

CHROM. 18 152

POSSIBILITY AND CONSEQUENCES OF USING DIFFERENT CONCENTRATION SCALES IN THE STUDY OF SOLUTION THERMODYNAMICS BY GAS-LIQUID CHROMATOGRAPHY

REYNALDO CÉSAR CASTELLS

CIDEPIINT, 52 entre 121 y 122, 1900 La Plata (Argentina)

(Received July 19th, 1985)

SUMMARY

Several concentration scales may be used to express the solute concentration, both in the condensed and in the vapour phase. Each choice of concentration units gives rise to a set of thermodynamic properties: distribution coefficient, activity coefficient, free energy, enthalpy and entropy of solution. The definitions and relationships between the different forms of activity coefficient are first reviewed. The standard states to which the thermodynamic properties obtainable from chromatographic data are referred are then unambiguously identified. Finally, some consequences on the correlation of the retention behaviour of members of homologous series are discussed.

INTRODUCTION

Different concentration scales have been used in chromatographic theory. Trivial as it may seem, a change in the concentration scale leads to a change in the standard state. Now that gas chromatography (GC) is a well established technique for the study of solution thermodynamics^{1,2}, it is very important to understand fully the meaning of the thermodynamic properties obtained through different treatments of experimental data and their interrelationships.

The partition coefficient

$$K = c_1/c_1^G \quad (1)$$

defined by the quotient between the solute molar concentrations in the liquid, c_1 , and the vapour phase, c_1^G , has been almost exclusively employed to describe the solute partitioning; other forms of distribution parameter, such as Henry's law constants, are very uncommon in the chromatographic literature. The infinite dilution rational activity coefficient, γ_1^{∞} , based on the mole fraction concentration scale and Raoult's law standard state, was introduced early in the development of GC³⁻⁵ to compare liquid phase selectivities. The partial molar and partial molar excess thermodynamic properties of solution for many years were calculated by measuring the temperature

dependence of K , of some form of retention volume or of γ_1^∞ , without paying too much attention to the standard states to which these properties were referred. Meyer⁶ demonstrated that, in accordance with the treatments of experimental chromatographic data current at that time, two sets of thermodynamic properties could be defined, based on totally different standard states for both phases. However, probably because his demonstration rested more on conceptual arguments than on formal thermodynamic equations, the importance of Meyer's paper has not been fully recognized.

When GC thermodynamic studies were extended to polymer solutions, the inadequacy of the rational activity coefficient was soon perceived. The stationary phase molecular weight, M_2 , needed to calculate γ_1^∞ is difficult to determine with adequate accuracy in the case of polymeric liquids, and difficult to specify for polydisperse polymers. Furthermore, $\ln \gamma_1^\infty \rightarrow -\infty$ when $M_2 \rightarrow \infty$ within a family of structurally identical polymers, indicating that γ_1^∞ is not a meaningful gauge of the interactions of the solute with its surroundings. To overcome this difficulty, Patterson *et al.*⁷ suggested using the infinite dilution weight fraction activity coefficient, Ω_1^∞ , while Fritz and Kováts⁸ and Martire⁹ proposed the usage of a molal-based activity coefficient, η_1^∞ . Both $\ln \Omega_1^\infty$ and $\ln \eta_1^\infty$ tend to a finite value as the polymer molecular weight increases, remaining almost constant for homologous solvents having molecular weights over 10^4 .

Partial molar excess thermodynamic properties are defined from these activity coefficients. Vapour solubility data, on the other hand, may also be expressed by using partial pressures in conjunction with molar fractions, weight fractions or molalities, instead of molar concentrations. Each of these forms of distribution coefficient gives rise to a set of partial molar thermodynamic properties of solution. The object of the present paper is to characterize unambiguously the standard states to which these properties are referred, and to obtain expressions that relate properties belonging to the different sets; for that purpose, the relationships between concentration scales and between activity coefficients need to be briefly discussed. The last section deals with some consequences on the correlation of the retention behaviour of homologous series.

Concentration scales

The solute concentration in the stationary phase is expressed in terms of the molar fraction, x_1 , weight fraction, w_1 , molality, m_1 and molarity, c_1 . The relationships between these concentration scales in a binary mixture, and their limits under conditions where $x_1 \rightarrow 0$, are

$$w_1/x_1 = w_1 + (1 - w_1)(M_1/M_2) \rightarrow M_1/M_2 \quad (2w)$$

$$m_1/x_1 = 1000/M_2(1 - x_1) \rightarrow 1000/M_2 \quad (2m)$$

$$c_1/x_1 = v^{-1} = [x_1\bar{v}_1 + (1 - x_1)\bar{v}_2]^{-1} \rightarrow v_2^{-1} \quad (2c)$$

where v is the solution molar volume, \bar{v}_i represents the partial molar volume of component i and v_2 is the molar volume of the pure stationary phase. The solute concentration in the gas phase is expressed either in terms of its partial pressure, p_1 , or its molarity, c_1^G .

