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$\Delta S^{\ominus}$ CALCULATION IN GAS CHROMATOGRAPHIC PROCESSES AND $\Delta H^{\ominus}$-CHARACTERISED POLARITY OF STATIONARY PHASE *

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ABSTRACT

An equation for calculating changes in enthalpy and entropy of solution in gas–liquid chromatography has been derived.

$\Delta H_s^{\ominus}$ and $\Delta S_s^{\ominus}$ values of 44 solution systems of alkanes, alcohols and aldehydes in squalane, tricresyl phosphate, SE-30, PEG-20M and ODPN were measured. The results were compared with those obtained using calorimetric and static methods.

The thermodynamic compensation effect and “iso-thermodynamic points” were found in homologues.

An index P_{BH} in terms of the $\Delta H_s^{\ominus}$ values of benzene and cyclohexane in a stationary phase is proposed to describe the relative polarity of a given GC column.

INTRODUCTION

Changes in enthalpy, entropy and Gibbs free energy of gas–solid adsorption or gas–liquid solution can be determined by using the pulse chromatographic technique. However, there seems to be discrepancies in the equations given by Katsanos et al. [1] and by Atkinson and Curthoys [2] for calculating the adsorption entropy ΔS_a. A new equation has been recently presented [3]

$$\ln V_g^0 = -\frac{\Delta H_a^{\ominus}}{RT_c} + \frac{\Delta S_a^{\ominus}}{R} + \ln(R273.2S) \tag{1}$$

Figgins et al. [4] have suggested the following equation

$$\ln V_g = -(\Delta H_s^m/RT) + (\Delta S_s^m/R) - \ln(1000/273R) \tag{2}$$

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In this paper, a similar equation, in which the logarithmic term on the R.H.S. is exactly defined, is derived for the chromatographic process of gas–liquid solutions.

EQUATION FOR DETERMINING $\Delta S_s^{\ominus}$ AND $\Delta G_s^{\ominus}$ BY GLC

When the column temperature is high enough and the pulsed sample injection is infinitesimally small, the partition, or equilibrium of the sample between the gaseous and liquid phases may be described using the dimensionless constant $K_{c,p}$

$$K_{c,p} = \frac{\text{mol of solute per unit volume of solvent}}{\text{partial pressure of solute in gaseous phase}}$$

$$= \frac{C}{P}\frac{P^{\ominus}}{C^{\ominus}} = \frac{n_s/V_s}{RT_c n_g/V_g}\frac{P^{\ominus}}{C^{\ominus}} \tag{3}$$

where, T_c refers to the column temperature (in K). V_g can be converted to the specific retention volume V_g^0 by the following equation [5]

$$V_g^0 = \frac{273.2 V_g n_s}{T_c W_s n_g} \tag{4}$$

Taking standard states in commonly used units, $C^{\ominus} = 1$ mol 1^{-1} and $P^{\ominus} = 1$ bar, and by taking the following relationship at T_c into account

$$\Delta G_s^{\ominus} = -RT_c \ln K_{c,p} = \Delta H_s^{\ominus} - T_c\, \Delta S_s^{\ominus} \tag{5}$$

we have

$$\Delta G_s^{\ominus} = -RT_c \ln K_{c,p} = -RT_c \ln\left(\frac{V_g W_s}{R \times 273.2 \times V_s}\right) \tag{6}$$

and

$$\ln V_g^0 = -\frac{\Delta H_s^{\ominus}}{RT_c} + \frac{\Delta S_s^{\ominus}}{R} + \ln(R \times 273.2 \times V_s/W_s) \tag{7}$$

The volume of a solvent divided by its weight gives the specific volume $1/\rho$ of the liquid stationary phase, which is related to the specific area S of solid stationary phase in eqn. (1).

At each given column temperature, $\Delta G_s^{\ominus}$ and $K_{c,p}$ can be determined by eqn. (6), where V_g^0 and the values in parentheses are known. Because the last term in eqn. (7) is a well defined constant, $\Delta S_s^{\ominus}$ can be determined directly from the intercept of the plot of $\ln V_g^0$ against $1/T_c$ by assuming that the changes in $\Delta H_s^{\ominus}$ and $\Delta S_s^{\ominus}$ are negligibly small in a certain range of temperatures. $\Delta G_{298.2}^{\ominus}$ can thereby be calculated.

EXPERIMENTAL

A Shimadzu GC-7A gas chromatograph was used in the GC experiments; for details, see our previous paper [6].

A home-made microcalorimeter of the heat-flux-type with twin cell and thermopile sensors for ΔT measurement was used. Its sensitivity is 127.3 μV/mW with precision of 0.2% when > 1 J [7].

A home-made B.E.T. adsorption apparatus with a quartz spring balance and a telescope was used for the static adsorption measurements.

