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ANALYTICAL COMPLEXATION

Objective

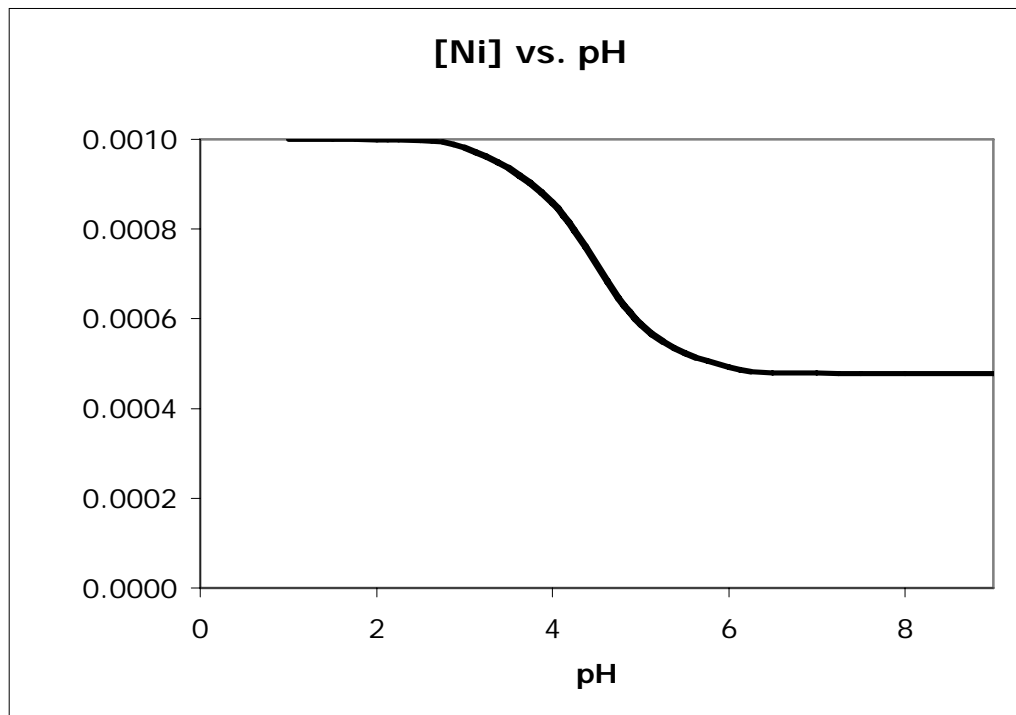
1. Be able to set up complexation equilibrium problems and solve those that are reasonable.
2. Become aware of some pitfalls in conventional approaches to complexation equilibrium.
3. Be able to calculate the analyte concentration at any point during a complexometric titration.

A 0.10F solution of acetic acid is prepared and treated with enough NiSO_4 so that it's 0.001F in NiSO_4 . Appropriate amounts of 1F NaOH are then added to achieve a number of pH values and the molar concentration of nickel ion observed at each using an electrode sensitive to the activity of Ni^{+2} . No precipitate is observed in the solution at any time during this process. Note that the ionic strength of this solution varies between 0.1 and 0.2 for this entire experiment and the volume only increases by about 10% by the end.

Here are the $[\text{Ni}^{+2}]$ values obtained by dividing the activity of Ni^{+2} by the appropriate activity coefficient at $\mu = 0.1$ (so if at some point you attempt to calculate these numbers ignoring activity you might not end up with perfect agreement):

pH	$[\text{Ni}^{+2}]$, M
1.00	1.00×10^{-3}
2.00	9.98×10^{-4}
3.00	9.81×10^{-4}
4.00	8.57×10^{-4}
5.00	5.68×10^{-4}
6.00	4.52×10^{-4}
7.00	4.42×10^{-4}
8.00	4.41×10^{-4}
9.00	4.40×10^{-4}

On the next page is the corresponding graph for you visual types:



1. NiSO₄ is generally considered a strong salt. At strongly basic pH we should expect Ni⁺² to form an insoluble hydroxide, but we evidently did not reach a pH sufficiently basic to cause this (or we'd have seen stuff precipitating out). Over what pH range does the molar concentration behave ideally without considering equilibrium?
2. Ni⁺² is known to form a 1:1 coordination complex with acetate ion in aqueous solution having $\log K_f = 1.43$. Write a balanced equilibrium equation showing this formation.
3. If there were somehow a small amount of acetate ion formed in a solution containing Ni⁺² what would you predict would happen to [Ni⁺²] based on Le Châtelier's Principle?
4. On the graph above imagine a second ordinate varying from 0.0 up to 0.1M. Roughly sketch a second graph of the concentration of acetate ion, [OAc⁻], due to the equilibrium dissociation of acetic acid as a function of pH. Does the Ni⁺² concentration vary with pH in a way that bears out your prediction?

Problem. A solution containing a 0.10F acetate buffer and 1.00×10^{-3} F NiSO_4 exhibits a pH of 5.00. Calculate $[\text{Ni}^{+2}]$ ignoring activity.

5. This is just an ordinary competitive equilibrium problem. In addition to the formation of the NiOAc^+ complex we have the dissociation of HOAc and the dissociation of water to be concerned about. Write the three mathematical equations expressing these equilibria in terms of K_f , K_a and K_w .

(Be very careful. $\text{p}K_a$ for acetic acid is 4.76, just as it's always been, and you can probably calculate K_a from that in your sleep. The $\log K_f$ for NiAOc^+ is 1.43. Note that this is given as a $\log_{10} K_f$, not a $\text{p}K_f$. You'll need to rouse from slumber just enough to operate your calculator in the correspondingly appropriate way)

6. Nickel gets into this system as NiSO_4 . There are a couple of ions in which nickel can end up given the equilibria described above. Write a suitable mass balance equation for nickel, taking into account all of these possible fates.

7. Acetate gets into this as acetic acid and acetate ion in the buffer. We aren't given values for C_{HOAc} or C_{OAc} but we do know that their sum is 0.10F. Notice that acetate in solution, in addition to ending up in the usual places, is also found in the complex NiOAc^+ . Write a suitable mass balance equation for the acetate ion.

8. We're given a value for the pH, so count up the number of equations and the number of unknowns and make sure they're equal (if they're not, now's the time to see what the problem is).

This problem can be solved algebraically in the usual way. You end up with a quadratic equation which, under some conditions, may require resorting to the quadratic formula. The unsettling part of this exercise is that this is the simplest possible case. Often ligands are the anions of polyfunctional acids (like EDTA, H_6Y^{+2} . You'll have six acid-base equilibria to contend with) and the complexes formed are often multi-coordinate (like $Cu(NH_3)_4$. There are four K_f expressions to sort out before you even consider the acid-base character of ammonia).

In general we only consider doing such problems on a routine basis when we can make one of a couple of assumptions that simplify things greatly. Likewise, we always insist on being told the pH up front. The success of any analytical method involving complexation hinges on the pH being correct. These solutions are always buffered appropriately. The approach to solving this particular problem, while strictly speaking unnecessary in this case, will illustrate some of the formalisms and assumptions ordinarily employed in this endeavor.

Consider the K_f expression:

$$K_f = 27 = \frac{[NiOAc^+]}{[Ni^{+2}][OAc^-]}$$

$[Ni^{+2}]$ is what we're looking for ultimately, so let's leave that alone. $[OAc^-]$ looks a little formidable in view of all the places acetate can go, but recall that we could actually calculate a value for it if we knew its formal concentration using α_{OAc} .

- Write an expression that one might use to calculate α_{OAc} given values for $[H^+]$ and K_a . Stick with algebraic symbols for now. There'll be an opportunity to plug in numbers and evaluate this stuff later.

