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The Determination of Partition Coefficients from Gas–Liquid Partition Chromatography

BY P. E. PORTER, C. H. DEAL AND F. H. STROSS

RECEIVED DECEMBER 9, 1955

Experimental data have been presented which show that partition coefficients which result from applying the Martin and Synge description of the GLPC process (as modified by James and Martin) to GLPC data are essentially sound equilibrium partition coefficients. From this it may be concluded that partition coefficients rather than retention volumes are the proper parameters for use in GLPC as has been pointed out by Littlewood, Phillips and Price in slightly different terms. It may also be concluded that the extensive data relating to the non-idealities of solutions may also be applied directly to the problems of understanding and predicting GLPC behavior.

Martin and his co-workers[1-3] have described the technique of gas–liquid partition chromatographic (GLPC) separation, have demonstrated its utility and have provided a good understanding of the essential nature of the process. They and others have clearly recognized the importance of solvent effects in determining the GLPC separations possible and have pointed to the potential application of GLPC measurements in the study of the non-idealities of solutions. The close relations between GLPC behavior and direct solution behavior have not yet been fully exploited, however, either with the object of applying existing knowledge of direct solutions to GLPC or with regard to the application of GLPC data to the study of solutions. It is the purpose of the present paper to describe an experimental technique and to present GLPC data to which the description of the GLPC process given by Martin and his co-workers can be applied so as to obtain sound equilibrium partition coefficients for a solute between liquid solvent and gas phases from GLPC measurement. On the basis of this work a companion paper[4] exploits direct vapor–liquid equilibrium studies in describing and correlating solvent effects in gas–liquid partition chromatography.

If the apparent partition coefficients from GLPC measurements are to be fundamentally sound and useful quantities, it is necessary that several conditions must be met. Coefficients determined in columns of different geometry and under different flow conditions must be consistent. Coefficients must not be markedly influenced by the solid support and must be substantially the same as those obtained from well defined equilibrium conditions. In the present work practical GLPC operations are discussed in the light of the Martin theory and in the light of some of the known aspects of solution behavior in order to delineate the conditions of GLPC operations which might be expected to lead to sound partition coefficients. Experimental GLPC data which confirm the consistency of partition coefficients (*i.e.*, the roughly equivalent V_g) obtained by Littlewood, Phillips and Price[5] but over a somewhat wider range of column length and gas flow rates are presented. In addition, experimental data obtained under appropriate GLPC conditions and under equilibrium conditions are presented. They show that the solid supports of diatomaceous earths have no substantial effect upon partition between gas and liquid phases and that partition coefficients by the two methods are in substantial agreement.

Relations of Retention Volume and Partition Coefficient.—The theory of Martin and Synge[2,3] provides the basis for a relationship between the partition coefficients for solute materials and the retention volumes for a purely GLPC process in which the solvent support is inert. In order to obtain rigorously valid partition coefficients or, conversely, in order to estimate suitable retention volumes from partition coefficients, however, due account must be taken of the simplifying assumptions of the theory. These are essentially as follows:

(a) No change in volume of a volume element of carrier gas occurs as it passes through a column.

(b) The partition coefficient for the distributing material is constant throughout the column.

(c) Samples are charged so that the initial charge is contained in the first plate.

(d) All rate effects can be taken into account by means of the concept of theoretical plates of which the heights are small relative to the column length and remain constant throughout the column. These simplifications lead Martin and Synge to an expression for the amount of material in the r'th plate after V volume of mobile gas is passed into the column. For purposes of the present discussion, this may be transformed into an expression for the concentration of the solute in the effluent gas (C), as a function of the volume of mobile gas passed into the column (V), the amount of material charged to the first plate (q_0), the number of plates in the column (r) and the retention volume (V_R^0). This becomes

$$C = \frac{r}{V_R^0}\,\frac{q_0}{\sqrt{2\pi r}}\,e^{(-r/2)(1-V/V_R^0)^2} \qquad \text{(I)}$$

The retention volume is the volume of mobile phase passed into the column when C is a maximum and is related to the column geometry and the partition coefficient for the solute by

$$V_R^0 = V_m + H^0 V_s \qquad \text{(II)}$$

where

V_m = vol. occupied by the mobile vapor phase in the column
V_s = vol. occupied by the stationary solvent phase in the column
H^0 = solute partition coefficient defined as the ratio of solute per unit vol. of the solvent phase to that of the gas phase, properly taken as indicated below when the solute is at infinite diln. in the liq. solvent phase

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(1) A. T. James and A. J. P. Martin, *Biochem. J.*, **50**, 679 (1952).

(2) A. J. P. Martin and R. L. M. Synge, *ibid.*, **35**, 1358 (1941).

(3) A. J. P. Martin, *Biochem. Soc. Symposia*, No. 3, 4 (1951).

(4) G. J. Pierotti, C. H. Deal, E. L. Derr and P. E. Porter, THIS JOURNAL, **78**, 2989 (1956).

(5) A. B. Littlewood, C. S. G. Phillips and D. T. Price, *J. Chem. Soc.*, 1480 (1955).

