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Nonlinear Distribution Coefficients in Gas Chromatography*

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Summary

Nonlinear partition coefficients of polar solutes on coated and uncoated diatomaceous-earth supports lend themselves to mathematical treatment when proper precautions are taken to reproducibly condition the chromatographic column. A previously derived equation was used to calculate the adsorption and distribution isotherms from adsorption-desorption chromatograms whose diffuse elution curves approached the base line asymptotically. In the concentration ranges studied, the adsorption of acetone on uncoated support obeyed the Temkin isotherm equation. A plot of the amount adsorbed vs. the log of the concentration of the solute in the carrier gas gave a straight line. The adsorption of acetone on coated columns under the same conditions followed a Freundlich isotherm equation, and log-log plots of amount adsorbed vs. concentration of the solute gave straight lines. The equations for the lines obtained from the isotherm plots of the coated and uncoated columns were used to calculate the retention volumes as a function of concentration, by means of the equation $V_{N_g} = dQ/dC$. The validity of the retention volume and adsorption equations were checked by the agreement of theoretical and experimental measurements.

Within limits retention volumes may be correlated with sample size, providing the contribution of the bulk liquid phase is known. It is expected that the retention volume–sample size relationship would be more useful in low-loaded columns, where the bulk liquid-phase contribution is either small or negligible. The temperature-effect studies showed that, as expected, stronger adsorption bonds are formed at lower temperatures. The sample size–temperature studies on the inactive (RIC) support coated with tri-*o*-tolyl phosphate showed that the liquid phase contributed to the nonlinearity of the distribution coefficient in a minor but unknown extent.

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The gas-chromatographic behavior of polar compounds frequently shows the results of nonlinear distribution coefficients due to combinations of nonideal solution and support adsorption effects. This is generally observed in the form of tailing peaks and variations of retention volumes with sample size, sample composition, and previous condition of the column.

Few studies have attempted a quantitative estimation of the effects of the nonlinear distribution coefficients upon retention volumes. de Vault (*18*) developed the basic mathematical expressions relating retention volumes to the slopes of adsorption isotherms. Gluckauf (*5*) extended and improved de Vault's results by making it possible to experimentally determine adsorption isotherms from the diffuse tailing portion of a chromatogram. Gregg and Stock (*6*) and Perrett and Purnell (*13*) used Gluckauf's equations to compare adsorption isotherms with statically determined adsorption isotherms. Papa (*10*) used the method of Gregg and Stock for relatively high solute pressure to saturation vapor pressure (P/P_0) ratios, and attempted to use a solute front breakthrough method for the lower P/P_0 ratios.

In a detailed study of the effects of the solid support upon the retention volumes of polar solutes (*17*), it was observed that the distribution coefficients of the polar solutes were obviously not linear for two series of acid-washed firebrick (AWFB) columns coated with varying amounts of squalane and tri-*o*-tolyl phosphate (TOTP), respectively. Two additional series of columns on supports deactivated by hexamethyldisilazane through a radiation-induced copolymerization (RIC) method (*16*) showed essentially linear distribution coefficients.

APPARATUS AND PROCEDURE

The apparatus and experimental procedure have been described previously (*17*). They consist of the usual gas-chromatographic techniques plus a method of exposing the chromatographic columns to known, constant amounts of solute in the carrier gas. The four series of columns as described above were studied at 75°C under various conditions of sample sizes and known concentrations in the helium carrier gas. Unless otherwise stated, reference is always made to the behavior of the columns using the nondeactivated (AWFB) support.

Effects of Previous Condition of Column

Figures 1 and 2 show the effects of a previous injection of an acetone sample upon the retention time of succeeding samples injected at definite time intervals on uncoated and coated surface active columns, respectively. In all cases the sample size was 0.70 μl. With short time intervals between injections the retention times became small. Longer periods between injections gave longer retention times. The first injection on a freshly conditioned column could not be detected. The second and following injections gave the retention volumes shown. In each instance the desorption of the tailing portion of the previous sample attained a reproducible level to give an apparent reproducible retention volume. Because of this phenomena, care has to be taken in interpreting gas-chromatographic retention data obtained from repeti-

