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## Regression against temperature of gas chromatographic retention data

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(First received August 23rd, 1989; revised manuscript received December 8th, 1989)

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### SUMMARY

Specific retention volumes were measured in the range 25–75°C for benzene + squalane, benzene + triethylene glycol and *n*-hexane + squalane and in the range 15–55°C for benzene + tetraethylene glycol dimethyl ether, each in steps of 5°C. Values for the solution thermodynamic properties and their errors were obtained by fitting the experimental data to equations with two or more constant by using the method of Clarke and Glew. The best thermodynamic results were obtained by means of the three-constant equation; adding a fourth constant did not improve the adjustment. However, when the objective is interpolation, the results obtained with the classical, two-constant equation, are of adequate accuracy.

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### INTRODUCTION

Gas chromatography (GC) has been widely used to measure the free energy change associated with the solution process. There is a high degree of agreement between activity coefficients measured by GC and those derived by extrapolating values obtained by means of static techniques at finite concentrations<sup>1–3</sup>. Values thus obtained can be correlated with the molecular or macroscopic properties of the solutes and of the stationary phases; the predictions of theoretical models have in many instances been successfully tested against chromatographic results<sup>4,5</sup>.

The dependence on temperature of the specific retention volume,  $V_g$ , can in principle be employed to determine first-order (enthalpy) and second-order (heat capacity) partial molar quantities. However, with the exception of a small number of

workers, a linear relationship between  $\ln V_g$  and  $1/T$  has been assumed, this implying a zero partial molar heat capacity. The exceptions are the papers by Meyer and Baiochi<sup>6-8</sup>, Hammers and de Ligny<sup>9</sup> and Roth and Novák<sup>10</sup>; the systems they studied were composed of hydrocarbon solutes and stationary phases that were either another hydrocarbon or a poly(dimethylsiloxane). The reproducibility of the results was tested in only one instance<sup>7</sup> where, unfortunately, an equation without a sound theoretical basis was employed.

In this work, the specific retention volumes of benzene were measured using three stationary phases with major chemical differences: squalane (SQ), triethylene glycol (TEG) and tetraethylene glycol dimethyl ether (TEGDME); data for the system *n*-hexane + SQ are also reported. Duplicate runs were performed over relatively broad temperature ranges; measurements were carefully made, using conventional equipment. Data were processed by the method of Clarke and Glew<sup>11</sup>, which furnishes values both for the standard thermodynamic functions and for their standard deviations.

The system benzene + TEG was chosen on the assumption that, TEG being a self-associating liquid, the dissolution of a non-polar solute could be decreasingly exothermic as the temperature increases<sup>12</sup>. Whereas it can be demonstrated that retention in chromatographic columns packed with TEG on Chromosorb W is due exclusively to gas-liquid partitioning<sup>13</sup>, important contributions from adsorption at the gas-liquid interface can be expected when more strongly associated liquids (such as formamide, glycerol or ethylene glycol) are used as stationary phases. Small temperature effects on the heats of solution were expected for the systems benzene + SQ and *n*-hexane + SQ, and an intermediate behaviour for the solutions of benzene in TEGDME. The system *n*-hexane + TEG could not be studied because of significant adsorption effects<sup>13</sup>.

The number of calorimetric studies on excess heats of solution and heat capacities has grown in recent years as a consequence of the introduction of very precise instruments<sup>14-16</sup>, and it is improbable that chromatographic data could compete in quality against them. A comparison between both sets of data is difficult because calorimetric measurements are regularly performed at finite concentrations and on mixtures with limited chromatographic interest; the two types of information can thus be complementary.