It will be noted that the retention volume here does not depend explicitly on the number of plates in the column but depends only on the column geometry through V_m and V_s. Equation II provides a basis for estimating partition coefficients from retention volumes provided that the retention volume used is that defined by the conditions imposed by the simplifying assumptions of the theory.

For present purposes the activity coefficient for the solute may be defined as is customary for solutions of non-electrolytes[6] by

$$yP = \gamma x P^0 \qquad \text{(III)}$$

so that

$$H = \frac{xM_s}{yM_m} = \frac{xP}{\gamma x P^0}\frac{M_s}{M_m} = \frac{M_sRT}{\gamma P^0} \qquad \text{(IV)}$$

where

x = mole fraction of solute in the liq. phase
y = mole fraction of solute in the gas phase
P = pressure of the substantially ideal gas phase
M_m = moles of mobile gas phase per unit vol.
M_s = moles of stationary liquid phase per unit vol.
γ = activity coefficient of the solute in the solvent phase, taking the pure liq. solute as standard state and the gas phase as ideal
P^0 = vapor pressure of the solute

Although non-idealities in the gas phase may become significant, these will not be considered here. Strictly, the assumption of constant partition coefficient implies either ideal solutions or infinitely dilute solutions. Thus equation II in these terms becomes

$$V_R^0 = V_m + \frac{M_sRT}{\gamma^0 P^0} V_s \qquad \text{(V)}$$

where γ^0 is the activity coefficient at infinite dilution. As is immediately apparent, expressing the partition coefficient in this manner has the advantage of clearly separating it into the fundamental solvent dependent (M_s), solute dependent (P^0) and solute–solvent dependent (γ^0) factors.

Volume Changes of Carrier Gas.—James and Martin[1] have shown that a limiting retention volume for the case of no gas expansion, that is, the V_R^0 of the Martin and Synge theory may be obtained from an apparent retention volume by

$$V_R^0 = V_R \Big/ \left[2/3\,\frac{(p_i/p_0)^3 - 1}{(p_i/p_0)^2 - 1}\right] \qquad \text{(VI)}$$

Here

V_R = apparent retention vol.; *i.e.*, vol. of gas phase passed into the column when the maximum in solute concn. appears in the column effluent
p_i = inlet pressure
p_0 = outlet pressure

In the present work inlet to outlet pressure ratios are less than two, and the conversion of V_R to V_R^0 involves a correction of less than 50%.

Variation in Partition Coefficients.—In normal GLPC column operations an over-all compromise condition between sample size and charging technique, partition coefficient magnitude (solvent nature and temperature),, column length and detecting sensitivity is arrived at. In practice, this compromise is frequently such that the initial concentrations of solute in the solvent at the beginning of a column may be as high as one or two tenths mole fraction. Since the activity coefficient, hence partition coefficient, is normally a sensitive function of concentration in this region (except for ideal solutions), and since the maximum concentration of a solute band falls as the band is developed through a column, this results frequently in considerable variation of the partition coefficient operative.

Although a quantitative accounting of the effects of a variable partition coefficient cannot be made conveniently, several qualitative conclusions can be drawn.

If $\gamma^0 < 1$, γ is greater and the partition coefficient is smaller along the more concentrated portions of a band than in the dilute portions. This results in a slower movement of material in the less concentrated portions of a band relative to that in the more concentrated portions, in a sharpening of the band front and in a broadening of the trailing edge of the band as it moves through the column. As the maximum concentration in the band falls, the net motion of the band becomes relatively slower approaching that obtained in the limiting case of zero concentration in the solvent. Under these circumstances the apparent retention volume is less than the limiting value (V_R^0) of the Martin and Synge theory and approaches this value in the limit in which the charge is put on the column at zero concentration. This effect opposes the effects of finite sample charging volume discussed below with regard to retention volume but augments the effect on band shape of a slowly falling concentration in the charging operation.

Activity coefficients of less than unity most frequently occur only when the solution components are very similar in polarity but have a large difference in molar volume or when the solution components tend to react chemically.

If $\gamma^0 = 1$, the solution is ideal, the partition coefficient is constant and the apparent retention volume is identical with the limiting retention volume insofar as partition coefficient effects are concerned.

If $\gamma^0 > 1$, γ is smaller and the partition coefficient is greater along the more concentrated portions of the band than in the dilute portions. This results in a faster movement of material in the less concentrated portions of a band relative to that in the more concentrated portion of the band, in a sharpening of the trailing portion of the band and in a broadening of the band front. As the maximum in the band falls, the net motion of the band becomes relatively faster and approaches that in the limiting case of the Martin and Synge theory. Under these circumstances the apparent retention volume is greater than the limiting value V_R^0. This effect augments the finite sample charging volume effect discussed below with regard to retention volume and opposes the effect on band shape of a slowly falling concentration in the charging step.

Activity coefficients greater than unity usually occur when there is a difference in polarity between the components. As a practical matter it may be noted in passing that solute–solvent systems in which there are large differences in polarity in general give relatively low partition coefficients (equa-

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(6) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold Publ. Corp., New York, N. Y., 1950.

tion IV) and consequently relatively low plate capacities. For some given separation, however, the low capacity effect may have to be tolerated in order to obtain a sufficiently large difference in partition coefficients (retention volumes) for any separation at all.