Activity coefficients

In accordance with the chosen concentration scale, the solute chemical potential in the condensed phase, ${}_L\mu_1$, may be expressed by one of the following equations

$${}_L\mu_1 = {}_L\mu_1^x + RT \ln \gamma_1 x_1 \quad (3x)$$

$$= {}_L\mu_1^w + RT \ln \Omega_1 w_1 \quad (3w)$$

$$= {}_L\mu_1^m + RT \ln \eta_1 m_1 \quad (3m)$$

$$= {}_L\mu_1^c + RT \ln \Gamma_1 c_1 \quad (3c)$$

where Γ_1 is the molar concentration activity coefficient, and ${}_L\mu_1^x$, ${}_L\mu_1^w$, ${}_L\mu_1^m$ and ${}_L\mu_1^c$ represent the solute chemical potential in the standard state, *i.e.*, the state with unitary solute activity and at the solution temperature, corresponding to the various concentration scales.

When the pure substance is chosen as the standard state for both components of the mixture (symmetrical or Raoult's law convention, identified by an exponent R), two direct consequences emerge from eqns. 3x-3c

$${}_L\mu_1^{xR} = {}_L\mu_1^{wR} = {}_L\mu_1^{mR} = {}_L\mu_1^{cR} = {}_L\mu_1^0 \quad (4)$$

where ${}_L\mu_1^0$ is the chemical potential of the pure solute at the solution temperature, and:

$$\gamma_1^R x_1 = \Omega_1^R w_1 = \eta_1^R m_1 = \Gamma_1^R c_1 \quad (5)$$

This convention is commonly applied in conjunction with molar and weight fractions; in these cases both the activities and the activity coefficients tend to one as the system approaches the standard state. Its usage with molalities^{8,9} is not as common; as $m_1 = \infty$ at the standard state, $\eta_1^R = 0$ in this state, in order to attain unit activity. The application of Raoult's law convention with molarities is also infrequent; in this case $c_1 \rightarrow (1/v_1)$, and consequently $\Gamma_1^R \rightarrow v_1$ when the system approaches the standard state. Under infinite dilution conditions for the solute, combining eqns. 5 and 2 it is possible to write

$$\gamma_1^\infty = \Omega_1^\infty (M_1/M_2) = \eta_1^\infty (1000/M_2) = \Gamma_1^\infty (1/v_2) \quad (6)$$

where the exponent R has been omitted in the activity coefficient symbols.

In the unsymmetrical (or Henry's law) convention the activity coefficients are defined by reference to a solution dilute enough as to behave in accord with Henry's law; the following limits are specified for the solute in such a solution

$$\gamma_1^H \rightarrow 1 \text{ when } x_1 \rightarrow 0 \quad (7x) \quad \Omega_1^H \rightarrow 1 \text{ when } w_1 \rightarrow 0 \quad (7w)$$

$$\eta_1^H \rightarrow 1 \text{ when } m_1 \rightarrow 0 \quad (7m) \quad \Gamma_1^H \rightarrow 1 \text{ when } c_1 \rightarrow 0 \quad (7c)$$

where the exponent H identifies the applied convention. The solute standard states

resulting when these limits are introduced in eqns. 3x-3c are purely hypothetical:

$$\left. \begin{array}{l} {}_L\mu_1^{xH}: \\ {}_L\mu_1^{wH}: \\ {}_L\mu_1^{mH}: \\ {}_L\mu_1^{cH}: \end{array} \right\} \begin{array}{l} \text{the solute chemical} \\ \text{potential in an hypo-} \\ \text{thetical solution} \\ \text{with} \end{array} \quad \left\{ \begin{array}{l} x_1 = 1 \text{ (8x)} \\ w_1 = 1 \text{ (8w)} \\ m_1 = 1 \text{ (8m)} \\ c_1 = 1 \text{ (8c)} \end{array} \right\} \begin{array}{l} \text{and with behaviour} \\ \text{characteristic of} \\ \text{the infinitely} \\ \text{dilute solution} \end{array}$$

