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APPLICATION OF A UNIFIED MOLECULAR THEORY TO GAS–LIQUID CHROMATOGRAPHY

DANIEL E. MARTIRE

Department of Chemistry, Georgetown University, Washington, DC 20057 (U.S.A.)

SUMMARY

A novel, unified molecular theory of chromatography is applied to derive equations for gas–liquid chromatography (GLC) and to treat representative GLC problems involving the interpretation and prediction of absolute retention (partition coefficients), the effect of the molecular weight of the stationary liquid phase on relative retention, and the isolation and quantitation of functional-group (energetic) contributions to retention. The utility and efficacy of this new theoretical approach to GLC are thereby demonstrated.

INTRODUCTION

A unified molecular theory of fluid–liquid (absorption) chromatography, encompassing gas, liquid and supercritical-fluid mobile phases, has recently been developed¹. This comprehensive theory, which is based on a lattice-fluid (or Ising-fluid) model and statistical thermodynamics is applied in the present paper to treat more rigorously several representative problems in gas–liquid chromatography (GLC) with a single-component stationary liquid phase (solvent): (1) the interpretation and prediction of absolute retention for simple, alkane solute plus alkane solvent systems; (2) the effect of the molecular weight (or chain length) of the solvent on solute relative retention and, cognately, the use of GLC for the determination of solvent molecular weight; (3) the isolation and quantitative assessment of functional-group (energetic) contributions to solute retention. The following derivations and analyses are intended to be indicative rather than exhaustive.

THEORY

In the lattice-fluid model^{1,2}, expansion (compression) effects, configurational entropy, and attractive and repulsive interactions are rigorously taken into account using the Bragg–Williams (random-mixing) approximation. In this model a molecule of component i is taken to consist of r_i segments, where r_i is proportional to the hard-core or van der Waals volume of the molecule. The attractive interaction energy between nearest-neighbor segments on molecules i and j is designated by ϵ_{ij} , where, adopting the Sanchez–Lacombe (SL) convention² here, $\epsilon_{ij} > 0$. Also, for a given pure

component ($j = i$), the segmental pair interaction energy, ε_{ii} , is related to the SL reduced temperature of that component, \tilde{T}_i , by^{1,2}

$$z\varepsilon_{ii}/2k_B T = \tilde{T}_i^{-1} = T_i^*/T \quad (1)$$

where z is the coordination number of the lattice, k_B is the Boltzmann constant, T is the absolute temperature, and T_i^* , the characteristic temperature of component i (a scale parameter, not to be confused with the critical temperature), is proportional to ε_{ii} . Similarly, the SL reduced density of pure component i , $\tilde{\rho}_i$, is related to the experimental, pure-component density, ρ_i^o , by^{1,2}

$$\tilde{\rho}_i = \rho_i^o/\rho_i^* = \theta_i^o \quad (2)$$

where ρ_i^* is the characteristic density of component i (the close-packed density; another scale parameter, not to be confused with the critical density) and θ_i^o is the occupied volume fraction of pure i .

In the following treatment, the subscripts a, b, c and d denote, respectively, solute molecules containing other functional groups in addition to paraffinic ones (a = "active" solute), paraffinic solute molecules (b = "reference" solute), solvent molecules containing other functional groups in addition to paraffinic ones (c = "active" solvent), and paraffinic solvent molecules (d = "reference" solvent). Eqn. 39 (or 40) in ref. 1 describes the distribution constant (partition coefficient), K , for ideal GLC (strictly, the value obtained by extrapolation to zero column pressure). Substituting $\tilde{\rho}_i$ for θ_i^o and using the convention $\varepsilon_{ij} > 0$ [rather than $\varepsilon_{ij} < 0$ (ref. 1)], the equation for the reference system (solute b + solvent d) becomes

$$\ln K_{b(d)} = r_b[(z\varepsilon_{bd}/k_B T)\tilde{\rho}_d - (z\varepsilon_{dd}/2k_B T)\tilde{\rho}_d^2 - (1 - r_d^{-1})\tilde{\rho}_d] \quad (3)$$

It sensibly predicts that K , hence the specific retention volume, will increase with increasing r_b , increasing ε_{bd} and decreasing ε_{dd} , and clearly shows that K depends on both T and $\tilde{\rho}_d$, where the latter governs the average distance between molecules (and non-bonded molecular segments) in the stationary phase. Note that the last term, $-r_b(1 - r_d^{-1})\tilde{\rho}_d$, is the configuration entropy contribution to $\ln K$.

