly good. No corrections have been made to the dispersion energy term. The geometric mean assumption seems to be valid in these cases. The negative  $\Phi_{\text{in}}$  term indicates the induction interaction between the solute and solvent molecules is favored. The success of this empirical evidence suggests that for a given binary system,  $\Phi_{\text{in}}$  depends on the dielectric constant of the mixture and hence, on the composition of the mixture.

Polar Solutes in Polar Stationary Phases. In mixing a polar solute with a polar solvent, the situation is more complicated. The interactions among the molecules are not only restricted to dispersion, induction interaction, dipole-orientation and hydrogen bonding (or in general, electron donor-acceptor interactions) also play an important role in the energy of mixing of the solution. Therefore,  $\Phi_h$  in Equation [60] can no longer be zero. Hensen et al. (18) and Bagley et al. (4) have published solubility parameters for hydrogen bonding,  $\delta_h$ , for a number of organic compounds, but there has been no theoretical proof whether  $\Phi_h$  is related to  $\delta_h$ . In the present studies,  $\Phi_h$  is used as an adjustable parameter to fit Equation [60] to experimental results. There are scarcely any data on the solubility parameters of polar stationary phases to be found in the

literature. Hensen (18) has published solubility parameters for a number of plasticizers for the use in paint technology. One of those plasticizers is di-n-butyl phthalate which is a stationary phase commonly used in gas chromatography. Activity coefficients data are obtained for five halo-alkanes in di-n-butyl phthalate at 20°C from Martire's (39) paper. The solubility parameters, molar volumes of halo-alkanes and di-n-butyl phthalate are given in Table 10. All interaction functions and  $\Phi_h$  values are listed in Table 20. The geometrical mean rule is assumed to be valid in all cases. These results show considerably dipole-dipole orientation between the solute and solvent molecules. Although  $\Phi_h$  values are subject to errors accumulated from the determinations of other energy terms, the large negative  $\Phi_h$  values suggest significant specific interactions (not restricted to hydrogen bonding) between the solute and solvent molecules. Goates et al. (16) discovered striking evidence of attraction between benzene and halo-alkanes in excess of that attributable to London forces alone and it is sufficiently strong to result in negative deviations from Raoult's Law. In these present cases, the chloride group attached on the methylene or ethylene molecules are electro-negative enough to cause the H atom positive to accept electrons from the electron rich aromatic ester, di-n-butyl phthalate. No correlations have also been found between  $\Phi_h$  and  $\delta_h$ . According to Keller et al. (29),  $\delta_h$  should be further separated into two solubility

parameters  $\delta_a$ , and  $\delta_b$ , where  $\delta_a$  is related to the electrons accepting power and  $\delta_b$  to the electrons donating power of the molecules. Keller also proposed that  $\Phi_h$  should be expressed in terms of  $\delta_a$  and  $\delta_b$  of both the solvent and the solute. Therefore,

$$\Phi_h = \frac{2V_2}{RT} [\delta_{a_1} \delta_{b_1} + \delta_{a_2} \delta_{b_2} - \delta_{a_1} \delta_{b_2} - \delta_{a_2} \delta_{b_1}] \quad [98]$$

If the equation suggested has the correct form, accurate  $\delta_a$  and  $\delta_b$  data are required. No scheme of  $\delta_a$  and  $\delta_b$  values has yet been developed to separate from  $\Phi_h$ , so that no quantitative test of the equation suggested can be made.

#### 4. PHILOSOPHY

The initial goals of this thesis are to

1. Investigate the theoretical and thermodynamic background of the Rohrschneider index system and the McReynold index system.
2. Study the solute-solvent interactions in gas-chromatographic solution system in view of these two schemes.
3. Estimate the solute polarity factors based on the McReynold's scheme and examine the behaviors of these solute polarity factors with reference to the molecular structures of the solutes. The results of these investigations which will be presented in the following discussion and the appearance of Keller, Karger and Snyder's publication (29) have convinced the author to abandon the investigation of solute-solvent interactions based on these two schemes and to undertake a more fundamental and difficult approach: the applications of the solubility parameters concept and the thermodynamic solution theory to study solute-solvent interactions in gas chromatographic solutions which have been described in the previous chapters.

### The Rohrschneider Index and the McReynold Index System

The purpose of the Rohrschneider Constants system and McReynold Index system is to characterize gas chromatographic stationary phases by their polarity factors. These polarity factors are represented by the retention index differences of various reference compounds in the polar stationary phase and squalane.

Rohrschneider (52, 53) has published polarity factors for a number of stationary phases. At first, Rohrschneider characterized a stationary phase by using three polarity factors, namely the retention index differences of benzene, ethanol and methyl ethyl ketone (53).

Rohrschneider later found that three polarity factors cannot fully express the many interaction potentials of a stationary phase, therefore two more polarity factors were added to the previous scheme (52).

Rohrschneider Constants system thus characterize a stationary phase by five polarity factors (benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine). McReynold (35), however, felt that the polarity of a stationary phase is better expressed by ten reference compounds (benzene, butanol, 2-pentanone, nitropropane, pyridine, 2-methyl-2-pentanol, 1-iodobutane, 2-octyne, 1,4-dioxane, and cis-hydridine). Each polarity factor has its own meaning. For example, the polarity factor represented by butanol or ethanol shows the H-bonding interaction potential and nitropropane or nitromethane

shows the dipole orientation interaction potential of the stationary phase.

With these polarity factors assigned to each stationary phase, the characteristic polarity constants (a, b, c, ...) for any organic compound can be estimated according to Equation [63].

$$\Delta I_p^{RX} = ax + by + cz + \dots \quad [63]$$

These polarity constants of an organic compound should bear the same meaning with their corresponding polarity factors of the stationary phase. Once the polarity factors (a, b, c, ...) are obtained, they are valid for the organic compound regardless of the column being used.

These constants can be determined by (a) chromatographing the compound on at least five columns with known polarity factors if Rohrschneider's scheme is used or at least ten columns if McReynold's scheme is used (one of the columns must be squalane), (b) the retention index for the compound on each column, (c) calculating the index difference. Rohrschneider (52) and McReynold (35) have already published polarity factors of a large number of stationary phases. Through private communications with McReynold, a compilation of retention index data of some organic compound has been obtained. These data are listed in Table 21. Since Equation [63] is a linear equation, the polarity constants of an organic compound have been

calculated by fitting the experimental data to Equation [63] by means of a multiple linear regression analysis computer program. The ten McReynold's polarity constants (designated by alphabets from a to j) for these organic compounds are given in Table 22. Rohrschneider (52) also published polarity constants for a few organic compounds. Table 23 is a duplication of Rohrschneider's data. With these polarity factors of the stationary phases and the organic compounds, retention index differences of an organic compound in various columns can then be calculated with a mean deviation of 6 index units for Rohrschneider's scheme and 1 index unit for McReynold's scheme. This result does not indicate McReynold's scheme is better simply because the more polarity factors terms used in Equation [63] will result in letting the computer more freedom to adjust the polarity constants of the organic compound, and hence the products of the polarity terms compensate one another to yield a better prediction of  $\Delta I$ .

Some polarity constants of organic compounds in McReynold's schemes shown in Table 20 seem to vary in a consistent pattern. For the alcohol family, the second polarity constants which measures the H-bonding potential have been plotted against the  $\delta_h$  value obtained from Hensen (18) in Figure 9. The hydrogen bonding potentials of the alcohols decrease with the hydrogen bonding solubility parameter  $\delta_h$  and start to level off after 1-hexanol. The behavior of methanol is exceptional. The sharp rise from ethanol to methanol indicates that

methanol is far more reactive and can form stronger hydrogen bonding with the stationary phase. Secondary and tertiary alcohols have larger values on the sixth polarity constants because the reference compound 2-methyl-2-pentanol has greater resemblance to these alcohols. However, this consistency cannot be found in Rohrschneider's scheme. Although some consistencies are found between the polarity constants and the physical nature of the organic compounds in McReynold's scheme, most of the polarity constants show an incongruent pattern in both schemes, e. g., the polarity factor "a" which is a measure of the polarizability of an organic molecule, has no correlations to  $\delta_d$ .

A detailed examination of Tables 21 and 22 may give rise to these questions:

1. How many polarity factors should be used to characterize a stationary phase?
2. Is each of these polarity factors in fact representing a unique interaction potential of the stationary phase?

These questions cannot be answered without studying the theoretical foundation of the scheme. The retention index difference of the reference compound which is the polarity factor is expressed by Equations [61] and [63]



$$\Delta I_p^{RX} = \frac{100}{\Delta F_p^{CH_2}} (\Delta F_p^{RX} - \Delta F_p^{n_u}) \quad [61]$$

where  $100/\Delta F_p^{CH_2}$  is just the slope of curve  $p$  in Figure 1. Each of the free energy of solution terms in Equation [61] actually includes two parts as shown by

$$\Delta F_i = RT(\ln P_i^0 + \ln \gamma_i^\infty) \quad [99]$$

$RT \ln \gamma_i$  is the excess free energy and should be expressed as Equation [57]. Each of the different interaction free energy terms in Equation [57] is further represented by solubility parameter terms as shown in Equation [60]. The free energy of solution  $\Delta F_p^{RX}$  of the polar organic compound  $RX$  should therefore include all interaction free energy terms such as dispersion interaction, dipole orientation, induction interaction, hydrogen bonding interaction and complex formation energies besides an entropy term and the vapor pressure of  $RX$ . However the free energy of solution  $\Delta F_p^{n_u}$ <sup>4</sup> includes only the dispersion interaction, and the induction interaction free energy terms, an entropy term and the vapor pressure of  $n_u$ . The difference of  $\Delta F_p^{RX}$  and  $\Delta F_p^{n_u}$  will not cancel out the vapor pressure term, the entropy term, the dispersion interaction term and the

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<sup>4</sup>The definition of  $\Delta F_p^{n_u}$  is on p. 115.

induction interaction term completely, because the molar volumes, the dispersion solubility parameters, the vapor pressure of RX and  $n_u$  are different. Therefore the  $\Delta I_p^{RX}$  value actually composes of the dipole orientation term, the hydrogen bonding interaction term of RX and the residuum resulting from the incomplete cancelation. If a reference compound is not chosen carefully, the polarity factor in fact does not represent a unique type of the interaction. For example the  $\Delta I$  of benzene, which is one of the polarity factors in both schemes, is very likely to contain induction interaction energy which results from the polarizable  $\pi$  electrons, and complex formation energy. The  $\Delta I$  value of nitromethane or nitropropane is another example. Both molecules differ from their corresponding  $n_u$  molecules by having a tendency to interact strongly with another dipole (dipole orientation), to induce a dipole on other polarizable molecules (induction) and to act as Lewis bases (electron donor and acceptor interaction). Wherefore in order to isolate a particular type of interaction from the reference compound for purpose of characterizing a stationary phase, the strength of the various interactions must be known separately in terms of retention indices.

Preceding investigations have also proven that interaction energies are related to the product of solubility parameters. The dispersion energy and the dipole orientation are proportional to the square of the difference of solubility parameters, while the induction

and hydrogen bonding energies are separately given by the summation of four solubility parameters product terms. In order to express the total interaction potentials of an organic compound or a stationary phase, at least five polarity factors are required.

In view of these arguments, the number of polarity factors in Rohrschneider scheme are probably enough to characterize a stationary phase; however, the five polarity factors used are by no means representing the various unique interactions. Some of the ten reference compounds in McReynold's scheme may be redundant. For example, 2-methyl-2-pentanol expresses a similar function as butanol; 1,4-dioxane and pyridine are both electron donors.

The controversial publication by Keller et al. (29) has simultaneously come to the same conclusion based on the solubility parameter concept that the reference substances are capable to interact with the stationary phase molecules by various types of interactions. Take nitromethane for example, nitromethane has these solubility parameters  $\delta_d = 7.30$ ,  $\delta_o = 8.00$ , and  $\delta_b = 1.00$  (approximate value). Therefore nitromethane can interact with the stationary phase molecules by dispersion force, dipole orientation and electron donor-acceptor interaction. Keller et al. (29) proposed that the classical solubility parameter concept and the Hildebrand-Scatchard equation can offer a starting basis for studying chromatographic retention of

non-polar solute-solvent systems. The modified Hildebrand-Scatchard equation for polar solute and solvent systems was predicted by Keller et al. (29) to be applicable to study solute-solvent interactions in gas chromatographic solutions.

## 5. SUMMARY

In connection to many problems in the field of physical separation it would be of great value to have at ones disposal an accurate method for the determination of solute activity coefficient at infinite dilution in a liquid phase. From the solute activity coefficient not only the specific retention volume but also the partition coefficient can be calculated. It is known that the solute activity coefficient yields much information on the nature of intermolecular forces between the solute and the solvent molecules.