It is of interest that effluent curve shapes attributable to each of the cases have been obtained.

It is clear from the above that equation V can be strictly applied only when solutions are ideal or when solutes are charged to very low concentrations in the solvent phase. The allowable concentration for at least semi-quantitative application of equation V depends critically upon the magnitude of the infinite dilution activity coefficient of the particular solute in the particular solvent being used. In the determination of partition coefficients from GLPC measurements of the present work cognizance has been taken of the above effects by introducing samples into the carrier gas at fairly low (*ca.* 0.05 mole fraction) and at roughly comparable vapor concentrations for all solutes. Although this procedure does not ensure that the partition coefficient remain constant (wide ranges of partition coefficients are covered at a given temperature and with a given solvent), it does provide a reproducible technique with sample sizes which can be conveniently handled and detected in the effluent gas. In addition, it provides apparent partition coefficients which are comparable to those encountered in practical work. An alternative procedure of charging the minimum detectable concentration of sample in a solution of sufficient size for convenient handling may give somewhat more constant partition coefficients through the column. In this case the second component of the charge should be of widely different volatility from the solute of primary interest in order that its band overlap the primary band for the minimum time in the column and have the least effect on the partition coefficient operative in the primary band.

Rate Effects.—Although the Martin and Synge theory exploits the concept of theoretical plates to avoid detailed consideration of mass transfer and diffusional effects, it is apparent from equation II that the number of theoretical plates is not explicitly involved in the retention volume. Variations in the heights equivalent to a theoretical plate along the length of a column, of themselves, would consequently not be expected to affect apparent retention volumes critically. Thus such factors as diffusion along the column length of a column would not be expected to affect the validity of equation V although it might be expected to affect the apparent number of theoretical plates in a column. As will be shown below quite consistent results are obtained over wide ranges of carrier gas flow rate.

Sample Charging.—Normally GLPC columns are charged by techniques which amount to inserting a charge into the carrier gas stream. Here the charge is vaporized at some indeterminate rate and is carried to the column for absorption into the solvent liquid. Under these conditions the sample size charged may affect apparent retention volumes by giving rise to high concentrations in the vapor carried to the column and thus to variable partition coefficients as discussed above. The sample size charged may also affect the apparent retention volume by being charged over a significant time (volume of carrier gas) and by forming an initial band spread out over a significant length of column, depending on the magnitude of the partition coefficient. It is clear that, although effects may be small, some correction must be made on the apparent retention volume in order to apply equation II.

As pointed out by Martin and Synge, each elemental amount of solute acts independently of every other such element if the partition coefficient is constant. If, in addition, the manner of charging can be characterized, the effects of the charging technique on the development of the solute through the column can be estimated.

If the concentration of solute in the charging gas is $C(S)$ where S is the volume of gas passed into the column since charging began, the solute charge can be thought of as being added in small increments $dq_0 = C(S)\,dS$. If a total volume of gas V, measured from the beginning of the charging, is passed to develop the band, then the amount of gas used to develop any given increment is $V - S$, and the contribution to the concentration of solute in the last plate is

$$dC_r = C(S)\,dS\left[\frac{r}{V_R^0} \times \frac{1}{\sqrt{2\pi r}} \times e^{-\frac{r}{2}\left(1-\frac{V-S}{V_R^0}\right)^2}\right] \tag{VII}$$

The total concentration in the last plate when V gas has been passed is then

$$C_r(V) = \int_0^{S_0} \frac{r}{V_R^0\sqrt{2\pi r}}\, C(S)\, e^{-\frac{r}{2}\left(1-\frac{V-S}{V_R^0}\right)^2} dS \tag{VIII}$$

where S_0 is the total volume of gas used in the charging cycle.

Two extreme cases may be considered: the case in which a plug of solute–gas mixture of constant composition is charged and the case in which the solute–gas mixture falls to zero solute composition exponentially. For the apparatus described here, these two cases correspond first to the case in which the sample is displaced plug-wise from the vaporizer chamber into the column and second to the case in which complete mixing occurs between developer gas and sample at all times after the sample chamber is switched into the gas stream.

For the first case

$$C(S) = C_0,\ 0 < S \leqq B$$
$$C(S) = 0,\ S > B$$

and

$$C_r(V) = \frac{r}{V_R^0}\,\frac{C_0}{\sqrt{2\pi r}}\int_0^B e^{-\frac{r}{2}\left(1-\frac{V}{V_R^0}+\frac{S}{V_R^0}\right)^2} dS \tag{IX}$$

where B is the volume of the sample chamber. In this case it can be shown by finding the maximum in C as a function of V that the apparent retention volume, that is, the volume of gas passed when the $C_r(V)$ is a maximum at plate r, is

$$V_R = V_R^0 + B/2 \tag{X}$$

The chromatogram is symmetrical about its center, and as in the Martin and Synge case the apparent retention volume is independent of the number of plates in the column. The chromatogram may be calculated in detail by the use of tables of values of the probability integral. Equation IX is of the form

$$C_r(V) = \frac{C_0}{2} \times \frac{2}{\sqrt{\pi}} \int_{X_0}^{X_1} e^{-X^2}\,\mathrm{d}X \qquad \text{(XI)}$$

where

$$X_0 = \sqrt{\frac{r}{2}}\left(1 - \frac{V}{V_\mathrm{R}^0}\right)$$

$$X_1 = X_0 + \sqrt{\frac{r}{2}}\,\frac{B}{V_\mathrm{R}^0}$$

The result of varying the sample size while holding the concentration of solute in the charging gas constant is shown by the calculation in Fig. 1. It is

