An Experiment to Demonstrate the Effect of pH on Partition Coefficients in Liquid–Liquid Extraction

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Liquid–liquid extraction remains an important separation technique for both preparative and analytical problems. It can be used to

- clean samples by separating desired components from contaminants
- transfer solutes from their original solvent to one that gives better results with a certain instrument
- concentrate dilute solutes

Liquid–liquid extraction is justifiably prominent in instructional labs, and excellent experiments have been developed to demonstrate it (*1, 2*).

Extraction typically involves allowing a mixture's components to partition between aqueous and nonpolar organic solutions. Extraction efficiency can be improved by carrying out multiple extractions (*3*) or by manipulating the partition coefficient. The pH of the aqueous phase can have an enormous effect on the partition coefficients of acidic and basic solutes. Adjusting the pH is a crucial part of the commonly used experiment to extract caffeine from tea (*1*) and indeed of any extraction involving weak acids or bases.

Unfortunately, many students do not appreciate the effect that pH can have on extraction and are unable to suggest appropriate buffering for a given extraction problem. Often they cannot even satisfactorily explain why they have added an acid or base to the aqueous phase before performing an extraction.

The experiment described here demonstrates the effect of pH on the partition coefficient of acidic, basic, and neutral species in liquid–liquid extraction. It also uses analytical gas chromatography and can be used to introduce internal standard quantitation. It can be adapted for either organic or analytical classes and can be completed in a single 3-h laboratory period.

Experimental

- ***Caution***: Eye protection, gloves, and a fume hood should be used. This experiment uses organic solutes, phosphoric acid, and concentrated base. Phosphoric acid is readily absorbed by the skin. Concentrated bases are extremely caustic and pose a particular danger to the eyes.

Reagents and Apparatus

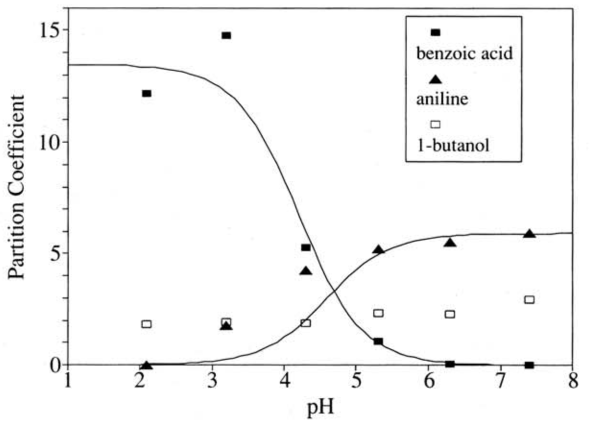
Students are given a standard diethyl ether solution containing benzoic acid, aniline, and an alcohol (butanol or pentanol) at concentrations of about 1 g/L. Optionally, *p*-xylene may be included in the ether solution as an internal standard. The aqueous phase is 0.1 M phosphoric and acetic acids. A separatory funnel, magnetic stirrer, pH meter, and concentrated base solution are also provided.

Procedure

An amount of aqueous buffer sufficient to complete the experiment is put in a beaker or Erlenmeyer flask, and its pH is adjusted by adding concentrated base with stirring. As the buffer's pH increases to predetermined values, 10-mL aliquots are withdrawn and used to extract 10-mL aliquots of the standard ether solution. Extractions should be carried out from the initial pH to at least pH 7. Another 10-mL aliquot of standard ether solution may be extracted with distilled water to provide comparison. The unextracted standard ether solution and all extracted ether solutions are analyzed by gas chromatography.

Equipment for Analysis

The data presented here were obtained by GC/MS using a Hewlett–Packard 5890 Series II gas chromatograph with a 7673 autoinjector and 5989A mass spectrometer with



Typical experimental and theoretical partition coefficients

split injection onto a fused-silica column (12-m × 0.2-mm, 0.33-µm methyl silicone gum) (Hewlett–Packard). This experiment does not require such expensive equipment; it can be done effectively with any capillary or packed-column GC equipped with a nonspecific detector such as a TCD or FID.

