

CHROM. 12,023

## EFFECT OF ADSORPTION ON SOLUTE RETENTION IN GAS-LIQUID CHROMATOGRAPHY

FRANÇOIS RIEDO\* and E. sz. KOVÁTS

*Laboratoire de Chimie Technique de l'École Polytechnique Fédérale de Lausanne, 1015 Lausanne (Switzerland)*

### SUMMARY

An equation is given that relates the retention volume to partition coefficients and that is easy to interpret in terms of thermodynamic functions. The partition coefficients allowing for the adsorption at the interfaces of the stationary liquids are discussed in the light of the „parallel layer” model of Defay and Prigogine. Proposals are made for the estimation of the different parameters of this model.

### INTRODUCTION

The equation first given by Martin<sup>1</sup> and extended by Martire<sup>2</sup> and Berezkin<sup>3,4</sup> relates the gas chromatographic retention to partition coefficients,  $K$ , as summarized in eqn. 1. The net retention volume of a solute,  $j$ , is given as

$$V_{N,j} = K_j^{(\lambda)} V_\lambda + K_j^{(\lambda\gamma)} A_{\lambda\gamma} + K_j^{(\lambda\sigma)} A_{\lambda\sigma} + K_j^{(\sigma\gamma)} A_{\sigma\gamma} \quad (1)$$

$$K_j^{(\lambda)} = c_j^{(\lambda)} / c_j^{(\gamma)}; K_j^{(\lambda\gamma)} = \Gamma_{j|\lambda}^{(\lambda\gamma)} / c_j^{(\gamma)}; K_j^{(\lambda\sigma)} = \Gamma_{j|\lambda}^{(\lambda\sigma)} / c_j^{(\gamma)}; K_j^{(\sigma\gamma)} = \Gamma_j^{(\sigma)} / c_j^{(\gamma)} \quad (1a)$$

where the superscripts  $\lambda$  and  $\gamma$  refer to the liquid and the gas phase and  $\sigma$  to the surface of the solid support. Concentrations are expressed as molar bulk,  $c$  (mol l<sup>-1</sup>), or molar surface concentrations,  $\Gamma$  (mol m<sup>-2</sup>),  $V_\lambda$  is the volume of the stationary liquid in the column and  $A$  is the corresponding area for an interface indicated by the subscripts. Eqn. 1 gives the net retention volume as a sum of four contributions: (i) due to dissolution of the solute in the bulk of the liquid film (first term), (ii) due to adsorption at the surface of the liquid (second term); (iii) due to adsorption at the liquid-solid interface (third term); and (iv) due to adsorption of the solute at the non-wetted surface of the support (last term).

At a first view it seems to be logical to refer all partition coefficients to a common concentration, the concentration of the solute in the gas phase,  $c_j^{(\gamma)}$ . In this paper it will be shown that eqn. 2, derived by simple transformation of eqn. 1, accounts

\* Partially from the Doctoral Thesis of F.R.

more clearly for the thermodynamic relationships of the individual partition coefficients:

$$V_{N,j} = K_j^{(\lambda)} [V_\lambda + \kappa_j^{(\lambda\gamma)} A_{\lambda\gamma} + \kappa_j^{(\lambda\sigma)} A_{\lambda\sigma}] + \chi_j^{(\sigma\gamma)} A_{\sigma\gamma} \quad (2)$$

where

$$K_j^{(\lambda)} = c_j^{(\lambda)} / c_j^{(\gamma)} \text{ and } \chi_j^{(\sigma\gamma)} = K_j^{(\sigma\gamma)} = \Gamma_j^{(\sigma)} / c_j^{(\gamma)} \quad (2a)$$

(as before) but

$$\kappa_j^{(\lambda\gamma)} = \Gamma_{j|\lambda}^{(\lambda\gamma)} / c_j^{(\lambda)} \text{ and } \kappa_j^{(\lambda\sigma)} = \Gamma_{j|\lambda}^{(\lambda\sigma)} / c_j^{(\lambda)} \quad (2b)$$

Two partition coefficients,  $K_j^{(\lambda)}$  and  $\chi_j^{(\sigma\gamma)}$ , refer as in eqn. 1 to the concentration of the solute in the gas phase but, for  $\kappa_j^{(\lambda\sigma)}$  and  $\kappa_j^{(\lambda\gamma)}$ , coefficients accounting for adsorption at the liquid interfaces, the reference concentration is that in the bulk of the liquid. Such a form was suggested implicitly by the results and evaluation described by Martin<sup>5</sup> and Martire<sup>2</sup>.

#### THE INTERFACE PARTITION COEFFICIENTS, $\kappa_j^{(\lambda\gamma)}$ AND $\kappa_j^{(\lambda\sigma)}$

Actually, liquid interfaces are not autonomous phases. There is only an adsorption, positive or negative, if the concentration in the surface phase is different from that of the bulk. Let us suppose first that the gas phase is composed only of the solute,  $j$ , or in other words that the inert gas present (carrier gas) is an ideal gas insoluble in the liquid and it is not adsorbed in the system. In this case there are three phases,  $\gamma$ ,  $\lambda$  and  $\sigma$ , the solute being soluble in two of them,  $\gamma$  and  $\lambda$ , and insoluble in  $\sigma$ . For the general case the excess surface concentration,  $\Gamma_j^{(\lambda\beta)}$  (the relative adsorption of the solute,  $j$ , to that of the solvent,  $\lambda$ ), at the interface between the liquid and the phase  $\beta$  is given by<sup>6</sup>

$$\Gamma_{j|\lambda}^{(\lambda\beta)} = \Gamma_j^{(\lambda\beta)} - \Gamma_\lambda^{(\lambda\beta)} \cdot \frac{c_j^{(\lambda)} - c_j^{(\beta)}}{c_\lambda^{(\lambda)} - c_\lambda^{(\beta)}} \quad (3)$$

where the phase  $\beta$  is either  $\gamma$  or  $\sigma$ . Thereby, the Gibbs' dividing plane is situated between the two phases and there will always be relative adsorption if the concentration of the solute  $j$  (or  $\lambda$ ) near the dividing plane is different on either side from its concentration at the corresponding side in the bulk. As an example, at the liquid-gas interface there will be adsorption either if the concentration of the solute near the dividing plane is different from that of the solute in the gas phase or if the concentration of the solute on the other side of the dividing plane, at the surface of liquid, is different from that in the bulk. With the aid of eqn. 3, let us examine the different adsorptions of the solute,  $j$ , in the system under consideration.

For the relative adsorption at the liquid-gas interface we obtain ( $\beta = \gamma$ )

$$\Gamma_{j|\lambda}^{(\lambda\gamma)} = \Gamma_j^{(\lambda\gamma)} - \Gamma_\lambda^{(\lambda\gamma)} \cdot \frac{c_j^{(\lambda)} - c_j^{(\gamma)}}{c_\lambda^{(\lambda)} - c_\lambda^{(\gamma)}} \approx \Gamma_j^{(\lambda\gamma)} - \Gamma_\lambda^{(\lambda\gamma)} \cdot \frac{c_j^{(\lambda)}}{c_\lambda^{(\lambda)}} \quad (4)$$

Following the generally accepted assumption (see, for instance, ref. 7) that the gas phase is homogeneous down to the Gibbs' dividing plane and therefore there is no adsorption from the side of the gas phase, we obtain the very close approximation indicated on the right-hand side in eqn. 4 [this assumption seems to give good results even for slightly soluble gases (nitrogen in water<sup>8</sup>) and it will be even better for conditions normally valid in gas chromatography where  $c_j^{(\gamma)} \ll c_j^{(\lambda)}$  and  $c_\lambda^{(\gamma)} \rightarrow 0$ ].

