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Spectrophotometric Method for Determination of Dissociation Constant of weak acid like 2, 4-Dinitrophenol in 1-Propanol-Water Mixtures at $24.5 \pm 0.5^\circ\text{C}$

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ABSTRACT

Spectrophotometrically dissociation constant (pK_a) of the indicator acid, 2,4-Dinitrophenol in 5,10,20,30 and 40 wt. % 1-propanol – water mixtures at $24.5 \pm 0.5^\circ\text{C}$ were determined. The experimental values of ϵ_{in} -potassium salt of indicator acid and the derived values of intercept of ϵ_{in} -values using Ion-pair intermediate model equation shows a good consistency, suggesting the ion-pair intermediate model is applicable in the present instance. The maximum drop in pK_a was found to occur around 20 wt. % 1-propanol- water mixtures. This has been explained as due to increase in solvation energy for anion of the acid by London- dispersion force mechanism. The drastic increase in pK_a values above 20 wt% propanol has been assumed to be due to decrease in dielectric constant of the medium. This method is suitable for determination of dissociation constant for weak acid and this method will be helpful for determination of dissociation constant for drugs are weak acid in nature.

Key words: Spectrophotometry, Dissociation Constant, Dinitrophenol,

INTRODUCTION

The study of aqueous mixtures has drawn an early attention of many investigators for various physiochemical properties of electrolyte solutions. Such studies in aqueous mixtures are standard potentials of the electrodes, solubility of single ions and electrometric method of determination of dissociation constant of weak acids.

Among the mixed solvents water and alcohol mixtures have been widely used both experimentally and theoretically to understand the type of interaction between the aqueous and non-aqueous polar molecules through hydrogen bonding.

The liquid alcohols, like water, are hydrogen bonded. Although this inter-molecular bonding has a strong influence on the properties of the liquid, it is clear that open structures are not formed as in water. Hydrogen bonding alone cannot account for the oddities in properties that are observed when alcohols are mixed with water.

Franks and Ives.[1] reviewed in detail the structure of alcohol-water mixtures. From the simple view, the hydrophobic hydrocarbon chain in alcohol may be regarded as opposing the effect of the hydrophilic-OH group in its attempt to pull the molecule into solution. The hydroxyl group can form hydrogen bonds with the solvent molecules,

acting either as donor or as acceptor. Glover. [2] determined the dissociation constant of hexanitrodiphenylamine (HNDA) in methanol, acetone, dioxane, water and various water-organic mixtures by spectrophotometric method.

Fong and Grunwald. [3] determined the acid – dissociation constant of HNDA in acetone-water mixtures at 25°C by spectrophotometric method. Study of dissociation of 2,4-dinitrophenol (pK_a in water = 4.09)[#] in 5, 10, 20, 30 and 40 wt.% Propanol – water solvent compositions has been undertaken in this investigation by spectrophotometric method. The proton donating ability of a solvent (Hammett acidity function H_0) to a neutral base was determined spectrophotometrically by Braude and Stern.[4] for solution of HCl in dioxane, water, ethanol, acetone and their mixtures, with m-, p- nitroanilines as proton acceptors. The dissociation constants of substituted phenols, amines, acetic acid, Benzoic, and nitrobenzoic acid have been measured spectrophotometrically by Rene Reynaude.[5] employing various mixtures of water with alcohols, amides, ketones, tetrahydrofuran, and sulfolane as solvents. Measurements were carried out both in the presence of NaOH and HCl. The values were compared in different solvents. Absolute pK_a values of two indicator acids, 2,4- and 2,5-dinitrophenol, have been determined spectrophotometrically by L.M. Mukherjee, J.J. Kelly, W. Baranetzky and J. Sica.[6]. Investigation of mixtures of these indicators with HBr and HNO_3 yield the pK_a value of the latter acids.

MATERIALS AND METHODS

Solvents and Reagents:

Reagents are 2, 4 – Dinitrophenol (98% pure), KOH, HNO_3 (65% pure), Propanol-1(99% pure) and double demineralized water. All other chemicals were high purity reagent grade products.

Method: Ion-pair intermediate model:

Ion-pair intermediate model equation is as below

$$\epsilon_{app.} = \epsilon_{In^-} - \frac{(\epsilon_{app.} - \epsilon')^2}{\epsilon_{In^-} - \epsilon'} \times \frac{f^2 C_t}{K_{HIn}}$$

$$\text{or } K_{HIn} = \frac{(\epsilon_{app.} - \epsilon')^2 f^2 C_t}{(\epsilon_{In^-} - \epsilon')(\epsilon_{In^-} - \epsilon_{app.})}$$

$$\text{or } pK_a = \frac{(\epsilon_{app.} - \epsilon')^2 f^2 C_t}{(\epsilon_{In^-} - \epsilon')(\epsilon_{In^-} - \epsilon_{app.})}$$

It follows from above equation that a plot of $\epsilon_{app.}$ vs. $\frac{(\epsilon_{app.} - \epsilon')^2 f^2 C_t}{(\epsilon_{In^-} - \epsilon')}$ at any wavelength will be a straight line and K_{HIn} will be given by the reciprocal of the slope.

