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## COMPARISON OF STATIC AND GAS CHROMATOGRAPHIC SOLUBILITY DATA

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### SUMMARY

The solubility data calculated by the use of static and gas chromatographic techniques are compared for polar and non-polar solutions. For non-polar solutions, partition coefficients and molar heats of solution were equal according to both techniques. Only carefully estimated partition coefficients (specific retention volumes) of polar solutes (acetone, alcohols) in squalane (with adsorption effects taken into account) were the same for both techniques, but molar heats of solution differed somewhat. Molar heats of solution for infinitely diluted solutions of polar solutes can be calculated only by the static technique. Adsorption and concentration effects were studied for alcohol solutions in squalane and oxydipropionitrile, and the contribution of these effects to the retention volume in gas-liquid chromatography was measured.

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### INTRODUCTION

Gas-liquid chromatography (GLC) is one of the most preferable physico-chemical methods for studying the solubility of non-electrolytes<sup>1,2</sup>. Unfortunately, a more detailed study has shown that a partition coefficient estimated from the retention volume data depends not only on solubility but also on inter-phase adsorption<sup>3,4</sup>. In general, the partition coefficients for the adsorption and the solubility depend on concentration ( $c$ )<sup>5,6,20</sup>.

The relationships between partition coefficients and concentration were studied in a previous paper<sup>5</sup>. It has been shown that partition coefficients vary with the nature of solutes and solvents. The solubility data calculated from gas chromatographic results are of importance for different absorption processes and for development of the theory of solubility. Therefore, a comparison of the solubility data calculated from gas chromatographic and static measurements shows the accuracy that we can obtain using the gas chromatographic technique. Some comparisons were made for non-polar, mainly hydrocarbon-hydrocarbon, solutions<sup>7,8</sup>. For such systems the static and gas chromatographic partition coefficients were the same within the limits of error of about 1%.

The aim of this paper is to compare static and gas chromatographic data on

the partition coefficients and thermodynamic functions for solutions consisting of at least one polar component. The concentration variation in partition coefficients were taken into account. Saturated  $C_2-C_5$  alcohols, acetone and benzene were chosen as solutes; and non-polar (squalane) and highly polar ( $\beta,\beta'$ -oxydipropionitrile) stationary phases were used.

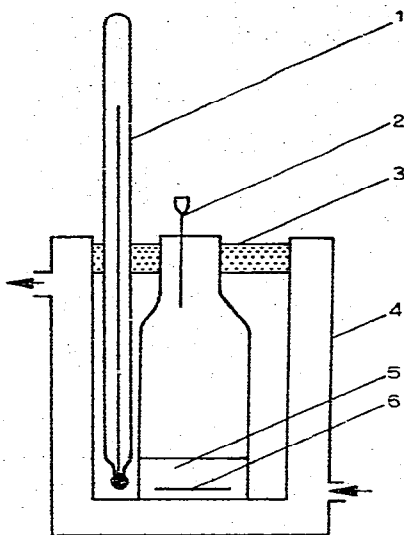


Fig. 1. The saturator for static measurements. 1, Thermometer; 2, syringe needle; 3, cork; 4, glass thermostat; 5, solution; 6, magnetic stirrer.

## EXPERIMENTAL

The static measurements were carried out in 50-ml thermostated vessels (Fig. 1) containing 5–10 ml of solutions of different concentrations. A magnetic stirrer stirred the solution. The time required to attain the phase equilibrium depended on temperature and was about 10–30 min. When the phase equilibrium was achieved, a sample of the gas phase (from the vessel) was taken by a 100- $\mu$ l Hamilton syringe provided with an adaptor. The sample was injected into a Chrom 31 chromatograph (Laboratorni pristroje, Prague, Czechoslovakia) with flame-ionization detector. A 100  $\times$  0.4 cm column was packed with 0.16–0.20 mm Chromaton N HMDS (Lachema, Czechoslovakia) coated with 10% polyethylene glycol adipate. The carrier gas was nitrogen. The column temperature was 140  $^{\circ}$ C. Quantitative analysis was made by an absolute calibration technique using the peak heights. The vapours saturated at 15  $^{\circ}$ C were used as the standard. All solutes were of the "chromatographically pure" grade.  $\beta,\beta'$ -Oxydipropionitrile was purified by vacuum distillation. Squalane was purified by preparative column chromatography on silica gel in an 80-cm column. The mean standard deviation in the determination of the partition coefficient by the static technique was about 2%. To compare the solubility data in the static and gas chromatographic experiments, the partition coefficients calculated in the static method were recalculated to the specific retention volume,  $V_g^*$ , as follows:

$$V_g^* = \frac{m_2 - c_g v_g}{(m_L + m_2 - c_g v_g) c_g} \cdot \frac{273.2}{T} \quad (1)$$

where  $T$  is temperature in  $^{\circ}\text{K}$ ,  $m_L$  is weight of the stationary phase,  $m_2$  is weight of the solute,  $c_g$  is concentration of the solute in the gas phase, and  $v_g$  is volume of the gas phase.

The  $V_g^*$  value measured from the static experiments refers to solution at finite concentration; therefore its physical nature differs from the specific retention volume,  $V_g$ , obtained from GLC data. It is possible to compare  $V_g^*$  and  $V_g$  values only when  $V_g^*$  is extrapolated to zero concentration.

The molar heats of solution  $\Delta H_s$  were estimated in the static experiments by the following thermodynamic equation:

$$\Delta H_s = \frac{R \partial[\ln(p_2/N_2)]}{\partial(1/T)} \quad (2)$$

where  $p_2$  is the vapour pressure of the solute and  $N_2$  is a molar fraction of the solute.

Our gas chromatographic experiment was carried out using the same chromatograph with a  $50 \times 0.4$  cm column. The column was packed with Chromaton N HMDS coated with 13–25% of the stationary phase by weight. The column was thermostated at 30–60  $^{\circ}\text{C}$ . The values of  $V_g$  and  $\Delta H_s$  were calculated as in refs. 9 and 10. The average standard deviations of  $V_g$  and  $\Delta H_s$  values were about 1% and 0.2 kcal/mole, respectively.

It is important to choose the proper sample size for non-ideal systems. The relationship between the sample size and the  $V_g$  value has a minimum<sup>11</sup>. Repeatable  $V_g$  values are obtained only when the sample size corresponds to this minimum. Under this condition the partition coefficients are constants for a first approximation<sup>5</sup>. Therefore, for all gas chromatographic measurements the  $V_g$  values corresponding to the minimum were used.

To calculate the partition coefficients  $(c_L/c_g)_T$  ( $c_L$  is the solute concentration in the liquid phase) it is necessary to measure the interphase adsorption using the following equation<sup>4,12</sup>:

$$V_N = V_g^T \cdot m_L + V_{Na} \quad (3)$$

where  $V_{Na}$  is the sum of all the interphase adsorption effects, and  $V_g^T$  is the specific retention volume corrected to the column temperature.

To estimate the adsorption on the surface in the static experiment the variation in the solute concentration  $\Delta c_g$  was measured in the gas phase after Chromaton had been added to the solution. The amount of solute adsorbed,  $a$ , was calculated as follows:

$$a = \frac{\Delta c_g^T \cdot K \cdot V_L}{m_c} \quad (4)$$

where  $V_L$  is volume of the liquid phase,  $m_c$  is the weight of added Chromaton, and  $K$  is the partition coefficient.

This technique for adsorption measurement is similar to that described in ref. 13. It is possible to obtain the adsorption isotherm by plotting  $a$  values against  $c_g$  or  $c_L$ . The mean standard deviation of the  $a$  values was about 10%.

## RESULTS AND DISCUSSION

*Benzene solution*

The specific retention volume of benzene solutions in the polar and non-polar stationary phases is independent of the sample volume over a wide concentration range.

The values  $V_g^T$  and  $V_{Na}$  are listed in Table I for squalane. As is shown in ref. 14, the adsorption at the liquid surface for non-polar stationary phases is negligible; therefore, the  $V_{Na}$  value for squalane depends on adsorption at the solid-liquid interphase. The contribution of adsorption into  $V_g$  for benzene is 3.5 and 3.8% at 50 and 20°C, respectively, the stationary phase amount being 15%. These values are very high for such an inert support as Chromaton N AW HMDS. But these values can be explained by adsorption on the silanized surface of the support having a hydrocarbon nature.