For the relative adsorption of the solute at the liquid-solid interface ( $\beta = \sigma$ ), the Gibbs' dividing surface will be placed exactly at the surface of the solid. Considering that neither of the components,  $\lambda$  or  $j$ , is soluble in the solid, we obtain

$$\Gamma_{j/\lambda}^{(\lambda\sigma)} = \Gamma_j^{(\lambda\sigma)} - \Gamma_\lambda^{(\lambda\sigma)} \cdot \frac{c_j^{(\lambda)} - c_j^{(\sigma)}}{c_\lambda^{(\lambda)} - c_\lambda^{(\sigma)}} = \Gamma_j^{(\lambda\sigma)} - \Gamma_\lambda^{(\lambda\sigma)} \cdot \frac{c_j^{(\lambda)}}{c_\lambda^{(\lambda)}} \quad (5)$$

It is interesting that at very low solute concentrations, where both  $\Gamma_j^{(\lambda\beta)}$  and  $c_j^{(\lambda)} \rightarrow 0$  [and at the same time  $\Gamma_\lambda^{(\lambda\beta)} \rightarrow \Gamma_\lambda^0$  and  $c_\lambda^{(\lambda)} \rightarrow c_\lambda^0$  where the superscript zero refers to the pure substance], and further, if  $c_j^{(\gamma)} \ll c_j^{(\lambda)}$ , the combination of eqn. 4 with eqn. 2b and eqn. 5 with eqn. 2b gives

$$\kappa_j^{(\lambda\gamma)} = [\Gamma_j^{(\lambda\gamma)}/c_j^{(\lambda)}] - (\Gamma_\lambda^0/c_\lambda^0); \quad c_j^{(\lambda)} \rightarrow 0 \quad (6)$$

and

$$\kappa_j^{(\lambda\sigma)} = [\Gamma_j^{(\lambda\sigma)}/c_j^{(\lambda)}] - (\Gamma_\lambda^0/c_\lambda^0); \quad c_j^{(\lambda)} \rightarrow 0 \quad (7)$$

where the term  $\Gamma_\lambda^0/c_\lambda^0 \equiv C^{(\lambda)}$  is constant for  $c_j^{(\lambda)} \rightarrow 0$  for a given solvent. The value of  $C^{(\lambda)}$ , however, is not independent of the model chosen for the calculation of  $\Gamma_\lambda^0$  and  $\Gamma_j$ . After rearrangement of eqns. 6 and 7 we obtain

$$\Gamma_j^{(\lambda\beta)} = [\kappa_j^{(\lambda\beta)} + C^{(\lambda)}]c_j^{(\lambda)}; \quad c_j^{(\lambda)} \rightarrow 0 \quad (8)$$

$\beta = \gamma \text{ or } \sigma$

meaning that not only the relative but also the actual surface concentration of the solute at the interfaces  $\lambda\gamma$  and  $\gamma\sigma$  is proportional to the concentration of the solute in the bulk,  $c_j^{(\lambda)}$ . The consequences of eqn. 8 for liquid-solid chromatography will be discussed in a forthcoming paper.

Returning to our main topic, eqns. 4 and 5 (and also eqn. 8) show that the relative adsorption of the solute at the solvent interfaces is a direct function of its concentration in the bulk.

In the Gibbs' equation:

$$d\gamma^{(\lambda\beta)} = -s_{j/\lambda}^{(\lambda\beta)}dT - \Gamma_{j/\lambda}^{(\lambda\beta)}d\mu_j \quad (9)$$

$\gamma$  is the surface or interfacial tension of the solution,  $\beta$  is equal to  $\gamma$  or  $\sigma$  and  $s_{j/\lambda}^{(\lambda\beta)}$  is the relative surface entropy<sup>6</sup>. For the dependence of the surface concentration of the solution on the concentration of the solute in the bulk [expressed in molality,  $m_j$  (mol kg<sup>-1</sup>)] we obtain for constant temperature

$$[\partial\gamma^{(\lambda\beta)}/\partial m_j^{(\lambda)}]_T = -\Gamma_{j/\lambda}^{(\lambda\beta)} [\partial\mu_j/\partial m_j^{(\lambda)}]_T \quad (10)$$

Henry's law for ideal dilute solutions gives

$$p_j = g_j m_j^{(\lambda)}; \quad p_j \rightarrow 0 \quad (11)$$

where  $p_j$  is the partial pressure of the solute in the gas phase and  $g_j$  is Henry's molal coefficient. Eqns. 12 and 13 are valid under the same conditions:

$$d\mu_j = RT d \ln p_j \quad \text{for } p_j \rightarrow 0 \quad (12)$$

$$\kappa_j^{(\lambda\beta)} = \Gamma_{j/\lambda}^{(\lambda\beta)} / c_j^{(\lambda)} = \Gamma_{j/\lambda}^{(\lambda\beta)} / m_j^{(\lambda)} \varrho_\lambda \quad (13)$$

$$\text{for } c_j^{(\lambda)} \rightarrow 0 \quad m_j^{(\lambda)} \rightarrow 0$$

where  $\varrho_\lambda$  is the density of the solvent. Combination of eqns. 10–13 gives

$$\kappa_j^{(\lambda\beta)} = - (1/\varrho_\lambda RT) (\partial \gamma^{(\lambda\beta)} / \partial m_j^{(\lambda)}); \quad m_j^{(\lambda)} \rightarrow 0 \quad (14)$$

This relationship was first given by Martin<sup>5</sup> for the interface  $\lambda\gamma$  in gas chromatography.

In order to find the temperature dependence of  $[\partial \gamma^{(\lambda\beta)} / \partial m_j^{(\lambda)}]_{T, m_j^{(\lambda)}=0}$  we have to examine the behaviour of this derivative around a standard temperature  $T^\dagger$ :

$$[\partial \gamma^{(\lambda\beta)} / \partial m_j^{(\lambda)}]_{m_j^{(\lambda)}=0} = [\partial \gamma^{(\lambda\beta)} / \partial m_j^{(\lambda)}]_{T^\dagger, m_j^{(\lambda)}=0} + [\partial^2 \gamma^{(\lambda\beta)} / \partial m_j^{(\lambda)} \partial T]_{T^\dagger, m_j^{(\lambda)}=0} (T - T^\dagger) \quad (15)$$

The expression

$$[\partial^2 \gamma^{(\lambda\beta)} / \partial m_j^{(\lambda)} \partial T]_{T^\dagger, m_j^{(\lambda)}=0} = - [\partial s^{(\lambda\beta)} / \partial m_j^{(\lambda)}]_{T^\dagger, m_j^{(\lambda)}=0} \quad (15a)$$

is the initial change of entropy of the solvent surface with the concentration,  $m_j^{(\lambda)}$  [note that  $s^{(\lambda\beta)}$  is not the same as  $s_{j/\lambda}^{(\lambda\beta)}$  in eqn. 9]. Experimental evidence shows<sup>9</sup> that its value is small and that it is constant in a relatively wide temperature range. Substitution of eqn. 15 into eqn. 14 gives finally

$$\kappa_j^{(\lambda\beta)} = - \frac{1}{\varrho_\lambda RT} \left\{ \left[ \frac{\partial \gamma^{(\lambda\beta)}}{\partial m_j^{(\lambda)}} \right]_{T^\dagger} - \left[ \frac{\partial s^{(\lambda\beta)}}{\partial m_j^{(\lambda)}} \right]_{T^\dagger} (T - T^\dagger) \right\} = - \frac{Y_j^{(\lambda\beta)}}{\varrho_\lambda RT}; \quad m_j^{(\lambda)} = 0 \quad (16)$$

where  $Y_j^{(\lambda\beta)}$  is introduced for the expression in brackets for simplicity. Eqn. 16 shows that  $\kappa_j^{(\lambda\beta)}$  depends essentially on the inverse of the temperature. The temperature dependence of  $Y_j^{(\lambda\beta)}$  is small and linear. This relationship is valid for both interfaces of the liquid, i.e., the liquid-gas and liquid-solid interfaces. In the first instance,  $\gamma^{(\lambda\gamma)}$  is the surface tension of the stationary liquid and in the second,  $\gamma^{(\lambda\sigma)}$  is the interfacial tension between the liquid and the solid.

