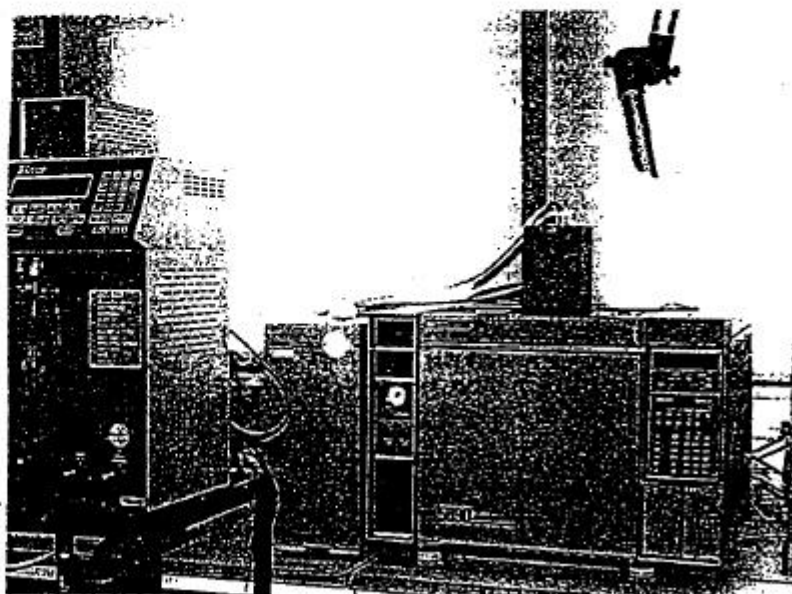
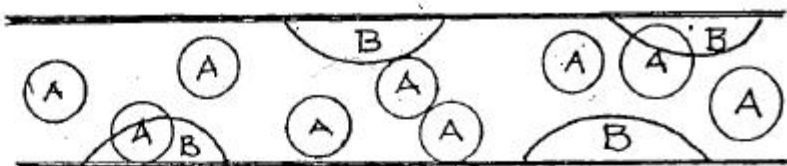
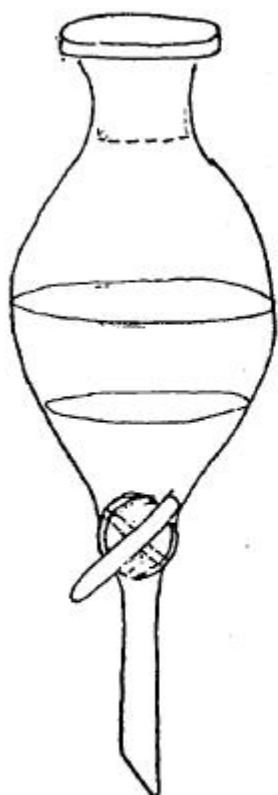


KEMS448 PHYSICAL CHEMISTRY ADVANCED LABORATORY WORK



DISTRIBUTION LAW

1 Theory

1.1 Distribution coefficient and association

Two immiscible liquids are connected to each other through the boundary surface between them. These liquids are called phases. If one of these phases also contains a third substance A, a part of that substance will be transferred into the the phase where its chemical potential is lower, until substance A's chemical potential in both phases is the same.

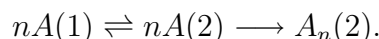
In practice, one can put in a separatory funnel two immiscible liquids like water and diethyl ether. The water also contains acetic acid, making the water phase in fact a liquid solution of acetic acid.

In equilibrium, the chemical potentials for A in both phases (1=water, 2=diethyl ether) are equal, from which can be derived that the equilibrium constant

$$K = \frac{a_A(2)}{a_A(1)} \approx \frac{c_A(2)}{c_A(1)}.$$

The activities (effective concentrations) of substance A, a_A in the different phases can be approximated as concentrations c_A in the phases.

The following reaction equation depicts substance A's distribution in the two different phases, and the possible molecular association in phase 2.



Let us rewrite the equilibrium constant

$$K_1^n = \frac{c_A^n(2)}{c_A^n(1)}. \quad (1)$$

The equilibrium constant of the second reaction step, the association of substance A's molecules with phase 2's molecules is

$$K_2 = \frac{c_{A_n}(2)}{c_A^n(2)}. \quad (2)$$

Combining the two equations a new distribution coefficient K is defined as

$$K = K_1^n K_2 = \frac{c_A^n(2) c_{A_n}(2)}{c_A^n(1) c_A^n(2)} = \frac{c_{A_n}(2)}{c_A^n(1)}. \quad (3)$$

Because only the total concentration of A in the system, C_A , can be measured with relative ease, here by titrating, we will first define the total concentration ratio D in the phases for non-associating molecules.

$$D = \frac{C_A(2)}{C_A^n(1)}. \quad (4)$$

Taking the logarithm from equation (4), we get a linear equation

$$\log C_A(2) = n \log C_A(1) + \log D, \quad (5)$$

the slope of which is n and the y -axis intercept is $\log D$.