Remember that we said a week or so ago that the distribution functions are only valid when the acid and any of its anions don't precipitate from solution or complex with anything. Strictly speaking, that's not the case here because acetate ion actively complexes with nickel. We can only use the distribution functions, therefore, if we consider as formal acetate for this purpose only that which is not involved in any metal-ion complex. This "partial" formal concentration is traditionally given the symbol C_T , for no reason I've ever been able to figure out.

- Write an expression for C_T , the total concentration of all the acetate in solution except that involved in a nickel complex, in terms of C_{HOAc} , C_{OAc} and any other concentration you think appropriate.

- Now write an expression for $[OAc^-]$ in terms of α_{OAc} and C_T .

12. Even though it seems a little earnest, this is a perfectly good expression for $[\text{OAc}^-]$, so rewrite the K_f expression replacing $[\text{OAc}^-]$ with your new expression.

13. Just for kicks, get rid of α_{OAc} in the denominator by multiplying both sides by it.

Assuming that you're doing this symbolically, the expression $\alpha_{\text{OAc}}K_f$ is what's known as the conditional formation constant, K_f' . It's the formation constant modified to take into account the effect of pH on the formation of the complex.

14. OK, time to get down to business. Calculate a value for α_{OAc} given the value of K_a you know and the fact that the $\text{pH} = 5.00$. Then use the K_f value you calculated earlier to get the conditional formation constant for NiOAc^+ at $\text{pH} = 5.00$, K_f' . Then write what's left of the K_f' expression, plugging in your value for K_f' itself.

15. Dig out that mass balance expression for NiSO_4 and rearrange it to get an expression for $[\text{NiOAc}^+]$ in terms of $[\text{Ni}^{+2}]$. Plug that into your K_f' expression.

16. Find your expression for C_T and plug in any values you know. What's the largest $[\text{NiOAc}^+]$ could possibly be? Consider ignoring it if that seems reasonable. Plug whatever you get into the K_f' expression and solve for $[\text{Ni}^{+2}]$.

The use of the conditional formation constant in the K_f expression along with substitution of C_T for the ligand molar concentration is always a legal move and doesn't introduce any error. It's only useful if a reasonable expression can be obtained for eventually getting a value for C_T . Assuming that some molar concentration in the C_T expression is insignificant does potentially introduce error, so it needs to be checked once you're done.

It's normal for inorganic ligands to form multiply-coordinate complex ions with metals. A familiar example is the royal blue $\text{Cu}(\text{NH}_3)_4^{+2}$ ion. As you might expect this gives rise to four complexation equilibria, four K_f values and three intermediate copper-amine complexes. In desperation, it's normal to try to assume that the complex forms fully and the concentrations of any intermediate complexes are negligible. Then it suffices to make use of the combined formation constant expression after the fashion of:

$$K_{f1}K_{f2}K_{f3}K_{f4} = \frac{[\text{Cu}(\text{NH}_3)_4^{+2}]}{[\text{Cu}^{+2}][\text{NH}_3]^4}$$

in which case it's essential to check to be sure that $[\text{Cu}(\text{NH}_3)_4^{+2}]$ is indeed large compared to any other copper-containing species. Frequently it's not, and then you're out of luck.

A word about looking up formation constant values in Harris. At least one of the tables offered therein provides $\log \beta$ values rather than $\log K_f$ values. If you want you can learn to use β values. This notation is not limited to Harris. On the other hand, if you're likely to attempt to do complexation equilibrium problems just as seldom as possible, it's probably more intuitive to stick with K_f and learn to get K_f values from β . The relationship isn't difficult:

$$\beta_1 = K_{f1}$$

$$\log \beta_1 = \log K_{f1}$$

$$\beta_2 = K_{f1}K_{f2}$$

$$\log \beta_2 = \log K_{f1} + \log K_{f2}$$

$$\beta_3 = K_{f1}K_{f2}K_{f3}$$

$$\log \beta_3 = \log K_{f1} + \log K_{f2} + \log K_{f3}$$

and so forth.