For the fugacity of the solute vapours, \hat{f}_1 , in equilibrium with a very dilute solution (identified by an asterisk) it is possible to write

$$\hat{f}_1 = H_x x_1^* = H_w w_1^* = H_m m_1^* = H_c c_1^* \quad (9)$$

or

$$\hat{f}_1 = \gamma_1^\infty x_1^* f_1^0 = \Omega_1^\infty w_1^* f_1^0 = \eta_1^\infty m_1^* f_1^0 = \Gamma_1^\infty c_1^* f_1^0 \quad (10)$$

where H_x , H_w , H_m and H_c are the Henry's coefficients on the different concentration scales, and f_1^0 is the fugacity of the vapours in equilibrium with pure solute at the solution temperature. From eqns. 9 and 10 we obtain:

$$H_x = \gamma_1^\infty f_1^0 \quad (11x)$$

$$H_w = \Omega_1^\infty f_1^0 \quad (11w)$$

$$H_m = \eta_1^\infty f_1^0 \quad (11m)$$

$$H_c = \Gamma_1^\infty f_1^0 \quad (11c)$$

Some confusion may arise in the identification of these standard states. Thus $x_1 = 1$ is obviously equivalent to $w_1 = 1$, and this could induce one to think that both standard states are also equivalent. However, while the state corresponding to ${}_L\mu_1^{xH}$ is obtained by extrapolating on a plot of \hat{f}_1 vs. x_1 the behaviour at infinite dilution (straight line of slope H_x) to the point where $x_1 = 1$, the state corresponding to ${}_L\mu_1^{wH}$ is obtained by an analogous mechanism but on a plot of \hat{f}_1 vs. w_1 (straight line of slope H_w).

In order to help to distinguish the different standard states, solute fugacities have been plotted in Figs. 1-4 against the four discussed concentration scales, for the system *n*-hexane (1) + *n*-dotriacontane (2) at 73°C. The data were taken from Van der Waals and Hermans¹⁰. Raoult's and Henry's standard states are indicated in the figures by a circle and the symbols RSS and HSS, respectively. The behaviours predicted from both laws have been plotted in each figure, besides the curve through the experimental points. As Raoult's law is defined in terms of molar fractions, the ideal behaviour is not represented by straight lines in the other three concentration scales (with the exception of \hat{f}_1 vs. w_1 in the fortuitous case in which $M_1 = M_2$).

For a very dilute solution

$${}_L\mu_1^0 + RT \ln \gamma_1^\infty x_1^* = {}_L\mu_1^{xH} + RT \ln x_1^* \quad (12x)$$

and one can write analogous expressions in w_1 , m_1 and c_1 . From them we obtain

$${}_L\mu_1^{xH} - {}_L\mu_1^0 = RT \ln \gamma_1^\infty \quad (13x)$$

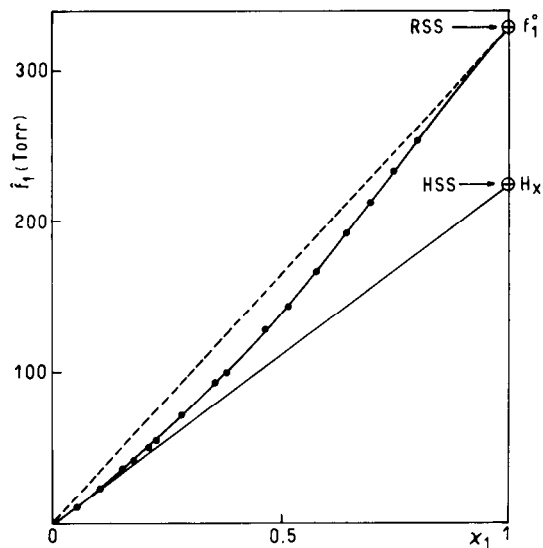


Fig. 1. Plot of fugacity against molar fraction for the system *n*-heptane (1) + *n*-dotriacontane (2), at 73°C, calculated from data in ref. 10. The dashed and the solid straight lines represent Raoul's and Henry's law behaviour, respectively. Further details in the text.

