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USE OF THE SOLUBILITY PARAMETER FOR PREDICTING SELECTIVITY AND RETENTION IN CHROMATOGRAPHY

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SUMMARY

The theoretical and practical aspects of the solubility parameter ("polarity") model for predicting retention behaviour and partition coefficients have been investigated. A critical discussion of the theoretical basis shows that sufficiently accurate data for the total solubility parameter can be obtained from generalized thermodynamic functions, rather than from the usual vapour pressure data. Partial polarities are obtained from theoretical and semi-empirical relations with simple physical parameters such as refractive index, dielectric constant and dipole moment. Internal pressure, calorimetric and spectroscopic experimental data are used for estimating the contributions of charge and proton transfer (acid-base interaction).

Tables of partial and total polarities are presented which replace older, less accurate data. The multicomponent model is tested with chromatographic and partition experiments and is proposed as an alternative method for selecting a proper phase system (in both chromatography and partition methods where, for example the Hansch method is frequently used).

INTRODUCTION

The main problem in all separation methods based on phase equilibria is the *a priori* prediction of selectivity. In the relatively simple gas chromatographic (GC) system, this problem can be solved by empirical methods such as Rohrschneider's method. However, the very large number of different phase systems (often mixtures) makes this approach impractical for liquid chromatography (LC), as the preliminary characterization would take too long. As retention in chromatography is controlled by the thermodynamic equilibrium of a solute between mobile and stationary phases, in principle the prediction of retention is possible from thermodynamic data of standard partial free molar enthalpies: $-\Delta\mu^0 = RT\ln K$.

Numerical values for $\Delta\mu^0$ are too scarce to be of any practical value, so use must be made of reliable models for mixtures of liquids, gases, etc. With the condition

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that the model utilizes only readily available and simple physical parameters, only one model can be considered, *viz.*, the solubility parameter model after Scatchard and Hildebrand and Scott^{1,2}. This model is extremely attractive because it uses only pure component data and is, by its definition on a volume basis, very convenient for mixtures (gradient elution). The attractive alternative of perturbation theories^{3,55} is under investigation.

Developed for non-polar substances, the solubility parameter, δ , has been extended to polar substances in the last decade, as has been reviewed by Barton⁴. In view of the many assumptions inherent in the δ model, a surprising number of experiments can be explained^{1,2,4}, pointing to a more fundamental justification of the concept. The present study supports the usefulness of the model, provided that a sufficient number of partial parameters is used.

The next section critically discusses the means of obtaining reliable and sufficiently accurate solubility parameters, the values of which are presented in Table I.

THEORETICAL

The usual differential migration or retention equation⁵:

$$V_R = V_m + K_t V_s$$

makes use of the practical partition coefficient,

$$K_t = c_i^s/c_i^m$$

based on concentrations rather than thermodynamic relevant activities.

At infinite dilution, K_t is related to activity coefficients, γ , and molar volumes, v :

$$K_t = \frac{\gamma_i^m}{\gamma_i^s} \cdot \frac{v_m}{v_s} \quad (1)$$

where γ describes the deviation from Raoult's law ($K_H = p/x = \gamma p^\circ$) when use is made of the pure liquid as a standard state. Prediction of retention thus requires activity coefficients, which in turn follow from thermodynamic excess functions as:

$$RT \ln \gamma_i = \mu_i^e = h^e - Ts^e = RT \ln \gamma_i^h + RT \ln \gamma_i^s \quad (2)$$

In common practice, the ("athermal") entropy contribution is found from the well known Flory-Huggins^{5,6} expression:

$$\ln \gamma_i^s = \ln \frac{v_i}{v_j} + \left(1 - \frac{v_i}{v_j}\right) \quad (3)$$

where molar volumes are used for convenience⁶. Eqn. 3, which gives values of $\gamma^s < 1$, is also used in the interpretation of our experiments. Although more sophisticated expressions exist^{7,8} they do not give better results than the simple Flory-Huggins theory, because the additional parameters introduced are not well known.

The next sections are concerned with the enthalpy contribution, γ_i^h , also called the regular, thermal or interactional contribution.

Solubility parameter and polarity

In regular solutions, defined by the absence of volume and entropy effects ($v^e = s^e = 0$; $h^e = u^e + pv^e = u^e$), the molar mixing energy is given by the Scatchard-Hildebrand mixing rule^{1,2}.

The solubility parameter, δ , is defined as the square root of the cohesive energy density (c.e.d. = $-u/v$), i.e., the internal potential energy compared with the ideal gas state. The partial molar excess enthalpy,

$$h^e = -\frac{\partial}{\partial n_i} (\Delta u^m_{ij})_{n_j}$$

now determines γ_i^h as

$$\ln \gamma_i^h = \frac{v_i}{RT} (\delta_i - \delta)^2 \quad (4)$$

In earlier chromatographic studies^{5,9-12}, this relationship has been shown to give useful predictions of retention behaviour. Based on these results, it is possible to interpret the solubility parameter as a quantitative measure of the "polarity", which in practical chromatography is often handled in an intuitive manner^{5,13}. Indeed both, polarity and the internal energy density are supposed to describe the total δ of molecular interactions. Hence, in the following discussion, solubility parameter and polarity are used interchangeably. One direct consequence of the exponential relationship between the activity coefficient, γ , and the solubility parameter, δ , is the need for highly accurate δ values. Indeed, a simple error analysis of eqn. 4 shows that δ must be known to better than 1% in order to make an estimate of chromatographic retention data possible. In the following sections, the possibility of obtaining such accurate δ values will be discussed.

