The Dimerization Effects of Some Solutes on the Partition Coefficient k_D in Binary Immiscible Solvents

V.O. Onyeocha¹, O.D. Akpan², I.A. Onuchukwu³, M.A. Chidiebere^{1*}

¹Electrochemistry and Material Science Research Laboratory, Department of Chemistry, Federal University of Technology Owerri, Nigeria

²Department of Chemistry, University of Uyo, Uyo, Nigeria

³Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University, Anambra State

*arinzechukwuchidiebere@gmail.com

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Abstract. The dimerization of a solute dissolved in binary immiscible solvents shows that the value of the partition coefficient k_D of the solutes are influenced by the dimerization constant K of the solute in one of the solvents according to the description: $\frac{C_X^A}{C_X^B} = k_D + 2k_D^2KC_x^B$, where C_x^A and C_x^B are the concentrations of the solute x in the solvents A and B respectively. Both k_D and K are parameters that predict the extent of beneficiation for most minerals. Also, k_D is a fundamental parameter that determines the extent of solute recovery during solvent extraction. In this study, it is found that the order $K > k_D$ and $K \gg k_D$ are the effects for acetic and succinic acids respectively in the binary solvents composed of carbon tetrachloride/water and diethylether/water systems respectively. These results suggest that the distributions of these solutes in the solvents are accompanied by the formation of succinic anhydride which is more favoured than the dimerization of the acetic acid. Also, the changes in the values of distribution enthalpies, ΔH_D are corroborated to explain these experimental observations.

1. Introduction

A solute introduced into two immiscible solvents and on attainment of equilibrium, the solute distributes itself between the solvents in accordance with the Nernst's distribution law. Thus, the ratio of the distributions of the solute in the two immiscible solvents is a constant at any temperature [1-9, 17, 21]. This principle is true provided the solute neither undergoes association, dissociation nor participates in a chemical reaction in any of these solvents [5, 10-11, 13-15, 17]. This distribution law is often represented by the relation:

$$\frac{C_X^A}{C_X^B} = k_D \quad (1.1)$$

where at equilibrium, C_X^A and C_X^B are the concentrations of the solute in the solvents, A and B respectively, while k_D is the distribution constant for any temperature. In a chemical reaction system, the distribution constant, is influenced by dimerization process which modifies the equation (1.1) by the expression:

$$\frac{C_X^A}{C_X^B} = k_D + 2k_D^2KC_x^B \quad (1.2)$$

where k_D retains its usual meaning, while K is the dimerization constant. This distribution coefficient K_D , identifies the extent of the solubility of a solute in the binary solutions, 'A' and 'B' at any temperature. The temperature (T), pH of the solution and any possible chemical reaction of the solute with one/or both of the solvents affect the distribution coefficient, K_D .

The organic solvents such as: carbon tetrachloride (CTC), acetic acid (Ac); exists in the form of a dimer [5, 10-11, 13-15, 17]. Acetic acid is miscible with carbon tetrachloride and exhibits dimerization from the process as shown in scheme I:

Scheme I

The solubility characteristics of non - ionic compounds are determined by their polarity. However, non-polar compounds dissolve in like solvents while highly polar compounds dissolve in highly polar solvents. Carbon tetrachloride (CTC) is known to be insoluble in water, as a polar solvent, because the highly polar water molecules are held to each other by strong dipole-dipole interactions [23-28]. In this consideration, it is envisaged that there could be only weak attractive forces between water molecules on one hand and the non-polar carbon tetrachloride on the other. Ac is miscible with water, and remains as a monomer in water but in CTC, it exists as a dimer. CTC is immiscible with water. Ac dimerizes in some organic solvents. The dimerization of Ac in organic solvents affects the distribution of the acid in immiscible binary solvents. The higher the dimerization constant, K, then the smaller the value of distribution coefficient, and the much less in the efficiency of distribution in the case of solvent extraction as described by expression:

$$\frac{C_X^A}{C_X^B} < 1. \quad (1.4)$$

However, succinic acid (SSA) is a dicarboxylic acid which is observed in an aqueous solution to ionize and form conjugate anions referred to as succinate ions [10-14] as shown in scheme II:

Scheme II

This process (eqn. 1.5), could undergo two successive reactions as a diprotic acid. The SSA is fairly soluble in water but, sparingly soluble in ether. However, on heating SSA, large amount sublimes, while the remainder is converted into the cyclic succinic anhydride, (CSSAH), which is shown in the scheme III:

Scheme III

Solvent/Solute Interaction

The interaction of solutes with a solvent brings about changes such that the solvent solubilization of the solute (solid) is achieved. The structure of the solute becomes separated from each other and the space in between becomes occupied by solvent molecules. This is the essence of solvation. The entire bulk may constitute a homogeneous phase that cannot be separated from each other by physical means. This homogeneous phase is the solution. The solvent is present in large excess amount over the solute. Factors such as temperature, the nature of the solute and type of solvent etc., are considered significant in this process.

