Studying Acid–Base Equilibria in Two-Phase Solvent Media

Analyzing Results Using Aqueous Surfactant Solutions with Organic Solvents in the Titration of Analytes with Low Solubilities and Low Dissociation Constants

Sheryl A. Tucker, Vicki L. Amszi, and William E. Acree, Jr.¹

University of North Texas, Denton, Texas 76203–5068

Acid–base titrations provide a very convenient experimental means for determining equivalent weights, percent compositions, and solution concentrations of unknown acid–base samples. Over the past few years many experimental titration methods have appeared in *this Journal* (1–7) and in standard laboratory manuals (8–12) for use in either general chemistry or quantitative analysis.

Titration Weak Acids

To our knowledge, none of these methods are applicable to acids having dissociation constants of 10^{-10} or less. Such acids are generally too weak to be titrated in aqueous media. Analytical textbooks (13, 14) approach the problem from the standpoint of selecting a nonaqueous solvent, listing pyridine, *t*-butylamine, dimethylformamide, and ethylene diamine as possibilities for very weak acids. Little attention is given to the experimental difficulties that may be encountered using glass pH electrodes to monitor acid–base titrations in nonaqueous media.

Titrations in Aqueous–Organic Two-Phase Systems

Aqueous–organic two-phase systems (15–19) can also serve as solvent media for acid–base titrations involving compounds or titration products with limited aqueous solubility, or for analytes that are too weakly acidic or basic in aqueous solution. Qualitatively, the effect of the additional organic phase can be explained as follows.

Titration an Ionic Acid

The acid (a trialkylammonium ion is assumed in the present case) partially dissociates in the aqueous phase to give the hydrogen ion and amine as products.

Activity coefficients are ignored. Equilibrium is “temporarily” established so as to obey the mathematical constraint imposed by K_a . The uncharged, neutral trialkylamine molecule then partitions into the organic phase, thus reducing the R_3N concentration in the aqueous phase.

Le Chatelier’s principle states that the system must compensate for the disturbance by shifting the equilibrium further to the right-hand side. More acid dissociates, and the hydrogen-ion concentration increases. The trialkylammonium ion thus behaves as a stronger acid.

Titration a Molecular Acid

Depending upon the actual numerical values of K_a and K_p , it may be possible to titrate R_3NH^+ to a sharp endpoint by measuring the pH of the aqueous phase with a glass electrode. An entirely opposite effect would be observed if the acid were molecular in nature.

Then partitioning of HA into the organic phase reduces the H^+ concentration, giving the appearance that HA is a much weaker acid.

Constructing a Titration Curve

At this point in time, two choices are available: be content with a qualitative explanation of how an organic phase affects the acid–base equilibria in the aqueous phase (general chemistry), or try to construct a titration curve of pH as a function of volume of KOH (base) added (quantitative analysis).

Deriving an Expression for $[\text{H}^+]_{\text{aq}}$

For each point on the titration curve, we can write both a charge balance equation

$$[\text{H}^+]_{\text{aq}} + [\text{K}^+]_{\text{aq}} + [\text{R}_3\text{NH}^+]_{\text{aq}} = [\text{X}^-]_{\text{aq}} + [\text{OH}^-]_{\text{aq}} \quad (3)$$

and a mass balance equation.

$$(n_{\text{R}_3\text{NH}^+\text{X}^-})_{\text{total}} = (n_{\text{R}_3\text{NH}^+})_{\text{aq}} + (n_{\text{R}_3\text{N}})_{\text{aq}} + (n_{\text{R}_3\text{N}})_{\text{org}} \quad (4)$$

$$\begin{aligned} C_{(\text{R}_3\text{NH}^+\text{X}^-)}^0 V_{\text{aq}} &= [\text{R}_3\text{NH}^+]_{\text{aq}}(V_{\text{aq}} + V_{\text{KOH}}) \\ &+ [\text{R}_3\text{N}]_{\text{aq}}(V_{\text{aq}} + V_{\text{KOH}}) + [\text{R}_3\text{N}]_{\text{org}} V_{\text{org}} \end{aligned} \quad (5)$$

where n_i is the number of moles of species i ; V_{KOH} is the volume of potassium hydroxide added; $C_{(\text{R}_3\text{NH}^+\text{X}^-)}^0$ is the initial concentration of the trialkylammonium salt in the aqueous phase; and V_{aq} and V_{org} are the initial volumes of the aqueous and organic phases, respectively. For simplicity, it is further assumed that the organic solvent is completely immiscible with the aqueous phase.