Calculation of numerical values for δ

Numerical values for δ follow directly from its definition, $\delta^2 = -u/v$. As an example, the Van der Waals equation of state gives the internal energy as $u = -a/v$ [of course, negative compared with the ideal gas state ($u \approx 0$) by the attractive nature of the intermolecular forces]. Indeed, this can be used as a crude estimate of δ values¹: $\delta^2 = a/v^2$. More accurate results are obtained by arguing that the potential energy of a saturated liquid equals the sum of the molar heat of evaporation, Δu^v , and the energy, Δu^g , needed to expand the saturated vapour to the ideal gas state ($p \rightarrow 0$ or $v \rightarrow \infty$):

$$-u = \Delta u^v + \Delta u^g = \Delta u^v + \int_v^\infty \left(\frac{\partial u}{\partial v} \right)_T dv \quad (5)$$

In terms of the usual heats of vaporization:

$$-u = \Delta h^v + \Delta h^g - RT + pv^g \quad (6)$$

Provided that the pressure and temperature are far from the critical conditions, Δh^g and pv^g can be neglected, which gives the commonly used expression

$$\delta^2 = \frac{\Delta h^v - RT}{v^g} \quad (7)$$

In LC, however, conditions may easily approach the critical region of many solutes ($\Delta h^g \rightarrow 0$). Now, Δh^g and pv^f determine to a large extent the value of δ^2 , which from eqn. 7 would be negative, and values based on eqn. 7 must therefore be used carefully. Another reason for this is the lack of sufficiently accurate Δh^g data, which are often estimated from vapour pressure data using the Clausius-Clapeyron equation.

It can be shown that

$$\delta^2 = -\frac{u}{v^f} = \left(\frac{\Delta h^g - RT}{v^f} \right) \cdot Z \left[1 - \left(\frac{v^f}{v^g} \right)^2 \right] \approx \frac{\Delta h^g - RT}{v^f} \cdot Z \quad (8)$$

In comparison with eqn. 7, the compressibility factor, Z , corrects for gas imperfection. This is probably sufficient in GC, where the conditions are still far removed from the critical region and indeed Hoy's tables¹⁴ are valuable here. For the much higher pressures encountered in LC, the correction remains doubtful, because the factor $1 - (v^f/v^g)^2$ is based on the Van der Waals equation, the validity of which is uncertain. Therefore, for LC the vapour pressure approach is abandoned in favour of the generalized thermodynamic functions, to be discussed next.

Solubility parameter and generalized thermodynamic properties

In principle, all generalized thermodynamic predictions are based upon Pitzer's acentric factor (ω) method to correlate compressibility factors as a function of reduced pressures and temperatures¹⁵. As $Z = Z(p_R, T_R)$ represents the complete equation of state, it is possible to derive internal energies and hence δ^2 values. Hildebrand *et al.*² used this approach and developed a correlation for δ^2 in terms of ω . This method, however, yields unreliable results, probably owing to a lack of sufficiently accurate data. Much better results can be obtained from the modern residual enthalpy tables^{15,16}, as δ^2 can be shown to be a simple function of this variable.

Because $h = u + pv = u + ZRT$, the residual internal energy, *i.e.*, δ^2 , is established as

$$\delta^2 = \left[\frac{h^0 - h}{RT_c} + T_R(Z - 1) \right] \frac{RT_c}{v} \quad (9)$$

Lee and Kesler's recent tabulation¹⁶ of $(h^0 - h)/RT_c$ and Z values extends to sufficiently low values of p_R and T_R to be of practical use for all forms of chromatography. Values of the constant ω are tabulated¹⁵ or can be derived from critical data¹⁵⁻¹⁷, which in turn can be obtained from group contributions^{15,18}. Table I gives values for a number of compounds covering a wide range of polarity. The results do not differ much from the values in the Hoy table¹⁴ but are more accurate and have a better background.

Cohesive energy density (c.e.d.) and internal pressure; multicomponent parameters

It is often stated that solubility parameters can be evaluated from internal pressures^{1,4}, defined by the thermodynamic equation of state, which follows from the first and second laws of thermodynamics:

$$p_i = \left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p = T\gamma_0 - p \quad (10)$$

The relationship between the c.e.d. ($= \Delta u^v/v$) (integral or total interaction) and the internal pressure, $(\partial u/\partial v)_T$ (a differential quantity), is obvious from Van der Waals' equation, where both are equal to a/v^2 . From this, it appears worthwhile to derive δ^2 from p_i . To this end, the following three possibilities were investigated.

Firstly, p_i can be derived from compressibility and specific heat data, but these attempts were unsuccessful. In a second attempt, we utilized a slightly corrected form of Lee and Kesler's compressibility correlation¹⁶. The results were promising, but it appeared that in order to reach an accuracy of 1% for δ , the correlation should be improved. The third approach is based directly upon eqn. 10 using the isochoric thermal pressure coefficient:

$$\gamma_v = \alpha_p/\beta_T \quad (11)$$

where α_p is the isobaric expansion coefficient and β_T is the isothermal compressibility. Existing correlations for α_p (ref. 15) and β_T (refs. 26 and 27) were not sufficiently accurate for our purposes, but direct experimental data for α_p and β_T or, better still, for γ_v (refs. 1, 4, 19-25) yielded good results. As shown by Bagley and co-workers²¹⁻²⁴ and Dack²⁵, these experiments strongly indicate the close relationship between p_i and c.e.d. for non-polar substances as

$$p_i = \frac{\Delta u^v}{v} + \frac{3}{2} \cdot \frac{RT}{v} \quad (12)$$

The correction term $(3/2) \cdot (RT/v)$ results from the difference in the external degrees of freedom of vibration and rotation in the gas and liquid phases.

