

Effect of Various Binary Gas Mixtures as Mobile Phases on Theoretical Plate Number in Capillary Gas Chromatography

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Abstract

The effect of mixtures of hydrogen and helium and hydrogen and nitrogen on the theoretical efficiency of gas phase open-tubular column separations are reported. Two mixtures of N_2-H_2 and $He-H_2$, as well as the three pure gases, are used as the mobile phase. These 7 mobile phases provide a range of densities, diffusivities, and viscosities for studying the effects of these mass transfer properties on the height equivalent of a theoretical plate (HETP). A commercially available test mixture composed of various chemical classes is analyzed in triplicate with each carrier gas. The average HETP for each compound in the mixture is calculated and plotted against average linear velocity, mobile phase density, and inlet pressure. The $He-H_2$ mixes are very similar to each other in their effect on HETP at high gas velocities; their close agreement appears to be predicated on the narrow range of densities calculated for each mixture. Hydrogen, on the other hand, strongly affects the performance of nitrogen at all velocities. The wide spread of HETP among the N_2-H_2 mixes is also commensurate with their densities. The HETP of the 40% N_2 -60% H_2 mobile phase at the lowest velocities is higher than the 60% N_2 -40% H_2 mix. As the velocity increases to 40 cm/s, the 40% N_2 mix actually matched the performance of the $He-H_2$ mixes. Little plate height is sacrificed, even at 50 cm/s average linear velocity. This 40% N_2 mix is somewhat analogous to a multiviscosity motor oil; its N_2 component limits longitudinal diffusion at low velocities, and the H_2 component facilitates rapid mass transfer at higher velocities. The influence of the molecular volume of the probes on HETP is studied. The aromatic solutes produce lower HETP than the hydrocarbons at linear velocities greater than the optimum, but the aromatics produce higher HETP at suboptimum velocities. The responsible factor here is the binary diffusion coefficient, which is a function of the molar volume or size of the molecule.

Introduction

Open tubular column gas-liquid chromatography with flame ionization detection (GC-FID) routinely utilizes 4 gases: carrier gas, fuel gas, oxidizer gas, and auxiliary (or make-up) gas. In general, the roles of the carrier and make-up gases in the chromatographic and detection process, respectively, are not completely understood. However, more attention appears to have been given to the mode of operation of different carrier gases in GC-FID than different auxiliary gases. For example, a commercially available open-tubular porous layer (e.g., PLOT) column has recently been used to study the influence of carrier gas on retention in gas-solid chromatography. Hydrogen (H_2), helium (He), nitrogen (N_2), and carbon dioxide (CO_2) were studied (1). Column efficiency could be improved by using heavier carrier gases, such as N_2 and CO_2 , with a series of gaseous hydrocarbon analytes (e.g., propylene, butane, and isobutylene). To date, N_2 and CO_2 have not been seriously considered as mobile phases, because the diffusion coefficients of the analytes in these gases are considerably lower than in He and H_2 (2). In this regard, literature references have been primarily limited to the kinetic aspects of the influence of the carrier gas on chromatographic analysis employing packed columns (3,4).

Because open-tubular columns are routinely used, a systematic investigation of the influence of carrier gas in open tubular GC applied to moderately-high-boiling analytes would be of interest. A limited search of the literature revealed that studies of this type have typically used hydrocarbons as the probe analyte and did not incorporate carrier gas mixtures. We have attempted to design an experiment that employs a set of neat gases and binary mixtures that display a variation in viscosity and density under GC conditions. Data that show the impact of density on van Deemter curve properties have resulted from this study. Such a study should prove valuable for a number of reasons: the number of theoretical plates of a column is a function of the

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probe compound that is used as the basis for its calculation; the efficiency specifications given to open tubular columns by vendors are relative values unless they are specified at the mobile phase optimum velocity; and to provide maximum efficiency for separating a multicomponent mix of analytes, a narrow range of velocities near the optimum linear velocity may be preferred.