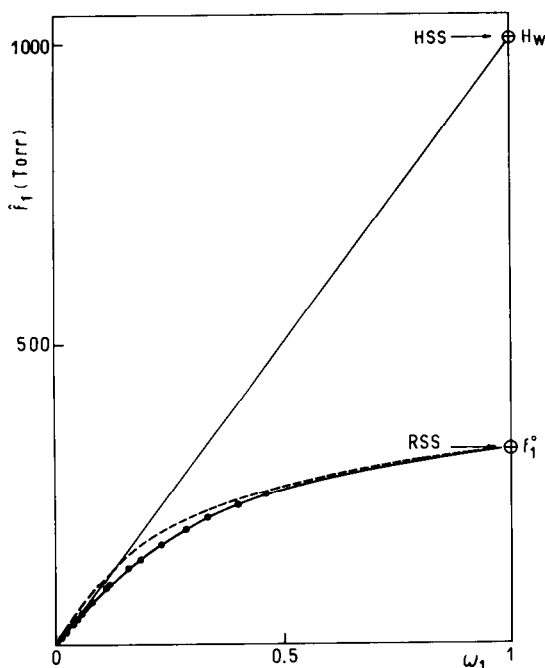


Fig. 2. As in Fig. 1, but expressing concentrations in weight fractions. The solid straight line represents Henry's law behaviour; the dashed curve corresponds to Raoul's law.

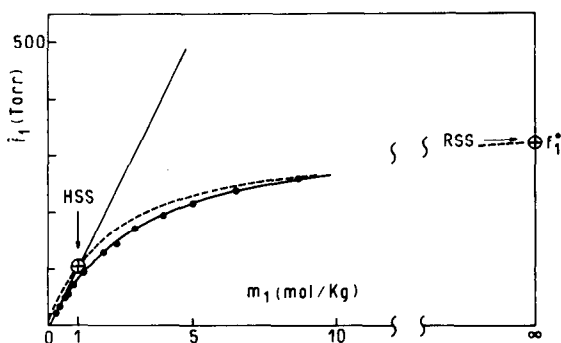


Fig. 3. As in Fig. 1, but expressing concentrations as molalities. The solid straight line represents Henry's law behaviour; the dashed curve corresponds to Raoul's law.

$${}_L\mu_1^{wH} - {}_L\mu_1^0 = RT \ln \Omega_1^\infty \quad (13w)$$

$${}_L\mu_1^{mH} - {}_L\mu_1^0 = RT \ln \eta_1^\infty \quad (13m)$$

$${}_L\mu_1^{cH} - {}_L\mu_1^0 = RT \ln \Gamma_1^\infty \quad (13c)$$

which remove any doubt about the standard states associated with the infinite dilution partial molar excess potentials on each of the four concentration scales.

For a given solution, without restrictions about the concentration range

$$\begin{aligned} {}_L\mu_1^{xH} + RT \ln \gamma_1^H x_1 &= {}_L\mu_1^{wH} + RT \ln \Omega_1^H w_1 \\ &= {}_L\mu_1^{mH} + RT \ln \eta_1^H m_1 = {}_L\mu_1^{cH} + RT \ln \Gamma_1^H c_1 \end{aligned} \quad (14)$$

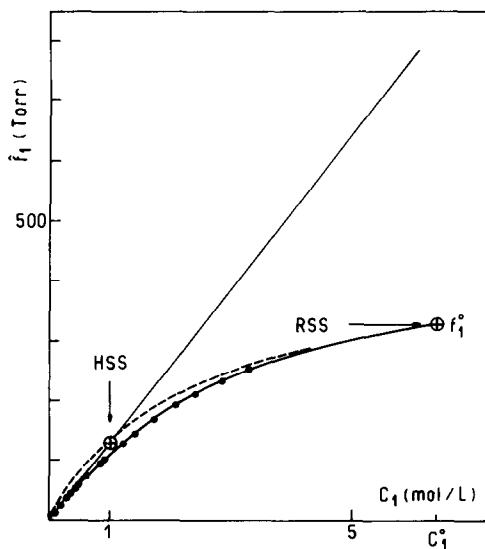


Fig. 4. As in Fig. 1, but expressing concentrations as molarities. The solid straight line represents Henry's law behaviour; the dashed curve corresponds to Raoul's law.

and by combining eqn. 14 with eqns. 13x-13c:

$$\gamma_1^H \gamma_1^\infty x_1 = \Omega_1^H \Omega_1^\infty w_1 = \eta_1^H \eta_1^\infty m_1 = \Gamma_1^H \Gamma_1^\infty c_1 \quad (15)$$

When eqn. 6 is introduced in eqn. 15, we obtain

$$\gamma_1^H x_1 = \Omega_1^H w_1 (M_2/M_1) = \eta_1^H m_1 (M_2/1000) = \Gamma_1^H c_1 v_2 \quad (16)$$

which, within Henry's law convention, is analogous to eqn. 5 for Raoul's law convention.

RETENTION VOLUME AND VAPOUR-LIQUID EQUILIBRIUM

The solute chemical potential in the vapour phase is given by

$${}_G\mu_1 = {}_G\mu_1^0 + RT \ln f_1 \quad (17)$$

where \hat{f}_1 is as defined earlier and ${}_G\mu_1^0$ is the chemical potential of component 1 in the state of unit fugacity (vapours of pure 1 behaving as an ideal gas at the solution temperature and $p = 1$ atm).

