Notes

Evaluation of hydrogen-bond energies by means of gas–liquid chromatography

In the paper by IOGANSEN, KURKCHI AND LEVINA[1], presented under the above title at the 6th International Symposium on Gas Chromatography in Rome, a simple approach to the evaluation of hydrogen-bond energies has been suggested. The controversy between the consistency claimed for the results obtained and the apparent inconsistency in the theoretical approach used deserve closer inspection.

The attempt at the determination of the H-bond energy from chromatographic data seems promising; but owing to the complexity of molecular interactions, especially in polar systems, and to the fact, that chromatographic data reflect all types of interaction along with statistical effects, it is unlikely that such a simple procedure as has been presented will elucidate the contribution of individual types of interaction. It would be more appropriate to speak of rough estimation or of correlation of the heats of mixing rather than of the evaluation of H-bond energies. Thus, it is questionable whether the so-called nonspecific interactions, involving, for the systems discussed, the contribution of inductive and dispersion forces, may be assumed the same both in polar electron donating and in nonpolar media. ΔH_{ib}, defined as ΔH_v (liquid b) $—\Delta H_v$ (liquid i), will in any case involve the contribution of inductive forces, which are playing a role only in liquid b. Moreover, the Raoult's law activity coefficient involves a geometric term, a distribution term and an interaction term[2]. On the one hand, the first two terms have been found[3] to be significant contributors to the total excess Gibbs free energy, and on the other hand, they obviously cannot be declared nonspecific.

The procedure for calculating ΔH_v seems to be ambiguous. The relation $V_g = \bar{v}t'/m$ corresponds to the well known equation:

$$V_g = RT/f^0 M_L \gamma = RT/M_L H \gamma^* \tag{1}$$

where f^0 is fugacity of pure solute, γ and γ^* are, respectively, the Raoult's law and the Henry's law activity coefficients of the solute in the given solvent at temperature T, M_L is the molecular weight of the solvent and H is the Henry's law constant. Differentiation of $\ln V_g$, expressed from eqn. (1), with respect to $1/T$, gives:

$$\text{d} \ln V_g/\text{d} (1/T) = (\Delta H_v/R) — T. \tag{2}$$

Hence for the determination of ΔH_v, as used in the earlier paper[1], it is necessary to use $V_g (273/T)$, i.e., V_g^0, for:

$$V_g^0 = R\,273/f^0 M_L \gamma = R\,273 x/M_L P y \tag{3}$$

where x and y are the mole fractions of solute in the gas and liquid phases and P is the total pressure of the sorption system.

and therefore:

$$\text{d} \ln V_g{}^0/\text{d}\,(1/T) = \Delta H_v/R. \tag{4}$$

The calculation of ΔS_v is not clear either. It is well known that:

$$\Delta G^0 = -RT \ln K \tag{5}$$

where K is the thermodynamic distribution coefficient defined as the ratio of solute activity in the gaseous and liquid phases, respectively, and $\Delta G°$ is the change of the standard Gibbs free energy per mole of solute. When choosing as standard states the I atm perfect gas state for the solute in the gas phase and an extremely dilute solute in the solvent for the solute in the liquid phase, it may be written as[4]:

$$K = Py/x. \tag{6}$$

Combining eqns. (3), (5) and (6) we obtain for the standard molar entropy change:

$$\Delta S_v{}^0 = \Delta H_v{}^0/T + R \ln (R\,273/V_g{}^0 M_L),$$

which relation can hardly be correlated with:

$$4.57 \times \log V_g = \Delta S_v - (\Delta H_v/T).$$

Concerning the relation between reaction enthalpy and equilibrium constant K_a, it is necessary to keep in mind that the relation $-\Delta H_a = R\ \text{d}\ln K_a/\text{d}(1/T)$ becomes valid only when ΔH_a is a change of standard enthalpy, which makes it necessary to define the standard states. K_a should also be defined by activities rather than by concentrations, which will both differ for the two systems discussed.

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Comments on the standard addition method used in quantitative gas chromatographic analysis

Quantitative analysis by gas chromatography, using the standard addition method, is based on the relation between the chromatogram of the initial sample under analysis and the chromatogram of a blend of this sample and a defined added