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PEAK DISPERSION AND MOBILE PHASE VELOCITY IN LIQUID CHROMATOGRAPHY: THE PERTINENT RELATIONSHIP FOR POROUS SILICA

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SUMMARY

The equations of Van Deemter, Giddings, Huber, Knox and Horváth for the height equivalent to a theoretical plate (H) are tested against over 25 data sets of experimental values of H and the mobile phase linear velocity (u) obtained for columns packed with silica gel. Each data set contains at least 10 complementary pairs of H and u values and furthermore, each H and u value was taken as the mean of at least three replicate measurements, thus, involving a total of over 750 individual and precise measurements of H and u . The maximum standard error for any set of replicate measurements was 2%. The data were obtained for silica gels having four different particle diameters, for six solvent mixtures and nine different solutes. It is shown that over the velocity range of 0.02–1 cm/sec, the Van Deemter equation accurately predicts the experimentally determined relationship between H and u . Consequently, under normal operating conditions in liquid chromatography, employing silica gel as the stationary phase Van Deemter equation can be employed with confidence in column design.

INTRODUCTION

Chromatography theory has developed extensively since the invention of gas chromatography (GC) nearly thirty years ago. In 1959, Purnell¹ derived the equation to calculate the number of theoretical plates necessary to affect a given separation*. Shortly after, Purnell and Quinn², Desty and Goldup³ and Scott and Hazeldean⁴ developed equations to calculate the total analysis time required for GC separations. Later, Snyder⁵, Martin *et al.*⁶, Halász *et al.*⁷ and Guiochon⁸ developed similar equations for liquid chromatographic (LC) separations. Equations that could be used to calculate the length of the column necessary to achieve a given separation were developed for GC by Scott and Hazeldean⁴, and for LC by Snyder⁵, Martin *et al.*⁶ and Halász *et al.*⁷. The effect of pressure on chromatographic performance which can have a major pertinence to LC was also investigated by Snyder⁵ and Martin *et al.*⁶,

* *Editor's Note:* Actually this had already been calculated by J. Beukenkamp, W. Rieman, III and S. Lindenbaum in 1954 (*Anal. Chem.*, 26 (1954) 505).

and also by Guiochon⁸, Kraak *et al.*⁹ and Knox and Saleem¹⁰. More recently, equations have been developed to calculate the minimum column radius for maximum solvent economy and maximum mass sensitivity in LC^{11,12} and the maximum permissible response time of the detecting system¹³⁻¹⁶. The calculation of all column parameters and operating conditions is ultimately contingent, however, on knowing the explicit equation that accurately predicts the variance per unit length of a column [more commonly known as the height equivalent to a theoretical plate of the column, (HETP or H)] from a knowledge of the mobile phase velocity. Furthermore, the explicit terms of the equation must accurately establish the interrelationship of the physical and chemical properties of the solute, phase system and column contents. The literature is not wanting in such equations. The first HETP equation was derived by Van Deemter *et al.*¹⁷ in 1956 and experimental support for the equation was published by Keulemans and Kwantes for GC¹⁸ at the first Gas Chromatography Symposium held in London in the same year. However, when the equation was applied to LC, it was found that the relationship predicted by Van Deemter *et al.*, did not appear to hold, probably due to the presence of artifacts such as those caused by extra column dispersion, large amplifier time constants, etc. Nevertheless, this poor agreement between theory and experiment provoked a number of workers in the field to develop alternative HETP equations in the hope that a more exact relationship between HETP and mobile phase linear velocity (u) could be obtained that would be compatible with experimental data. In 1961, Giddings¹⁹ produced an HETP equation, of which the Van Deemter equation was a special case. Giddings was dissatisfied with the Van Deemter equation inasmuch as it predicted a finite contribution to dispersion independent of the solute diffusivity in the limit of zero mobile phase linear velocity, which appeared to him to be unreasonable. Giddings also suggested that there was a coupling term that accounted for increased diffusion that resulted from the tortuous path followed by the solvent between the particles. However, when the mobile phase velocity was sufficiently high, the equation simplified to the Van Deemter equation as, at practical mobile phase velocities, the other functions in the equation were similar to those of Van Deemter. The coupling function introduced by Giddings was not strictly a term that described a multipath effect, although at high values of u , the value of the function extrapolated to a constant independent of the mobile phase velocity. The dispersion phenomenon that the coupling function described was more comparable to a resistance-to-mass transfer contribution arising solely within the interparticulate voids in the column packing. Furthermore, a dispersion effect independent of solvent velocity is not necessarily unacceptable. There must be a range of paths of different length that a molecule can take when passing through the interstices of a packed bed and this range of path-lengths must lead to dispersion that is independent of the solvent velocity. Nevertheless, the constant in the Van Deemter equation independent of mobile phase velocity could include both the multipath term, as such, together with the limiting value of the coupling term of Giddings at high linear velocities.

The next HETP equation to be developed was that of Huber and Hulsman in 1967²⁰. These authors introduced a term similar to the coupling term of Giddings which also allowed the dispersion factor due to the multi-path effect to become zero, at zero mobile phase velocity. These authors, however, used a different model from that of Van Deemter or Giddings in deriving the resistance to mass transfer in the

mobile phase located solely between the particles. They arrived at an additional term involving the square root of the mobile phase velocity, as opposed to the linear function postulated by Van Deemter and Giddings. However this mobile phase mass transfer factor of Huber has a distinct similarity to that of the coupling term of Giddings in its physical interpretation and its velocity dependence. It is difficult to evoke a physical process that would reduce the resistance to mass transfer between the particles other than the coupling effect postulated by Giddings. It appears, therefore, that both the resistance-to-mass transfer effect containing the fractional power of u and the coupling term in the Huber equation could be describing the same dispersion phenomenon.

During 1972 and 1973, Knox and co-workers²¹⁻²³ carried out a considerable amount of work on different packing materials with particular reference to the effect of particle size on the reduced plate height of a column. These workers produced a fourth HETP equation which was significantly different from those mentioned previously and was developed from a curve fitting procedure applied to their fairly extensive experimental data. Consequently, although empirically interesting, the equation of Knox and his co-workers was not explicit with respect to the physical and chemical properties of solvent-solute and column packing and thus cannot be used for column design. Finally, Horváth and Lin^{24,25} used yet another model to derive an HETP equation similar to that of Huber and Hulsman, but the term describing the resistance to mass transfer in the mobile phase involved the square of the cube root of the mobile phase velocity and not the square root. Once more the resistance-to-mass transfer term involving the fractional power of the linear velocity in the Horváth equation was introduced to characterize a dispersion effect similar to the coupling term of Giddings and in fact, may be accounting for the same phenomenon that is described by a coupling term he also included in his equation.

All the above equations are significantly different and it is the purpose of this work to identify *that* equation which best describes the relationship between variance per unit length of a column and linear velocity of the mobile phase over the range of linear velocities normally employed in LC analysis. The equation identified can then be employed with confidence in chromatographic calculations and in particular, column design.

THEORETICAL CONSIDERATIONS

The five equations that will be considered are given in chronological order of their derivation as follows:

Van Deemter *et al.* (1956)¹⁷

$$H = A + \frac{B}{u} + Cu \quad (1)$$

Giddings (1961)¹⁹

$$H = \frac{A}{1 + E/u} + \frac{B}{u} + Cu \quad (2)$$

Huber and Hulsman (1967)²⁰

$$H = \frac{A}{1 + E/u^{1/2}} + \frac{B}{u} + Cu + Du^{1/2} \quad (3)$$

Kennedy and Knox (1972)²¹

$$H = Au^{1/3} + \frac{B}{u} + Cu \quad (4)$$

Horváth and Lin (1976)²⁴

$$H = \frac{A}{1 + E/u^{1/3}} + \frac{B}{u} + Cu + Du^{2/3} \quad (5)$$

where A , B , C , D and E are appropriate constants for a given solute chromatographed on a given column and phase system.

