

Passage III (Questions 13 - 18)

Thin layer chromatography (TLC) helps to identify the quantity and the nature of a product mixture in terms of components and residual starting material. It can be used to determine the best solvent system for carrying out column chromatography. The optimal column length and degree of separation can both be extrapolated from the TLC results.

A series of unknown compounds is studied using TLC on silica gel plates. The R_f values for each of eight compounds in three unique solvents are listed in Table 1. The R_f value (ratio of the fronts) is the distance traveled by the material (spot) divided by the distance traveled by the solvent front. As the R_f value increases, the solubility of the compound in the solvent is said to be increasing.

Compound	<i>n</i> -Hexane	Et ₂ O	CH ₂ Cl ₂ /MeOH
Q	0.19	0.27	0.51
R	0.10	0.24	0.40
S	0.49	0.58	0.71
T	0.06	0.19	0.38
V	0.33	0.39	0.53
X	0.13	0.23	0.44
Y	0.37	0.46	0.59
Z	0.46	0.49	0.66

Table 1

The data in Table 1 can be used to approximate the relative solubilities of each compound in the various solvents. Each experiment is repeated several times to verify the R_f values. The values in the table represent the average results of the trials.

13. Which column chromatography separation would require the longest column?
- Compound Q from Compound V, using diethyl ether.
 - Compound T from Compound Y, using diethyl ether.
 - Compound R from Compound S, using *n*-hexane.
 - Compound X from Compound Z, using *n*-hexane.
14. The R_f value can be used to estimate all of the following EXCEPT:
- the solubility of a solute in a solvent.
 - the elution time of a solute from a column in a chromatography experiment.
 - the nature of intermolecular forces between a solute and solvent.
 - the reactivity of a solute in different solvents.
15. If Compound X is polar, what else must be TRUE?
- Compound Q is nonpolar.
 - Methylene chloride and methanol are nonpolar.
 - Compound Z is polar.
 - Compound T is polar.
16. To separate a mixture of Compounds X, Y, and Z using column chromatography, it would be BEST to:
- use *n*-hexane, where Compound X elutes from the column first, followed by Compound Y, then Compound Z.
 - use *n*-hexane, where Compound Z elutes from the column first, followed by Compound Y, then Compound X.
 - use methylene chloride mixed with methanol, where Compound X elutes from the column first, followed by Compound Y, then Compound Z.
 - use methylene chloride mixed with methanol, where Compound Z elutes from the column first, followed by Compound Y, then Compound X.
17. A large R_f value can be attributed to what factors?
- High affinity of the solute for the TLC plate.
 - Low affinity of the solute for the solvent.
 - High heat of solvation ($\Delta H_{\text{solvation}}$) between the solute and solvent.
 - High heat of coordination ($\Delta H_{\text{binding}}$) between the solute and silica gel.
18. The BEST separation of Compounds T and X is found using column chromatography with:
- pure *n*-hexane.
 - pure diethyl ether.
 - a mixture of *n*-hexane and diethyl ether.
 - a mixture of methylene chloride and methanol.

