TO STUDY THE EFFECT OF ADDITION OF ANTIBIOTIC DRUGS ON AQUEOUS ALCOHOL AND AQUEOUS ACETONITRILE

Final report of

Minor Research Project

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Regional Office, Ganeshkhind, Pune

By

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I N D E X

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In the present project work the experimental procedure requires the measurement of density, viscosity, Ultrasonic velocity of different solvents and solution.

Experimental Work: For the determination of density, viscosity, and Ultrasonic velocity following method is used.

Water: Deionised water was distilled thrice .0.2 gm $KMnO_4$ and 0.5 gm NaOH was added to each liter of distillate. This solution was distilled and was used for the preparation of different composition of Acetonitrile and Ethyl alcohol.

Solvent Acetonitrile and ethyl alcohol (Hi Media) was purified by standard procedures. The purity of solvents was checked by comparing densities, viscosities, with literature values.

Sample liquid	T. Density gm/cm^3 at 27^0	T. Viscosity centipoise	E. Density gm/cm^3	E.Viscosity Centi poise
Ethyl Alcohol	0.7869	1.201	0..7865	1.2141
Acetonitrile	0.78	0.3435	0.77584	0.3435

Solutes Ampicillin, streptomycin, ciprofloxacin hydrochloride of Himedia were used after checking their purity.

For the measurement of density, viscosity and ultrasonic velocity values different systems were prepared as follows 10%, 20%, 30 % aqueous ethanol and aqueous Acetonitrile solvent solutions were prepared. From these solvents 0.002, 0.004, 0.005, 0.006, 0.008, .01 M solutions of Ampicillin, ciprofloxacin, Streptomycin ternary solutions were prepared.

Density Measurement:

For the determination of partial Molal Volume, apparent Molal volume , partial Molal compressibility , apparent Molal Compressibility values of different systems , density values were determined with the help of specific gravity bottle and water is used as reference.

Density bottle was washed with chromic acid and then with distilled water. The density bottle was dried. The weight of density bottle was taken on digital balance .The density bottle was filled with triple distilled water. The water sticking the outer wall was dried by clean Whatmann paper. The weight of distilled water was weighed and weight was recorded.

Similarly weights of 10%, 20%, 30%, aqueous ethyl alcohol and aqueous Acetonitrile were recorded. Similarly weights of 0.002 , 0.004 ,0.005, 0.006 , 0.008 , .01 M solutions of Ampicillin , ciprofloxacin , Streptomycin ternary solutions in 10% , 20%, 30% ,aqueous ethyl alcohol and aqueous Acetonitrile was recorded.

Viscosity measurement:

Mansingh Survismeter (Borosil make) was used to determine time flows of 10% , 20%, 30% ,aqueous ethyl alcohol and aqueous Acetonitrile and 0.002 , 0.004 ,0.005, 0.006 , 0.008 , .01 M solutions of Ampicillin , ciprofloxacin , Streptomycin ternary solutions in 10% , 20%, 30% ,aqueous ethyl alcohol and aqueous Acetonitrile . The instrument was cleaned and washed with acetone and distilled water. The time flow was recorded for each solution.

Coefficient of viscosity was calculated from equation $\eta = \frac{d}{d_0}\frac{t}{t_0} \times \eta_0$

Where η = Coefficient of viscosity of solution , η_0 = Coefficient of viscosity of solvent , d= density of solution , d_0 = density of solvent, t= time flow of solution , d_0 = time flow of solvent .

Ultrasonic Measurements:

For the Ultrasonic Measurement m-81 ultrasonic Interferometer supplied by Mittal Enterprises Delhi , was used with measuring frequency 2 MHZ and frequency tolerance of ± 20 .2 % .

Principle : It employees the principle of formation of standing wave between transducers and flat reflector . The x- cut quartz crystal fitted at the of measuring cell produces ultrasonic waves of known frequency. These waves travels through the liquid and get reflected back from the movable metallic plate kept parallel to current through the plate is integral multiple of half of the wavelength , standing waves are set up in the .

The reflected waves arriving back at the crystals are out of phase. This causes decrease in amplitude of crystal oscillation and is accompanied by alternating current through the crystal. The driving oscillator is closely coupled to l. c circuit with quartz crystal in parallel with capacitor . Both l.C circuit and an oscillator are tuned to resonant frequency of the crystal and current through the crystals is measured. When the position of reflector is changed their is variations in crystal current . The distance between sharp minima or maxima is half wavelength in medium . Knowing the crystal frequency the wavelength , velocity of sound in medium can be calculated

Assembly of interferometer:

The main parts of interferometer are 1) quartz crystal 2) Radio frequency oscillator 3) Cell and measuring assembly