The application of solution theories to the study of the solute-solvent interactions and to the prediction of the solute activity coefficient have been achieved in this thesis. This thesis has demonstrated that the logarithm of the solute activity coefficient (or the partial molar excess free energy of mixing) can be calculated by a combination of the Flory-Huggins equation, (Equation 35) which is associated with the statistical effects due to the size difference between the solvent and solute molecules, and the Hildebrand-Scatchard equation (Equation 49) which is associated with the interaction energy between the solute and solvent molecules. Three different methods have been tested by the author to estimate the solubility parameters of pure solute and pure solvent components. Some of the results have been compared with published data on solubility parameters estimated at 20° C from

accurate vapor pressure data which have been corrected for gas phase imperfection. According to Hildebrand's definition, the solubility parameter of a pure component is calculated by the heat of vaporization. The heat of vaporization which is calculated from the Antoine Constants have been shown by the author to be unable to estimate solubility parameters of higher alkanes at low temperatures. The rationale is that Antoine constants for higher alkanes are not defined at low temperatures. The refractive index method has been chosen by the author to estimate the solubility parameters of the higher n-alkanes because this method yields solubility parameters in better agreement with the published data. The solubility parameters estimated directly from the internal pressures of pure components have been shown by the author to be more theoretically sound. The interaction energies of nonpolar solute and nonpolar solvent systems have been calculated by two sets of solubility parameters. Set I consists of solubility parameters calculated from the heat of vaporization method for the lower alkanes and from refractive index method for the higher alkanes. Set II are solubility parameters calculated directly from the internal pressures. The interaction energies (or  $\ln \gamma_t^e$ ) in nonpolar solvent and nonpolar solute solution systems calculated both by Set I and Set II solubility parameters by the author show significant deviations from the experimental results ( $\ln \gamma_{ex}^e$ ). These deviations are attributed to the failure of the geometric mean assumption (Equation

94) which is inherent in the Hildebrand-Scatchard equation. The binary coefficients ( $l_{12}$ ) which serves as a correction factor for the geometrical mean assumption have been calculated by the author for various nonpolar solute and nonpolar solvent solution systems.  $l_{12}$  values which are small compared to unity are related to the branching ratio of the solutes.  $l_{12}$  values also increase with the temperature and the number of carbon atoms of the solvents. The deviations can also be attributed to the use of molar volume as the true volume of the solute in a solution. Replacing the molar volume of the solute by the partial molar volume, estimation of the interaction energies of mixture containing nonpolar components have been improved.

The solute activity coefficients of nonpolar mixture systems have been predicted by combining the values obtained from the Flory-Huggins and Hildebrand-Scatchard equations. In most cases, the predicted solute activity coefficients are within  $\pm 20\%$  relative error compared to published experimental values. This poor agreement is attributed to the breakdown of the geometrical mean assumption in the Hildebrand-Scatchard equation.

A few cases of polar solute and nonpolar solvent solution systems have also been examined in this thesis. The solute-solvent interaction energies have been estimated by the modified Hildebrand-Scatchard equation. The results show that the excess partial molar

free energy of mixture is contributed by their interaction energies, namely the dispersion interaction energy between the polar solute and nonpolar solvent molecules, the dipole interaction energy between solute molecules, and a negative induction interaction energy between the polar solute and the nonpolar solvent molecules. None of these energies has shown to be negligible. The overall predictions of the solute activity coefficients are within  $\pm 10\%$  relative error.

Mixtures containing polar solute and polar solvent molecules have been studied by the author. The solute-solvent interaction energies have also been estimated by the modified Hildebrand equation. The excess partial molar free energy of mixture includes an additional interaction energy term. This energy term has a large negative value and is responsible for the formation of hydrogen bond or the formation of complex between the solute and solvent molecules.

In view of these findings, the reference substances used in the Rohrschneider Index System in classifying stationary phases are subject to further examination. The retention index differences of these reference substances does not reflect a unique type of interaction but rather a combination of various interactions. It is not surprising that the polarity factors of organic compounds (the  $a, b, c, d, e, \dots$  values) estimated from the polarity factors of the stationary phases ( $x, y, z, u, s, \dots$  values) appear in a confusing pattern rather than a systematic variation according to the molecular structure of the solute



molecules.

In order to select a reference substance characterizing an unique interaction, a complete quantitative isolation of the various interaction forces must be achieved. The isolation of forces of interaction can be clearly seen in the preceding studies of the predictions of solute activity coefficients by solution theory in various solute-solvent mixtures.

For purposes of future investigations in the classification of stationary phases, the author would like to suggest that the polarity of the stationary phases may be examined in terms of the solubility parameters. More research should be directed toward the measurements of solubility parameters of gas chromatographic stationary phases. In view of the solution theory, the polarity factors of the stationary phases are more appropriate to be expressed in terms of the logarithm of solute activity coefficients. It is because the logarithm of solute activity coefficients are directly related to the interaction forces. The retention index differences are related to the free energies of solution which include according to Equation [26] the ideal and excess free energy of solution. In order to achieve quantitative isolation of interaction forces, it is necessary to examine in light of the interaction energies terms in the modified Hildebrand-Scatchard equation: Equations [60] and [95], and this cannot be done without a true knowledge of the solubility parameters of the solutes

and stationary phases. It is possible to apply the homomorph concept to isolate the polar interaction forces from the dispersion interaction force. The configurational interaction force can be easily isolated if the solute activity coefficient of a nonpolar substance which has the same  $\delta_d$  value as the stationary phase is known. The dispersion and induction interaction forces may also be isolated as a sum if the molar volume of a nonpolar solute is approximately at same as the stationary phase. So far there is scarcely any information concerning the relationship between  $\delta_h$ , and the hydrogen bonding formation and electron donor-acceptor interaction forces. It may be necessary to relate  $\delta_h$  with  $\delta_a$  and  $\delta_b$  as suggested by Keller et al. (29).

Although this thesis has tested the applicability of solubility parameters concept and solution theory to gas chromatographic solute activity coefficients data, yet these theories should be subject to further refinements and verification.

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## APPENDIX

## APPENDIX

Solute Components

1. n-Butane
2. n-Pentane
3. n-Hexane
4. n-Heptane
5. n-Octane
6. n-Nonane
7. Isopentane
8. 3-Methylpentane
9. 2, 2-Dimethylpentane
10. 2, 4-Dimethylpentane
11. 3, 3-Dimethylpentane
12. 2, 3-Dimethylpentane
13. 2-Methylhexane
14. 3-Methylhexane
15. 3-Ethylpentane
16. 2, 2, 4-Trimethylpentane
17. 1-Chlorobutane
18. Dichloromethane
19. Chloroform
20. Trichloroethylene
21. 1, 2-Dichloroethane

Table 1. Activity coefficients of solutes at infinite dilution.

Source	Solvents	Temp	Solute Components <sup>a</sup>										
			1	2	3	4	5	6	7	8	9	10	11
10	squalane	20	0.578	0.617	0.635	0.671	0.705	0.737	0.618	0.632	0.695	0.704	0.617
19, 62	n-C <sub>16</sub>	30		0.904	0.916	0.929							
		40			0.910								
		50			0.898								
		60			0.889								
8	n-C <sub>18</sub>	35		0.871	0.877	0.893	0.914						
		50		0.861	0.869	0.887							
19, 62	n-C <sub>20</sub>	40		0.830	0.852	0.875							
19, 62	n-C <sub>22</sub>	60		0.791	0.804								
19, 62	n-C <sub>24</sub>	50		0.767	0.771	0.809	0.830						
		60		0.760	0.776	0.813	0.832						
58		76		0.794	0.818	0.850	0.875			0.708		0.874	
19, 62	n-C <sub>28</sub>	70		0.719	0.735								
58	n-C <sub>30</sub>	76			0.694	0.718	0.737	0.770		0.694		0.780	
19, 62	n-C <sub>32</sub>	50				0.697	0.726						
		76				0.695	0.723						
58	n-C <sub>36</sub>	76			0.640	0.653	0.680	0.727		0.632		0.714	
58 <sup>b</sup>	n-C <sub>24</sub>	20											
58 <sup>b</sup>	n-C <sub>30</sub>	20											
58 <sup>b</sup>	n-C <sub>36</sub>	20											
58 <sup>b</sup>	Di-n-butyl phthalate	20											

(continued)

Table 1. Continued.

Source	Solvents	Temp	Solute Components <sup>a</sup>									
			12	13	14	15	16	17	18	19	20	21
10	squalane	20	0.632	0.684	0.658	0.633	0.721					
19, 62	n-C <sub>16</sub>	30										
		40										
		50										
		60										
8	n-C <sub>18</sub>	35										
		50										
19, 62	n-C <sub>20</sub>	40										
19, 62	n-C <sub>22</sub>	60										
19, 62	n-C <sub>24</sub>	50										
		60										
		76			0.817							
19, 62	n-C <sub>28</sub>	70										
58	n-C <sub>30</sub>	76			0.717							
19, 62	n-C <sub>32</sub>	59										
		76										
58	n-C <sub>36</sub>	76			0.658							
58 <sup>b</sup>	n-C <sub>24</sub>	20						0.951				1.570
58 <sup>b</sup>	n-C <sub>30</sub>	20						0.819				1.250
58 <sup>b</sup>	n-C <sub>36</sub>	20						0.732				1.052
58 <sup>b</sup>	Di-n-butyl phthalate	20						0.844	0.309	0.319	0.598	0.533

<sup>a</sup>The nomenclature of the solute components are given in Appendix I.

<sup>b</sup>Extrapolated from experimental data.

Table 2. Molar volume of alkanes (c. c. / mole).

	20	30	35	40	50	60	70	76
n-Butane	99.98							
n-Pentane	114.80	116.65	117.60	118.56	120.41	122.61	124.75	
n-Hexane	130.19	132.01	132.95	133.90	135.84	137.86	139.94	141.21
n-Heptane	145.93	147.79	148.74	149.70	151.61	153.70		157.07
n-Octane				164.83	167.76	169.90		173.34
n-Nonane								189.73
n-Hexadecane	291.67	294.19		296.76	299.37	302.07		
n-Octadecane	324.24		328.30		332.24			
n-Eicosane				362.67				
n-Docosane	389.50					402.03		
n-Tetraconsane	422.19				431.95	435.35		441.03
n-Octacosane	489.51						506.08	
n-Triacontane	520.22							542.19
n-Dotriacontane	552.90				564.96			575.48
n-Hexatriacontane	618.25							643.36
Isopentane	116.78							
2,2-Dimethyl pentane	148.05							
2,4-Dimethyl pentane	148.31							
3,3-Dimethyl pentane	143.96							
2,3-Dimethyl pentane	143.59							
2-Methyl hexane	147.05							
3-Methyl hexane	145.24							
3-Ethyl pentane	143.53							
2,2,4-Trimethyl pentane	164.38							
Squalane	520.31							

Table 3. Solubility parameters of alkanes estimated by heat of vaporization data.<sup>a</sup>

	20°C	30°C	35°C	40°C	50°C	60°C	70°C	76°C
n-Butane	7.01	6.89	6.84	6.78	6.67	6.56	6.46	
n-Pentane	7.22	7.11	7.06	7.00		6.80	6.69	
n-Hexane	7.39	7.28	7.22	7.14	7.06	6.96	6.86	6.80
n-Heptane	7.53	7.41	7.35	7.30		7.08	6.98	6.92
n-Octane	7.66		7.47	7.41		7.19	7.09	7.02
n-Nonane	7.80				7.53		7.18	7.12
n-Hexadecane	8.88	8.64		8.42	8.22	8.03	7.86	
n-Octadecane	9.37							
n-Eicosane	9.82							
n-Docosane	10.19				9.12	8.84		
n-Tetracosane	10.74					9.16		8.70
n-Octacosane	12.07				10.32	9.89	9.50	
n-Triacontane	12.87							9.63
n-Dotriacontane	13.89							
n-Hextriacontane	16.28							10.86
Isopentane	6.96	6.85				6.54		
2,2-Dimethyl pentane	7.02							
2,4-Dimethyl pentane	7.07					6.65		6.51
3,3-Dimethyl pentane	7.18							
2,3-Dimethyl pentane	7.33				6.77			
2-Methyl hexane	7.31							
3-Methyl hexane	7.38	7.27				6.96		6.80
3-Ethyl pentane								
2,2,4-Trimethyl pentane	6.94							

<sup>a</sup>The unit of solubility parameter is (cal/cc)<sup>1/2</sup>.

Table 4. Comparison of solubility parameters of n-heptane estimated from accurate heat of vaporization method and index of refraction method.<sup>a</sup>

Temp °C	Index of Refractive Method Obtained from Eq. 65	Accurate Heat of Vaporization Method Obtained from Ref. 4
25	7.23	7.45
35	7.14	7.33
45	7.04	7.20
55	6.96	7.07
76	6.76	6.80

<sup>a</sup>Unit for solubility parameter is  $(\text{cal/cc})^{1/2}$ .