The following stationary phases were used: SE-30 (methyl siloxane polymer), OV-17 (methyl phenyl (50 : 50) silicon), PEG-20M (polyethylene glycol), TCP (tricresyl phosphate), squalane (Sinwa Chemical Co., Japan); ODPN (β,β'-oxydipropionitrile) (First Reagent Factory of Shanghai); Porapak R,Q,N,T, (Waters Associates, U.S.A.).

Samples of alkanes, alcohols and aldehydes (AnalaR) were purchased from the First and the Third Reagent Factory of Shangai.

RESULTS AND DISCUSSIONS

The raw experimental data from 44 solution systems were all processed using the method of least-squares. The changes in enthalpy $\Delta H_s^{\ominus}$, entropy $\Delta S_s^{\ominus}$, and Gibbs function $\Delta G_{298.2}^{\ominus}$ are listed in Table 1.

Accuracy of $\Delta H_s^{\ominus}$

Changes in enthalpy were detected calorimetrically. The curve of differential heat of solution was obtained with the heat flux microcalorimeter, and the initial differential heat Q_s was obtained by extrapolating the curve to zero concentration. This is, therefore, comparable to the GC result in which the solution is infinitely dilute. Table 2 shows that the data are in accordance with each other.

Equilibrium constants

$K_{c,p}$ can easily be obtained from the GC results. A static experiment was also carried out using the B.E.T. method. The solubility curve is virtually straight in the low pressure range where Henry's law is obeyed: the equilibrium constant can be determined from the slope. Some of our experiments showed that the higher the GC-column temperature range, the higher the $\Delta G_{298.2}^{\ominus}$ calculated, which resulted in a smaller equilibrium constant. This may explain why the results obtained by GC are somewhat smaller than those obtained from the static method (see Table 3). However, the differences between the two sets of data are within reasonable limits.

TABLE 1

Values of $\Delta H_s^{\ominus}$, $\Delta S_s^{\ominus}$ and $\Delta G_{298.2}^{\ominus}$

	$-\Delta H_s^{\ominus}$ (kJ mol^{-1})	$-\Delta S_s^{\ominus}$ (J mol^{-1} K^{-1})	$\Delta G_{298.2}^{\ominus}$ (kJ mol^{-1})
Alkane–squalane (348–383K) [a]			
n-Hexane	24.3	173	27.3
n-Heptane	28.7	179	24.6
n-Octane	33.2	184	21.6
n-Nonane	37.8	190	18.8
n-Decane	42.3	196	16.1
Alkane–SE30 (333–423K)			
n-Heptane	32.6	141	9.3
n-Octane	36.7	146	6.9
n-Nonane	40.8	152	4.4
n-Decane	44.5	156	2.1
n-Undecane	48.6	162	−0.3
Alkane–OV-17 (323–363K)			
n-Hexane	26.9	166	22.6
n-Heptane	31.0	172	20.2
n-Octane	35.2	178	17.8
n-Decane	43.9	190	12.7
n-Undecane	48.1	196	10.3
Alkane–PEG-20M (333–393K)			
n-Heptane	26.8	139	14.6
n-Octane	30.8	145	12.4
n-Nonane	34.5	150	10.2
n-Decane	38.5	156	7.9
n-Undecane	42.7	162	5.6
Alcohol–TCP (353–393K)			
Ethanol	29.5	182	24.7
Propan-1-ol	35.9	194	21.9
Butan-1-ol	39.6	198	19.4
Pentan-1-ol	43.5	202	16.7
Hexan-1-ol	47.5	207	14.2
Alcohol–PEG-20M (333–373K)			
Propan-1-ol	37.3	213	26.2
Butan-1-ol	41.0	218	23.9
Pentan-1-ol	44.9	224	21.8
Hexan-1-ol	48.5	229	19.7
Heptan-1-ol	52.3	235	17.7
Alcohol–ODPN (313–343K)			
Ethanol	32.7	142	9.6
Propan-1-ol	35.8	146	7.9
Butan-1-ol	39.1	151	6.0
Pentan-1-ol	42.2	156	4.2

TABLE 1 (continued)

	$-\Delta H_s^{\ominus}$ (kJ mol^{-1})	$-\Delta S_s^{\ominus}$ (J mol^{-1} K^{-1})	$\Delta G_{298.2}^{\ominus}$ (kJ mol^{-1})
Aldehyde–TCP (353–393K)			
Methanal	21.1	138	20.0
Ethanal	24.9	142	17.4
Propanal	27.2	144	15.7
Butanal	30.6	147	13.2
Pentanal	34.2	150	10.5
Aldehyde–PEG-20M (343–383K)			
Ethanal	25.8	164	23.1
Propanal	28.4	167	21.4
Butanal	31.9	173	19.6
Pentanal	34.8	176	17.6
Heptanal	42.3	187	13.4

[a] Solute–solvent and the temperature range measured.