## THEORY

It can be proved<sup>17</sup> that the change in the partial molar free energy of a solute on its transfer from the pure ideal vapour phase at  $p = 1$  atm to a hypothetical solution at unit molar fraction and obeying Henry's law is related to the specific retention volume,  $V_g$ , by the equation

$$\Delta \bar{G}_1^0 = -RT \ln(V_g M_2 / 273.15R) + (2B_{13} - v_1) p_o J_3^4 / 41.303 \quad (1)$$

where  $M_2$  is the molecular weight of the stationary phase,  $B_{13}$  is the second virial coefficient for the interactions between the solute and the carrier gas,  $v_1$  is the solute molar volume and  $J_3^4$  is a function of the outlet ( $p_o$ ) and inlet ( $p_i$ ) pressures. Using the definition of Gibbs free energy, eqn. 1 becomes

$$\ln V_g = -(\Delta\bar{H}_1^0/RT) + (\Delta\bar{S}_1^0/R) - \ln(M_2/273.15R) + (2B_{13} - v_1)p_0J_3^4/41.303RT \quad (2)$$

If it is assumed that  $\Delta\bar{H}_1^0$  and  $\Delta\bar{S}_1^0$  are independent of temperature and that effects of non-ideality of the vapour phase are negligible, eqn. 2 can be simplified to

$$\ln V_g = A + (B/T) \quad (3)$$

where  $B = -\Delta\bar{H}_1^0/R$  and  $A = (\Delta\bar{S}_1^0/R) - \ln(M_2/273.15R)$ . In the usual GC practice, experimental  $V_g$  values are fitted to eqn. 3 by the least-squares method, thus obtaining the best estimates for  $\Delta\bar{H}_1^0$  and  $\Delta\bar{S}_1^0$  and their standard errors. This approach is justified over short temperature ranges or with retention volumes of limited accuracy.

When accurate  $V_g$  values are obtained over a broad temperature range, non-linearity in the plots of  $\ln V_g$  against  $1/T$  can sometimes be detected. This effect, which cannot be ascribed to experimental error, can in principle be attributed to changes in  $\Delta\bar{H}_1^0$  and  $\Delta\bar{S}_1^0$  with temperature. According to eqn. 1, the problem of improving the regression of chromatographic retention data against temperature pertains to the more general problem of obtaining  $\Delta H$ ,  $\Delta S$  and  $\Delta C_p$  values by fitting  $\Delta G$  data (obtained through measurements of equilibrium constants, solubilities, vapour pressures, etc.) to some reasonable function of  $T$ . With this objective, and although there are some other options available<sup>18</sup>, the method of Clarke and Glew<sup>11</sup>, or some variant of it, is still one of the preferred choices.

Clarke and Glew begin with the very plausible assumption that the standard enthalpy change in a given process,  $\Delta H_T^0$ , can be expressed as a perturbation on the value  $\Delta H_\theta^0$  at some reference temperature  $\theta$  by means of Taylor's series expansion. Then, using formal thermodynamic equations, they deduced the following expression for the standard free energy change:

$$-\Delta G_T^0/T = -\Delta G_\theta^0/\theta + \Delta H_\theta^0[(1/\theta) - (1/T)] + \Delta C_{p\theta}^0[(\theta/T) + \ln(T/\theta) - 1] + \\ + (\theta/2)(\partial\Delta C_p^0/\partial T)_\theta[(T/\theta) - (\theta/T) - 2\ln(T/\theta)] + \dots \quad (4)$$

By introducing the temperature variable  $x = (T - \theta)/\theta$ , eqn. 4 can be written as

$$-\Delta G_T^0/T = -\Delta G_\theta^0/\theta + \sum_{j=0}^q \frac{\theta^{j-1}}{j!} \left( \frac{\partial^j \Delta H^0}{\partial T^j} \right)_\theta \left[ x^{j+1} \sum_{n=0}^{\infty} (n/n+j) (-x)^{n-1} \right] \quad (5)$$

In order to fit this equation to a set of experimental values by the method of least squares, the following definitions are adopted:

$$b_0 = -\Delta G_\theta^0/\theta \quad (6)$$

$$b_{j+1} = (\theta^{j-1}/j!) (\partial^j \Delta H^0/\partial T^j)_\theta \quad (7)$$

$$u_{j+1} = x^{j+1} \sum_{n=0}^{\infty} (n/n+j) (-x)^{n-1} \quad (8)$$

In this way eqn. 5 is reduced to a linear function in the variables  $u_1, u_2, \dots, u_{q+1}$ :

$$-\Delta G_T^0/T = b_0 + b_1 u_1 + b_2 u_2 + \dots + b_{q+1} u_{q+1} \quad (9)$$

The number of terms in the series is based on the application of the  $t$ -test:  $q$  is taken as the highest value of  $j$  for which  $b_{j+1}$  is significantly different from zero. Alternatively, the results obtained by applying successive polynomials may be compared by means of the  $F$ -test, in order to determine if the inclusion of an additional term produces a meaningful improvement in the regression<sup>19</sup>.

