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THE DETERMINATION OF SOLUTION AND ADSORPTION ENTHALPIES IN SYSTEMS WITH MIXED MECHANISMS

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SUMMARY

In systems involving mixed mechanisms, temperature affects the retention volume according to the equation $\ln V_N = -(\Delta H_s/RT) +$ a constant, where ΔH_s is the heat of sorption. The relationship between ΔH_s and the heats of solution and adsorption is derived, and an equation is presented for computing changes in ΔH_s with the percentage of stationary phase. Expressions are also derived for estimating the errors in the computation of the heats of solution and adsorption.

INTRODUCTION

The contribution of mixed mechanisms to chromatographic retention has been known since Martin's paper[1] in 1961, and the various possibilities (depending on solute, stationary phase and solid-support peculiarities) have been extensively discussed by Conder *et al.*[2]. However, one particular case has received much more attention than the others, *i.e.*, systems in which retention is caused by solution in the stationary phase and adsorption on the gas–liquid interface. Systems that behave in this way generally involve non-polar solutes and highly polar stationary phases, and the expression for the net retention volume per gram of packing, V_N, in this case is

$$V_N = K_L V_L + K_A A_L \tag{1}$$

where K_L and K_A are the partition and adsorption coefficients, respectively, and V_L and A_L represent the volume and the exposed area of liquid per gram of packing.

Thermodynamically, K_L and K_A are the meaningful parameters; to obtain them, V_N is measured on a series of columns having different ratios of stationary phase to solid support, and the following relationships are then applied:

$$K_L = \left[\frac{\partial (V_N/A_L)}{\partial (V_L/A_L)} \right]_T \tag{2a}$$

$$K_A = \left[\frac{\partial (V_N/V_L)}{\partial (A_L/V_L)} \right]_T \tag{2b}$$

The preceding reasoning implies the possibility of obtaining the partial molar enthalpies of solution (ΔH_L) and adsorption (ΔH_A) at infinite dilution:

$$\Delta H_L = -R\frac{\partial \ln K_L}{\partial(1/T)} \tag{3a}$$

$$\Delta H_A = -R\frac{\partial \ln K_A}{\partial(1/T)} \tag{3b}$$

This possibility has seldom been exploited. an example of it being the study of various water–hydrocarbon systems by Karger et al.[3].

It is obvious that, when mixed mechanisms are involved. the combination of data from different columns will determine for the heats of solution and adsorption a precision lower than that obtained in systems where retention occurs by a single mechanism. The object of the present paper is to develop some form of calculation that permits us to establish confidence limits to these enthalpies, and also to discuss some not completely clear aspects of the effect of temperature changes on the retention volume in systems where solution and adsorption processes occur simultaneously. Infinite dilution will be assumed in every instance, and non-idealities in the vapour phase will be neglected.

THE ENTHALPY OF SORPTION

If mixed processes take place in the column, the retention volume will be affected by the temperature in accordance with the equation

$$\ln V_N = -\frac{\Delta H_s}{RT} + \text{a constant} \tag{4}$$

In this expression. rigidly obeyed over not-too-wide temperature intervals, ΔH_s is the "enthalpy of sorption"; this quantity, which has been defined[3] without further precision, is obviously related to the heats of solution and adsorption. By differentiating eqn. 1 with respect to $1/T$, multiplying the result by $1/V_N$ and assuming that, over a narrow temperature range, the changes in V_L and A_L are negligible compared with those in V_N, we arrive at the expression

$$\frac{1}{V_N}\cdot\frac{\partial V_N}{\partial(1/T)} = \frac{\partial \ln V_N}{\partial(1/T)} = \left[\frac{V_L}{V_N}\right]\frac{\partial K_L}{\partial(1/T)} + \left[\frac{A_L}{V_N}\right]\frac{\partial K_A}{\partial(1/T)} \tag{5}$$

Combination of this result with eqns. 3 and 4 leads to

$$\Delta H_s = \left[\frac{V_L}{V_N}\right]K_L\,\Delta H_L + \left[\frac{A_L}{V_N}\right]K_A\,\Delta H_A \tag{6}$$