Eqn. 12 is very important as it proves that p_i and not c.e.d. should be used in the regular mixing rule, as pointed out by Bagley and co-workers²¹⁻²⁴. This means that solubility parameters should be evaluated from internal pressures ($p_i = \delta^2_v$) rather than from vaporization data (c.e.d. = δ^2) and according to eqn. 12 have higher values than tables of δ^2 suggest:

$$\delta_v^2 = \delta^2 + \frac{3}{2} \cdot \frac{RT}{v} \quad (13)$$

Indeed, the internal pressure is very sensitive to small volume changes, as it describes the volume differential of the potential energy. Hence the strongly distance-dependent classical interactions such as dispersion are covered. Thus, for non-polar substances $p_i = -(u_{disp}/v)$. On the other hand, the integral quantity Δu^v covers the whole of the energy changes involved in phase changes and thus contains the kinetic terms associated with vibration and rotation as well as the dispersion interaction. As the mixing rule applies strictly to symmetrical potential energy interactions (e.g., dispersion) and not to kinetic energy changes, there is no doubt that it is p_i that plays the role of $-u/v$ in the mixing rule. This reasoning gives the solubility parameter concept a sound thermodynamic basis.

For polar substances, this has the important consequence that the determination of p_i as well as c.e.d. gives insight into both classical and chemical interactions, as shown by Bagley and co-workers²¹⁻²⁴. The residual parameter $\delta^2_R = \delta^2 - \delta^2_v$

now describes not only kinetic effects ($[3/2] \cdot [RT/v]$) but also transfer (acid-base) interactions. The latter can thus be described as $\delta_h^2 = - (u_{ab}/v)$, such that

$$\delta_T^2 = \delta^2 + \frac{3}{2} \cdot \frac{RT}{v} = \delta_o^2 + \delta_h^2 \quad (14)$$

Compared with the method of Hansen²⁸⁻³⁰ both our total polarity, δ_T , and δ_h have higher values than δ and δ_H according to eqn. 14, caused by the kinetic term. Furthermore, as Hansen's values are based upon vapour pressure data and a statistical interpretation of certain physical experiments (*e.g.* surface tension), we prefer the method outlined above. Hansen's method bears some resemblance to some calculation procedures recently applied to chromatography, such as factor analysis³² and the Rohrschneider method^{5,37}. These methods are of great value for a limited number of compounds, but obscure physical insight and also are too laborious for the universal prediction of retention.

The two-component model expressed by eqn. 14 shows some resemblance with the model of Prausnitz and co-workers^{2,10,12} (which, however, applies the uncertain homomorph concept and, notwithstanding its relative success, is unattractive and rather complex to handle). A two-parameter model cannot, however, be conclusive in describing at least three types of interactions (if we neglect the influences of induction³³ and multipoles, *i.e.*, if present their influence is reflected on the other parameters). The differences in all possible partial polarities rather than the differences in total polarities determine the interaction energies. As proposed by Hansen and suggested by eqn. 14, there is some logical basis for defining partial polarities $\delta_d^2 = - (u_{dis}/v)$ and $\delta_o^2 = - (u_{or}/v)$ for dispersion and orientation, respectively.

Keiler *et al.*³⁴ performed the important task of proving that the mixing rule remains unaffected for symmetrical interactions such as dispersion and orientation. For asymmetrical (induction and transfer) interactions, they formulated revised mixing rules. They describe the important contribution of transfer interaction by

$$h^e = \Delta h_{i,j}^m = \Delta u_{i,j}^m = 2v_i(\delta_{a,i} - \delta_{a,j})(\delta_{b,i} - \delta_{b,j}) \quad (15)$$

where $\delta_h^2 = - (u_{ab}/v) = 2\delta_a\delta_b$. Note that eqn. 15 can give rise to exothermal mixing ($h^e < 0$), as is actually the case in many transfer interactions. All other partial interactions are necessarily endothermal from eqn. 4 (except the neglected induction, which has a form like eqn. 15).

In conclusion, we now have a well defined four-parameter solubility parameter model:

$$\delta_T^2 = \delta_a^2 + \delta_o^2 + 2\delta_a\delta_b \quad (16)$$

If accurate enough partial polarities can be obtained, the main problems in chromatography, those of selectivity and choice of an optimal phase system, may be tackled. It is obvious that no universal list of phases with increasing polarity (elutropic series) can be obtained, but rather lists of partial polarities. When the solutes are characterized in the same way, optimal separation conditions may be predicted. The only tasks that remain are to prove the model to be correct and to perform the charac-

terization in terms of partial polarities. The latter must be carried out such that the method becomes attractive to the practical chromatographer.

Retention and partial polarities

Written in terms of partial polarities, the activity coefficient is now expressed as

$$\ln \gamma_i^h = \frac{v_i}{RT} [(\delta_{a,i} - \delta_{a,j})^2 + (\delta_{o,i} - \delta_{o,j})^2 + 2(\delta_{a,i} - \delta_{a,j})(\delta_{b,i} - \delta_{b,j})] \quad (17)$$

which replaces eqn. 4. From eqns. 1, 3 and 17, an expression for the partition coefficient is obtained:

$$\begin{aligned} \ln K_i = \frac{v_i}{RT} [(\delta_{T,m}^2 - \delta_{T,s}^2) + 2\delta_{a,i}(\delta_{a,s} - \delta_{a,m}) + 2\delta_{o,i}(\delta_{o,s} - \delta_{o,m}) + \\ + 2\delta_{a,i}(\delta_{b,s} - \delta_{b,m}) + 2\delta_{b,i}(\delta_{a,s} - \delta_{a,m})] + v_i \left(\frac{1}{v_s} - \frac{1}{v_m} \right) \quad (18) \end{aligned}$$

from which all other retention data can be found.

In GC, there is even a possibility of obtaining p_i^σ from the δ model, which yields

$$\ln \alpha_{21} = \ln \frac{\gamma_1 p_1^{\sigma_1}}{\gamma_2 p_2^{\sigma_2}} \approx \ln \frac{v_1}{v_2} + (v_1 - v_2) \left[\frac{\delta_s^2}{RT} - \frac{1}{v_s} \right] - 2 \frac{\delta_s}{RT} (v_1 \delta_1 - v_2 \delta_2) \quad (19)$$

which is almost the same as Rohrschneider's expression³⁷. Experimental verification (see Chromatographic Experiments) shows that eqn. 19 is not bad as a rule of thumb (Table IV). Kováts retention indices can be obtained from eqn. 19.