Table 5. Solubility parameters of alkanes estimated by index of refraction method. <sup>a</sup>

	20°C	30°C	35°C	40°C	50°C	60°C	70°C	76°C
n-Butane	6.34	6.22	6.16	6.10	5.98		5.74	
n-Pentane	6.76	6.66	6.60	6.55		6.33	6.22	
n-Hexane	7.06	6.96	6.91	6.86	6.77	6.67	6.57	6.51
n-Heptane	7.28	7.18	7.14	7.09		6.91	6.82	6.76
n-Octane	7.44			7.26		7.09	7.00	6.95
n-Nonane	7.57			7.40			7.15	7.10
n-Hexadacane	8.04	7.97		7.90	7.84	7.77	7.70	
n-Octadacane	8.11		8.01					
n-Eicosane	8.17							
n-Docosane	8.22				8.03	7.96		
n-Tetracosane	8.26					8.00		7.91
n-Octacosane	8.32				8.14	8.08	8.01	
n-Triacontane	8.35							8.01
n-Dotriacontane	8.37							
n-Hexatriacontane	8.41							8.08
Isopentane	6.65	6.54				6.20		
2,2-Dimethyl pentane	7.17							
2,4-Dimethyl pentane	7.16							6.62
3,3-Dimethyl pentane	7.38							
2,3-Dimethyl pentane	7.39							
2-Methyl hexane	7.22							
3-Methyl hexane	7.31	7.22				6.95		6.80
3-Ethyl pentane								
2,2,4-Trimethyl pentane	7.33							
Squalane	8.43							

<sup>a</sup>Unit for solubility parameter is (cal/cc)<sup>1/2</sup>.



Table 6. Thermal pressure coefficients (43).

n-Alkanes	$\gamma$ bars deg <sup>-1</sup>
n-Hexane	$\gamma = 9.595 - 6.22 \times 10^{-2}t + 1.732 \times 10^{-4}t^2 - 0.339 \times 10^{-6}t^3$
n-Octane	$\gamma = 10.255 - 5.822 \times 10^{-2}t + 1.330 \times 10^{-4}t^2 - 0.166 \times 10^{-6}t^3$
n-Hexadecane	$\gamma = 11.876 - 6.744 \times 10^{-2}t + 2.292 \times 10^{-4}t^2 - 0.477 \times 10^{-6}t^3$
n-Docosane	$\gamma = 12.050 - 5.536 \times 10^{-2}t + 0.892 \times 10^{-4}t^2$
n-Hexatriacotane	$\gamma = 13.168 - 6.424 \times 10^{-2}t + 1.153 \times 10^{-4}t^2$

Table 7. Solubility parameters ( $\delta' = (\text{cal/cc})^{1/2}$ ) of n-alkanes estimated by internal pressures ( $P_i = \text{atm}$ ).

	20°C		40°C		60°C		70°C		76°C	
	$P_i$	$\delta'$	$P_i$	$\delta'$	$P_i$	$\delta'$	$P_i$	$\delta'$	$P_i$	$\delta'$
Hexane	58.95	7.68	55.08	7.42	51.04	7.14	48.97	6.99	47.60	6.89
Octane	64.02	8.00	60.81	7.80	57.34	7.57	55.54	7.45	54.91	7.41
Hexadecane	74.34	8.62	71.18	8.43	68.06	8.25	66.52	8.16	65.86	8.12
Docosane	76.88	8.79	74.65	8.64	72.02	8.49	70.60	8.40	68.86	8.30
Hexatriacontane	79.08 <sup>a</sup>	8.89	76.60 <sup>a</sup>	8.75	74.43 <sup>a</sup>	8.63	72.30 <sup>a</sup>	8.50	7.98 <sup>a</sup>	8.48
Pentane <sup>b</sup>	53.6	7.33								
Heptane <sup>b</sup>	61.2	7.82								
Nonane <sup>b</sup>	66.0	8.12								
Decane <sup>b</sup>	67.0	8.19								
Dodecane <sup>b</sup>	69.5	8.34								
Tetradecane <sup>b</sup>	71.5	8.47								
Isopentane <sup>b</sup>	54.8	7.40								
2-Methyl pentane <sup>b</sup>									6.86 <sup>c</sup>	
2-Methyl hexane <sup>b</sup>	52.4	7.71								
2,2-Dimethyl pentane <sup>b</sup>	55.8	7.47							6.83 <sup>c</sup>	
2,3-Dimethyl pentane <sup>b</sup>	61.8	7.86							6.98 <sup>c</sup>	
2,4-Dimethyl pentane	56.3	7.50							7.07 <sup>c</sup>	
3-Methyl pentane <sup>b</sup>	60.2	7.76							7.25 <sup>c</sup>	
3-Ethyl pentane	63.9	7.99								
3,3-Dimethyl pentane <sup>b</sup>	59.9	7.74								
3-Methyl pentane									7.01 <sup>c</sup>	
2,2,4-Trimethyl pentane <sup>b</sup>	63.0	7.94								

<sup>a</sup> Linear extrapolation of  $P_i$  vs  $1/N$  plots in Figure 6.

<sup>b</sup> From Allen *et al.* (50).

<sup>c</sup> Calculated by Equation 83.

Table 8. Comparison of  $\delta$  values estimated by various methods. <sup>a</sup>

	A Equation (64) at 20°C	B Allen <u>et al.</u> (1) at 20°C	C Equation (67) at 20°C	D Equation (81) at 20°C
n-Butane	7.01		6.34	6.80
n-Pentane	7.22	7.09	6.76	7.33
n-Hexane	7.39	7.33	7.06	7.68
n-Heptane	7.53	7.49	7.28	7.82
n-Octane	7.66	7.61	7.44	8.00
n-Nonane	7.80	7.71	7.57	8.12
n-Hexadacane	8.88	8.02	8.04	8.62
n-Octadacane	9.37	8.06	8.11	8.66
n-Eicosane	9.82	8.10	8.17	8.71
Docane	10.19	8.13	8.22	8.77
Tetracosane	10.74	8.15	8.26	8.75
Octacosane	12.07	8.19	8.32	8.81
Triacontane	12.87	8.20	8.35	8.85
Doctriacontane	13.89	8.21	8.37	8.87
Hexatriacontane	16.28	8.24	8.41	8.89
Squalane			8.34	8.68
Isopentane	6.96	6.78	6.65	7.40
2, 2-Dimethyl pentane	7.02	6.97	7.17	7.47
2, 4-Dimethyl pentane	7.07	7.02	7.16	7.50
3, 3-Dimethyl pentane	7.18	7.14	7.38	7.74
2, 3-Dimethyl pentane	7.33	7.29	7.39	7.86
2-Methyl hexane	7.31	7.27	7.22	7.71
3-Methyl hexane	7.38	7.35	7.31	7.76
3-Eethyl pentane		7.42		7.99
2, 2, 4-Trimethyl pentane	6.94	7.31	7.33	7.94

A = heat of vaporization method.

B = corrected heat of vaporization method.

C = refractive index method.

D = internal pressure method (50).

<sup>a</sup>  $\delta = (\text{cal/cc})^{1/2}$ .

Table 9. Internal pressure and energies of vaporization for heptane (1).

T°C	$P_i V$ cal/mole	$\Delta E^V$ cal/mole	$\Delta nRT$ cal/mole
20	9008	8201	807
35	8835	7911	924

Table 10. Molar volumes and solubility parameters ( $\text{cal}^{1/2}/\text{cc}^{1/2}$ ) for selected polar organic compounds obtained from Hensen (18).

Solute or Solvent	$V_{cc}$	$\delta_d$	$\delta_o$	$\delta_n$
1, 2-Dichloroethane	104.4	9.20	2.60	2.00
1-Chlorobutane	78.79	7.95	2.70	1.00
Dichloromethane	63.62	8.91	3.10	3.00
Chloroform	80.03	8.65	1.50	2.80
Trichloroethylene	92.61	8.78	1.50	2.60
Di-n-butyl phthalate	265.27	8.20	4.20	2.00

Table 11. Athermal contribution to solute activity coefficient ( $-\ln \gamma^s$ ).

$$\ln \gamma_2^s = -\Delta S^M / R.$$

Solvent	Temp	Solute Components							
		1	2	3	4	5	6	7	8
Squalane	20°C	0.843	0.732	0.636	0.552			0.718	
n-C <sub>16</sub>	30°C		0.322	0.250	0.191				
	40°C			0.247					
	50°C			0.244					
	60°C			0.241					
n-C <sub>18</sub>	35°C		0.385	0.309	0.245	0.191			
			0.377	0.303	0.241				
n-C <sub>20</sub>	40°C		0.445	0.366	0.298				
n-C <sub>22</sub>	60°C		0.493	0.413					
n-C <sub>24</sub>	50°C		0.556	0.471	0.398	0.334			
	60°C		0.549	0.467	0.394	0.331			
	76°C			0.459	0.389	0.327	0.274		0.466
n-C <sub>28</sub>	70°C		0.647	0.562					
n-C <sub>30</sub>	76°C			0.606	0.529	0.460	0.400		0.618
n-C <sub>32</sub>	50°C				0.584	0.511			
	76°C				0.572	0.501			
n-C <sub>36</sub>	76°C			0.736	0.654	0.581	0.516		0.744
		9	10	11	12	13	14	15	16
Squalane	20°C	0.541	0.540	0.562	0.563	0.546	0.555	0.564	0.468
n-C <sub>16</sub>	30°C								
	40°C								
	50°C								
	60°C								
n-C <sub>18</sub>	35°C								
n-C <sub>20</sub>	40°C								
n-C <sub>22</sub>	60°C								
n-C <sub>24</sub>	50°C								
	60°C								
	76°C		0.375				0.393		
n-C <sub>28</sub>	70°C								
n-C <sub>30</sub>	76°C		0.519				0.538		
n-C <sub>32</sub>	50°C								
	76°C								
n-C <sub>36</sub>	76°C		0.638				0.659		

Table 12. "Experimental" excess partial molar heat of mixing in terms of  $\ln \gamma_{ex}^e$ .  $\ln \gamma_{ex}^e = \ln \gamma^\infty - \ln \gamma_2^s$   $\ln \gamma_{ex}^e = (\Delta H^E/RT)$

Solvent	Temp	Solute Components							
		1	2	3	4	5	6	7	8
Squalane	20°C	0.294	0.249	0.182	0.153			0.237	
n-C <sub>16</sub>	30°C		0.220	0.163	0.117				
	40°C			0.153					
	50°C			0.136					
	60°C			0.123					
n-C <sub>18</sub>	35°C		0.247	0.178	0.132	0.101			
			0.228	0.163	0.121				
n-C <sub>20</sub>	40°C		0.259	0.205	0.164				
n-C <sub>22</sub>	60°C		0.258	0.194					
n-C <sub>24</sub>	50°C		0.291	0.211	0.186	0.148			
	60°C		0.275	0.213	0.187	0.147			
	76°C			0.228	0.188	0.164	0.140		0.227
n-C <sub>28</sub>	70°C		0.318	0.253					
n-C <sub>30</sub>	76°C			0.241	0.197	0.155	0.139		0.253
n-C <sub>32</sub>	50°C				0.222	0.191			
	76°C				0.208	0.177			
n-C <sub>36</sub>	76°C			0.290	0.228	0.195	0.197		0.295
		9	10	11	12	13	14	15	16
Squalane	20°C	0.178	0.189	0.079	0.105	0.167	0.137	0.107	0.141
n-C <sub>16</sub>	30°C								
	40°C								
	50°C								
	60°C								
n-C <sub>18</sub>	35°C								
n-C <sub>20</sub>	40°C								
n-C <sub>22</sub>	60°C								
n-C <sub>24</sub>	50°C								
	60°C								
	76°C		0.240					0.191	
n-C <sub>28</sub>	70°C								
n-C <sub>30</sub>	76°C		0.270					0.206	
n-C <sub>32</sub>	50°C								
	76°C								
n-C <sub>36</sub>	76°C		0.301					0.240	

Table 13. Theoretical excess partial molar heat of mixing in terms of  $\ln \gamma_t^e$  calculated by Set I solubility parameters.  
 $\ln \gamma_t^e = (\Delta H_t^E/RT) = (V_2/RT)(\delta_1 - \delta_2)^2$

Solvent	Temp	Solute Components								
		1	2	3	4	5	6	7	8	
Squalane	20°C		0.248	0.202	0.165	0.305		0.383	0.260	
n-C <sub>16</sub>	30°C		0.144	0.105	0.007					
	40°C									
	50°C									
	60°C			0.137						
n-C <sub>18</sub>	35°C		0.174	0.136	0.107	0.079				
	50°C									
n-C <sub>20</sub>	40°C		0.207	0.175	0.132					
n-C <sub>22</sub>	60°C									
n-C <sub>24</sub>	50°C									
	60°C		0.268	0.226	0.197	0.169				
	76°C			0.252	0.223	0.199	0.171		0.296	
n-C <sub>28</sub>	70°C									
n-C <sub>30</sub>	76°C			0.299	0.270	0.246	0.217		0.347	
n-C <sub>32</sub>	50°C									
	76°C				0.280	0.256				
b-C <sub>36</sub>	76°C			0.335	0.306	0.282	0.253		0.385	
			9	10	11	12	13	14	15	16
Squalane	20°C	0.444	0.412	0.334	0.252	0.269	0.231			0.555
n-C <sub>16</sub>	30°C									
	40°C									
	50°C									
	60°C									
n-C <sub>18</sub>	35°C									
	50°C									
n-C <sub>20</sub>	40°C									
n-C <sub>22</sub>	60°C									
n-C <sub>24</sub>	50°C									
	60°C									
	76°C		0.455					0.278		
n-C <sub>28</sub>	70°C									
n-C <sub>30</sub>	76°C		0.522					0.331		
n-C <sub>32</sub>	50°C									
	76°C									
n-C <sub>36</sub>	76°C		0.572					0.370		

