• ***Учебни опити и демонстрации*** •
• ***Teaching Chemical Experiment*** •

RAPID DETERMINATION OF PARTITION COEFFICIENTS OF SOME COMMON ORGANICS BETWEEN ORGANIC AND AQUEOUS SOLVENTS

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Abstract. Determination of partition coefficients of (1) acetic acid between n-butanol and water and (2) benzoic acid between water and benzene have been carried out by a different approach, where volumetric titration is completely avoided. This method yields results in excellent agreement with those obtained by conventional titrations. The inherent advantages of the suggested method are its easy execution in reduced time with less number of chemicals.

Keywords: partition coefficient, digital balance, rapid method, classroom teaching

Introduction

The term partition coefficient commonly refers to the equilibrium distribution of a solute between two immiscible solvent phases. Partition coefficients are also known as distribution coefficients. The concept of partition coefficient is of great significance and is applied extensively in diverse fields like medicinal chemistry and drug design, eco-toxicology, chemical engineering, geochemistry, hydrogeology and environmental chemistry. The partition coefficient has also been widely used in calculating numerous physical properties such as membrane transport and water solubility.

Depending upon the nature of the complexities involved in the experiment and type of problem to be addressed, measurement of partition coefficient has been con-

ducted by (i) shake-flask method [1], where the experiment is conventionally carried out by the titrimetric estimation of concentration of the solute in two immiscible solvents layers after their distinct separation (ii) HPLC (high-performance liquid chromatography) method [2]. In HPLC method the partition coefficients are determined by correlating the retention time of a solute of interest with similar compounds with known values, (iii) spectroscopic method (cf. Stanley, Aspaas & Solberg[1)]) and (iv) electrochemical method where experiments are conducted using polarized liquid interfaces to examine the thermodynamics and kinetics of the transfer of charged species from one phase to another [3].

Owing to the large number of applications in diverse fields as mentioned above, the concept of partition coefficient is imparted to undergraduate/graduate students of many universities by demonstrating simple laboratory experiment in practical classes. Estimating the partition coefficient of acetic acid between n-butanol and water and that of benzoic acid between water and benzene are the commonly conducted experiments. In these experiments the concentration of either benzoic acid (in both water and benzene layers) or acetic acid (in both n-butanol and water) is measured by conventional titration method after distinct solvent-layer separation using shake-flask method [1].

The motivation of this article is to suggest an alternative approach where the weight of a fixed volume of each solvent layer is measured with the help of a digital balance thereby completely avoiding the volumetric determination. The experiment can therefore be completed in less time with use of fewer numbers of chemicals. In order to establish the authenticity of the suggested approach, I determined partition coefficients for (1) acetic acid between n-butanol and water and (2) benzoic acid between water and benzene. These results are then validated by conventional titration method.

The Partition Coefficient

Explicitly, the partition coefficient (K_D) is defined as the ratio of the equilibrium concentrations (C_i) of a dissolved substance in a two-phase system consisting of two largely immiscible solvents. In other words, when a solute is added to a mixture of two immiscible liquids A and B, where it is soluble in both the liquids and does not undergo any association or dissociation in any of the solvent, it (the solute) distributes itself between the two solvents in such a way that the ratio of the concentration of the solute in solvent A and B (C_A and C_B) is constant at a particular temperature T,

$$K_D = C_A / C_B = const \tag{1}$$

The partition coefficient (K_D) is the quotient of two concentrations; hence it is dimensionless and is usually represented in the form of its logarithm to the base ten ($\log K_D$).

The above definition of partition coefficient holds if the solute molecules in phase A are in equilibrium with those in phase B (i.e. the species of solute molecules present in both A and B phases are same). However, if the solute has normal molecular form in one solvent in which the concentration is C_A, while in the other solvent it exists predominantly as associated molecule B_n (the total concentration being C_2), then the equilibrium between associated and simple molecule is represented as

$$B_n \rightleftharpoons nB$$

where B and B_n are the simple and associated molecules, respectively. The equilibrium constant in phase B is given by:

$$K = C_B^n / C_B \tag{2}$$

where C_B is the concentration of the simple molecules and C_{B_n} that of associated molecules.