In the discussion below, eqn. 18 is applied in two ways. Firstly, it is used to predict retention data, which are then compared with experimental data taken from our own measurements or from the literature. Secondly, partial polarities for novel stationary phases are obtained from a linear regression analysis of retention data for a number of solutes for which δ parameters are known. This approach is analogous to Rohrschneider's, but yields meaningful parameters. With these parameters, it might be possible to characterize, *e.g.*, chemically bonded stationary phases and adsorbents. Furthermore it should be possible to replace the popular semi-empirical Hansch model, used in predicting partition coefficients within^{38,39} and outside⁴⁰ chromatography, by a more flexible and probably more accurate model. Having established the relationship between the Hansch and δ models, a more sophisticated prediction of retention and partition seems possible in the near future, based on Hammett and Taft constants or other group solution models.

ESTIMATE OF PARTIAL POLARITIES

Dispersion

The London-Van der Waals interaction can be related to the refractive index, n , via the Lorentz-Lorenz expression for the polarizability^{34,41}. However, the correlations thus obtained are based on uncertain latent heats and extended over a high

polarity range, which means that a contribution of other interactions is included. Also, the kinetic term must be taken into account. Hence we propose a new correlation between δ_d^2 and $(n^2-1)/(n^2+2)$. Based on eqn. 13, where $\delta_o^2 = \delta_d^2$ for non-polar liquids, we obtain the correlation

$$\delta_d^2 = 228.0 \cdot \frac{n^2 - 1}{n^2 + 2} + 5.2 \quad (20)$$

(relative standard deviation = 2%; $1.35 < n < 1.45$) for 42 *n*-alkanes and branched alkanes. Values for the c.e.d. were obtained from the residual enthalpy method (see above). We used eqn. 20 for all tabulated substances, even when the refractive index lies out the range of the correlation.

Polar interaction or orientation

Following the suggestions of Hansen and Beerbower³⁰ and Bagley²¹⁻²⁴, the polar (dipole-dipole) interaction, $\delta_p^2 = \delta_o^2 = - (u_p/v)$, is calculated from the Böttcher expressions for u_p (ref. 42):

$$\delta_o^2 = \frac{1.2099 \cdot 10^4}{v^2} \cdot \frac{(\epsilon - 1)(n^2 + 2)}{(2\epsilon + n^2)} \cdot \mu^2 \approx \frac{RT}{v} \cdot \frac{(\epsilon - 1)(\epsilon - n^2)}{(n^2 + 2)\epsilon} \quad (21)$$

In our experience, the more simple second expression, involving only the dielectric constant and avoiding uncertainties in the dipole moments, gives reliable results except for alcohols, where the first expression is recommended. Beerbower's³¹ simple relationship, $\delta_o = 18.3 \mu/v^{\frac{1}{2}}$, yields values which may be in error by up to $\pm 2 \delta$ units [(cal/cm³)^{1/2}], which is much too large for our purposes.

Chemical or acid-base interaction

Estimate of δ_h^2 . Transfer interactions, which are of utmost importance in chromatographic selectivity, are described by the asymmetrical Keller³⁴ expression, $\delta_h^2 = 2\delta_a\delta_b$, which shows a striking resemblance with the Drago⁵⁹ *E* and *C* equation ($\Delta h = \Sigma E \cdot C$). This useful equation for acid-base phenomena was recently provided with a theoretical basis⁴³ and has been used in two recent chromatographic studies^{44,45}. Reliable *E* and *C* coefficients are still too scarce to be used for the universal prediction of δ_h^2 , however. Beerbower and co-workers^{30,31} proposed a group solution model, as is in common use for non-polar interactions, which contains, however, too great uncertainties to be used. The same applies to Hansen's rule of thumb³⁰ for *n*-fold hydrogen bonding, $\delta_h^2 = 4650n/v$.

Besides the correlation with surface tension^{30,31,46}, two methods for estimating values for δ_h^2 remain, which in our opinion also give the most reliable data. These methods are based on the formerly derived relationship between δ_h^2 and δ_R^2 . The latter is known either from internal pressures or from the estimated partial polarities discussed in the previous sections. Where possible, p_i measurements²⁰ are used to calculate δ_h^2 in Table I ($\delta_h^2 = \delta_T^2 - p_i$), otherwise dispersion and orientation were used ($\delta_h^2 = \delta_T^2 - \delta_d^2 - \delta_o^2$).

Separate acid and base parameters. As discussed above, it is necessary to subdivide the total transfer parameter into separate acid and base parameters in order to explain the exothermal character of this type of interaction. It is also not impossible

that further differentiation in hard (electrostatic) and soft (covalent) interactions is desired, as suggested by Keller *et al.*³⁴ as a consequence of the analogy with Drago's acid-base treatment. For the time being, we chose the simple two-parameter model $\delta_n^2 = 2\delta_a\delta_b$ in order to keep the model as simple as possible.

In order to obtain the two unknowns, δ_a and δ_b , from estimated values of δ_n^2 , another relationship is necessary. As shown by Drago⁵⁹, the usefulness of the model is not affected when an arbitrary choice of either the acid or the base scale is made. This is due to the fact that only product terms of acid and base parameters occur (*e.g.*, eqns. 15 and 18). The same applies to the Rohrschneider method, where the partial polarity scales are defined by arbitrary choices of standard substances.

We prefer, however, to define the parameters in our model such that they are related to absolute physical properties as closely as possible in a realistic sense, *i.e.*, the parameters should have absolute rather than only relative significance.