Eqn. 5 can be applied to the distribution of a volatile solute between a solution and a vapour phase. Thus, when  $q = 0$ , eqn. 5 reduces to

$$-\Delta \bar{G}_{1,T}^0/T = -\Delta \bar{G}_{1,\theta}^0/\theta + \Delta \bar{H}_{1,\theta}^0[(1/\theta) - (1/T)] = \Delta \bar{S}_{1,\theta}^0 - \Delta \bar{H}_{1,\theta}^0/T \quad (10)$$

The combination of eqns. 10 and 1 under the assumption of an ideal vapour phase results in eqn. 3. The same calculation, but for  $q = 1$ , gives

$$\ln V_g = A' + (B'/T) + C' \ln T \quad (11)$$

where

$$A' = (1/R) \{ \Delta \bar{S}_{1,\theta}^0 - \Delta \bar{C}_{p1,\theta}^0 \ln(1 + \theta) \} - \ln(M_2/273.15R)$$

$$B' = -(1/R) (\Delta \bar{H}_{1,\theta}^0 - \theta \Delta C_{p1,\theta}^0)$$

$$C' = \Delta \bar{C}_{p1,\theta}^0/R$$

Infinite dilution activity coefficients measured at several temperatures have been fitted by Roth and Novák<sup>10</sup> to an equation similar in form to eqn. 11.

## EXPERIMENTAL

### Apparatus

Measurements were carried out in a modified Perkin-Elmer Sigma 300 gas chromatograph, equipped with a thermal conductivity detector and an LCI-100 computing integrator. Hydrogen, dried by passing it through a trap containing molecular sieve 5A, was used as the carrier gas. The instrument flow controller was connected by means of an 1 m  $\times$  1/8 in. copper coil (immersed in the same bath as the column) with a stainless-steel H, the other arms of which were connected to a mercury manometer, to a silicone gum septum and to the analytical column. A Haake N3B water-bath, constant to  $\pm 0.01^\circ\text{C}$ , was used as a column thermostat. A short stainless-steel tube, 0.51 mm I.D., wrapped with heating tape, was used to connect the column outlet to the detector. The inlet and outlet pressures were measured to  $\pm 0.5$  Torr by means of a mercury manometer and a barometer, respectively; a soap-bubble flow meter with an air jacket was used to measure the flow-rates. Temperatures were measured to  $\pm 0.05^\circ\text{C}$  by means of a mercury thermometer with  $0.1^\circ\text{C}$  graduations that had been calibrated against two certified thermometers (Cannon, for ASTM kinematic viscosity, 28.5–31.5 $^\circ\text{C}$  and 58.5 to 61.5 $^\circ\text{C}$ , respectively).

### Columns and reagents

The columns were stainless-steel tubes of 0.53 cm I.D.; Chromosorb W (60–80 mesh) was used as the solid support. The following columns were used: 9.29% (w/w) SQ (Hewlett-Packard), 1 m in length; 8.18% (w/w) TEGDME (Aldrich), 0.6 m in length; and 10.82% (w/w) TEG (Carlo Erba, RPE), 1 m in length. Packings were prepared in a rotary evaporator under a flow of dry nitrogen using *n*-hexane as the solvent for SQ and dry methanol for TEG and TEGDME. A 25-cm precolumn, containing the same packing as the analytical column and immersed in the same water-bath, was intercalated in the runs with TEGDME and TEG. The solutes were of 99 + % purity (Aldrich) and were used as received.

### Procedure

The columns were preconditioned before each run by heating for 4 h at the maximum operating temperature under a flow of hydrogen. All measurements were made in quadruplicate over a temperature range from 25 to 75°C for SQ and TEG and from 15 to 55°C for TEGDME, each in steps of about 5°C. After each run the  $V_g$  of the solute was measured at the lower temperature and compared with the value initially obtained; no significant loss of stationary phase could be detected. On-column injection of the solutes in the vapour form were made with 100- and 250- $\mu$ l Hamilton syringes. Carrier gas flow-rate measurements (about 30 ml/min) were started as soon as the solute was injected, and repeated as many times as was possible during the time required for its elution.