The effect of mixtures of H₂ with He and N₂ on the theoretical efficiency of gas-phase open-tubular column separations is reported here. Three areas were investigated: (a) how does the addition of H₂ to He affect the relationship between minimum plate height and average linear velocity, (b) is it possible to obtain significant performance improvement at high linear velocities from helium modified with various amounts of H₂, and (c) does the same situation apply for varying compositions of N₂ and H₂?

Experimental

The studies were performed with a Hewlett-Packard (Wilmington, DE) 5890 series II GC equipped with a 7673 autosampler and an HP-5 fused-silica open-tubular column (25 m × 0.32-mm i.d., 1.05-μm film thickness). The injector was heated to 220°C, and the split ratio was set at 100:1 for each injection. The column head pressure was varied from 4 to 35 psig to provide a sequence of increasing mobile phase densities. The column oven temperature was maintained at 100°C for the duration of each run. All samples were detected by flame ionization, and the detector was maintained at 220°C. Methane was used to determine the mobile phase linear velocity as the column head pressure was varied. Data were collected with an HP 3392 integrator.

A Supelco (Bellefonte, PA) nonpolar isothermal test mix (500 mg/mL per component) that contained several chemical classes was analyzed in triplicate at each parameter change to generate peak area, peak height, and retention time data. The mixture contained 2-octanone, *n*-decane, 1-octanol, *n*-undecane, 2,6-dimethylphenol (DMP), 2,6-dimethylaniline (DMA), *n*-dodecane, and *n*-tridecane dissolved in methylene chloride. Retention fac-

tors for the analytes ranged from 3 to 9 (Figure 1).

The properties of the mobile phase were varied by using H₂, He, N₂, and two mixtures each of helium and hydrogen (60:40 and 40:60) and nitrogen and hydrogen (60:40 and 40:60). The density of each gas at 4 and 35 psi was calculated from the ideal gas law.

The study was conducted by varying the linear velocity of each mobile phase by changing the inlet pressure, measuring the retention time of an unretained compound at each pressure, running the probe mix in triplicate under each new set of conditions, and calculating the number of theoretical plates, height equivalent of a theoretical plate (HETP), and the retention or capacity factor from the averaged experimental data for each analyte. The total number of theoretical plates (*N*) for each analyte in each run was calculated via the height/area method given by Bidlingmeyer and Warren (5) using the following formula:

$$N = \frac{2\pi(ht_R)^2}{A^2} \quad \text{Eq. 1}$$

where *h* is the integrator's measure of peak height, *t_R* is the retention time, and *A* is the integrator's measure of peak area (6). Martin and Synge first described this calculation in 1941.

Results and Discussion

Seven gases were used as experimental mobile phases. Three gases were of a single component, and four gases were binary mixtures. The gases and their density are tabulated in Table I for inlet pressures of 4 and 35 psig at 100°C. We chose to ignore the pressure and density gradients across the column in this work. The data in Table I suggest the following: (a) N₂ is 10 times more dense than H₂ and 7 times more dense than He at an inlet pressure of 4 psig, (b) mixes of N₂ and H₂ cover a larger density range (0.77–0.54 g/L) than mixes of He and H₂ (0.14–0.12 g/L), (c) the density of N₂ increases at a more rapid rate with an increase in pressure than the density of He and H₂, and (d) the viscosity of pure helium is greater than the viscosity of pure nitrogen.

On the HP-5 column, propane and *n*-butane were retained in part as evidenced by the decrease in retention time with the increase in temperature. Methane consequently proved to be the optimal compound for the calculation of linear velocity (μ). Table II gives the retention time data for methane at different GC head pressures at 100°C. In this case, retention time increased with an increase in temperature, which reflects the increase in mobile phase viscosity with a temperature increase for a nonretained analyte.