Introducing eqn. 1 into eqn. 3, one obtains an expression in terms of the reduced variables of the solvent component:

$$\ln K_{b(d)} = r_b[2(\varepsilon_{bd}/\varepsilon_{dd})(\tilde{\rho}_d/\tilde{T}_d) - (\tilde{\rho}_d^2/\tilde{T}_d) - (1 - r_d^{-1})\tilde{\rho}_d] \quad (4)$$

Allowing for a deviation from the geometric-mean approximation for ε_{bd} , one has

$$\varepsilon_{bd} \approx (\varepsilon_{bb}\varepsilon_{dd})^{1/2}(1 + \eta_{bd}) \quad (5)$$

where η_{bd} , which reflects the deviation, is expected to be small with respect to unity. Substituting eqns. 1 and 5 into eqn. 4, one obtains

$$\ln K_{b(d)} = r_b[(2/\tilde{T}_b^{1/2})(1 + \eta_{bd})(\tilde{\rho}_d/\tilde{T}_d^{1/2}) - (\tilde{\rho}_d^2/\tilde{T}_d) - (1 - r_d^{-1})\tilde{\rho}_d] \quad (6)$$

which may be written as follows:

$$\ln K_{b(d)} = r_b \{ A [(1 + \eta_{bd}) / \tilde{T}_b^{1/2}] - B \} \quad (7)$$

where

$$A = (2\rho_d / \tilde{T}_d^{1/2}) \quad (8)$$

$$B = (\tilde{\rho}_d^2 / \tilde{T}_d) + (1 - r_d^{-1}) (\tilde{\rho}_d) \quad (9)$$

Note that A and B depend only on properties of the pure solvent. Therefore, if the molecular-size parameters r_b and r_d , and the reduced variables $\tilde{\rho}_d$, \tilde{T}_d and \tilde{T}_b are known, and the binary molecular parameter η_{bd} can be determined, then it should be possible to utilize eqn. 6 (or eqns. 7–9) for the prediction of absolute partition coefficients of alkane solutes in alkane solvents. The feasibility of this approach will be investigated in the next section.

It follows from eqn. 4 that, for the system (solute a + solvent d), one can write

$$\ln K_{a(d)} = r_a [2(\varepsilon_{ad}/\varepsilon_{dd}) (\tilde{\rho}_d / \tilde{T}_d) - (\tilde{\rho}_d^2 / \tilde{T}_d) - (1 - r_d^{-1}) \tilde{\rho}_d] \quad (10)$$

If one now chooses a and b such that $r_a \approx r_b$ (*vide infra*), then eqns. 4 and 10 give

$$\ln [K_{a(d)} / K_{b(d)}] = \ln R_{(a/b)(d)} \approx 2r_b [(\varepsilon_{ad}/\varepsilon_{dd}) - (\varepsilon_{bd}/\varepsilon_{dd})] [\tilde{\rho}_d / \tilde{T}_d] \quad (11)$$

where $R_{(a/b)(d)}$ is the relative retention of solutes a and b in solvent d. Note that eqn. 11 predicts that R will increase with increasing r_b , increasing ε_{ad} , decreasing ε_{bd} , increasing $\tilde{\rho}_d$ and decreasing \tilde{T}_d . Also, a modified geometric-mean expression, similar to eqn. 5, can be written for ε_{ad} :

$$\varepsilon_{ad} \approx (\varepsilon_{aa}\varepsilon_{dd})^{1/2} (1 + \eta_{ad}) \quad (12)$$

Applying eqns. 1, 5 and 12 to eqn. 11 yields

$$\ln R_{(a/b)(d)} \approx 2r_b \{ [(1 + \eta_{ad}) / \tilde{T}_a^{1/2}] - [(1 + \eta_{bd}) / \tilde{T}_b^{1/2}] \} (\tilde{\rho}_d / \tilde{T}_d^{1/2}) \quad (13)$$

Eqn. 13 describes, in terms of the reduced temperatures of the pure components, the reduced density of the solvent component and three molecular parameters, r_b , η_{ad} and η_{bd} , the relative retention of an "active" solute and a "reference" solute in a given "reference" solvent. It will be applied in the next section to examine the dependence of this relative retention on the molecular weight (or chain length) of n -alkane solvents.