Spectrophotometric Measurements:

The spectra and all absorbance values reported in the thesis were obtained using two spectrophotometers (one is SHIMADZU UV-Visible Recording Spectrophotometer and another Spectro UV-VIS RS spectrophotometer) by selecting wavelength length range 325-600nm. Teflon capped silica cells of 1.00 cm. light path were used throughout. The cells were calibrated and the constancy of calibration was checked periodically by measuring the absorbance of standard potassium chromate in 0.2M KOH solution. All measurements were carried out at the room temperature which was maintained at $24 \pm 0.5^\circ\text{C}$.

Preparation of solution of 2,4 – Dinitrophenol and K-salt of 2,4 – Dinitrophenol:

The initial concentration of 2,4-Dinitrophenol was known by weight and the solvent was 1-propanol – water mixtures. The experimental solutions were made by dilution of concentrated solution with the help of micropipette.

A solution of KOH was prepared by weight and the solvent was 1-propanol – water mixtures. The actual strength of KOH was known by titration with succinic acid by using phenolphthalein indicator. Dilute solution was made by dilution of concentrated KOH solution. The initial concentration of K-salt of 2,4 – dinitrophenol was known by weight and the solvent was the solution of KOH. The experimental solutions were made by dilution of concentrated solution and the solvent used was dilute solution of KOH.

Experimental procedure:

Step1. Determination of absorption maxima of 2,4-Dinitrophenol (DNP) in 1-Propanol – Water Mixtures, Potassium Salt of 2,4-Dinitrophenol (DNP) in 1-Propanol – Water Mixtures, 2,4-Dinitrophenol (DNP) in 1-Propanol – Water Mixtures in presence of non-absorbing acid (Nitric Acid).

Step2. Spectrophotometric study with 2,4-Dinitrophenol (DNP) in 5wt.%, 10wt%, 20wt%, 30wt% & 40wt% 1-Propanol-Water Mixtures at 360 nm & 400nm and determination of ϵ_{app} .

Step3. Spectrophotometric study of Mixtures of 2,4-Dinitrophenol (DNP) and Nitric Acid (HNO_3) in 5wt.%, 10wt%, 20wt%, 30wt%, 40wt% 1-Propanol-Water Mixtures at 360nm and 400nm and determination of ϵ' .

4. Spectrophotometry with potassium salt of 2,4-Dinitrophenol (K-DNP) in 5wt%,10wt%, 20wt%, 30wt% & 40wt% 1-Propanol- Water Mixtures at 360nm and 400nm and determination of ϵ_{in-} .

5. Finally determination of acid dissociation constant pKa from ion pair intermediate model equation..

RESULTS

TABLE- 1: Spectrophotometry of Mixtures of 2,4-Dinitrophenol (DNP) and Nitric Acid (HNO_3) in 5wt.% 1-Propanol-Water Mixtures at 360nm and 400nm.

Con. of 2,4-DNP $\text{M} \times 10^4$	Con. of HNO_3 M	Absorbance at wavelength		$\epsilon_{360} \times 10^4$	$\epsilon_{400} \times 10^4$
		360nm	400nm		
0.8195	0.2	0.150	0.043	0.1830	0.0524
1.6234		0.218	0.047	0.1342	0.0289
2.4629		0.302	0.052	0.1226	0.0211
3.2812		0.388	0.063	0.1182	0.0192
4.0907		0.464	0.069	0.1134	0.0168
4.9145		0.542	0.071	0.1102	0.0144
5.7304		0.625	0.077	0.1090	0.0134
6.5521		0.710	0.085	0.1083	0.0129

Similarly Spectrophotometry of Mixtures of 2, 4-Dinitrophenol (DNP) and Nitric Acid (HNO_3) in 10wt.%, 20wt%, 30wt%, 40wt% 1-Propanol-Water Mixtures at 360nm and 400nm. Calculated all results are presented in figure 1A & 1B and ϵ' at 360nm ϵ' at 400nm was determined.

TABLE- 2: Spectrophotometry with potassium salt of 2,4-Dinitrophenol (K-DNP) in 5wt% 1-Propanol- Water Mixtures at 360nm and 400nm.

Con. of K- DNP $\text{M} \times 10^5$	Absorbance at wavelength		$\epsilon_{in-360} \times 10^4$	$\epsilon_{in-400} \times 10^4$
	360nm	400nm		
0.5210	0.049	0.054	0.8349	0.9210
1.0420	0.095	0.099		
2.0901	0.177	0.195		
3.102	0.260	0.298		
4.1700	0.342	0.382		
5.2140	0.440	0.481		
6.2602	0.523	0.580		
7.3001	0.620	0.681		

Similarly Spectrophotometry with potassium salt of 2,4-Dinitrophenol (K-DNP) in 10wt%, 20wt%, 30wt%, 40wt% 1-Propanol- Water Mixtures at 360nm and 400nm. Calculated all results data represented on figure 2A & 2B.