System of Variable Composition/Solution

The composition of the phases of a solution can be varied continuously, within a certain limit. A binary solution is formed from two substances. The basic parameters for the state of the solution

are temperature, pressure and concentration that express the relative amounts of the components in the solution.

Literature

The distribution coefficient as defined by equation 1.1 depends on relative solubility of a solute in the two immiscible solvents. In a solvent extraction principles, when $C_X^A/C_X^B = 1$; the solute is distributed equally in two solvents used, and is extracted completely. This principle was used in the solvent extraction of Gold from Alkaline Cyanide solution by Tetradecylmethylbenzylammonium Chloride [6]. When the distribution coefficient $C_X^A/C_X^B > 1$, complete extraction of the solute is done in more than one step [10].

Solvent extraction is an important technique in an industrial beneficiation of minerals. Log k_D (distribution coefficient) is reported as useful tool in drug recovery, beneficiation, and development. Cells are likened to filters which are identical to solvent extraction in the use of organic solvents. This is applied in research and development (R&D), and in the production of drugs [6].

Dimerization of Solutes

This is the formation of a bi-molecular compound (dimer). This involves as follows:

(i) Association of molecules

Association of molecule is defined by the hypothetical chemical equation as:

(ii) Dissociation of molecules.

This is like in the association of molecules; large molecules such as proteins and acids dissociate in solvents to give dimers [21]. Dimerization of a compound affects its distribution in a binary solution.

In this work, investigations were carried out on Ac and SSA to determine the distribution coefficients, k_{DS} , and the effect of dimerization on the distribution coefficients in immiscible binary solutions, namely carbon tetrachloride/water and diethylether/water.

2. Materials and Methods

Materials

Sources of materials were of AnalaR Grade reagents of acetic acid, carbon tetrachloride, diethylether, succinic acid, phenolphthalein, 0.5M and 0.1M sodium hydroxide and distilled water.

Method

The various solutions of immiscible solvents were prepared to obtain the stock solution as follows:

Preparation of Immiscible Solvents I

One ml pipette was used to pipette 1.00ml of acetic acid into two immiscible solvents of 25.00ml of water and 25.00ml of carbon tetrachloride in a separating funnel and shaken up vigorously for several times and allowed to stand for over one hour. Also 2.00ml, 3.00ml, and 4.00ml, of acetic acid were subsequently pipetted separately into several freshly prepared two immiscible solvents of 25.00ml of water and 25.00ml of carbon tetrachloride respectively.

Preparation of Immiscible Solvents II

One ml pipette was used to pipette 1.00ml of acetic acid into two immiscible solvents of 25.00ml of water and 25.00ml of diethylether in a separating funnel and shaken up vigorously for several times and allowed to stand for over one hour. Also 2.00ml, 3.00ml, and 4.00ml, of acetic acid were respectively pipetted separately into freshly prepared two immiscible solvents of 25.00ml of water and 25.00ml of diethylether in a separating funnel.

Preparation of Immiscible Solvents III

1g of succinic acid was weighed out using the weighing balance and put into two immiscible solvents of 25.00ml of water and 25.00ml of diethylether in a separating funnel and shaken up vigorously for several times and allowed to stand for over one hour. Later, 2.00g, 3.00g, and 4.00g of succinic acid were weighed out respectively with the weighing balance and put into freshly prepared two immiscible solvents of 25.00ml of water and 25.00ml of diethylether, respectively.

These stock solutions were used to determine the distribution coefficient of the acids in the binary solutions as involved. Each solution gave two phases; aqueous and organic phases. Titrations were carried out with the aqueous and organic solutions using phenolphthalein indicator and sodium hydroxide solutions. The concentrations of the respective acids involved were then calculated.