THE PARTITION COEFFICIENTS,  $K_j^{(\lambda)}$  AND  $\chi_j^{(\sigma)}$ 

The interpretation of these coefficients will be given for the sake of completeness. Assuming that the carrier gas is an ideal gas insoluble in the solvent,  $\lambda$ ,

$$K_j^{(\lambda)} = \rho_\lambda RT / 1000 g_j; \quad m_j^{(\lambda)} \rightarrow 0 \quad (17)$$

where  $g_j$  is Henry's molal coefficient. Under the same conditions

$$\chi_j^{(\sigma)} = RT / k_j^{(\sigma)}; \quad \Gamma_j^{(\sigma)} \rightarrow 0 \quad (18)$$

where  $k_j^{(\sigma)} = p_j / \Gamma_j^{(\sigma)}$  is Henry's coefficient for the solid surface, which is the inverse of the initial slope (at  $p_j = 0$ ) of the adsorption isotherm  $\Gamma_j^{(\sigma)} = \Gamma_j^{(\sigma)}(p_j)$ .

The thermodynamic relation for  $g_j$  is

$$RT \ln g_j = \Delta \mu_j^{(\lambda)} = \Delta H_j^{(\lambda)} - T \Delta S_j^{(\lambda)} + \Delta C_{p,j}^{(\lambda)} [T - T^\dagger - T \ln (T/T^\dagger)] \quad (19)$$

where  $R = 1.98719 \text{ cal mol}^{-1} \text{ }^\circ\text{K}^{-1}$  is the gas constant to give the thermodynamic functions in calories,  $\Delta \mu_j^{(\lambda)}$  is the difference of the standard chemical potential of the solute,  $j$ , between the gas phase and the liquid phase at ideal dilution and  $\Delta H_j^{(\lambda)}$ ,  $\Delta S_j^{(\lambda)}$  and  $\Delta C_{p,j}^{(\lambda)}$  are the corresponding differences of the molar enthalpy, entropy and heat capacity at constant pressure, all functions measured at  $T^\dagger$  [it should be noted that  $\Delta \mu_j^{(\lambda)}$  is related to Henry's molal coefficient,  $g_j$ , meaning that the standard state in the solution is given in molality<sup>10</sup>].

The analogous expression for  $k_j^{(\sigma)}$  is

$$RT \ln k_j^{(\sigma)} = \Delta \mu_j^{(\sigma)} = \Delta H_j^{(\sigma)} - T \Delta S_j^{(\sigma)} + \Delta C_{p,j}^{(\sigma)} [T - T^\dagger - T \ln (T/T^\dagger)] \quad (20)$$

with analogous definitions of the symbols as above but referred to the solid surface,  $\sigma$ .

## RELATIONSHIPS FOR RETENTION VOLUMES

Combination of eqns. 2, 16, 17 and 18 gives the net retention volume as a function of terms of thermodynamic parameters as

$$V_{N,j} = \frac{RT}{1000 g_j} \left[ w_\lambda - \frac{Y_j^{(\lambda\gamma)}}{\mathcal{R}T} \cdot A_{\lambda\gamma} - \frac{Y_j^{(\lambda\sigma)}}{\mathcal{R}T} \cdot A_{\lambda\sigma} \right] + \frac{RT}{k_j^{(\sigma)}} \cdot A_{\sigma\gamma} \quad (21)$$

Thereby, the following gas constants have to be used:  $R = 82.0544 \text{ ml atm mol}^{-1} \text{ }^\circ\text{K}^{-1}$  and  $\mathcal{R} = 8.31440 \text{ joule abs. mol}^{-1} \text{ }^\circ\text{K}^{-1}$ , together with the individual terms measured in the following units:  $V_N$  (ml);  $w_\lambda$  (g);  $A$  ( $\text{m}^2$ );  $Y$  ( $\text{erg kg cm}^{-2} \text{ mol}^{-1}$ );  $g_j$  ( $\text{atm kg mol}^{-1}$ );  $k_j^{(\sigma)}$  ( $\text{atm m}^2 \text{ mol}^{-1}$ ).

The specific retention volume measured at the column temperature,  $V_{g,j} = V_{N,j} / w_\lambda$ , is given by

$$V_{g,j} = V_{g,j}^0 \left[ 1 - \frac{Y_j^{(\lambda\gamma)}}{\mathcal{R}T} \cdot \frac{A_{\lambda\gamma}}{w_\lambda} - \frac{Y_j^{(\lambda\sigma)}}{\mathcal{R}T} \cdot \frac{A_{\lambda\sigma}}{w_\lambda} \right] + \frac{RT}{k_j^{(\sigma)}} \cdot \frac{A_{\sigma\gamma}}{w_\lambda} \quad (22)$$

Thereby  $V_{g,j}^0 = RT/1000 g_j$  is the specific retention volume without any adsorption effects.

The essential feature of eqns. 21 and 22 is that they show the retention volume as explicit functions of the coefficients  $g_j$ ,  $k_j^{(\sigma)}$  and the two  $Y_j$ , which are easy to interpret. The temperature dependence of  $g_j$  and  $k_j$  is strong and they vary exponentially with  $1/T$ . In contrast, the two terms allowing for the adsorption at the liquid interfaces are essentially different. Their main temperature dependence is proportional to that of  $g_j$ , and their relative importance, expressed in  $Y$ , diminishes slightly with  $1/T$ .

For the experimental determination of the four parameters  $g_j$ ,  $k_j^{(\sigma)}$ ,  $Y_j^{(\lambda\gamma)}$  and  $Y_j^{(\lambda\sigma)}$ , specific retention volumes should be available at different values of  $A_{\lambda\gamma}/w_\lambda$ ,  $A_{\lambda\sigma}/w_\lambda$  and  $A_{\sigma\gamma}/w_\lambda$ . Unfortunately, the parameters  $A_{\lambda\gamma}/w_\lambda$  and  $A_{\lambda\sigma}/w_\lambda$  are closely correlated. Actually, the areas of the interfaces  $\lambda\gamma$  and  $\lambda\sigma$  are the two sides of the duplex film and therefore about equal. However, in certain instances, by the use of a first support one of the parameters,  $Y_j$ , can be determined experimentally and accepted for the evaluation of the results on a second support.