Table 14. Theoretical excess partial molar heat of mixing in terms of  $\ln \gamma_t^e$  calculated by Set II solubility parameters.

$$\ln \gamma_t^e = (\Delta H_t^e / RT) = (V_2 / RT)(\delta_1 - \delta_2)^2$$

Solvent	Temp	Solute Components							
		1	2	3	4	5	6	7	8
Squalane	20°C	0.446	0.384	0.281	0.186	0.141	0.096	0.330	
n-C <sub>16</sub>	30°C		0.349	0.216	0.139				
	40°C			0.234					
	50°C			0.252					
	60°C			0.272					
n-C <sub>18</sub>	35°C		0.389	0.254	0.168	0.114			
	50°C		0.446	0.286	0.188				
n-C <sub>20</sub>	40°C		0.448	0.291	0.200				
n-C <sub>22</sub>	60°C		0.556	0.070					
n-C <sub>24</sub>	50°C		0.525	0.353	0.247	0.181			
	60°C		0.569	0.381	0.267	0.195			
	76°C			0.424	0.295	0.212	0.159		0.354
n-C <sub>28</sub>	70°C		0.663	0.445					
n-C <sub>30</sub>	76°C			0.484	0.349	0.261	0.203		0.410
n-C <sub>32</sub>	50°C				0.297	0.227			
	76°C				0.361	0.276			
n-C <sub>36</sub>	76°C			0.516	0.378	0.287	0.227		0.439
		9	10	11	12	13	14	15	16
Squalane	20°C	0.373	0.356	0.219	0.166	0.238	0.212	0.118	0.394
n-C <sub>16</sub>	30°C								
	40°C								
	50°C								
	60°C								
n-C <sub>18</sub>	35°C								
	50°C								
n-C <sub>20</sub>	40°C								
n-C <sub>22</sub>	60°C								
n-C <sub>24</sub>	50°C								
	60°C								
	76°C		0.370				0.263		
n-C <sub>28</sub>	70°C								
n-C <sub>30</sub>	76°C		0.430				0.314		
n-C <sub>32</sub>	50°C								
	76°C								
n-C <sub>36</sub>	76°C		0.463				0.342		



Table 15. Deviations from the geometrical mean assumption in terms of binary coefficient ( $-l_{12} \times 10^{-2}$ ).

Solvent	Temp	Solute Components							
		1	2	3	4	5	6	7	8
Squalane	20°C	1.54	0.46	0.34	0.10	0.03	0.03	0.36	
n-C <sub>16</sub>	30°C		0.54	0.19	0.07				
	40°C			0.30					
	50°C			0.45					
	60°C			0.60					
n-C <sub>18</sub>	35°C		0.61	0.28	0.11	0.04			
	50°C		1.00	0.47	0.22				
n-C <sub>20</sub>	40°C		0.82	0.31	0.11				
n-C <sub>22</sub>	60°C		1.41	0.70					
n-C <sub>24</sub>	50°C		1.05	0.54	0.20	0.10			
	60°C		1.39	0.66	0.27	0.14			
	76°C			0.83	0.40	0.15	0.05		0.54
n-C <sub>28</sub>	70°C		1.70	0.79		0.34	0.18		
n-C <sub>30</sub>	76°C			1.03	0.55				0.65
n-C <sub>32</sub>	50°C				0.24	0.10			
	76°C				0.55	0.32			
n-C <sub>36</sub>	76°C			0.95	0.54	0.29	0.09		0.64
		9	10	11	12	13	14	15	16
Squalane	20°C	0.59	0.50	0.42	0.18	0.21	0.22	0.03	0.69
n-C <sub>16</sub>	30°C								
	40°C								
	50°C								
	60°C								
n-C <sub>18</sub>	35°C								
	50°C								
n-C <sub>20</sub>	40°C								
n-C <sub>22</sub>	60°C								
n-C <sub>24</sub>	50°C								
	60°C								
	76°C		0.47				0.27		
n-C <sub>28</sub>	70°C								
n-C <sub>30</sub>	76°C		0.58				0.39		
n-C <sub>32</sub>	50°C								
	76°C								
n-C <sub>36</sub>	76°C		0.58				0.36		

Table 16. Predictions of solute activity coefficients at infinite dilution with Watson's partial molar volumes.

Solvent	Solute	Temp °C	$\bar{V}_{cc}$	$-\ln \gamma_{ex}^s$	$\ln \gamma_{ex}^e$	$\ln \gamma_t^e$	$\gamma^\infty$	R. D. %
n-C <sub>18</sub>	n-C <sub>5</sub>	50	109.2	0.441	0.291	0.405	0.964	-12.01
n-C <sub>20</sub>	n-C <sub>5</sub>	40	108.3	0.507	0.321	0.409	0.906	- 9.22
n-C <sub>22</sub>	n-C <sub>5</sub>	60	110.1	0.569	0.334	0.499	0.933	-18.02
n-C <sub>24</sub>	n-C <sub>5</sub>	50	109.2	0.628	0.363	0.476	0.859	-11.98
	n-C <sub>5</sub>	60	110.1	0.628	0.354	0.511	0.890	-17.08
	n-C <sub>6</sub>	60	128.3	0.526	0.295	0.385	0.868	- 9.36
n-C <sub>28</sub>	n-C <sub>5</sub>	70	111.0	0.736	0.407	0.590	0.864	-20.04
	n-C <sub>6</sub>	70	127.6	0.629	0.321	0.406	0.799	- 8.87
n-C <sub>30</sub>	n-C <sub>6</sub>	76	128.3	0.678	0.313	0.440	0.788	-13.55
n-C <sub>36</sub>	n-C <sub>6</sub>	76	128.3	0.812	0.366	0.469	0.710	-10.88

Table 17. Predictions of solute activity coefficients at infinite dilution ( $\gamma_2^\infty$ )<sup>a</sup> from Set I solubility parameters.

Solvent	Temp	Solute Components							
		1	2	3	4	5	6	7	8
Squalane	20°C		0.616	0.648	0.679	0.584		0.714	0.683
			0.09	-2.11	-1.22	-17.10		-15.70	-10.73
n-C <sub>16</sub>	30°C		0.837	0.865	0.893				
			8.62	4.35	3.92				
	40°C								
	50°C			0.901					
n-C <sub>18</sub>	35°C		0.810	0.841	0.871	0.894			
			7.02	3.42	2.51	2.21			
n-C <sub>20</sub>	40°C		0.788	0.826	0.848				
			5.05	2.78	3.14				
n-C <sub>22</sub>	60°C								
n-C <sub>24</sub>	50°C								
			0.755	0.786	0.821	0.850			
	76°C		0.81	-1.66	-0.99	-2.18			
			0.813	0.847	0.879	0.903			0.844
		-2.35	-3.56	-3.48	-3.16			-7.12	
n-C <sub>28</sub>	70°C								
n-C <sub>30</sub>	76°C		0.736	0.772	0.807	0.833			0.767
			-6.02	-7.53	-9.51	-8.19			-10.4
n-C <sub>32</sub>	50°C								
	76°C			0.811	0.782				
				-12.3	-8.19				
n-C <sub>36</sub>	76°C			0.669	0.706	0.741	0.769		0.699
				-4.60	-8.08	-9.03	-5.73		-10.6

(continued)

Table 17. Continued.

Solvent	Temp	Solute Components							
		9	10	11	12	13	14	15	16
Squalene	20°C	0.908	0.880	0.796	0.733	0.758	0.722		1.091
		-30.61	-24.95	-29.01	-15.92	-10.72	-9.85		-51.34
n-C <sub>16</sub>	30°C								
	40°C								
	50°C								
	60°C								
n-C <sub>18</sub>	35°C								
	50°C								
n-C <sub>20</sub>	40°C								
n-C <sub>22</sub>	60°C								
n-C <sub>24</sub>	50°C								
	60°C								
	76°C		1.083				0.892		
			-23.9				-9.16		
n-C <sub>28</sub>	70°C								
n-C <sub>30</sub>	76°C		1.009				0.817		
			-29.3				-13.9		
n-C <sub>32</sub>	50°C								
	76°C								
n-C <sub>36</sub>	76°C		0.936				0.749		
			-31.1				-13.8		

<sup>a</sup>All relative deviations are listed in the second row.

Table 18. Predictions of solute activity coefficients at infinite dilution  $(\gamma_2^\infty)^a$  with Set II solubility parameters.

Solvent	Temp	Solute Components							
		1	2	3	4	5	6	7	8
Squalane	20°C	0.791	0.665	0.701	0.694	0.713	0.727	0.678	
		36.8	11.8	10.4	3.37	1.22	-1.32	9.68	
n-C <sub>16</sub>	30°C			1.028	6.966	0.949			
				13.7	5.43	2.16			
	40°C			0.987					
				8.41					
				1.008					
50°C			12.3						
60°C			1.031						
				15.9					
n-C <sub>18</sub>	35°C		1.004	0.947	0.926	0.926			
			15.2	7.94	3.66	1.28			
	50°C		1.071	0.983	0.948				
			24.4	13.1	6.87				
n-C <sub>20</sub>	40°C		1.003	0.928	0.907				
			20.8	8.88	3.65				
n-C <sub>22</sub>	60°C		1.066	0.957					
			34.8	19.2					
n-C <sub>24</sub>	50°C		0.969	0.889	0.859	0.858			
			26.3	15.3	6.22	3.34			
	60°C		1.021	0.918	0.880	0.873			
			34.2	18.2	8.28	4.88			
76°C			0.965	0.911	0.892	0.891		0.894	
				21.5	11.4	4.89	1.85		13.5
n-C <sub>28</sub>	70°C		1.016	0.889					
			41.2	21.1					
n-C <sub>30</sub>	76°C			0.886	0.836	0.819	0.821		0.812
				27.6	16.4	11.7	6.65		16.9
n-C <sub>32</sub>	50°C				0.751	0.752			
					7.77	3.63			
	76°C				0.809	0.799			
				16.5	10.5				
n-C <sub>36</sub>	76°C			0.803	0.759	0.745	0.749		0.737
				25.4	16.2	9.62	3.05		16.7

(continued)

Table 18. Continued.

Solvent	Temp	Solute Components							
		9	10	11	12	13	14	15	19
Squalane	20°C	0.845	0.932	0.710	0.672	0.735	0.709	0.640	0.929
		21.6	18.1	15.0	6.37	7.45	7.80	1.13	28.8
n-C <sub>16</sub>	30°C								
	40°C								
	50°C								
	60°C								
n-C <sub>18</sub>	35°C								
	50°C								
n-C <sub>20</sub>	40°C								
n-C <sub>22</sub>	60°C								
n-C <sub>24</sub>	50°C								
	60°C								
	76°C		0.995				0.879		
			13.8				7.55		
n-C <sub>28</sub>	70°C								
n-C <sub>30</sub>	76°C		0.915				0.799		
			17.4				11.5		
n-C <sub>32</sub>	50°C								
	76°C								
n-C <sub>36</sub>	76°C		0.839				0.728		
			17.5				10.7		

<sup>a</sup>All relative deviations are listed in the second row.

Table 19. Interaction parameters of halo-alkanes in paraffinic solvents at 20° C.

	$-\ln \gamma_{ex}^s$	$\ln \gamma_{ex}^e$	$\Phi_d$	$\Phi_o$	$-2\Phi_{in}$	$\ln \gamma_t^e$	$\gamma_t^\infty$	R. D.
<u>1-Chloro-butane</u>								
n-C <sub>24</sub>	0.647	0.597	0.0943	1.290	0.698	0.687	1.041	-9.2 %
n-C <sub>30</sub>	0.809	0.609	0.131	1.290	0.821	0.599	0.811	+0.85%
n-C <sub>36</sub>	0.950	0.638	0.147	1.290	0.867	0.571	0.683	+6.60%
<u>1, 2-Dichloroethane</u>								
n-C <sub>24</sub>	0.8680	1.319	0.0362	0.905	-0.361	1.299	1.540	-2.4 %
n-C <sub>30</sub>	1.040	1.265	0.0198	0.905	-0.271	1.197	1.168	-6.5 %
n-C <sub>36</sub>	-1.190	1.139	0.0155	0.906	-0.236	1.157	0.967	+8.2 %

$$\Phi_d = \frac{V_2}{RT} (\delta_{d1} - \delta_{d2})^2$$

$$\Phi_o = \frac{V_2}{RT} (\delta_{o1} - \delta_{o2})^2 \text{ for paraffinic solvents } \delta_{o1} = 0$$

$$\Phi_{in} = (\delta_{o2} \delta_{d2} - \delta_{o2} \delta_{d1})$$

Table 20. Interaction parameters for halo-alkanes in di-n-butyl phthalate solvent at 20°C.