Molarity as the expression of solution concentration

Under vapour-liquid equilibrium conditions, from eqns. 3c and 17 we can write

$$L\mu_1^f - {}_G\mu_1^0 = -RT \ln (\Gamma_1 c_1 / \hat{f}_1) = -RT \ln \mathbf{K} \quad (18)$$

where the bold face identifies a thermodynamic equilibrium constant; \mathbf{K} , therefore, will depend only on the temperature and on the choice of standard state. The solute fugacity is given by

$$\hat{f}_1 = \hat{\psi}_1 p_1 = \hat{\psi}_1 c_1^G RT \quad (19)$$

where $\hat{\psi}_1$ represents the solute fugacity coefficient. Then, using eqn. 1, we obtain:

$$\mathbf{K} = (\Gamma_1 / \hat{\psi}_1) (K/RT) \quad (20)$$

The unsymmetrical convention is a convenient choice for the condensed phase, as under the high dilution conditions of a chromatographic experiment, $\Gamma_1^H = 1$. Furthermore, if ideal behaviour is assumed for the vapour phase, $\hat{\psi}_1 = 1$ and eqn. 20 may be written

$$\mathbf{K}^H = K^\infty / RT \quad (21)$$

where K^∞ represents the chromatographic, *i.e.*, infinite dilution, partition coefficient, related to the specific retention volume, V_g , by the wellknown equation

$$V_g = 273 K^\infty / T \rho_2 \quad (22)$$

where ρ_2 is the density of the stationary phase. Symbolizing with ${}_G\mu_1^\dagger$ the chemical potential of the vapours of pure component 1 in an ideal vapour phase at unit molar concentration, *i.e.*, at $p/RT = 1$, we have:

$${}_G\mu_1 - {}_G\mu_1^\dagger = RT \ln (1/RT) \quad (23)$$

By combining eqns. 18–23, the standard partial molar free energy of solution may be written as:

$$\Delta G_K^0 \equiv {}_L\mu_1^{\text{cH}} - {}_G\mu_1^\dagger = -RT \ln K^\infty = -RT \ln (V_g T \rho_2 / 273) \quad (24)$$

The standard partial molar enthalpy and entropy of solution are obtained by studying the effect of temperature on the retention volume

$$\Delta H_K^0 = RT^2 (d \ln K^\infty / dT) = RT^2 (d \ln V_g / dT) + RT(1 - \alpha_2 T) \quad (25)$$

$$\Delta S_K^0 = (\Delta H_K^0 - \Delta G_K^0) / T \quad (26)$$

where $\alpha_2 = (1/v_2) (\partial v_2 / \partial T)$, the thermal expansion coefficient of the stationary phase.

Molar fraction as the expression of solution concentration

In this particular case, from eqns. 3x and 17, under equilibrium conditions:

$${}_L\mu_1 - {}_G\mu_1^0 = -RT \ln (\gamma_1 x_1 / f_1) = -RT \ln K_x \quad (27x)$$

At infinite dilution, $K_x = \gamma_1 / H_x$ and, if Henry's law reference state is adopted for the activity coefficients, eqn. 27x may be written as:

$$\Delta G_x^0 \equiv {}_L\mu_1^{\text{cH}} - {}_G\mu_1^0 = -RT \ln K_x^{\text{H}} = RT \ln H_x \quad (28x)$$

By successive application of eqns. 1, 19, 9, 2c and 22 it is possible to deduce the following relationship between H_x and V_g

$$H_x = 273 R \hat{\psi}_1 / M_2 V_g \quad (29x)$$

and assuming ideal behaviour for the vapour phase:

$$\Delta G_x^0 = -RT \ln (M_2 V_g / 273 R) \quad (30x)$$

From eqns. 28x and 30x, the standard partial molar enthalpy of solution is given by

$$\Delta H_x^0 = -RT^2 (d \ln H_x / dT) = RT^2 (d \ln V_g / dT) \quad (31x)$$

while the standard partial molar entropy of solution is obtained by combination of eqns. 30x and 31x. Meyer⁶ identified this set of properties by the suffix *k*; as he points, his partition coefficient, *k*, represents the inverse of the Henry's law constant, H_x . In order to simplify the notation, so avoiding confusion with the next section, I have omitted *k*.