A fruitful proposal for the estimation of the areas is that of Martin<sup>1</sup>. Assuming that the stationary phase wets completely the solid support and that it forms a film of uniform thickness, it was proposed that

$$A_{\sigma\gamma} = 0 \text{ and } A_{\lambda\gamma} = A_{\lambda\sigma} = a_\sigma w_\sigma \equiv A_\sigma$$

where  $a_\sigma$  is the specific surface area of the solid support and  $w_\sigma$  is its weight in the column. Thus, eqn. 22, on introducing the variable  $\zeta = a_\sigma w_\sigma / w_\lambda$ , yields the well known equation

$$V_{g,j} = V_{g,j}^0 \{1 - [Y_j^{(\lambda\gamma)} + Y_j^{(\lambda\sigma)}] \zeta / RT\} \quad (23)$$

Eqn. 23 permits the experimental evaluation of the sum of the two interfacial adsorption terms with the knowledge of  $a_\sigma$ , from data measured at different values of  $\zeta$ . For partially wetted supports this model can be extended by assuming that

$$A_{\sigma\gamma} + A_{\lambda\gamma} = A_\sigma; \quad \alpha = A_{\lambda\gamma}/A_\sigma = A_{\lambda\sigma}/A_\sigma$$

where  $\alpha$  is the proportion of the surface wetted by the stationary phase, the proportion of the non-wetted part being  $1-\alpha$ , giving

$$V_{g,j} = V_{g,j}^0 \{1 - \alpha [Y_j^{(\lambda\gamma)} + Y_j^{(\lambda\sigma)}] \zeta / RT\} + (1 - \alpha) RT \zeta / k_j^{(\sigma)} \quad (24)$$

Eqn. 24 permits the evaluation of  $k_j^{(\sigma)}$  and  $\alpha$  with the knowledge of  $V_{g,j}^0$  and of the sum of the interfacial terms. The difficulty lies in the fact that the partially wetted support is partially wetted because its surface energy is different from that of the completely wetted support, and consequently

$$Y_j^{(\lambda\sigma_w)} \neq Y_j^{(\lambda\sigma_n)} \quad (25)$$

where  $w$  refers to the wetted and  $n$  to the partially wetted interface. Martin<sup>5</sup> and Martire<sup>2</sup> showed that for polar stationary liquids and small molecules as solutes the

term  $Y_j^{(\lambda\sigma)} \approx 0$  for the usual gas chromatographic supports. With this assumption, data on the two supports, wetted and non-wetted by the stationary phase, allow for the evaluation of  $k_j^{(\sigma)}$  values, but of course for only the low-energy, partially wetted support.

#### MODEL FOR THE INTERPRETATION OF $Y_j^{(\lambda\gamma)}$

In this paper only the term  $Y_j^{(\lambda\gamma)}$  will be discussed and therefore, for the sake of simplicity, all superscripts referring to this interface,  $\lambda\gamma$ , will be omitted throughout this section. The parameter  $g_j$  and the interpretation of the related thermodynamic functions are the subject of many papers on gas-liquid chromatography. The same is valid for the Henry coefficient,  $k_j^{(\sigma)}$ , in treatments of gas-solid chromatography. Finally, the term  $Y_j^{(\lambda\sigma)}$ , important in liquid-solid chromatography, is negligible in gas-liquid chromatography if supports of low surface energy are used and/or the surface tension of the applied stationary phase is considerable<sup>2</sup>.

The surface tension of an athermal mixture of molecules of equal size ("perfect mixture") as a function of the composition was given by Zhukhovitskii<sup>11</sup>. Assuming that the adsorption at the liquid surface is related only to a surface phase one monolayer thick ("monolayer model"), the expression for the surface tension of the mixture,  $\gamma$ , is given by

$$\exp(-\gamma\omega/\mathcal{R}'T) = x_j^{(\lambda)} \exp(-\gamma_j\omega/\mathcal{R}'T) + x_\lambda^{(\lambda)} \exp(-\gamma_\lambda\omega/\mathcal{R}'T) \quad (26)$$

where  $\gamma_j$  and  $\gamma_\lambda$  (erg cm<sup>-2</sup>) are the surface tensions of the pure liquids,  $j$  and  $\lambda$ ;  $\omega$  is the average molar surface of a monomolecular layer of  $j$  and  $\lambda$ ;  $x_j^{(\lambda)}$  and  $x_\lambda^{(\lambda)}$  are the molar fractions in the bulk of the mixture; and  $\mathcal{R}'$  (erg mol<sup>-1</sup> °K<sup>-1</sup>) = 10<sup>7</sup>  $\mathcal{R}$ . By using the relationship

$$\left[ \frac{\partial\gamma}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0} = \left[ \frac{\partial\gamma}{\partial x_j^{(\lambda)}} \right]_{x_j^{(\lambda)}=0} \left[ \frac{\partial x_j^{(\lambda)}}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0} \quad (27)$$

one calculates from eqn. 26 for the case where component  $j$  is at infinite dilution

$$\left[ \frac{\partial\gamma}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0}^* = \frac{M_\lambda \mathcal{R}'T}{1000 \omega} \{1 - \exp[(\gamma_\lambda - \gamma_j)\omega/\mathcal{R}'T]\} \quad (28)$$

where  $M_\lambda$  is the molar mass (g mol<sup>-1</sup>) of the component  $\lambda$ , identified as the solvent. The asterisk refers to the specific assumptions under which eqn. 26 is valid. The exponential in brackets can be expanded around  $(\gamma_\lambda - \gamma_j)\omega/\mathcal{R}'T = 0$ . Retaining the two first terms, we obtain

$$\left[ \frac{\partial\gamma}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0}^* \approx \frac{M_\lambda}{1000} \left[ -(\gamma_\lambda - \gamma_j) - \frac{1}{2}(\gamma_\lambda - \gamma_j)^2 \cdot \frac{\omega}{\mathcal{R}'T} \right] \quad (29)$$

If the components differ in size and the solution is non-athermal, the relation of  $\gamma$  to the composition is as given by Defay<sup>12</sup>, generalizing the treatment of Prigogine and Maréchal<sup>13</sup> for the athermal mixtures (see also ref. 7). The following assumptions were made. Let us assume first that the mixture of small and large molecules is non-

athermal but the entropy of mixing is that of an athermal mixture ("regular" mixture). Let us assume further that the large elongated molecules are parallel to the surface ("parallel-layer model") and that adsorption will occur only in this layer. Under these assumptions

$$\gamma = \gamma_j \Phi_j^{(\lambda)} + \gamma_\lambda \Phi_\lambda^{(\lambda)} - \frac{q_j \beta}{\omega_j} \cdot \Phi_j^{(\lambda)} \Phi_\lambda^{(\lambda)} - \frac{1}{2} \cdot \frac{r_\lambda \Phi_j^{(\lambda)} \Phi_\lambda^{(\lambda)}}{\Phi_j^{(\lambda)} + r_\lambda \Phi_\lambda^{(\lambda)}} \left\{ \gamma_\lambda - \gamma_j + \frac{q_j \beta}{\omega_j} [\Phi_\lambda^{(\lambda)} - \Phi_j^{(\lambda)}] \right\}^2 \cdot \frac{\omega_j}{\mathcal{R}'T} \quad (30)$$

where  $\Phi_j^{(\lambda)}$  and  $\Phi_\lambda^{(\lambda)}$  are volume fractions in the bulk,  $\omega_j$  is the molar surface of a mono-molecular layer of the substance  $j$  (small molecules) and  $q_j$  is the molar enthalpy of mixing ("configurational enthalpy"), supposedly independent of the composition of the mixture. The small molecule has a certain coordination number in the bulk higher than that in the surface layer. The proportion of the coordination number lost referred to that in the bulk is  $\beta$ . The large molecule is considered to be composed of  $r_\lambda$  segments, every segment having the same volume as the solute  $j$ . By using the rule

$$\left[ \frac{\partial \gamma}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0} = \left[ \frac{\partial \gamma}{\partial \Phi_j^{(\lambda)}} \right]_{\Phi_j^{(\lambda)}=0} \left[ \frac{\partial \Phi_j^{(\lambda)}}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0} \quad (31)$$

we obtain for the ideal dilute solution of  $j$  in  $\lambda$

$$\left[ \frac{\partial \gamma}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0} = \frac{M_\lambda}{1000 r_\lambda} \left[ - \left( \gamma_\lambda - \gamma_j + \frac{q_j \beta}{\omega_j} \right) - \frac{1}{2} \left( \gamma_\lambda - \gamma_j + \frac{q_j \beta}{\omega_j} \right)^2 \frac{\omega_j}{\mathcal{R}'T} \right] \quad (32)$$