For this discussion, it is assumed that column efficiency (e.g., plate height or HETP) is described in terms of contributions to solute zone broadening by both diffusion and mass

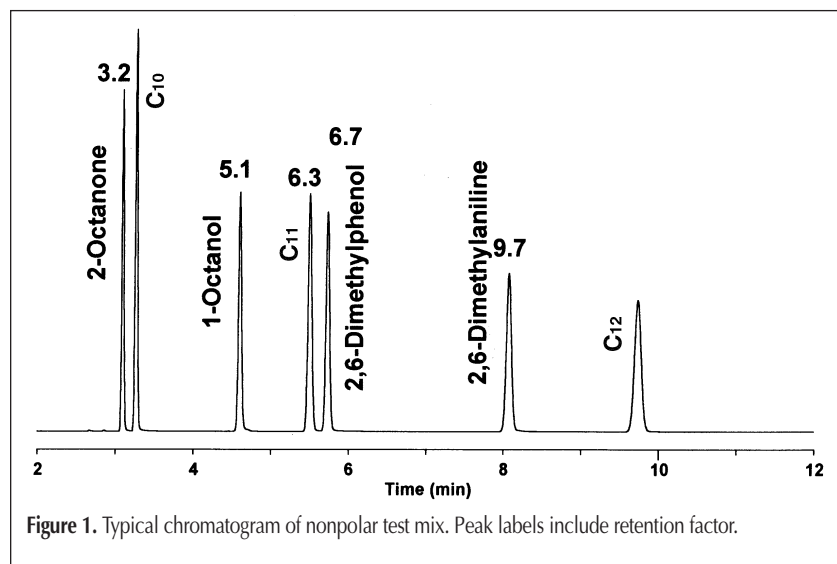


Figure 1. Typical chromatogram of nonpolar test mix. Peak labels include retention factor.

transfer in the mobile phase. The gas compressibility factor or the contribution of resistance to mass transfer in the stationary phase were not included. Because the same column at the same temperature was used for our studies, these terms were considered to account for less than 5% variation in HETP. At low linear

velocities, longitudinal diffusion determines plate height, and the radial diffusion contribution is minimal. As the linear velocity increases, longitudinal diffusion becomes limited to the point where it has little effect on plate height and elution bandwidth. More importantly, the resistance to mass transfer in the mobile phase increases linearly with linear velocity.

Plots of plate height (HETP) versus linearly velocity (μ) are termed van Deemter plots. The value for μ at which the HETP reaches its minimum value is the optimum carrier gas velocity for the specific combination of analyte, carrier gas, and temperature. At this point, the independent contributions to zone broadening from longitudinal diffusion and gas-phase mass transfer are minimized. Chromatographic theory predicts that N_2 at its optimal linear velocity will yield more theoretical plates than He and H_2 in the same column, because its minimum HETP is smaller. However, at velocities slightly above optimum, N_2 as a mobile phase becomes very inefficient. That is, the property of N_2 that limits longitudinal diffusion at low velocities severely inhibits effective and uniform mass transfer at higher velocities. Although the helium plot is intermediate between N_2 and H_2 curves, it is vastly different from the former and quite similar to the latter. The property of He and H_2 that permits significant band broadening at low velocities due to enhanced longitudinal diffusion does not strongly impair effective mass transfer at high velocities.

The effect of two mixtures of N_2 and H_2 and two mixtures of He and H_2 on the efficiency of open tubular column separations for various chemical classes is reported experimentally (Table III). The average HETP for each compound in the mixture was calculated and plotted against average linear velocity. In Figure 2, the HETP of a single probe compound (2,6-dimethyl phenol) is plotted against m for the 4 gas mixtures and for pure H_2 , He, and N_2 . At low velocities, the N_2 - H_2 mixtures produce smaller HETPs than the He- H_2 mixtures. The nitrogen component of the binary mixtures apparently limits longitudinal diffusion at low velocities. The dramatic rise in plate height caused by the N_2 - H_2 mixtures at high velocities is not surprising. The interesting point is that the HETP decreases regularly and substantially (at all linear velocities

