Journal of Chromatography, 387 (1987) 85–93
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 057

THERMODYNAMICS OF SOLUTION OF HALOGENATED HYDROCARBONS IN MIXTURES OF TRI-*n*-OCTYLPHOSPHINE OXIDE AND SQUALANE USING GAS–LIQUID CHROMATOGRAPHY

A. M. NARDILLO, R. C. CASTELLS* and E. L. ARANCIBIA
CIDEPINT, 52 entre 121 y 122, 1900 La Plata (Argentina) and Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata (Argentina)

(Received August 6th, 1986)

SUMMARY

The retention behaviours of ten halogenated and five saturated hydrocarbons were measured in stationary phases consisting of pure squalane (SQ), pure tri-*n*-octylphosphine oxide (TOPO) and seven mixtures of SQ and TOPO, at four temperatures within the range 55–65.5°C. Equilibrium constants and standard enthalpies for complex formation were extracted from the data using a lattice model developed by Martire (D. E. Martire, *J. Phys. Chem.*, 87 (1983) 2425). The interactions of the solutes with TOPO are of a relatively strong type and, with the exception of trichlorobromomethane, the effects of other-end interactions can be neglected.

INTRODUCTION

We have previously studied[1] the molecular interactions between halogenated hydrocarbons and tri-*n*-octylphosphine oxide (TOPO) by a modification of the two-column gas chromatographic (GC) method of Martire and Riedl[2]. The association constants measured were markedly larger than those determined by Martire and co-workers[3,4] for the same solutes with ethers, thioethers and tertiary amines. The interaction mechanisms operating in these systems have not been fully identified, and the observed trends in retention behaviour and in the association constants cannot be explained exclusively on the basis of the solute's hydrogen-bonding propensities; charge-transfer n → σ^* interactions between the n-donor and the halogen atoms and classical electrostatic interactions may constitute important alternative or simultaneous mechanisms. This is especially true in the case of TOPO, since trilkylphosphine oxides are not only very strong electron donors but also display very high dipole moments, about 4.5 D[5]. The interactions between TOPO and solutes with none or very remote possibilities of hydrogen bonding, *e.g.*, carbon tetrachloride and bromotrichloromethane, were by no means negligible, although much weaker than those observed for the haloforms.

A model designed to cover a broad range of interactions, from very strong to very weak, was proposed by Martire[6]. The rôle of the inert solvent as of a second

0021-9673/87/$03.50 © 1987 Elsevier Science Publishers B.V.

and weaker solute–additive interaction are explicitly taken into account. The study of the TOPO + halogenated hydrocarbon systems by means of this model was interesting for several reasons: (1) the previous results[1] indicated large differences in association constants; (2) the possibility of discriminating between different, simultaneous interaction mechanisms; (3) the ability to compare results obtained through quite different theoretical and experimental approaches.

Scott's[7] quasi-chemical calculations for a lattice of monomeric donor, acceptor and inert solvent molecules were extended by Martire by allowing the molecules to be heterogeneous and different in size. The solute (a), inert solvent (b) and additive solvent (c) molecules contain r_a, r_b and r_c segments, respectively. The solute molecules have a fraction, f_{1a}, of the type 1 segments and a fraction, f_{2a}, of segments of type 2; only paraffinic segments (type 3) constitute the inert solvent molecule. The additive solvent molecules have a fraction, f_{3c}, of segments of type 3 and a fraction, f_{4c}, of segments of type 4. The exchange energy for the formation of an pair ij from the pairs $i3$ and $j3$ is defined as

$$\Delta W_{ij} = \Delta\omega_{ij} - \Delta\omega_{i3} - \Delta\omega_{j3} \tag{1}$$

where $\Delta\omega_{mn} = \omega_{mn} - 1/2(\omega_{mm} + \omega_{nn})$ is the usual interchange energy. The only strong interaction is that between segments of type 2 in the solute and of type 4 in the additive solvent. In the limit of infinite dilution of the solute, the conventional counting of segment pairs and the quasi-chemical approximation (with the restriction $|\Delta W_{ij}| \ll kT$, except for the pair 24) lead to the following expression for the thermodynamic solute–additive association constant

$$K_{ac} = f_{4c} V_c^0 \kappa \tag{2}$$

where V_c^0 is the molar volume of additive c and $\kappa = \exp(-\Delta W_{24}/kT)$. The equilibrium constant for a totally random mixture, K_{ac}^T, is obtained by making $\kappa = 1$; hence, the excess or "sociation" constant[8], K_{ac}^e, is given by

$$K_{ac}^e = K_{ac} - K_{ac}^T = f_{4c} V_c^0(\kappa - 1) \tag{3}$$

and represents a measure of the degree of association in excess over that wich would be formed in a random mixture.

