PROCEEDING
The 2nd International Seminar on Chemical Education 2017
September, 12-13th 2017

What Can Be Learned from the Integrative Titration Curves of Acetic Acid and Glycine?

Bhinyo Panijpan[1], Parames Laosinchai[2,*]

[1]Faculty of Science, 272 Rama VI Road, Bangkok 10400, Mahidol University, Thailand
[2]Institute for Innovative Learning, 999 Phutthamonthon 4 Road, Nakhon Pathom 73170
*email: parames.lao@mahidol.edu

Abstract

Titration is a standard laboratory exercise used to find the concentration of a known analyte. In a typical laboratory session, students would follow the titration procedure while interpreting the obtained titration curves according to the explanation given by the instructor/textbook. In so doing, they would concentrate on the macroscopic and symbolic levels of chemistry without thinking much, if at all, about the corresponding microscopic level. Here, we superimpose the graphs of the amounts of relevant species on the titration curves of acetic acid and glycine to help elucidate the interactions among those species during the titrations. The integrative graphs come with detailed explanations so that they can be used as teaching aids in a classroom or laboratory.

Keywords: titration dynamics, buffering, integrative titration curve, diprotic acid, acetic acid, glycine

Introduction

Titration of a weak acid by NaOH is a routine laboratory exercise performed by first- or second-year undergraduate or even by some high-school science-stream students. During the exercise, they may be instructed to plot the titration curve, the graph of the pH of the solution as a function of the volume of the titrant added. Usually, the exercise is considered successful if the obtained titration curve is comparable to that given in a textbook. The class would then focus on how the equivalence/end point can be used to determine the concentration of the weak acid and on the buffering range around the pK_a of the acid where the titration curve is relatively flat. The Henderson-Hasselbalch equation would usually be invoked to describe the pH of the solution around that range. Typically, little to no attention would be paid to the amounts of different chemical species during the titration.

For several decades teaching science, life science, and science education at both the undergraduate and graduate levels, we have asked our students about what actually goes on at the microscopic level during titration; In particular, what are

the amounts of different ionic species at different points and how do they interact? Usually, students would neither know where to begin nor how to think about this kind of question. Although several approaches were suggested to help students grasp different aspects of titration (Barnum, 1999; Barrette-Ng, 2011; Cavalho & Nantes, 2008; Clark et al., 1995; Curtright et al., 2004; Heck et al., 2009) and most employed some kinds of graphs, none was comprehensive enough to facilitate the creation of a coherent concept of titration dynamics. Here we wish to propose integrative titration curves, titration curves superimposed by the graphs of relevant ionic species, of acetic acid and glycine as teaching aids to help teachers and students alike see the amounts of relevant ionic species and deduce their interactions during monoprotic- and diprotic-acid titration.