At first sight, it might appear adequate to test the above equations to a number of data sets of H and u and to identify the equation that gives the best fit. Unfortunately, in practice this is of little use as, due to the nature of the functions, all five equations would provide an excellent fit to any given experimentally derived data set provided it was obtained with adequate precision. However, all the individual terms for each equation purport to describe a specific dispersive effect; that being so, all the constants for the above equations derived from a curve fitting procedure must be positive and real if the dispersion effect described is to be physically significant over the mobile phase velocity range examined. Any equation that did not consistently provide positive and real values for all constants would obviously not be an appropriate explicit equation to describe the dispersion effects occurring over the said range of velocities. However, any equation that *did provide a good fit* to a series of experimentally determined data sets and meet the requirement that all constants were positive and real *would not uniquely identify the appropriate equation for use*. The constants A , B , C etc., would then have to be replaced by the explicit functions, derived from the specific theory employed, incorporating the physical properties of solvent, solute and stationary phase. The physical properties of the solute and phase system could then be varied in a defined manner and the change in the nature of the constants A , B , C etc. tested against the relationship predicted by the explicit functions.

The identification of the pertinent HETP equation has therefore to be carried out employing a sequential series of tests. Firstly, all the equations have to be tested against a series of (H, u) data sets and those equations giving positive and real values for the constants identified. The explicit form of those equations that satisfy the preliminary criteria has then to be tested against a series of data sets that have been obtained employing different chromatographic systems. Such systems would have different particle size packing or have different but known solute and solvent physical properties. In this way, the most appropriate equation that describes the relationship between H and u over the mobile phase velocity range examined will be identified.

EXPERIMENTAL

The accurate measurement of solute dispersion in a column operated at different mobile phase linear velocities requires that the contribution to the peak dispersion from the injection system, connecting tubes and detector to be very small compared with that due to the column. Inattention to this obligatory condition can easily lead to the misinterpretation of the results. To reduce extra column dispersion to a minimum, a Valco valve (volume $0.2 \mu\text{l}$) was employed as the sample valve which, for work on the effect of different particle diameter packing, was also used in conjunction with an intra-column injection system²⁶. This device ensured that, even if there was bed settlement at the top of the column, the accuracy of the peak dispersion measurements would not be impaired. All connecting tubes were 0.007 in. I.D. and their lengths kept to a minimum ($< 5 \text{ cm}$). The detector employed was the LC-85B (cell volume $1.4 \mu\text{l}$) with an electronic amplifier that had an effective time constant of about 28 msec. The columns employed had internal diameters of 8 or 9 mm to ensure a large peak volume relative to any caused by instrument dispersion. As a result of these precautions, the extra-column dispersion was maintained at a level of less than 2% of the peak volume for all measurements and in most instances less than 1%. The initial work was carried out using a column 25 cm long, 9 mm in diameter packed with Partisil 10, a microparticulate silica that had an actual mean diameter of $8.5 \mu\text{m}$. The column was situated in an oven and thermostated at 25°C .

In the first series of experiments, six data sets were obtained for H and u employing six solvents having different viscosities. This served two purposes as, not only were there six different data sets with which the dispersion equations could be tested but, the coefficients in those equations supported by the data sets could be subsequently correlated with solute diffusivity. The solvents employed were approximately 5% (v/v) ethyl acetate in *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane. The solutes used were benzyl acetate and hexamethylbenzene. The diffusivities of the solutes in the different solvents were determined in the manner

TABLE I
PROPERTY DATA FOR MOBILE PHASES AND SOLUTES

Mobile phase	Benzyl acetate			Hexamethylbenzene
	k'	k_e	$D_m (10^{-5} \text{ cm}^2/\text{sec})$	$D_m (10^{-5} \text{ cm}^2/\text{sec})$
1 4.58% (w/v) ethyl acetate in <i>n</i> -pentane	2.05	4.07	3.61	3.51
2 4.86% (w/v) ethyl acetate in <i>n</i> -hexane	1.97	3.94	3.06	2.73
3 4.32% (w/v) ethyl acetate in <i>n</i> -heptane	2.04	4.06	2.45	2.23
4 4.50% (w/v) ethyl acetate in <i>n</i> -octane	2.01	4.01	2.01	1.71
5 4.41% (w/v) ethyl acetate in <i>n</i> -nonane	2.12	4.20	1.65	1.35
6 4.82% (w/v) ethyl acetate in <i>n</i> -decane	2.01	4.01	1.46	1.17

previously described by Katz *et al.*²⁷ and the results obtained are included in Table I. The solvent mixtures were adjusted to provide capacity ratio (k') of 2 for benzyl acetate in all experiments. The k' discussed here is the conventional value obtained from the dead volume measured as the retention volume of the fully permeating unretained solute, hexamethylbenzene. In fact, the strict definition of k' relates to the ratio of the volume of the stationary phase and the volume of the moving phase, and thus, as the true moving phase is only that portion of the mobile phase situated between the particles, a capacity ratio, k_e , was also calculated from the excluded volume as: $k_e = (V_R - V_e)/V_e$, where V_R is the retention volume of the solute and V_e is the excluded volume of the column. The excluded volume, V_e , was taken as the retention volume of the completely excluded solute, polystyrene (having a molecular weight of 83,000) determined by employing tetrahydrofuran as the mobile phase. The composition of each solvent mixture, the k' and k_e values for benzyl acetate and hexamethylbenzene together with the diffusivity values for these solutes in each solvent are given in Table I.

HETP values for these data sets were obtained over a linear velocity range of about 0.02–0.6 cm/sec. The HETP was taken as the ratio of the column length to column efficiency and the column efficiency was calculated as four times the square of the ratio of the retention distance to the peak width measured at 0.6065 of the peak height. Each measurement was made in triplicate and if any individual measurement differed from the others by more than 3%, then further replicate measurements were made. HETP values were obtained for 10 to 12 different linear mobile phase velocities over the range examined. The linear velocity was measured in two ways, firstly, as the ratio of the column length to the column dead time (the elution time of hexamethylbenzene). This is the conventional value for the linear velocity, u . However, the dead volume of a silica gel column includes a significant proportion of the mobile phase that is trapped in the pores and is therefore static. Consequently, a more correct value for the linear velocity would be taken from the excluded retention volume of the column. Thus a second value for the velocity, u_e , was taken as the ratio of the column length to the retention time of the fully excluded solute polystyrene (molecular weight 83,000).

Thus

$$u_e = uV_0/V_e$$

where V_0 was the retention volume of the fully permeating solute hexamethylbenzene.

Values of H , u_e and u for both solutes, hexamethylbenzene and benzyl acetate are given in Tables II and III for each different solvent mixture examined, inclusive. In all subsequent calculations the velocity, u_e , is taken as the true value for the linear velocity; however, values for u are also included so that alternative procedures can be employed if desired. The data given in Table II for benzyl acetate employing H and u_e was curve fitted to the different equations for H and the results are given in Table IV. The details of the fit to the Van Deemter equation *only* are also included in Tables II and III. In Fig. 1 the HETP curve for benzyl acetate in 4.8% (w/v) ethyl acetate-*n*-hexane gives an indication of the quality of the fit of the data to the Van Deemter equation. The multipath term (A), the longitudinal diffusion term (B/u) and the resistance-to-mass transfer term (Cu), as calculated from the values of the constants A , B and C obtained from the fit procedure are also included in Fig. 1.