Weight fraction or molality as expressions of solution concentration

In these cases, by combining eqn. 17 with eqn. 3w or 3m, respectively, we get:

$${}_L\mu_1^w - {}_G\mu_1^0 = -RT \ln (\Omega_1 w_1 / f_1) = -RT \ln K_w \quad (27w)$$

$${}_L\mu_1^m - {}_G\mu_1^0 = -RT \ln (\eta_1 m_1 / f_1) = -RT \ln K_m \quad (27m)$$

At infinite dilution, and adopting Henry's law reference state for the condensed phase, two different standard partial molar free energies of solution may be defined:

$$\Delta G_w^0 \equiv {}_L\mu_1^{wH} - {}_G\mu_1^0 = -RT \ln K_w^H = RT \ln H_w \quad (28w)$$

$$\Delta G_m^0 \equiv {}_L\mu_1^{mH} - {}_G\mu_1^0 = -RT \ln K_m^H = RT \ln H_m \quad (28m)$$

By combining eqn. 29x with eqns. 11 and 6, we get:

$$H_w = 273 R\hat{\psi}_1 / M_1 V_g \quad (29w)$$

$$H_m = 273 R\hat{\psi}_1 / 1000 V_g \quad (29m)$$

Therefore, under the assumption of an ideal vapour phase

$$\Delta G_w^0 = -RT \ln (M_1 V_g / 273 R) \quad (30w)$$

$$\Delta G_m^0 = -RT \ln (1000 V_g / 273 R) \quad (30m)$$

and the corresponding partial molar enthalpies are given by:

$$\Delta H_w^0 = -RT^2 (d \ln H_w / dT) = RT^2 (d \ln V_g / dT) \quad (31w)$$

$$\Delta H_m^0 = -RT^2 (d \ln H_m / dT) = RT^2 (d \ln V_g / dT) \quad (31m)$$

It should be noted that $\Delta H_x^0 = \Delta H_w^0 = \Delta H_m^0$; this is not surprising, since the three processes involve the same vapour phase standard state, and the measured interactions in the condensed phase are those corresponding to isolated solute molecules, surrounded only by solvent molecules. From eqns. 25 and 31

$$\Delta H_k^0 = \Delta H_x^0 + RT - \alpha_2 RT^2 \quad (32)$$

where the RT term is a consequence of the adoption of different vapour phase standard states, and $-\alpha_2 RT^2$ accounts for the changes in molarity resulting from thermal expansion. Standard partial molar entropies are calculated from eqns. 30 and 31.

CONSEQUENCES ON THE CORRELATION OF RETENTION BEHAVIOUR OF HOMOLOGOUS SERIES

In discussions about the retention index system and the polarity of stationary phases¹¹⁻¹⁴ it is frequently assumed, following Martin's approach¹⁵, that the standard molar free energy of solution may be formally expressed as an additive function of the contributions of the individual groups in the solute molecule. For compounds with a general formula $H(CH_2)_N Y$, where N represents the number of carbon atoms and Y is a functional group;

$$\Delta G^0 = N \Delta G^0(CH_2) + \Delta G^0(H) + \Delta G^0(Y) \quad (33)$$

The value of $\Delta G^0(\text{CH}_2)$, the contribution per methylene group to the standard free energy of solution, is virtually the same for different homologous series when studied in a given stationary phase. Because of this characteristic, $\Delta G^0(\text{CH}_2)$, together with the corresponding group contribution to the excess free energy of solution, $\Delta G^e(\text{CH}_2)$, has been employed to correlate the polarity of stationary phases¹¹⁻¹⁴.

By combining eqn. 33 with eqn. 24 or 30, four methylene group contributions to the standard free energy of solution may be defined:

$$\begin{aligned} -RT \left(d \ln V_g / dN \right) &= \Delta G_k^0(\text{CH}_2) = \Delta G_x^0(\text{CH}_2) \\ &= \Delta G_w^0(\text{CH}_2) + RT \left(d \ln M_1 / dN \right) \\ &= \Delta G_m^0(\text{CH}_2) \end{aligned} \quad (34)$$

Two different correlations of retention behaviour within an homologous series would then be possible. The first one is the classical plot of $\ln V_g$ vs. N , with a slope that may be considered as $-\Delta G_k^0(\text{CH}_2)/RT$, $-\Delta G_x^0(\text{CH}_2)/RT$ or $-\Delta G_m^0(\text{CH}_2)/RT$. The second correlation involves plotting $\ln(V_g M_1)$ against N , the slope in this case being equal to $-\Delta G_w^0(\text{CH}_2)/RT$.