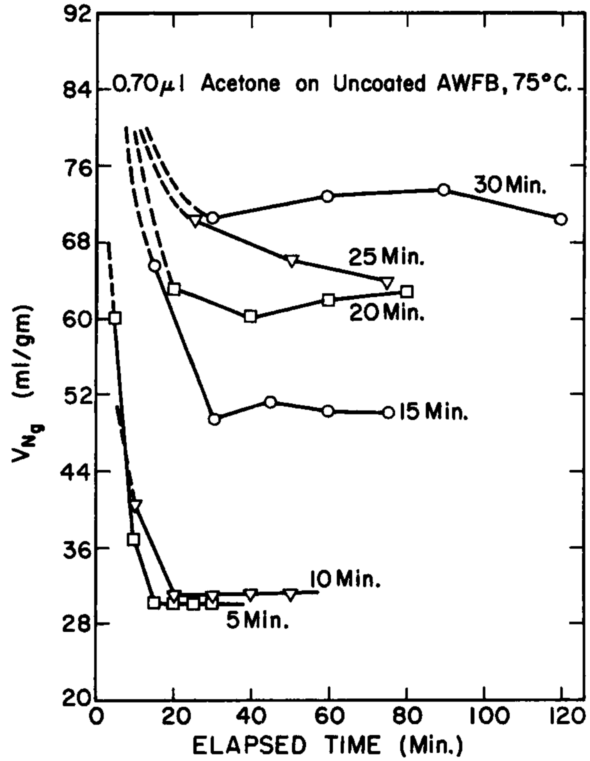

FIG. 1. Repeated injections of acetone on A. W. Firebrick.

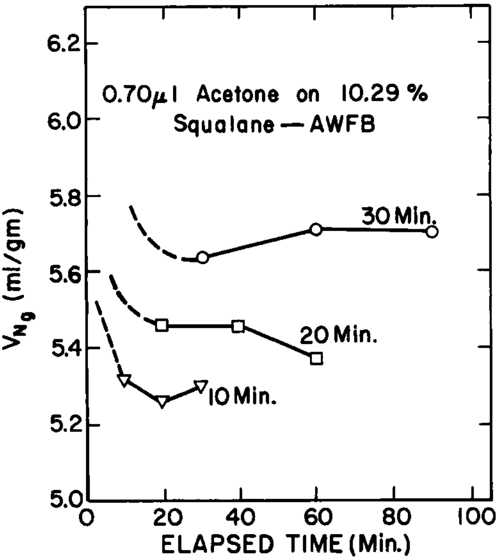

FIG. 2. Repeated injections of acetone on 10.29% squalane on AWFB.

tive injections until "reproducible" retention times are obtained. In this study extreme care was taken to ensure minimum effects from previous injections. Columns were conditioned for a minimum of 2 hours—frequently overnight.

Distribution Isotherms

Distribution isotherms were determined by using the front of a constant load adsorption-desorption chromatogram, or frontalgram, to indicate the total amount adsorbed and Gluckauf's method of calculating the isotherm from the diffuse rear boundary of an elution chromatogram (*12*). The term "distribution isotherm" (*7*) is used in preference to either "partition" or "adsorption" isotherms, because in many instances—especially for low-loaded columns—it is difficult to know whether partitioning or adsorption is the predominant process taking place.

Distribution isotherms obtained by gas-chromatographic methods may not necessarily be the same as those obtained by static methods, because of possible kinetic effects. However, other workers have demonstrated that gas-chromatographic isotherms

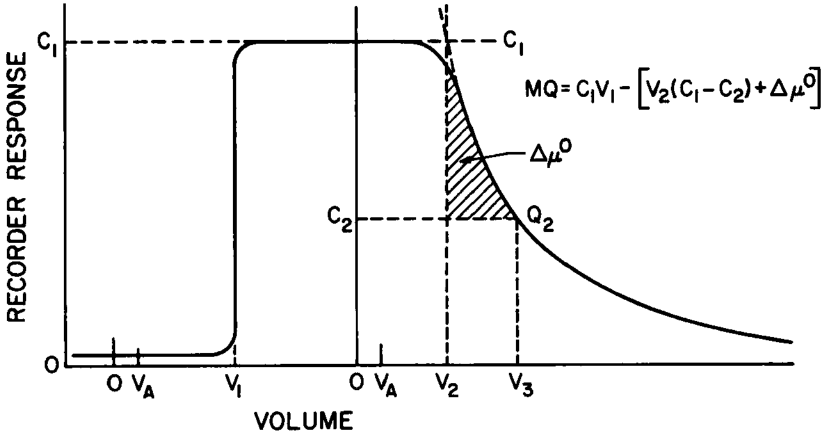

FIG. 3. Typical adsorption-desorption chromatogram for a constant load of solute in carrier gas.