The infinite-dilution partial molar excess Gibbs free energy of the solute is considered to be the sum of a combinatorial (or "geometrical") and an energetic contribution; the former is expressed in terms of the well-known Flory–Huggins equation[9,10], while the latter is approximated by the partial molar excess configurational energy, this in turn being computed from the contributions of each segment pair type. The expression obtained for the relationship between the infinite-dilution vapour–liquid partition coefficient of the solute in a mixture (m) of an inert solvent and an additive to that in the pure inert solvent (b) is

$$\begin{aligned}\ln[K_{a(m)}^0/K_{a(b)}^0] = {} & r_a(r_c^{-1} - r_b^{-1})\varphi_c - zr_a f_{1a}(\varphi_c f_{4c})(\Delta W_{14}/kT) + \\ & + zr_a f_{2a} \ln[1 + (K_{ac}^e \varphi_c)/V_c^0] - zr_a(\varphi_c f_{4c})^2(\Delta\omega_{34}/kT)\end{aligned} \tag{4}$$

where z is the lattice coordination number and φ_c is the volume fraction of the additive in the mixture. For a paraffinic solute (p), eqn. 4 gives:

$$\ln [K^0_{p(m)}/K^0_{p(b)}] = r_p(r_c^{-1} - r_b^{-1})\varphi_c - zr_p(\varphi_c f_{4c})^2(\Delta\omega_{34}/kT) \quad (5)$$

Subtracting eqn. 5 from eqn. 4 gives

$$Q + \varepsilon = -zr_a f_{1a}(\varphi_c f_{4c})(\Delta W_{14}/kT) + zr_a f_{2a} \ln[1 + (K^e_{ac}\varphi_c/V^0_c)] \quad (6)$$

where

$$Q \equiv \ln[K^0_{a(m)}/K^0_{p(m)})/(K^0_{a(b)}/K^0_{p(b)})] \quad (7)$$

and

$$\varepsilon \equiv (r_p - r_a)(r_c^{-1} - r_b^{-1})\varphi_c - z(r_p - r_a)(\varphi_c f_{4c})^2(\Delta\omega_{34}/kT) \quad (8)$$

An important point about eqn. 6 is that only relative retention times need to be measured to calculate Q. The methods to measure ε (which becomes zero when the solute of interest and the reference solute have very nearly equal molar volumes) will be considered in the Discussion.

When only one of the zr_a contacts made by the solute molecule results in a strong interaction, the assignments $zr_a f_{2a} = 1$ and $zr_a f_{1a} = zr_a - 1$ may be made in eqn. 6. Further, when retention data are obtained at several temperatures it is possible to introduce in eqn. 6 the expression for K^e_{ac} resulting from eqn. 3 and from the definition of κ, yielding

$$Q + \varepsilon = (A\varphi_c/T) + \ln\{1 + f_{4c}[\exp(C/T) - 1]\varphi_c\} \quad (9)$$

with $A = -(zr_a - 1)f_{4c}(\Delta W_{14}/k)$ and $C = -\Delta W_{24}/\mathrm{k}$.The values of A and C may be obtained by a non-linear fit to the $Q + \varepsilon$ data corresponding to a range of temperature and stationary phase compositions. The excess association constant at a given temperatures can be calculated from isothermal data by means of eqn. 6, or from data obtained at several temperatures by use of:

$$K^e_{ac} = f_{4c}V^0_c[\exp(C/T) - 1] \quad (10)$$

The standard enthaply, ΔH^e_{ac}, and entropy, ΔS^e_{ac}, of excess complex formation are computed with eqn. 11 and 12

$$\Delta H^e_{ac} = -R[\mathrm{d}(\ln K^e_{ac})/\mathrm{d}(1/T)] = R\left[\alpha T^2 - \frac{C}{1 - \exp(-C/T)}\right] \quad (11)$$

$$\Delta S^e_{ac} = \Delta H^e_{ac}/T + R \ln K^e_{ac} \quad (12)$$

where $\alpha = (1/V^0_c)(\mathrm{d}V^0_c/\mathrm{d}T)$, the thermal expansion coefficient of the additive solvent.