### Data treatment

Specific retention volumes were calculated from corrected peak retention times and operating conditions using the expression derived by Littlewood *et al.*<sup>20</sup>.  $\Delta\bar{G}_1^0$  values were calculated by means of eqn. 1 using mixed second virial coefficients computed from the corresponding states equation of McGlashan and Potter<sup>21</sup>. Critical constants for the pure compounds were taken from the compilation by Kudchadker *et al.*<sup>22</sup>; critical volumes and temperatures for the mixtures were calculated by means of the Lorentz rule and the equation proposed by Hudson and McCoubrey<sup>23</sup>, respectively.

Temperatures, which were measured with greater accuracy than the retention volumes, were considered to be error free. The coefficients of variation, C.V. =  $[s(V_g)/\bar{V}_g] \cdot 100$ , where  $\bar{V}_g$  represents the mean and  $s(V_g)$  the standard deviation for the sample of data obtained at a given temperature, ranged between 0.05 and 0.25%. As the influence of temperature on the C.V. values calculated for a given run was erratic, it was assumed that the retention volumes were affected by the same percentage random error over all the temperature range. In other words, it was assumed that the experimental data resulting from a run can be considered as a set of  $\ln V_g$  values with constant precision, measured at exactly known temperatures. On the basis of this simplifying hypothesis,  $\Delta\bar{G}_1^0/T$  data were fitted to eqn. 9 by means of least-squares multiple linear regression<sup>19</sup>. Best estimates of the  $b_j$  coefficients and their standard deviations were thus obtained; these, in turn, were transformed into thermodynamic functions by means of eqns. 6 and 7.

## RESULTS AND DISCUSSION

The results of the regression analysis for  $q = 0, 1$  and  $2$  are given in Tables I–III. The values for runs A and B in Tables I and II correspond to regressions performed with experimental data obtained in this work (eleven points per run), whereas those for run W correspond to regressions performed on the seven data points reported by Wicarová *et al.*<sup>24</sup>. Values for runs TEG A, TEG B and TEGDME in Table III correspond to the fitting of the experimental data obtained using TEG (eleven points per run) or TEGDME (nine points) as the stationary phase. The  $s$  values are the residual standard deviations, *i.e.*, the square root of the quotient between the residual sum of squares for the  $N$  observed values about the corresponding regression equation (as defined by  $q$ ) and the number of degrees of freedom,  $N - q - 2$ ;  $s$  is an estimator of the standard error in the measurement of  $\Delta\bar{G}_1^0/T$ . Numbers preceded by  $\pm$  are the standard deviations of the thermodynamic properties, calculated from  $s$  and from the elements of the inverse matrix. Values for the thermodynamic properties and for their standard deviations at the reference temperature are given in the tables; however, values at any other temperature within the experimental range are easily calculated by means of the computer program, and are independent of the chosen reference temperature. Figures in parentheses are the percentage significance level for the values of the thermodynamic functions; they were calculated by the  $t$ -test and represent estimates of the probability that the value of the function calculated in the last place for a given value of  $q$  differs from zero by chance.

The value of  $s$  suffers a considerable decrease on passing from  $q = 0$  to  $q = 1$ , and the values obtained for  $\Delta\bar{C}_{p1,0}^0$  are significantly different from zero in all instances;