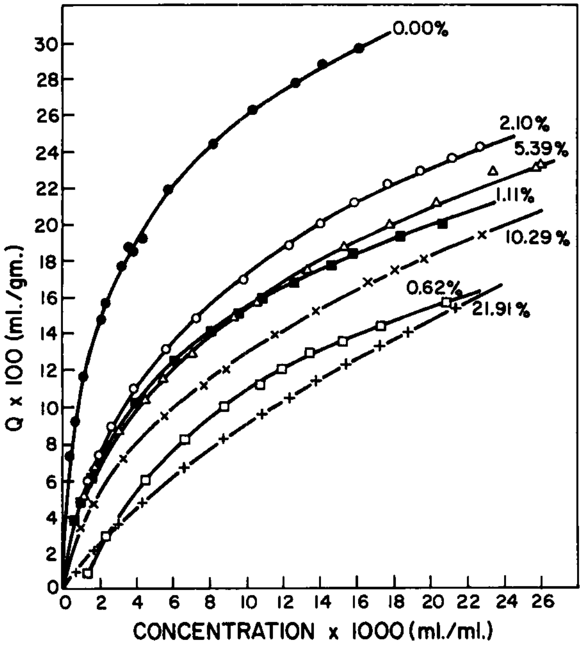

FIG. 4. Distribution isotherms for acetone/squalane/AWFB at 75°C.

duplicated those obtained by static methods (*6*). In this investigation essentially the same isotherms were obtained, with flow rates varying from 10 to 30 ml/min. A more systematic study of the effect of flowrates is presently being undertaken.

Figure 3 shows a typical frontalgram, where C is the mole fraction concentration of the solute in the carrier gas, Q is the amount of sample adsorbed, V is the volume of the carrier gas measured from the air peak (V_A), and $\Delta\mu^0$ is the area under the elution curve between the point (V_2), where the curve drops below the original concentration (C_1), and the optional point ($\bar{C}$), at which the amount adsorbed ($\bar{Q}$) is to be measured (*12*).

Figure 4 shows the distribution isotherms of acetone on a series of squalane-coated columns. The equation

$$Q = C_1V_1 - [V_2(C_1 - C_2) + \Delta\mu^0] \tag{1}$$

was used to calculate the amount of acetone adsorbed from frontal-

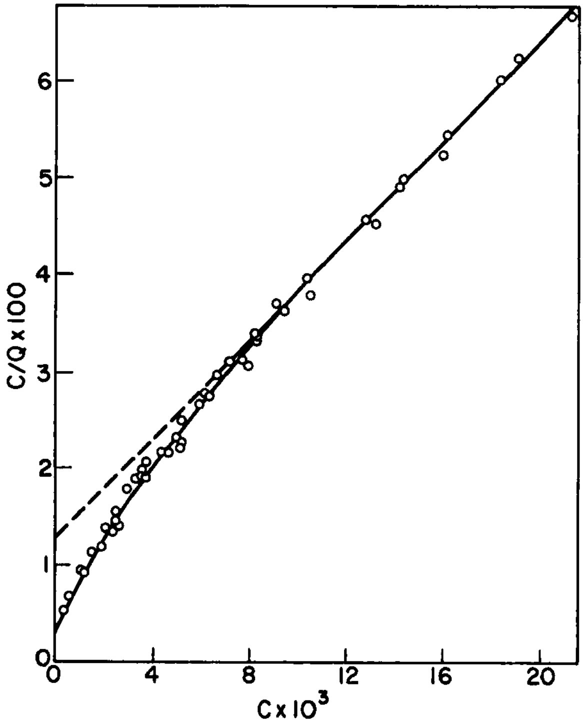

FIG. 5. Langmuir plot for acetone/AWFB.

grams of each column. In this study, Q is defined as the amount of solute adsorbed in the liquid phase plus that adsorbed on the solid support per gram of coated support.

The uncoated columns exhibited the greatest amount of adsorption; the coated columns exhibited a minimum of adsorption at approximately 0.5% liquid load, a maximum near 2%, and a gradual decrease as the liquid load increased. All isotherms are curved, showing that the distribution coefficients are nonlinear in the concentrations studied. These concentrations ($0-20 \times 10^{-3}$ ml/ml) are those generally encountered in gas chromatography. Independently measured retention volumes also showed the same liquid-load dependence (*17*).