Table I. Viscosity and Density of Gases at 100°C

Gas	Viscosity (μ poise)*	Density (4 psig)/L	Density (35 psig)/L
N_2	210	1.23	3.08
N_2 - H_2 (60:40)	195	0.77	1.94
N_2 - H_2 (40:60)	177	0.54	1.36
He	230	0.18	0.44
He- H_2 (60:40)	(160)	0.14	0.35
He- H_2 (40:60)	(142)	0.12	0.31
H_2	104	0.09	0.22

* N_2 and H_2 viscosity values from Reference 9, N_2 - H_2 binary mix viscosity values linearly interpolated from data in Reference 9, He viscosity value from reference 10, He- H_2 binary mix viscosity values estimated from Reference 11 and chromatographic data.
† Densities calculated from ideal gas law.

Table II. Retention Times of Methane at Different GC Head Pressures*

Head pressure (psi)	Retention time (min, $n = 3$)		
	Average	SD	%RSD
4	6.076	0.0113	0.185
8	2.124	0.0045	0.212
12	1.244	0.0038	0.304
15	0.996	0.0025	0.253
20	0.705	0.0010	0.142
24	0.589	0.0036	0.612
30	0.469	0.0010	0.213
35	0.399	0.0023	0.578

* Oven temperature was 100°C.
† SD, standard deviation.
‡ %RSD, percent relative standard deviation.

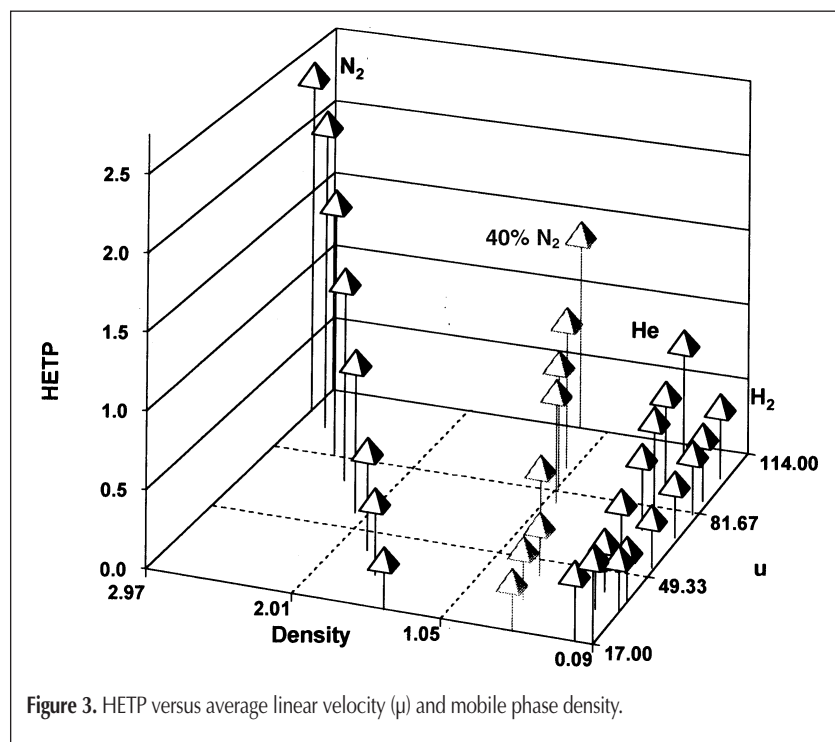
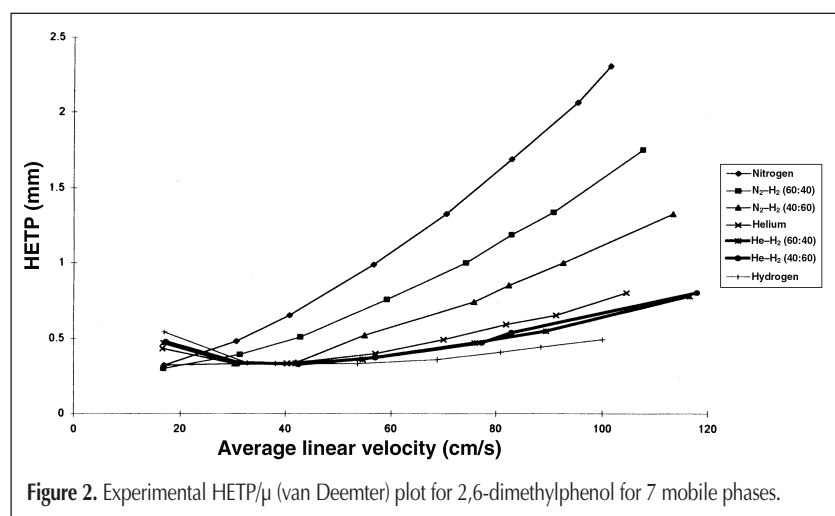
Table III. Typical Data Collected in this Study*