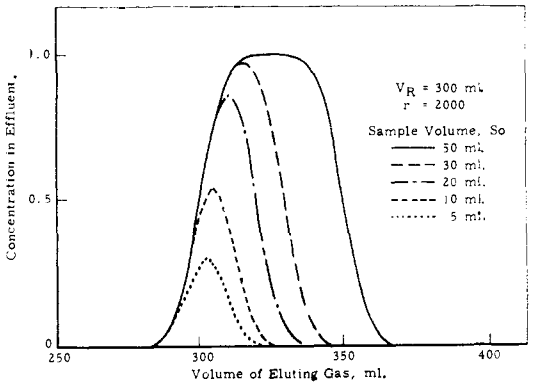

Fig. 1.—Elution curves for variable sample of constant concentration.

clear that the flattened top on the upper curve corresponds to the case in which the sample is so large that it fills a substantial portion of the column before the charging step is complete. With a lower partition coefficient (higher activity coefficient or higher P°), this flattened curve occurs at a lower sample size. Likewise it is clear that the apparent number of plates in a column calculated by the procedure frequently used which does not take into account sample size, is dependent upon the sample size.

For the second extreme case the solute charging may be approximated by

$$C(S) = C_0e^{-S/B},\ S \geqq 0$$

where B is the volume of the sample container. The concentration of solute in the effluent is

$$C_r(V) = \frac{r}{V_\mathrm{R}^0}\,\frac{C_0}{\sqrt{2\pi r}} \int_0^V e^{-S/B - \frac{r}{2}\left(1 - \frac{V}{V_R^0} + \frac{S}{V_R^0}\right)^2}\,\mathrm{d}S \qquad \text{(XII)}$$

In this case the apparent retention volume is greater than V_R^0 and is dependent on both B and the number of plates. The chromatogram is not symmetrical about its maximum and is steepest on its front. Equation XII also may be evaluated by the use of the probability integral tables. It has the form

$$C_r = \frac{C_0}{2}\left[e^{\frac{V_R^0}{2B^2r}}\,e^{-\frac{V_R^0}{B}\left(1 - \frac{V}{V_R^0}\right)}\right]\frac{2}{\pi}\int_{X_0}^{X_1} e^{-X^2}\,\mathrm{d}X \qquad \text{(XIII)}$$

$$X_0 = \frac{V_\mathrm{R}^0}{\sqrt{2r}}\left[\frac{1}{B} + \frac{r}{V_\mathrm{R}^0}\,(1 - V/V_\mathrm{R}^0)\right]$$

$$X_1 = X_0 + \frac{r}{\sqrt{2}}\,\frac{V}{V_\mathrm{R}^0}$$

The result of varying the charging period while holding the sample size constant is shown by the calculation summarized in Fig. 2. As indicated

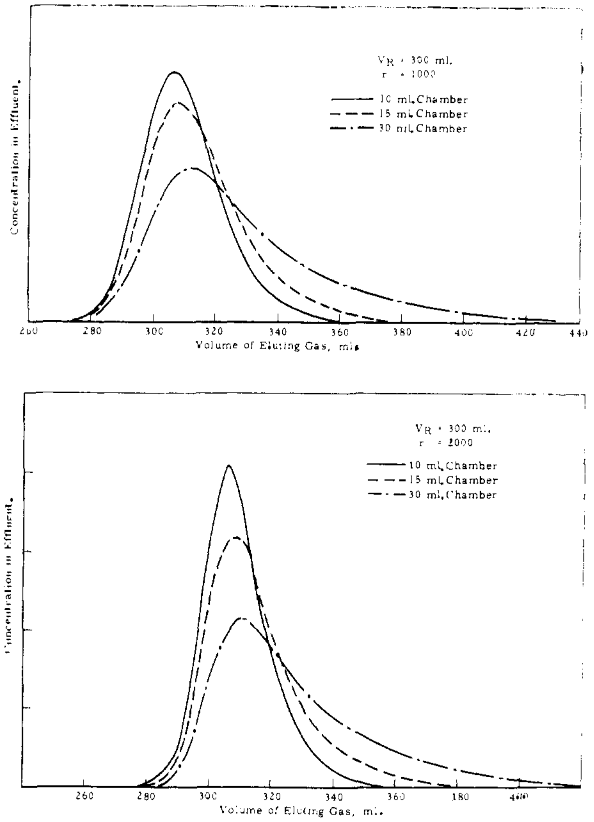

Fig. 2.—Elution curves for variable charging period and constant sample size.

previously, the apparent retention volume is fairly sensitive to the length of the charging period (sample chamber volume) but is fairly insensitive to the number of plates assumed. As in the former case the resolution of two components not easily separable and the apparent number of plates are critically affected by the charging period.