EXPERIMENTAL

Materials

TOPO, from Eastman Kodak, was purified as described[1]. Squalane was obtained from Hewlett-Packard, and was used as received. The names of the ten halogenated hydrocarbons and the five reference hydrocarbons are given in Table I; dichlorobromomethane, trichloroethylene and bromotrichloromethane were taken from standard kits from Analabs, and the remaining solutes were C. Erba standards for gas–liquid chromatography (GLC).

TABLE I

MOLAR VOLUMES AT 60°C, V^0,VOLUME RATIOS RELATIVE TO DICHLOROMETHANE, r, AND SOLVENT THERMAL EXPANSION COEFFICIENTS, α

Compound	V^0 *(cm³ mol⁻¹)*	r
Cyclohexane	113.6	1.67
n-Hexane	138.5	2.04
n-Heptane	154.3	2.27
n-Octane	170.5	2.51
n-Nonane	186.7	2.75
Carbon tetrachloride	101.5	1.49
Bromotrichloromethane	103.0	1.52
Chloroform	82.03	1.21
Dichlorobromomethane	85.94	1.27
Dichloromethane	67.96	1.00
Bromochloromethane	70.27	1.03
1,2-Dichloroethane	82.87	1.22
1,1,1,2-Tetrachloroethane	113.6	1.67
trans-1,2-Dichloroethylene	81.64	1.20
Trichloroethylene	94.32	1.39
TOPO	457.2	6.73
Squalane	539.9	7.94

$\alpha_{TOPO} = 7.53 \cdot 10^{-4}\ K^{-1}$
$\alpha_{SQ} = 7.54 \cdot 10^{-4}\ K^{-1}$

Columns

The liquid phases were coated on Johns-Manville Chromosorb W AW DMCS (60–80 mesh). The packings, containing between 6 and 7% (w/w) of stationary phase, where prepared in a rotatory evaporator; *n*-hexane, used as the volatile solvent, was evaporated at room temperature under a slow stream of nitrogen. Data were obtained for pure TOPO, pure squalane and the following volume fractions (φ_c at 60°C) of TOPO: 0.113, 0.227, 0.355, 0.480, 0.620, 0.755 and 0.891. The coated supports were packed into stainless-steel tubes (0.5–1.0 m × 6 mm O.D.).

Apparatus and procedures

The GLC apparatus has been described[11]. The column bath temperature was controlled to within ±0.05°C. The nitrogen carrier gas was passed through a molecular-sieve (Davidson 5A) trap; flow-rates ranged between 15 and 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. Solute vapours were injected, together with one or two of the reference hydrocarbons and a small quantity of methane, by means of 10- and 50-μl Hamilton syringes; sample sizes were of the order of 10^{-2} μmol and produced symmetrical peaks. Relative retention times were calculated from the distances measured on the chart between the methane peak and the maxima of the solute and reference peaks. The experiments were carried at 55.0, 58.5, 62.0 and 65.5°C. Relative retention times were measured not less than three times on each column at all temperatures.

Density measurements

Densities at six temperatures within the range 55–65°C were measured for TOPO, squalane and three mixtures by using a 5-ml picnometer. The excess volumes of mixing were less than 0.1%.

RESULTS AND DISCUSSION

The molar volumes at 60°C of the solutes [12–14] and pure solvents are given in Table I. The Table also includes the corresponding molar volume ratios, r, relative to dichloromethane, the smallest solute molecule in the series. The thermal expansion coefficients of TOPO and squalane are coincident within experimental error, thus fully justifying the neglecting of the equation of state contribution to the excess free energy of solution.

In order to obtain the correction term, ε, Martire resorted to a method based on the measurement of the retention time for a solute (di-*n*-propyl ether) with the same functional group as the additive solvent molecule (di-*n*-octyl ether). Since trialkylphosphine oxides, including the lower homologues, have vapour pressures low enough to preclude their elution from our columns in a reasonable retention time, an alternative method was adopted. Subtraction from eqn. 5 of the corresponding equation for a second paraffinic solute (p′) yields.

$$\ln[(K^0_{\mathrm{p(m)}}/K^0_{\mathrm{p'(m)}})/(K^0_{\mathrm{p(b)}}/K^0_{\mathrm{p'(b)}})] - (r_\mathrm{p} - r_{\mathrm{p'}})(r_\mathrm{c}^{-1} - r_\mathrm{b}^{-1})\varphi_\mathrm{c} = -z(r_\mathrm{p} - r_{\mathrm{p'}})f_{4\mathrm{c}}^2(\Delta\omega_{34}/kT)\varphi_\mathrm{c}^2 \quad (13)$$

where only relative retention times are involved. The value of the term $-zf_{4\mathrm{c}}^2(\Delta\omega_{34}/kT)$ can be calculated from the slope of the straight line obtained by plotting the left-handside against φ_c^2. When cyclohexane is taken as the reference solute, the mean of the values for this term obtained with the remaining four hydrocarbons was 0.168 and its standard deviation was 0.002 at 60°C.