17. Calculate the six $\log K_f$ values for the hexamine cobalt(II) complex $\text{Co}(\text{NH}_3)_6^{+2}$ (yes, $\log K_f$ values can be, and occasionally are, negative).

18. Write the K_{f6} expression for the formation of hexamine cobalt(II) using the actual value of K_{f6} . Suppose that $[\text{NH}_3]$ is 1.0 and that it's available in such huge excess compared to the amount of Co^{+2} available that there's no reason for any of the intermediate ammonia complexes to form from a stoichiometric point of view. Does it seem reasonable to assume that $[\text{Co}(\text{NH}_3)_6^{+2}]$ is much larger than any other Co^{+2} containing ion? Justify your answer with an appropriate calculation.

Problem. 50mL of 0.1F CaCl_2 is titrated with 0.2F EDTA at pH 10.00. Calculate pCa following addition of 35mL of titrant.

19. Write a balanced chemical equation for the reaction of Ca^{+2} with EDTA. It's customary to represent the neutral EDTA molecule as H_4Y . Of the many possible acid-base forms of EDTA, the only one that's active as a ligand in this application is Y^{-4} . The reaction between any metal ion and EDTA is always one to one. This is an important part of why EDTA and other amino polycarboxylic acids like it are useful.

20. Calculate the moles of Ca^{+2} to start with and the moles of Y^{-4} added. Use these to calculate the moles of CaY^{-2} formed and the moles of any reagent left over. Then calculate the formal concentrations of CaY^{-2} and whatever reagent was left over.

21. Write the K_f expression for the formation of CaY^{-2} . $\log K_f = 10.69$.

22. Recall that $[\text{Y}^{-4}] = \alpha_Y C_T$ where C_T is the sum of the concentrations of all ions in solution containing Y except that involved in complexation with Ca^{+2} . The value of α_Y at pH 10 is 0.36. Yeah, you can calculate it by looking up all four K_a values for EDTA and grinding through the appropriate distribution function, but I just looked it up in the table in chapter 13 of Harris. I encourage you to do the same. Calculate the value of the conditional formation constant, K_f' , and rewrite the K_f expression so as to accommodate it.

23. Now you'll need some ingenuity. If Ca^{+2} was the limiting reagent, come up with expressions for C_T and $[\text{CaY}^{-2}]$ in terms of $[\text{Ca}^{+2}]$, which is likely to be small. If EDTA was the limiting reagent you'll probably find it easier to come up with expressions for $[\text{Ca}^{+2}]$ and $[\text{CaY}^{-2}]$ in terms of C_T , which we'll expect to be small. Whichever you do, make the appropriate substitutions into the K_f' expression and solve for the variable you've chosen.
24. Check any instance in which you ignored a value because it might be small. If you're one of these people that neglects the equilibrium entirely when Ca^{+2} isn't limiting, watch out if K_f' is small.
25. Once you get a result that you're satisfied represents something like reality, use it to get pCa.

This approach to complexometric titration problems works for one-to-one titrations anywhere on the titration curve. Since complexes other than one-to-one are problematic for titration (the sudden rise in pCa that would ordinarily be enjoyed all at once at the endpoint is instead frittered away piecemeal during the course of the titration as each intermediate form of the complex gives way to the next) there is little need for greater complexity.

Exercise 1

A solution containing 0.1F NH_3 and 0.001F AgNO_3 is adjusted to pH 9.5 with a suitable buffer, resulting in the formation of the diamine silver complex, $\text{Ag}(\text{NH}_3)_2^+$. Calculate pAg.

Exercise 2

10mL of 0.05*F* MgSO₄ is titrated with 0.02*F* EDTA at pH 7.0. Calculate pMg following addition of 10, 25 and 30mL of titrant.