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Gas Chromatography Evaluation of HELP

Purpose

A sample of butanol mixes in ethanol was used to evaluate HETP, height equivalent to a theoretical plate for a chromatographic column. Under three different column pressures, chromatograms were obtained and used to calculate HETP, van Deemter Equation coefficients, and resolution.

Data and Procedure

The apparatus used were HP 6890N GC w/ flame ionization detector and 1500 cm x 0.2 mm i.d. DB-1 capillary column. The analyte was prepared as 0.01% isobutanol and 0.01% butanol mix in ethanol (V/V). We injected 1 μL mix into the gas chromatography injection point for each run, and obtained chromatograms of the analyte under three different column pressures of 5.00 psi, 7.50 psi, and 10.00 psi. In each injection, conditions other than column pressures and corresponding flow rate remained the same. The retention time (t_r) and peak width (W_b) of each peak were reported and HETP and plate number (N) were analyzed as shown in Table 1.

Pressure (psi)	Flow rate (cm/s)	2-butanol			1-butanol			N_{avg}	HETP (cm)
		t_r (min)	W_b (min)	N	t_r (min)	W_b (min)	N		
5.00	22	2.352	0.0223	177985.6	2.667	0.0306	121541.1	149763.4	0.0100
7.50	33	1.646	0.0145	206178.6	1.856	0.0198	140587.1	173382.9	0.0087
10.00	43	1.159	0.0103	202587.4	1.318	0.0140	141806.0	172196.7	0.0087

Table 1: Chromatogram data for 3 runs

Calculations and Results

(a) Evaluations of N and HETP

The plate number (N) of a column is determined by $N = \frac{16(t_r)^2}{(W_b)^2}$ where t_r is the retention time and W_b is the base peak width. Under the flow rate of 22 cm/s, 2-butanol gives t_r = 2.352 min and W_b = 0.0223 min, and thus, the plate number is determined by $N = \frac{16(t_r)^2}{(W_b)^2} = (16) (2.352)^2 (0.0223)^2 = 177985.6$. The plate number of 1-butanol is calculated as 121541.1, and thus it gives us an average plate number N_{avg} = 149763.4.

HETP can be then determined by HETP = $\frac{L}{N}$, where L is the column length (1500 cm) and N is the number of theoretical plates. Under 5.00 psi, HETP (average) = L/N_{avg} = 1500/149763.4 = 0.0100 cm.

(b) Evaluations of A, B, and C

By applying van Deemter Equation, which states that $HETP = A + \frac{B}{\mu} + C\mu$, where μ is the flow rate in cm/s, we have 3 equations with 3 unknowns and therefore we can evaluate Eddy diffusions (A), longitudinal diffusion (B), and mass-transfer equilibria (C).

$$HETP_{22} = 0.0100 = A + \frac{B}{22} + C(22)$$

$$HETP_{33} = 0.0087 = A + \frac{B}{33} + C(33)$$

$$HETP_{43} = 0.0087 = A + \frac{B}{43} + C(43)$$

Using the method of determinants, where $D = \begin{bmatrix} 1 & \frac{1}{22} & 22 \\ 1 & \frac{1}{33} & 33 \\ 1 & \frac{1}{43} & 43 \end{bmatrix} = -0.07$, we have the parameters as

$$A = \frac{\begin{bmatrix} 0.0100 & \frac{1}{22} & 22 \\ 0.0087 & \frac{1}{33} & 33 \\ 0.0087 & \frac{1}{43} & 43 \end{bmatrix}}{D} = -0.00190 \qquad B = \frac{\begin{bmatrix} 1 & 0.0100 & 22 \\ 1 & 0.0087 & 33 \\ 1 & 0.0087 & 43 \end{bmatrix}}{D} = 0.19325$$

$$C = \frac{\begin{bmatrix} 1 & \frac{1}{22} & 0.0100 \\ 1 & \frac{1}{33} & 0.0087 \\ 1 & \frac{1}{43} & 0.0087 \end{bmatrix}}{D} = 0.00014$$

Therefore, van Deemter Equation for this experiment is $HETP = -0.00190 + \frac{0.19325}{\mu} + 0.00014\mu$.

(c) Plot of HETP vs. flow rate
By applying different values of flow rate to the equation, HETP has the following values as shown in Table 2. The HETP vs. flow rate graph is shown in Plot 1.