Although δ_a and δ_b themselves do not have a true physical meaning (only their product), they are clearly related to acid strength and base strength, respectively. Acid strength can be interpreted as the energy (enthalpy) that accompanies the process of donating a proton or accepting an electron, whereas for base strength the reverse applies. Thus, we propose to interpret the square of the ratio of δ_a and δ_b as the ratio of the energies that accompany the processes of donating and accepting a proton. As only a few substances are both acids and bases, we are almost forced to choose water as the standard substance. This choice has the further advantage that many experiments, together with confirming M.O. calculations⁴⁷, can furnish the desired energies. Thus we obtain

$$\left(\frac{\delta_b}{\delta_a}\right)_{\text{H}_2\text{O}}^2 = \frac{u_{\text{H}_2\text{O}} - u_{\text{H}_3\text{O}^+}}{|u_{\text{H}_2\text{O}} - u_{\text{OH}^-}|} = 0.43 \quad (22)$$

from which $\delta_{a,\text{H}_2\text{O}}$ and $\delta_{b,\text{H}_2\text{O}}$ follow because $\delta_{n,\text{H}_2\text{O}}^2$ is known to be 363.7 (Table I). Depending on the reliability of the literature data for the energies, this defines the scales for acid and base strength such that water is roughly twice as acidic as it is basic.

For the benefit of the reader, the way in which the acid and base parameters are obtained from water is described below in some detail.

Step 1. Collect values of δ_n^2 . Here the calculation method involving p_i measurements or δ_R^2 is preferred.

Step 2. Combine the data on water with enthalpy data from the literature. A recent useful source of such data is the work of McTigue and Renowden⁴⁸. For a number of substances, δ_a and δ_b are now obtained from $\delta_n^2 = 2\delta_a\delta_b$ and eqn. 15, where $v_i = v_{\text{H}_2\text{O}} = 18$.

Step 3. In the literature, many spectroscopic studies on hydrogen bonding and association enthalpies are reported⁴⁹⁻⁵¹, mainly with respect to some standard substances such as phenol. Most reliable are the recent results of Rao *et al.*⁵¹, which were obtained at infinite dilution in order to avoid solvent effects (note however, the wrong conversion of kilocalories into kilojoules by these workers). From our table, we combined δ_n^2 values for phenol and water with the Rao *et al.* enthalpy values to obtain from eqn. 15 the key values of δ_a and δ_b for phenol.

Step 4. These values enable us to calculate δ_a and δ_b values for the compounds on which enthalpy data (on association with phenol) are reported in the literature. If

possible, we used values at infinite dilution⁵¹, otherwise at uncertain (but low) concentration⁵⁰.

Step 5. The now known data on electron donors (basic compounds) are combined with enthalpy data on interactions with various other acceptors. Repeated application of eqn. 15 using δ_R^2 values obtained from step 1 yields a series of δ_a and δ_b values for each of the acceptors used. The spread of such a series is a very important indication of the usefulness and consistency of our model (eqn. 16).

Step 6. For those compounds on which no enthalpy data on phenol are available, we might now use other acceptors as "key compounds". The deviations in δ_a and δ_b values for one donor compound (base) is another way of testing the model's internal consistency.

CHROMATOGRAPHIC EXPERIMENTS

In order to test the tabulated partial polarities in connection with the reported retention equations, both GC and LC retention experiments were carried out. Some other interesting test cases were selected from the literature. Retention data are reported in terms of activity coefficients and partition coefficients where sufficient data could be obtained (*e.g.*, amounts of both phases, pressure). Otherwise, relative retention capacity factors and retention indices are used.

Gas-liquid chromatography

A modified Perkin-Elmer F11 and a Becker 1452D gas chromatograph, both equipped with an FID detector, were used. Columns were packed with deactivated and sieved Chromosorb support materials. The columns used were constructed from light materials (alumina and glass packed capillaries) in order to obtain reliable values for the amount of stationary phase by weighing. During experiments, repeated weighing gave information on the loss of stationary phase by bleeding. In calculating specific retention volumes, V_g^0 (based on peak maxima), bleeding was corrected for, whereas activity coefficients were calculated from V_g^0 by the method of Martire and Pollara⁵².

Vapour pressures, p_i^σ (mm Hg), were obtained from tables^{15,35,36}, whereas second virial coefficients followed from the compilation of Dymond and Smith⁵³ or from acentric factor correlations^{15,16}.

Activity coefficients were corrected for entropy contributions according to eqn. 3. The results of these measurements are used in regression analysis to obtain the solubility parameters of GLC stationary phases (Table II). Other measurements yielded experimental Kováts indices, which are reported in Table IV.

Liquid chromatography

A Waters and a Packard-Becker liquid chromatograph were used. Chemically bonded stationary phases were prepared in our laboratory⁵³, and the columns were always filled by slurry packing techniques. From measured capacity factors, relative retention data were calculated and used in regression analysis.

RESULTS AND DISCUSSION

Table I presents a selection of values obtained as described above. Starting from these values, our first concern is to prove the internal consistency of the proposed four-parameter model. Conclusive information on this point can be obtained from