The heat of sorption should thus change when the percentage of stationary phase in the packing is changed. unless the condition $\Delta H_L = \Delta H_A$ is fulfilled. In order to be able to compute this change, eqn. 6 is differentiated with respect to A_L/V_L at constant temperature; this gives

$$\frac{\partial(\Delta H_s)}{\partial(A_L/V_L)} = K_L\,\Delta H_L\,\frac{\partial(V_L/V_N)}{\partial(A_L/V_L)} + K_A\,\Delta H_A\,\frac{\partial(A_L/V_N)}{\partial(A_L/V_L)} \tag{7}$$

From eqns. 2a and 2b, it can easily be shown that

$$\frac{\partial(V_L/V_N)}{\partial(A_L/V_L)} = -K_A \left[\frac{V_L}{V_N}\right]^2 \tag{8a}$$

$$\frac{\partial(A_L/V_N)}{\partial(A_L/V_L)} = K_L \left[\frac{V_L}{V_N}\right]^2 \tag{8b}$$

By introducing eqns. 8a and 8b into eqn. 7, we arrive at

$$\frac{\partial(\Delta H_s)}{\partial(A_L/V_L)} = K_L K_A \left[\frac{V_L}{V_N}\right]^2 (\Delta H_A - \Delta H_L) \tag{9}$$

In passing from a column with a ratio $(A_L/V_L)_1$ to another with a ratio $(A_L/V_L)_2$, ΔH_s will show a change given by

$$\Delta(\Delta H_s) = K_L K_A (\Delta H_A - \Delta H_L) \int_1^2 \left[\frac{V_L}{V_N}\right]^2 d(A_L/V_L) \tag{10}$$

By using eqn. 1 to express (V_L/V_N) in terms of (A_L/V_N) and then integrating, we get

$$\Delta(\Delta H_s) = K_L (\Delta H_A - \Delta H_L) \left[\frac{1}{K_L + K_A(A_L/V_L)}\right]_{(A_L/V_L)_1}^{(A_L/V_L)_2} \tag{11}$$

To obtain an approximation of the magnitude of the change of ΔH_s, eqn. 11 has been applied to two different systems, viz., n-nonane plus formamide, and benzene plus formamide, each at 25°, using data from a paper soon to be published. The transition considered in each instance was from a column with 6.80% of stationary phase on Chromosorb P $(A_L/V_L \approx 2.0 \times 10^5 \, cm^{-1})$ to one with 21.9% $(A_L/V_L \approx 2.1 \times 10^4 \, cm^{-1})$; the results are shown in Table I.

TABLE I

CHANGES IN VALUES OF VARIOUS PARAMETERS WITH DIFFERENT CONTENTS OF STATIONARY PHASE

System	K_L	K_A (cm)	$-\Delta H_L$ (kcal/mole)	$-\Delta H_A$ (kcal/mole)	$-(\Delta H_s)$ (kcal/mole)
n-Nonane + formamide	16.7	$8.86 \cdot 10^{-4}$	8.8	9.4	0.2
Benzene + formamide	93.6	$0.95 \cdot 10^{-4}$	6.3	6.5	0.04

Later in this paper it will be shown that ΔH_L and ΔH_A can be measured with only poor precision, but, in any event, it is evident from Table I that, unless the heats of solution and adsorption differ by at least 3 kcal/mole, the change in ΔH_s will be of the same order as the experimental error.