TABLE II

PEAK DISPERSION DATA FOR BENZYL ACETATE ($k_e = 4.0$)

u (cm/sec)	u_p (cm/sec)	H (cm)	Van Deemter coefficients
<i>4.68% (w/v) ethyl acetate in n-pentane</i>			
0.01819	0.03027	0.004788	
0.02721	0.04527	0.003704	
0.03911	0.06507	0.003116	$A = 0.001189$ cm
0.06024	0.10023	0.002526	$B = 0.0001079$ cm ² /sec
0.07847	0.1306	0.002292	$C = 0.002525$ sec
0.09937	0.1653	0.002176	
0.1495	0.2488	0.002246	($r = 0.999844$)
0.1914	0.3185	0.002360	(std. error = $5.9 \cdot 10^{-5}$)
0.2880	0.4792	0.002678	
0.3623	0.6028	0.002856	
<i>4.86% (w/v) ethyl acetate in n-hexane</i>			
0.01825	0.03037	0.004182	
0.02711	0.04521	0.003352	
0.03923	0.06527	0.002731	
0.06112	0.1017	0.002293	$A = 0.001144$ cm
0.07784	0.1295	0.002246	$B = 0.00009045$ cm ² /sec
0.09968	0.1659	0.002110	$C = 0.003008$ sec
0.1500	0.2496	0.002305	
0.1852	0.3082	0.002407	($r = 0.999885$)
0.2908	0.4839	0.002778	(std. error = $4.8 \cdot 10^{-5}$)
0.3631	0.6042	0.003098	
<i>4.32% (w/v) ethyl acetate in n-heptane</i>			
0.01763	0.02933	0.003982	
0.02692	0.04479	0.003109	
0.03817	0.06351	0.002605	
0.05631	0.09369	0.002251	$A = 0.001114$ cm
0.07167	0.1193	0.002191	$B = 0.00008141$ cm ² /sec
0.08596	0.1430	0.002208	$C = 0.003362$ sec
0.1294	0.2153	0.002199	
0.1729	0.2877	0.002365	($r = 0.999955$)
0.2718	0.4523	0.002849	(std. error = $2.9 \cdot 10^{-5}$)
0.3623	0.6028	0.003253	
<i>4.50% (w/v) ethyl acetate in n-octane</i>			
0.01821	0.03030	0.003439	
0.02741	0.04561	0.002829	
0.03954	0.06579	0.002428	
0.06059	0.1008	0.002163	$A = 0.001210$ cm
0.07862	0.1308	0.002195	$B = 0.00006460$ cm ² /sec
0.09992	0.1663	0.002252	$C = 0.003661$ sec
0.1506	0.2506	0.002356	
0.1956	0.3255	0.002602	($r = 0.999946$)
0.2894	0.4815	0.003120	(std. error = $3.2 \cdot 10^{-5}$)
0.3771	0.6275	0.003602	

(Continued on p. 58)

TABLE II (continued)

u (cm/sec)	u_e (cm/sec)	H (cm)	Van Deemter coefficients
<i>4.41% (w/v) ethyl acetate in n-nonane</i>			
0.01813	0.03017	0.002985	
0.03037	0.05053	0.002385	
0.03945	0.06564	0.002186	
0.05447	0.09063	0.002119	$A = 0.001208$ cm
0.07230	0.1203	0.002143	$B = 0.00004893$ cm ² /sec
0.08735	0.1453	0.002184	$C = 0.004298$ sec
0.1316	0.2190	0.002384	
0.1753	0.2917	0.002640	$(r = 0.999934)$
0.2706	0.4503	0.003307	(std. error = $3.4 \cdot 10^{-5}$)
0.3561	0.5925	0.003789	
<i>4.82% (w/v) ethyl acetate in n-decane</i>			
0.01813	0.03017	0.002888	
0.02720	0.04526	0.002464	
0.03932	0.06542	0.002226	
0.06053	0.10072	0.002123	$A = 0.001237$ cm
0.07862	0.1308	0.002256	$B = 0.00004587$ cm ² /sec
0.09937	0.1653	0.002324	$C = 0.004786$ sec
0.1490	0.2479	0.002625	
0.1883	0.3133	0.002864	$(r = 0.999935)$
0.2848	0.4739	0.003544	(std. error = $3.6 \cdot 10^{-5}$)
0.3570	0.5940	0.004194	

TABLE III

PEAK DISPERSION DATA FOR HEXAMETHYLBENZENE ($k_e = 0.67$)

u (cm/sec)	u_e (cm/sec)	H (cm)	Van Deemter coefficients
<i>4.68% (w/v) ethyl acetate in n-pentane</i>			
0.01819	0.03027	0.003676	
0.02721	0.04527	0.002849	
0.03911	0.06507	0.002208	$A = 0.0009097$ cm
0.06024	0.10023	0.001828	$B = 0.00008309$ cm ² /sec
0.07847	0.1306	0.001656	$C = 0.001021$ sec
0.09937	0.1653	0.001531	
0.1459	0.2488	0.001542	$(r = 0.999803)$
0.1914	0.3185	0.001564	(std. error = $4.7 \cdot 10^{-5}$)
0.2880	0.4792	0.001590	
0.3623	0.6028	0.001617	
<i>4.86% (w/v) ethyl acetate in n-hexane</i>			
0.01825	0.03037	0.003132	
0.02711	0.04521	0.002408	
0.03923	0.06527	0.001968	$A = 0.0009713$ cm
0.06112	0.1017	0.001655	$B = 0.00006317$ cm ² /sec
0.07784	0.1295	0.001659	$C = 0.001260$ sec
0.09968	0.1659	0.001529	
0.1500	0.2496	0.001615	$(r = 0.999693)$

TABLE III (continued)

u (cm/sec)	u_e (cm/sec)	H (cm)	Van Deemter coefficients
0.1852	0.3082	0.001632	(std. error = $5.5 \cdot 10^{-5}$)
0.2908	0.4839	0.001699	
0.3631	0.6042	0.001798	
<i>4.32% (w/v) ethyl acetate in n-heptane</i>			
0.01763	0.02933	0.002800	
0.02692	0.04479	0.002078	
0.03817	0.06351	0.001777	$A = 0.0010014$ cm
0.05631	0.09369	0.001620	$B = 0.00004870$ cm ² /sec
0.07167	0.1193	0.001561	$C = 0.001536$ sec
0.08596	0.1430	0.001579	
0.1294	0.2153	0.001606	($r = 0.999011$)
0.1729	0.2877	0.001719	(std. error = $9.4 \cdot 10^{-5}$)
0.2718	0.4523	0.001917	
0.3623	0.6028	0.001880	
<i>4.50% (w/v) ethyl acetate in n-octane</i>			
0.01821	0.03030	0.002363	
0.02741	0.04561	0.001892	
0.03954	0.06579	0.001677	$A = 0.001036$ cm
0.06059	0.10082	0.001496	$B = 0.00003673$ cm ² /sec
0.07862	0.1308	0.001605	$C = 0.001952$ sec
0.09992	0.1663	0.001602	
0.1506	0.2506	0.001733	($r = 0.999576$)
0.1956	0.3255	0.001844	(std. error = $6.1 \cdot 10^{-5}$)
0.2894	0.4815	0.002073	
0.3771	0.6275	0.002259	
<i>4.41% (w/v) ethyl acetate in n-nonane</i>			
0.01813	0.03017	0.002101	
0.03037	0.05053	0.001647	
0.03945	0.06564	0.001559	$A = 0.001081$ cm
0.05447	0.09063	0.001565	$B = 0.00002651$ cm ² /sec
0.07230	0.1203	0.001586	$C = 0.002353$ sec
0.08735	0.1453	0.001652	
0.1316	0.2190	0.001756	($r = 0.999607$)
0.1753	0.2917	0.001920	(std. error = $5.8 \cdot 10^{-5}$)
0.2706	0.4503	0.002206	
0.3561	0.5925	0.002474	
<i>4.82% (w/v) ethyl acetate in n-decane</i>			
0.01813	0.03017	0.001899	
0.02720	0.04526	0.001613	
0.03932	0.06542	0.001518	$A = 0.001174$ cm
0.06053	0.10072	0.001592	$B = 0.00001751$ cm ² /sec
0.07862	0.1308	0.001658	$C = 0.002501$ sec
0.09937	0.1653	0.001695	
0.1490	0.2479	0.001906	($r = 0.999550$)
0.1883	0.3133	0.002116	(std. error = $6.4 \cdot 10^{-5}$)
0.2848	0.4739	0.002328	
0.3570	0.5940	0.002680	

TABLE IV

EXPERIMENTAL VALUES FOR DISPERSION EQUATION COEFFICIENTS OBTAINED BY CURVE FITTING PROCEDURES TO THE DATA GIVEN IN TABLE II