Mobile phase	Head pressure	CH_4 t_R (min)	Linear average velocity (cm/s)	t_{R1} (min)	t_{R2} (min)	t_{R3} (min)	Average t_R (min)											
								Peak height 1	Peak height 2	Peak height 3	Peak average height	Peak area 1	Peak area 2	Peak area 3	Peak average area	HETP (mm)		
40% H_2 -60% He	24	0.496	84.20	3.083	3.081	3.08	3.081											
40% H_2 -60% N_2	28	0.496	84.20	3.010	3.008	3.009	3.009											
60% H_2 -40% He	21	0.505	82.70	3.156	3.153	3.156	3.155											
60% H_2 -40% N_2	26	0.491	85.06	3.002	2.999	2.997	2.999											
40% H_2 -60% He								27182	26683	28129	27331	62974	62424	64882	63426			0.628
40% H_2 -60% N_2								29248	29127	29063	29146	100632	101071	100042	100581			1.457
60% H_2 -40% He								21964	22074	22348	22128	49070	48990	49457	49172			0.549
60% H_2 -40% N_2								26956	26709	26909	26858	79995	79525	79586	79702			1.085

* Compound is 1-octanol.

greater than the optimum) as the proportion of H₂ in the carrier gas increases. It appears that an increase in the concentration of H₂ leads to more efficient mass transfer in the mobile phase. The slopes of the curves also become more hydrogen-like as the H₂ concentration of the mobile phase increases.

The He-H₂ mixtures are also intermediate between the pure helium and hydrogen curves, but their range of HETP values is much narrower than that of the N₂-H₂ mixes. Increasing the concentration of hydrogen improves the efficiency of the gas as a mobile phase at high linear velocities and decreases its efficiency at suboptimum velocities. The hydrogen component clearly improves the mass transfer processes in the binary mixes at high velocities and permits greater longitudinal diffusion at velocities below the optimum. The slopes of the HETP/ μ curves of the He-H₂ mixtures become more hydrogen-like as the concentration of hydrogen increases.



Obviously, those gas properties which directly affect the slopes of the van Deemter curves are intermediate for the mixes. As stated previously, the wide spread in the N₂ mix curves and the narrow range of the He mix curves reflect the gas density data (i.e., large variation in the density of N₂-H₂ mixtures but small differences in the density of He-H₂ mixtures). Although the viscosity of the mobile phases change, it cannot be correlated with the van Deemter curves and slopes. Because the study was performed isothermally, one has to consider only density changes increasing pressure. Because higher linear velocities were attained by increasing the inlet pressure, the density of each gas was raised mechanically along the x -axis with a concomitant increase in HETP. The conclusion is that the mobile phase density increase apparently accounts for much of the loss in efficiency.