Several workers (*10,13,14*) have suggested that the nonlinear distribution coefficients found, in particular, in gas-solid chromatography, followed the Langmuir isotherm equation (9). This was not found to be true in the concentration ranges and for the type of support studied in this investigation. The uncoated AWFB support showed a marked departure from the Langmuir equation at the low solute concentrations normally found in gas chromatography. The amount adsorbed was greater than predicted (Fig. 5).

The data obtained from the columns were plotted to check for their fit into the Langmuir, Freundlich, or Temkin isotherm equations (*1,4,9*). The Langmuir equation is restricted to monomolecular layer adsorption. It also assumes that each adsorption site is equivalent and is not affected by the filling in of neighboring sites. The Freundlich equation was developed empirically but implies that the heat of adsorption decreases exponentially as the adsorption sites are filled. This predicts inordinately high heats of solution at low concentrations when only a small fraction of adsorption sites are occupied. The Temkin equation is an extension of the Langmuir equation to heterogeneous surfaces and assumes a linear decrease in the heat of adsorption with surface coverage.

Uncoated Columns

The data from the uncoated AWFB columns best fit into Temkin isotherm plots. These are shown in Fig. 6, where the open circles are experimental points obtained through Eq. (1) from constant-load adsorption curves. The line is the best fit for the data and follows the equation $Q = 0.151 \log (C_m \times 10^3) + 0.133$, where C_m is

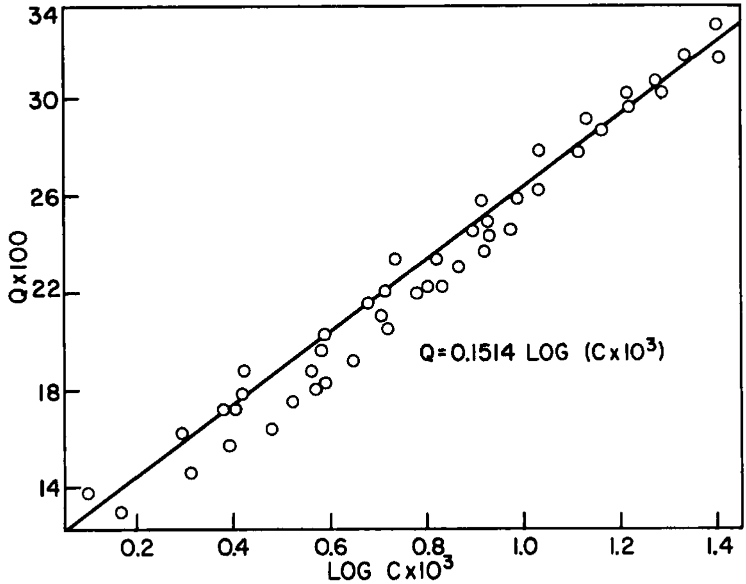

FIG. 6. Temkin plot for acetone/AWFB.

the concentration of the solute in the mobile phase. Once the equation for the isotherm has been determined, it can be related to the retention volume as follows (*11*):

$$Q = 0.151 \log (C_m \times 10^3) + 0.133 \quad (2)$$

$$\frac{dQ}{dC_m} = \frac{0.0657}{C_m} \quad (3)$$

However, in this study

$$Q = C_L V_L + C_S A_S \quad (4)$$

where C_L and C_S are the concentrations of the solute in the liquid and solid phases, V_L is the volume of the liquid phase, and A_S is the surface area of the support.

$$\frac{dQ}{dC_m} = \frac{dC_L}{dC_m} V_L + \frac{dC_S}{dC_m} A_S \quad (5)$$

If the partition coefficient of the solute in the liquid phase is constant, then

$$\frac{dC}{dC_m} = K_L V_L + \frac{dC_S}{dC_m} A_S \quad (6)$$

Equation (6) shows that dQ/dC_m can be related to the retention contributions of the liquid phase, $K_L V_L$, and the solid support, $(dC_S/dC_m)A_S$.