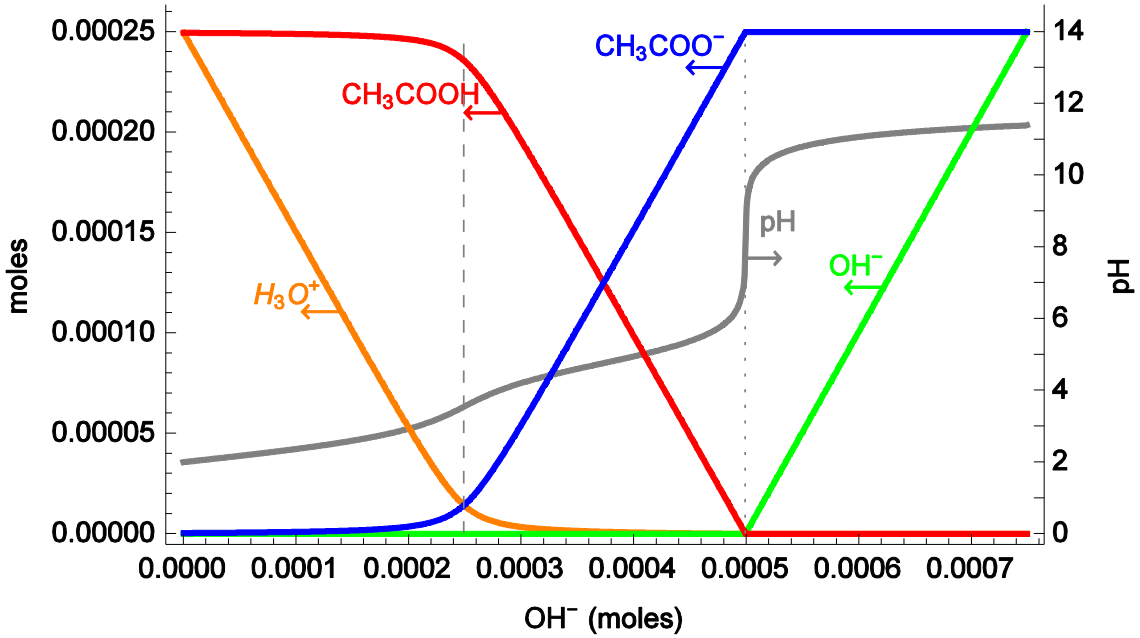

Fig.1. Integrative titration curve of 0.01 M acetic acid by 0.01 M OH^-

Integrative Titration Curve of Acetic Acid

Fig. 1 shows the titration curve of 0.01 M acetic acid by 0.01 M OH^- and amounts of different ionic species during the titration. The initial volume of acetic acid solution is 25 mL. The horizontal axis represents the amount of OH^- added (in moles). The left vertical axis represents the amount of each species in the solution while the right one is the pH scale. Infinitely concentrated H_3O^+ is added (left of the vertical dashed line) until the pH of the solution is 2 before the titration with

OH^- begins in order to demonstrate the effect of strong-acid titration. As can be seen from the figure, the amount of OH^- (late increasing green line) is negligible before the end point, indicating that each drop of OH^- added is completely neutralized during this stage of the titration.

At the early stage of the titration (pH < 3), H_3O^+(early decreasing orange line)decreases almost linearly while CH_3COOH (red line decreasing in the middle)is practically unchanged,indicating that added OH^- is neutralized mostly by H_3O^+. This is due to the fact that there are plenty of H_3O^+so that the amount used for neutralization represents only a small proportion of total H_3O^+.Thus the equilibrium of the dissociation reaction

$$H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$$

is very slightly disturbed by the addedOH^-.Notice also that even thoughH_3O^+decreases at slightly decreasing rates, the pH of the solution(curvy increasing gray line) increases at increasing rates. This is because a logarithmic graph measures the percentage change of the original quantity. That is, pH measures the percentage change of H_3O^+.

At the dashed line, there are equal amounts of H_3O^+ and CH_3COO^-, signifying the start of the titration had H_3O^+not been added. Even though H_3O^+decreases at significantly slower rates around the dashed line, the pH curve exhibits a slight kink, again due to the logarithmic nature of pH. CH_3COOH plays a bigger role in the neutralization of added OH^- from this point on and turns into CH_3COO^- (blue line increasing in the middle) during this buffering stage of monoprotic titration. Thus the original amount ofCH_3COOH represents the buffer capacity. Notice that the pH curve in the buffering zone is steeper than that in the acidic zone, indicating that H_3O^+, while still present, is more effective at neutralizing added OH^- than CH_3COOH.

At the equivalence point (the vertical dotted line)where CH_3COOH has run out, pH jumps to a new level before entering a new flat stage. even though the OH^-just starts to increase linearly, once again illustrating the logarithmic nature of pH. This new flat stage is a reflection of that in the acidic zone. (Recall that pOH = 14 – pH. So the graph of pOH is as flat as that of pH.)

