# Spectrophotometric method of determination of dissociation constants of 2,5-dinitrophenol in ethanol-water mixtures at 25±0.5ºC

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## ABSTRACT

*Dissociation constants ($K_a$) of an indicator acid, 2,5-dinitrophenol in 20, 40, 50, 60 and 70 wt.% ethanol-water mixtures at $25\pm0.5^0C$ temperature were determined spectrophotometrically. The pure indicator acid and potassium salt of indicator acid show maxima at 450 nm in the visible range. At first the spectrophotometric data have been analyzed in terms of an ion-pair intermediate model. But the experimental values of $\epsilon_{In^-}$ potassium salt of indicator acid and the derived values of intercept of $\epsilon_{In^-}$ using ion-pair intermediate model show a sharp difference. So this model was not applicable in this case. For this an alternative treatment, simple dissociation model has been applied. The maximum drop in $pK_a$ was found to occur around 20 wt.% ethanol-water mixtures. This has been explained as due to increase in solvation energy for anion of the acid by London Dispersion Force Mechanism. The dramatic increase in $pK_a$ values above 20 wt.% ethanol has been assumed to be due to decrease in dielectric constant of the medium.*

**Key words**: dielectric constant, 2,5-dinitro phenol, dissociation constant, ethanol.
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## INTRODUCTION

There has been much attention on the use of binary solvent systems for many purposes and practical applications. These mixtures have also been used as solvents in the study of various physiochemical properties of electrolyte solutions [1-4]. Among the mixed solvents, water and alcohol mixtures have been widely used both experimentally and theoretically to follow the type of interaction between the polar and non-polar molecules through hydrogen bonding.

Liquid water according to the view of Frank and Wen [5] has been considered to have a remarkable self-stabilizing three dimensional hydrogen bonded flickering clusters with life times of the order of $10^{-11}$ seconds. These entities are maximally hydrogen bonded and voluminous making water open structured liquid full of cavities.

The liquids, alcohols, like water are hydrogen bonded. Although this intermolecular 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 oddity in properties that is observed when alcohols are mixed with water.

Franks and Ives [6] reviewed in detail the structure of alcohol-water mixtures. From the simple view, the hydrophobic hydrocarbon group in alcohol may be regarded as opposing the effect of the hydrophilic hydroxyl 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 acceptor.

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It now seems clear that the initial addition of alcohol to the mixture increases the degree of structure through co-operative effort to which hydrogen bonding is the key. The alcohol molecules though opposing have a certain affinity for water and become trapped in the interstices of the existing three dimensional cluster network. With more introduction of alcohol, the structural breakdown in water ensues, the sooner the more foreign is the invader alcohol. On the other hand, with the addition of small amount of water to alcohol, the changes in the physical properties of alcohol are less profound than observed on adding small amount of alcohol to water as alcohol is less structured than water.

This is why, to show a medium effect and to gather evidence on the role of ethanol in the ethanol-water mixtures as solvents, a study of dissociation of 2,5-dinitrophenol in 20, 40, 50, 60 and 70 wt.% ethanol-water solvent compositions has been undertaken in this investigation by spectrophotometric method.

## MATERIALS AND METHODS

2,5-Dinitrophenol (Aldrich, 80% pure), KOH (E. Merck, 99.8% pure), $HNO_3$ (E. Merck, 65% pure) and Ethanol (E. Merch, 99.9% pure) were used as reagents. 2,5-dinitrophenol was purified by recrystallization from ethanol. The vacuum dried product melted at 113ºC [7]. The recrystallized 2,5-dinitrophenol was kept over $CaCl_2$ in a vacuum desiccator. Analysis of the recrystallized sample gave a purity of 100%. The recrystallized sample was carried out free from moisture and carbondioxide. Double distilled water with the specific conductance $1.2$-$1.3 \times 10^{-6}$ $ohm^{-1}cm^{-1}$ was used for sample preparation.