TABLE 2

Heats of solution (kJ mol^{-1}) obtained by GC and microcalorimetry

	Benzene		Cyclohexane	
	$-\Delta H_s^{\ominus}$	$-Q_s$	$-\Delta H_s^{\ominus}$	$-Q_s$
Squalane	32.0	29.6	32.3	34.2
SE-30	30.0	32.3	30.1	29.4
TCP	30.3	32.8	25.9	28.6
ODPN	31.8	29.4	21.6	–

TABLE 3

Comparison of equilibrium constants ($K_{c,p} \times 10^{-1}$) at 298.2 K using GLC and static methods

	Benzene		Cyclohexane	
	GC	Static	GC	Static
Squalane	2.21	2.81	2.81	3.01
SE-30	1.41	1.76	1.47	1.89
TCP	2.58	2.73	0.80	1.22
ODPN	2.04	2.16	0.13	0.21

The "iso-thermodynamic point"

Many of the physical properties of a homologue relate to its carbon number. Table 1 shows that $-\Delta H_s^{\ominus}$ and $-\Delta S_s^{\ominus}$ also obey this relation. As a matter of fact, the slopes of the ln V_g^0 versus $1/T_c$ plots increase with the carbon number of the homologue. If the plots are extropolated in the

TABLE 4

Comparison of "iso-thermodynamic points" $(1/T_c)_{iso}$ and slopes of compensation effect ($K^{-1}\times10^{-3}$)

		$(1/T_c)_{iso}$	m
Alcohols	PEG-20M	1.42	1.47
Aldehydes	PEG-20M	1.39	1.40
Alcohols	TCP	1.13	1.05
Aldehydes	TCP	0.93	0.96
Alkanes	OV-17	1.44	1.41
Alkanes	Squalane	1.27	1.26
Alkanes	SE-30	1.29	1.30

direction of decreasing $1/T_c$, an intersection point, $\ln(V_g^0)_{iso}$ and $(1/T_c)_{iso}$, of the plots can be found. Obviously, the $\Delta G_s^\ominus$ of a homologue should be the same as that at a hypothetical temperature $(T_c)_{iso}$. Therefore we call this point the "iso-thermodynamic point" as has been reported in adsorption processes [6]. The data are given in Table 4.

Compensation effect

As is the case in adsorption process, a linear relationship has also been found between the $\Delta H_s^\ominus$ and $\Delta S_s^\ominus$ of solution of a homologue in a liquid stationary phase

$$\Delta S_s^\ominus = m\ \Delta H_s^\ominus + n \tag{8}$$

By combining eqns. (5) and (8), G_T can be expressed in terms of m, n and $\Delta H_s^\ominus$

$$\Delta G_T^\ominus = \Delta H_s^\ominus (1 - mT_c) - T_c n \tag{9}$$

At $T_c = 1/m$, the changes in Gibbs function of the solutions of a homologue in a certain liquid stationary phase are all equal to $-n/m$. The difference between $(1/T_c)_{iso}$ and m in the homologue is small (see Table 4). This verifies the reliability of the determination and the internal relationship between compensation effect and iso-thermodynamic point.

Relative polarity of stationary phase

Some indices are used to describe the polarities of the stationary phase in GC [8,9]. Most of them are estimated by the retention volumes at a given temperature. Undoubtedly, $\Delta G^\ominus$ and $\Delta H^\ominus$ are parameters which reflect the interaction between the sample and the stationary phase, both solid and liquid. Therefore, thermodynamic parameters are more universal. Furthermore, it is possible to measure $\Delta H^\ominus$ by methods other than GC itself, e.g. by calorimetry.

TABLE 5

P_{BH} values of some stationary phases

	$-\Delta H_B^\ominus$	$-\Delta H_H^\ominus$	P_{BH}
Porapak Q	48.0	48.8	−8
Squalane	32.0	32.3	−5
SE-30	30.0	30.1	−2
Porapak R	50.5	50.6	−1
Porapak N	51.4	50.9	5
Porapak T	51.7	48.8	29
TCP	30.3	25.9	78
PEG-20M	32.9	25.0	149
ODPN	31.8	21.4	195

Benzene and cyclohexane are two commonly used samples because of their similar sizes and shapes.

A simple index P_{BH} in terms of the $\Delta H_s^\ominus$ values of benzene and cyclohexane in a stationary phase is now proposed to describe the relative polarity of a given column

$$P_{BH} = \frac{\Delta H_B^\ominus - \Delta H_H^\ominus}{\Delta H_B^\ominus + \Delta H_H^\ominus} \times 1000 \tag{10}$$

The data of some stationary phases in the order of their relative polarities P_{BH} can be seen in Table 5. Porapak Q seems to be less polar than squalane. This agrees with the results already reported [10] and was explained by the impurity squalene present in the squalane, identified by IR.

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