Solute Components	$-\ln \gamma_{ex}^s$	$-\ln \gamma_{ex}^e$	$\Phi_d$	$\Phi_o$	$2\Phi_{in}$	$\Phi_h$	$\gamma_2^\infty$
Dichloromethane	0.668	0.505	0.054	0.130	-0.168	-0.5214	0.309
Chloroform	0.500	0.641	0.027	0.989	-0.328	-1.329	0.319
Trichloroethylene	0.326	0.401	0.336	1.145	-0.273	-1.322	0.598
1, 2-Dichloroethane	0.401	0.511	0.134	0.342	-0.427	-0.166	0.5331
1-Chlorobutane	0.511	0.326	0.011	0.398	+0.135	-0.387	0.844

$$\Phi_d = \frac{V_2}{RT} (\delta_{d_1} - \delta_{d_2})^2$$

$$\Phi_o = \frac{V_2}{RT} (\delta_{o_1} - \delta_{o_2})^2$$

$$\Phi_{in} = (\delta_{d_1} \delta_{o_1} + \delta_{d_2} \delta_{o_2} - \delta_{d_1} \delta_{o_2} - \delta_{d_2} \delta_{o_1})$$



Table 21. Retention indexes of organic compounds in various stationary phases.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Propanol	481	502	537	637	615	648	661	663	711
Isopropanol	430	442	473	563	547	579	591	592	632
Butanol	587	606	644	746	725	757	769	773	822
t-Butanol	471	480	507	584	579	609	619	617	649
1-Hexanol	792	812	852	957	933	967	980	985	1035
2-Hexanol	739	754	785	876	861	892	902	905	850
3-Hexanol	742	757	782	872	857	886	896	898	944
2-Methyl-2-pentanol	688	698	722	801	795	822	832	831	872
3-Methyl-3-pentanol	714	728	744	831	820	841	851	851	901
2-Methyl-2-heptanol	881	891	919	998	988	1018	1028	1028	1068
3-Methyl-3-heptanol	898	910	931	1013	1001	1026	1036	1037	1083
Cyclopentanol	719	748	774	907	860	888	904	907	1000
Allyl alcohol	456	477	527	637	624	657	670	670	723
Propionaldehyde	435	453	478	599	544	542	554	579	657
Hexanal	741	759	784	904	856	849	862	889	970
Crotonaldehyde	582	609	633	788	732	721	735	772	875
Acetone	422	441	478	597	547	543	558	584	661
Methyl ethyl ketone	531	546	580	703	651	644	658	686	769
2-Pentanone	625	640	670	791	740	734	748	774	857
2-Hexanone	726	741	773	893	845	837	851	879	961
2,4-Dimethylpentane	632	628	632	623	633	632	632	630	619
2-Methylheptane	766	764	767	762	766	766	766	765	758
3-Methylheptane	775	774	776	774	776	775	775	775	772
2,2,3-Trimethylhexane	782	773	788	771	779	781	781	777	758
Cyclohexane	679	694	679	721	692	684	688	687	743
1-Octene	783	787	789	809	802	801	803	803	823
2-Octene	804	808	814	839	826	821	823	825	851
2-Ethylhexene	780	783	788	810	801	798	800	801	822
1-Octyne	784	793	811	875	848	850	856	859	910
2-Octyne	841	850	864	948	886	890	895	906	978
Benzene	653	682	668	774	761	725	736	737	835
Toluene	760	790	771	878	871	831	842	845	942
Ethylbenzene	851	879	864	974	952	921	931	937	1035
Mesitylene	971	1001	968	1077	1069	1039	1049	1058	1151
Hydrindane	1005	1034	1004	1077	1039	1017	1024	1024	1118
Decalin	1118	1152	1110	1194	1157	1129	1138	1139	1242
Styrene	878	915	891	1023	1011	972	986	989	1104
Ethynylbenzene	837	873	872	1019	990	967	982	984	1099
Methanol	329	348	364	477	445	469	489	486	527
Ethanol	378	393	436	530	502	539	551	555	602
1-Iodo-butane	817	849	821	939	893	885	894	901	995
Carbon Tetrachloride	659	686	673	751	729	707	713	712	799
Nitroethane	557	585	626	812	738	748	764	802	881
Pyridine	697	734	742	905	865	822	840	859	997
1,4-Dioxane	652	679	699	842	791	760	779	793	929

(continued)

Table 21. Continued.

	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
Propanol	742	849	852	866	941	991	804	710
Isopropanol	664	754	762	770	833	883	714	643
Butanol	854	957	964	975	1051	1103	915	822
t-Butanol	679	749	766	764	815	875	720	679
1-Hexanol	1066	1167	1178	1186	1263	1317	1129	1037
2-Hexanol	973	1054	1072	1072	1136	1194	1026	961
3-Hexanol	961	1036	1057	1052	1114	1175	1017	947
2-Methyl-2-pentanol	892	955	978	969	1022	1087	937	894
3-Methyl-3-pentanol	909	972	998	987	1041	1112	958	913
2-Methyl-2-heptanol	1088	1149	1175	1165	1218	1286	1133	1095
3-Methyl-3-heptanol	1092	1150	1199	1166	1219	1291	1141	1102
Cyclopentanol	995	1106	1116	1126	1212	1276	1068	966
Allyl alcohol	752	892	892	911	1003	1036	832	702
Propionaldehyde	595	678	725	690	746	870	682	753
Hexanal	904	976	1035	991	1044	1188	995	1077
Crotonaldehyde	795	896	965	915	988	1141	911	993
Acetone	611	690	747	708	766	916	694	803
Methyl ethyl ketone	711	783	843	799	855	1008	793	895
2-Pentanone	800	867	930	883	937	1092	881	987
2-Hexanone	905	968	1034	984	1038	1200	985	1096
2,4-Dimethylpentane	627	625	626	625	621	622	624	645
2-Methylheptane	763	761	762	761	759	756	761	773
3-Methylheptane	775	775	775	774	773	776	773	785
2,2,3-Trimethylhexane	772	768	769	767	760	768	762	809
Cyclohexane	703	721	720	724	748	759	720	709
1-Octene	805	821	832	824	836	843	823	811
2-Octene	828	847	858	850	865	875	847	831
2-Ethylhexene	804	820	831	823	835	845	821	811
1-Octyne	867	929	957	938	983	994	922	874
2-Octyne	913	970	999	979	1021	1031	974	894
Benzene	761	837	866	849	912	957	833	797
Toluene	868	939	972	951	1013	1063	940	905
Ethylbenzene	957	1027	1063	1038	1099	1150	1032	993
Mesitylene	1080	1142	1175	1155	1215	1245	1146	1093
Hydrindane	1054	1080	1084	1087	1119	1159	1084	1064
Decalin	1174	1200	1203	1207	1242	1283	1206	1184
Styrene	1018	1109	1151	1124	1204	1261	1110	1062
Ethynylbenzene	1015	1151	1191	1169	1275	1289	1127	1038
Methanol	575	695	688	716	796	839	643	531
Ethanol	635	742	740	761	834	880	694	605
1-Iodo-butane	922	982	1008	993	1045	1116	990	956
Carbon tetrachloride	731	794	810	803	852	847	794	733
Nitroethane	796	955	1002	973	1075	1245	949	1031
Pyridine	945	1023	1059	1046	1122	1219	1006	1013
1,4-Dioxane	849	937	964	945	1014	1118	913	937

(continued)



Table 21. Continued.

	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(25)
Propanol	749	838	824	1033	1072	1059	1213	1347
Isopropanol	673	779	741	914	953	955	1091	1217
Butanol	858	952	934	1143	1185	1172	1326	1460
t-Butanol	694	815	755	883	921	948	1060	1175
1-Hexanol	1070	1171	1147	1361	1402	1389	1537	1658
2-Hexanol	983	1095	1050	1220	1257	1266	1396	1511
3-Hexanol	972	1074	1037	1196	1231	1248	1369	1485
2-Methyl-2-pentanol	905	1032	967	1093	1130	1160	1269	1381
3-Methyl-3-pentanol	921	1046	985	1113	1149	1188	1299	1411
2-Methyl-2-heptanol	1103	1229	1165	1291	1327	1361	1464	1563
3-Methyl-3-heptanol	1107	1231	1169	1292	1327	1367	1470	1572
Cyclopentanol	995	1099	1084	1318	1361	1357	1536	1664
Allyl alcohol	772	845	853	1110	1150	1126	1309	1460
Propionaldehyde	632	842	688	812	842	886	998	1170
Hexanal	939	1167	996	1110	1139	1198	1299	1464
Crotonaldehyde	837	1120	905	1076	1108	1159	1316	1507
Acetone	645	926	710	838	867	933	1054	1251
Methyl ethyl ketone	742	1010	804	926	955	1018	1135	1330
2-Pentanone	830	1100	889	1004	1033	1100	1210	1396
2-Hexanone	933	1208	994	1108	1136	1205	1312	1499
2,4-Dimethylpentane	633	654	632	615	614	622	627	597
2-Methylheptane	766	775	766	757	757	761	759	759
3-Methylheptane	776	788	778	774	775	778	780	780
2,2,3-Trimethylhexane	783	809	783	754	754	768	754	746
Cyclohexane	693	702	712	763	767	765	814	837
1-Octene	817	833	825	849	852	863	884	907
2-Octene	839	854	851	882	886	897	922	950
2-Ethylhexene	814	836	825	850	854	867	891	918
1-Octyne	906	945	940	1033	1043	1063	1128	1189
2-Octyne	943	979	974	1067	1076	1098	1231	1226
Benzene	788	882	832	980	994	1006	1148	1256
Toluene	891	1004	934	1079	1094	1109	1249	1359
Ethylbenzene	982	1084	1026	1167	1179	1201	1333	1439
Mesitylene	1093	1237	1132	1280	1294	1300	1452	1550
Hydrindane	1031	1066	1065	1156	1163	1162	1243	1281
Decalin	1144	1195	1181	1282	1291	1288	1376	1413
Styrene	1049	1171	1102	1292	1309	1321	1490	1614
Ethylbenzene	1072	1158	1137	1385	1406	1395	1578	1685
Methanol	578	682	655	894	931	897	1077	1226
Ethanol	639	732	714	925	966	949	1111	1249
1-Iodo-butane	930	964	972	1106	1117	1117	1237	1337
Carbon tetrachloride	749	801	788	906	914	918	1018	1048
Nitroethane	889	1120	967	1185	1213	1274	1440	1653
Pyridine	933	1169	1015	1225	1266	1285	1516	1642
1,4-Dioxane	861	1128	943	1101	1132	1214	1366	1521

Table 22. McReynold's polarity factors for organic compounds.

	a	b	c	d	e
2, 4-Dimethylpentane	- 4. 81	-39. 45	-24. 46	20. 66	26. 35
2-Methylheptane	10. 74	- 7. 74	2. 23	2. 54	0. 89
3-Methylheptane	3. 08	- 7. 83	1. 40	1. 03	2. 50
2, 2, 3-Trimethylhexane	2. 47	-21. 05	- 4. 72	16. 56	2. 45
Cyclohexane	-14. 62	13. 00	- 7. 89	- 9. 86	- 5. 35
1-Octene	17. 45	0. 44	- 6. 26	2. 93	-14. 43
2-Octene	11. 12	5. 41	-12. 24	3. 97	-15. 82
2-Ethylhexene	15. 69	- 2. 26	- 6. 01	2. 23	-13. 83
1-Octyne	33. 29	20. 63	-52. 80	35. 48	-28. 35
2-Octyne	-23. 47	-54. 71	-102. 32	29. 29	18. 58
Benzene	100. 76	- 0. 38	- 1. 59	0. 14	-15. 53
Toluene	104. 34	-10. 08	8. 83	- 4. 95	-10. 12
Ethylbenzene	79. 00	- 9. 50	- 2. 06	0. 34	-17. 60
Mesitylene	114. 55	-12. 36	33. 03	-28. 98	
Hydrindane	-36. 86	- 3. 21	-16. 63	-15. 02	8. 04
Decalin	-40. 18	- 5. 77	-16. 69	-15. 87	19. 54
Styrene	112. 14	-11. 07	- 5. 96	7. 42	- 5. 30
Ethynlbenzene	103. 15	42. 92	-95. 39	68. 00	10. 98
Methanol	40. 55	151. 62	47. 54	-48. 52	-54. 66
Ethanol	6. 29	99. 34	5. 91	-15. 72	-29. 94
Propanol	1. 30	86. 05	-12. 44	1. 73	-19. 71
Isopropanol	- 7. 53	62. 09	-24. 48	7. 71	-47. 07
Butanol	- 4. 19	79. 11	-14. 01	3. 43	-11. 79
t-Butanol	18. 07	16. 89	4. 35	- 1. 21	-34. 18
1-Hexanol	-30. 80	67. 03	-38. 56	22. 13	8. 11
2-Hexanol	- 5. 82	30. 84	-17. 67	9. 74	-11. 30
3-Hexanol	- 3. 15	19. 98	-13. 59	4. 15	-24. 29
2-Methyl-3-pentanol	9. 19	0. 71	3. 08	- 1. 33	-28. 25
3-Methyl-3-pentanol	3. 42	-10. 33	- 7. 67	- 0. 61	-34. 32
2-Methyl-2-heptanol	-16. 79	-11. 31	-22. 64	16. 59	-16. 22
3-Methyl-3-heptanol	- 2. 68	-29. 14	-11. 16	8. 76	-17. 81
Cyclopentanol	-44. 05	62. 10	-51. 59	13. 09	- 5. 52
Allyl alcohol	41. 82	110. 88	-37. 04	17. 89	-20. 05
Propional	21. 03	27. 62	66. 53	16. 34	-28. 68
Hexanal	- 2. 27	- 9. 05	55. 83	28. 98	-13. 97
Crotonal	23. 74	0. 98	66. 78	34. 20	10. 30
Acetone	19. 37	11. 88	91. 86	8. 79	-27. 47
Methyl ethyl ketone	16. 22	8. 40	99. 19	1. 86	-29. 11
2-Pentanone	7. 50	- 0. 60	97. 15	4. 46	-24. 66
2-Hexanone		-10. 94	95. 42	7. 63	-18. 76
1-Iodobutane	10. 30	4. 55	5. 07	- 1. 42	-19. 74
Carbon tetrachloride	55. 41	- 4. 91	-59. 11	28. 28	27. 46
Nitroethane	9. 07	25. 86	-30. 36	117. 20	-31. 95
Pyridine	- 1. 15	-38. 36	-18. 72	6. 35	78. 78
1, 4-Dioxane	- 2. 64	-12. 94	-15. 72	8. 95	-19. 31