TABLE I

VALUES OF  $V_g^T$  (ml/g) AND  $V_{Na}$  (ml) MEASURED ON SQUALANE UNDER GAS-CHROMATOGRAPHIC CONDITIONS

Solute	50°C		20°C	
	$V_g^T$	$V_{Na}$	$V_g^T$	$V_{Na}$
Ethanol	17.4	0.7	32.4	2.2
<i>n</i> -Propanol	54.6	1.8	127	2.9
<i>n</i> -Butanol	159	5.6	476	9.8
Isopropanol	30.4	0.9	64.5	3.1
<i>sec.</i> -Butanol	100	1.6	259	7.1
<i>tert.</i> -Butanol	47.6	1.3	106	5.6
Isobutanol	113	2.7	286	12.5
Acetone	28.9	0.3	56.0	0.9
Benzene	274	3.0	784	9.3

When the polar stationary phase coats the solid support surface the adsorption is decreased rapidly because the real nature of the interphase surface is changed. Our gas chromatographic experiments show that the contribution of adsorption into  $V_g$  for benzene in  $\beta,\beta'$ -oxydipropionitrile was about 0.6%. (The support was coated with 15% of stationary phase.) This value is similar to that calculated by Berezkin for the adsorption on the polar liquid phase<sup>15</sup>.

Only in the static experiments was it possible to measure the concentration relationships of the  $V_g$  values. We used the Krichevski equation<sup>20</sup>, modified for GLC<sup>5</sup>:

$$\log V_g^* = \log V_g + A(2N_2 - N_2^2) \quad (5)$$

where  $V_g$  is the specific retention volume extrapolated to zero concentration, and  $A$  is the concentration coefficient.

The experimental data for benzene in squalane are plotted in Fig. 2. The  $V_g^*$  value extrapolated to  $N_2 = 0$  is 720 ml/g which is somewhat smaller than that estimated from the gas chromatographic experiment. To explain this difference let us

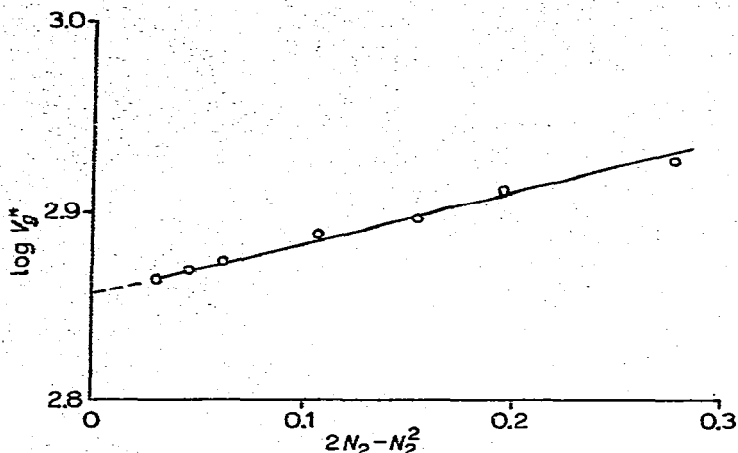


Fig. 2. Relationship between  $\log V_g^*$  and  $2N_2 - N_2^2$  for solutions of benzene in squalane at 20°C (static measurements).

plot  $\log (p_2/N_2)$  instead of  $\log V_g$  versus  $2N_2 - N_2^2$  (Fig. 3). Indeed, Fig. 3 shows that, at very low concentrations, there is a small area where  $p_2/N_2^2$  is constant, which corresponds to Henry's law. The values of  $K$  calculated for benzene both from static and gas chromatographic data are in good agreement. (The deviation is about 1% which is within experimental error.)

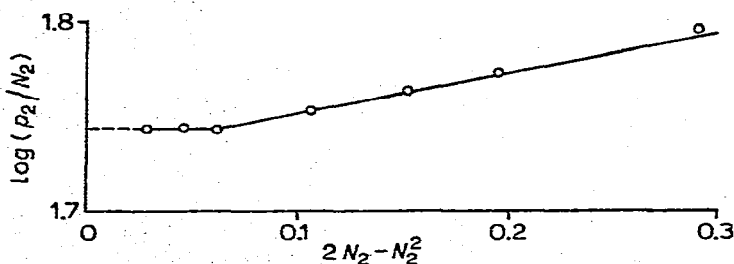


Fig. 3. Relationship between  $\log (p_2/N_2)$  and  $2N_2 - N_2^2$  for benzene solutions in squalane at 20°C.