There is a close analogy between the form of eqn. 32 and 29, suggesting that eqn. 32 is also obtained by expansion of an exponential, analogously to the derivation of eqn. 29 from 28. Therefore, it follows that

$$\left[ \frac{\partial \gamma}{\partial m_j^{(\lambda)}} \right]_{m_j^{(\lambda)}=0} = \frac{M_\lambda \mathcal{R}'T}{1000 r_\lambda \omega_j} \left\{ 1 - \exp \left[ \left( \gamma_\lambda - \gamma_j + \frac{q_j \beta}{\omega_j} \right) \frac{\omega_j}{\mathcal{R}'T} \right] \right\} \quad (33)$$

The practical use of eqn. 33 presumes the knowledge or estimation of a series of parameters. The molecular mass of the solvent,  $M_\lambda$ , must be known and the surface tension of the pure substances,  $\gamma_j$  and  $\gamma_\lambda$ , must be available at the desired (column) temperature. The next section is devoted to a possible estimation of the configurational enthalpy,  $q_j$ , from gas chromatographic data. From the definition of  $r_\lambda$  it follows that this number can be approximated by

$$r_\lambda = V_\lambda / V_j \quad (34)$$

where  $V_\lambda$  and  $V_j$  are the molar volumes of the solvent and of the solute. For the estimation of the remaining parameters  $\omega_j$  and  $\beta$ , two methods are proposed as follows.

#### Method A

First a substance,  $z$ , is needed whose solution is athermal, proved to be ather-



mal by calorimetric measurements or by a good working hypothesis (in the case of polymeric solvents, "segment"-like molecules are to be preferred: dimer, trimer, etc.). For such substances the configurational energy,  $q_z$ , is zero. Assuming that for any substance

$$\omega_\lambda/\omega_j = V_\lambda/V_j \quad (35)$$

substitution of eqns. 34 and 35 into eqn. 33 gives

$$\left[ \frac{\partial \gamma}{\partial m_z^{(A)}} \right]_{m_z^{(A)}=0}^{(ath)} = \frac{M_\lambda \mathcal{R}'T}{1000 \omega_\lambda} \left\{ 1 - \exp \left[ \left( \gamma_\lambda - \gamma_z \right) \frac{V_z}{V_\lambda} \cdot \frac{\omega_\lambda}{\mathcal{R}'T} \right] \right\} \quad (36)$$

Thereby, the only unknown parameter will be the molar surface of the solvent,  $\omega_\lambda$ , if experimental (E) values for  $(\partial \gamma / \partial m_z)_{m_z=0}^{(E)}$  are available from gas chromatographic (or static) measurements. This value,  $\omega_\lambda^{(A)}$ , will be now accepted for the general case (the superscript A refers to Method A). Having experimental values,  $(\partial \gamma / \partial m_j)_{m_z=0}^{(E)}$ , at hand we can equate them as indicated:

$$\left[ \frac{\partial \gamma}{\partial m_j^{(A)}} \right]_{m_j^{(A)}=0}^{(E)} = \frac{M_\lambda \mathcal{R}'T}{1000 \omega_\lambda^{(A)}} \left\{ 1 - \exp \left[ \left( \gamma_\lambda - \gamma_j \right) \frac{V_j}{V_\lambda} \cdot \frac{\omega_\lambda^{(A)}}{\mathcal{R}'T} + \frac{q_j \beta}{\mathcal{R}'T} \right] \right\} \quad (37)$$

The unknown quantity,  $q_j \beta$ , can now be calculated giving values related, of course, to this method of proceeding:  $(q_j \beta)^{(A)}$ . Comparison of these results with values for  $q_j$  from other sources [e.g., by plotting  $(q_j \beta)^{(A)}$  versus  $q_j$ ] permits the evaluation of  $\beta$ .

#### Method B

The molar surface of the solute is assumed to be given by

$$\omega_j = N^{1/3} V_j^{2/3} = 8.445 \cdot 10^7 V_j^{2/3} \quad (38)$$

Accepting again eqns. 34 and 35, substitution of eqn. 38 into eqn. 39 gives

$$\left[ \frac{\partial \gamma}{\partial m_j^{(A)}} \right]_{m_j^{(A)}=0}^{(E)} = \frac{\rho_\lambda V_j^{1/3} \mathcal{R}'T}{1000 N^{1/3}} \left\{ 1 - \exp \left[ \left( \gamma_\lambda - \gamma_j \right) \frac{N^{1/3} V_j^{2/3}}{\mathcal{R}'T} + \frac{q_j \beta}{\mathcal{R}'T} \right] \right\} \quad (39)$$

Values of  $(q_j \beta)^{(B)}$  can now be calculated, proceeding as for Method A.

For practical work, note that

$$4.184 \cdot 10^7 (q_j \beta)^{(A \text{ or } B)} \text{ cal mol}^{-1} = (q_j \beta)^{(A \text{ or } B)} \text{ erg mol}^{-1} \quad (40)$$

#### ESTIMATION OF THE CONFIGURATIONAL ENTHALPY FROM GAS CHROMATOGRAPHIC DATA

The configurational enthalpy, identified as the heat of mixing of the solute,  $j$ , with a stationary phase, X, could of course be calculated as the difference of the enthalpy of dissolution  $\Delta H_j^{(X)}$  and the enthalpy of condensation  $\Delta^{\text{cond}} H_j^0$ . The first can be calculated from gas chromatographic data (cf., eqn. 19); the determination of the

latter involves a certain amount of experimental work on a larger sample of the pure compound. Gas chromatographic data can be determined with traces of a compound, not necessarily pure, with high precision and little effort. In the following it will be shown that the configurational enthalpy in the liquid, X, might be estimated by comparing data on X with those on a non-polar stationary phase, A. By definition A is an alkane,  $C_{2n}H_{2n+2}$ , or a mixture of alkanes.