Determination of Distribution Coefficients, k_d from the Immiscible Solvents

Acetic acid in Water/Diethylether as Immiscible Solvents

One ml pipette was used to pipette 1.00ml of acetic acid into two immiscible solvents of 25.00ml of water and 25.00ml of diethylether in a separating funnel, and shaken up for several times until equilibrium was attained. The solution was allowed to separate in each case for 5-10 minutes and clamped until separation was attained within 15-20min. The layer of diethylether (organic layer) was decanted into a clean beaker, and the aqueous layer was decanted into another clean beaker. 10.00ml of the organic layer was pipetted into a conical flask and was titrated with 0.1M sodium hydroxide with phenolphthalein as the indicator until a pink color was obtained. The volume of the sodium hydroxide used was recorded. Also, 10.00ml of the aqueous solution was titrated with 0.5M sodium hydroxide to the phenolphthalein end point. The volume of sodium hydroxide used in each case was recorded. The concentrations of the acids in the two layers were then determined from the appropriate ratios of these acid concentration of Ac in each case as obtained in equation 1.1. The experiment was repeated separately for 2.00, 3.00, and 4.00ml of acetic acid. The concentration of acetic acid in the two layers were calculated. Similarly, the other systems were obtained with the repetitive values of the end point.

Succinic Acid in Water/Diethylether as Immiscible Solvents

1.00g of succinic acid was weighed into equal volume of the immiscible solvents of 25.00ml each of water and diethylether in a separating funnel. The immiscible solvents in the separating funnel were shaken vigorously for 10-15mins until the acid dissolved. The solution was then allowed to stand for 15-20 mins. The lower organic layer was decanted into a clean beaker while the upper aqueous layer was discharged into another clean beaker. 10.00ml of the organic layer was titrated with 0.1M sodium hydroxide with phenolphthalein as indicator until end point was attained. The volume of sodium hydroxide used was recorded. 10.00ml of the aqueous layer was titrated with 0.5M sodium hydroxide with phenolphthalein until a pink colour was obtained as end point. Also the volume of sodium hydroxide used was recorded. The experiment was repeated separately for 2.00, 3.00, and 4.00g of succinic acid. The concentration of succinic acid in the two layers were calculated. Similarly, the other systems were obtained with the repetitive values of the end point.

Determination of the Changes of Enthalpy for Water/ CCl_4 Immiscible Solvents

A container was packed with glass wool (as an insulator) and built to a temperature of 5°C with ice blocks of water with a thermometer to measure the temperature changes. 1 ml pipette was

used to pipette 1.00ml of acetic acid into the immiscible solvents of equal volumes of water and carbon tetrachloride of 25.00ml each in a separating funnel with an inserted thermometer in the chamber as described above, at 5°C. The separating funnel was left for 10-15mins in the chamber. The solution was then taken out and shaken up vigorously for 10-15mins. The solution was allowed to settle for another 15-20mins. The lower layer of carbon tetrachloride was decanted into a clean beaker, and the aqueous layer also was decanted into another beaker. Titrations were carried out using 10.00ml of the solution from the two layers. The concentrations were once more calculated. The experiment was repeated using 1.00ml of acetic acid at 10°C, 20°C, and 25°C.

The change of enthalpy of the distribution of the solute (i.e. acetic acid) in the immiscible solvents of diethylether and water was repeated as in the case of acetic acid in carbon tetrachloride and water system, using diethylether and water as immiscible solvents.

3. Results

Table 1. The values of the distribution coefficient (k_D) for acetic acid in the binary solution of Carbon tetrachloride and Water, at 30°C and atmospheric pressure.

Volume of Acetic acid (99.9%) @ 30°C (ml)	Acid concentration in CCl_4 (C_x^A) (M)	Acid concentration in water (C_x^B) (M)	$C_x^B/\sqrt{C_x^A}$ (M) ^{1/2}
1.00	0.04	0.01	0.05
2.00	0.15	0.02	0.05
3.00	0.16	0.02	0.05
4.00	0.30	0.03	0.05

From this table, it is observed that acetic acid is more soluble in CCl_4 than in water. Linear fitting plots using Origin 8 software were made. A plot of C_x^A/C_x^{*B} against C_x^{*B} as shown in equation 1.2 above gave a straight line with intercept k_D and slope equal to $2k_D^2K$. The dimerization constant (K) was calculated using the slope of the plot according to the relations:

$$K = \text{Slope}/2k_D \quad (3.1)$$

Table 2 shows the values of the ratio of concentrations, C_x^A/C_x^{*B} , and C_x^B (M) in the binary immiscible solution at 30°C and atmospheric pressure.

Table 2. The values of the ratio of concentrations, C_x^A/C_x^{*B} , and C_x^B (M) in the binary immiscible solution at 30°C and atmospheric pressure.