Mathematical manipulation of eqs 1–5, gives the following cubic expression.

$$A([\text{H}^+]_{\text{aq}})^3 + B([\text{H}^+]_{\text{aq}})^2 + C[\text{H}^+]_{\text{aq}} + D = 0$$

where

$$A = \frac{V_{\text{aq}} + V_{\text{KOH}}}{V_{\text{aq}} + V_{\text{KOH}} + K_p V_{\text{org}}}$$

$$B = K_a + \frac{V_{\text{KOH}} C_{\text{KOH}}^0}{V_{\text{aq}} + V_{\text{KOH}} + K_p V_{\text{org}}}$$

¹ Author to whom correspondence should be addressed.

$$C = \frac{K_a C_{\text{KOH}}^0 V_{\text{KOH}}}{V_{\text{aq}} + V_{\text{KOH}}} - \frac{K_a C_{(\text{R}_3\text{NH}^+\text{X}^-)}^0 V_{\text{aq}}}{V_{\text{aq}} + V_{\text{KOH}}} - \frac{K_w(V_{\text{aq}} + V_{\text{KOH}})}{V_{\text{aq}} + V_{\text{KOH}} + K_p V_{\text{org}}}$$

and

$$D = -K_a K_w$$

Solving for $[\text{H}^+]_{\text{aq}}$

The cubic expression can be solved easily for $[\text{H}^+]_{\text{aq}}$ via Newton's method of convergence, provided that numerical values are known or assumed for the following:

- acid dissociation constant (K_a)
- partition coefficient (K_p)
- autoprotolysis constant of water ($K_w = 10^{-14}$)
- initial concentrations of
 - the trialkylammonium salt ($C_{(\text{R}_3\text{NH}^+\text{X}^-)}^0$)
 - the potassium hydroxide base (C_{KOH}^0)
- the following volumes
 - organic (V_{org})
 - initial aqueous (V_{aq})
 - titrant (V_{KOH})

Computerized calculations significantly reduce the amount of time needed to solve eq 5 for the hydrogen ion concentration. If a computer program is available, or can be written by the students, then simulated titrations can be assigned before the actual laboratory experiment using different sets values for K_a , K_p , and $V_{\text{org}}/V_{\text{aq}}$. Students can observe first-hand how pH titration curves would be affected using different organic solvents (the K_p values would vary) and different phase-volume ratios ($V_{\text{org}}/V_{\text{aq}}$).

Experimental Measurements

Titration Lidocaine Hydrochloride Solutions

Experimentally, the effect of a two-phase solvent media on acid-base equilibria can be easily illustrated by measuring the pH during the titration of lidocaine hydrochloride with potassium hydroxide, both with and without organic solvent.

Using Aqueous Surfactant Solutions Alone

A typical experiment involves dissolving 0.5500 g of accurately weighed lidocaine hydrochloride monohydrate (Sigma) in 100 mL of an aqueous 0.0125 M cetylpyridinium chloride (Aldrich) surfactant solution. The surfactant forms a micellar region (pseudo-two-phase solvent media), which helps to solubilize the lidocaine produced during the titration reaction. The surfactant also increases the degree of acid dissociation by removing the neutral amine from the aqueous solution as discussed above.

Potassium hydroxide (0.10 M) is slowly added, and the pH is recorded at incremental V_{KOH} values before and after the equivalence point, using a standard glass/calomel combination electrode. (To eliminate potential shifts caused by the surfactant, the saturated KCl solution inside the salt bridge is replaced by 0.10 M NaCl (15).)

Using Aqueous Surfactant Solutions with Organic Solvent

A known volume ($V_{\text{org}} = 100$ mL, etc.) of methylene chloride or other immiscible organic solvent is added to an identically prepared lidocaine hydrochloride aqueous surfactant solution. Again, the pH is recorded after each incremental addition of KOH. In this particular titration, the solution turns an emulsion-like milky white after a few drops of KOH are added. A steady pH reading is obtained in 2 or 3 min with vigorous stirring.

We have found that there is no real need to wait for the solution to visually separate back into its two phases. The measured pH of the milky white solution differs by less than 0.2 pH units from the value that one would obtain whenever two distinct phases are visually present. The cetylpyridinium chloride solution can be replaced by 1.25×10^{-3} M cetyltrimethylammonium bromide (Aldrich) if two visual phases are desired. However, it takes slightly longer to reach a steady pH reading.

Variations

The experiment can be modified to include other surfactants and weak acids, to compare titration curves for various $V_{\text{org}}/V_{\text{aq}}$ ratios, and to compare titration curves for different organic solvents. As an experiment in our instrumental analysis course, each student examines one acid, two organic solvents, and two different surfactants for a total of six titrations.

Discussion

Maximizing pH Changes

Representative two-phase titration curves are depicted in Figures 1 and 2 for the titration of lidocaine hydrochloride in two different surfactant mixtures: cetylpyridinium chloride (CPC) and cetyltrimethylammonium bromide (CTAB). Examination of the figures reveals that lidocaine hydrochloride can be titrated in each aqueous surfactant solution without addition of organic cosolvent. Small pH changes make equivalence point detection difficult.

$$\Delta\text{pH} = 1.1 \text{ for CPC}$$

$$\Delta\text{pH} = 0.9 \text{ for CTAB}$$

More dramatic pH changes are observed in the two-phase aqueous-organic solvent media.