From eqns. 1 and 11:

$$\ln R_{(a/b)(d)} \approx r_a (z/k_B T) (\varepsilon_{ad} - \varepsilon_{bd}) (\tilde{\rho}_d) \quad (14)$$

where r_b has now been replaced by r_a ($\approx r_b$). Similarly, the relative retention of solutes a and b in an "active" solvent (c), $R_{(a/b)(c)}$, is given by

$$\ln R_{(a/b)(c)} \approx r_a(z/k_B T)(\varepsilon_{ac} - \varepsilon_{bc})(\tilde{\rho}_c) \quad (15)$$

If one chooses solvents c and d such that $\tilde{\rho}_c \approx \tilde{\rho}_d$ [solvents having comparable chain lengths ($r_c \approx r_d$) and expansion coefficients^{1,2}], then subtracting eqn. 14 from eqn. 15 yields

$$\ln[R_{(a/b)(c)}/R_{(a/b)(d)}] = \ln Q \approx r_a(z/k_B T)(\varepsilon_{ac} - \varepsilon_{bc} - \varepsilon_{ad} + \varepsilon_{bd})(\tilde{\rho}_d) \quad (16)$$

where Q is the ratio of two relative retention quantities.

Recalling the nature of molecules a, b, c and d, and assuming that the "active" solute molecules (a) consist of type-p (paraffinic) and type-x chemical groups and the "active" solvent molecules (c) consist of type-p and type-y chemical groups, while the "reference" molecules (b and d) consist only of type-p groups, the ε_{ij} values in eqn. 16 may be decomposed as follows^{3,4}:

$$\varepsilon_{bd} = \varepsilon_{pp} \quad (17a)$$

$$\varepsilon_{ad} = f_{ap}\varepsilon_{pp} + f_{ax}\varepsilon_{px} \quad (17b)$$

$$\varepsilon_{bc} = f_{cp}\varepsilon_{pp} + f_{cy}\varepsilon_{py} \quad (17c)$$

$$\varepsilon_{ac} = f_{ap}f_{cp}\varepsilon_{pp} + f_{ap}f_{cy}\varepsilon_{py} + f_{ax}f_{cp}\varepsilon_{px} + f_{ax}f_{cy}\varepsilon_{xy} \quad (17d)$$

where ε_{kl} ($k, l = p, x, y$) now denotes the attractive interaction energy, per unit segment, between type- k and type- l moieties on adjacent molecules, and f_{jk} ($j = a, b, c, d$; $k = p, x, y$) denotes the fraction of a molecule of type- j that contains type- k functional groups. Note that the number of segments on molecule j containing type- k moieties, r_{jk} , is related to f_{jk} by

$$r_{jk} = f_{jk}r_j \quad (18a)$$

$$\sum_k r_{jk} = \sum_k f_{jk}r_j = r_j \quad (18b)$$

where $f_{ap} + f_{ax} = 1$, $f_{cp} + f_{cy} = 1$, $f_{bp} = 1$ and $f_{dp} = 1$.

Use of eqns. 17 and 28 in eqn. 16 leads to, after much algebra

$$\ln[R_{(a/b)(c)}/R_{(a/b)(d)}] = \ln Q_{xy} \approx (\tilde{\rho}_d)(r_a f_{ax} f_{cy})(z/k_B T)(\varepsilon_{xy} - \varepsilon_{py} - \varepsilon_{px} + \varepsilon_{pp}) \quad (19)$$