From results of n and D the distribution coefficient can be calculate if for total concentration we approximate $C_A(1) \approx c_A(1)$ and the relation $C_A(2) = n c_A(2)$. It follows that

$$D = \frac{C_A(2)}{c_A^n(1)} = \frac{n c_{A_n}(2)}{c_A^n(1)} = nK,$$

or

$$K = \frac{D}{n}. \quad (6)$$

1.2 Elution with a constant distribution coefficient K

Elution with a greater number of small amounts of substance is far more efficient than using all of the solvent at once. Proceeding with the elution: V millilitres of solution containing the amount n of a substance is eluted with v millilitres of another solvent that does not dissolve into the first solvent. Therefore, after a great number of N elutions, the amount of substance left uneluted, n_N can be calculated as follows.

After one elution, the concentration of the eluted solvent is $\frac{n_1}{V}$ and the eluting solvent concentration is $\frac{n_0 - n_1}{v}$. Here the distribution coefficient, defined as the ratio of concentrations of the eluted solvent (diethyl ether) and and the uneluted solvent (water), which is exactly the situation of equation (1):

$$K = \frac{\frac{n_0 - n_1}{v}}{\frac{n_1}{V}}, \quad (7)$$

from which the amount of substance in the eluted solvent is

$$n_1 = n_0 \left(\frac{V}{Kv + V} \right). \quad (8)$$

After the second elution the amount of substance of the original solution is n_2 , for which

$$n_2 = n_1 \left(\frac{V}{Kv + V} \right) = n_0 \left(\frac{V}{Kv + V} \right)^2. \quad (9)$$

Expanding this gives the amount of substance n_N in the original solvent (water) after N elutions

$$n_N = n_0 \left(\frac{V}{Kv + V} \right)^N. \quad (10)$$

The superiority of continuous elution, in which the solvent is distilled back into use, is therefore explicit.

In some books, the elution equation (10) is in the form of

$$n_N = N_0 \left(\frac{K'V}{K'V + v} \right)^N. \quad (11)$$

Show that equations 10 and 11 are equal by using, instead of the Nernst dissociation law equilibrium constant K , its inverse $K' = \frac{1}{K}$.

2 Experimental methods

Use $\sim 1.5 - 2.0 M$ acetic acid solution (or propionic acid in its stead) 200 ml. Define the exact concentration by titrating with exact concentration $NaOH$ solution. From this base solution, five differing concentrated dilutions (for example 0.2, 0.4, 0.6, 0.8 and 1.0 M) are prepared.

In five separatory funnels, measure 25 ml of each acetic acid solution. Shake each funnel in turns for 30 minutes (NOTE: Knowledge of the shaking mechanics is crucial for safety reasons!) and leave the solutions standing still for about an hour. After opening the cork, the separation of phases goes as normal. Drain the water phase completely out of the funnel through the valve and set the phase boundary at midpoint of the valve region (it is glass, so it is easily seen). The diethyl ether phase is left in the funnel with the cork shut as soon as possible to avoid evaporation and change in concentration due to it.

From the separated layers pipette samples for the titrations: for example from the water phase 5 ml and from the ether phase 10 ml, so that titer consumption is reasonable, but greater than 10 ml. Add 10 ml of water into the ether phase, because there the titrating reaction itself will happen in the water phase of the titrant. Titrate using a magnetic stirrer, and phenolphthalein as indicator (it may take time for the colour to stay in the ether phase in the equilibrium point - try to find a way to determine the same colour intensity formed and the amount of titrant used)

As titrant, use 0.1 M NaOH solution, the concentration of which has first been confirmed with HCl solution with a known concentration. The way the concentration was confirmed should be found both in the lab log book and the lab report written.

3 Results

The following results should be in the form of table(s):

Ether phase sample: volume, titer concentration, titer expenditure, concentration $C_A(ether)$

Water phase sample: volume, titer concentration, titer expenditure, concentration $C_A(water)$

Total concentration calculated: $C_A(ether) + C_A(water)$, the ratio $\frac{C_A(ether)}{C_A(water)}$

Results: $y = \log C_A(ether)$, $x = \log C_A(water)$

From the results an (x,y) -graph as indicated by equation 5 is drawn. From the slope, constant n is determined, and from the y -axis intercept the ratio of total concentrations, both with errors.

4 Additionally

Comment on your results. What does n tell about the association of acetic acid? Provide clarification for why n the constant depicting association gets this particular value.

To confirm the superiority of continuous elution, calculate through dissociation coefficient how much acetic acid will be left in the water phase when 100 *ml* of 1.0 *M* acetic acid water solution is eluted with a) one 100 *ml* volume of ether or a) ten 10 *ml* volumes of ether.

Also think how the elution amount parameter N and the eluting solution's volume v should be chosen, so that the acid could be *most* efficiently eluted from water to ether.