The densities of the N₂-H₂ mixtures are much greater and more widely spread than the densities of He, H₂, and the He-H₂ mixtures. The slopes and relative magnitudes of the HETP/ μ curves at high linear velocities appear to reflect these density differences among the pure and binary mixes of the gases. In addition, the similarity of the HETP/ μ curves for helium and hydrogen is commensurate with the fact that their densities are different by a factor of 2, in contrast with the 7- to 10-fold difference between their densities and that of nitrogen. Thus, the steep slopes and high HETP values of N₂ and the N₂-H₂ mixes with respect to the shallow slopes and low HETP values of He, H, and the He-H₂ mixtures appear to be based on the gas density values.

Does the gas density impact the HETP? This is a question that will stimulate a resounding chorus of "no" from the theoreticians. Gas density does not appear explicitly in the Golay equation or its derivatives. However, there is evidence in Figure 2 that suggests density does have an effect. The density of the gases in Figure 2 changes on both the x - and y -axis; along the y -axis because of the decreasing concentration of hydrogen in the mixes, and on the x -axis because the inlet pressure of each gas was raised mechanically to obtain higher linear velocities. Although increasing linear velocity can account for the loss of efficiency along the x -axis, only increasing gas density can account for the loss of efficiency along the y -axis, holding the linear velocity constant.

Is there any theoretical basis for considering the effect of the gas density on HETP? Although there is no explicit gas density variable in the Golay equation (1), the binary diffusion coefficient (D_m), which describes the diffusivity of a specific solute in a specific mobile phase, can be related to density.

The Schettler-Fuller-Giddings (2) empirical equation for estimating D_m shows that D_m is a function of gas density and the molecular weight and volume of the diffusing molecules (8).

$$D_m = (1.00 \times 10^{-3}) \left[\frac{T^{1.75}}{P} \right] \left\{ \frac{[(1/M_A) + (1/M_B)]^{1/2}}{[V_A^{1/3} + V_B^{1/3}]^2} \right\} \quad \text{Eq. 2}$$

where T is the temperature (K), P is the pressure (atm), M_A and M_B are molecular weights (g/mole) of solute and carrier gas, and V_A and V_B are "special atomic volume increments".

D_m is inversely proportional to the pressure at low to medium pressures. Additionally, density (ρ) (from the ideal gas law) is directly proportional to pressure. Thus, D_m is inversely related to a density function $P = \rho RT$, and $D_m \propto (\rho RT)^{-1}$.

We can relate HETP to density by substituting $(\rho RT)^{-1}$ for D_m in the second term of the Golay equation and inverting the reciprocal term.

$$\text{HETP} \propto \left[\frac{\rho RT \bar{u} r^2 (1 + 6k + 11k^2)}{(24)(1 + k^2)} \right] \quad \text{Eq. 3}$$

It was concluded that HETP is indeed directly proportional via the binary diffusion coefficient to the density of the mobile phase at high linear velocities. Clearly, holding the linear velocity con-

stant and varying the gas density will change the plate height. This suggests the possibility of deriving an alternative expression for plate height, relating it to gas density. Furthermore, it raises the question concerning the impact of the localized density increase at the inlet end of the column on the plate height.

Figure 3 plots HETP versus both the average linear velocity and density of the gas mixture mobile phase. The plot shows explicitly the impact of gas density at low and high mobile phase linear velocities. The plate height at low velocities decreases as density increases, whereas at high velocities, HETP increases sharply with an increase in density. The shallow curves of He and H_2 with respect to N_2 are clearly seen to be a function of the gas densities.

The impact of the molecular volume of the probes on HETP is indicated in Figures 4 and 5, where the HETP values of the probe compounds are plotted against the linear velocity of the three straight gases and a single mixed mobile phase (e.g., 40% He mix). Not all mixture components are separated with equal efficiency in the same system, even under isothermal conditions, unless the linear velocity is controlled at the optimum. At high linear velocities, aromatic probes experience less band broadening than the acyclic hydrocarbon derivatives. In other words, aromatics produce lower plate heights at linear velocities greater than the optimum, but the same analytes yield higher HETP at suboptimum velocities. The reason for this behavior cannot be related to functional groups, because our mixture contained both aromatic and acyclic alcohols. It also cannot be attributed to differences in molecular weight or carbon number, because all components in both groups are similar. It also cannot be retention factor differences, because undecane and DMP, for example, have almost identical retention factors.