From Eq. (2)

$$C_B = const \sqrt[n]{C_B} \tag{3}$$

If the solute in phase B is mainly in associated form, C_{B_n} may be identified with C_2, the total concentration in the second solvent, and hence above Eq. (3) becomes:

$$C_B = const \sqrt[n]{C_2} \tag{4}$$

The modified expression of partition coefficient under such condition therefore becomes

$$K_D = C_A / \sqrt[n]{C_2} = const \tag{5}$$

As benzoic acid remains as simple molecule in water but becomes associated forming dimer in benzene, the expression for partition coefficient of benzoic acid between water and benzene thus can be written as

$$K_D = C_{aq} / \sqrt{C_{org}} \tag{6}$$

It is also important to note that the partition coefficient is a ratio and hence if one wants to express partition coefficient of benzoic acid between benzene and water, it is estimated as

$$\sqrt{C_{org}} / C_{aq}$$

Method

There is minor deviation in the calculation of partition coefficients of (1) acetic acid between n-butanol and water and (2) benzoic acid between water and benzene.

In the following, I therefore describe the methodologies adopted for both the experiments separately; so that the readers are able to appreciate the basis as to why minor deviation was desirable (see also section 4 for further details).

Partition coefficient of acetic acid between n-butanol and water

The mass of 10 ml n-butanol (W_1) taken in a relative density bottle is measured. Four stopper bottles marked #1 to #4 are filled with n-butanol, water and glacial acetic acid (Table 1). The bottles are stoppered tightly and then shaken for about 50-60 minutes. They are then allowed to stand in a large beaker containing water at room temperature. The contents are separated in two layers; lower aqueous layer and upper organic layer. 10 ml of the organic layer is taken in a relative density bottle with the help of a pipette with bulb. The mass of the content is recorded (W_1*).

Table 1. Result of partition co-efficient measurement of acetic acid between n-butanol and water

Room temperature: 25.2^0 C

Mass of 10 ml n-butanol (W_1 = 8.187 gm)

Difference in the mass when 1 ml n-butanol is replaced by 1 ml acetic acid = 0.2293 gm

Bottle Number	1	2	3	4
Volume of acetic acid (V ml)	0.3	0.6	0.9	1.2
Volume of n-butanol added (ml)	50	50	50	50
Volume of water added (ml)	49.7	49.4	49.1	48.8
Mass of 10 ml organic layer (W_1* gm)	8.225	8.264	8.300	8.342
Volume of acetic acid dissolved in 50 ml n-butanoll solution $V^I_{org} = (W_1^* - W_1)/0.2293$ (ml)	0.1657	0.3358	0.4928	0.676
Mass of acetic acid dissolved in 50 ml organic solution $W^I_{org} = V^I_{org}$ x 1.048 (gm)	0.1737	0.3519	0.5165	0.7084
Conc. of acetic acid solution in n-butanol $C^I_{org} = W^I_{org}$ x (1000 / 60) x (1/50) (M)	0.0579	0.1173	0.1722	0.2361

Total mass of the acetic acid dissolved in 100 ml mixture $W_T = V$ x 1.048 (gm)	0.3144	0.6288	0.9432	1.2576
Mass of acetic acid dissolved in 50 ml aqueous solution $W^I_{aq} = WT - W^I_{org}$ (gm)	0.1407	0.2769	0.4267	0.5492
Conc. of acetic acid solution in water $C^I_{aq} = W^I_{aq}$ x (1000 / 60) x (1/50) (M)	0.0469	0.0923	0.1422	0.1831
Partition coefficient $K_D = C^I_{org} / C^I_{aq}$	1.23	1.27	1.21	1.29

From Figure 1 the slope of the line is K_D = 1.2826

Conventional titration is performed on each aliquot to estimate the concentrations of acetic acid in both n-butanol layer and in aqueous layer using freshly prepared standard NaOH solution in presence of phenolphthalein as indicator. These results are presented in Table 2.

Table 2. Experimental data on partition coefficient measurement of acetic acid between n-butanol and water by conventional titration method

Stopper bottle Number	1	2	3	4
Volume of 0.1M NaOH solution required for the neutralization of 10 ml organic layer (V^I_{org}) ml	5.9	11.7	17.3	23.6
Volume of 0.1 M NaOH solution required for the neutralization of 10 ml aqueous layer (V^I_{aq}) ml	4.6	9.2	14.1	18.4
Concentration of acetic acid in n-butanol (C^I_{org}, M)	0.059	0.117	0.173	0.236
Concentration of acetic acid in water (C^I_{aq}, M)	0.046	0.092	0.141	0.184
Partition coefficient $K_D = C^I_{org}/C^I_{aq}$	1.28	1.27	1.226	1.282

Partition coefficient of benzoic acid between benzene and water

The readers must take a note that the experiments in this case were conducted only during laboratory classes assigned to students and the measurements were not taken on a single day.