Flow rate (cm/s)	HETP (cm)
0.10	1.931
0.25	0.771
0.50	0.385
1.00	0.191
2.00	0.095
3.00	0.063
4.00	0.047
5.00	0.037
6.00	0.031
7.00	0.027
8.00	0.023
9.00	0.021
10.00	0.019

Table 2: HETP values
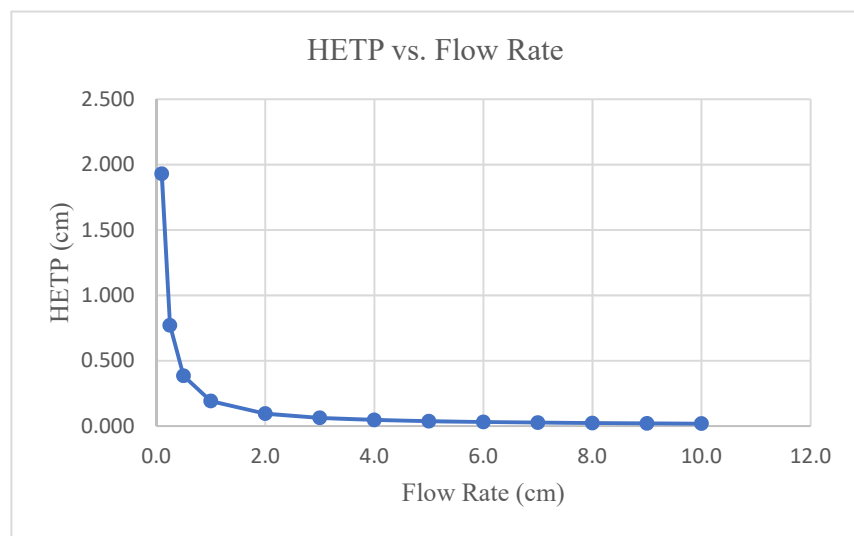
Plot 1: HETP vs. Flow Rate

From the plot, we can see the optimum flow rate (local minimum) occurs when the flow rate $\mu = 10.0\ cm/s$. However, this point may not be global minimum because our experimental flow rates have lower HETP. By taking the derivatives (HETP'=0), we find the global minimum HETP occurs at $\mu = 36.9\ cm/s$ (more details in Question section).

(d) Evaluation of resolution (R)

Resolution is defined as $R = \frac{2(t_2 - t_1)}{W_1 + W_2}$ where t_1 and t_2 are retention times of two peaks, and W_1 and W_2 are the peak widths. For flow rate of 22 cm/s, we have $t_1 = 2.352$ min and $t_2 = 2.667$ min, $W_1 = 0.0223$ min and $W_2 = 0.0306$ min. Thus, $R_{22} = \frac{2(t_2 - t_1)}{W_1 + W_2} = \frac{2(2.667 - 2.352)}{0.0223 + 0.0306} = 11.9$. Similarly, $R_{33} = 12.2$, $R_{43} = 13.1$.

Discussion and Conclusion

Under 5.00 psi, 7.50 psi, and 10.00 psi, we separated sample alcohol mix and determined 3 chromatograms for GC. We found the van Deemter Equation in this experiment satifies $\text{HETP} = -0.00190 + \frac{0.19325}{\mu} + 0.00014\mu$, and the system achieved good resolution and separation. The overall optimum flow rate does not fit in the flow rate range from 0.1 cm/s to 10.0 cm/s as expected, but occurs at $\mu = 36.9\ cm/s$. The major source of error is the poor injection of the sample that led to poor injection reproducibility and some sample loss, but this does not greatly affect the precision and accuracy of the data.

Question

$$HETP = A + \frac{B}{\mu} + C\mu$$

Taking the derivative: $HETP' = -\frac{B}{\mu^2} + C = 0$. Thus,

$$\frac{B}{\mu^2} = C \text{ or, } \frac{B}{C} = \mu^2$$

Therefore, optimum rate occurs at $\mu = \sqrt{\frac{B}{C}}$ $(\mu > 0)$.

In this lab, $\text{HETP} = -0.00190 + \frac{0.19325}{\mu} + 0.00014\mu$, $B = 0.19325$ and $C = 0.00014$. Thus,

Optimum rate occurs at $\mu = \sqrt{\frac{B}{C}} = \sqrt{\frac{0.19325}{0.00014}} = 36.87\ \frac{cm}{s}$.