An experimental chromatogram is compared with curves calculated on each of the above two bases in Fig. 3. The experimental case taken for this comparison is one in which the activity coefficient is only slightly less than unity so that the partition coefficient is approximately constant. As is apparent the chromatogram obtained has a somewhat elongated "tail" corresponding more closely to the complete mixing case rather than to the plug flow case.

In the present work cognizance of the charging volume effect has been taken by using a small, fairly well characterized charging volume and by applying a small correction to the retention volume. The correction is based on the calculated curve in Fig. 4 which corresponds to the complete mixing case discussed above.

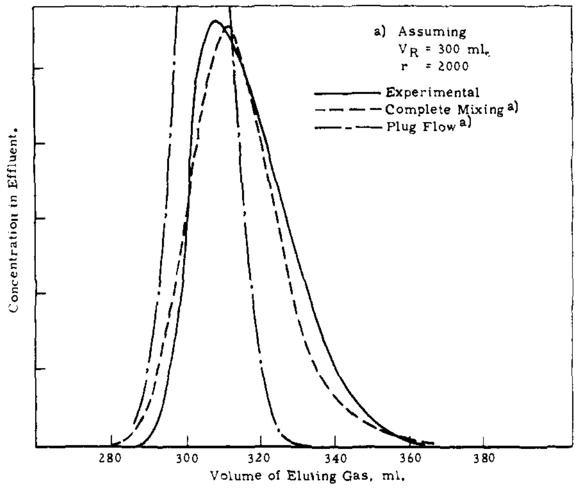

Fig. 3.—Comparison of elution curves.

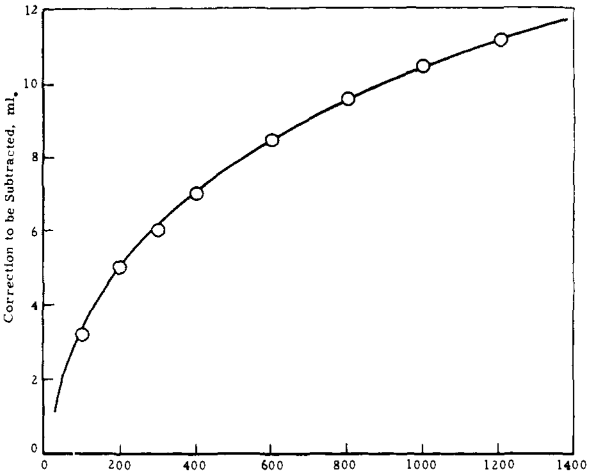

Fig. 4.—Correction for sample volume (complete mixing, 10 ml. chamber).

Experimental

Gas-Liquid Partition Chromatographic Apparatus.—The apparatus used in determining apparent GLPC retention volumes is given in detail in another paper.[7] Carrier gas, regulated by means of a Moore Nullmatic 40-30 regulator, is preheated in a small coil in the thermostat and is fed to a reference thermal conductivity cell. It is then fed through a sample introduction device, which can be by-passed by means of a valve network, into the thermostated column and finally into the sensing thermal conductivity cell. The columns consist of $^1/_4$ to $^3/_8$ inch o.d. copper tubing coiled into spirals approximately 15 cm. in diameter after packing. Column lengths up to 6 m. have been used here but most of the work is with a one meter column. The sample introduction device consists of a 10 ml. chamber into which a glass bulblet containing sample can be introduced and later broken by means of a magnetically activated crusher.

Column Operation.—Normally helium is used as a carrier gas at flow rates in the vicinity of 150-200 ml. per minute per square centimeter of column cross sections. This flow is obtained with an inlet pressure of less than roughly 1.5 atmospheres, depending on the particular column used; the outlet pressure is allowed to ride at ambient pressures. Samples of 2-4 mg. of pure solute in sealed glass bulblets are introduced into the chamber with the carrier gas by-passed, the chamber is evacuated to remove air, the bulblet is broken, and the sample is allowed to vaporize and come to thermal equilibrium with the thermostat. When equilibrium is reached, the valving system is manipulated so as to purge the totally vaporized sample into the column. The thermostat temperature is maintained to within a few tenths of a degree centigrade of the nominal operating temperature.

Apparent retention volumes are estimated from the time of sample introduction to the column, the time of efflux of the peak maximum and the flow rate corrected to the temperature of operation, as determined by the time required to collect a fixed volume of effluent gas. V_m and V_s for each column are estimated from the net packing density, the densities of solvent and solid support, the volume of the column and weight of solvent per unit weight of packing material. No account is taken of any small changes in the packing density or of solvent evaporation from continued use.

Equilibrium Apparatus.—Apparatus used to determine the equilibrium partition of solute between liquid solvent and gas phases consists of (1) several gas wash bottles thermostated at an appropriate temperature which serve to saturate the incoming carrier gas with the solute under test to a known partial pressure of solute, (2) a gas preheater coil submerged in a liquid thermostat, (3) a U-shaped thermostated tube of about 100 ml. volume containing either bulk liquid or liquid supported on GLPC packing material and (4) a thermal conductivity cell to determine when supported liquid becomes saturated with the solute in the carrier gas. The equilibrium concentration of solute in the liquid is determined by a material balance over the operation of the U-tube. The loss of solvent was found to be negligible. In the case of supported liquid, equilibrium was obtained between the entire liquid charge and the incoming gas mixture in about 60 minutes. When determining the partition between gas mixture and bulk liquid, the liquid level in the U-tube was adjusted so that the gas mixture bubbled through the bottom of the U-tube with the minimum pressure drop possible to still maintain the stirring action of the bubbles. In this case, equilibrium was obtained in about 5 hr.