Retention volumes can be designated as (*18*)

$$V_R = V_m + \frac{dQ}{dC_m} \tag{7}$$

$$V_{N_g} = V_R - V_m = \frac{dQ}{dC_m} \tag{8}$$

Hence, for the uncoated support

$$V_{N_g} = \frac{0.0657}{C_m}$$

V_{N_g} is used to denote the retention volume per gram of coated support, corrected for void volume and pressure drop, and adjusted to the column temperature (75°C) rather than 0°C. It can be measured at the maximum height of an elution peak or at a given concentration on the tailing portion of a frontalgram or an elution chroma-

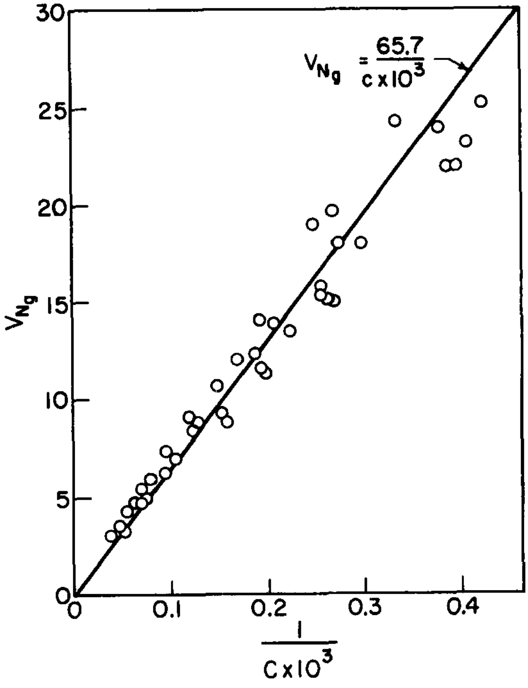

FIG. 7. Plot of retention volume vs. 1/*C*.

togram. In the latter case it is a measure of the volume of carrier gas required to elute a given concentration of solute from the column. A plot of the retention volumes of various points on the elution curve vs. the reciprocal of the concentration of the solute in the carrier gas at the selected point should give a straight line with a slope of 0.0657 and passing through the origin. This is shown in Fig. 7, where the line is from the derived equation and the open circles are experimental points.

If the observations from the present investigation are combined with the work of Papa (*10*) and Perrett and Purnell (*13*), one may surmise that the surfaces of the diatomaceous supports act as if they were homogeneous at very low and very high values of C_m (or P/P°) and heterogeneous in the intermediate ranges. This strongly suggests two principal types of adsorption sites, which, in the supports studied, are probably the hydrogen-bonding silanol groups and the acidic aluminum, iron, and other metal oxide impurities present on the support surfaces.

Coated Columns

Two squalane-coated columns were studied in detail. These were the 10.29% and the 22.07% squalane-coated AWFB columns, respectively. The isotherms were of the Freundlich type, with a slight divergence at the lower concentrations of solute in the carrier gas. Neither isotherm fit a Temkin equation, even when the liquid-phase contribution, obtained from the deactivated RIC columns, was subtracted out of the V_R term. When the data obtained from the tailing portions of the elution curves of either an injected sample or a constant-load frontalgram were plotted in the form of log V_{N_a} vs. log C_m a linear relationship was obtained. For the 22% squalane column the equation obtained from the plot was (*11*)

$$\log V_{N_a} = -0.429 \log C_m + 0.018 \tag{9}$$

$$V_{N_a} = 1.04 C_m^{-0.429} = \frac{dQ}{dC_m} \tag{10}$$

Hence, by integration,

$$Q = 1.82 C_m^{0.571} \tag{11}$$

Figure 8 compares the points obtained from the above equation with those obtained from Eq. (1) and those obtained from breakthrough points of constant-load frontalgrams, where Q equals the product of the concentration times the retention volume. A separate frontalgram was required for each of the latter points. There is very good agreement among the points, and it can be concluded that the equation describes the distribution isotherm for the column, which in itself obeys a Freundlich-type adsorption equation.

The columns coated with tri-*o*-tolyl phosphate (TOTP) were not

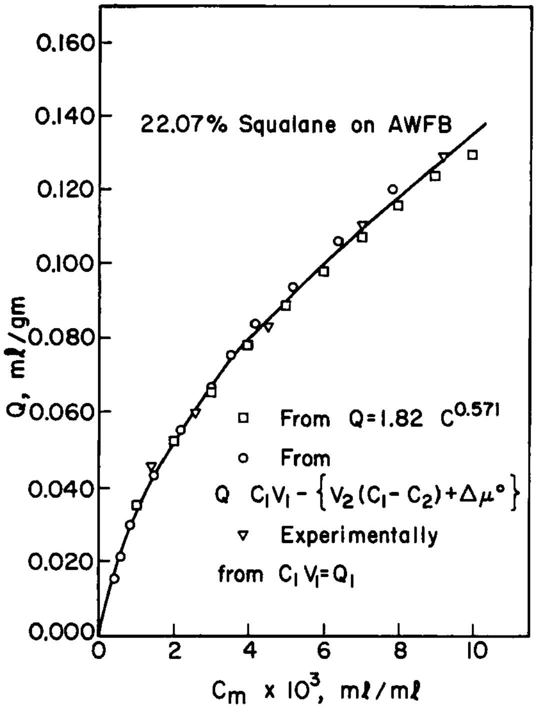

FIG. 8. Distribution isotherm for acetone/squalane/AWFB.