13. **Choice A is the best answer.** A long column is chosen when compounds require an ample distance over which to separate. This means that a long column is employed when the two solutes do not separate readily. This occurs when the two species have similar R_f values. To answer this question, you are looking for an R_f ratio that is closest to 1.0, rather than just large R_f values. In diethyl ether, Compound Q has an R_f value of 0.27 and Compound V has an R_f value of 0.46. The two values are very small and produce a ratio less than 2 : 1 for choice A. In diethyl ether, Compound T has an R_f value of 0.19 and Compound Y has an R_f value of 0.46. The two values produce a ratio greater than 2 : 1. The large ratio of the two R_f values leads allows us to use a short column, because the two compounds will separate quickly. This eliminates choice B. In *n*-hexane, Compound R has an R_f value of 0.10 and Compound S has an R_f value of 0.49. The two values produce a ratio of of roughly 5 : 1. The R_f values are extremely different, so a very short column could be employed. This eliminates choice C. In *n*-hexane, Compound X has an R_f value of 0.13 and Compound Z has an R_f value of 0.46. The two values produce a ratio greater than 3 : 1. This ratio is not the smallest of the answer choices, so choice D is eliminated. Only in choice A is the ratio less than 2 : 1, so that combination would require the longest column for adequate separation.
14. **Choice D is the best answer.** The more soluble a solute in a solvent, the greater its R_f value, so R_f values can approximate solubility, making choice A valid. The R_f value measures the migration of solute in a solvent against resistance from the gel on the plate. This is exactly what transpires during column chromatography (but with the aid of gravity), so choice B is valid. Again, the more soluble the solute in a solvent, the greater the R_f value, so R_f values can be used to approximate the nature of intermolecular interactions, making choice C valid. Finally, R_f values measure affinities between compounds, not their reactivity. Choice D is invalid, and thus the best answer.
15. **Choice D is the best answer.** Compound X and Compound Q show approximately equal R_f values in each of the three solvents, so the two compounds must have similar solubility properties. If Compound X is polar, then Compound Q must also be polar, eliminating choice A. Compound X travels the farthest in the methylene chloride/methanol mixture. This means that if Compound X is polar, then the methylene chloride/methanol mixture is also polar. This eliminates choice B. Compound X and Compound Z show different R_f values in each of the three solvents, so the two compounds must have different solubility properties. If Compound X is polar, then Compound Z must be nonpolar, eliminating choice C. Compound X and Compound T show similar R_f values in each of the three solvents, so the two compounds must have similar properties (in terms of solubility and miscibility). If Compound X is polar, then Compound T must also be polar, making choice D the best answer.
16. **Choice B is the best answer.** According to the R_f values in Table 1, it is easy to separate Compound X from Compounds Y and Z. The difficult part involves separating Compound Y and Compound Z. In all solvents, Compound X has the lowest R_f value, and therefore migrates slowest and comes off of the column last. This eliminates choices A and C. We must now compare the R_f values for Compounds Y and Z. In *n*-hexane, the R_f values are 0.46 and 0.37. In the methylene chloride with methanol mixture, the R_f values are 0.66 and 0.59. The R_f values differ more in *n*-hexane than they do in the methylene chloride with methanol mixture, so the better separation is observed in *n*-hexane. This makes choice B, the best answer.
17. **Choice C is the best answer.** A large R_f value is associated with solutes that migrate a great distance. Thus, a large R_f value is associated with solutes that have a high affinity for the mobile phase (solvent) and low affinity for the stationery phase (plate). This eliminates choices A and B. High affinity for the mobile phase involves a favorable interaction between the solvent and solute, so there should be a high heat of solvation between the two compounds. This makes choice C the best answer. A high heat of coordination between the solute and silica gel implies that there is a high affinity for the plate, which would hinder migration and lower R_f values. Because the R_f value is being maximized, not minimized, choice D is eliminated.
18. **Choice A is the best answer.** The best separation of the two compounds will occur in the solvent that offers the greatest ratio of (not difference in) the R_f values. For instance, R_f values of 0.10 and 0.05 offer great separation, because the one value is twice the other. On the other hand, R_f values of 0.60 and 0.70, although they differ by a great deal on a linear scale, differ by less than 20% (0.70 divided by 0.60 is 1.167). The separation is not that good. In *n*-hexane, Compound T has an R_f value of 0.06, while Compound X has an R_f value of 0.13. The ratio of 0.13 to 0.06 is greater than 2 : 1. In diethyl ether, Compound T has an R_f value of 0.19, while Compound X has an R_f value of 0.23. The ratio of 0.23 to 0.19 is only slightly greater than 1 : 1, which is so small that choices B and C can be eliminated. In a mixture of methylene chloride and methanol, Compound T has an R_f value of 0.38, while Compound X has an R_f value of 0.44. The ratio of 0.44 to 0.38 is only slightly greater than 1 : 1, which is so small that choice D can be eliminated.. Pure *n*-hexane offers the largest ratio, so choice A is the best answer.