<i>Mobile phase</i>						
<i>n-Pentane</i> 4.68% (w/v)	<i>n-Hexane</i> 4.86% (w/v)	<i>n-Heptane</i> 4.32% (w/v)	<i>n-Octane</i> 4.50% (w/v)	<i>n-Nonane</i> 4.41% (w/v)	<i>n-Decane</i> 4.82% (w/v)	
<i>Van Deemter equation</i> $H = A + \frac{B}{u} + Cu$						
<i>A</i>	0.001189	0.001144	0.001114	0.001210	0.001208	0.001237
<i>B</i>	0.0001079	0.00009045	0.00008141	0.00006460	0.00004893	0.00004539
<i>C</i>	0.002525	0.003008	0.003362	0.003661	0.004298	0.004786
<i>Giddings equation</i> $H = \frac{A}{1 + Eju} + \frac{B}{u} + Cu$						
<i>A</i>	0.001189	0.001144	0.001123	0.001210	0.001407	0.001257
<i>B</i>	0.0001079	0.00009045	0.00008622	0.00006460	0.00006651	0.00005297
<i>C</i>	0.002525	0.003008	0.003348	0.003661	0.004001	0.004754
<i>E</i>	0	0	0.005243	0	0.03370	0.008100
<i>Huber equation</i> $H = \frac{A}{1 + Eju^{1/2}} + \frac{B}{u} + Cu + Du^{1/2}$						
<i>A</i>	0.001455	0.001048	0.0009864	0.001196	0.0007022	0.1612
<i>B</i>	0.0001035	0.00009204	0.00008345	0.00006483	0.00005710	0.00005624
<i>C</i>	0.003302	0.002728	0.002979	0.003622	0.002769	0.02310
<i>D</i>	-0.0009161	0.0003309	0.0004472	0.00004591	0.001775	-0.06804
<i>E</i>	0	0	0	0	0	2.131
<i>Knox equation</i> $H = Au^{1/3} + \frac{B}{u} + Cu$						
<i>A</i>	0.002509	0.002422	0.002390	0.002545	0.002608	0.002626
<i>B</i>	0.0001232	0.0001051	0.00009518	0.00008025	0.00006389	0.006111
<i>C</i>	0.0008720	0.001407	0.001754	0.002003	0.002518	0.0023035
<i>Horváth equation</i> $H = \frac{A}{1 + Eju^{1/3}} + \frac{B}{u} + Cu + Du^{2/3}$						
<i>A</i>	0.001366	0.001057	0.001013	0.001197	0.0008252	0.005583*
<i>B</i>	0.0001044	0.00009215	0.00008332	0.00006486	0.00005625	0.00005139
<i>C</i>	0.003572	0.002495	0.002744	0.003585	0.001948	0.009169
<i>D</i>	-0.001104	0.0005411	0.0006474	0.00007991	0.002454	-0.008577
<i>E</i>	0	0	0	0	0	*

* The best fit obtained for *E* sufficiently large that the first term reduced to $A/Eu^{-1/3}$. The value given is for A/E .

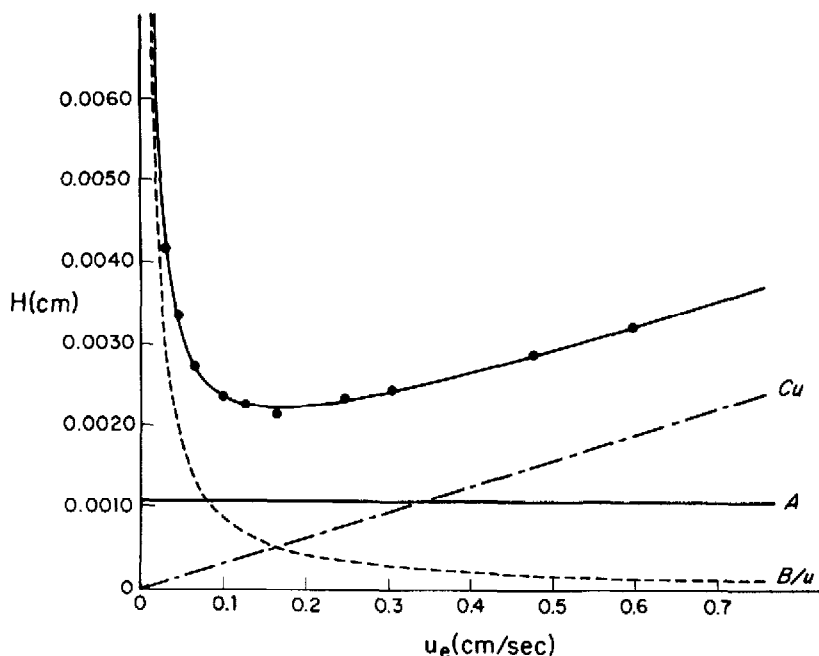


Fig. 1. H versus u curve. Partisil-10; 5.4% ethyl acetate in n -hexane; benzyl acetate. Fit to Van Deemter eqn.; $r = 0.999699$.

RESULTS

Examination of Table IV shows rational fits of the data given in Tables II and III were obtained with the equations developed by Van Deemter, Giddings and Knox. The fit of the data to both the Huber and Horváth equations gave alternating positive and negative values for the D constant which is the coefficient of the fractional power functions of u . Furthermore, for the Huber equation the value for the coupling coefficient E is consistently zero and for the Horváth equation is zero for four solvent mixtures out of six with an extreme value of 97.3 for one solvent. On the basis of the irrational fits of the data to the Huber and Horváth equations these equations will be eliminated from those that can satisfactorily describe the relationship between H and u . The same irrational behaviour of the Huber and Horváth equations can be observed if the data for hexamethylbenzene are also fitted to them but the results are not included here. The data given in Tables II and III are precisely measured and can be tested against the Horváth and Huber equations or any other HETP equation if so desired.

It is seen that a good fit is also obtained for the equation of Giddings but it is also seen that the coupling coefficient E is numerically equal to zero. Thus the Van Deemter equation could be considered a special case of the Giddings equation where, at the linear velocities employed, the term involving the constant E is not significant (*i.e.* the coupling effect is complete). Although through the remainder of this paper the Van Deemter equation will continually be employed and referred to by name, the equation of Giddings might well be correct over a wider or different linear velocity

range. Consequently, the two equations to be tested further for validity are the Van Deemter equation (as a special case of the Giddings equation) and the Knox equation.

It is now necessary to refer to the detailed equations of Van Deemter and Knox.

The Van Deemter equation is

$$H = 2\lambda d_p + \frac{2\gamma D_m}{u_e} + \frac{f_1(k_e)d_p^2 u_e}{D_m} + \frac{f_2(k_e)d_f^2 u_e}{D_s} \quad (6)$$

where D_m and D_s are the diffusivities of the solute in the mobile and stationary phases, respectively; d_p is the particle diameter; d_f is the effective film thickness of the stationary phase; λ and γ are constants; and H , k_e and u_e have the meanings previously ascribed to them. The Knox equation is

$$H = Au_e^{1/3} + \frac{2\gamma D_m}{u_e} + \frac{g'f_m(k_e)d_p^2 u_e}{D_m} + \frac{gf_s(k_e)d_f^2 u_e}{D_s} \quad (7)$$

where A , γ , g and g' are constants, and the other symbols have the meaning previously ascribed to them.

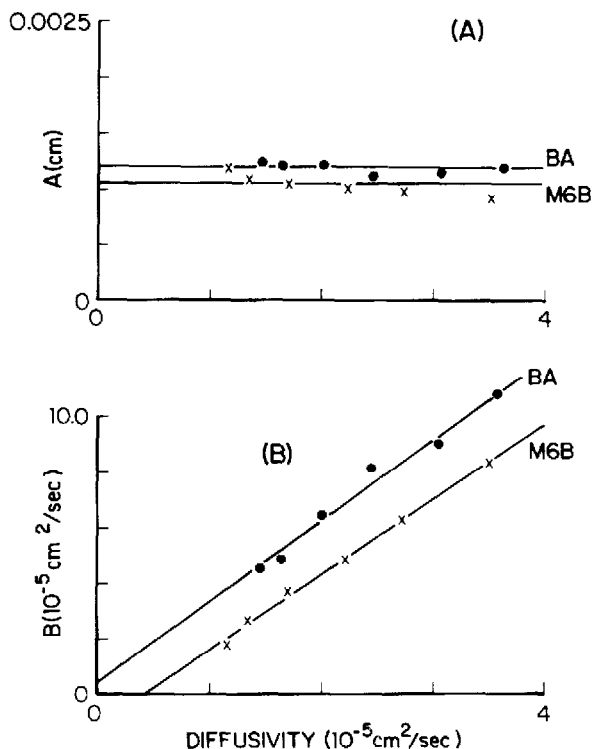


Fig. 2. Van Deemter coefficients as a function of solute diffusivity; Partisil 10 silica. (A) Multipath coefficient; (B) longitudinal diffusion. BA = benzyl acetate; M6B = hexamethylbenzene.