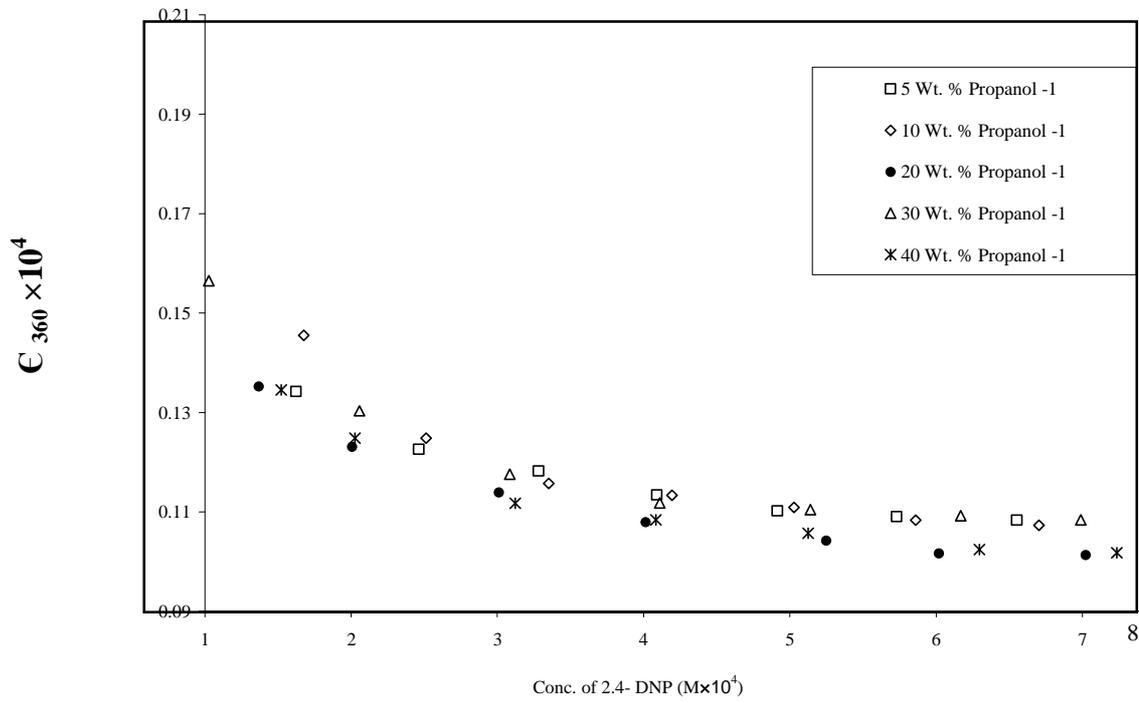


Fig. 1A: Determination of E'_{360} at 360nm

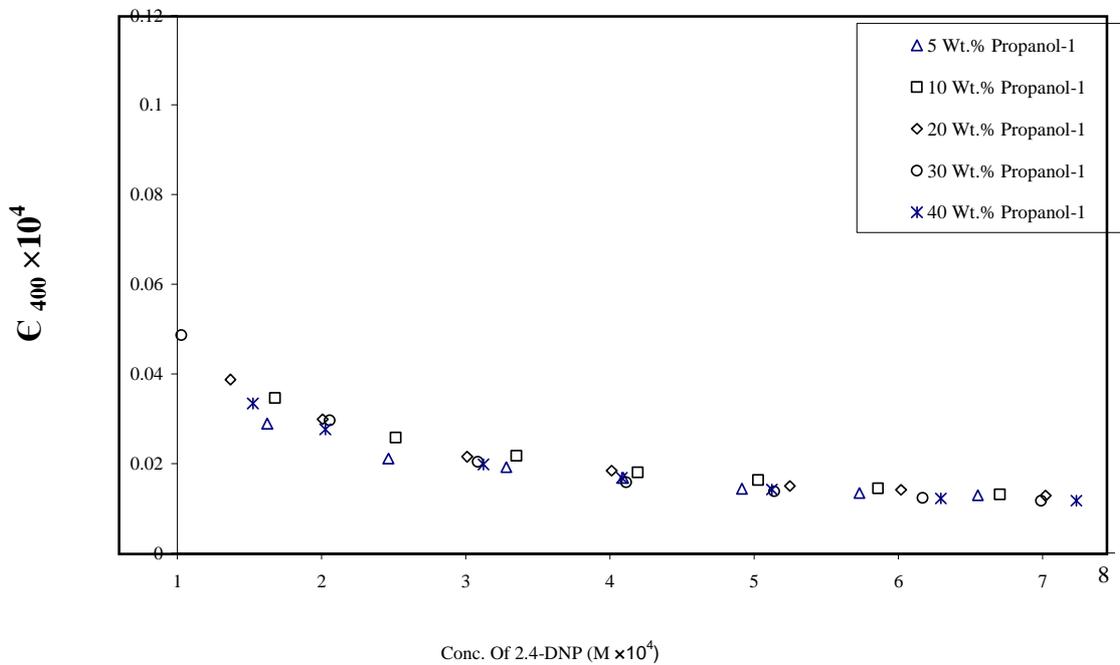


Fig. 1B: Determination of E'_{400} at 400nm

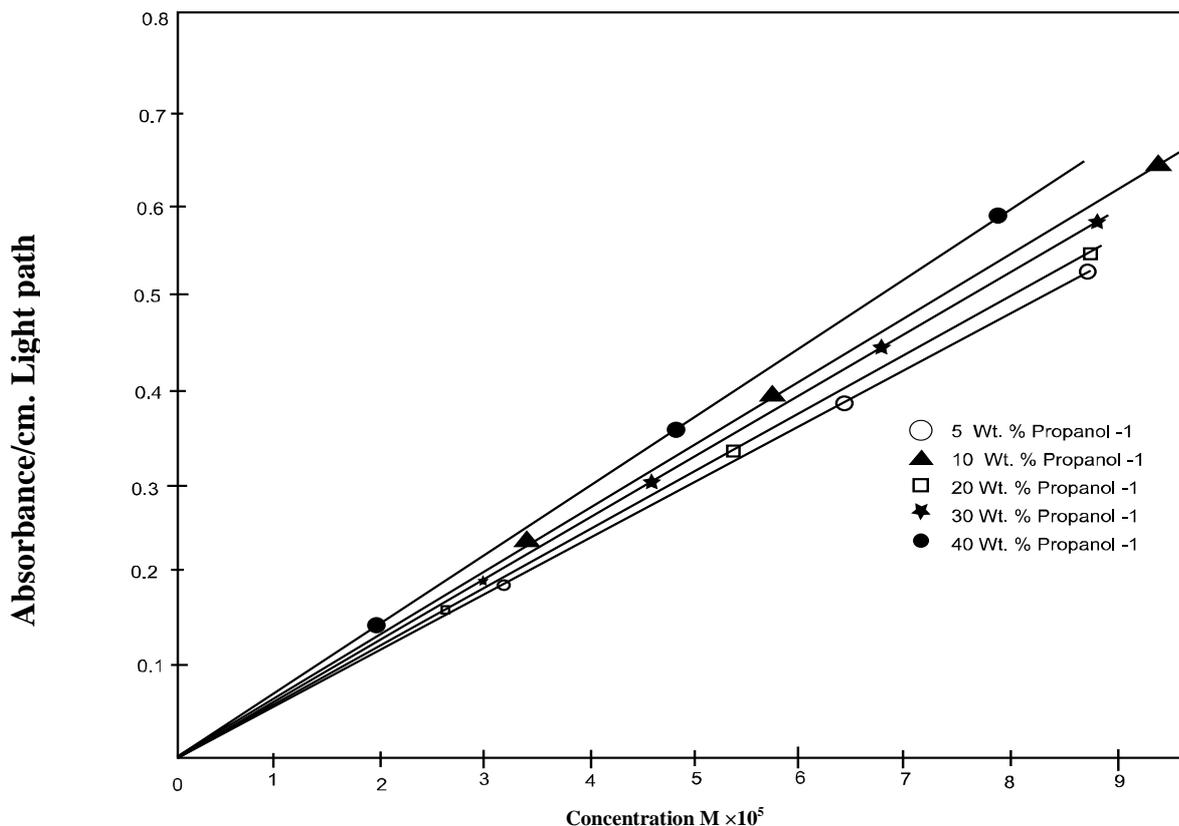


Fig. 2A: Absorbance vs. Concentration of potassium salt of 2,4- Dinitrophenol in 1-propanol –water Mixtures at 360nm. The slopes were calculated by Least- squares method.

TABLE – 3.1 Spectrophotometry with 2,4-Dinitrophenol (DNP) in 5wt.% 1-Propanol-Water Mixtures at 360 nm.

Concentration of 2,4- DNP $M \times 10^5$	Absorbance A	$\epsilon_{app360} \times 10^4$	f^2	$f^2 (\epsilon_{app360} - \epsilon'_{360})^2 \times C_t$
				$(\epsilon_{In_{360}} - \epsilon'_{360})$
0.6681	0.060	0.8980	0.9999	0.0568
1.0023	0.087	0.8680	0.9999	0.0788
1.6701	0.140	0.8382	0.9999	0.1211
2.0043	0.165	0.8232	0.9999	0.1394
2.6721	0.218	0.8158	0.9999	0.1820
3.0064	0.242	0.8049	0.9999	0.1985
3.6765	0.288	0.7833	0.9999	0.2277
4.0082	0.310	0.7734	0.9999	0.2410
4.6761	0.353	0.7549	0.9999	0.2655
5.0121	0.370	0.7382	0.9999	0.2699

$A' = 0.564; \epsilon_{In_{360}} = 0.8349 \times 10^4; \epsilon'_{360} = 0.1158 \times 10^4$

Similarly Spectrophotometry with 2,4-Dinitrophenol (DNP) in 10wt.%, 20wt.%, 30wt.%, 40wt.% 1-Propanol-Water Mixtures at 360 nm was performed. Resulting data presented in figure 3A.