Therefore, the reason for somewhat underestimated  $V_g$  values calculated by the static technique lies in the erroneous extrapolation of the Krichevski equation to Henry's region of concentrations. It is true for solutions that are close to the ideal (for example, hydrocarbons in hydrocarbons) to find the Henry region of concentrations and to calculate the  $V_g^*$  values (or  $K$  values) for this region.

Taking into account that  $c_g = p_2/RT$  we may rewrite eqn. 1 as follows:

$$p_2 = \frac{273R (m_2 - c_g v_g)}{V_g^* (m_L + m_2 - c_g v_g)} \quad (6)$$

As  $c_g v_g \ll m_2$  the  $c_g v_g$  term in eqn. 6 may be neglected. Let us denote  $n$  as the

TABLE II

COMPARISON OF SPECIFIC RETENTION VOLUMES MEASURED BY GAS CHROMATOGRAPHIC ( $V_g$ ) AND STATIC ( $V_g^*$ ) TECHNIQUES AT 20°C

Solute	Squalane		$\beta,\beta'$ -Oxydipropionitrile	
	$V_g$	$V_g^*$	$V_g$	$V_g^*$
Ethanol	30.3	30.6	729	729.5
<i>n</i> -Propanol	118.5	118	1570	1560
<i>n</i> -Butanol	444	447	3480	3470
<i>n</i> -Pentanol	—	—	7800	7730
<i>sec.</i> -Butanol	242	238	1460	1470
<i>tert.</i> -Butanol	98.8	99.1	618	617
Isobutanol	266	264	2150	—
Isopropanol	60.1	60.1	714	—
Acetone	51.2	52.2	—	—
Benzene	731	722	610	602

number of moles, then  $m_2 = n_2 M_2$  and  $m_L = n_L M_L$ , where  $M$  is the molecular weight. Then:

$$p_2 = \frac{n_2 M_2}{n_L M_L + n_2 M_2} \cdot \frac{273R}{V_g^*} \quad (7)$$

Let us divide this equation by a mole fraction  $N_2 = n_2/(n_L + n_2)$ :

$$\frac{p_2}{N_2} = \frac{(n_L + n_2) \cdot 273R}{(n_L M_L/M_2 + n_2) V_g^*} \quad (8)$$

The left part of eqn. 8 is the partition coefficient between the gas and liquid phases.

Let us discuss three possible cases.

(1)  $p_2/N_2 = \text{constant}$ . The solution is obeyed Henry's law. Taking into account that  $M_2 < M_L$  for gas chromatographic systems, we can consider the term  $n_L M_L/M_2 + n_2$  as a constant. When  $n_2$  is increased, the term  $\frac{n_L + n_2}{n_L M_L/M_2 + n_2}$  is also increased.

Hence, when  $n_2$  rises  $V_g^*$  rises too.

(2) For a non-ideal solution with positive deviations,  $p_2/N_2$  decreases and  $V_g^*$  increases with increasing solute concentration.

(3)  $p_2/N_2$  increases as the concentration of solute is increased (non-ideal solution with negative deviations). In this case it is possible that  $V_g^*$  may also increase with increasing solute concentration because  $p_2/N_2$  is varied far less than

$\frac{n_L + n_2}{n_L M_L/M_2 + n_2}$  for gas chromatographic systems. These conclusions are similar to those made by Henly *et al.*<sup>6</sup>

Unfortunately, when a solute and a solvent have different physico-chemical properties (for example, polarity) it is difficult to find the Henry region and, therefore, an extrapolation according to eqn. 5 is expedient.

The molar heat of solution extrapolated to  $N_2 = 0$  from the static experiment was the same as in the gas chromatographic experiment (Table III).