The only variables in the Golay Equation (1) that are specific to the analytes are the retention factor and the binary diffusion coefficient D_m . The larger the D_m value, the smaller the contribution of this term to the overall HETP. Holding all variables except D_m constant, analytes with varying D_m will thus lead to different efficiencies. The Schettler-Fuller-Giddings Equation (2) shows that D_m is also dependent on the molecular weight and volume of the analyte molecule. The reciprocal of the molecular weight of a large organic molecule is very small with respect to the inverse molecular weight of the carrier gas, so it will have no effect on D_m . However, it was observed that the molecular volume term will be significant and will inversely affect D_m . The smaller the molecule, regardless of molecular weight, the higher the D_m . Thus, the more compact aromatic molecules (DMP and DMA) will have larger D_m values than undecane, 1-octanol, and 2-octanone. Although the aliphatic analytes have molecular weights and carbon numbers similar to the aromatic analytes, the former have greater molar volumes.

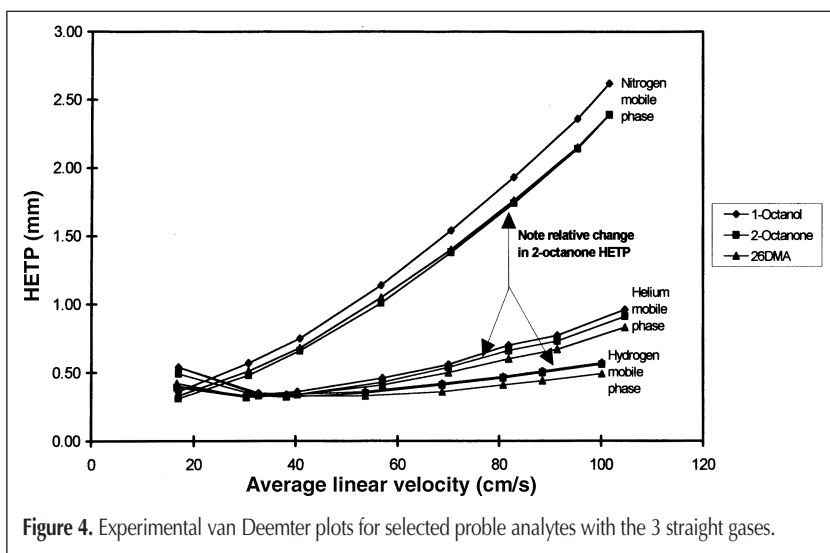


Figure 4. Experimental van Deemter plots for selected probe analytes with the 3 straight gases.

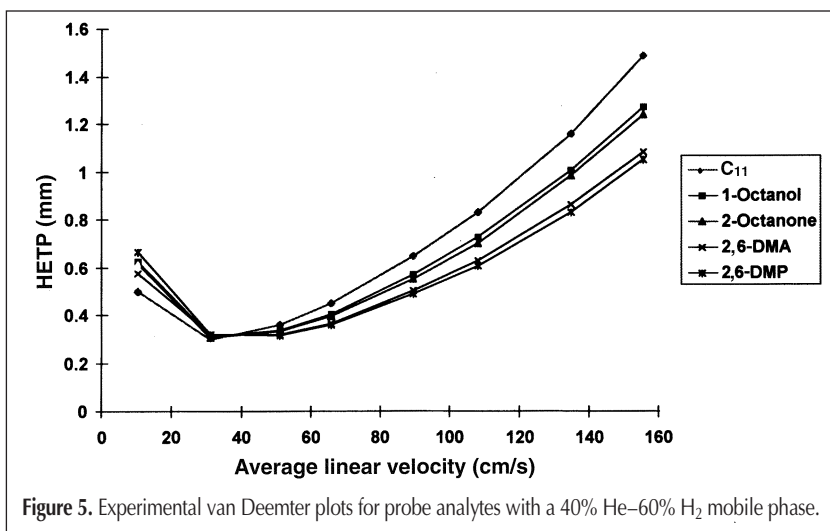


Figure 5. Experimental van Deemter plots for probe analytes with a 40% He-60% H_2 mobile phase.