For the purposes of the present paper, type 4 segments are identified with the group PO in the TOPO molecule. The estimation of $f_{4\mathrm{c}}$ is problematic, since there are no available data for the contribution of the PO group to the van der Waals molecular volumes; this was calculated as 16.0 $\mathrm{cm}^3\ \mathrm{mol.}^{-1}$, by summing the contributions assigned by Bondi[15] to a phosphorus atom attached to three alkyl groups and the upper limit (5.5 $\mathrm{cm}^3\ \mathrm{mol.}^{-1}$) obtained for an oxygen atom. This results in $f_{4\mathrm{c}} = 0.06$.

Fig. 1 is a plot of $Q + \varepsilon$ against φ_c for carbon tetrachloride and chloroform,

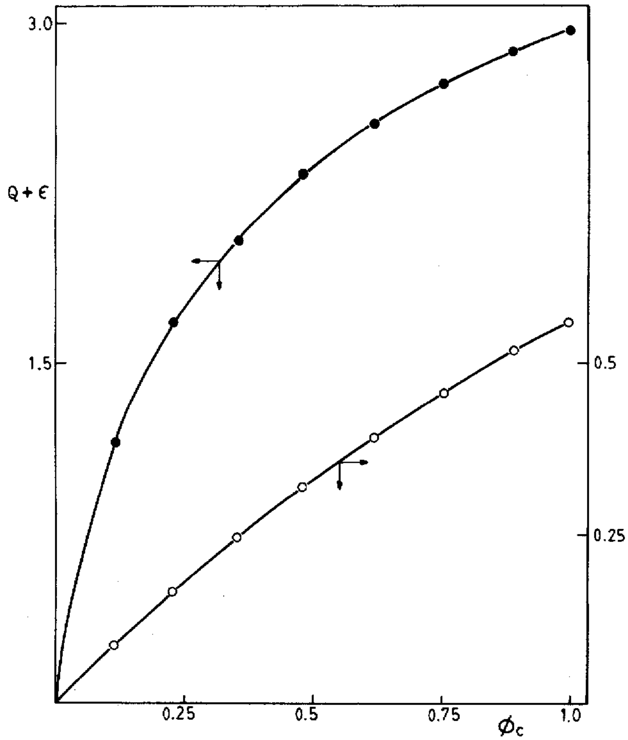

Fig. 1. Plots of $Q + \varepsilon$ against φ_c at 60°C for chloroform (left-hand scale) and carbon tetrachloride (right-hand scale).

the two solutes that exhibited the smallest and the largest association constants in our previous work[1]. The plots are clearly non-linear, pointing to the fact that a strong interaction requiring a logarithmic term in eqn. 9 exists in both cases. This behaviour is very different from that observed by Martire and co-workers[16] in their study of the interactions between haloforms and di-*n*-octyl ether, where this type of plot was linear in the case of carbon tetrachloride, indicating the existence of weak interactions only, expressed through the linear term in eqn. 9.

The experimental data were analyzed through eqn. 9, by means of the IBM routines FMCG and DGMCG based on the calculation of an unconstrained minimum of a function of several variables using conjugate gradients[17]. The correlation coefficients were in excess of 0.9995 with the exception of that for carbon tetrachloride, which yielded a value of 0.9993.

Perhaps more important than the goodness of the fit is the fact that the coefficient A is 74.5 K for bromotrichloromethane and zero for the remaining solutes. This behaviour suggests that in all the studied systems there is one type of solute–solvent interaction that is much stronger than the interactions of other types, *ie.*, $|\Delta W_{24}| \gg |\Delta W_{14}|$, thus making unnecessary the inclusion of a linear term in eqn. 9. The nature of the interaction cannot be established on the basis of thermodynamic evidence alone; however, it is predictable that hydrogen bonds, when feasible as in molecules CHX_3 and CH_2X_2 (X = halogen atom), represent stronger interactions than those established between the X atoms in the same molecules and PO groups, these in turn being stronger than the paraffinic segment – PO group interactions. The difference between the PO/Br and the PO/Cl interaction energies would not be very large, thus making necessary a linear term in the correlation of the experimental data for bromotrichloromethane; the coefficients A and C obtained for this solute in the non-linear fit lead to $\Delta W_{14} = -0.2$ kcal mol^{-1} and $\Delta W_{24} = -2.3$ kcal mol^{-1}, respectively, when used in conjunction with the f_{4c} anbd f_{2a} values calculated from Bondi's[15] tabulation of group contributions to van der Waals molecular volumes.