TABLE I

STANDARD PARTIAL MOLAR THERMODYNAMIC PROPERTIES FOR SOLUTIONS OF BENZENE IN SQUALANE AT  $\theta = 323.15$  K

| Run <sup>a</sup> | Parameter   | $q = 0$           | $q = 1$                   | $q = 2$                   |
|------------------|---|-------------------|---------------------------|---------------------------|
| A                | $s \times 10^3$   | 11.725            | 4.852                     | 5.089                     |
| B                |   | 11.766            | 8.181                     | 7.701                     |
| W                |   | 12.796            | 7.428                     | 8.567                     |
| A                | $\Delta\bar{G}_{1,0}^0$   | $-944.3 \pm 1.18$ | $-940.8 \pm 0.71$         | $-940.7 \pm 0.78$         |
| B                |   | $-947.9 \pm 1.15$ | $-944.9 \pm 1.22$         | $-945.0 \pm 1.16$         |
| W                |   | $-935.9 \pm 1.57$ | $-932.9 \pm 1.27$         | $-932.9 \pm 1.56$         |
| A                | $\Delta\bar{H}_{1,0}^0$   | $-7250 \pm 24$    | $-7276 \pm 11$            | $-7264 \pm 26$            |
| B                |   | $-7283 \pm 24$    | $-7273 \pm 17$            | $-7218 \pm 42$            |
| W                |   | $-7320 \pm 44$    | $-7274 \pm 29$            | $-7280 \pm 77$            |
| A                | $\Delta\bar{C}_{p1,0}^0$  |                   | $9.42 \pm 1.412 (<0.1\%)$ | $9.94 \pm 1.781$          |
| B                |   |                   | $8.19 \pm 2.514 (1.2\%)$  | $7.57 \pm 2.408$          |
| W                |   |                   | $15.46 \pm 4.695 (3.4\%)$ | $15.92 \pm 7.699$         |
| A                | $\left(\frac{\partial\Delta\bar{C}_{p1}^0}{\partial T}\right)_\theta$ |                   |                           | $-0.177 \pm 0.342 (63\%)$ |
| B                |   |                   |                           | $-0.798 \pm 0.560 (10\%)$ |
| W                |   |                   |                           | $0.159 \pm 1.870 (>80\%)$ |

<sup>a</sup> Runs A and B, experimental data obtained in this work; run W, experimental data from ref. 26.

TABLE II

STANDARD PARTIAL MOLAR THERMODYNAMIC PROPERTIES FOR SOLUTIONS OF  $n$ -HEXANE IN SQUALANE AT  $\theta = 323.15$  K

| Run <sup>a</sup> | Parameter   | $q = 0$           | $q = 1$                   | $q = 2$                  |
|------------------|---|-------------------|---------------------------|--------------------------|
| A                | $s \times 10^3$   | 15.085            | 9.089                     | 8.410                    |
| B                |   | 12.989            | 4.345                     | 3.890                    |
| W                |   | 10.138            | 4.911                     | 4.747                    |
| A                | $\Delta G_{1,\theta}^0$   | $-711.7 \pm 1.47$ | $-707.4 \pm 1.36$         | $-707.6 \pm 1.26$        |
| B                |   | $-711.6 \pm 1.27$ | $-707.4 \pm 0.65$         | $-707.5 \pm 0.59$        |
| W                |   | $-693.9 \pm 1.24$ | $-691.5 \pm 0.84$         | $-691.1 \pm 0.86$        |
| A                | $\Delta \bar{H}_{1,\theta}^0$   | $-7390 \pm 31$    | $-7377 \pm 19$            | $-7312 \pm 45$           |
| B                |   | $-7393 \pm 26$    | $-7376 \pm 9$             | $-7343 \pm 21$           |
| W                |   | $-7393 \pm 35$    | $-7355 \pm 19$            | $-7398 \pm 43$           |
| A                | $\Delta \bar{C}_{p1,\theta}^0$  |                   | $11.45 \pm 2.793$ (0.4%)  | $10.71 \pm 2.269$        |
| B                |   |                   | $11.35 \pm 1.334$ (<0.1%) | $10.74 \pm 1.247$        |
| W                |   |                   | $12.91 \pm 3.104$ (1.5%)  | $16.35 \pm 4.266$        |
| A                | $\left(\frac{\partial \Delta \bar{C}_{p1}^0}{\partial T}\right)_\theta$ |                   |                           | $-0.936 \pm 0.612$ (18%) |
| B                |   |                   |                           | $-0.484 \pm 0.281$ (14%) |
| W                |   |                   |                           | $1.173 \pm 1.036$ (37%)  |

<sup>a</sup> See Table I.