Comparing eqns. 6 and 7 it is seen that there is a significant difference between them, in that, only the Van Deemter equation should provide a term independent of both the linear velocity of the mobile phase and the solute diffusivity. In Fig. 2 the upper graph relates the A term (calculated from the curve fitting procedure for the Van Deemter equation) to the diffusivity of the solute in the mobile phase (see Tables I and IV) for both benzyl acetate and hexamethylbenzene. It is seen that the A term is independent of the solute diffusivity as predicted by the Van Deemter equation. The values of the A term for benzyl acetate give a horizontal line parallel with the diffusivity axis. The values for hexamethylbenzene appear to decrease slightly as the solute diffusivity increases but the value for the slope has no statistically significant difference from zero. Furthermore, the mean values of the multipath term for the two solutes statistically do not differ significantly.

It is important to emphasize that the type of tests that are utilized here are only valid if the columns are well packed. Katz and Scott²⁶ showed that data from poorly packed columns that exhibited channeling, or with large column void volumes, gave very large values for the Van Deemter multipath term A . In other words, gross imperfections in the column packing appeared as excessive multipath terms. Any dispersion process arising from gross packing defects and not included in the theoretical development of an HETP equation may well involve solute diffusivity dependent terms and thus the A term, determined by a curve fitting procedure for a number of different solutes, could be found diffusion dependent if the column was not well packed. It is recommended, therefore, that HETP data are not used to test dispersion relationships if the multipath term, A , is found to be greater than two particle diameters; *i.e.*, only columns that are reasonably well packed should be employed.

Examination of eqns. 6 and 7 indicates that both the Knox and Van Deemter equations predict a linear relationship between the value of B (the longitudinal diffusion coefficient) and solute diffusivity. A plot of B , derived from the Van Deemter curve fit, against diffusivity for both benzyl acetate and hexamethylbenzene are shown in the lower part of Fig. 2. It is seen that the predicted linear relationship is obtained. However, it can be shown that the values of B from the Knox curve fit also give a linear relationship so that the lower linear curves in Fig. 2 do not *exclusively* support the Van Deemter equation.

In eqn. 6, D_s is the diffusivity of the solute in the stationary phase which, for a silica gel column, consists almost entirely of that portion of the 'mobile phase' that is static and is trapped in the pores of the silica gel. It would therefore appear reasonable to assume that $D_s = D_m$. Now this would not be quite true as, due to layers of the more polar solvent that is absorbed on the surface of silica²⁸, the mean composition of the solvent in the pores will not be quite that of the mobile phase. However, it would be reasonable to assume that $D_s = \alpha D_m$ where α is a constant probably close to unity.

Now if D_s can be replaced by αD_m then eqn. 6 can be simplified to

$$H = 2\lambda d_p + \frac{2\gamma D_m}{u_e} + \frac{b u_e}{D_m} \quad (8)$$

where $b = f_1(k_e)d_p^2 + f_2(k_e)\frac{d_f^2}{\alpha}$

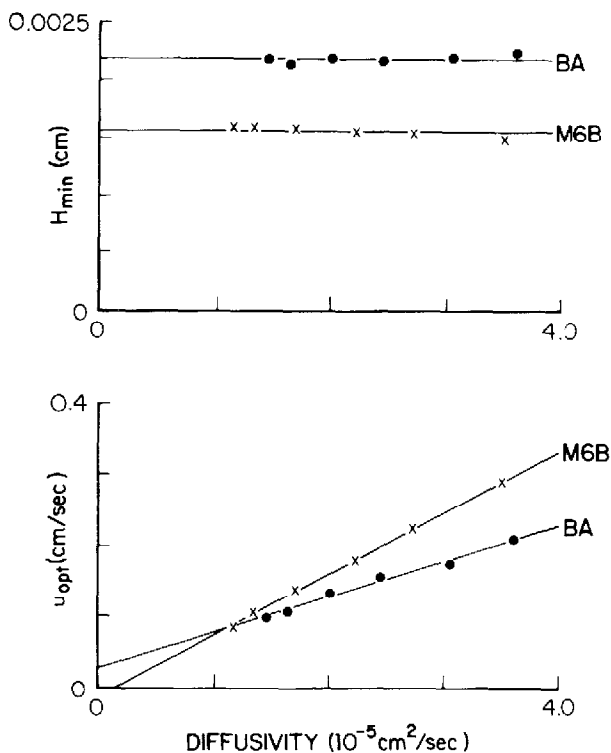


Fig. 3. H_{\min} and u_{opt} as functions of solute diffusivity; Partisil 10 silica.

Differentiating eqn. 8 with respect to u_e , equating to zero and solving for u_e it can be seen that

$$u_{\text{opt}} = D_m \left(\frac{2\gamma}{b} \right)^{1/2} \quad (9)$$

where u_{opt} is the optimum velocity.

Further substituting for u_e in eqn. 8 from eqn. 9 it is also seen that the minimum plate height,

$$H_{\min} = 2\lambda d_p + 2(2\gamma b)^{1/2} \quad (10)$$

Now it is seen from eqns. 9 and 10 that the optimum linear velocity should be linearly related to the solute diffusivity, D_m , whereas the value for the minimum HETP should be constant and independent of D_m (for solutes eluted at a constant k_e).

Values for H_{\min} and u_{opt} are plotted against solute diffusivity for both hexamethylbenzene and benzyl acetate in the upper and lower graphs, respectively, in Fig. 3. It is seen that the relationships predicted by eqns. 9 and 10 are confirmed. A similar treatment of the Knox equation does not predict a value of H_{\min} independent of D_m , nor does it predict a linear relationship between u_{opt} and solute diffusivity.

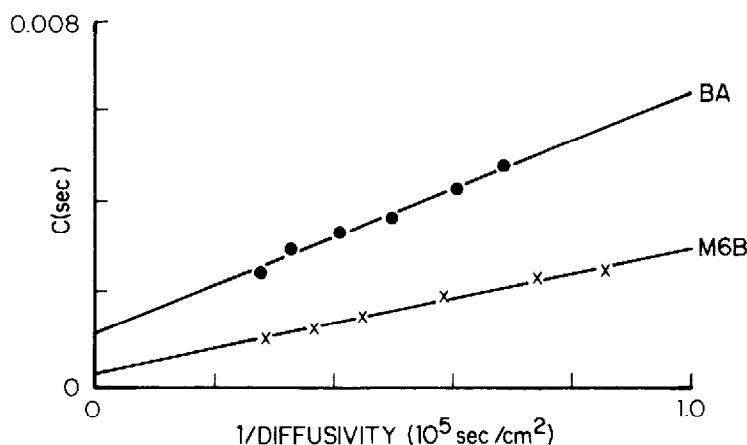


Fig. 4. Van Deemter resistance-to-mass-transfer coefficient (C) as a function of solute diffusivity; Partisil 10 silica.

Returning to eqn. 8 it is seen that the Van Deemter resistance-to-mass transfer coefficient (C) should be linearly related to the reciprocal of the solute diffusivity and in Fig. 4, the values of the C coefficient for both solutes hexamethylbenzene and benzyl acetate are shown plotted against the reciprocal of the diffusivity. It is seen that an excellent linear relationship is obtained as predicted by eqn. 8. However, these linear curves are also *not an exclusive* validation of the Van Deemter equation as the C coefficient from the curve fit of the HETP data to the Knox equation also gives a reasonable linear relationship. It is interesting to note that the curve for the unretained solute hexamethylbenzene gives an intercept that is not statistically significant. The linear curve for benzyl acetate, however, gives a larger intercept that is significant. At this time it is tentatively suggested that this intercept may possibly represent a small resistance-to-mass transfer factor that is associated with the layers of ethyl acetate molecules on the silica surface where the retentive interactions take place.