In order to assess which of both correlations renders a better representation of the experimental results, a study on a group of literature data of comparable reliability has been performed. Many systems had to be discarded as the excellence of the $\ln V_g$ vs. N correlation (unitary correlation coefficient) revealed that the reported data were the result of this type of adjustment. For the majority of the remaining systems (including data of Meyer and Baiocchi¹⁶ for C_5 - C_8 *n*-alkanes and C_3 - C_7 1-chloroalkanes on eicosane and dinonyl ketone at 60°C, of Martire and co-workers^{17,18} for C_6 - C_9 *n*-alkanes and 1-alkenes and C_4 - C_7 1-chloroalkanes on *n*-tetracosane, *n*-triacontane and *n*-hexatriacontane at 76-88°C, of Meyer and Gens¹⁹ for C_5 - C_8 alkanes on 2-nonadecanone and eicosanyl nitrile at 76°C, of Meyer *et al.*²⁰ for C_5 - C_{11} linear and cyclic ketones on *n*-hexatriacontane at 100°C and of Pease and Thorburn²¹ for C_5 - C_{12} *n*-alkanes on *n*-octacosane and squalane at 80-100°C) the standard deviations of the plots of $\ln(V_g M_1)$ vs. N , as given by a linear least squares analysis of the data, were two to three times larger than those obtained from the plots of $\ln V_g$ against N . An analysis of the residuals (difference between experimental and fitted values) demonstrated that the $\ln V_g$ vs. N plots for this group of systems were concave towards the abscissa axis. In a few instances (the data for C_6 - C_{11} *n*-alkanes in dinonyl phthalate and in squalane at 100°C reported by Pecsok and Apfel²²) a better representation was obtained by plotting $\ln(V_g M_1)$ against N ; the plots of $\ln V_g$ vs. N were concave towards the ordinate axis in these cases.

The molecular weight of a member of the homologous series $\text{H}(\text{CH}_2)_N\text{Y}$ is given by

$$M_1 = 14.027 \left(N + 0.072 + \frac{M_Y}{14.027} \right) = 14.027 (N + c) \quad (35)$$

where M_Y is the molecular weight of the functional group Y and c is a constant characteristic of the series. The plots of $\ln M_1$ against N should, therefore, be concave towards the N axis; this characteristic explains the opposite effects that a change in

the correlation technique has on the slope standard deviation as revealed by the direction of the curvature of the $\ln V_\theta$ vs. N plots. Since there are no means to calculate this curvature *a priori*, a comparison of both correlations is advisable in work with unknown systems when the object is, for instance, an highly precise interpolation of experimental data.

There is, however, a definite advantage in using the classical correlation, $\ln V_\theta$ vs. N , particularly in a comparison of the behaviours of different homologous series in a given stationary phase. From eqns. 34 and 35:

$$\Delta \equiv \Delta G_x^0(\text{CH}_2) - \Delta G_w^0(\text{CH}_2) = RT/(N + c) \quad (36)$$

If N_1 and N_2 are used to designate the carbon atom numbers of the lower and the higher members of the series employed in the measurements, the difference between the resulting methylene group contributions may be calculated from

$$\bar{\Delta} \equiv \int_{N_1}^{N_2} \Delta dN / \int_{N_1}^{N_2} dN \quad (37)$$

with the result:

$$\Delta G_x^0(\text{CH}_2) - \Delta G_w^0(\text{CH}_2) = [RT/(N_2 - N_1)] \ln (M_2/M_1) \quad (38)$$

Therefore, the experimental results for $\Delta G_x^0(\text{CH}_2)$, or for $\Delta G_w^0(\text{CH}_2)$, or for both, will depend on the members of the series employed in the measurements. There are many

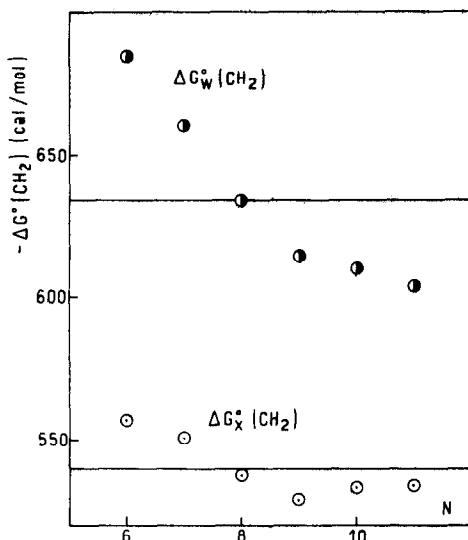


Fig. 5. Methylene group contributions to the standard partial molar free energy of solution of *n*-alkane solutes in *n*-octacosane at 120°C against solute carbon atom number, calculated from data in ref. 21. Each point was calculated from data for three consecutive *n*-alkane solutes, and plotted against the N value for the middle component in the group. Upper and lower horizontal lines correspond to values of $\Delta G_w^0(\text{CH}_2)$ and $\Delta G_x^0(\text{CH}_2)$, respectively, calculated by using the data for all the solutes.