The results of the analysis of the experimental data are given in Table II, which also includes the results for K^e_{ac} and for ΔH^e_{ac} at 60°C, calculated by means of eqns. 10 and 11, respectively; for comparative purposes, the values of the association constants, K'_{ac}, obtained previously[1] have also been included.

An estimate of f_{4c} is necessary in order to calculate K^e_{ac} by applying eqns. 9 and 10: this estimation, like any other involving group contributions to van der Waals molecular volumes, is highly uncertain. The isothermal version of eqn. 9, however, does not include f_{4c}:

$$Q + \varepsilon = (A\varphi_c/T) + \ln[1 + (K^e_{ac}\varphi_c/V^0_c)] \qquad (14)$$

When retention data at 60°C (obtained by interpolation) are analyzed through eqn. 14, the results for K^e_{ac} differ by less than 0.5% from those appearing in Table II. This coincidence shouldn't be attributed to a very accurate (or lucky) estimation of f_{4c}, but to the fact that the results arrived at by means of eqns. 9 and 10 are sparingly affected by large changes in f_{4c}.

Although the same general trends are shown by the association constants calculated in the present and in our previous work[1], some of the results require additional comments. While equal values of K^e_{ac} are obtained for chloroform and for dichlorobromomethane by the present approach, the result for dichlorobromomethane was 5% larger in our former work. In a similar fashion, Martire and co-

TABLE II

RESULTS OF ANALYSIS OF DATA BY MEANS OF EQN. 9 AND THERMODYNAMIC PROPERTIES AT 60°C

Compound	*C(K)*	*K^e_{ac} (l mol^{-1})*	*$-\Delta H^e_{ac}$ (kcal mol^{-1})*	*K'_{ac} (l mol^{-1})**
Carbon tetrachloride	874.5	0.351	1.71	0.378
Bromotrichloromethane	1135	0.801	2.17	1.22
Chloroform	1928	8.92	3.68	8.82
Dichlorobromomethane	1928	8.92	3.68	9.22
Dichloromethane	1563	2.98	2.97	2.79
Bromochloromethane	1573	3.04	2.99	3.00
1,2-Dichloroethane	1438	2.03	2.73	2.01
1,1,1,2-Tetrachloroethane	1430	1.98	2.71	2.06
t-1,2-Dichloroethylene	1218	1.03	2.32	1.00
Trichloroethylene	1298	1.32	2.47	1.34

* Data from ref. 1.

workers[16] determined the same $K^{\mathrm{e}}_{\mathrm{ac}}$ values for four haloforms with di-*n*-octyl ether, more than one interaction mechanism being taken into consideration, but the values increased as bromine replaced chlorine in the series when the retention characteristics were attributed exclusively to hydrogen bonding. These results reflect the capability of the Martire lattice model to isolate the most important interaction and, for the systems under consideration, they indicate an equal hydrogen-donor capacity in the haloform family. On the other hand, trialkylphosphine oxides are basic enough[18] to make their interactions with the haloform halogen atoms almost negligible in comparison to hydrogen bonding; a linear term is therefore not necessary in the fit of eqn. 9 to the experimental data.

Carbon tetrachloride is a chemically homogeneous solute; its interactions with TOPO, albeit much weaker than those shown by the haloforms, are strong enough to yield a markedly non-linear $Q + \varepsilon$ *vs.*φ_{c} plot; the $K^{\mathrm{e}}_{\mathrm{ac}}$ computed from these data, by no means negligible, is more than doubled when a bromine atom replaces a chlorine atom. These facts could be explained by postulating the existence of a $\mathrm{n} \rightarrow \sigma^{\star}$ charge-transfer mechanism between the n-donor and the halogen atoms or, more probably when the very high dipole moment of TOPO is taken into account, by dipole–induced dipole classical electrostatic interactions. Since the stronger hydrogen-bonding interactions are not possible with the pair carbon tetrachloride–bromotrichloromethane, the substitution of one halogen atom results in a more important effect than in the haloform family; furthermore, the presence of two sites of not very different interaction energies in the molecule bromotrichloromethane results in the only case, among those studied in the present work, where a linear term becomes necessary in the adjustment of the data. The behaviour within the pair dichloromethane–bromochloromethane is similar to that observed for the haloforms: almost equal $K^{\mathrm{e}}_{\mathrm{ac}}$ values when analyzed in terms of the lattice model, and a larger association constant for bromochloromethane when only one type of interaction mechanism was assumed. A double bond produces a marked decrease in the sociation constants of the solutes with two carbon atoms, most probably as a consequence of the repulsion with the high-electron-density PO groups.