It was of interest to examine the resistance-to-mass transfer factor for a totally excluded polystyrene (molecular weight 83,000). HETP curves were obtained employing the same approach as that used previously but now using different concentrations of glycerol in tetrahydrofuran containing 5% of methanol. (The methanol was included to ensure that the polystyrene was not retained in any way by adsorption.) HETP curves were obtained for six different concentrations of glycerol in tetrahydrofuran, thus changing the solute diffusivity and consequently the magnitude of the C term. Each data set was not fitted directly to the Van Deemter equation as the longitudinal diffusion term could be eliminated because due to the high molecular weight of the solute the diffusivity was extremely small. Consequently, the data were fitted to a simple linear function ($y = a + bx$). The constant (a) gives the magnitude of the multipath coefficient (A) and the slope (b), the magnitude of the resistance-to-mass transfer coefficient (C). The results are given in Table V. It is seen that the magnitude of the C coefficient from Table V are commensurate with those for hexamethylbenzene given in Table III. The commensurate values for the C coefficients of the two solutes have a considerable significance. Katz and Scott²⁹ have shown that

TABLE V
RESISTANCE-TO-MASS TRANSFER COEFFICIENTS FOR POLYSTYRENE (MOLECULAR WEIGHT 83,000)

Glycerol* (%, v/v)	Viscosity (cP)	Resistance-to-mass transfer coefficient (sec)
0	0.343	0.001465
0.6	0.479	0.001500
1.0	0.489	0.001504
5.0	0.586	0.001876
8.0	0.752	0.002422
11.0	0.869	0.002360

* Balance was 5% methanol in tetrahydrofuran.

the diffusivity of a solute is inversely proportional to the molecular weight of a solute raised to the power of 0.833; that being so the C coefficient for polystyrene should be one to two orders of magnitude larger than the C coefficient for hexamethylbenzene. However, the polystyrene is completely excluded; *ipso facto*, the resistance to mass transfer between the particles is one to two orders in magnitude less than that trapped inside the pores of the particle due to the static mobile phase. Therefore by far the major resistance to mass transfer for a silica gel column takes place within the particle and not between the particles. In light of the work by Tijssen³⁰ describing secondary flow that can occur in tightly coiled capillary tubes, the solute transfer is obviously aided by the eddies (radial flow) formed between the particles due to the continual change in direction of the solute flow as it winds its way through the interstices between the particles of the packing. These eddies do not constitute turbulence, although it might be considered that they can form the source of turbulent flow at much higher velocities. This effect is, in fact, the coupling phenomenon to which Giddings refers, and which constitutes the resistance-to-mass transfer effect for which he includes a hyperbolic function of u_e . The results described here, however, demonstrated that u_e is sufficiently high for the coupling term to increase D_m sufficiently and the only significant resistance-to-mass transfer effect resides in the static mobile phase within the pore, and this predominates at high velocities. However, it is interesting to note that for a true pellicular packing, with a very small pore volume, the inverse would apply. There would be no significant resistance to mass transfer in a static layer of mobile phase and the only residual resistance-to-mass transfer term would be in the voids between the particles of the packing and thus be controlled by the coupling term of Giddings. Consequently, the magnitude of the resistance-to-mass transfer term could still be relatively small even when the column is operated at high mobile phase velocities.

The effect of particle size and capacity factor on the resistance-to-mass transfer factors in a silica gel column

In general the Van Deemter equation, as a special case of the Giddings equation, has been well substantiated over the linear mobile phase velocity range of 0.05–0.6 cm/sec for columns packed with silica gel. There remains the effect of two more variables to be examined in order to validate completely the use of the Van

TABLE VI

PEAK DISPERSION DATA FOR BENZYL ACETATE ($k' \approx 2.0$)Mobile phase: 4.3% w/v ethyl acetate in *n*-hexane.

u (cm/sec)	u_e (cm/sec)	H (cm)	Van Deemter coefficients
$d_p = 17.5 \mu\text{m}$; packing, Partisil 20; column, 25×0.8 cm I.D.			
0.0220	0.0366	0.004831	
0.0298	0.0497	0.004137	
0.0373	0.0621	0.003683	$A = 0.001539$ cm
0.0526	0.0875	0.003634	$B = 0.0000976$ cm ² /sec
0.0754	0.1254	0.003955	$C = 0.012859$ sec
0.1014	0.1687	0.004346	
0.1353	0.2251	0.004936	($r = 0.999862$)
0.1916	0.3188	0.006018	(std. error = $1.1 \cdot 10^{-4}$)
0.2435	0.4052	0.007058	
0.3695	0.6148	0.009605	
0.4678	0.7784	0.011596	
$d_p = 7.8 \mu\text{m}$; packing, Partisil 10; column: 25×0.8 cm I.D.			
0.0225	0.0374	0.003063	
0.0301	0.0501	0.002520	
0.0377	0.0628	0.002202	$A = 0.000515$ cm
0.0527	0.0877	0.001785	$B = 0.0000910$ cm ² /sec
0.0754	0.1255	0.001637	$C = 0.003319$ sec
0.1016	0.1691	0.001611	
0.1312	0.2183	0.001640	($r = 0.99927$)
0.1841	0.3063	0.001834	(std. error = $3.1 \cdot 10^{-5}$)
0.2336	0.3887	0.002078	
0.3036	0.5052	0.002422	
0.3782	0.6293	0.002749	
0.4457	0.7416	0.003076	
0.4678	0.7784	0.003193	
$d_p = 4.4 \mu\text{m}$; packing, Partisil 5; column, 14×0.8 cm I.D.			
0.0199	0.0331	0.002960	
0.0266	0.04426	0.002315	
0.0338	0.0562	0.002012	$A = 0.000623$ cm
0.0478	0.0795	0.001719	$B = 0.0000744$ cm ² /sec
0.0693	0.1153	0.001448	$C = 0.001569$ sec
0.0929	0.1546	0.001376	
0.1199	0.1995	0.001291	($r = 0.999858$)
0.1727	0.2873	0.001341	(std. error = $3.3 \cdot 10^{-5}$)
0.2179	0.3626	0.001395	
0.3257	0.5419	0.001556	
0.3849	0.6404	0.001770	
0.4140	0.6888	0.001837	
0.4712	0.7840	0.001937	
$d_p = 3.2 \mu\text{m}$; packing, Partisil 3; column: 9×0.8 cm I.D.			
0.0201	0.0334	0.002884	
0.0271	0.0451	0.002460	
0.0342	0.0569	0.002024	$A = 0.000644$ cm

(Continued on p. 68)

TABLE VI (continued)

u (cm/sec)	u_e (cm/sec)	H (cm)	Van Deemter coefficients
0.0483	0.0804	0.001621	$B = 0.0000750 \text{ cm}^2/\text{sec}$ $C = 0.001284 \text{ sec}$
0.0696	0.1158	0.001437	
0.0945	0.1572	0.001355	$(r = 0.999739)$ (std. error = $1.3 \cdot 10^{-3}$)
0.1225	0.2038	0.001286	
0.1721	0.2864	0.001270	
0.2172	0.3614	0.001307	
0.2648	0.4406	0.001335	
0.3177	0.5286	0.001494	
0.3497	0.5819	0.001527	

Deemter equation for column design, namely, the particle diameter of the packing, d_p , and the solute capacity factor, k_e . The explicit function of the capacity factor that is included in the resistance-to-mass transfer factor has been examined elsewhere²⁹ and that work will only be briefly referred to here. However, the effect of the capacity ratio of the solute and the particle diameter of the packing on the resistance-to-mass transfer factor will be directly examined.