Since $r_a f_{ax} = r_{ax}$ and $f_{cy} = r_{cy}/r_c \approx r_{cy}/r_d$ (eqn. 18), then eqn. 19 may be written as

$$\ln Q_{xy} \approx (\tilde{\rho}_d)(r_x r_y / r_d)(z/k_B T)(\Delta w_{xy} - \Delta w_{px} - \Delta w_{py}) \quad (20)$$

where the first subscript on r_{ax} and r_{cy} has become unnecessary and been deleted, and

$$\Delta w_{kl} = \varepsilon_{kl} - (\varepsilon_{kk} + \varepsilon_{ll})/2 \quad (21)$$

where Δw_{kl} is the interchange energy for the formation of a k - l pair interaction¹. Inspection of eqn. 20 reveals that, provided $r_a \approx r_b$, $r_c \approx r_d$ and $\tilde{\rho}_c \approx \tilde{\rho}_d$, Q should have the same value whether type- x groups are located on solute a and type- y groups on solvent c , or *vice versa*; that is, Q should exhibit solute-solvent invariance ($Q_{xy} \approx Q_{yx}$). Therefore, writing eqn. 22 in terms of interaction parameters¹, χ_{kl} , one obtains

$$\ln Q_{xy} \approx \ln Q_{yx} \approx (\tilde{\rho}_d)(r_x r_y / r_d)(\chi_{px} + \chi_{py} - \chi_{xy}) \quad (22)$$

where

$$\chi_{kl} = -(z/k_B T)\Delta w_{kl} \quad (23)$$

To continue, if the "active" solute (a) and solvent (c) molecules have common functionality ($y = x$ or $x = y$), then $\chi_{px} = \chi_{py}$ and $\chi_{xy} = 0$ (ref. 3) and from eqn. 24

$$\ln Q_{xx} \approx (\tilde{\rho}_d)(r_x^2 / r_d)(2\chi_{px}) \quad (24)$$

$$\ln Q_{yy} \approx (\tilde{\rho}_d)(r_y^2 / r_d)(2\chi_{py}) \quad (25)$$

Eqns. 24 and 25 thus permit the characterization of px and py interactions. Substituting these equations into eqn. 22 gives

$$\ln Q_{xy} \approx \ln Q_{yx} \approx (r_y / 2r_x) \ln Q_{xx} + (r_x / 2r_y) \ln Q_{yy} - (\tilde{\rho}_d)(r_x r_y / r_d) \chi_{xy} \quad (26)$$

which permits the characterization of xy interactions and the testing of solute-solvent invariance.

Eqns. 24-26 will be applied in the next section to isolate and quantify functional group contributions to solute retention. It is important to note that products such as $(r_x r_y / r_d) \chi_{xy}$ regularly appear in theoretical (lattice-model) expressions for solute activity coefficients, absolute and relative partition coefficients in gas and liquid chromatography, as well as hydrocarbon-water bulk partition coefficients^{3,4}. Also, an additional novel feature of the theory presented above is the emergence of the factor $\tilde{\rho}_d$ in the various equations (*e.g.*, eqns. 11 and 13, and eqns. 24-26). This factor, which does not appear in earlier (incompressible) lattice-model results, explicitly accounts for the effect of the degree of expansion (or free volume) of the stationary liquid on solute retention.

APPLICATIONS

We start by considering the application of eqn. 6 (or eqns. 7-9) to the interpretation and prediction of absolute retention [$K_{b(d)}$] for relatively simple alkane solute (b) + n -alkane solvent (d) systems. As will become evident, the first term in this equation (retention-enhancing contribution from solute-solvent interactions) is comparable in magnitude to, but greater than, the sum of the second and third terms (retention-diminishing contributions from solvent-solvent interactions and configurational entropy, respectively) for the systems in question.

The initial test systems are six alkane solutes in n -C₂₄H₅₀ at 80.0°C. Listed in Table I are the r_b and \tilde{T}_b values of the solutes (from the Sanchez-Lacombe tabulation²)

TABLE I

ANALYSIS OF PARTITION COEFFICIENTS, $K_{b(d)}$, OF ALKANE SOLUTES (b) IN n -C₂₄H₅₀ (d) AT 80.0°C

Solute	r_b^a	\tilde{T}_b^a	$K_{b(d)}$ (experimental) ^b	$K_{b(d)}$ (calculated) ^c
<i>n</i> -Hexane	8.37	0.7416	61.9	61.5
<i>n</i> -Heptane	9.57	0.7248	146.6	148.2
<i>n</i> -Octane	10.34	0.7032	339.1	336.2
<i>n</i> -Nonane	11.06	0.6828	783.0	783.2
2,2-Dimethylbutane	8.10	0.7759	35.9	35.7
2,3-Dimethylbutane	8.29	0.7624	46.5	46.8