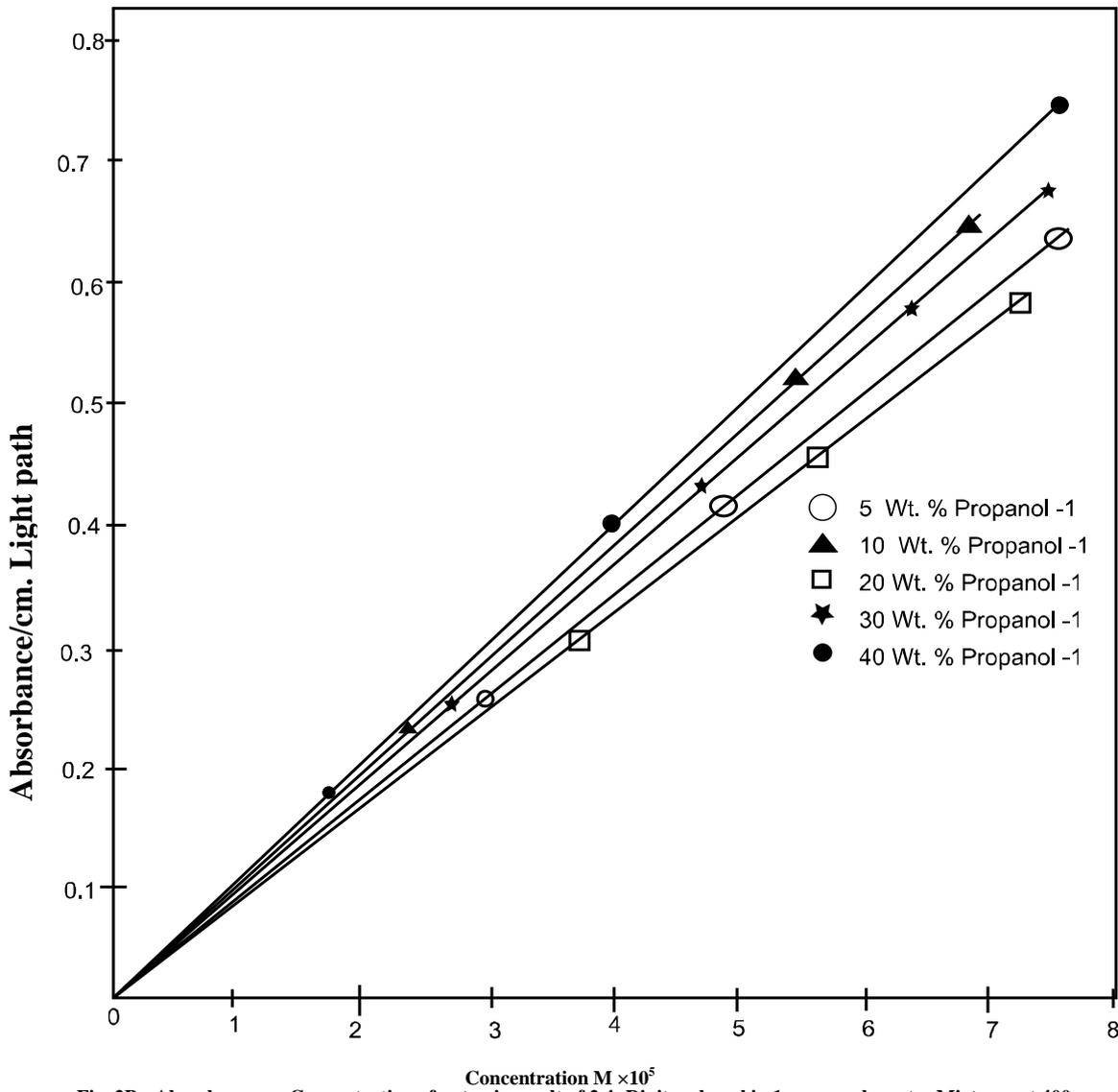


Fig. 2B: Absorbance vs. Concentration of potassium salt of 2,4- Dinitrophenol in 1-propanol –water Mixtures at 400nm. , The slopes were calculated by Least- squares method.