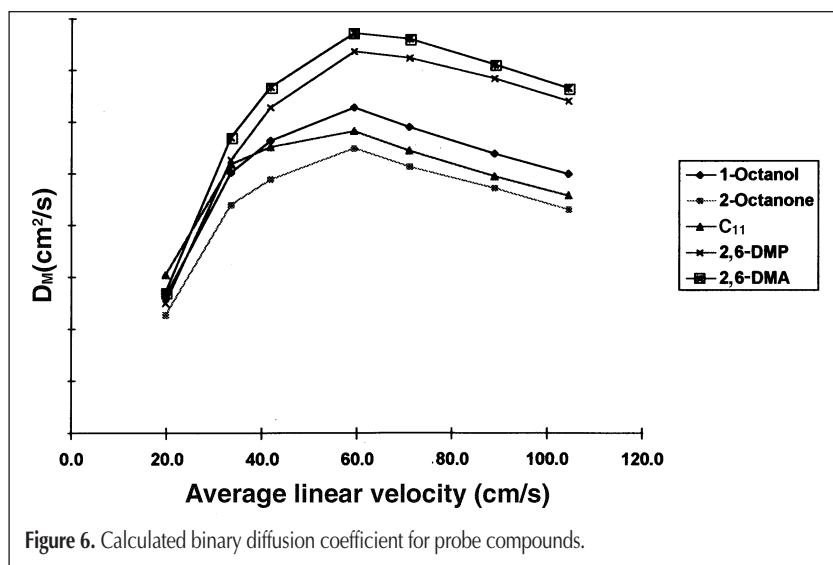


Figure 6. Calculated binary diffusion coefficient for probe compounds.

The net result is that under all conditions of gas density, the aromatics will yield better efficiency (e.g., lower HETP) than linear acyclics. For example, benzene exhibits a higher D_m in H_2 than He or N_2 , whereas D_m is smaller for C_3 and larger saturated acyclic molecules. By setting the second term in the Golay Equation equal to the HETP and ignoring all contributions at high linear velocities from longitudinal diffusion, D_m can be calculated from the experimental data. The results are plotted in Figure 6, where it can be seen that the smaller, more compact aromatics have larger D_m values at all linear velocities greater than 40 cm/s. These results therefore suggest that a chromatographer can tailor his analytical system for specific analytes in terms of their molecular volume to improve analytical performance.

Conclusion

In conclusion, we report that HETP is a function of mobile phase density, solute molecular volume, and mobile phase linear velocity. The HETP of solutes in binary mobile phases falls between the pure gases at higher linear velocities. The 40% N_2 binary mobile phase with H_2 was most effective for low- to high-linear-velocity separations. The van Deemter plot (for this mixture) shows that there will be a relatively "flat" HETP across the linear velocity range of 20–40 cm/s. This happens to be the typ-

ical operating range for capillary GC mobile phase velocities. An analyst who does not use H_2 in the mobile phase and does not have flow control will, therefore, experience a 40% drop in linear velocity across a temperature program ramp. This change in linear velocity would mean a sliding HETP (or efficiency) value across a range of eluting solutes. In this case, the later eluting solutes would be separated with a different HETP than the early eluting solutes. The constant HETP maintained by the 40% N_2 –60% H_2 mix across the 20–40 cm/s linear velocity range should yield the same efficiency throughout a temperature programmed analysis when the mobile phase is controlled at constant pressure.

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