^a From ref. 2.^b From ref. 5.^c Calculated from eqn. 30, with $\eta_{bd} = -0.020$ for the normal alkane solutes and $\eta_{bd} = -0.017$ for the branched alkane solutes.

and the GLC partition coefficients⁵. The scale parameters (ρ_d^* and T_d^*) needed to evaluate $\tilde{\rho}_d/\tilde{T}_d^{1/2}$ (hence, $\tilde{\rho}_d^2/\tilde{T}_d$) are not directly available for n -C₂₄H₅₀. However, since T^* and ρ^* values have been tabulated for n -C₆H₁₄ through n -C₁₄H₃₀ (ref. 2), $\tilde{\rho}_d/\tilde{T}_d^{1/2}$ was determined as a function of n -alkane molecular weight, M_d , by fitting this available data to the form

$$\tilde{\rho}_d/\tilde{T}_d^{1/2} = C - [D/(M_d + E)] \quad (27)$$

The optimum correlation coefficient (0.9990) is obtained with the assignment $E = 121.4$, giving $C = 1.3477$ and $D = 91.628$:

$$\tilde{\rho}_d/\tilde{T}_d^{1/2} = 1.3477 - [91.628/(M_d + 121.4)] \quad (28)$$

By extrapolation to $M_d = 338.6$, eqn. 28 gives $\tilde{\rho}_d/\tilde{T}_d^{1/2} = 1.1485$ and $\tilde{\rho}_d^2/\tilde{T}_d = 1.3191$ for n -C₂₄H₅₀ at 80°C. Similarly, the value of $(1 - r_d^{-1})\tilde{\rho}_d$ is obtained by fitting available data² for the n -alkanes as a function of M_d^{-1} and then extrapolating to $M_d = 338.6$:

$$(1 - r_d^{-1})\tilde{\rho}_d = 0.8422 - (13.290/M_d) \quad (29)$$

with a correlation coefficient of 0.9997, giving $(1 - r_d^{-1})\tilde{\rho}_d = 0.8030$ for n -C₂₄H₅₀ at 80°C.

Accordingly, from eqns. 7-9 we have $A = 2.2970$, $B = 2.1221$ and

$$\ln K_{b(d)} = r_b \{ [2.2970(1 + \eta_{bd})/\tilde{T}_b^{1/2}] - 2.1221 \} \quad (30)$$

Using eqn. 30, the best fit to the experimental $K_{b(d)}$ values is found by letting $\eta_{bd} = -0.020$ for the normal alkane solutes and $\eta_{bd} = -0.017$ for the branched alkane solutes, indicating slight negative deviations from the geometric-mean

TABLE II

PREDICTION OF PARTITION COEFFICIENTS, $K_{b(d)}$, OF ALKANE SOLUTES IN n -C₃₀H₆₂ AND n -C₃₆H₇₄ AT 80.0°C

Solute	n -C ₃₀ H ₆₂		n -C ₃₆ H ₇₄	
	Experimental ^a	Predicted ^b	Experimental ^a	Predicted ^b
n -Hexane	57.0	56.7	52.8	53.2
n -Heptane	134.7	136.2	125.3	127.3
n -Octane	317.5	310.2	289.6	290.8
n -Nonane	728.2	727.2	684.8	684.5
2,2-Dimethylbutane	32.9	32.7	30.6	30.5
2,3-Dimethylbutane	43.2	43.1	39.9	40.2

^a From ref. 5.^b Calculated from eqns. 31 and 32, respectively, with $\eta_{bd} = -0.020$ for the normal alkane solutes and $\eta_{bd} = -0.017$ for the branched alkane solutes, and using the r_b and \tilde{T}_b values from Table I.

approximation for ε_{bd} . The goodness of this fit is seen in Table I, where where the average difference between the experimental and calculated $K_{b(d)}$ values is only 0.6%.

As a preliminary test of the predictive ability of this approach, the same procedure as that leading to eqn. 30 is applied to n -C₃₀H₆₂ and n -C₃₆H₇₄ at 80°C. From eqns. 7–9, 28 and 29, one obtains for the two respective solvents

$$\ln K_{b(d)} = r_b \{ [2.3587(1 + \eta_{bd}) / \tilde{T}_b^{1/2}] - 2.2016 \} \quad (31)$$

$$\ln K_{b(d)} = r_b \{ [2.4038(1 + \eta_{bd}) / \tilde{T}_b^{1/2}] - 2.2606 \} \quad (32)$$

Shown in Table II is a comparison of the experimental and predicted $K_{b(d)}$ values for the same set of solutes. The average difference between the two is less than 0.8%.