(continued)

Table 22. Continued.

	f	g	h	i	j
2, 4-Dimethylpentane	42.71	-20.66	- 3.27	-12.13	- 0.96
2-Methylheptane	8.69	-14.12	- 0.53	- 4.67	- 0.75
3-Methylheptane	7.28	- 5.75	- 0.82	- 0.70	- 0.51
2, 2, 3-Trimethylhexane	18.97	-27.36	- 4.87	0.80	- 2.11
Cyclohexane	-36.12	54.68	- 0.33	36.11	2.03
1-Octene	7.31	- 1.27	3.57	13.34	- 1.67
2-Octene	- 7.25	10.40	4.03	26.07	- 4.50
2-Ethylhexene	5.83	4.32	2.97	17.64	- 3.95
1-Octyne	- 1.71	-21.32	11.71	46.76	- 1.04
2-Octyne	60.43	64.81	18.32	64.75	-20.96
Benzene	3.57	- 0.84	1.20	15.45	1.37
Toluene	16.36	- 7.99	2.14	6.49	3.49
Ethylbenzene	14.07	11.04	6.45	22.76	1.54
Mesitylene	37.33	-40.56	9.11	- 8.10	15.87
Hydrindane	-29.69	102.40	- 3.01	51.00	- 0.09
Decalin	-28.71	94.61	- 2.26	46.83	8.33
Styrene	26.59	- 9.81	4.91	1.36	8.51
Ethynlbenzene	-24.33	-71.27	13.90	24.60	17.51
Methanol	-54.76	- 9.69	- 6.64	44.21	25.45
Ethanol	2.44	21.64	- 6.76	33.82	- 6.47
Propanol	18.87	15.18	- 4.97	23.85	- 5.20
Isopropanol	44.19		- 4.93	62.00	6.52
Butanol	27.23	16.79	- 3.29	18.45	- 6.88
t-Butanol	92.78	- 7.83	4.93	20.79	- 0.92
1-Hexanol	38.14	13.29	- 0.43	18.26	- 6.91
2-Hexanol	73.76	8.57	- 1.40	18.24	- 5.32
3-Hexanol	84.34	24.24	0.98	22.49	- 5.78
2-Methyl-3-pentanol	106.85	2.05	- 0.26	18.36	- 2.31
3-Methyl-3-pentanol	108.29	24.36	- 0.98	35.28	- 2.67
2-Methyl-2-heptanol	116.16	8.15		25.19	- 4.71
3-Methyl-3-heptanol	131.62	21.53	6.06	11.54	- 7.11
Cyclopentanol	27.27	61.68	- 0.89	58.86	- 5.83
Allyl alcohol	9.01	-11.11	- 6.36	14.71	-10.28
Propional	-13.74	- 7.48	1.24	23.75	2.36
Hexanal	0.31	7.12	0.60	15.43	- 1.97
Crotonal	- 0.41	-27.34	3.14	- 6.83	4.09
Acetone	- 9.08	-13.89	- 5.22	28.29	- 4.97
Methyl ethyl ketone	- 7.21	0.97	- 1.13	22.78	- 3.59
2-Pentanone	2.61	- 1.16	- 0.65	19.89	- 0.54
2-Hexanone	14.05	5.18	- 0.45	15.25	- 3.96
1-Iodobutane	- 3.20	99.90	- 0.31	10.80	- 0.48
Carbon tetrachloride	0.63	-26.33	13.40	8.20	6.03
Nitroethane	-26.76	-17.37	- 7.94	47.82	5.99
Pyridine	47.00	29.46	- 1.59	24.30	-12.20
1, 4-Dioxane	15.69	7.61	- 0.50	124.71	- 3.98

Table 23. Rohrschneider's polarity constants for organic compounds.

	a	b	c	d	e
2, 4-Dimethylpentane	-19.63	0.74	12.97	- 1.94	0.68
2-Ethylhexene-1	19.14	- 0.69	4.86	- 1.29	0.10
Cyclohexane	32.06	-22.47	-21.64	4.07	29.72
Toluene	108.33	3.77	8.75	- 7.01	- 7.61
Styrene	127.00	0.02	- 8.08	10.67	- 8.94
Phenylacetylene	125.20	2.53	-74.82	57.97	0.90
Acetone	- 5.30	- 4.61	94.94	7.90	5.64
Propional	13.27	- 1.01	74.86	4.79	1.33
Crotonal	- 7.86	-17.59	65.75	37.49	17.21
n-Butylacetate	- 3.77	-13.31	57.29	13.88	19.98
Actonitrile	2.86	-16.38	30.09	84.10	0.03
Nitroethane	- 5.41	-11.07	43.66	75.66	- 1.28
Oioxane	45.86	- 2.89	40.20	- 7.49	40.24
n-Dibutylether	17.34	9.77	29.73	-12.48	- 2.79
Thiophene	105.69	- 4.19	-31.53	20.10	11.22
Chloroform	69.71	28.91	-72.62	53.05	- 6.29
Carbon tetrachloride	63.28	-20.94	-57.47	28.28	33.75
Methyliodide	71.06	-14.95	-42.57	31.77	21.58
Ethylbromide	46.05	- 7.74	- 1.28	18.34	9.11
Difluorotetrachloroethane	14.89	-16.12	-35.03	29.09	33.35
n-Propanol	- 9.42	105.26	0.25	6.63	- 7.49
Isopropanol	-18.15	95.89	15.76	- 6.53	2.09
Allyl alcohol	18.11	116.45	-21.27	22.06	-23.35
t-Butanol	-11.42	76.51	33.75	-12.77	0.21

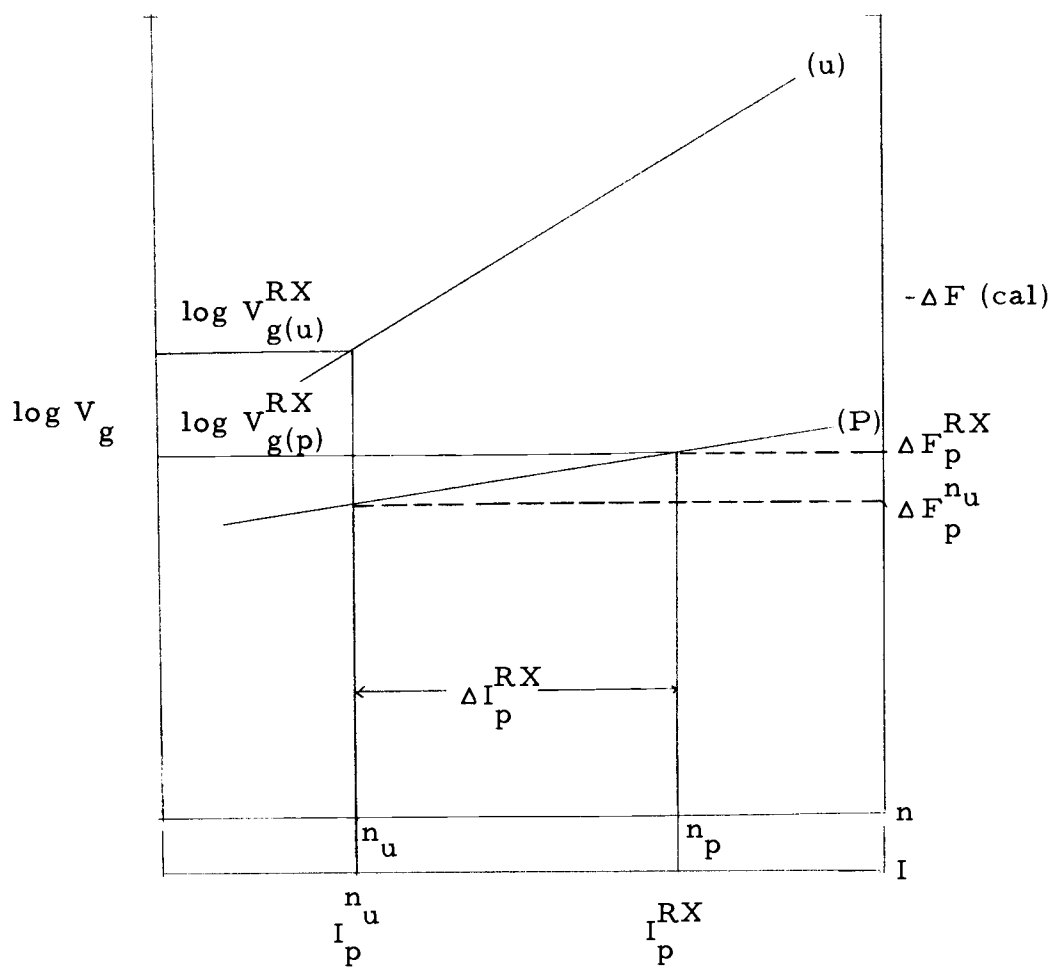
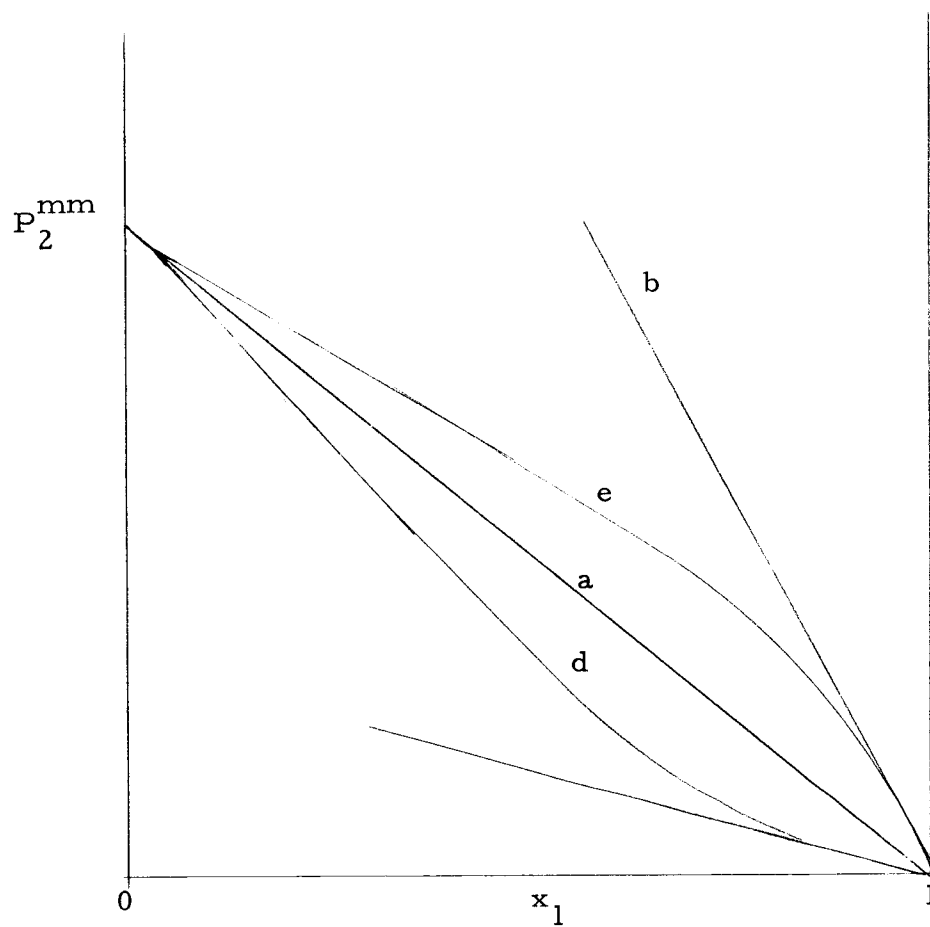


Figure 1. The retention index system.





- Curve a: Raoult's law
- Curve b: Henry's law
- Curve c: positive deviation
- Curve d: negative deviation

Figure 2. Behavior of solute vapor pressure in ideal and nonideal solution.