TABLE I
CALCULATED MULTICOMPONENT SOLUBILITY PARAMETERS AT 20°C

Compound	δ_T	δ_d	δ_o	δ_h	δ_a	δ_b	δ
Acetone	10.51	7.44	6.41	5.47	0.90	16.6	9.93
Acetonitrile	13.15	7.33	10.27	3.70*	0.39	17.6	12.50
Acetophenone**	10.79	8.74	3.80	2.67	0.27	13.1	10.44
Aniline	12.21	9.04	2.30	7.88*	3.49	8.9	11.81
Benzaldehyde**	11.34	8.80	4.38	5.65*	1.15	13.9	10.95
Benzene	9.71	8.51	0.16	1.95	0.18	10.4	9.19
Benzonitrile	11.38	8.69	5.42	4.96*	0.94	13.1	11.00
Benzophenone**	10.87	9.15	2.79	5.16*	1.11	12.0	10.62
1-Butanol	11.47	7.77	2.64	7.74	3.15	9.1	11.05
tert.-Butanol	10.53	7.65	2.47	5.47	2.51	6.1	10.08
Carbon-tetrachloride	9.19	8.22	0.29	1.43	0.34***	3.0***	8.68
Chloroform	9.87	8.12	1.95	3.02	1.54	3.1	9.31
Cyclohexanone**	10.76	8.16	4.57	4.13	0.61	13.9	10.36
Dibutyl ether**	8.26	7.77	0.86	2.67*	0.30	11.9	7.94
1,2-Dichloroethane	10.64	8.11	3.71	3.35	1.68	3.3	10.12
Dichloromethane	10.68	7.96	3.67	4.07	1.92	4.3	10.02
Diethyl ether	7.92	7.38	1.68	2.33	0.19	14.0	7.37
N,N-Dimethylaniline**	10.29	8.87	1.43	5.02*	1.58***	8.0***	9.95
Dimethyl sulphoxide	13.45 [‡]	8.34	9.49	7.51	1.32	21.4	12.98 [‡]
1,4-Dioxane	10.65	7.95	0.43	7.07*	1.47	17.1	10.16
Ethanol	13.65	7.46	4.29	10.81	5.17	11.3	13.09
Ethyl acetate	9.57	7.55	2.32	5.40	0.26	13.5	9.09
Ethylbenzene	9.35	8.47	0.34	1.80	0.15	10.6	8.96
n-Heptane	7.91	7.91	0.03***	0	0	0	7.52
n-Hexane	7.74	7.74	0.02	0	0	0	7.29
Methanol	15.85	7.18	6.72	13.53	7.18	12.9	15.15
Methyl acetate	10.19	7.44	2.83	3.90	0.51	15.0	9.63
N-Methylaniline**	11.69	8.93	1.85	7.31*	3.28	8.2	11.34
Methyl ethyl ketone	9.96	7.60	5.12	4.18	0.58	15.0	9.46
Nitromethane	13.83	7.63	9.58	6.42*			13.23
n-Octanol**	9.13	8.00	1.49	4.14*	1.85***	4.6***	8.82
n-Pentane	7.65	7.65	0.03	0	0	0	7.14
Phenol	12.76	8.33	2.52	8.86*	5.20	8.7	12.37
1-Propanol	12.27	7.65	3.54	9.04	4.12	10.0	11.78
2-Propanol	12.37	7.59	3.12	9.27	4.21	10.2	11.90
Pyridine	11.12 [‡]	8.56	3.94	5.90*	0.91	19.1	10.62 [‡]
Tetrahydrofuran	9.88	7.96	2.97	5.04*	0.78	16.3	9.32
Toluene	9.53	8.47	0.32	2.45	0.29	10.2	9.09
2,2,4-Trimethylpentane	7.33	7.33	0.04	0	0	0	6.96
Water	25.52	7.22	15.35	19.07	16.65	10.9	24.55

* Residual term from eqn. 16.

** Estimated critical data.

*** Estimated from related compound data.

[‡] Estimated from literature data²⁵.

the variation in acid and base parameters obtained from key compounds other than phenol. The relative standard deviation (in some instances based on too few compounds tested) rarely exceeds 10%. This is satisfactory, because deviations are not only caused by errors in the spectroscopic data used, but also reflect the cumulative error in the remaining partial polarities (dispersion, orientation and kinetic terms), as δ_a is often obtained as a "residual term" (see *Estimate of δ_a^2*).

TABLE II
CHARACTERIZATION OF GLC STATIONARY PHASES

Phase	$T(^{\circ}C)$	δ_T^*	δ_d	δ_o	δ_a	δ_b	δ_T^{**}
β, β' -Oxydipropionitrile	80	14.31	13.13	4.85	0.56	7.82	12.40
Dibutyl phthalate	90	10.01	9.37	1.13	0.68	8.18	8.89
Dinonyl phthalate	85.8	8.34	7.56	0.50	0.77	7.92	7.43
Diphenyl phthalate	81	11.33	10.68	1.47	0.76	7.98	10.18
Dicyclohexyl phthalate	97	12.24	11.81	1.71	0.45	8.15	10.44

* Sum of all partial parameters (eqn. 16).

** Value obtained from residual enthalpies.

Further proof of the consistency of the model is shown in Table II, which presents partial solubility parameters for some phthalate phases and β, β' -oxydipropionitrile, obtained from linear regression of eqn. 18, using GLC data. In this regression, the values of $\delta_{T,s}$ for the stationary phases were derived from residual enthalpies and used as fixed entries, instead of obtaining their values as an individual parameter from the regression analysis. It is illustrative to note that the δ_T obtained from the four parameters resulting from the regression analysis indeed approaches the original estimate within 10%. This proves the validity of the four-parameter model. Obviously, no important interactions are left out.

The observed deviation of 10% in δ_T (Table II) is acceptable, as the solubility parameters for the solutes used in the regression analysis had to be corrected for temperature variations. The best known means of executing temperature corrections in partial polarities is that described by Hansen and Beerbower³⁰. Although we suspect that their method overcorrects at least the dispersion polarity, we decided to use it in all appropriate instances. Except for non-polar substances, for which the temperature dependence is easily obtained from residual enthalpies, no better alternative exists. The molar volumes were corrected for temperature according to Pitzer's correlation¹⁵. Thus the observed differences of 10% in Table II may be attributed to a large extent to the uncertain correction method.

Having proved the consistency of the model, we now turn to its ability to predict retention data (Tables III and IV). Table III shows good agreement between experimental and predicted retention data on dinonyl phthalate for solutes not included in the regression analysis in Table II. This is apparent not only for relative retention data (where some cancellation of errors may occur), but also for absolute activity coefficients. It is noteworthy that on applying $\delta_a = 0$ (from Table I) for alkanes, no good results are obtained. A value of $\delta_a = 0.68$ fitted to the experimental data for 2,4-dimethylpentane (second footnote in Table III), however, yields good

TABLE III

ESTIMATE OF GLC RETENTION DATA ON DINONYL PHTHALATE AT 74.1°C

Data on dinonyl phthalate were calculated from regression at 85.8°C (Table II).