Experimental Data and Discussion

Apparent retention volumes determined as described above have been corrected for pressure drop according to Martin and James (equation VI) and for charging volume according to Fig. 4. From the resulting limiting retention volume (expressed in milliliters of carrier gas at atmospheric pressure and the temperature of the operation), partition coefficients have been calculated (equation II). Detailed data from the determination of partition coefficients from GLPC measurements are given in Table I; average values for a number of systems are given in Table II. Several direct measurements of equilibrium coefficients are given in Table III.

Apparent partition coefficients from GLPC measurements in a wide variety of column lengths (cross-sectional areas less than 2.8 cm.^{2}) and flow conditions have in general been consistent to within 5-10% of their values for any given solute component at a given temperature. Carefully obtained data from operations in columns of large differences in length (6-fold) and large differences in carrier gas velocities (10-fold) are presented in Table I for several solute materials. The magnitudes of the retention times (t_R) and the apparent (uncorrected) retention volumes (V_R) involved are also shown for orientation. In these cases no well defined trend in the apparent partition coefficients as the gas velocity changes can be noted. The partition coefficients with the 630-cm. column agree within about 5% with those of the 100-cm. column in spite of coincident changes in the amount of solvent phase per unit weight of support and in the physical structure of the support of diatomaceous earth. They consequently provide a further verification of the essential validity of the Martin and

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[7] M. Dimbat, P. E. Porter and F. H. Stross, *Anal. Chem.*, **28**, 290 (1956).

Table I

Comparison of Partition Coefficients from GLPC Measurements

Diisodecyl phthalate solvent at 105°

Column properties:											
Length, cm.			99						629		
Area, cm.^{2}			0.181						0.181		
Solvent support			Johns-Manville Celite 545						Crushed C-22 (Johns-Manville) Fire Brick		
Solvent charge, g. solvent/100 g. support			40						20		
Packing density, g./cm.^{3}									0.565		
V_m, cm.^{3}			13.1						81.3		
V_s, cm.^{3}			2.58						11.8		
Operating conditions											
$p_i - p_0$, mm.			129	208	399	580			738	1055	1475
Flow rate, ml./min. at 105°, 760 mm.			6.89	12.2	24.7	40.2			21.4	34.3	55.2
Gas velocity, cm./min.			52	92	187	305			165	266	428
Partition data	Range of t_R, min.	Range of V_R, cm.^{3}	H	H	H	H	Range of t_R, min.	Range of V_R, cm.^{3}	H	H	H
n-Hexane	3–11	88–121	27.0	27.1	26.9	27.0	31–16	657–895	82.8	29.0	28.3
n-Heptane	6–25	170–243	57.0	56.9	57.0	59.6	56–30	1200–1675	58.3	58.2	59.1
n-Octane	12–49	340–477	121	120	120	123	...	....	...	....	....
Propanol-1	5–20	136–192	44.8	44.8	47.9	47.5	...	....	...	....	....
Butanol-1	11–43	295–426	104	105	103	109	...	....	....	....	....

Table II

Average Partition Coefficients from GLPC Measurements

Variation with temperature

Solvent	Diisodecyl phthalate					Squalane[a]	
Temp., °C. →	75	95	105	115	135	80	105
Partition coefficients							
n-Pentane	...	...	...	...	...	26.6	16.3
n-Hexane	...	34.6	27.0	...	...	62.5	34.8
n-Heptane	127	74.4	57.6	44.2	31.3	146	72.9
n-Octane	297	165	121	91	58.3	...	...
n-Nonane		333	240	176	...	...	...
Methylcyclopentane	76.0	46.0	38.2	31.3	23.4	...	...
Cyclohexane	...	65.9	52.3	39.2	...	112	60.1
Methylcyclohexane	180	106	83.5	65.3	45.4	193	97.4
Toluene	...	238	180	134	...	...	...
Ethylbenzene	...	209	144	120	72.4	...	...
Methanol	...	15.4	12.6	...	...	...	...
Ethanol	...	25.0	20.9	...	...	...	...
1-Propanol	103	56.0	46.2	33.5	23.4	...	...
1-Butanol	246	139	107	82.5	48.5	...	...
2-Propanol	...	33.1	26.1	...	...	...	...
2-Methyl-2-butanol	181	99.0	73.5	55.7	36.2	...	...
3-Methyl-2-butanol	274	139	105	76.2	43.4	...	...

[a] 2,6,10,15,19,23-Hexamethyltetracosane.

Synge description of the operation and of the James and Martin correction for expansion of the carrier gas.

Average partition coefficients obtained from a number of columns operated under a variety of flow conditions are shown in Table II for a number of solutes.