The effect of particle diameter on the resistance-to-mass transfer coefficient

Experimental procedure. The same apparatus and procedure were employed as used previously, except that four columns were packed with Partisil 3, 5, 10 and 20 silica gel having actual particle diameters of 3.2, 4.4, 7.8 and 17.5 μm , respectively. Each column was examined, in exactly the same way as those previously but only one mobile phase was employed, *viz.* 5% ethyl acetate in *n*-hexane. HETP values were obtained over a range of mobile phase linear velocities from 0.02–0.8 cm/sec and the results obtained shown in Table VI. The data were fitted to the Van Deemter equation and the results of this fit are included in Table VI together with the values

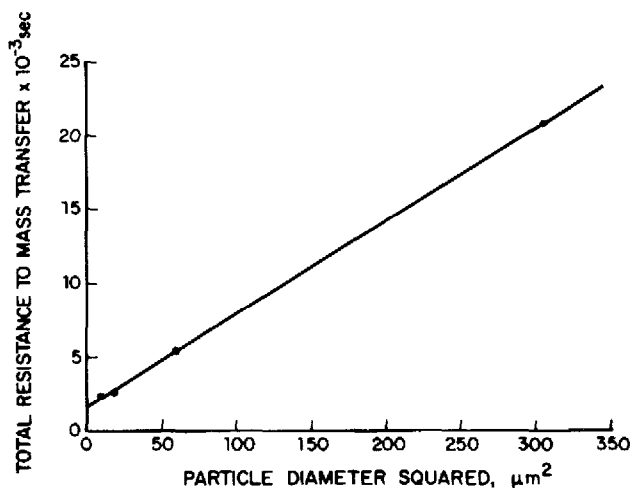


Fig. 5. Graph of total resistance to mass transfer against particle diameter squared; solute, benzyl acetate $k' = 2$.

of the multipath term (A), longitudinal diffusion coefficient (B) and the resistance-to-mass transfer coefficient (C).

Discussion. Examination of eqn. 6 indicates that the resistance-to-mass transfer term (C) should increase linearly as the square of the particle diameter of the packing. In Fig. 5 the values of the C coefficients from Table VI are shown plotted against the square of the particle diameter. It is seen that an excellent linear relationship is obtained as predicted by the Van Deemter equation. The intercept in Fig. 5 can be compared with the intercept shown in Fig. 4 and could also account, in a similar way, for a resistance-to-mass transfer effect that takes place in the layers of absorbed ethyl acetate on the surface of the silica gel.

The effect of solute capacity factor on the resistance-to-mass transfer coefficient

Experimental procedure. The column used was 25 cm \times 8 mm I.D., packed with Partisil 10 silica gel and the mobile phase employed was a mixture of 5% ethyl acetate in *n*-hexane. The apparatus was similar to that previously described and (H , u) data sets were obtained for eight different solutes of diverse molecular weight and consequently, diverse diffusivities, eluted over a range of k' values from zero to twelve. Values for the linear velocity and capacity ratios were calculated from the retention time of the fully permeating non-retained solute, tridecylbenzene, and not from the retention time of a completely excluded solute. Dispersion functions determined for each solute, such as that due to resistance to mass transfer will thus describe correctly the dependence of the C coefficient on solute diffusivity but the numerical values will not be absolute. The data obtained for each solute are given in Table VII which also includes values of A , B and C from the results of fitting the data to the Van Deemter equation. The H , u curves for each solute are shown in Fig. 6. It is seen that each solute has a unique curve with its own distinct value for the longitudinal diffusion coefficient (B) and the resistance-to-mass transfer coefficient (C). It should also be noted that both the minimum value of H and the optimum values of u are different for each solute as predicted by eqns. 9 and 10.

DISCUSSION

At high values for the linear velocity, u , the function $2\gamma D_m/u$ becomes negligible and eqn. 8 reduces to:

$$H = 2\lambda d_p + \frac{bu}{D_m} \quad (11)$$

where b is the function of k' as previously defined.

In Fig. 7 values of H for each solute taken at a liner velocity of 0.21 cm/sec are plotted against k' . It is seen that the relationship between H and k' is irregular and it appears that there is no clear correlation between them. This explains the confusion that presently exists in the general opinion of many workers in the field as to how H or the column efficiency varies with the k' of the eluted solute. Examination of eqn. 11 indicates that the value of the C term is determined not only by the magnitude of the function of k' but also by the value of the diffusivity, D_m . Furthermore, as apparently there is no relationship between the capacity factor of a

TABLE VII
PEAK DISPERSION DATA FOR DIFFERENT SOLUTES

Packing, Partisil 10; column, 25×0.8 cm I.D.; mobile phase, 5% (v/v) ethyl acetate in *n*-hexane.

u (cm/sec)	H (cm)	Tridecylbenzene ($k' = 0$)	<i>p</i> -Xylene ($k' = 0.09$)	Anisole ($k' = 0.51$)	Nitrobenzene ($k' = 1.55$)
0.0163		0.002230	0.004273	0.004753	0.004920
0.0244		0.001710	0.003147	0.003474	0.003664
0.0325		0.001407	0.002469	0.002871	0.003112
0.0426		0.001228	0.001994	0.002271	0.002477
0.0596		0.001194	0.001537	0.001912	0.002013
0.0847		0.001190	0.001367	0.001678	0.001659
0.1101		0.001174	0.001190	0.001512	0.001580
0.1474		0.001230	0.001179	0.001356	0.001493
0.2094		0.001409	0.001115	0.001432	0.001564
0.2632		0.001551	0.001227	0.001561	0.001720
0.3636		0.002037	0.001458	0.001906	0.002051
0.4651		0.002502	0.001692	0.002170	0.002422
<i>Van Deemter</i>		$A = 0.0004863$ cm	$A = 0.0003672$ cm	$A = 0.0005337$ cm	$A = 0.0005684$ cm
<i>coefficients</i>		$B = 0.00002716$ cm ² /sec	$B = 0.00006428$ cm ² /sec	$B = 0.00006914$ cm ² /sec	$B = 0.00007225$ cm ² /sec
		$C = 0.003849$ sec	$C = 0.002498$ sec	$C = 0.003113$ sec	$C = 0.003495$ sec
		($r = 0.999684$)	($r = 0.999763$)	($r = 0.999658$)	($r = 0.999418$)
		(std. err. = $4.4 \cdot 10^{-5}$)	(std. err. = $5.0 \cdot 10^{-5}$)	(std. err. = $7.0 \cdot 10^{-5}$)	(std. err. = $9.7 \cdot 10^{-5}$)

TABLE VII (continued)

μ (cm/sec)	H (cm)	Diethyl phthalate ($k' = 1.89$)	Acetophenone ($k' = 2.95$)	Dipropyl phthalate ($k' = 4.25$)	<i>o</i> -Cresol ($k' = 4.87$)
0.0163	0.002536	0.004920	0.003548	0.003490	0.004490
0.0244	0.001987	0.003649	0.002493	0.003326	0.003326
0.0325	0.001838	0.002992	0.002135	0.002755	0.002755
0.0426	0.001565	0.002420	0.001797	0.002297	0.002297
0.0596	0.001818	0.002053	0.001725	0.001984	0.001984
0.0847	0.001996	0.001726	0.001723	0.001878	0.001878
0.1101	0.002112	0.001612	0.001801	0.001855	0.001855
0.1474	0.002409	0.001623	0.001982	0.001952	0.001952
0.2094	0.002834	0.001785	0.002408	0.002214	0.002214
0.2632	0.003518	0.001958	0.002776	0.002546	0.002546
0.3636	0.004733	0.002452	0.003626	0.003089	0.003089
0.4651	0.005712	0.002897	0.004413	0.003589	0.003589
<i>Van Deemter</i>	$A = 0.0006096$ cm	$A = 0.0004873$ cm	$A = 0.0004636$	$A = 0.0006230$ cm	
<i>coefficients</i>	$B = 0.00002800$ cm ² /sec	$B = 0.00007269$ cm ² /sec	$B = 0.00004467$ cm ² /sec	$B = 0.00006159$ cm ² /sec	
	$C = 0.01085$	$C = 0.004754$ sec	$C = 0.008289$ sec	$C = 0.006206$ sec	
	($r = 0.999517$)	($r = 0.999719$)	($r = 0.999945$)	($r = 0.999931$)	
	(std. err. = $1.0 \cdot 10^{-4}$)	(std. err. = $7.0 \cdot 10^{-5}$)	(std. err. = $3.0 \cdot 10^{-5}$)	(std. err. = $3.6 \cdot 10^{-5}$)	