Let us now apply eqn. 13 to the analysis of the partition coefficient of chlorobenzene (a) relative to n -hexane (b) in the three n -alkane solvents. Listed in Table III are the $R_{(a/b)(d)}$ values of the solute pair⁵ and the M_d values of the solvents.

TABLE III

ANALYSIS OF PARTITION COEFFICIENTS OF CHLOROBENZENE (a) RELATIVE TO NORMAL HEXANE (b), $R_{(a/b)(d)}$, IN NORMAL ALKANE SOLVENTS AT 80.0°C

Solvent	$R_{(a/b)(d)}$ ^a	$R_{(a/b)(d)}$ (calculated) ^b	M_d ^c	M_d (calculated) ^d
n -C ₂₄ H ₅₀	6.531	6.526	338.6	339.7
n -C ₃₀ H ₆₂	6.850	6.863	422.8	419.1
n -C ₃₆ H ₇₄	7.128	7.120	507.0	509.8

^a Experimental data from ref. 5.^b Calculated using actual M_d values and eqns. 33 and 34, with $\eta_{ad} = -0.040$.^c Molecular weight (g/mol).^d Calculated from experimental $R_{(a/b)(d)}$ values and eqns. 33 and 34, with $\eta_{ad} = -0.040$.

For the solutes, $r_a = 8.38$ (ref. 2) and $r_b = 8.37$, thus clearly satisfying the condition $r_a \approx r_b$. Also, $\tilde{T}_a = 0.6034$ (ref. 2), $\tilde{T}_b = 0.7416$, $\eta_{bd} = -0.020$ and $\tilde{\rho}_d/\tilde{T}_d^{1/2}$ is given by eqn. 28, leaving η_{ad} as the only unknown. (Here, both η_{ad} and η_{bd} are assumed to be independent of M_d .)

It follows from eqns. 13 and 28 that $R_{(a/b)(d)}$ must have the form

$$\ln R_{(a/b)(d)} = F\{1.3477 - [91.628/(M_d + 121.3)]\} \quad (33)$$

where

$$F = 2.4998 + 21.5494\eta_{ad} \quad (34)$$

The determination of η_{ad} is therefore accomplished by finding the F value that best satisfies eqn. 33. (The goodness of the fit is evident from comparison of the second and third columns in Table III). From the result ($F = 1.6332$) and eqn. 34 one calculates $\eta_{ad} = -0.040$, indicating a small, but more negative (compared to η_{bd}), deviation from the geometric-mean approximation for ε_{ad} . Additional physical insight is obtained by noting that the dependence of $R_{(a/b)(d)}$ on M_d stems solely from $\tilde{\rho}_d/\tilde{T}_d^{1/2}$, *i.e.*, the increase in $R_{(a/b)(d)}$ with increasing M_d at fixed T (Table III) is primarily due to the increase in $\tilde{\rho}_d$ (decrease in the molar free volume and the average distance between molecular segments) with increasing M_d .

In addition to its predictive and interpretive aspects, the utility of this approach is that once the solute pair and solvent series have been characterized, eqns. 33 and 34 can then be employed to determine M_d for any solvent in the series by measuring $R_{(a/b)(d)}$ in that solvent⁶. The precision of such a determination of M_d for high-molecular-weight *n*-alkanes (and, presumably, the number average M_d for linear polyethylenes) may be estimated by subjecting eqn. 33 to a propagation-of-errors analysis⁶, yielding

$$(\sigma_{M_d}/M_d) = [(M_d + 121.4)^2/91.628M_d](\sigma_R/R) \quad (35)$$

where σ_{M_d}/M_d and σ_R/R are the fractional errors in M_d and $R_{(a/b)(d)}$, respectively. With an estimate of $\sigma_R/R = 0.001$ (ref. 6), eqn. 35 gives the following per cent errors in M_d : $M_d = 500$ (0.5%; see Table III), $M_d = 5000$ (3.5%), $M_d = 10\,000$ (6.8%) and $M_d = 20\,000$ (13.5%). Therefore, the per cent error increases with increasing M_d , but remains tolerable ($< 10\%$) for M_d values up to *ca.* $1.5 \cdot 10^4$. Based on the form of eqn. 13, it is anticipated that an equation having the same general form as eqn. 33 should apply to other solvent series, including polymeric ones.