Solute	γ	γ (exp)*	I	I (exp)**
Benzene	0.377	0.552	749	724 (80°C)
Toluene	0.435	0.598	843	819 (70°C)
n-Pentane	0.935***	1.043	500	500
n-Hexane	1.008***	1.132	600	600
2,4-Dimethylpentane	1.281***	1.281	614	640 (80°C)
2,3-Dimethylpentane	1.110***	1.153	662	—
Dichloromethane	0.414	0.363	597	626 (80°C)
Chloroform	0.249	0.331	730	716 (80°C)
Carbon tetrachloride	1.096	0.609	618	703 (80°C)
1,2-Dichloroethane	0.561	0.494	719	—

* Experiments after Martire *et al.*⁵⁶.

** ASTM Gas Chromatographic Data Compilation.

*** δ_a (= 0.68) of alkanes fitted to experimental γ of 2,4-dimethylpentane.

TABLE IV

PREDICTION OF KOVÁTS INDICES USING TOTAL SOLUBILITY PARAMETERS (EQN. 19) WITH n-HEXANE AND n-HEPTANE AS REFERENCES

Solute	Squalane (20°C)		Hexadecane (20°C)		Squalane (50°C)	
	Calc.	Exptl.*	Calc.	Exptl.*	Calc.	Exptl.
1-Hexene	611	582	609	573	—	—
3-Methylpentane	590	584	590	573	—	—
2,3-Dimethylpentane	662	669	663	674	—	—
Benzene	642	631	633	630	651	644
Cyclohexane	623	655	618	646	622	662
2-Methylhexane	670	666	672	676	—	—
3-Methylhexane	673	675	674	687	—	—
2,2-Dimethylpentane	623	624	—	—	—	—
2,4-Dimethylpentane	625	629	629	633	—	—
2,2,4-Trimethylpentane	666	686	—	—	816	692
Acetone	—	—	604	432	—	—
Toluene	—	—	725	738	748	751
3,3-Dimethylpentane	644	654	—	—	—	—
3-Ethylpentane	676	684	—	—	—	—
Carbon tetrachloride	—	—	—	—	637	646
Ethylbenzene	—	—	—	—	826	840

* ASTM Gas Chromatographic Data Compilation.

results for the other alkanes. This suggests that alkanes are able to donate protons to some measurable extent, and this effect is supported by some literature data^{1,57}.

Although a much better prediction of such activity coefficients has been reported by Funke *et al.*⁵⁶ using factor analysis, we consider our results to be more promising. Firstly, the present data were obtained from first principles, and secondly, they were obtained without the considerable experimental effort required in factor analysis. Even the use of the simple one-parameter (δ_T) model (eqn. 19) may give

useful results for non-polar combinations, as demonstrated in Table IV. However, as soon as the polarity becomes even moderate, this simple model breaks down, as illustrated by the example of acetone. Obviously, a multiparameter model is mandatory for the universal prediction of retention. Turning our attention to LC, it must be stressed that the use of the partial polarity data from Table I is permitted only, at atmospheric pressure and room temperature. Minor extensions to higher pressures and temperatures can still be made well below the critical region, but in the case of modern LC, where average pressures approach 50 atm, the present data cannot be used as such. Indeed, eqn. 8 shows that near the critical pressure the value of δ is reduced, so that the direct application of the data in Table I may easily overestimate the retention behaviour. It is simple to obtain accurately corrected data for the total parameter from residual enthalpies at any desired pressure and temperature. No reliable method, however, is available that will correct partial polarities for pressure changes. The possibility of using a reliable correlation for internal pressures is under investigation. Thus, at present we are forced to restrict ourselves to low-pressure liquid-liquid partition data, at least as far as *a priori* prediction is concerned.

The characterization of stationary phases through partial polarities, demonstrated earlier for GC phases (Table II), can also be applied to LC phases. This is illustrated for chemically bonded phases in Table V, which presents the results of linear regression of retention data using the solute data from Table I. In view of the above-mentioned lack of a suitable pressure correction, this characterization should be regarded as preliminary. Nonetheless, the resulting partial polarities are in the expected

TABLE V

CHARACTERIZATION OF STATIONARY PHASES IN LC (20°C)

Phase	N^*	δ_d	δ_o	δ_a	δ_b	δ_T^{**}	δ_T^{***}
<i>Chemically bonded phases[†]:</i>							
Methoxyphenyl	22	6.46	1.06	0.14	2.57	6.61	6.60
Aminophenyl ^{§§}	26	6.66	0.81	0.18	2.32	6.77	6.77
	12	7.21	1.41	0.19	2.23	7.88	7.40
Triglycine	23	8.27	0.59	0.38	1.20	9.10	8.35
N,N-Dimethylaminophenyl	11	7.60	1.13	0.13	2.04	8.11	7.72
<i>Temperature-treated silicas^{†††}:</i>							
200°C†	7	—	—	—	—	—	—
400°C	9	7.64	2.43	-0.32	5.09	7.37	—
500°C	9	7.52	2.61	-0.61	5.29	6.79	—
600°C	9	7.25	2.48	-0.64	5.29	6.37	—
700°C	9	7.20	2.49	-0.46	4.71	6.55	—
800°C	9	7.13	2.03	-0.30	4.79	6.66	—
900°C	9	7.14	2.01	-0.19	4.61	6.85	—

* Number of solutes used in regression analysis.

** Independent parameter from regression analysis.

*** Obtained by summation of partial parameters (eqn. 16).

† Characterized by active groups.

§§ Different batches.

††† Retention data from Scott and Kucera²⁴.