Let us imagine a hypothetical gas, composed of detached segments of a high molecular weight solvent. Let gas  $a$  be composed of segments of a non-polar hydrocarbon, A, and gas  $x$  of those of another solvent, X. The segments will be chosen by assuming that every small part of the large molecule of the solvent has the same interaction characteristics and so we can cut it at any point. In this case a basic segment can be chosen in such a manner that

$$\dot{V}_a = \dot{V}_x = 1 \text{ cm}^3 \quad (41)$$

where  $\dot{V}_i$ 's are molar volumes, the asterisk referring to the basic segments. The volume of a given segment can now be expressed as multiples,  $i$ , of the basic segment:

$$V_a = i_a \dot{V}_a \text{ and } V_x = i_x \dot{V}_x \quad (42)$$

Let us now examine the difference in the standard chemical potential for the dissolution processes of segments,  $a$  and  $x$ , in the solvents, A and X. Gas chromatographic evidence shows that the standard chemical potential is a linear function of the molecular mass. Obviously, linearity in the function of the molar volume will only be an approximation but later this assumption will permit a generalization of the results. For the four possible dissolution processes of the segments in the solvents, A and X, it can now be written

$$\Delta\mu_a^{\dagger(A)} = \Delta H_a^{\dagger(A)} + i\Delta\dot{H}_a^{\dagger(A)} - T\Delta S_a^{\dagger(A)} \quad (43)$$

$$\Delta\mu_x^{\dagger(X)} = \Delta H_x^{\dagger(X)} + i\Delta\dot{H}_x^{\dagger(X)} - T\Delta S_x^{\dagger(X)} \quad (44)$$

$$\Delta\mu_x^{\ddagger(A)} = \Delta H_x^{\ddagger(A)} + i\Delta\dot{H}_x^{\ddagger(A)} - T\Delta S_x^{\ddagger(A)} \quad (45)$$

$$\Delta\mu_a^{\ddagger(X)} = \Delta H_a^{\ddagger(X)} + i\Delta\dot{H}_a^{\ddagger(X)} - T\Delta S_a^{\ddagger(X)} \quad (46)$$

The correction,  $\Delta H^c$ , can be considered as the additional interaction energy of both ends of the segment (eventually end groups) with the solvent. Let us assume now that the "segment gas" forms "regular" solutions in both solvents, and further, that the molar volumes of both solvents,  $V_A$  and  $V_X$  are the same. In this instance the entropy contribution due to size differences is the same in all four cases and

$$\Delta S_a^{\dagger(A)} \approx \Delta S_x^{\dagger(X)} \approx \Delta S_x^{\ddagger(A)} \approx \Delta S_a^{\ddagger(X)} \quad (47)$$

$$i = \text{constant and } V_A = V_X$$

for equal  $i$  (refs. 14 and 15).

Let us examine now the enthalpic terms in eqns. 43-46. It is obvious that if a

segment is dissolved in its own environment the mixture would be athermal and so the enthalpy of dissolution should be equal to the enthalpy of condensation of the pure segment:

$$\begin{aligned}\Delta H_2^{(A)} &= \Delta H_2^{c(A)} + i\Delta \dot{H}_2^{d(A)} \approx \Delta^{\text{cond}} \cdot H_2^c \\ \Delta H_2^{(X)} &= \Delta H_2^{c(X)} + i\Delta \dot{H}_2^{d(X)} \approx \Delta^{\text{cond}} \cdot H_2^c\end{aligned}\quad (48)$$

The dissolution process can be composed of two hypothetical steps. In the first step a cavity is formed to fit in size and shape the molecule to be dissolved, and in the second the interacting molecule is placed in the cavity. Let us assume that both segment a and solvent A are able to interact only by dispersion forces, d, and that segment x and solvent X can in addition interact by polar forces, p. Applying this model we obtain

$$\Delta H_2^{(A)} = [\Delta H_2^{c,d(A)} + i\Delta \dot{H}_2^{d(A)}] + (0 + 0) - i\Delta^{\text{cav}} \cdot \dot{H}^{(A)} \quad (49)$$

$$\Delta H_2^{(X)} = [\Delta H_2^{c,d(X)} + i\Delta \dot{H}_2^{d(X)}] + (0 + 0) - i\Delta^{\text{cav}} \cdot \dot{H}^{(X)} \quad (50)$$

$$\Delta H_2^{(A)} = [\Delta H_2^{c,d(A)} + i\Delta \dot{H}_2^{d(A)}] + (0 + 0) - i\Delta^{\text{cav}} \cdot \dot{H}^{(A)} \quad (51)$$

$$\Delta H_2^{(X)} = [\Delta H_2^{c,d(X)} + i\Delta \dot{H}_2^{d(X)}] + [\Delta H_2^{c,p(X)} + i\Delta \dot{H}_2^{p(X)}] - i\Delta^{\text{cav}} \cdot \dot{H}^{(X)} \quad (52)$$

Thereby it was assumed that the work to form a cavity in a given solvent depends only on the size of the cavity. For reasons of symmetry the two terms  $\Delta \dot{H}_2^{d(X)}$  and  $\Delta \dot{H}_2^{d(A)}$  should be equal. However, the terms  $\Delta H_2^{c,d(X)}$  and  $\Delta H_2^{c,d(A)}$  are different, the end of a segment being in general different in nature to the segment itself. From eqns. 50 and 51, together with eqn. 47, we obtain

$$\begin{aligned}\Delta \mu_x^{\dagger(A)} - \Delta \mu_x^{\dagger(X)} &\approx \Delta H_2^{(A)} - \Delta H_2^{(X)} = [\Delta H_2^{c,d(A)} - \Delta H_2^{c,d(X)}] - \\ &\quad - i[\Delta^{\text{cav}} \cdot \dot{H}^{(A)} - \Delta^{\text{cav}} \cdot \dot{H}^{(X)}]\end{aligned}\quad (53)$$

which is a linear equation in  $i$  and could permit an estimation of the difference of the work needed to form a cavity in solvent X and solvent A, respectively, from gas chromatographic data for "segments" (segment-like molecules).

In the following, we put forward the question for conditions for a given substance,  $j$ , to form an athermal solution in X. Any segment,  $x$ , without end groups, forms an athermal mixture with the solvent, and consequently substances with equal volume and polarity to a segment might also show the same behaviour. Let us assume that for every substance

$$\Delta H_j^{d(X)} = k^{(X)} \Delta H_j^{d(A)} \quad (54)$$

where  $k^{(X)}$  is a constant characteristic for the pair of solvents X and A but independent of the substance. For a segment of variable size one can now compare the chromato-

graphic properties on the two stationary phases by measuring its retention volume and calculating with the aid of eqns. 45, 46, 47, 51, 52 and 54

$$\begin{aligned} i\delta\mu_x^{\dagger(X)} &\equiv \Delta\mu_x^{\dagger(X)} - \Delta\mu_x^{\dagger(A)} \approx \Delta H_x^{(X)} - \Delta H_x^{(A)} = \\ &C^c + i\Delta\hat{H}_x^{d(A)}(k^{(X)} - 1) + i\Delta\hat{H}_x^p - i[\Delta^{cav}\hat{H}^{(X)} - \Delta^{cav}\hat{H}^{(A)}] \end{aligned} \quad (55)$$

where the terms responsible for the ends of the segment are summed in  $C^c$ . For the dissolution of the substance  $j$ , the cavity to be formed in  $X$  is, to a first approximation, proportional to its molar volume, and consequently

$$\Delta^{cav}H_j^{(X)} = (V_j/1)\Delta^{cav}\hat{H}^{(X)} \text{ and } \Delta^{cav}H_j^{(A)} = (V_j/1)\Delta^{cav}\hat{H}^{(A)} \quad (56)$$

the molar volume of the basic segment being unity. The analogous expression to that of the segment in eqn. 55 for the substance  $j$  is then given by

$$\begin{aligned} \Delta\mu_j^{\dagger(X)} - \Delta\mu_j^{\dagger(A)} &\approx \Delta H_j^{(X)} - \Delta H_j^{(A)} = \\ \Delta H_j^{d(A)}[k^{(X)} - 1] + \Delta H_j^p - V_j[\Delta^{cav}\hat{H}^{(X)} - \Delta^{cav}\hat{H}^{(A)}] \end{aligned} \quad (57)$$