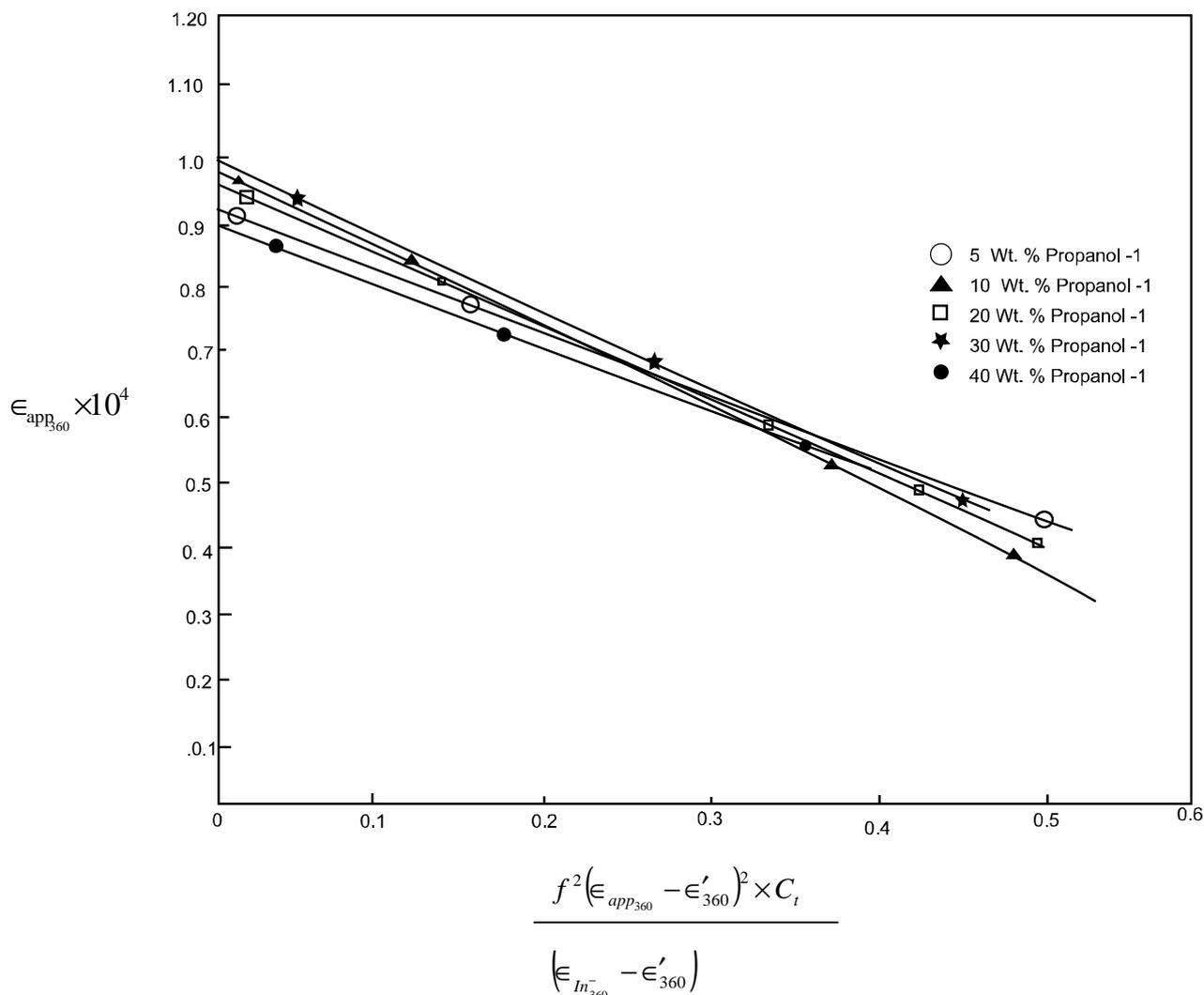


Fig. 3A: Plots of equation (3.13) for 2,4-Dinitrophenol in 1-propanol-water Mixtures at 360nm. The slopes and intercepts were obtained from the Least – Square method.

TABLE 3.2 Spectrophotometry with 2,4-Dinitrophenol (DNP) in 5wt.% 1-Propanol-Water Mixtures at 400 nm.

Concentration of 2,4- DNP M × 10 ⁵	Absorbance A	ε _{app400} × 10 ⁴	f ²	$f^2(\epsilon_{app400} - \epsilon'_{400})^2 \times C_t$
				$(\epsilon_{m400} - \epsilon'_{400})$
0.6681	0.062	0.9280	0.9999	0.0613
1.0023	0.090	0.8979	0.9999	0.0860
1.6701	0.143	0.8562	0.9999	0.1301
2.0043	0.168	0.8381	0.9999	0.1495
2.6721	0.220	0.8233	0.9999	0.1922
3.0064	0.245	0.8149	0.9999	0.2117
3.6765	0.291	0.7915	0.9999	0.2440
4.0082	0.313	0.7808	0.9999	0.2587
4.6761	0.357	0.7634	0.9999	0.2882
5.0121	0.380	0.7581	0.9999	0.3045

A' = 0.564; ε_{m400} = 0.9210 × 10⁴; ε'400 = 0.0168 × 10⁴

Similarly Spectrophotometry with 2,4-Dinitrophenol (DNP) in 10wt.%, 20wt.%, 30wt.%, 40wt.% 1-Propanol-Water Mixtures at 360 nm was performed. Resulting data presented in figure 3B.