During each experiment the masses of 10 ml benzene (W_2) and 10 ml distilled water (W_3) taken in relative density bottles are measured with the help of a single pan digital balance capable of yielding quick and accurate mass measurement.

Five stopper bottles marked #1 to #5 are filled with variable volumes of benzoic acid solution, solvent benzene and solvent distilled water (see Table 3 along with date of each experiment). Since these experiments are conducted by a different approach, purposely I avoid measurement of initial masses of benzoic acid that is added to solvent benzene in any of the stopper bottles. The partition coefficient value thus obtained would ensure authenticity of the adopted approach, provided the result is comparable within the limits of experimental error to that obtained by conventional titration method.

The bottles are stoppered tightly and shaken for 50-60 minutes and then allowed to stand in a water bath at room temperature. The contents are separated in two layers; lower aqueous layer and upper benzene layer. From each stopper bottle, 10 ml of the benzene layer is transferred to a relative density bottle with the help of a bulb-pipette. The use of bulb-pipette is important as it helps to avoid sucking chemicals by mouth. The mass of the content is recorded (W_2*). The difference between W_2* and W_2 (i.e. W_2* - W_2) gives the mass of benzoic acid in 10 ml organic layer. Similarly the mass of 10 ml lower aqueous layer is recorded (W_3*). The difference in mass (W_3* - W_3) gives the mass of benzoic acid in 10 ml aqueous layer.

Table 3. Experimental data on partition coefficient measurement of benzoic acid between water and benzene

Room temperature: 23.5 ± 0.1^0 C

Mass of 10 ml benzene (W_2 gm) = 8.612±0.001
Mass of 10 ml water (W_3 gm) = 9.892±0.001

Stopper bottle Number	1	2	3	4	5
Date of experimentation (January 2008)	4th	4th	7th	9th	11th
Volume of benzoic acid solution in benzene (ml)	10	20	30	40	50

Volume of benzene added (ml)	40	30	20	10	0
Volume of water added (ml)	50	50	50	50	50
Mass of 10 ml organic layer (W_2* gm)	8.665	8.720	8.766	8.790	8.815
Mass of benzoic acid in10 ml organic layer (W_2*-W_2) gm	0.053	0.108	0.154	0.178	0.203
Mass of the 10 ml aqueous layer (W_3* gm)	9.900	9.904	9.905	9.906	9.908
Mass of benzoic acid in10 ml aqueous layer (W_3*-W_3) gm	0.008	0.012	0.013	0.014	0.016
Concentration of benzoic acid solution in benzene (C^{II}_{org}, M)	0.0434	0.087	0.125	0.1447	0.165
Concentration of benzoic acid solution in water (C^{II}_{aq}, M)	0.0065	0.0097	0.010	0.0114	0.013
$\frac{C^{II}_{aq}}{C^{II}_{org}}$	0.1498	0.1115	0.0800	0.0788	0.0788
Partition coefficient $K_D = \frac{C^{II}_{aq}}{\sqrt{C^{II}_{org}}}$	0.031	0.033	0.030	0.030	0.032
log C^{II}_{org}	-1.3625	-1.0534	-0.8993	-0.8364	-0.7793
log C^{II}_{aq}	-2.1837	-2.0076	-1.9728	-1.9407	-1.8827

From Figure 2 the slope of the line, $s = 1/n = 0.4803$
Therefore $n = 1/s = 2.08$
Intercept on y-axis I = log K_D = -1.5238 (i.e. K_D = 0.03)

Conventional titration is carried out to estimate the concentrations of benzoic acid in both aqueous layer and in benzene layer using freshly prepared standard solution of NaOH in presence of phenolphthalein as an indicator. These results are presented in Table 4.

Table 4. Experimental data on partition coefficient measurement of benzoic acid between water and benzene by conventional titration method

Stopper bottle Number	1	2	3	4	5
Volume of 0.1M NaOH solution required for the neutralization of 10 ml organic layer (V^{II}_{org}) ml	4.2	8.5	12.6	14.5	16.4
Volume of 0.01 M NaOH solution required for the neutralization of 10 ml aqueous layer (V^{II}_{aq}) ml	6.6	9.8	10.4	11.3	13.5
Partition coefficient $K_D = C^{II}_{aq} / C^{II}_{org} =$ $= V^{II}_{aq} / (100 \text{ x } V^{II}_{org})$	0.0322	0.0336	0.0293	0.0297	0.033