Direct measurements of partition coefficients for two solute materials, *n*-heptane and 2-propanol, from both supported and bulk liquid diisodecyl phthalate are compared in Table III. These solutes, which form close to ideal solutions with the solvent (log $\gamma^\circ = -0.03$ and $+0.02$, respectively), would be expected to show markedly different behavior if the solid support is active. As is apparent the equilibrium partition coefficients for each solute are independent of the solvent support within about 5%, and it is clear that the solvent support has no significant effect upon the equilibrium between gas and liquid phases. It may in addition be noted that the values of the partition coefficients are substantially identical with those obtained from the GLPC data for the respective solutes and at the same temperature.

Solvent effects are discussed in a companion paper, but it is worthy of note here that the activity coefficients estimated from the partition coefficients (equation IV) in Table II are of a reasonable order of magnitude. Thus in the case of the only slightly polar diisodecyl phthalate solvent, the apparent activity coefficients of the low molecular weight paraffin solutes are less than unity as a result primarily of molecular size effects, whereas those of the more polar or polarizable solutes are

TABLE III

PARTITION COEFFICIENTS FROM EQUILIBRIUM MEASUREMENTS

Solvent, diisodecyl phthalate at 105°, 760 mm.; support, Crushed C-22 Fire Brick.

Solute ⟶	*n*-Heptane	2-Propanol
Supported solvent (40 g. solvent/100 g. support)		
Solute concn. in liq. (mole fraction)	0.012	0.0090
Partition coefficient[a]	55 ± 3	28 ± 3
Supported solvent (50 g. solvent/100 g. support)		
Solute concn. in liq. (mole fraction)	0.063	....
Partition coefficient[a]	57.2 ± 1	....
Infinite dilution partition coefficient[b]	56.4	....
Bulk liquid		
Solute concn. in liq. (mole fraction)	0.063	0.0304
Partition coefficient[a]	57.1 ± 1	25.8 ± 1
Infinite dilution partition coefficient[b]	56.3	25.9

[a] The ranges indicated are rough estimates of the errors which might be expected to arise from weighing, etc. [b] Estimated by means of a Margules extrapolation of the activity coefficient to infinite dilution [$\log \gamma = (1 - x)^2 \log \gamma^0$].

TABLE IV

APPARENT HEATS OF SOLUTION FROM GLPC MEASUREMENTS

Solute	Solvent	$(\Delta H_v - RT - \overline{\Delta H_s}^E)$exp., kcal.	ΔH_v, kcal.	$(\overline{\Delta H_s}^E)$exp., kcal.	$\overline{\Delta H_s}^{E\,a}$, kcal.
n-Pentane	Squalane	5.22	5.25	−0.72	−0.75
n-Hexane		6.21	6.36	− .60	− .69
n-Heptane		7.37	7.58	− .54	− .64
Cyclohexane		6.60	6.77	− .58	....
Methylcyclohexane		7.28	7.53	− .50	....
n-Hexane	Diisodecyl phthalate	6.54	6.36	− .93	....
n-Heptane		7.00	7.58	− .17	....
n-Octane		8.00	8.64	− .11	....
n-Nonane		9.14	9.77	− .12	
Methylcyclopentane		5.95	6.45	− .25	
Cyclohexane		7.35 ?	6.77	−1.33 ?	
Methylcyclohexane		6.90	7.53	−0.12	
Ethylcyclohexane		8.46	8.63	− .58	
Toluene		7.78	8.13	− .40	
Methanol		4.91	8.15	+3.24	
Ethanol		5.00	9.61	+4.61 ?	
Propanol-1		7.35	9.94	+1.41	
Butanol-1		7.45	10.00	+1.80	
2-Methyl-2-butanol		8.08	9.28	+0.45	
3-Methyl-2-butanol		8.54	...	....	

[a] Estimated by the method of Brønsted and Koefoed[8] from the data of van der Waals and Hermans.[9]

somewhat greater than unity as a result of the predominance of other solvent effects.

It may also be noted that the changes in partition coefficient with temperature for the solutes in Table II are of a reasonable magnitude. From equation IV above

$$\ln H^0 = + \ln M_sRT - \ln \gamma^0 - \ln P^0$$

From the known relation of γ^0 and P^0 to temperature

$$\ln H^0 = \ln M_sR - \ln \frac{1}{T} - \frac{\overline{\Delta H_s}^E}{RT} + \frac{\Delta H_v}{RT} + \text{Const.}$$

where $\overline{\Delta H_s}^E$ is the excess partial heat of solution of the solute in the solvent and ΔH_v is the heat of vaporization of the solute. Since the molal volume for the solvent is normally not very temperature dependent and its variation can be neglected

$$\frac{\partial \ln H^0}{\partial\left(\frac{1}{T}\right)} = - T - \frac{\overline{\Delta H_s}^E}{R} + \frac{\Delta H_v}{R} = \frac{\Delta H_v - RT - \overline{\Delta H_s}^E}{R}$$

and plots of the logarithm of the partition coefficient against reciprocal absolute temperature are expected to be substantially linear over a range of temperature such that RT is small with respect to the heat terms. Heat data calculated from the partition coefficients in Table II are summarized in Table IV. As a practical matter, it may be noted that the heat of vaporization of the solute predominates in determining the change in partition coefficient with temperature and that reasonable estimates of partition coefficients as functions of temperature can be based on a single temperature point and the above observation. As is evident from the comparison of the apparent heats of solution in the squalane case by independent methods with those obtained from the partition coefficients, substantial agreement is obtained. In other cases the magnitudes of the heats of solution are of a reasonable order of magnitude and except in the cases of cyclohexane and ethanol change in a reasonable manner as the solute structure changes. These observations further verify the essential soundness of partition coefficients as determined from GLPC measurements.