reasons to attribute this dependence exclusively to variations in $\Delta G_w^0(\text{CH}_2)$; the correlation $\ln V_g$ vs. N , for instance, has been intensively studied and applied to innumerable systems (since it constitutes the basis of the retention index system) and the anomalies, if extant, would have been detected long ago. However, to corroborate this fact fully, values of both methylene group contributions have been calculated for groups of three n -alkanes in the range C_5 – C_{12} , utilizing the experimental data of Pease and Thorburn²¹ with n -octacosane at 120°C. In Fig. 5 these results have been plotted against the number of carbon atoms of the middle component of the group.

As mentioned in the Introduction, weight fraction-based thermodynamic properties are usual in chromatographic work with polymeric stationary phases. There are no problems in the comparison of partial molar enthalpies, since these are independent of the concentration scale. However, if the object is to compare free energies of solution or, more probably, weight fraction activity coefficients of solutes belonging to different homologous series to detect, for instance, the effect of a given substituent Y on these properties, the effect depicted in eqn. 38 will distort the comparison. This distortion will be minimal when solutes with the same number of carbon atoms are chosen for each family; anyway, the effect of the molecular weight ratio in the logarithmic term will persist and may be important. For C_5 – C_7 n -alkanes and 1-chloroalkanes at 60°C, for instance, the right-hand term of eqn. 38 amounts to 109 and 77 cal/mol, respectively. Thermodynamic properties based on molal concentrations are free from this defect and, in my opinion, are preferred for work with polymeric stationary phases.

ACKNOWLEDGEMENTS

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). CIDEPIINT, Centro de Investigación y Desarrollo en Tecnología de Pinturas, is a Research Center supported by CIC and CONICET.

REFERENCES

- 1 R. J. Laub and R. L. Pecsok, *Physicochemical Applications of Gas Chromatography*, Wiley-Interscience, New York, 1978.
- 2 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, New York, 1979.
- 3 M. R. Hoare and J. H. Purnell, *Research (London)*, 8 (1955) 541.
- 4 A. B. Littlewood, C. S. G. Phillips and D. T. Price, *J. Chem. Soc.*, (1955) 1480.
- 5 P. E. Porter, C. H. Deal and F. H. Stross, *J. Am. Chem. Soc.*, 78 (1956) 2999.
- 6 E. F. Meyer, *J. Chem. Educ.*, 50 (1973) 191.
- 7 D. Patterson, Y. B. Tewari, H. P. Schreiber and J. E. Guillet, *Macromolecules*, 4 (1971) 356.
- 8 D. F. Fritz and E. sz. Kováts, *Anal. Chem.*, 45 (1973) 1175.
- 9 D. E. Martire, *Anal. Chem.*, 46 (1974) 626.
- 10 J. H. van der Waals and J. J. Hermans, *Recl. Trav. Chim. Pays-Bas*, 69 (1950) 971.
- 11 J. Novák, J. Ruzickova, S. Wicar and J. Janak, *Anal. Chem.*, 45 (1973) 1365.
- 12 J. Novák, *J. Chromatogr.*, 78 (1973) 269.
- 13 J. Novák and J. Růžicková, *J. Chromatogr.*, 91 (1974) 79.
- 14 M. Roth and J. Novák, *J. Chromatogr.*, 234 (1982) 337.
- 15 A. J. P. Martin, *Biochem. Soc. Symp.*, 3 (1949) 4.

- 16 E. F. Meyer and F. A. Baiocchi, *J. Am. Chem. Soc.*, 99 (1977) 6206.
- 17 Y. B. Tewari, D. E. Martire and J. P. Sheridan, *J. Phys. Chem.*, 74 (1970) 2345.
- 18 Y. B. Tewari, J. P. Sheridan and D. E. Martire, *J. Phys. Chem.*, 74 (1970) 3263.
- 19 E. F. Meyer and T. H. Gens, *J. Chem. Thermodyn.*, 9 (1977) 535.
- 20 E. F. Meyer, R. H. Weiss and T. H. Gens, *J. Chem. Thermodyn.*, 9 (1977) 439.
- 21 E. C. Pease and S. Thorburn, *J. Chromatogr.*, 30 (1967) 344.
- 22 R. L. Pecsok and J. Apffel, *Anal. Chem.*, 51 (1979) 594.