as surface-active as the squalane. The TOTP competed more strongly for the adsorption sites, and it was only at low liquid-phase loads or with the most polar solutes that nonlinearity of the distribution coefficients was clearly apparent. Above 2 to 3% liquid phase, the retention volumes increased linearly with increase in liquid-phase load. Seemingly the effect of the support surface had been masked. However, the retention volumes of the same polar solutes were consistently greater than the retention volumes of the same solute on the matching RIC columns.

Figure 9 shows the distribution isotherms for acetone on columns coated with 0.5, 10, and 24% TOTP, respectively. The isotherms for the 0.5 and 10% columns are curved throughout the concentration range shown, and the isotherm for the 24% column is curved at the lower concentrations. Under these conditions, the Freundlich isotherm equation holds. At higher liquid-phase loads and solute concentrations, the distribution coefficient becomes linear and dQ/dC_m approaches zero. The retention volumes consequently parallel, but remain above, the retention volumes of the inert RIC columns as the percentage of liquid is increased.

Correlation of Sample Size and Concentration

The retention-volume equation given in Eq. (7) is not in its most useful form. The usual experimental parameter is the sample size rather than the concentration of the solute in the carrier gas. It would be better to have the equation in the form $V_R = V_m + K_L V_L + f(\eta) A_S$, where η represents sample size.

The relation between concentration in the mobile phase and sample size is rather complicated and is a function of the isotherm equation. If the detector has a linear response to concentration and the adsorption isotherm is linear, the elution peaks will be symmetrical and the retention volume will be independent of both concentration and sample size. However, linear isotherms are rarely encountered for polar solute on coated or uncoated columns using common solid supports.

If the isotherm follows the Freundlich equation, i.e., $Q = kC_m^{1/n}$, where k and n are constants, then the retention volume is given by

$$V_R = V_m + K_L V_L + \frac{dQ}{dC_m} A_S \tag{12}$$

$$V_R = V_m + K_L V_L + \frac{k}{n} C_m^{(1-n)/n} A_S \tag{13}$$

$$V_{N_a}^{\circ} = \frac{k}{n} C_m^{(1-n)/n} A_S \tag{14}$$

where $V_{N_a}^{\circ}$ is the net retention volume corrected for void volume and contribution of the liquid phase.

Assuming a linear detector response, the concentration of the solute in the carrier gas may be obtained by (2)

$$C_m = \frac{h}{S_p} \tag{15}$$

$$S_p = \frac{AF}{BRT\eta} \tag{16}$$

where h is the peak height, A the peak area, F the flow rate at T, B the chart speed, R the gas constant, T the absolute temperature of detector, and η the sample size in millimoles.

From Eqs. (14), (15), and (16),

$$V^{\circ}_{N_u} = \frac{k}{n} A_S \left(\frac{h}{A} \frac{BRT}{F} \eta\right)^{(n-1)/n} \tag{17}$$

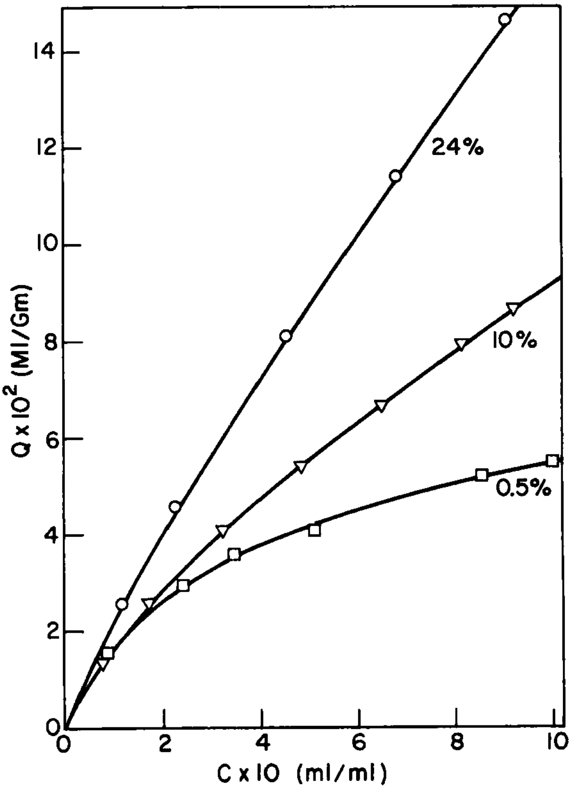

FIG. 9. Distribution isotherms for TOTP/AWFB.

