DISTRIBUTION OF BENZOIC ACID BETWEEN TOLUENE AND WATER AND DIMERIZATION OF BENZOIC ACID IN TOLUENE

OBJECTIVE: In this experiment we will use the volumetric technique of acid-base titration to determine the distribution of benzoic acid in the water-toluene system. From these distribution measurements we will be able to examine the two equilibria:

(1) dimerization of benzoic acid in toluene and,
(2) distribution of benzoic acid monomers between water and toluene.

INTRODUCTION: A general treatment by Moelwyn-Hughes[1] allows examination of the above two equilibria from distribution measurements. The benzoic acid water-benzene system has been studied by Huq and Lodhi[2]. This treatment has been extended to other acids (e.g. acetic and propionic acids) distributed between water and other organic solvents[3].

In the benzoic acid-water-toluene system, there are three equilibria which must be considered. In the aqueous layer, benzoic acid, being a weak acid will dissociate:

$$\mathrm{HBz} \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{Bz}^-(aq) \qquad (1)$$

and we can write the acid dissociation constant, K_a for the equilibrium as

$$K_a = \frac{[\mathrm{H}^+]\,[\mathrm{Bz}^-]}{[\mathrm{HBz}]_\mathrm{W}} \qquad (2)$$

In the toluene layer, benzoic acid exists both as a monomer and dimer (i.e. two benzoic acid molecules bonded together by hydrogen bonding to form a new species). This dimerization is also an equilibrium:

$$2\,\mathrm{HBz} \rightleftharpoons (\mathrm{HBz})_2 \qquad (3)$$

$$K_D = \frac{[(\mathrm{HBz})_2]_\mathrm{T}}{[\mathrm{HBz}]_\mathrm{T}^2} \qquad (4)$$

where $[\mathrm{HBz}]_\mathrm{T}$, is the equilibrium molar concentration of the monomer in toluene and $[(\mathrm{HBz})_2]_\mathrm{T}$ is the equilibrium molar concentration of the dimer in toluene.

The third equilibrium is the equilibrium constant for the distribution of benzoic acid monomers between water and benzene:

$$(\mathrm{HBz})_\mathrm{W} \rightleftharpoons (\mathrm{HBz})_\mathrm{T} \qquad (5)$$

$$K_M = \frac{[\mathrm{HBz}]_\mathrm{T}}{[\mathrm{HBz}]_\mathrm{W}} \qquad (6)$$

The total concentrations of benzoic acid in water and toluene, C_W and C_T respectively, is obtained by titration of the appropriate phase with sodium hydroxide.

$$C_W = [HBz]_W + [Bz^-]_W = C_W(1 - \alpha) + \alpha C_W \qquad (7)$$

where α is the degree of dissociation of benzoic acid; and

$$C_T = [HBz]_T + 2\,[(HBz)_2]_T \qquad (8)$$

Using Eqs.(6) and (4) as well as noting that $[HBz]_W = C_W(1 - \alpha)$ allows Eq.(8) to be rearranged to,

$$\frac{C_T}{C_W(1 - \alpha)} = K_M + 2K_M^2 K_D C_W(1 - \alpha) \qquad (9)$$

Eq.(9) predicts that a plot of $C_T/C_W(1 - \alpha)$ vs. $C_W(1 - \alpha)$ will be linear with a slope of $2K_M{}^2K_D$ and an intercept of K_M. The value of of α used in Eq.(9) is obtained from the known value of K_a.

$$K_a = \frac{\alpha^2 C_W}{1 - \alpha} = 6.3 \times 10^{-5} \text{ for benzoic acid at } 20°C$$

PROCEDURE:

A. Preparation of the toluene/benzoic acid/water mixtures

Eight mixtures of toluene/benzoic acid/water are to be studied so that the distribution can be observed over a wide range of concentration. These mixtures are to be made according to Table I, using the burettes for toluene and the benzoic acid solution in toluene, the water should be added using the 50.00 mL pipette.

Make up the mixtures in the stoppered bottles and allow the equilibrium distribution to be attained over a period of about 30 minutes, shaking frequently. During the equilibration period, practice the two titrations involved on samples of benzoic acid in toluene and in water as supplied in the laboratory.

TABLE I

Mixture	Benzoic acid in toluene	Toluene	Water
I	50 mL	+ 0 mL	+ 50 mL
II	45 mL	+ 5 mL	+ 50 mL
III	40 mL	+ 10 mL	+ 50 mL
IV	35 mL	+ 15 mL	+ 50 mL
V	30 mL	+ 20 mL	+ 50 mL
VI	25 mL	+ 25 mL	+ 50 mL
VII	20 mL	+ 30 mL	+ 50 mL
VIII	15 mL	+ 35 mL	+ 50 mL

At the end of the equilibration period, allow the mixture to separate into two layers. Decant the upper toluene layer into a large, clean, dry test tube, and cork it at once. (This separation need not be perfect).