TABLE III

STANDARD PARTIAL MOLAR THERMODYNAMIC PROPERTIES FOR SOLUTIONS OF BENZENE IN TEG AND TEGDME AT  $\theta = 323.15$  K

| Run    | Parameter   | $q = 0$           | $q = 1$                   | $q = 2$                  |
|--------|---|-------------------|---------------------------|--------------------------|
| TEG A  | $s \times 10^3$   | 15.298            | 6.732                     | 6.064                    |
| TEG B  |   | 14.489            | 5.164                     | 5.521                    |
| TEGDME |   | 12.354            | 4.564                     | 4.959                    |
| TEG A  | $\Delta G_{1,\theta}^0$   | $168.9 \pm 1.49$  | $173.7 \pm 1.01$          | $173.9 \pm 0.92$         |
| TEG B  |   | $172.5 \pm 1.41$  | $177.1 \pm 0.77$          | $177.1 \pm 0.83$         |
| TEGDME |   | $-846.8 \pm 2.01$ | $-848.2 \pm 0.77$         | $-848.1 \pm 0.90$        |
| TEG A  | $\Delta \bar{H}_{1,\theta}^0$   | $-7621 \pm 32$    | $-7604 \pm 14$            | $-7655 \pm 33$           |
| TEG B  |   | $-7603 \pm 30$    | $-7581 \pm 11$            | $-7581 \pm 30$           |
| TEGDME |   | $-8228 \pm 30$    | $-8017 \pm 33$            | $-8006 \pm 55$           |
| TEG A  | $\Delta \bar{C}_{p1,\theta}^0$  |                   | $13.43 \pm 2.165$ (<0.1%) | $14.24 \pm 2.009$        |
| TEG B  |   |                   | $12.84 \pm 1.620$ (<0.1%) | $12.85 \pm 1.840$        |
| TEGDME |   |                   | $13.50 \pm 2.005$ (<0.1%) | $16.08 \pm 9.594$        |
| TEG A  | $\left(\frac{\partial \Delta \bar{C}_{p1}^0}{\partial T}\right)_\theta$ |                   |                           | $0.794 \pm 0.469$ (14%)  |
| TEG B  |   |                   |                           | $0.002 \pm 0.411$ (>80%) |
| TEGDME |   |                   |                           | $0.169 \pm 0.612$ (70%)  |

the  $s$  values for  $q = 2$  are not very different from those for  $q = 1$ , and all the results for  $(\partial \Delta \bar{C}_p^0 / \partial T)_\theta$  are of poor significance. On the other side, the smallest standard errors for the heat of solution are obtained with the three-constant equation; it can be concluded that this equation gives a better fit to the experimental data than the two- or four-constant equation.

The results show a very good reproducibility between runs. In Tables I and II they are compared with those obtained by applying the same regression technique to the experimental data reported by Wicarová *et al.*<sup>24</sup>. They measured the specific retention volumes for benzene and *n*-hexane in SQ in a high-precision instrument; even though their measurements were performed at only seven different temperatures, over a temperature range narrower than ours, each  $V_g$  value represents the arithmetic mean of 15–20 measurements. With the exception of the  $\Delta \bar{C}_{p1,g}^0$  value for benzene in SQ, the comparison with our results is very encouraging. Unfortunately, there are no calorimetric data available for the systems studied in this work.

Corrections for non-ideality of the vapour phase are hardly justifiable when hydrogen is used as the carrier gas: corrected and uncorrected values for the heats of solution of *n*-hexane and benzene differ by less than 5 cal/mol when the equation of McGlashan and Potter<sup>21</sup> is used to calculate second virial coefficients and their dependence on temperature. However, when nitrogen is the carrier gas this difference can amount to 30 cal/mol, and the correction cannot be neglected.

Differences between experimental  $V_g$  values and the values calculated by means of the two-constant equation can amount to a maximum of about 1%, and this at the extremes of a broad temperature range. When the objective is interpolation, the use of more sophisticated regression techniques is not justified, at least for the heat capacity values of the systems studied here.

To summarize, the application of Clarke and Glew's regression method to chromatographic data leads to an improvement in the measurement of thermodynamic solution properties, but not in the interpolation of retention volumes.

#### 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).

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