Of the four solvents considered, methylene chloride gave the sharpest endpoints. Calculated pH changes for the methylene chloride systems were 2–3 pH units greater than those observed with the aqueous surfactant system alone. Procaine hydrochloride behaved similarly. However, the experimental pH changes near the equivalence point were smaller:

$$\Delta\text{pH} < 0.5 \text{ for CPC and CTAB}$$

$$\Delta\text{pH} \approx 1.8 \text{ with methylene chloride present}$$

Figure 1. Titration of lidocaine hydrochloride with potassium hydroxide in various two-phase aqueous-organic cetylpyridinium chloride systems. From top to bottom the curves correspond to the solvent used: no organic solvent, toluene, and methylene chloride. When an organic solvent was used, the system was prepared with equal volumes of aqueous surfactant solution and organic solvent.

Figure 2. Titration of lidocaine hydrochloride with potassium hydroxide in various two-phase aqueous-organic cetyltrimethylammonium bromide systems. From top to bottom the curves correspond to the solvent used: no organic solvent, toluene, and methylene chloride. When an organic solvent was used, the system was prepared with equal volumes of aqueous surfactant solution and organic solvent.

Class Treatment of Results

Two-phase solvent media affords an interesting application of Le Chatelier's Principle, which can be introduced in both beginning and upper level chemistry courses. At the freshman level, the effect of two-phase solvent media on acid-base equilibria can be explained in a qualitative manner: Removal of the neutral amine (R_3N) shifts the equilib-

ria farther to the right-hand side (see eq 1), thus leading to an increased hydrogen ion concentration. The protonated amine then behaves as a stronger acid.

The more eloquent mathematical treatment can be saved for the quantitative analysis course, when students are actually solving numerical problems that require manipulation of equilibrium constant, charge balance, and mass balance equations. Experimentally, the effect can be observed at any level by titrating lidocaine hydrochloride with potassium hydroxide both with and without organic solvent.

Literature Cited

1. Forland, K. S.; Hauge-Nilsen, G. S. *J. Chem. Educ.* **1991**, *68*, 674-675.
2. Russo, S. O.; Hanania, G. I. H. *J. Chem. Educ.* **1987**, *64*, 817-819.
3. Kilner, C. J. *J. Chem. Educ.* **1988**, *65*, 80-81.
4. Lieu, V. T.; Kalbus, G. E. *J. Chem. Educ.* **1988**, *65*, 184-185.
5. Thompson, R. Q. *J. Chem. Educ.* **1988**, *65*, 179-180.
6. Murphy, J. J. *J. Chem. Educ.* **1983**, *60*, 420-421.
7. Kauffman, G. B.; Houghten, R. A. *J. Chem. Educ.* **1967**, *44*, 408.
8. Harris, W. E.; Kratochvil, B. *Chemical Separations and Measurements: Background and Procedures for Modern Analysis*; Saunders College: Philadelphia, PA, 1974; pp 56-64.
9. Hargis, L. G. *Laboratory Manual for Analytical Chemistry: Principles and Techniques*; Prentice-Hall: Englewood Cliffs, NJ, 1988; pp 29-33.
10. Kennedy, J. H. *Analytical Chemistry: Practice*; Harcourt Brace Jovanovich: New York, NY, 1984; pp 67-71.
11. Sawyer, D. T.; Heineman, W. R.; Beebe, J. M. *Chemistry Experiments for Instrumental Methods*; John Wiley and Sons: New York, NY, 1984; pp 24-28.
12. Boikess, R. S.; Edelson, E. *Chemical Principles in the Laboratory*, 3rd ed.; Harper and Row: New York, NY, 1985; pp 323-328.
13. Pietrzyk, D. J.; Frank, C. W. *Analytical Chemistry*, 2nd ed.; Academic: New York, NY, 1979; Chapter 9.
14. Skoog, D. A.; West, D. M.; Holler, F. J. *Fundamentals of Analytical Chemistry*, 5th ed.; Saunders College: Philadelphia, PA, 1988; pp 245-250.
15. Johansson, P.-A.; Hoffmann, G.; Stefansson, U. *Anal. Chim. Acta* **1982**, *140*, 77-88.
16. Johansson, P.-A.; Stefansson, U.; Hoffmann, G. *Anal. Chim. Acta* **1983**, *151*, 49-63.
17. Korenman, I. M.; Gur'ev, I. A. *Zhurnal Anal. Khim.* **1975**, *30*, 1898-1902.
18. Hux, R. A.; Puon, S.; Cantwell, F. F. *Anal. Chem.* **1980**, *52*, 2388-2392.
19. Brandstrom, A. *Acta Chem. Scand.* **1979**, *33B*, 731-734.