The conditions for this substance to form an athermal solution are that

$$V^j = i$$

and

$$\Delta H_j^{d(A)}[k_x^{(X)} - 1] + \Delta H_j^p = V_j\{\Delta\hat{H}_x^{d(A)}[k_x^{(X)} - 1] + \Delta\hat{H}_x^p\} \quad (58)$$

Let us define now a "thermal" activity coefficient,  $\varphi$ , which is 1 for an athermal solution of substance  $j$  in  $X$ . Then

$$q = -RT \ln \varphi \quad (59)$$

whereby we identify this  $q$  as an estimate for the configurational enthalpy. Under conditions

$$\begin{aligned} q_j &= \Delta H_j^{(X)} - \Delta H_j^{(A)} - V_j[\Delta\hat{H}_x^{(X)} - \Delta\hat{H}_x^{(A)}] - C^c \\ &= [\Delta H_j^{d(A)} - V_j\Delta\hat{H}_x^{d(A)}][k^{(X)} - 1] + [\Delta H_j^p - V_j\Delta\hat{H}_x^p] - C^c \end{aligned} \quad (60)$$

The first term of the right-hand side of eqn. 60 could be small. It is the difference of the dispersion energy contribution in the non-polar solvent of the substance,  $j$ , with solvent  $A$  and that of a segment,  $x$ , of the same molar volume. In a zeroth approximation it can therefore be neglected, and thus  $q_j$  will originate principally from polarity differences of the substance and the segment. By combining eqn. 60 with eqns. 55 and 59 we obtain as a rough interpretation of  $q_j$

$$\begin{aligned} -RT \ln \varphi_j = q_j &\approx \Delta\mu_j^{\dagger(X)} - \Delta\mu_j^{\dagger(A)} - [V_j\delta\mu_x^{\dagger(X)} + C^c] \\ &\approx \Delta H_j^p - [V_j\Delta\hat{H}_x^p + C^c] \end{aligned} \quad (61)$$

In order to use eqn. 59, the individual terms have to be calculated from gas chromatographic data by using the middle part of the equation. The calculation of  $\Delta\mu_j^{(X)} - \Delta\mu_j^{(A)}$  is straightforward:

$$\Delta\mu_j^{(X)} - \Delta\mu_j^{(A)} = RT \ln [V_g(j|A)/V_g^0(j|X)] \quad (62)$$

where  $V_g(j|A)$  is the specific retention volume of substance  $j$  on phase A and  $V_g^0(j|X)$  is that on phase X, the superscript zero meaning that the value is corrected for adsorption effects.

To calculate  $\delta\mu_x^{(X)}$ , certain precautions have to be taken. The estimation will be explained by taking dimethoxypoly(ethylene glycol) with a molecular weight of  $2177 \pm 27$  as the stationary phase X<sup>9,16</sup>. The formula of this polymer is  $H(CH_2-O-CH_2)_nH$ . The end groups are hydrogen atoms. Small molecules having this formula are as follows:

$y$	Compound
1	2-Oxapropane (dimethyl ether)
2	2,5-Dioxahexane (1,2-dimethoxyethane)
3	2,5,8-Trioxanonane
4	2,5,8,11-Tetraoxadodecane

First the non-polar standard has to be carefully chosen. Actually, the molar volume of A should be the same as that of X. Not having data on such a hydrocarbon, we chose the hydrocarbon  $C_{37}H_{176}$  as a standard<sup>17</sup>, with a molecular weight of 1222.37 and  $V_A = 1540 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$  at  $100^\circ$  compared with  $M_X = 2177 \pm 27$  and  $V_X = 2077 \pm 27 \text{ cm}^3 \text{ mol}^{-1}$ .

By determining the gas chromatographic data of these substances on these two phases, a good linearity was observed for  $y = 2, 3$  and 4 in the  $\Delta\mu_y^{(A)}$  versus molecular weight plot on both phases,  $\lambda = A$  or X. It was also observed that  $\Delta I$  values:

$$\Delta I_y = I_y^X - I_y^A$$

where  $I$  is retention index, also increased monotonously (see Table I).

The difference between  $y = 1$  and 2, 2 and 3 etc. is always a  $CH_2-O-CH_2$  unit. Assuming additivity of the polar forces, the  $\Delta I$  value should also increase by the same

TABLE I

SPECIFIC RETENTION VOLUMES,  $V_g^0$ , RETENTION INDICES,  $I_{100}$ , AND MOLAR VOLUMES,  $V_y$ , OF SEGMENT-LIKE MOLECULES ON TWO STATIONARY PHASES A AND X. All data are given for  $100^\circ$ . A is a  $C_{37}H_{176}$  branched alkane; X is a dimethoxypoly(ethylene glycol) of molecular weight  $2177 \pm 27$ . Values marked with an asterisk are estimated from data determined at higher temperatures. Solutes have the general formula  $H(CH_2-O-CH_2)_nH$ .

$y$	$V_g^0 \text{ (ml g}^{-1}\text{)}$		$I_{100}$		$\Delta I_{100} = I_{100}^X - I_{100}^A$	$V_y \text{ (ml mol}^{-1}\text{)}$
	A	X	A	X		
2	36.6	50.2	604.5	920.9	316.4	115.6
3	259.3	511.6*	867.4	1320.7*	453.3	154.9
4	1727.7	5041.7*	1126.4	1716.6*	590.2	195.3

amount for every additional  $\text{CH}_2\text{-O-CH}_2$  unit. Further, the additional  $\Delta I$  value should be the same as that of an ether with similar steric hindrance, e.g., dipentyl ether, for which  $\Delta I = 115$  i.u.<sup>9</sup> This figure is lower than that for the segment. The exact periodicity of the position of the ether oxygens in "segment molecules" fitting exactly that of the polymer might account for the higher  $\Delta I$  increment for the segments<sup>18,19</sup>. The ends of the dimethoxypoly(ethylene glycol) chains are sterically less hindered and therefore have a higher polarity. This means at the same time that one cannot consider these small molecules to be representative of segments *inside* a chain. Only the additional segment of the oxaalkane shows this behaviour. Consequently, we can estimate the value of  $\delta\bar{\mu}_x^{\dagger(X)}$  from the data of the members of this homologous series as follows:

$$\begin{aligned}\delta\bar{\mu}_x^{\dagger(X)} &= \{[\Delta\mu_{(y+1)}^{\dagger(X)} - \Delta\mu_y^{\dagger(X)}] - [\Delta\mu_{(y+1)}^{\dagger(A)} - \Delta\mu_y^{\dagger(A)}]\} (V_{y+1} - V_y) \\ &= \frac{RT \ln [V_g^0(y|X) \cdot V_g(y+1|A)/V_g^0(y+1|X) \cdot V_g(y|A)]}{V_{y+1} - V_y}\end{aligned}\quad (63)$$

where  $y = 2, 3 \dots$  are the corresponding oxaalkanes and  $V_y$  their molar volumes. In our case we had, with the aid of data listed in Table I, two estimates for  $\delta\bar{\mu}_x^{\dagger(X)}$  from the two pairs of oxaalkanes and their average was used in the following calculations:

$$\delta\bar{\mu}_x^{\dagger(X)} = [(\delta\bar{\mu}_x^{\dagger(X)}(2/3) + \delta\bar{\mu}_x^{\dagger(X)}(3/4))/2] = (6.84 + 7.18)/2 = 7.0 \text{ cal cm}^{-3}$$

The numerical values were calculated from data determined at  $100^\circ$ ; the values are assumed to be valid in a certain temperature range around this temperature, let us say  $100 \pm 30^\circ$ .