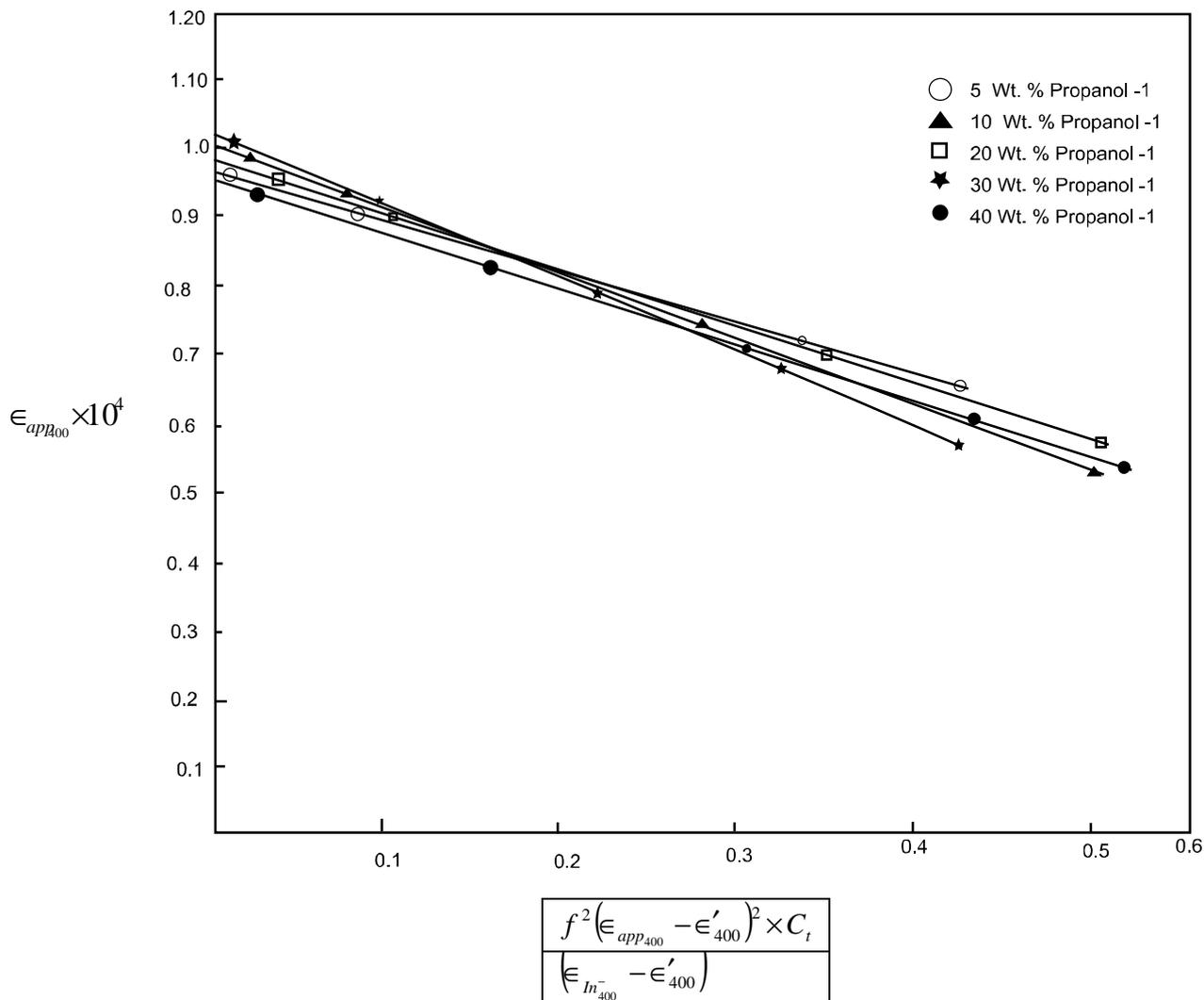


Figure 3B: Plots of equation (3.13) for 2,4 –Dinitrophenol in 1-propanol-water Mixtures at 400nm. The slopes and intercepts were obtained from the Least – Square method.

TABLE-4 Summary of ϵ_{in-} values of 2,4-Dinitrophenol (DNP) at different wt.% of 1-Propanol-Water Mixtures at 360nm and 400nm.

Wt.% of Propanol	$\epsilon_{in_{360}} \times 10^4$		$\epsilon_{in_{400}} \times 10^4$	
	Experimental	Intercept	Experimental	Intercept
5	0.8349	0.9245	0.9210	0.9538
10	0.8603	0.9884	0.9514	1.0197
20	0.8430	0.9539	0.9146	0.9671
30	0.8595	0.9936	0.9447	1.0284
40	0.8717	0.9062	0.9776	0.9339

RESULTS AND DISCUSSION

Typical spectra of 2,4 – Dinitrophenol (DNP) in 5,10,20,30, and 40 wt.% 1-propanol- water mixtures shows that in all the media the system exhibits absorption maxima at 360nm and 400 nm . The spectra of the Potassium salt of 2, 4 – Dinitrophenol (K-DNP) shows the maxima at 360 nm and 400nm. In the presence of a non-absorbing acid (HNO₃)

the peak tends of shift towards low wavelength region.

The results of 2,4-Dinitrophenol at the two absorbance maxima i.e, 360 nm and 400nm in different 1-propanol – water mixtures are summarized in separate tables. The absorbance vs. concentration plots of 2,4-Dinitrophenol reveal that Beer’s law is not obeyed at 360nm and 400nm. Based on this small curvature of the plots at 360 nm and 400nm. From spectral result it was decided to use the wavelength 360 nm and 400nm to test the applicability of ion-pair intermediate model equation in the present case.

Accordingly, the values of ϵ' at 360 nm and 400nm was determined from the limiting spectrum of the indicator containing different amounts of nitric acid which does not absorb at the selected wavelength. Plots of molar absorptivities of the indicator vs. the concentration of 2,4 -Dinitrophenol at 360 nm. and 400nm which are in Figure 1A and 3.7. The linear portions of the Figure 3.6 and 3.7 are extrapolated to zero acid concentration and the extrapolated values of ϵ' so obtained are taken to give ϵ' (equation 3.11) for the wavelength 360 nm and 400nm.

Beer’s law is valid at 360 nm and 400nm for solutions of potassium salt of 2,4-Dinitrophenol over the range of concentration of interest. The results of spectrophotometry with Potassium salt of 2,4-Dinitrophenol in different wt.% 1-propanol- water mixtures at 360 nm and 400nm. The constant ϵ_{in} . at 360 nm and 400nm was evaluated from the slope of the absorbance vs. concentration plots of the Potassium salt of 2,4- Dinitrophenol, the final trial of the ion-pair intermediate model equation is illustrated in Figure 3A and 3B and the derived values of the intercepts (ϵ_{in}) for different solvent compositions are given in Tables 4 along with the experimental values of the constant based on the absorbance data of the Potassium salt used. The two sets of ϵ_{in} . values, obtained from the experimental values based on the absorbance data of Potassium salt (Figure 2A and 2B) and the derived values of intercept for different solvent compositions (Figure 3A and Figure 3B) using ion-pair intermediate model equation, show a good consistency, suggesting that ion - pair mechanism is applicable in the present instance.

The values of pK_a of 2,4-Dinitrophenol in 5,10,20,30 and 40 wt. % have been given in table 5. The plot of pK_a vs. wt.% of 1-propanol-water given in figure 4 shows that at first the pK_a values of 2,4-Dinitrophenol in 1-propanol-water mixtures decreases up to 20 wt.% of propanol and then increases with the increase of propanol content.