B. Titration of the toluene layer

Pipette 15.00 mL of the toluene solution from the upper layer in the test tube into a clean (*not necessarily dry*) Erlenmeyer flask. **WIPE THE OUTSIDE OF THE PIPETTE BEFORE ADJUSTING THE TRANSFER VOLUME TO AVOID CARRYING OVER ANY EXTRA, UNMEASURED SOLUTION.** Pipette 25.00 mL of the 0.030 *M* NaOH and titrate with 0.0200 *M* HCl **(Record exact concentrations)** until the pink color of the phenolphthalein indicator disappears (this is the end point for the titration. Since neutralization of the benzoic acid in the toluene layer with the NaOH in aqueous solution is slow because of the immiscibility of the two layers, the two layers of solution must be stoppered and well shaken before the back titration with the 0.020 *M* HCl.

NOTE: Stir slowly when doing the titration because the low molarity of NaOH leads to problems with CO_2 absorption causing the end point to be reached faster than expected. The CO_2 forms carbonic acid which causes the weak solution of NaOH to be neutralized.

Repeat the titration, cleaning the pipette between samplings.

Follow the same procedure in duplicate for each of the other eight solutions and record your titration values on the blackboard in the laboratory for other students to record.

C. Titration Blank for the toluene layer

This is a necessary correction to the titration in part B due to the fact that CO_2 is absorbed and reacts with the dilute NaOH added when the aqueous & toluene layers are well shaken before back titration with the HCl solution.

Pipette 15.00 mL of pure toluene into a clean Erlenmeyer flask. Pipette 25.00 mL of the 0.030 *M* NaOH, stopper and shake well for the same period of time as you did for each of your titrations in part B. Titrate with the 0.0200 *M* HCl in exactly the same fashion as you did in part B. Repeat the titration with a second sample.

D. Titration of the aqueous layer

Titrate 20.00 mL of the lower, aqueous layer with the 0.006 *M* NaOH. The lower, aqueous layer must be reached through the upper, toluene layer. This is best done by blowing gently through the pipette as it is inserted to ensure that none of the toluene layer enters. Transfer the 20.00 mL to a clean Erlenmeyer flask, wipe the pipette before adjusting the transfer volume as before. Since the concentration of the benzoic acid in the water layer will be low, expect small amounts of titrant to be used in this titration. Repeat the titration.

Follow the same procedure in duplicate for the other eight solutions and record your titration values on the blackboard in the laboratory for other students to record.

CALCULATIONS:

1. Calculate how many mL of 0.020 *M* HCl should have been used to neutralize the 25.00 mL of 0.030 *M* NaOH in the titration blank of the toluene layer (Part C). The difference between the calculated volume and the actual volume it took to do the titration is the correction factor which must be added to each of your titration volumes for the toluene layer titrations of solution I to V.

2. From the volumes of titrant used for each solution you can calculate the concentration of benzoic acid in the toluene and water layers, C_T and C_W respectively.

3. You should also calculate the total amount benzoic acid present in each mixture (I to VIII). You should find that the amount of benzoic acid present follows the ratios you placed in mixtures I to VIII.

4. From equation (10), calculate the value of α for each value of C_W. You should tabulate your results under the following headings: solution number, mL of HCl used for toluene layer, C_T, mL of NaOH used for water layer, C_W, (C_T/C_W), α, $C_W(1 - \alpha)$ and $C_T/C_W(1 - \alpha)$.

   NOTE: You should show one complete calculation in your lab report. All of the data point obtained by the class can be input into the spread sheet on the computer which will automatically calculate the above values.

5. Plot all of the individual values of $C_T/C_W(1 - \alpha)$ vs. $C_W(1 - \alpha)$ obtained by the class and from this plot obtain tbe value K_M(intercept) and K_D (which can be obtained from the slope of this line as indicated in the introduction). **USE THE LINEAR REGRESSION PROGRAM ON YOUR CALCULATOR OR ON THE COMPUTER IN THE LAB TO OBTAIN THIS PLOT AS WELL AS THE BEST VALUES FOR THE SLOPE AND INTERCEPT.**

6. You should also calculate the concentration of benzoic acid in tbe original toluene solution used (i.e. 4.5 g/L).

QUESTIONS:

1. Comment on the size of these equilibrium constants (i.e. what do they imply about the system?).

2. Suggest a reason for the fact that benzoic acid exists as a monomer in aqueous solution but mainly as a dimer in toluene.

3. Draw the structure of the benzoic acid dimer.

4. Suggest how this experiment could be extended so that we might obtain information as to the $\Delta H°$ and $\Delta S°$ for the dimerization of benzoic acid in toluene as well as for the distribution of benzoic acid monomers between toluene and water.

REFERENCES:

1. E.A. Moelwyn-Hughes, J.Chem.Soc., 850 (1940).
2. A.K.M. Shamsul Huq and S.A.K. Lodhi, J. Phys. Chem., 70, 1354(1966).
3. M. Davies, P. Jones, D. Patnaik and E.A. Moelwyn-Hughes, J. Chem. Soc., 1249 (1951).