† Insufficient data available.

ranges. This may be helpful in interpreting the retention mechanism of chemically bonded phases. The results indicate at least some similarity with the bulk liquid partitioning mechanism. Only the orientation parameter is systematically lower than expected. Together with pressure influences, this results in somewhat lower values for the total solubility parameter. However, the tentative conclusion that the chemically bonded phases listed behave as if they were conventionally coated appears to be valid. Again, the consistency of the model is proved by the fair agreement between the total polarity calculated from the partial parameters and that obtained as a separate parameter in the regression analysis (final two columns in Table V).

Table V presents another demonstration of the characterizing capability of the model. The influence of temperature treatment of silica⁵⁴ is quantitatively described by the variation in partial polarities obtained from regression analysis. The observed variation in orientation and base parameters with pre-treatment temperature are possibly to be interpreted in terms of changes in free and bound hydroxyl groups at the silica surface. Obviously, the slightly negative values of the acid parameter can have no physical significance and probably result from the fact that no retention data on acceptor solutes or even strongly interacting bases were available. In view of our present inability to correct for the influence of elevated pressures, it is not surprising that most of our attempts to predict liquid chromatographic retentions failed. As low-pressure data (*e.g.*, TLC) on interesting solutes are scarce, we considered static partition equilibria to test the *a priori* predictions in liquid-liquid systems. A useful source of such data forms the extensive compilation by Leo *et al.*⁴⁰. Besides experimental partition data, Leo *et al.* present a method for deriving partition data in octanol-water from those measured in an arbitrary solvent-water system. We tested the ability of the present model to perform the same task. Representative results with two solvent-water systems are presented in Table VI. It can be seen that the predictions are not better, but within the same magnitude of error as with the Hansch method, using the present data on partial polarities. In our opinion, all large deviations must be attributed either to excessive orientation values or to uncertain acid-base parameters in Table I. Together with pressure and temperature corrections, these parameters require more attention in the future.

TABLE VI

PREDICTION OF PARTITION COEFFICIENTS COMPARED WITH HANSCH METHOD IN LIQUID-LIQUID SYSTEMS

<i>Solute</i>	<i>Solvent</i>	$\log K^*$	$\log K(\text{Oct})^{**}$	$\log P_H(\text{Oct})^{***}$	$\log P(\text{Oct})^\dagger$
Ethanol	CCl ₄	-1.61	0.18	0.47	-0.32
Phenol	CCl ₄	-0.42	1.46	1.55	1.46
Aniline	CCl ₄	0.25	1.83	1.11	0.94
Methanol	CHCl ₃	-1.63	-1.47	-0.66	-0.66
Ethanol	CHCl ₃	-0.85	-0.42	-0.18	-0.32
Phenol	CHCl ₃	0.35	0.97	1.53	1.46
Aniline	CHCl ₃	1.32	1.01	0.90	0.94

* Experimental data in solvent-water.

** Predicted from present model in octanol-water.

*** Predicted by Leo *et al.*⁴⁰ in octanol-water.

† Experimental data in octanol-water.

CONCLUSION

The results of this study show that a four-component solubility parameter model with a sound thermodynamic basis is able, in principle, to describe all of the important molecular interactions that determine retention behaviour. Greatly improved partial polarities already result in reliable *a priori* prediction of GC retention data, both relative and absolute. As the method only uses simple physical constants it is well suited for the practical chromatographer. Valuable use can be made of the method in characterizing phase systems in all kinds of chromatographic or partition methods. This application provides some insight into the partitioning mechanisms of, e.g., chemically bonded phases and temperature treated silicas.

The prediction of retention and partition in liquid-liquid systems is not yet completely satisfactory. In addition to more accurate data on orientation and transfer interactions, a better insight into the influences of pressure and temperature is needed.

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SYMBOLS

a	Van der Waals' constant
C	constant in Drago's equation describing covalent interaction
c	concentration (mole/cm ³)
E	constant in Drago's equation describing electrostatic interaction
h	molar enthalpy
Δh^σ	apparent latent heat (eqn. 8) = $RT^2 \cdot \frac{\partial}{\partial T} (\ln p^\sigma)$
K	$K = c_s/c_m$, partition coefficient
k	capacity factor
K_H	Henry coefficient
M	molecular weight
n	refractive index; number of moles
R	gas constant
T	temperature (°K)
T_R	reduced temperature, T/T_c
p	pressure
p_i	internal pressure
p_R	reduced pressure, p/p_c
u	molar energy
V	volume (cm ³)

v	molar volume (cm^3/mole)
V_R	retention volume (cm^3)
x_i	mole fraction, $n_i/\Sigma n_i$
Z	compressibility factor, pV/RT
α	relative retention; $\alpha_{2,1} = k_2/k_1$
α_p	isobaric thermal expansion, $\frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p$
β_T	isothermal compressibility, $-\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T$
γ	activity coefficient
γ_v	isochoric thermal pressure coefficient, $\left(\frac{\partial p}{\partial T} \right)_v$
Δ	difference of states (final — original)
δ	solubility parameter, $\left(\frac{-u}{v} \right)^{\frac{1}{2}}$ [$(\text{cal}/\text{cm}^3)^{\frac{1}{2}}$]
δ_R	residual solubility parameter
δ_v	solubility parameter based on internal pressure, ($\delta_v^2 = p_i$)
ϵ	dielectric constant
μ	(partial) free molar enthalpy thermodynamic potential; dipole moment in eqn. 21 (D)
ρ	density (g/cm^3)
ω	acentric factor (Pitzer)

Superscripts

s	stationary phase; entropy
m	mobile phase; mixing
h	enthalpy
σ	saturated liquid or gas
e	excess
v	vaporization
g	gas
l	liquid
o	ideal gas state or standard state

Subscripts

i	compound of interest
s	stationary phase
m	mobile phase
j	stationary or mobile phase
g	gas
c	critical
v	volume

<i>p</i>	pressure; polar
<i>T</i>	temperature; total
<i>a</i>	acid
<i>b</i>	base
<i>H</i>	Hansen
<i>h</i>	acid-base phenomenon
<i>d</i>	dispersion
<i>o</i>	orientation

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