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Acknowledgments.—The authors wish to acknowledge the coöperation of their associates at Shell Development Company laboratories, particularly that of Francis Powell and G. A. Harlow, who determined the equilibrium partition coefficients.

EMERYVILLE, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF UTAH]

Complex Ions of Chromium. VI. Kinetics of Formation of Diol Bonds in Chromium(III) Solutions[1-3]

BY DAVID M. GRANT[4] AND RANDALL E. HAMM

RECEIVED NOVEMBER 1, 1955

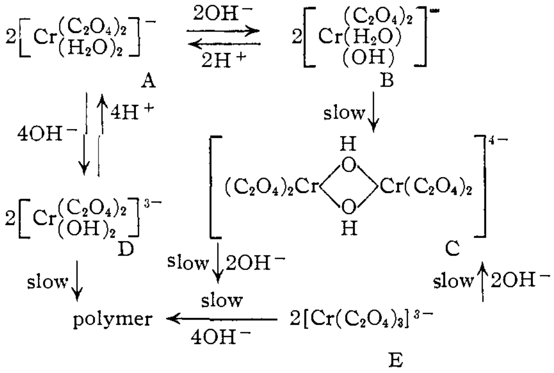
By a spectrophotometric method, the rates of dimerization of *cis*-hydroxydioxalatoaquochromate(III) were determined over a range of temperatures and ionic strengths. After a short induction period, the dimerization reaction was found to be first order in chromium concentration, when at concentrations above 0.01 molar. A mechanism is proposed for the dimerization reaction which accounts for the induction period of the reaction and the deviation from first-order kinetics at low concentrations. The activation energies and entropies were determined at the various ionic strengths and extrapolated values at zero ionic strength have been estimated.

Werner[5] characterized the *cis*-hydroxydioxalatoaquochromate(III) and *cis*-dihydroxydioxalatochromate(III) and recognized that the monohydroxy compound would dimerize to form a relatively stable ion, which he claimed would not revert to the original dioxalatodiaquochromate(III) ion upon the addition of acid, although he recognized that the freshly prepared hydroxy compounds would immediately revert to the aquo ions upon the addition of acid.

A number of investigators[6-8] have studied the process of aging in chromium(III) solutions. Although there is still some question of the exact extent to which it takes place there is now general agreement that it involves the formation of ol or diol linkages. Mattock[9] has shown that polymerization through formation of ol bonds is normal for several metal ions, including chromium(III).

The absorption spectra of solutions of either *cis*-hydroxydioxalatoaquochromate(III) of *cis*-dihydroxydioxalatochromate(III) showed changing spectral absorption indicating the occurrence of a slow reaction. The first of these reactions has been identified as a dimerization, while the second involves some replacement of oxalato groups by hydroxy groups followed by polymerization to some degree through diol bond formation. The monohydroxy dimer was found to split slowly and give back the original dioxalatodiaquochromate(III) ion upon the addition of acid. The dihydroxy aged product gave an immediate precipitate upon the addition of acid. This precipitate then slowly went into solution, as the oxalate slowly recombined to form dioxalatochromate(III).

The authors believe that by studying the formation of the diol linkage in the case of dioxalatochromate(III) where the process will stop at the formation of the dimer, one may get information to better understand the process where polymer formation is likely. The following are the interrelations which have been developed in the course of the present investigation.



The tris-(oxalato)-chromate(III) ion is included in this reaction scheme because spectrophotometric investigation showed that the products formed using it as starting material gave the same absorption curves as were obtained by using dioxalatodiaquochromate(III) as starting material.

This investigation has attempted to quantitatively study the slow step in the dimerization reaction and to suggest a reasonable mechanism for the process.

Experimental

Reagents.—The potassium dioxalatodiaquochromate(III) was prepared by the method of Werner.[5] Carbonate-free sodium hydroxide was used for preparation of the hydroxy salts in solution.

Procedure.—The equipment and methods were those reported in previous papers from this Laboratory.[10]

Potassium Bis-(dioxalato)-chromate(III)-μ-diol (C).—A (0.1 mole in 100 ml. H_2O) was treated with 0.1 mole of KOH and maintained at a temperature just below the boiling point for two hours, after which the solution was cooled to room temperature and slowly poured into 200 ml. of cool rapidly stirred dioxane. The precipitate was filtered off and washed with alcohol and ether. The solid obtained was dried at 100° and analyzed for chromium and oxalate.

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[1] This investigation has been supported by a research grant from the National Science Foundation.

[2] Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society meeting, September 16, 1955, in Minneapolis, Minn.

[3] Paper V in this series, THIS JOURNAL, **77**, 2083 (1955).

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