C_x^A/C_x^{*B}	4	7.5	8	10
C_x^B (M)	0.01	0.02	0.02	0.03

Figure 1. A plot of C_X^A/C_X^{*B} against C_X^{*B} for acetic acid in the binary immiscible solution of Carbon tetrachloride and Water, at 30°C and atmospheric pressure.

The K_D values for acetic acid in diethylether and water is as shown in Table 3. The data is obtained at 30°C and atmospheric pressure.

Table 3. The K_D values for acetic acid in diethylether and water obtained at 30°C and atmospheric pressure.

Volume of Acetic acid (99.9%) @ 30°C (ml)	Acetic concentration in diethylether (M)	Acetic concentration in acid (C_X^A)	Acetic concentration in water (C_X^B) (M)	$C_X^B/\sqrt{C_X^A}$ (M) ^{1/2}
1.00	0.02		0.13	0.92
2.00	0.04		0.19	0.92
3.00	0.07		0.26	0.98
4.00	0.08		0.28	0.99

From the Table 3, it is observed that acetic acid is more soluble in water than in diethyl ether. A plot of C_X^A/C_X^{*B} versus C_X^{*B} from Table 3 gave a straight line as shown in Fig. 2, with intercept k_D and slope equal to $2k_D^2K$. The dimerization constant, K , was calculated in the usual way from equation 1.1 above.

Table 4 shows the values of the ratio of concentrations, and the C_X^B (mole/liter or M) @ 30°C and 1atm.

Table 4. The values of the ratio of concentrations, and the C_X^B (mole/liter or M) @ 30°C and 1atm.

C_X^A/C_X^{*B}	0.15	0.21	0.27	0.29
C_X^B (M)	0.13	0.19	0.26	0.28

Figure 2. A plot of C_x^A/C_x^{*B} against C_x^B for acetic acid in diethylether and water obtained at 30°C and atmospheric pressure.

Table 5. The k_D values for succinic acid in the binary solution of immiscible solvents of diethyl ether and water at 30°C and atmospheric pressure.

Mass of Succinic acid (g)	Succinic acid concentration in diethyl ether (DEE) (M) (C_x^A)	Succinic acid concentration in water (C_x^B) (M)	$C_x^B/\sqrt{C_x^A}$ (mole/liter) ^{1/2}
1.00	0.05	0.75	3.35
2.00	0.11	1.13	3.41
3.00	0.13	1.19	3.30
4.00	0.13	1.20	3.33

From Table 5 it is obvious that succinic acid is more soluble in water than in diethyl ether.

A plot of C_x^A/C_x^{*B} versus C_x^{*B} from Table 5 gave a straight line as shown in Fig. 3. The intercept k_D and slope, $2k_D^2K$ were calculated. The dimerization constant, K , was also calculated using the equation 1.2 in the usual way.

Table 6. The values for the ratio C_x^A/C_x^{*B} and C_x^{*B} (M)

C_x^A/C_x^{*B}	0.07	0.10	0.11	0.11
C_x^{*B} M	0.75	0.13	0.19	0.20

Figure 3. The plot of C_x^A/C_x^{*B} Vs C_x^{*B} for succinic acid in diethylether/water at 30°C and atmospheric pressure.

The results obtained for the k_D and dimerization constant K for the two solutes in the binary solvents are compared in Table 7.

Table 7. Distribution Coefficient, k_D and Dimerization Constant, K , values @ 30°C and atmospheric pressure.

Binary Solutions	Immiscible	Distribution Coefficient k_D Value	Dimerization Constant K (mole/liter)
Acetic acid in CCl_4 /Water		1.37500	79.34
Acetic acid in Diethylether/Water		0.03177	456.40
Succinic acid in Diethylether/Water		0.00360	3409.30

Table 8. Values for the enthalpy of the distribution of Acetic acid in carbon tetrachloride at atmospheric pressure and varying temperatures.

Acetic acid concentration in CCl_4 (C_x^A) (M)	0.76	0.75	0.73	0.71
T (K)	278	283	293	298

Figure 4. A plot of the values of concentration against T of Acetic acid in water.

Table 9. Values for the enthalpy of the distribution of Acetic acid in water at atmospheric pressure and varying temperatures.

Acetic acid concentration in water (C_x^A) (M)	0.54×10^{-4}	0.54×10^{-4}	0.71×10^{-4}	0.75×10^{-4}
T (K)	278	283	293	298

Figure 5. A plot of the values of concentration against 1/T Acetic acid in water.