The initial concentration of 2,5-dinitrophenol was known by weight using ethanol-water mixtures as solvent. The experimental solutions were made by dilution of concentrated solution with the help of micropipette. A solution of KOH was prepared by weight and ethanol-water mixture was also used as solvent. The actual strength of KOH solution was determined by titration with succinic acid using phenolphthalein as an indicator. Dilute solutions were made by dilution of concentrated KOH solution. The initial concentration of K-salt of 2,5-dinitrophenol was known by weight and the solution of KOH was used as solvent. The experimental solutions were made by dilution of concentrated solution and the solvent used was dilute solution of KOH.

The spectra and absorbance values were obtained using two spectrophotometers (one was SHIMADZU UV-Visible Recording Spectrophotometer–Model 180 and another was CINTRA UV-Visible Spectrophotometer) by selecting wavelength at 450 nm. Teflon capped silica cells of 1.00 cm light path were used throughout. The cells were calibrated and the constancy of calibration was checked by measuring the absorbance of standard potassium chromate in 0.05 M KOH solution periodically. All the measurements were carried out at 25±0.5ºC temperature.

## RESULTS AND DISCUSSION
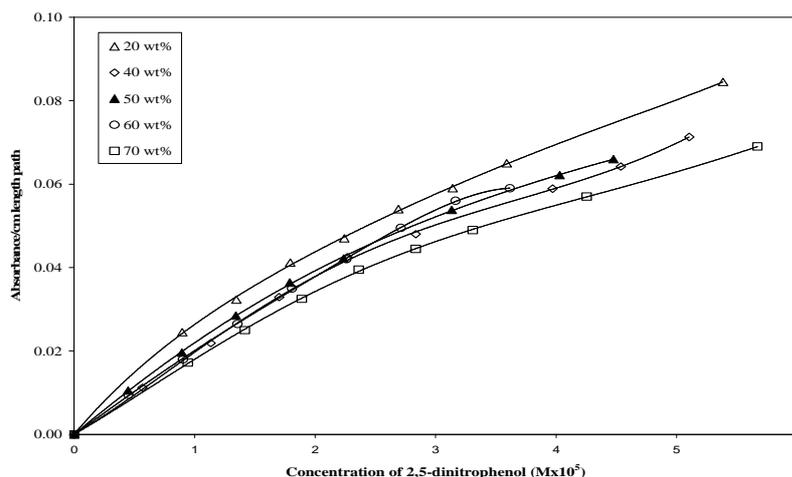


**Fig. 1. Plots of absorbance versus concentration of 2,5-dinitrophenol in ethanol-water mixtures at 450 nm**

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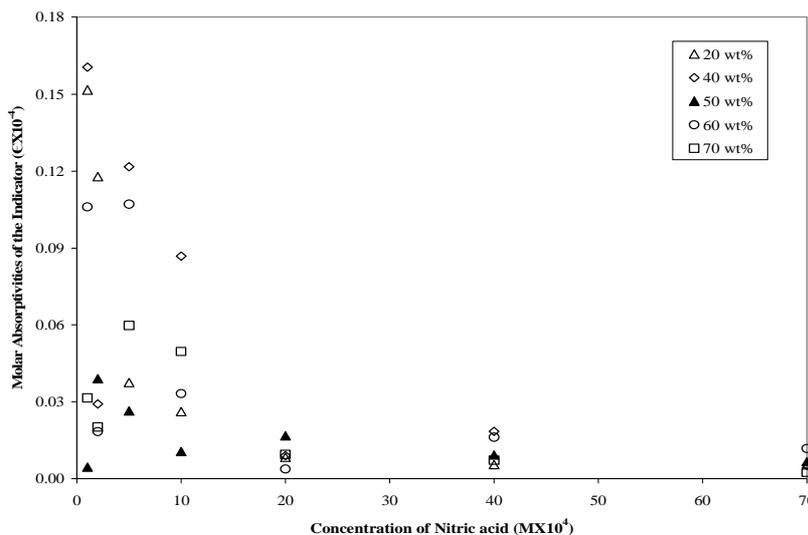