$$V^*_{N_0} = Dn^{(n-1)/n} \tag{18}$$

$$\log V^*_{N_0} = \log D + \frac{1-n}{n} \log \eta \tag{19}$$

where D is a collection of the constant terms in Eq. (16) and h/A is assumed to be nearly constant at all sample sizes. A plot of log $V^*_{N_0}$ vs. log sample size should give a straight line of slope $(1-n)/n$. Once this is determined, retention volumes can be obtained for different sample sizes. However, if h/A is not constant, because of severe tailing, the exponential relationship between $V^*_{N_0}$ and η will not hold, and h/A will become some function of the sample size; i.e., $h/A = f(\eta)$. Equation (17) becomes

$$V^*_{N_0} = D' \,[\eta f(\eta)]^{(1-n)/n} \tag{20}$$

$$\log V_{N_0} = \log D' + \frac{1-n}{n} \log \eta + \frac{1-n}{n} \log f(\eta) \tag{21}$$

where D' differs from D by the removal of h/A.

In the case of badly tailing peaks, the function $f(\eta)$ is not easily obtained, and the retention volume Eq. (13) cannot be conveniently altered to allow the substitution of sample size for concentration of the solute in the mobile phase.

Temperature Effects

The retention volumes of methanol, ethanol, and acetone were studied as functions of temperature and sample size on TOTP-coated columns. Figure 10 shows a Clausius-Clapeyron plot of the temperature dependence of the retention volume of 0.25-μl samples of acetone on an 18.4% TOTP-AWFB column and a 20.5% TOTP-RIC column, respectively. V_g' is the net retention volume taken at the peak maximum and calculated at column temperature. The double set of experimental points per line is used to indicate the reproducibility of the measurements. Each set was obtained from two independent series of temperature runs using different pressures and flow rates.

The retention volumes on the surface-active (AWFB) support (Fig. 10) are consistently higher than those on the inactive (RIC) supports. There is a tendency for the two lines to run parallel to one another. The line for the surface-active support, however, tends to curve upward at the lower column temperatures. This is interpreted to mean that more hydrogen bonds are being formed at these temperatures.

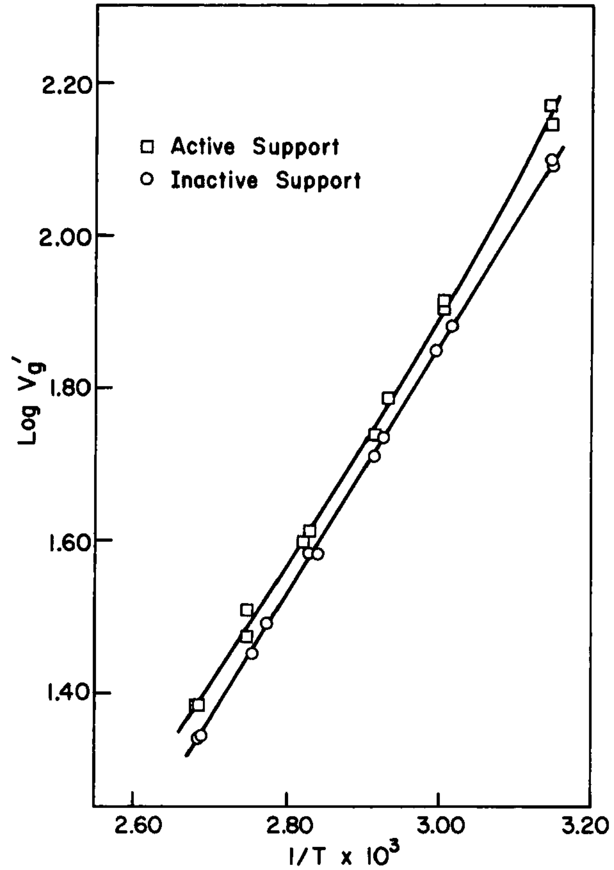

FIG. 10. Log retention volume vs. $1/T$ for acetone, 0.25 μl sample size.