Discussion

Benzoic acid and aniline were selected because they are generally available and have comparable pK_a values: 4.20 for benzoic acid and 4.58 for anilinium ion. Butanol and pentanol were found to be suitable un-ionizable solutes; isopropanol and 1-hexanol were difficult to chromatographically resolve from ether and *p*-xylene, respectively.

The concentration of the extracted ether solutions can be obtained from a one-point calibration based on the peak areas (or heights) obtained with the unextracted standard ether solution. Alternatively, internal standard calibration can be used. This is advisable because imprecision can result in obtaining peak areas for extracted solutions greater than those for the unextracted solution.

Internal Standard Calibration

Internal standard calibration reduces the error caused by evaporation of the solvent and by injection technique, which can be substantial for manual injection by inexperienced students. It is widely used for gas chromatographic analysis. Response factors R_f's for each solute may be calculated from the concentrations C and peak areas A for the unextracted standard ether solution.

$$\frac{C_{\text{solute}}}{C_{\text{standard}}} = R_{\text{f}} \frac{A_{\text{solute}}}{A_{\text{standard}}} \tag{1}$$

The concentrations of solutes in extracted ether solutions may be obtained by solving eq 1 for C_{solute}, with C_{standard} assumed to be constant. The internal standard is added by the instructor before extraction, so it must not be extractable. Toluene, *p*-xylene, naphthalene, anthracene, and 9-methylanthracene were tested for use as internal standards; *p*-xylene was found to be best.

Calculating the Partition Coefficient

Because the volumes of the aqueous and ether solutions are identical and assumed to be unchanged by the extraction, the aqueous concentration is simply the difference between the extracted and unextracted concentrations. From these concentrations, the partition coefficient K_{P} can be calculated.

$$K_{\text{P}} = \frac{C_{\text{ether}}}{C_{\text{aqueous}}} = \frac{C_{\text{ether}}}{C_{\text{unextracted}} - C_{\text{ether}}} \tag{2}$$

Because the ionized forms of acidic or basic solutes are more hydrophilic than the un-ionized forms, acids are expected to have lower partition coefficients at high pH, and bases are expected to have lower partition coefficients at low pH. The partition coefficients of solutes that cannot be ionized in aqueous solution (e.g., alcohols) are unaffected by pH.

A rule of thumb states that an acidic solute is essentially completely ionized at a pH that is 2 units greater than its pK_a and almost completely un-ionized at a pH that is 2 units less than its pK_a. Basic solutes show the opposite behavior. The ionized and un-ionized forms have different partition coefficients, which should be equal to those observed at the extremes of the experimental pH range.

Predicting the Partition Coefficient and Producing a Theoretical Plot

The partition coefficient observed at a pH near a solute's pK_a can be predicted from the values of the partition coefficients of its ionized and un-ionized forms and the fraction of the solute that is un-ionized, α.

$$K_{\text{P}} = \alpha K_{\text{P, un-ionized}} + (1 - \alpha) K_{\text{P, ionized}} \tag{3}$$

Equations to describe the effect of pH on α may be derived from the expression for the acid ionization constant. These will suffer from activity effects but are qualitatively instructive. Equation 5 uses the ionization constant for the conjugate acid.

$$\alpha_{\text{acid}} = \frac{[\text{H}^+]}{[\text{H}^+] + K_{\text{a}}} \tag{4}$$

$$\alpha_{\text{base}} = \frac{K_{\text{a}}}{[\text{H}^+] + K_{\text{a}}} \tag{5}$$

Equations 3–5 can be combined to produce a theoretical plot of partition coefficient vs. pH for acidic or basic solutes based on observed high-pH and low-pH partition coefficients and theoretically calculated degrees of ionization. This is a good exercise for analytical chemistry students because it develops spreadsheet skills and reinforces previously learned material about weak acid–base equilibria. Typical experimental results and the resulting theoretical curves are plotted in the figure.

Conclusion

This experiment was carried out by three pairs of students in a course in analytical chemistry for non-chemistry majors. They performed extractions at intervals of 1 pH unit from pH 1.5 to 7.5, calculated experimental partition coefficients, and prepared theoretical curves with satisfactory results. A month later, the students uniformly gave good answers to a test question designed to probe their understanding of the effect of pH on liquid–liquid extraction.

Literature Cited

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