**Fig. 2. Plots of molar absorptivities of the indicator versus concentration of nitric acid in ethanol-water mixtures at 450 nm**
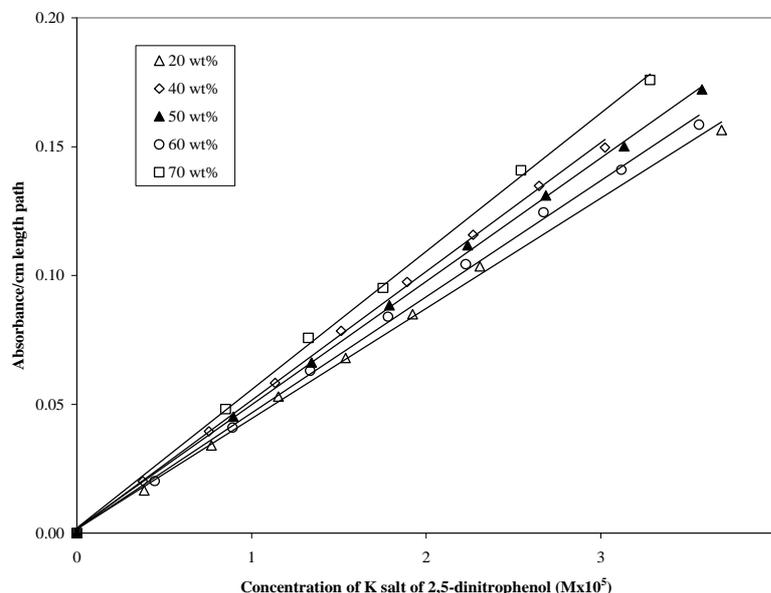


**Fig. 3. Plots of absorbance versus concentration of potassium salt of 2,5-dinitrophenol in ethanol-water mixtures at 450 nm**
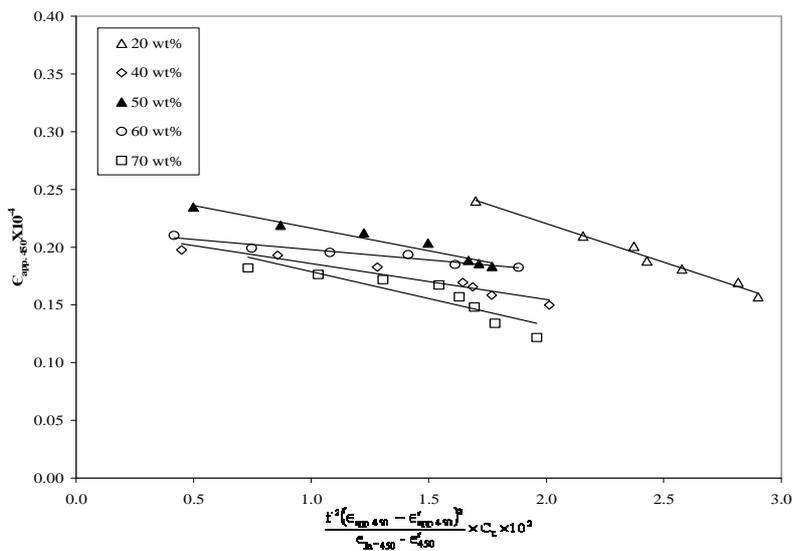


**Fig. 4. Plots of $\epsilon_{app.}$ versus $\dfrac{f^2\left(\epsilon_{app.\ 450} - \epsilon'_{450}\right)^2}{\epsilon_{In^-\ 450} - \epsilon'_{450}} \times C_t$ for 2,5-dinitrophenol in ethanol-water mixtures at 450 nm**

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**Table 1. Summary of $\epsilon_{In^-}$ and $pK_a$ values of 2,5-dinitrophenol in different wt.% of ethanol-water mixtures at 450 nm**

| Wt.% of Ethanol | $\epsilon_{In^-} \times 10^{-4}$ | | $pK_a$ |
|---|---|---|---|
| | Experimental | Intercept | |
| 20 | 0.4550 | 0.3540 | 5.04 |
| 40 | 0.4920 | 0.2370 | 5.30 |
| 50 | 0.4926 | 0.2524 | 5.42 |
| 60 | 0.4780 | 0.2160 | 5.53 |
| 70 | 0.4270 | 0.3382 | 6.63 |

From the typical spectra of 2,5-dinitrophenol (2,5-DNP) and potassium salt of 2,5-dinitrophenol (K salts of 2,5-DNP) in 20, 40, 50, 60, and 70 wt.% ethanol-water mixtures we can find that in all the media the indicator 2,5-DNP exhibits absorption maxima at 350 nm (ultraviolet) and 450 nm (visible) but K salts of 2,5-DNP exhibits absorption maxima at only one of these two wavelengths i.e., at 450 nm (visible). In the presence of a non absorbing acid ($HNO_3$) the peak tends to shift towards low wavelength (350 nm) region.