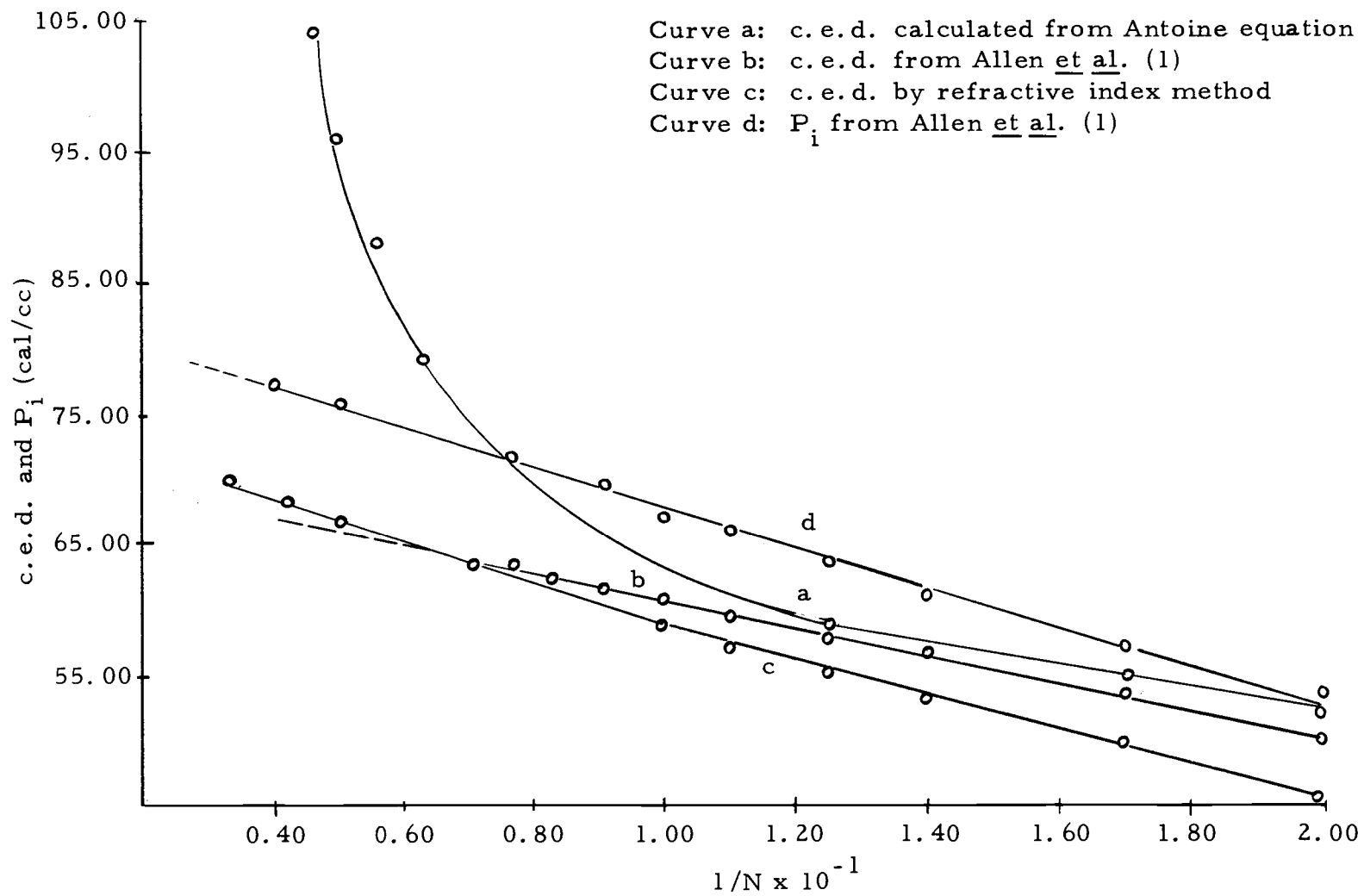


Figure 3. The relation between cohesive energy densities and internal pressures with n-alkanes carbon atom number.

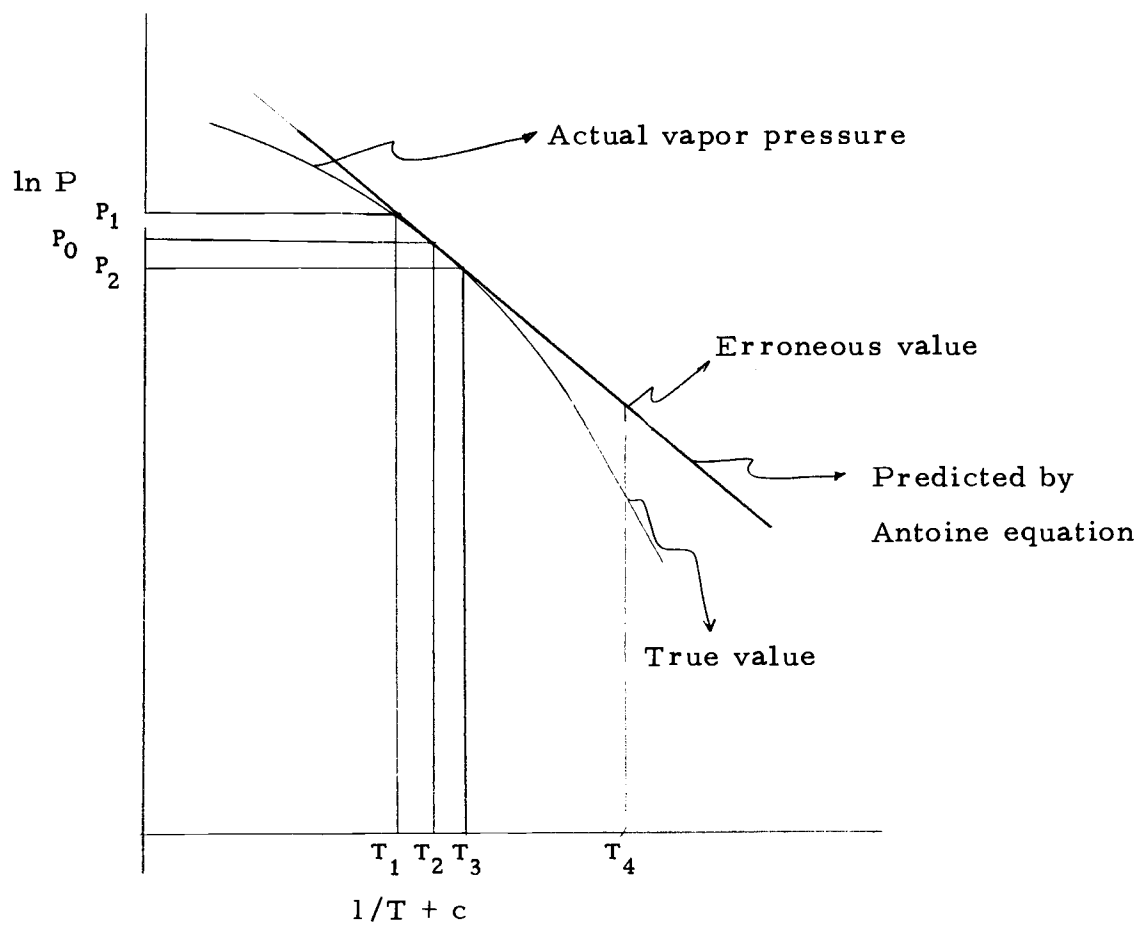


Figure 4. Illustration of fit of Antoine equation of experimental data (exaggerated for visual interpretation).

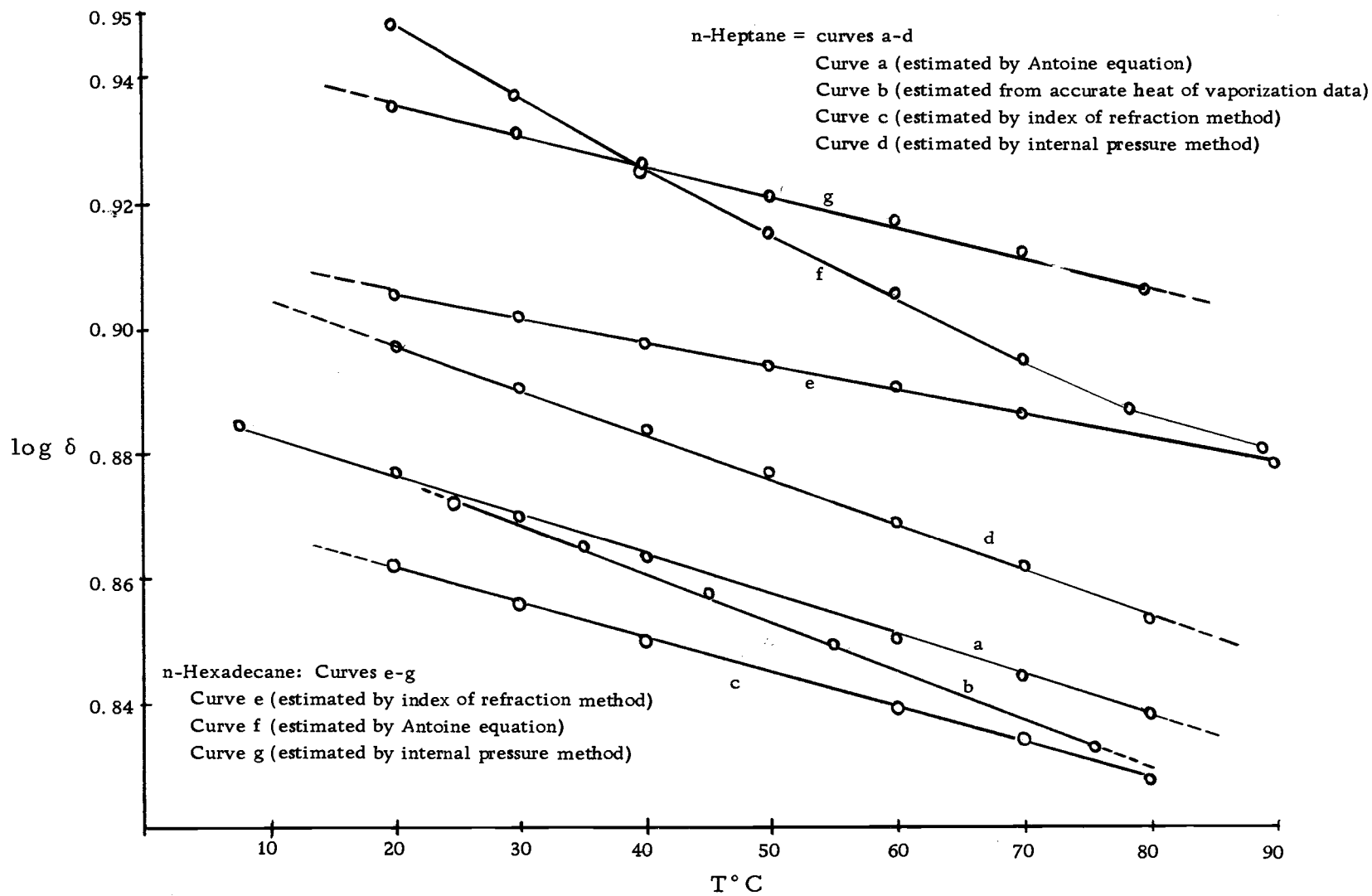


Figure 5. Temperature dependence of  $\delta$ .

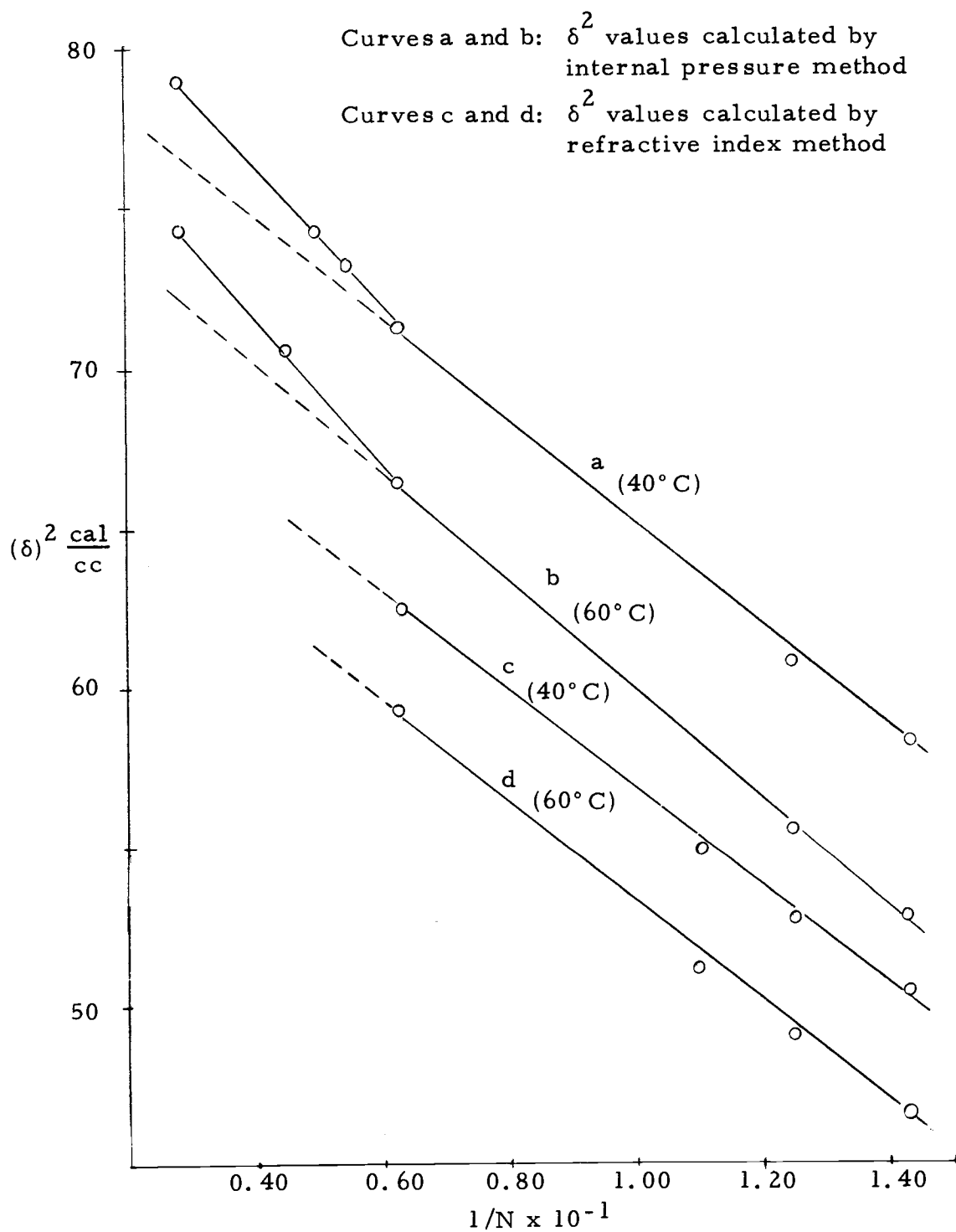


Figure 6. Comparison of  $(\delta)^2$  values estimated by index of refraction method and internal pressure method.