TABLE III

COMPARISON OF MOLAR HEATS OF SOLUTION IN SQUALANE MEASURED BY GAS CHROMATOGRAPHIC ( $\Delta H_{sc}$ ) AND STATIC ( $\Delta H_{ss}$ ) TECHNIQUES AND CALCULATED FROM THE DISPERSION INDICES ( $\Delta H_d$ ) (kcal/mole)

Solute	$\Delta H_{sc}$	$\Delta H_{ss}$	$\Delta H_d$
Ethanol	4.5	2.8	2.8
<i>n</i> -Propanol	6.0	4.5	4.0
<i>n</i> -Butanol	7.3	5.3	5.2
Isopropanol	5.3	—	3.7
<i>tert.</i> -Butanol	5.5	—	4.9
Acetone	4.9	4.3	4.3
Benzene	7.2	7.2	—

### Acetone solutions

Table I shows that the contribution of adsorption in  $V_g$  for acetone in squalane is 3.6 and 5% at 50 and 20 °C, respectively, the amount of stationary phase on the support being 15%. The specific retention volumes of acetone calculated from the static and gas chromatographic techniques agree sufficiently well (Table II).

The molar heat of solution calculated from the static technique by extrapolation of  $N_2 \rightarrow 0$  was somewhat smaller than that calculated from GLC data (Table III). In our previous paper<sup>16</sup> an assumption about concentration effects in GLC was made. From calculation according to the cited paper the molar heat of solution for acetone in squalane without the concentration effects was 4.35 kcal/mole, which is in excellent agreement with that found in the static experiment. Thus, this assumption is very well confirmed by direct static measurements.

### Alcohol solutions

Alcohol solutions in polar and moderately polar stationary phases are examples of solutions with great positive deviations from Raoult's law (Fig. 4). These solutions are the extreme case of non-ideality. Therefore, it is expedient to compare the gas chromatographic and static data obtained for these systems to check the

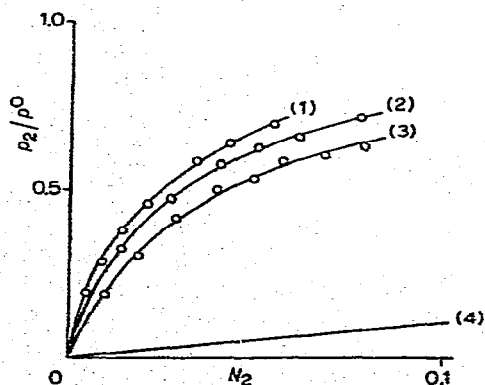


Fig. 4. Deviations from Raoult's law at 20°C. (1) Ethanol; (2) *n*-propanol; (3) *n*-butanol (all in squalane). Line (4) corresponds to Raoult's law.  $p^0$  = pressure of saturated vapours of the solute.

reliability of the solubility parameters calculated from the retention volumes in gas-liquid chromatography. Alcohol solutions in squalane were investigated in some works<sup>3,13,16,17</sup> by both static and gas-liquid chromatographic techniques. The contribution<sup>19</sup> of the adsorption in  $V_g$  for such systems is about 60% (on Inz-600 solid support).

The adsorption data for *n*-propanol on a squalane-Chromaton system were obtained by the static technique. At different concentrations of *n*-propanol in squalane after the addition of Chromaton, the adsorption isotherm, calculated at 20° (Fig. 5), had a linear form as did that reported in ref. 13 on Celite 545. Our static data have been recalculated to obtain the contribution of adsorption to the retention volume. This was 8.5%, and close to the gas chromatographic results (Table I). For such a system on Celite 545 (ref. 13) the contribution of adsorption under the same conditions was 30% which shows the great importance of the support surface.

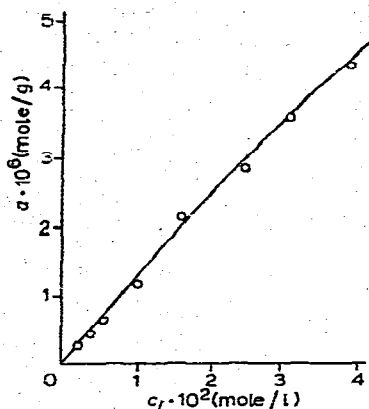


Fig. 5. Adsorption isotherm of *n*-propanol at 20°C on Chromaton coated with squalane.