One more question remains open, namely whether this correction can or cannot be used without a constant allowing for the effect of the end groups. To answer this question an additional constant,  $C^e$ , can be introduced to give

$$\begin{aligned}\delta\bar{\mu}_x^{\dagger(X)} &= [\delta\bar{\mu}_x^{\dagger(X)}(2/3) + \delta\bar{\mu}_x^{\dagger(X)}(3/4)]/2 = (-6.84 - 7.18)/2 = -7.0 \text{ cal cm}^{-3} \\ q_j &= RT \ln [V_g(j|A)/V_g^0(j|X)] - (V_j\delta\bar{\mu}_x^{\dagger(X)} + C^e)\end{aligned}\quad (64)$$

Its numerical value can be determined by comparing the  $q_j$  values of "segments" determined by calorimetric measurements with those calculated from eqn. 64. It can also be determined by correlating experimental with calculated adsorption data. Finally, if one finds a small oxaalkane for which  $\Delta H_y^{\dagger(X)} = \Delta^{\text{cond.}}H_y$ , then we can assume that its solution in X is athermal and  $q_y = 0$ . In our series it was almost the case for dimethoxyethane [ $y = 2$ ;  $\Delta H_2^{\dagger(X)} = -7669$  and  $\Delta^{\text{cond.}}H_2^0 = -7681 \text{ cal mol}^{-1}$  (ref. 20)], so that

$$\begin{aligned}0 &= RT \ln [V_g(2|A)/V_g^0(2|X)] - (V_2\delta\bar{\mu}_x^{\dagger(X)} + C^e) = \\ &= RT \ln (36.6/50.2) - 115.6(-7.0) - C^e = 575 - C^e\end{aligned}$$

giving  $C^e = 575 \text{ cal mol}^{-1}$ .

In this derivation it was always assumed that data on solution enthalpies are not available. It is evident that if such enthalpies were measured on both phases, A and X, all calculations should be made with these values instead of using the approximations via the chemical potential. The definition of  $\delta\hat{H}_x^{(X)}$ , the analogous term to  $\delta\hat{\mu}_x^{(X)}$ , is obvious from eqn. 55.

#### FINAL REMARKS

The relationships given in this paper describe the adsorption properties of solute molecules in well defined extreme cases. In intermediate cases there will be ambiguity as to what kind of adsorption isotherm is valid. Let us imagine a series of solvents, X, arranged in series in the order of increasingly strict inner structure, up to a solvent which cannot dissolve any organic molecules. It is clear that the activity coefficient of an organic molecule will increase in this series, finally approaching infinity. With a low activity coefficient the problem is clear, the Gibbs' dividing plane can be placed at the surface of liquid and adsorption can be neglected from the side of the gas phase. The other extreme is also straightforward, for the adsorption of insoluble substances the same thermodynamic treatment can be applied for the liquid surface as that for solid surfaces ("insoluble films"). To a certain extent, the parameter  $\beta$  could account for intermediate cases. In solvents with a stricter structure the solute will be "expelled" more strongly to the surface, meaning that the decrease in coordination number compared with that in a better solvent,  $\beta$ , will be larger. The question is open as to the value of  $\beta$  at which the phenomenon can no longer be considered as being an adsorption *at* a liquid-gas interface but rather *on* the surface of the liquid. A further interesting question is the effect of the adsorption of the carrier gas at the liquid-gas interface and its influence on the adsorption of the solutes,  $j$ . Chromatography with water vapour seems to eliminate the adsorption of solutes in certain cases<sup>21</sup>.

#### ACKNOWLEDGEMENTS

This paper reports part of a project supported by the Fonds National Suisse de la Recherche Scientifique. We thank Araksi Sahil and G. Kőrösi for unpublished experimental data and Dr. D. F. Fritz for valuable discussions.

#### NOTE ADDED IN PROOF

Using a different approach, Eon and Guiochon<sup>22</sup> derived an equation which is equivalent to our eqn. 33 if the thermal correction term,  $q_j\beta/RT$ , is replaced by the expression  $\ln(\gamma_j^{b,\infty}/\gamma_j^{s,\infty})$ . Thereby,  $\gamma_j^{b,\infty}$  and  $\gamma_j^{s,\infty}$  (symbols used in ref. 22) stand for the bulk and the surface activity coefficient, respectively, of the solute,  $j$ , at infinite dilution.

#### REFERENCES

- 1 R. L. Martin, *Anal. Chem.*, 33 (1961) 347.
- 2 D. E. Martire, in J. H. Purnell (Editor), *Progress in Chromatography*, Interscience, New York, 1968, p. 93.
- 3 V. G. Berezkin, *J. Chromatogr.*, 159 (1978) 359.

- 4 V. G. Berezkin, *Wiss. Z. Karl-Marx-Univ. Leipzig, Math.-Naturwiss. Reihe*, 26 (1977) 419.
- 5 R. L. Martin, *Anal. Chem.*, 35 (1963) 116.
- 6 A. Sanfield, in H. Eyring, D. Henderson and W. Jost (Editors), *Physical Chemistry*, Academic Press, New York, London, 1971, p. 245.
- 7 R. Defay and I. Prigogine (coauthors A. Bellemans and D. H. Everett), *Surface Tension and Adsorption*, Longmans, London, 1966.
- 8 R. Defay and I. Prigogine (coauthors A. Bellemans and D. H. Everett), *Surface Tension and Adsorption*, Longmans, London, 1966, p. 87.
- 9 D. F. Fritz, A. Sahil and E. sz. Kováts, *J. Chromatogr.*, (1979) in press.
- 10 D. F. Fritz and E. sz. Kováts, *Anal. Chem.*, 45 (1973) 1175.
- 11 A. A. Zhukhovitskii, *Acta Physicochim. URSS*, 19 (1944) 176.
- 12 R. Defay, *J. Chim. Phys.*, 51 (1954) 299.
- 13 I. Prigogine and J. Maréchal, *J. Colloid Sci.*, 7 (1952) 122.
- 14 P. J. Flory, *J. Chem. Phys.*, 9 (1941) 600.
- 15 M. L. Huggins, *J. Phys. Chem.*, 9 (1941) 440.
- 16 D. F. Fritz, A. Sahil, H.-P. Keller and E. sz. Kováts, *Anal. Chem.*, 51 (1979) 7.
- 17 F. Riedo, D. Fritz, G. Tarján and E. sz. Kováts, *J. Chromatogr.*, 126 (1976) 63.
- 18 M. Chastrette and G. Tagand, *Chromatographia*, 11 (1978) 379.
- 19 M. Chastrette and G. Tagand, *Chromatographia*, 11 (1978) 447.
- 20 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, CRC Press, Cleveland, Ohio, 58th ed., 1977, p. C-733.
- 21 I. Lysyj and K. H. Nelson, *Anal. Chem.*, 40 (1968) 1365.
- 22 C. Eon and G. Guiochon, *J. Colloid Interface Sci.*, 45 (1973) 188.