Finally, we give an example of the application of Eqns. 24–26 to isolate and quantify functional-group energetics, as measured by $\tilde{\rho}_d(r_k r_l / r_d) \chi_{ml}$, where $k, l = x, y$ and $m = p$ ($k = l$) or $m = k$ ($k \neq l$). Listed in Table IV are the *n*-alkyl chloride (a or c) and di-*n*-alkyl thioether (a or c) systems under consideration and the experimental values of $\ln Q_{kl}$ at 40.0°C (ref. 7). The reference solute (b) and solvent (d) are *n*-C₇H₁₆ and *n*-C₁₇H₃₆, respectively. From Bondi's tabulation of group van der Waals volumes⁸ it is seen that $r_S \approx r_{Cl} \approx r_{CH_2}$. Therefore, $r_k \approx r_l$, $r_a \approx r_b$ and $r_c \approx r_d$, as required. Also, from density measurements on the active and reference solvents it is found that $\tilde{\rho}_c \approx \tilde{\rho}_d$ (ref. 7). Accordingly, the conditions leading to the derivation of eqns. 24–26 are satisfied.

TABLE IV
ANALYSIS OF FUNCTIONAL GROUP ENERGETICS AT 40.0°C

Solute (a)–solvent (c) ^a	<i>k</i>	<i>l</i>	<i>m</i>	$\ln Q_{kl}^b$	$\bar{\rho}_d(r_x r_l / r_d) \chi_{ml}$
Di- <i>n</i> -propyl thioether–di- <i>n</i> -octyl thioether	x	x	p	0.350	0.175 ^c
<i>n</i> -Hexyl chloride– <i>n</i> -hexadecyl chloride	y	y	p	0.386	0.193 ^d
Di- <i>n</i> -propyl thioether– <i>n</i> -hexadecyl chloride	x	y	x	0.384	–0.016 ^e
<i>n</i> -Hexyl chloride–di- <i>n</i> -octyl thioether	y	x	y	0.386	–0.018 ^e

^a Reference solute (b): *n*-C₇H₁₆; reference solvent (d): *n*-C₁₇H₃₆.

^b Experimental data from ref. 7.

^c Calculated from eqn. 24.

^d Calculated from eqn. 25.

^e Calculated from eqn. 26, with $r_x \approx r_y$.

As is evident from the results in the last column of Table IV, paraffin–sulfur (px), paraffin–chloride (py), sulfur–chloride (xy) and chloride–sulfur (yx) energetics can be readily characterized, and solute–solvent invariance is confirmed ($\chi_{xy} \approx \chi_{yx}$). The unfavourable energetics associated with the paraffin segment–“active” segment interchange process (eqn. 23, with $k = p$ and $l = x$ or y) leads to the expected positive values of χ_{px} and χ_{py} . However, the energetics of the S + Cl pairing is nearly ideal [$\bar{\rho}_d(r_x r_y / r_d) \chi_{xy} \approx -0.017$]. An estimate of the absolute value of χ_{xy} may be obtained by using Bondi's data⁸ (from which, $r_x r_y / r_d \approx 0.693$) and the Sanchez–Lacombe tabulation² (from which, $\bar{\rho}_d \approx 0.868$), giving $\chi_{xy} \approx -0.028$. Similar estimates yield $\chi_{px} \approx 0.313$ ($x = S$) and $\chi_{py} \approx 0.299$ ($y = Cl$). In the same manner the energetics of other functional groups can be quantified.

CONCLUSIONS

As mentioned at the outset, the derivations and analyses presented above were meant to be representative rather than exhaustive. Certainly, additional and more complex chemical systems need to be evaluated, and the dependence of retention on the reduced temperature and reduced density of the stationary liquid phase needs to be more thoroughly studied. Nevertheless, the utility, efficacy and promise of this new theoretical approach have been demonstrated.

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