Table I shows that the contribution of adsorption to the retention volume for lower alcohols rapidly increased with a decrease of temperature. This effect was caused by the difference between heat of solution and heat of adsorption. The latter is much greater than the former and, therefore, the adsorption increases more rapidly with decreasing temperature than the solubility, as follows from the equation

$$\Delta H_s = \frac{R \partial(\ln V_g)}{\partial(1/T)} \quad (9)$$

The contribution of adsorption for branched alcohols is smaller than for *n*-alcohols. The greater the solubility, the smaller the contribution of adsorption. The increments of the adsorption part of the retention volume (15% of squalane) for alcohols (Table I) decreased with increasing the hydrocarbon chain in the alcohol molecule from 12.5 to 11% at 50 °C and from 21.3 to 7% at 20 °C.

The concentration relationships for alcohol solubility have the same equation as that for benzene (eqn. 5). The relationships between the concentration coefficient  $A$



and the number of carbon atoms in the alcohol molecule is plotted in Fig. 6. The  $A$  values in squalane are much higher than in  $\beta,\beta'$ -oxydipropionitrile. A similarity in the physico-chemical nature of alcohols and stationary phase molecules is increased for squalane (or decreased for  $\beta,\beta'$ -oxydipropionitrile) when the alkyl radical in the alcohol molecule is increased. The  $A$  values for branched alcohols lie lower than those for  $n$ -alcohols in squalane and higher in  $\beta,\beta'$ -oxydipropionitrile. Shielding the hydroxyl group by an alkyl radical reduces the  $A$  value in the non-polar liquids.

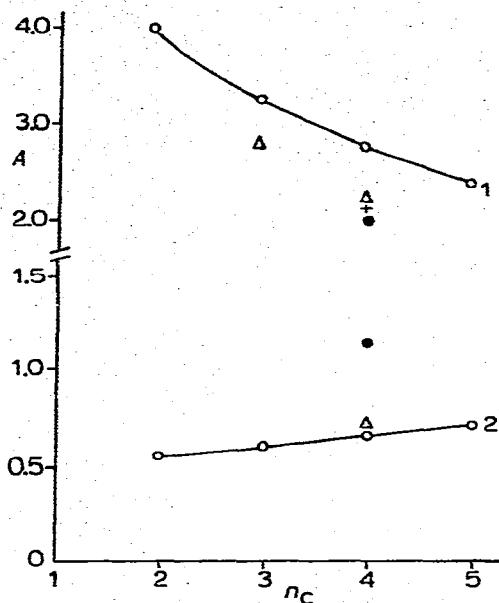


Fig. 6. Relationship between the concentration coefficient  $A$  and number of carbon atoms  $n_c$  in an alcohol molecule.  $\circ$ ,  $n$ -Alcohols;  $\Delta$ ,  $sec.$ -alcohols;  $+$ , isoalcohols;  $\bullet$ ,  $tert.$ -alcohols. 1, Solutions in squalane; 2, solutions in  $\beta,\beta'$ -oxydipropionitrile.

Table II lists the  $V_a$  values calculated from gas chromatographic data (taking into account the interphase adsorption) and from the static data extrapolated to an infinite dilution. All the data agree satisfactorily within experimental error (2%). Hence, the solubility (liquid-gas equilibrium) can be found from carefully calculated GLC data even for very non-ideal solutions.

Molar heats of solution for alcohols in squalane are listed in Table III. The experimental heats of solution calculated from data measured by the static technique for infinitely diluted solutions agree satisfactorily with those calculated from the dispersion indices<sup>16</sup>. A comparison of heats of solution calculated from gas chromatographic and static experiments shows that the concentration effects take place even for very small samples in GLC ( $2 \cdot 10^{-5}$ – $1 \cdot 10^{-4}$  g).

Experimental results show that the partition coefficients and specific retention volumes carefully calculated from GLC data characterize quantitatively the solubility for the polar and non-polar systems. Thermodynamic functions of solution calculated

from GLC data are close to those calculated from the static measurements only for non-polar systems. Thus, the partition coefficients calculated from GLC data can be used for different purposes; for example, for extraction processes.

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