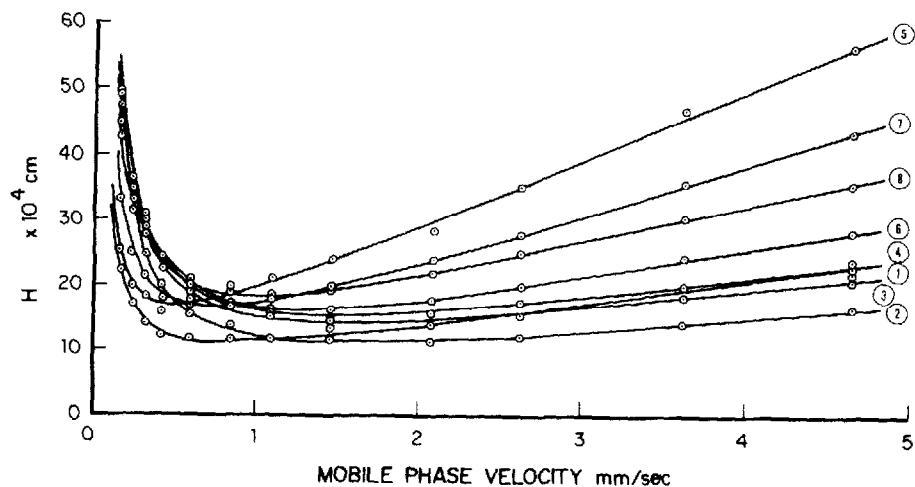


Fig. 6. H versus u curves for different solutes; packing, Partisil 10. Curves: 1 = tridecylbenzene; 2 = *p*-xylene; 3 = anisole; 4 = nitrobenzene; 5 = dioctyl phthalate; 6 = acetophenone; 7 = dipropyl phthalate; 8 = *o*-cresol.

given solute and its diffusivity, the irregular relationship between H and k' is to be expected. Now it is seen from eqn. 10 that the minimum values of H are independent of D_m and thus values for H_{\min} should be smoothly related to k' . In Fig. 8 the values of H_{\min} (calculated from eqn. 10 using the data for the Van Deemter coefficients B and C for each solute from Table VII) are plotted against k' . It is seen that a smooth relationship between H and k' is now obtained once the effect of solute diffusivity is eliminated. Thus H increases (and consequently, the column efficiency decreases) with increasing values of k' but this will only be observed in practice for solutes with the

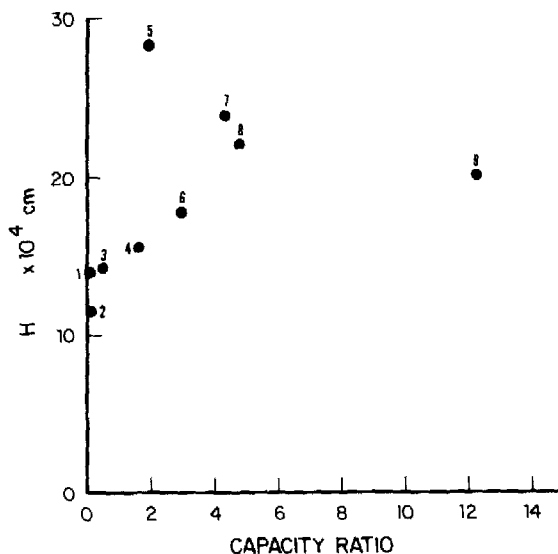


Fig. 7. Graph of H versus k' ; mobile phase linear velocity, 0.21 cm/sec. Column, 25×0.8 cm I.D.; Partisil 10. Compounds 1-8 as in Fig. 6; 9 = dimethyl phthalate.

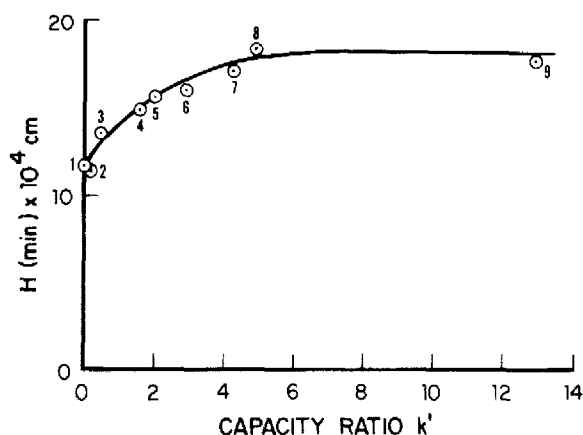


Fig. 8. Dependence of H_{\min} on k' at optimum linear velocity for each solute. Compounds 1-9 as in Fig. 7.

same diffusivity or if the value of H is taken at the optimum velocity where the effect of solute diffusivity is eliminated. It should be reemphasized that extra column dispersion must also be insignificant. The smooth curve shown in Fig. 8 is also further evidence that the relationship between H and u is most accurately described by the Van Deemter equation as the Knox equation does not predict that the value of U_{opt} is independent of D_m .

The precise function of k_e that controls the magnitude of the resistance-to-mass-transfer factor is, at this time, a subject of some uncertainty—even confusion. The original equation of Van Deemter did not include a function for the resistance-to-mass transfer term in the mobile phase, but only a function for the resistance to mass transfer in the stationary phase. Subsequently, an expression for the resistance to mass transfer in the mobile phase was put forward³¹ but the function of k' was not acceptable as it predicted no resistance to mass transfer in the mobile phase for an unretained solute. Purnell² suggested that an appropriate function of k_e would be that derived by Golay³² for capillary columns, and Horváth²⁴, Huber²⁰ and Knox³³, all provided alternative and different functions of k_e that they considered to be appropriate. More recently Katz and Scott²⁹ approached the problem by testing various functions of k_e against an experimental data set obtained for 69 different substances. The expression they arrived at for the resistance-to-mass transfer coefficient was as follows:

$$C = \frac{(0.37 + 4.69k_e + 4.04k_e^2) d_p^2 u_e}{24 (1 + k_e)^2 D_m} \quad (12)$$

It is seen that the appropriate function for k_e identified experimentally is very similar to that developed by Golay³² viz.

$$\frac{1 + 6k_e + 11k_e^2}{24 (1 + k_e)^2}$$

Until more experimental evidence becomes available to suggest an alternative function of k_e , eqn. 12 can be used with reasonable confidence in column design.

CONCLUSIONS

Virtually any hyperbolic or pseudo hyperbolic function will algebraically fit experimentally determined (H , u) data sets but will not necessarily provide the correct physical interpretation of the dispersion processes that take place. The HETP equation that most accurately describes the relationship between H and u over the velocity range of 0.02 to 1.00 cm/sec for columns packed with porous silica is that of Van Deemter which, itself, appears to be a special case of the Giddings equation. The Van Deemter equation, in the following form, can be used with confidence in column design

$$H = 2 \lambda d_p + \frac{2\gamma D_m}{u_e} + \frac{(a + bk_e + ck_e^2) d_p^2 u_e}{24 (1 + k_e)^2 D_m}$$

where λ and γ may vary with the quality of the packing but for a reasonably well packed column can be taken as 0.5 and 0.8; a , b and c can be taken as 0.37, 4.69 and 4.04, respectively.

There are indications that the coupling term of Giddings could become extremely important for pellicular type packing materials when the particle porosity is very low and the major resistance-to-mass-transfer effect occurs between the particles. This could also be true for reversed-phase packings if the pores of the silica are sealed by the silanization process used in the bonding procedure. Even if only a proportion of the pores are sealed, then the quantity of static mobile phase held in the packing will be less and consequently, the overall resistance-to-mass transfer effect is reduced and the contribution of the mass transfer effects between the particles becomes more significant. It should be emphasized that simple curve fitting procedures of (H , u) data sets to a proposed dispersion equation are, by themselves, inadequate to validate its applicability. Any equation in question must also be examined with respect to how it predicts the effect of solute diffusivity, particle diameter and solute capacity ratio on optimum velocity, minimum H values and the different individual dispersion processes taken into account by the theory. Finally, *it cannot be overemphasized* that the validity of any HETP equation can only be tested with extremely precise and accurate data. A standard deviation of 2% in measured values of H , or the mobile phase velocity, u_e , is the maximum that can be tolerated; data less precise than this can only lead to uncertainty in any conclusions and even completely fallacious interpretations.

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