A similar trend in pK_a vs. 1/D plots of other weak acids was reported [1,2,7] earlier in alcohol- water binary mixtures. In cases of indicator acids like mono-,di-, tri- and hexa-nitro phenolic acid, an initial decrease in pK_a with the increase of non – aqueous liquid concentration in water- non-aqueous liquid mixtures was observed by Fong and Grunwald [2] and Habibullah.[7] They considered that for an initial decrease in pK_a at lower alcohol/non-aqueous liquid region, the dispersive force is dominant over the electrostatic force caused by the lowering of dielectric constant and thereby an overall decrease in pK_a was observed up to 20 wt.% concentration of alcohol / non-aqueous component in the solvent mixture. In our case, the initial increase of the dissociation of the DNP upto 20 wt% propanol is a results of large preferential increase in solvation energy of the anion of DNP through London-dispersion interaction of the propanol molecules with the chromophoric nitrogen atom and the two nitro groups of the DNP. After that composition range, the electrostatic force of attraction predominates over the dispersive force as a result of which pK_a increases with the increase of the concentration of the non – aqueous component of the binary solvent mixture.

Table-5 Summary of pK_a values of 2,4-Dinitrophenol (DNP) in 1-Propanol-Water ,Mixtures at 360nm and 400nm.

Wt.% of propanol	pK_a at 360nm.	pK_a at 400nm.
0	4.09 \neq	4.09 \neq
5	3.81	3.82
10	3.74	3.73
20	3.66	3.64
30	3.85	3.87
40	3.89	3.91

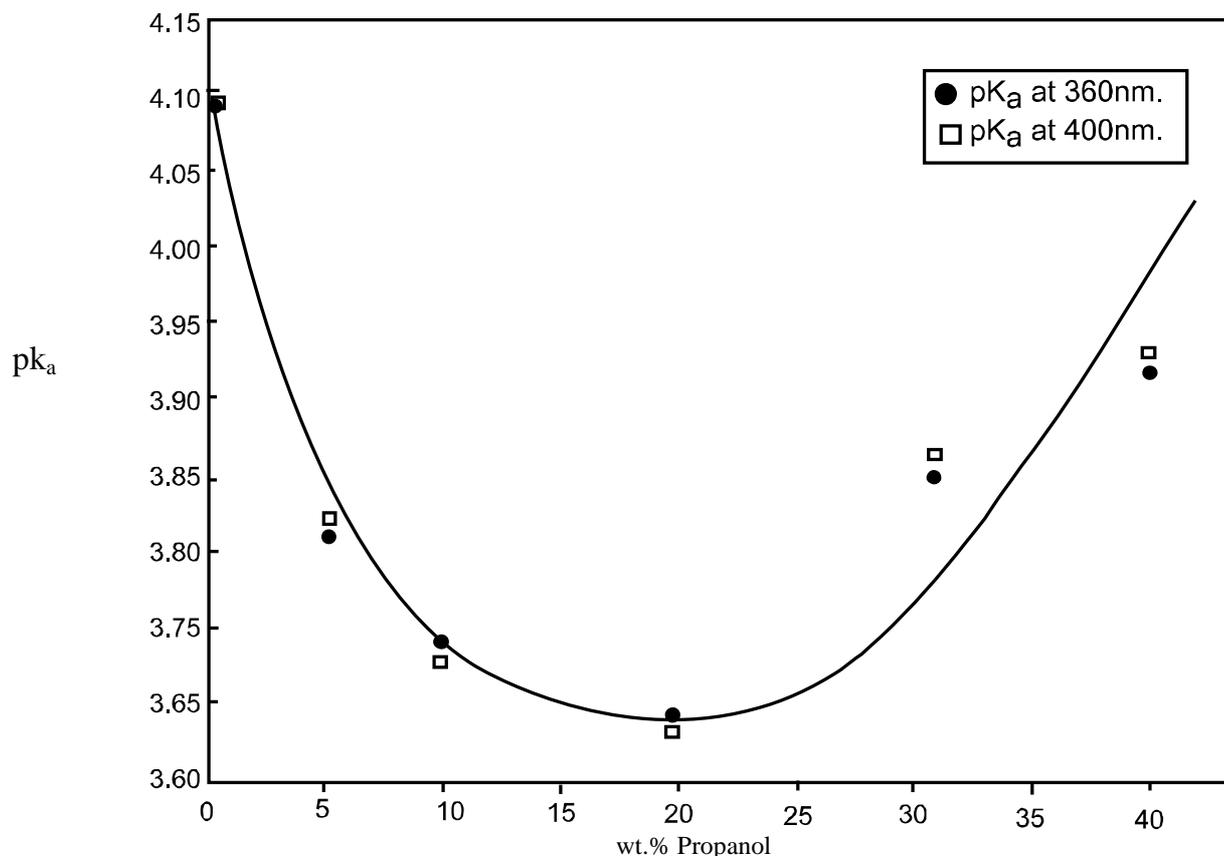


Fig. 4 :Plot of (pKa) 2,4- Dinitrophenol vs. wt.% Propanol

CONCLUSION

The study helps to determine the dissociation constant of weak acid. The dissociation constant of weak acid will help in understanding the chemistry of weak acid in aqueous medium as well as provide information in the area of electrochemistry. Similarly this type of study helps us to understand the dissociation, solubility of drugs are weak acid in nature. The values of pKa and pH are especially important to understand solubility profile, absorption, distribution of drug and drug product. So this study will contribute greatly in the field of pre-formulation study, formulation & dosage form development and drug delivery of drugs are weak acid in nature.

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