ISBN: 978-602-73192-1-9

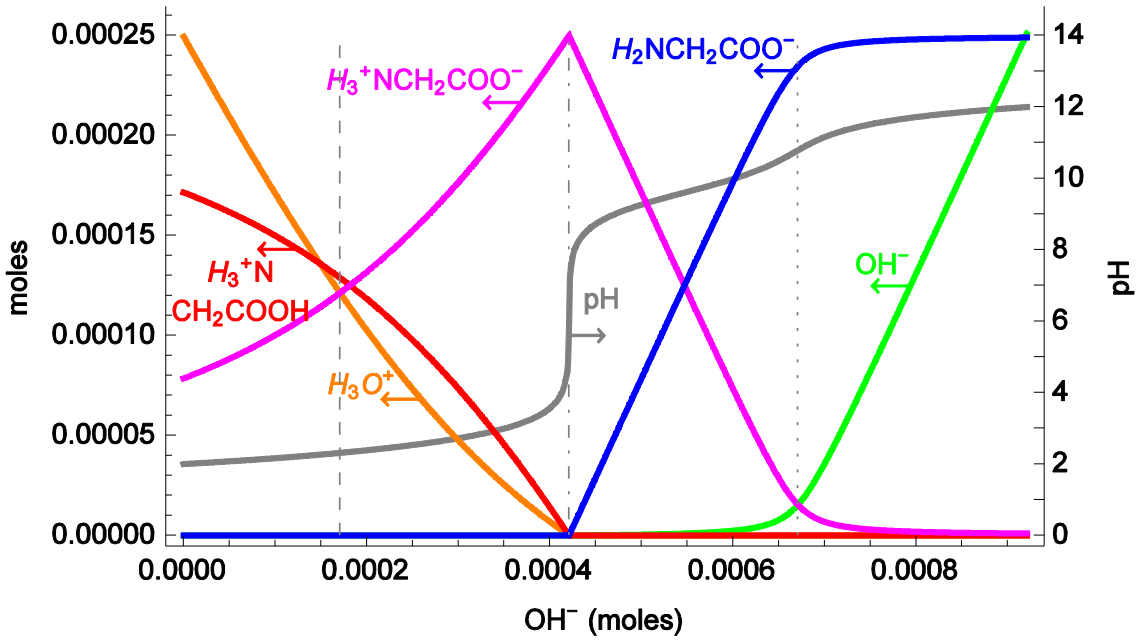

Fig.2. Integrative titration curve of 0.01 M glycine by infinitely concentrated OH^-

Integrative Titration Curve of Glycine

Fig. 2 illustrates the titration curve of 0.01 M glycine by infinitely concentrated OH^- and amounts of different ionic species during the titration. The initial volume of glycine solution is 25 mL andinfinitely concentrated H_3O^+ is added (left of the vertical dashed line) until the pH of the solution is 2 before the titration with OH^- begins. Because the starting pH is close to the first pK_a of glycine (2.34), the titration begins in the middle of the first buffering stage (left of the vertical dash-dotted line) during which each drop of OH^- added is neutralized by both H_3O^+ (due to relatively low pH and concentration, early concave-up orange line) and the carboxylic group of $H_3^+NCH_2COOH$ (early concave-down red line), the latter of which turns into $H_3^+NCH_2COO^-$ (concave-up then decreasing magenta line), which, in turn, neutralizes added OH^- after the first equivalence point (the dash-dotted line). The second equivalence point (the dotted line) is relatively hard to find due to the high second pK_a (9.6) and low concentration. A significant amount of $H_3^+NCH_2COO^-$ is present in the solution well after the second equivalence point because the fewer the amount of $H_3^+NCH_2COO^-$, the higher the concentration of OH^- required to neutralize them. At this point, there is practically no H_3O^+ left to neutralize OH^-. If the last pK_a is even higher (for example, 10.53,

the last pK_a of ε-NH_3^+ of lysine), then we can observe amount of OH^- that is more or less the reverse of the amount of H_3O^+ around the dashed line in this figure which means that there are plenty of OH^- during the last buffering stage (just like there are a lot of H_3O^+ during the first buffering stage). Notice that around the dotted line, the titration curve and amounts of species are the reverses of those around the dashed line in Fig. 1 and the kink in the pH curve is also due to its logarithmic nature. It should be noted that interacting with ε-NH_3^+ by OH^- species at higher pHs would be much slower than with H_3O^+.

Conclusion

A titration exercise helps improve students' laboratory skills and helps them become familiar with buffering phenomena, among others. However, it is hard to think about what really goes on at the microscopic level looking only at a standard titration curve. Here, we present integrative titration curves of acetic acid and glycine at the hope of providing teachers and students with a tool to help visualize about the interactions among relevant species in the solution during titration.

References

Barnum, D. 1999.Predicting acid-base titration curves without calculations, Journal of Chemical Education76: 938–942.

Barrette-Ng, I.H. 2011. The pH ruler: A Java applet for developing interactive exercises on acids and bases, Biochemistryand Molecular Biololgy Education39: 332–338.

Carvalho, E.O., Nantes, I.L. 2008. A novel tool to facilitate the learning of buffering mechanism by undergraduate students of the biological area, Biochemistryand Molecular Biololgy Education36: 189–195.

Clark, R.W., White, G.D., Bonicamp J.M., Watts, E.D. 1995. From titration data to buffer capacities: A computer experiment for the chemistry lab or lecture,Journal of Chemical Education 72:746–750.

Curtright, R., Emry, R., Heaton, R.M.,Markwell, J. 2004.Facilitating student understanding of buffering by an integration of mathematics and chemical concepts,Biochemistryand Molecular Biololgy Education32: 71–77.

Heck, A.,Kędzierska, E., Rogers, L., Chmurska, M. 2009. Acid-base titration curves in an integrated computer learning environment, The Chemical Educator14: 164–174.