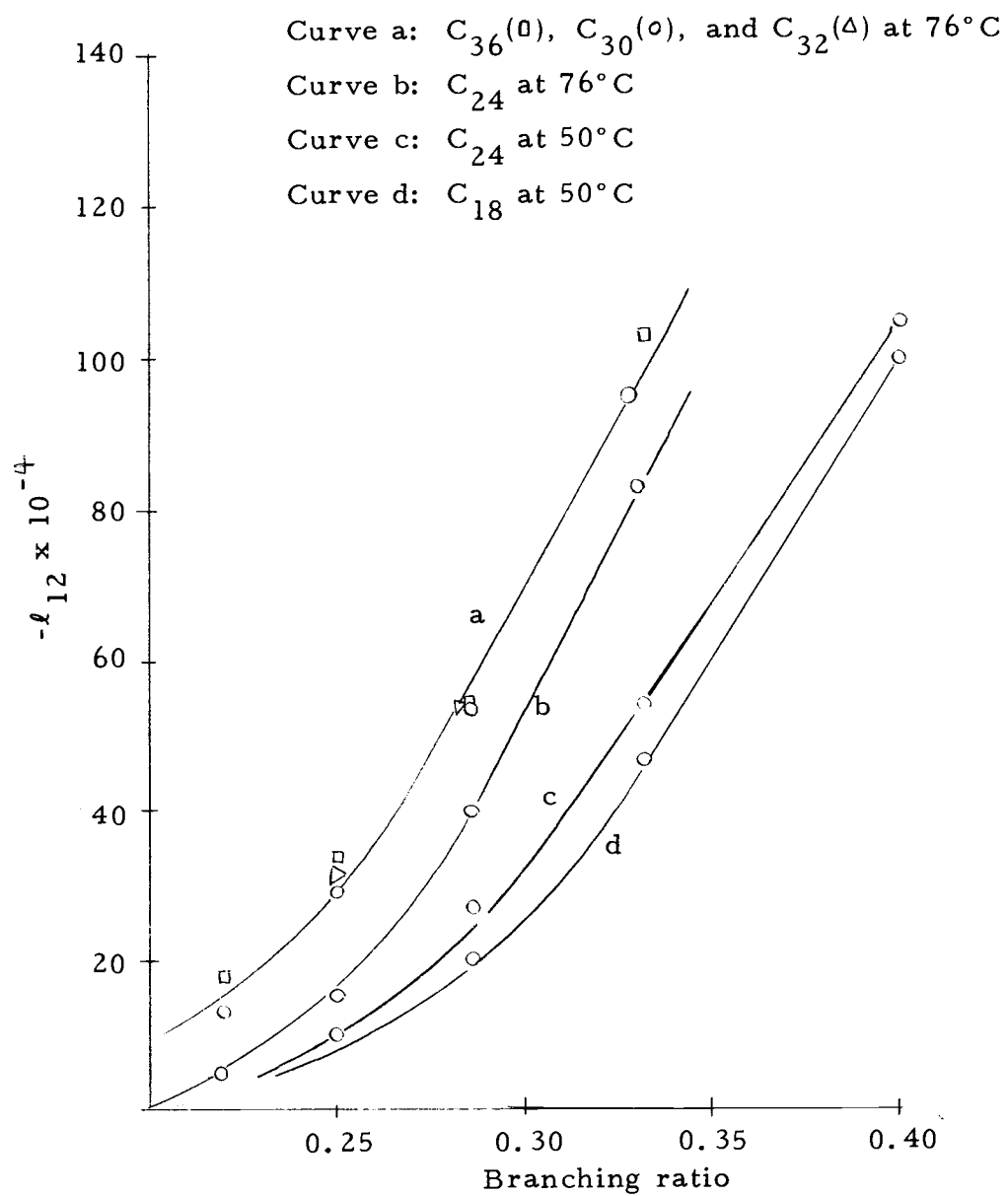


Figure 7. Deviations of geometrical mean assumption of n-paraffinic mixtures: the effect of solvent carbon atom number.

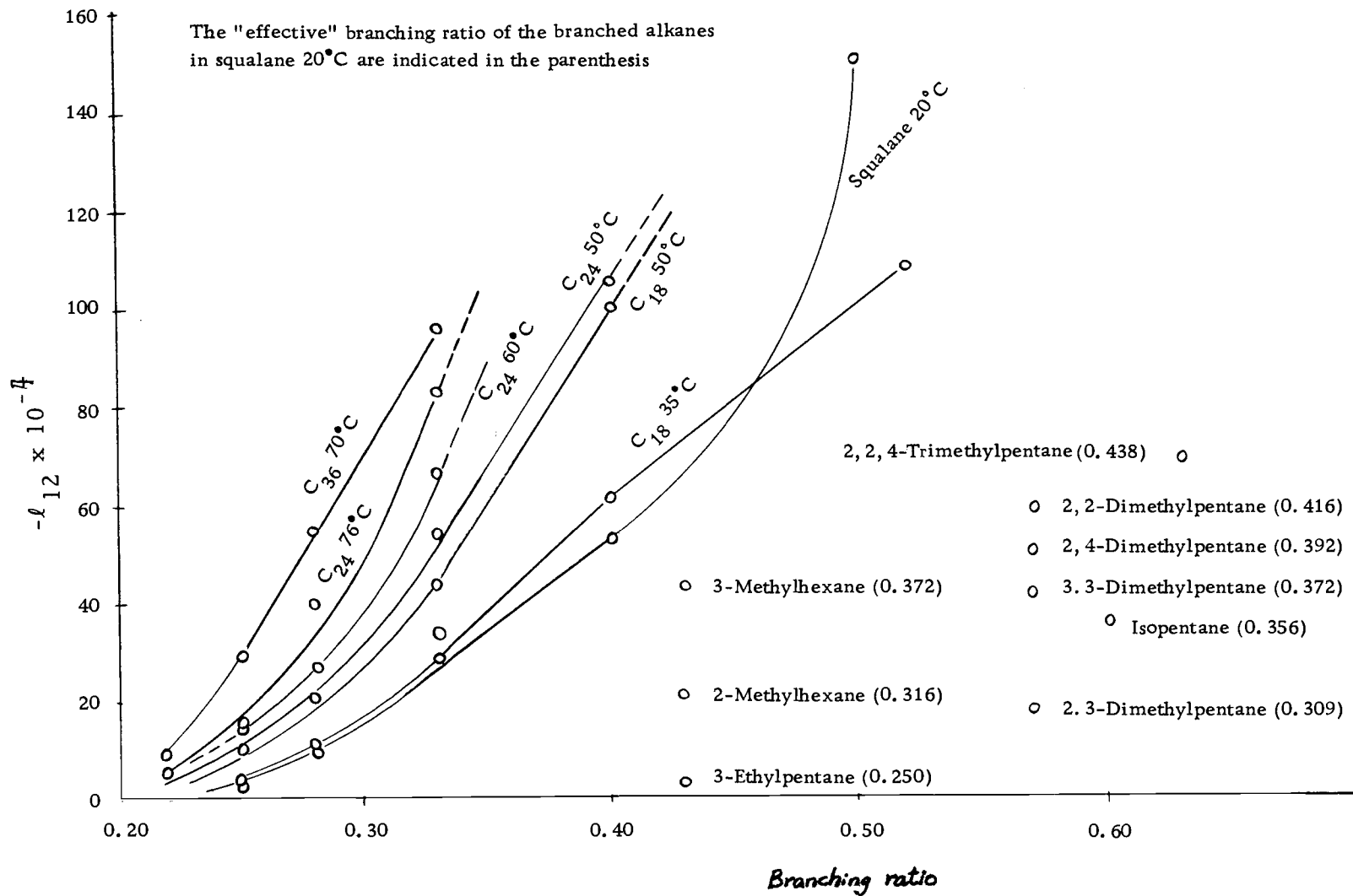


Figure 8. Variation of  $l_{12}$  with temperature in linear and branched solvents.

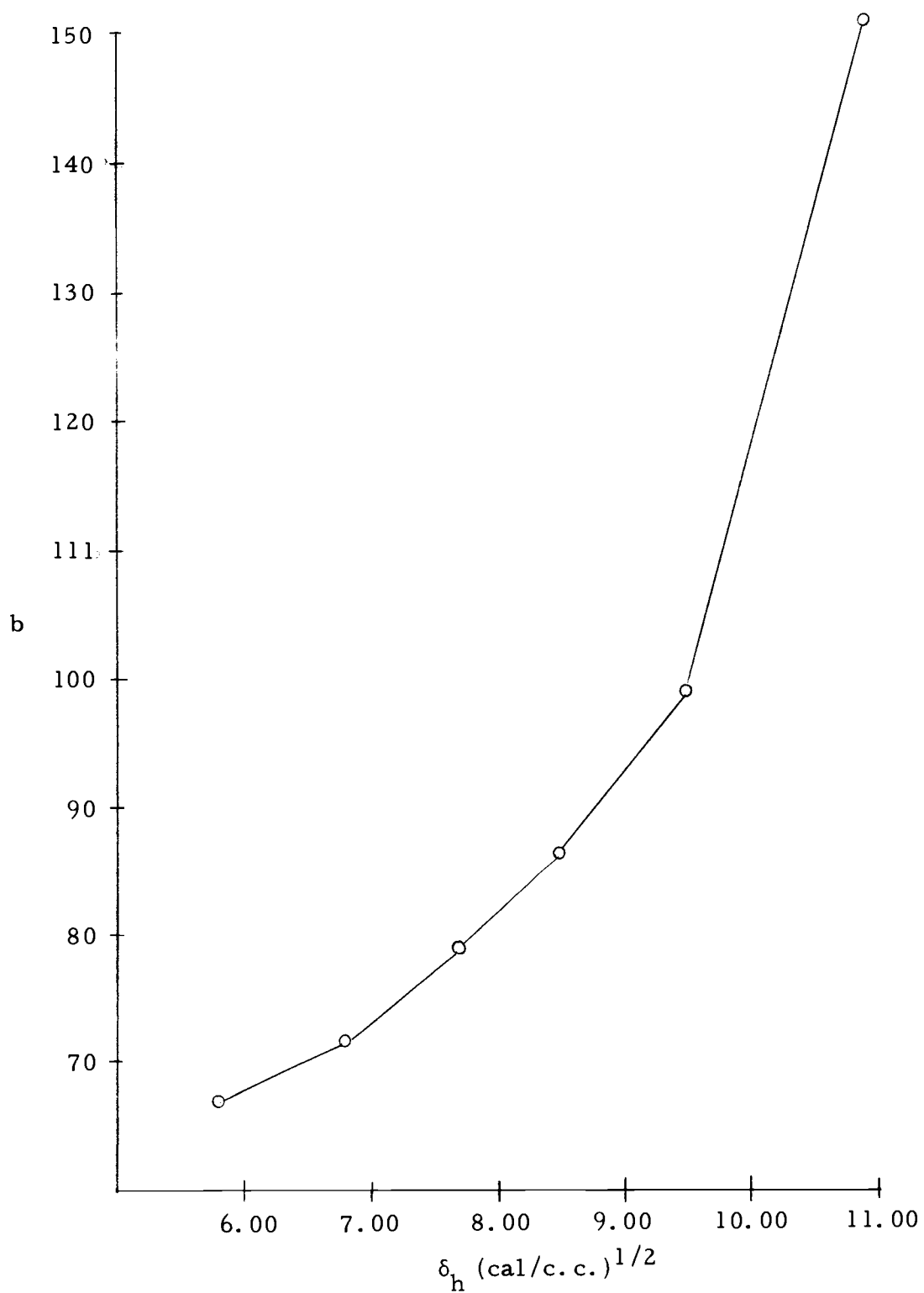


Figure 9. Relation of polarity factor "b" with  $\delta_h$ .