The values of absorbance as a function of concentration of 2,5-dinitriphenol in ethanol-water mixtures at 450 nm represented by the Fig.1 reveal that Beer's law is not obeyed at 450 nm. Based on this small curvature of the plots at 450 nm, it was decided to use the wavelength 450 nm to test the applicability of ion-pair intermediate model [7] in the present case. The ion-pair intermediate model equation is as follows:

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

where, the apparent molar absorptivity, $\epsilon_{app.}$, is defined as, $\epsilon_{app.} = \dfrac{A}{bc_t}$ here, A is the observed

absorbance at a particular wavelength, b is the light path (cm) and $C_t$ is the total analytical concentration of the indicator.

For evaluation of f, the Debye-Huckel limiting law was used. Thus, in terms of the experimental quantities

$$-\log f = A' \sqrt{\frac{\epsilon_{app.} - \epsilon'}{\epsilon_{In^-} - \epsilon'} \times C_t}$$

where the limiting slope A′ will assume values characteristic of the dielectric constant of the different ethanol-water mixtures used [8].

Therefore, $A' = 1.8246 \times 10^6 / (DT)^{3/2}$

where, D and T are the dielectric constant and the temperature in absolute scale respectively.

The values of $\epsilon'$ at 450 nm were determined from the limiting spectrum of the indicator containing different amounts of nitric acid which does not absorb at the selected wavelength. The values of molar absorptivities, $\epsilon$ of the indicator as a function of concentration of an added non-absorbing acid ($HNO_3$) at 450 nm are shown in Fig. 2. The linear portions of the plots were extrapolated to zero acid concentration and the extrapolated values of $\epsilon$ so obtained were taken to give $\epsilon'$ for the wavelength 450 nm.

Beer's law is valid at 450 nm for solutions of potassium salt of 2,5-dinitrophenol over the studied concentration range. The values of absorbance as a function of concentration of potassium salt of 2,5-dinitrophenol are shown in Fig. 3. The values of the constant $\epsilon_{In^-}$ at 450 nm was evaluated from the slope of the absorbance versus concentration plots of the potassium salt of 2,5-dinitrophenol. The final trial of ion-pair intermediate model is illustrated in Fig. 4.

The two sets of $\epsilon_{In^-}$ values, obtained from the experimental values based on the absorbance data of potassium salt of 2,5-dinitrophenol and the derived values from the intercept of ion-pair intermediate model equation plots for different solvent compositions as shown in Fig. 4 are represented in Table 1. The values show a remarkable

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difference suggesting that ion-pair model is not applicable in the present instance. So, an alternative simple dissociation model has been used to calculate the $pK_a$ of 2,5-dinitrophenol.

The values of $pK_a$ of 2,5-dinitophenol in 20, 40, 50, 60 and 70 wt.% ethanol-water mixtures ($pK_a$ of 2,5-DNP in water is 5.24 [9]) represented in Table-1 shows that at first the $pK_a$ values of 2,5-dinitrophenol in ethanol-water mixtures decreases up to 20 wt.% of ethanol and then increases with the increase of ethanol content. Presently found values are almost in agreement with the earlier workers [10-11]. This trend is due to the initial decrease in $pK_a$ at lower alcohol 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 component in the solvent mixture. 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 mixtures.

## CONCLUSION

The study of dissociation constants of 2,5-dinitrophenol in different composition of ethanol-water mixtures helps us to understand the behaviour of weak acid in alcohol-water mixtures. This type of study also provides an opportunity to find the applicability of ion-pair intermediate model and simple dissociation method in the determination of $pK_a$ of weak acid in ethanol-water mixtures. From our study we can find that ion-pair intermediate model is not applicable but simple dissociation model is applicable in our case.

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