Both $K^{\mathrm{e}}_{\mathrm{ac}}$ and $\Delta H^{\mathrm{e}}_{\mathrm{ac}}$ are calculated from C; since this is the only parameter depending on the solute in eqns. 9 and 10, there is an obvious correlation between both sets of thermodynamic properties. When $\kappa = \exp(C/T)$ is large compared to unity, eqn 12 leads to:

$$\Delta S^{\mathrm{e}}_{\mathrm{ac}} = R \ln f_{4\mathrm{c}} V^0_{\mathrm{c}}$$

Correspondingly, almost coincident complex-formation entropies, ranging between -6.7 and -7.1 cal K^{-1} mol^{-1}, were obtained for all the solutes in the present work. This may be considered as a weakness of the lattice model, and is a consequence of approximating the energetic contribution to the partial molar excess free energy by the partial molar excess configurational energy.

In conclusion, it is experimentally demonstrated that when one of the solute–additive solvent interactions is much stronger than the rest of the interactions, the equations of Martire's lattice model (eqn. 14) simplify to:

$$\exp(Q + \varepsilon) = 1 + K^{\mathrm{e}}_{\mathrm{ac}} \varphi_{\mathrm{c}} / V^0_{\mathrm{c}} \qquad (15)$$

Had the molecular volumes of the solute of interest and the reference solute been comparable, thus making $\varepsilon = 0$, eqn. 15 would have further simplified, yielding an expression of the type used in GLC studies of complexing[19,20]. The behaviour of the system trichlorobromomethane + TOPO demonstrates that other-end interactions cannot be neglected when their exchange energies amount about one tenth of the most important exchange energy.

ACKNOWLEDGEMENT

This work was sponsored by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and by the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC).

REFERENCES

1 R. C. Castells and A. M. Nardillo, *J. Solution Chem.*, 14 (1985) 87.
2 D. E. Martire and P. Riedl, *J. Phys. Chem.*, 72 (1968) 3478.
3 J. P. Sheridan, D. E. Martire and Y. B. Tewari, *J. Am. Chem. Soc.*,94 (1972) 3294.
4 J. P. Sheridan, D. E. Martire and F. P. Banda, *J. Am. Chem. Soc.*, 95 (1973) 4788.
5 R. R. Carlson and D. W. Meek, *Inorg. Chem.*, 13 (1974) 1741.
6 D. E. Martire, *J. Phys. Chem.*, 87 (1983) 2425.
7 R. L. Scott, *J. Phys. Chem.*, 75 (1971) 3834.
8 E. A. Guggenheim *Trans. Faraday Soc.*, 56 (1960) 1159.
9 P. J. Flory, *J. Chem. Phys.*, 10 (1942) 51.
10 M. L. Huggins, *Ann. NY Acad. Sci.*, 43 (1942) 1.
11 R. C. Castells, *An. Asoc. Quim. Argent.*, 64 (1976) 155.
12 R. R. Dreisbach, *Adv. Chem. Ser.*, 15 (1955).
13 R. R. Dreisbach, *Adv. Chem. Ser.*, 22 (1959).
14 R. R. Dreisbach, *Adv. Chem. Ser.*, 29 (1961).
15 A. Bondi, *J. Phys. Chem.*, 68 (1964) 441.
16 T. J.Bruno, D. E. Martire, M. W. P. Harbison, A. Nikolić and C. F. Hammer, *J. Phys. Chem.*, 87 (1983) 2430.
17 R. Fletcher and C. M. Reeves, *Comput. J.*, 7 (1964) 149.
18 E. M. Arnett, E. J. Mitchell and T. S. S. R. Murty, *J. Am. Chem. Soc.*, 96 (1974) 3975.
19 R. J. Laub and X. A. Wellington, in R. Foster (Editor), *Molecular Association*, Vol. 2, Academic Press, London, 1979, Ch. 3.
20 J. R. Conmder and C. L. Young, *Physicochemical Applications of Gas Chromatography*, Wiley, New York, 1979, Ch. 6.