Figure 11 shows the same type of data obtained from 0.10-μl samples. The lines tend to be separated further from one another, indicating a greater surface adsorption effect by the AWFB support. At the lower temperatures and for smaller sample sizes on the AWFB supports, the peak maxima become difficult to find and measure because of the excessive tailing that develops.

Table 1 lists the partial molar excess heats of solution calculated from the slopes of Clausius-Clapeyron plots by (3)

$$d(\log V_g')/d(1/T) = \frac{\Delta H_v - \overline{\Delta H}_S^E}{2.303R} \tag{22}$$

TABLE 1

Excess Heats of Solution as Functions of Sample Size on an 18.3% TOTP-Coated Deactivated Support

Compound	Sample size, μl	2.303R slope	$\overline{\Delta H}_S^E$, kcal/mole
Methanol	1.00	9.632	−0.69
	0.75	9.257	−0.32
	0.50	8.969	−0.03
	0.25	8.594	+0.35
	0.10	7.482	1.46
Ethanol	1.00	9.655	0.47
	0.75	9.761	0.36
	0.50	9.335	0.79
	0.25	9.060	1.06
	0.10	8.649	1.47
Acetone	1.00	8.10	−0.88
	0.75	7.76	−0.54
	0.50	7.73	−0.51
	0.25	7.44	−0.22
	0.10	7.21	+0.01

where ΔH_v is the heat of vaporization, $\overline{\Delta H}_S^E$ the excess partial molar heat of solution, and R the gas constant. The heats of vaporization were obtained from Rossini et al. (*15*) and the International Critical Tables (*8*).

The data are shown only for TOTP on the inactive RIC column. The data for TOTP on the active AWFB column in general gave nonlinear plots which cannot easily be interpreted. However, even for the "inactive" RIC support, the excess heats of solution of all three solutes increased with decreases in sample size. The increase in the heat of solution as the concentration of solute in the carrier gas became smaller resulted in a greater retention of the solute by the substrate and consequently caused a nonlinear increase in the partition coefficient. That these effects can be observed for an inactive support, coated with approximately 20% of a relatively polar liquid phase, strongly suggests that solution nonideality

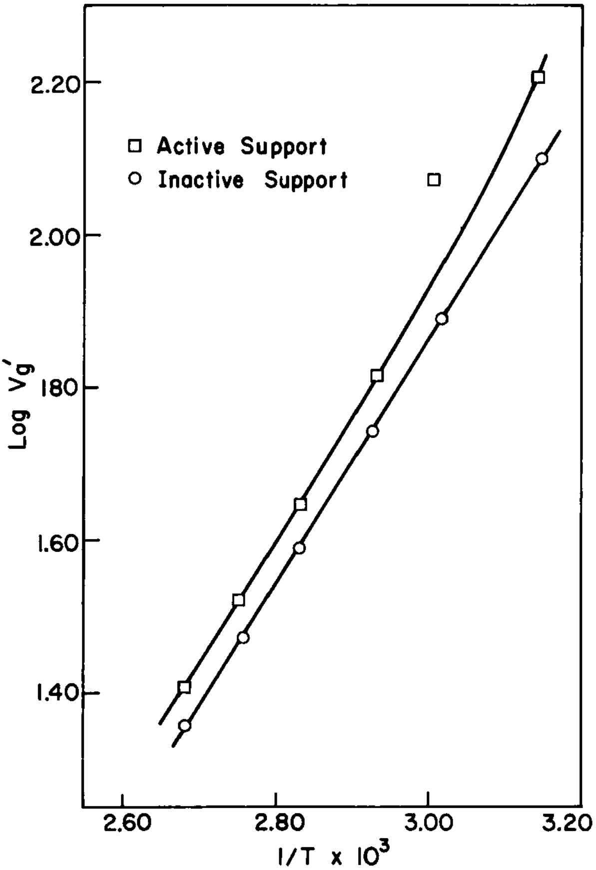

FIG. 11. Log retention volume vs. $1/T$ for acetone, 0.10 μl sample size.

contributes to the nonlinearity of the partition coefficients observed for the columns using surface-active supports. The magnitude of this contribution would depend upon the relative surface activities and solute-solution interactions. In these studies the effect has been small compared to the active support effects.

Acknowledgments

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