Results and discussion

Partition coefficient of acetic acid between n-butanol and water

The results of the partition coefficient determination of acetic acid between n-butanol and water are presented in Table 1. The volume of acetic acid dissolved in 50 ml of n-butanol solution can be calculated from V^{I}_{org} (in cm^3) = $\frac{(W_1^* - W_1)}{0.2293}$, where 0.2293 g represents the difference in mass when 1 ml n-butanol solvent is replaced by 1 ml glacial acetic acid. The volume is converted to mass using the equation, $W^{I}_{org} = V^{I}_{org}$ x 1.048 (gm/ml of glacial acetic acid = 1.048). The concentration of the acetic acid solution in n-butanol is given by $C^{I}_{org} = W^{I}_{org}$ x (1000/60) x (1/50) where 60 is the molecular weight of acetic acid. The mass of acetic acid dissolved in 50 ml. aqueous solution can be calculated as $W^{I}_{aq} = W_T - W^{I}_{org}$ where W_T = total mass of acetic acid in 100 ml. mixture of each bottle = volume of acetic acid added in each bottle {V x 1.048). Then $C^{I}_{aq} = W^{I}_{aq}$ x (1000/60) x (1/50). The partition coefficient $K_D = C^{I}_{org} / C^{I}_{aq}$ (see Table 1) can therefore be calculated. The independent estimates for C^{I}_{org} and C^{I}_{aq} values shown in Table 1 are also plotted as Fig. 1. The best fit line through data points defines a straight line with high correlation coefficient of 0.9957 and is characterized by positive slope passing almost through the origin as indicated by insignificant y-intercept of 0.0031. The slope of the best fit line yields the value of partition coefficient as

K_D = 1.2826, which is in fairly good agreement with that obtained by conventional titration method (see Table 2) and the value reported in the literature [4].

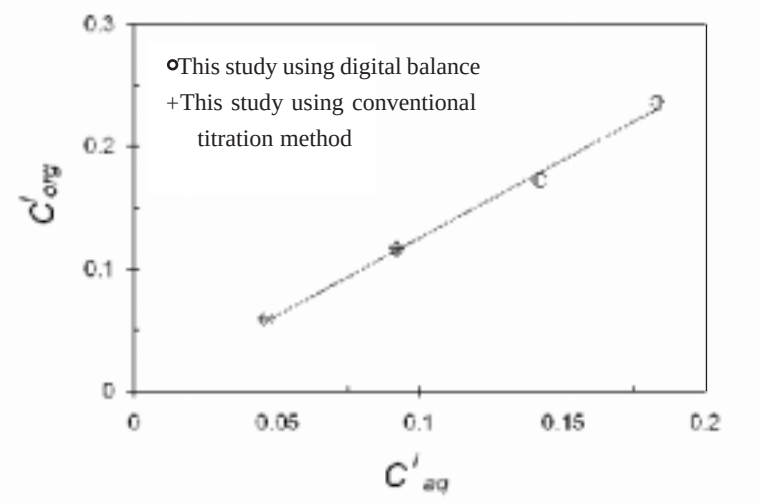

Fig. 1. Concentration of acetic acid between aqueous (C^I_{aq}) and organic (C^I_{org}) layers estimated and shown in Table 1. The plot shows linear relationship between C^I_{aq} and C^I_{org} with high correlation coefficient (R^2 = 0.9957). The partition coefficient K_D =1.2826 is estimated from the slope of the regression line through the data points (open circle). Data points related to conventional titration (cross) are shown for comparison.

Partition coefficient of benzoic acid between benzene and water

The results of this experiment are presented in Table 3. The concentration of benzoic acid in the organic layer can be calculated from the measured masses using the simple equation $C^{II}_{org} = \frac{1000 \times \left(W_2^* - W_2\right)}{(\mathrm{M}_{C_6H_5COOH} \times 10)}$ where $\mathrm{M}_{C_6H_5COOH}$ represents the molecular weight of benzoic acid = 122.12. Similarly, C^{II}_{aq} gives the concentration of benzoic acid in the aqueous layer as $C^{II}_{aq} = \frac{1000 \times \left(W_3^* - W_3\right)}{(\mathrm{M}_{C_6H_5COOH} \times 10)}$. Using the values of C^{II}_{aq} and C^{II}_{qrg}, it can be seen from Table 3 that the concentration ratio $\frac{C^{II}_{aq}}{C^{II}_{org}}$ is dependent on the concentration of benzoic acid in water and vice versa. The partition coefficient, which can be estimated from $K_D = \frac{C^{II}_{aq}}{\sqrt[n]{C^{II}_{org}}}$, however, does not change and remain close to 0.03 (see Table 3) over the concentration range.