Table 10. Values for the enthalpy of the distribution of Acetic acid in diethyl ether at atmospheric pressure and varying temperatures.

Acetic acid concentration in DDE (C_x^A) (M)	0.48	0.50	0.48	0.51
T (K)	278	283	293	298

Figure 6. A plot of the values of concentration against $1/T$ of the distribution of Acetic acid in diethyl ether at atmospheric pressure and varying temperatures.

These plots were drawn with the Origin 8.0 software. From the equation below, equation 3.2, the slopes and intercepts were read out accordingly for Figs. 4-6.

Thus:

$$\ln x = \frac{-\Delta H}{RT} + C. \quad (3.2)$$

where x is the concentration. The slope is equal to $-\Delta H/R$.

Change in the enthalpy (ΔH) of the distributions as shown in the Tables above.

Table 11. Change in the enthalpy (ΔH) of the distributions.

System	ΔH (KJ/mole)
Acetic acid in CCl_4	-128.0
Acetic acid in water	748.3

System	ΔH (KJ/mole)
Acetic acid in DDE	107.3
Acetic acid in water	142.2

System	ΔH (KJ/mole)
Acetic acid in DDE/ CCl_4	107.3/-128.0

Discussion

Acetic acid has an appreciable distribution coefficient $k_D = 1.38$ in carbon tetrachloride and water. There was an observed dimerization of the acid in CCl_4 /Water; and diethylether/water solutions used. Carbon tetrachloride and water system is the best binary solution for acetic acid. They are completely immiscible. Acetic acid has a low distribution coefficient value of 0.03 in diethylether and water. Therefore solvent extraction for example is not encouraging in this binary solution. Succinic acid is very reactive in carbon tetrachloride, and as such, the investigation could not be carried out in this solution, by titration method. In diethylether and water system, succinic acid has a very low distribution coefficient value of 0.0036. Solvent extraction of the acid is not encouraging with this binary solution.

These findings are also represented in the values of the distribution enthalpies. Acetic acid in carbon tetrachloride/water has the enthalpies of -128/748.3, and 107.3/142.0 in diethylether/water. Exothermic process ($\Delta H_D = -ve$) is favoured by solubility of solutes in a solvent.

Acetic acid has a place in organic chemical industry because there is a tendency of extensive recycling and recovery of both unreacted and product formed, when used in the preparation of pharmaceuticals. Acetic acid is used in form of vinegar. It is used directly as a condiment and pickling of vegetables and foodstuffs. It is sprayed on silage as a preservative to discourage bacterial and fungal growth.

Succinic acid is a crystalline solid. It is moderately soluble in water and ethanol, sparingly soluble in ether, but highly soluble in methanol. When heated, a large amount sublimes, the rest is converted into cyclic anhydride, succinic anhydride. When heated with excess of glycol, succinic acid forms high polymer ester (the alkyd resins). In aqueous solution, it ionizes to anions (succinate). It is a precursor to some polyesters. It is also a precursor to polybutylene terephthalate, a thermoplastic the automotive and electronic industries use for the production of connectors, insulators, etc. It is used in food and beverage industry.

Nernst's Distribution law

The phenomenon of distribution coefficient is a direct evidence of the thermodynamic requirement for equilibrium [1-9]. According to Nernst's distribution law, a solute distributes between two solvents. Therefore the ratio of the activities of the substance in the two layers is constant at any given temperature. When a chemical reaction (association, dissociation, etc.) occurs in one of the solvents, then the usual expression is modified by:

$$\frac{C_X^{*A}}{C_X^{*B}} = k_D$$

or

$$\frac{C_X^{*B}}{C_X^{*A}} = \frac{1}{K_D} \quad (3.3)$$

C_X^{*A} is the free concentration of the solute 'X' in solvent A while C_X^{*B} is the free concentration of the solute 'X' in B. k_D is the distribution coefficient.

In the case of dimerization of the solute 'X' in solvent A; both k_D (distribution constant) and the constant for the dimerization reaction, K are used to determine the degree of the distribution of the solute in a chemically reacting system.

Conclusion

Carbon tetrachloride and water system is a good binary solution for the recovery of pure acetic acid by solvent extraction.

Distribution coefficient, k_D is shown herein as a good analytical parameter for the investigation of a solute in a binary immiscible solvents. However, dimerization process is considered a serious interference in solvent extraction principles and calls for the use of more complex relation of the ratio.

The formula $\frac{C_X^A}{C_X^{*B}} = k_D + 2k_D^2 K C_X^{*B}$ is used.

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