In Fig. 1, the heats of sorption for the systems n-nonane plus formamide and benzene plus formamide are represented as a function of the percentage of stationary phase in the packing. For each point, the 95% confidence interval is indicated; this interval was calculated from the standard deviation of the slope of the plot of $\ln V_N$
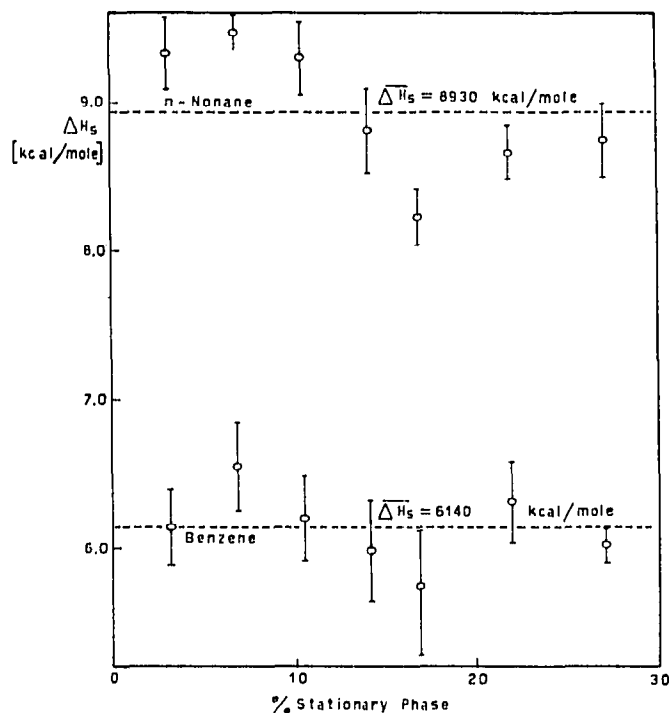
Fig. 1. Heat of sorption of *n*-nonane and benzene as a function of the percentage of stationary phase·

vs. $1/T$ and the corresponding value of *t* (see ref. 4). The broken lines correspond to mean heats of sorption. From Fig. 1 it can be seen that the values do not follow any given trend, their deviations from the mean being of the same order as the experimental error.

The experimental inability to detect changes in the heat of sorption casts doubt on the validity of the values of ΔH_L and ΔH_A obtained by using eqns. 3a and 3b.

ESTIMATION OF THE ERRORS

From eqn. 3a the heat of solution can be computed; two kinds of error will affect the values thus obtained. First, the slope of the plot of ln K_L *vs.* $1/T$ must be measured. As the partition coefficient is determined at each temperature starting from retention-volume data, the uncertainty in the knowledge of the heat of solution should be at least equal to the uncertainty related to the heat of sorption. If $\Delta H'_L$ and ΔH_L are the true and the experimental values for the heat of solution, respectively, then

$$\Delta H'_L = \Delta H_L \pm t_T R s(m) = \Delta H_L \pm t_T s(\Delta H_s) \tag{12}$$

where $s(m)$ is the standard deviation of the slope of ln V_N *vs.* $1/T$, obtained by a least-squares analysis of the experimental data; from eqn. 4, the product $R s(m)$ is the

standard deviation of the heat of sorption, $s(\Delta H_s)$. The Student t factor corresponding to the confidence level selected and a number of degrees of freedom two less than the number of temperatures used is designated t_T (see ref. 4).

Secondly, the partition coefficient at a given temperature is computed by combining data from different columns, with use of eqn. 2a. Although, in fact, A_L and V_L for a given column are the actual uncertain values, it can reasonably be assumed that each value is exactly known, the uncertainty in the value of V_N corresponding to those (correct) values of V_L and A_L. As the retention volume at a given temperature can be precisely interpolated by means of expressions such as eqn. 4 with constants obtained by the least-squares method, we shall assume that, in plotting V_N/A_L vs. V_L/A_L at a given temperature, the only error introduced is the one associated with assigning the calculated value of V_N to the correct values of V_L and A_L, the error introduced by interpolating with respect to temperature being negligible. Then, errors of this second type are measured by the standard deviation of the slope of the plots V_N/A_L vs. V_L/A_L, which we represent by $s(K_L)$. If K'_L is the true value of the partition coefficient and K_L is the experimentally determined value, we can write

$$K'_L = K_L \pm t_C\, s(K_L) \tag{13}$$

where t_C is the Student t factor corresponding to the confidence level selected and a number of degrees of freedom two less than the number of columns used.