The expression for K_D can also be written as $\log C^{II}_{aq} = \frac{1}{n}\log C^{II}_{org} + \log K_D$ and can be solved graphically to evaluate values of K_D as well as n (n is the molecularity of benzoic acid in benzene). Fig. 2 shows the plot of log C^{II}_{aq} against log C^{II}_{org}, which is a straight line with high correlation coefficient ($R^2 = 0.9753$). From the slope of the line, molecularity of benzoic acid in benzene (n = 1/slope) and from the intercept on y-axis, the partition coefficient log K_D is determined. The calculated n-value from the slope of the line (n = 2.08) is very close to 2. The log K_D value from the intercept of the line is -1.5238 (i.e. K_D = 0.03) (see Fig. 2 and Table 3), which is in reasonably good agreement with the measured partition coefficient value by conventional method (for comparison see Table 4). The results obtained in this study at 23.5^0 C are also compared with the available published data (see Fig. 2) reported at a lower temperature of 6^0 C [5]. It may be noted that as temperature increases the value of partition coefficient tends to increase in favor of the phase in which the solutes are less soluble.

There are several advantages of the new method suggested here. The method is simple and easy to execute. The duration of experimentation is reduced drastically compared to other methods involving titration and IR[1)] spectroscopy [1]. The number of chemicals used in the experiment is less (use of NaOH and phenolphthalein indicator needed for titration method is completely avoided) and hence the method is cost-effective.

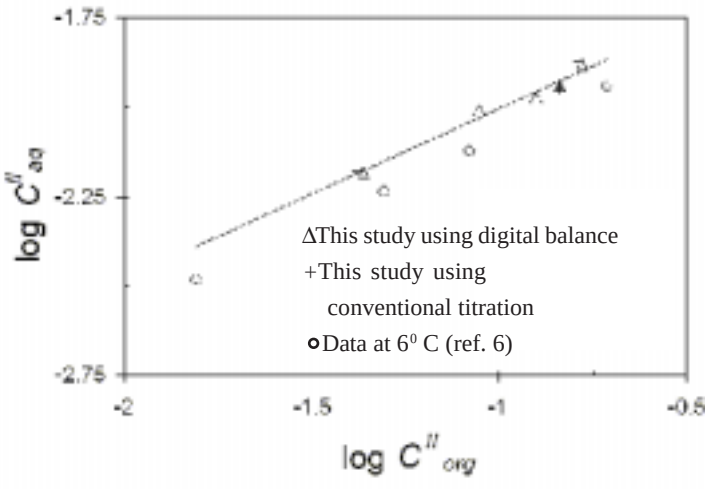

Fig. 2. Plot of log C^{II}_{aq} against log C^{II}_{org} showing linear relationship with high correlation coefficient. The partition coefficient value estimated from the best fit linear trend through experimental data points (open triangle) is tabulated in Table 3. Data points related to conventional titration (cross) are shown for comparison.

Points plotted as open circles represent data at 6^0 C from the literature [5].

Conclusion

The principle of partition coefficient is the basis for the solvent extraction and chromatographic separation methods. The use of liquid-liquid extraction methods for the separation of organic compounds is very common for laboratory-scale and industrial-scale separations.

The methods suggested here efficiently impart the concept of partition coefficient in a simple way by measurement of masses with the help of a digital balance. Other similar laboratory assignments for undergraduate classes such as distribution of (i) succinic acid between ether and water, (ii) salicylic acid between water and benzene, (iii) salicylic acid between water and chloroform and (iv) acetic acid between water and various organic solvents can be conducted easily by the suggested method. However, it should be noted that depending upon the system to be studied, some innovation in the proposed approach might be necessary as brought out in this study as well.

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NOTES

1. http://ed.augie.edu/~awaspaas/pchem/labs/dimerization/dimerization.html

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БЪРЗ МЕТОД ЗА ОПРЕДЕЛЯНЕ НА КОЕФИЦИЕНТИТЕ НА РАЗПРЕДЕЛЕНИЕ В ТЕЧНИ СМЕСИ

Резюме. Предложен е бърз метод за определяне на коефициенти на разпределение в течни смеси. Определен е коефициентът на разпределение на: 1. оцетна киселина в смес на н-бутанол и вода; 2. бензоена киселина в смес на бензен и вода. Методът печели пред традиционните методи с икономията на време и по-ниския разход на химикали.

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