From eqn. 13, it is easily deduced that

$$\ln K'_L = \ln K_L \pm t_C\, \frac{s(K_L)}{K_L} \tag{14}$$

As $s(K_L)$ is calculated from data obtained on different columns, all operated at the same temperature, changes in $s(K'_L)$ with temperature will be only fortuitous, so that

$$\frac{\partial \ln K'_L}{\partial(1/T)} = \frac{\partial \ln K_L}{\partial(1/T)} \pm t_C\, \frac{s(K_L)}{K_L}\, \frac{\partial \ln K_L}{\partial(1/T)} \tag{15}$$

By combining eqns. 15 and 3a,

$$\Delta H'_L = \Delta H_L \pm t_C\, \frac{s(K_L)}{K_L}\, \Delta H_L \tag{16}$$

Assuming that both types of error are independent, eqns. 12 and 16 can be combined to provide an estimate of the total error, thus

$$\Delta H'_L = \Delta H_L \pm \left[t_T\, s(\Delta H_s) + t_C\, \frac{s(K_L)}{K_L}\, \Delta H_L \right] \tag{17a}$$

By analogy, for the adsorption process we obtain

$$\Delta H'_A = \Delta H_A \pm \left[t_T\, s(\Delta H_s) + t_C\, \frac{s(K_A)}{K_A}\, \Delta H_A \right] \tag{17b}$$

A series of experimental values for systems involving formamide with n-nonane, cyclohexane and benzene is shown in Table II. These three solutes were selected

TABLE II

EXPERIMENTAL VALUES OF VARIOUS PARAMETERS FOR SEVEN COLUMNS AND FIVE TEMPERATURES

The energies are expressed in cal/mole.

Parameter	n-Nonane	Cyclohexane	Benzene
$-\Delta H_s$	8930	5570	6140
$s(\Delta H_s)$	66	104	93
K_L	16.7	9.72	93.6
$s(K_L)$	0.227	0.075	0.509
$-\Delta H_L$	8810	5890	6320
K_A (cm)	$8.86 \cdot 10^{-4}$	$0.48 \cdot 10^{-4}$	$0.95 \cdot 10^{-4}$
$s(K_A)$ (cm)	$3.11 \cdot 10^{-6}$	$0.62 \cdot 10^{-6}$	$3.66 \cdot 10^{-6}$
$-\Delta H_A$	9410	4760	6500
$t_T \, s(\Delta H_s)$	210	330	296
$t_c \, \dfrac{s(K_L)}{K_L} \, \Delta H_L$	311	117	84
$t_c \, \dfrac{s(K_A)}{K_A} \, \Delta H_A$	86	162	653

because they are representative of different situations, *viz.*, adsorption-dominated (*n*-nonane), partition-dominated (benzene) and intermediate (cyclohexane) retention. As the heat of sorption and its standard deviation change from column to column, their mean values $\overline{\Delta H_s}$ and $\overline{s(\Delta H_s)}$ are indicated. A confidence level of 95% was selected, and seven stationary phase–solid support ratios were studied; each column was run at five different temperatures, so that $t_c = 2.57$ and $t_T = 3.18$.

The heat of sorption has been determined with a precision of $\pm$ 300 cal/mole; this is a realistic range, especially if we consider that, for these solutes, the enthalpies of vaporization change by 10–20 cal/mole for each degree (Celsius) and the measurements were made within a range of 10°.

Further, as could have been foreseen, the heat of solution of benzene (a solute retained fundamentally by solution in the stationary phase) is determined with a precision only slightly worse than that associated with the heat of sorption; however, its heat of adsorption is very uncertain. For *n*-nonane, retained principally by adsorption on the gas–liquid interface, the behaviour is the opposite, and for cyclohexane it is intermediate.

To summarize, when a solute is retained by a process involving mixed mechanisms, the enthalpy associated with the principal mechanism can be computed with a precision of the same order as that associated with the heat of sorption; as the importance of a given mechanism diminishes, the uncertainty in the knowledge of the corresponding differential enthalpy will increase.

REFERENCES

1 R. L. Martin, *Anal. Chem.*, 33 (1961) 347.
2 J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 700.
3 B. L. Karger, P. A. Sewell, R. C. Castells and A. Hartkopf, *J. Colloid Interface Sci.*, 35 (1971) 328; *J. Phys. Chem.*, 75 (1971) 3870.
4 O. L. Davies, *Statistical Methods in Research and Production*, 3rd ed., Oliver & Boyd, Edinburgh, London, 1957, Ch. 7.