1) Quartz crystal : Quartz crystal is crystalline form of silicon di oxide. The crystal possesses three polar axes at 600 to each other. The axes are called x, y, z axis. The x- cut quartz crystal is widely used. When electric field is applied to the crystal in x- direction ,strain is produced in crystal along x-direction . Hence such crystals are used to produce and detect compressional wave in x-direction. A transducers for producing ultrasonic wave is circular plate of diameter 1 cm cut from x-cut crystal. The circular plate is gold plated on both sides such that sides act as electrodes . When the potential difference is of 1 volt is applied across the electrodes the thickness of plate changes by about $2x10^{-12}$ m . on reversing the voltage strain changes sign , it

changes from extension to compression and vice versa .So when sinusoidal voltage is applied across the transducers it vibrates and when natural frequency of vibration of plate is equal to the frequency of applied voltage , resonance takes place and plate vibrates with large amplitude . If the amplitude of oscillation becomes very large , due to increased strain , the quartz crystal may crack . Hence a.c voltage applied is kept low.

Radio Frequency oscillator:

This is fixed frequency oscillator , the frequency of which is controlled by quartz crystal in the power of amplitude for the circuit . when R.F power is drawn , the micrometer show constant current due to d.c . Voltage applied across it. The oscillator provides the voltage of about 400 volt across this crystal. R. F generator is used to excite the x- cut quartz crystal fitted at the bottom of the measuring cell .

Cell and Assembly measurements :

It is specially designed double wall cylindrical vessel of outer diameter 3.96 cm and inner diameter 0.87 cm. Height of the cell is 9.25 cm. It has capacity to hold 12 ml liquid .Water can be circulated through the annular space between the walls for maintaining the temperatures of liquid in the cell . X- Quartz crystal described above is fitted at the bottom of the cell. Inner wall of the cell is corrugated to prevent the cell wall reflection . The electrical contact to lower the face of crystal is made by vertical electrodes coming from the solid base . The fitting of the cell in solid

base is made by the screw . The reflector is connected to cylindrical plug. The upper end of the plug is connected to lower end of the screw by means of locking ring . A fine micro meter having least count of 0.001 cm for the motion of reflector . Hence position of reflector can be accurately measured upto the 4^{th} decimal . The distance 2.5 cm is available for the movement of the micro meter screw.

Procedure for the measurements of ultrasound velocity:

The cell of the interferometer was filled with redistilled water . The cell assembly was connected to interferometer .The needle of the ammeter was adjusted in the range of 10 to 40 , with the help of adjusting knob. Instrument was allowed to warm for some time to get steady range . Micro meter reading was noted. Screw was moved clock wise to get maximum deflection . The movement of screw was continued for 5 maxima , after returning back of the needle to the original position , micro meter reading was noted .

The distance between initial and last reading after 5 deflection gives the distance traveled by five maxima . The distance traveled by for one maxima is determined by dividing the distance traveled by five maxima . Same procedure is repeated many times to get accurate values of distance . The cell is made empty , dried and then filled with water ,again the procedure is repeated . With the help of water ultrasound velocity , accuracy of the instrument was checked . For the measurement of sound

velocity of different sample solution , same procedure is repeated , to get distance traveled by micro meter screw for one maxima . In the present work all the measurements of of ultrasound velocity was made at 2 MHZ. frequency .

The observed value of sound velocity of distilled water was found to be 1499.50 at 30^0 temperature which was in agreement with literature value 1496.3 m/s . All the values were made at constant temperature of 30^0 . Temperature was controlled by using thermostatic bath.

Calculation of Ultrasonic Velocity :

From the interferometer we get the value of 'D ' distance traveled by micro meter screw to get one maxima . From the value of D the wavelength of ultrasonic wave was calculated by equation 2D = wavelength

Velocity of ultrasonic wave is calculated by equation

Ultrasonic Velocity = wavelength x Frequency

U= wavelength x2

Velocity in this case m/s .

Result And Discussion :

Thermodynamic properties are generally convenient parameters for interpreting solute – solvent interactions in solution phase . Various concept regarding molecular process in solution such as electrostriction [1] , hydrophobic hydration [2], micellization [3] and cosphere overlap during solute –

solvent interactions [4,5] have to some extent been derived from the partial molar volume data of derived compounds viscosity , density , ultrasonic velocity measurements of electrolyte solution are excellent tool to detect solute – solvent , solute – solute interactions . These interactions in case of electrolytes in water -n-alkanol mixture have been studied by many workers, but such investigations in aqueous alcohol and aqueous acetonitrile mixture are scanty . Hence in order to investigate solute – solvent , solute – solute interactions , the apartment molal compressibilities (φ_k) , apartment molal volumes (φ_v), of different drugs such as Ampiciiln , Ciprofloxacin ,and Streptomycin were determined by measuring their sound velocities , densities , viscosities in 10%, 20 % ,30% binary solvent aqueous acetonitrile and aqueous alcohol. The limiting apartment molal volumes ($\varphi^0 v$) of these drugs have also been evaluated in solvent - water mixture at low concentration version (0.001 to 0.01) at room temperatures 30 ^{0}. The values of apartment molal volumes (φ_v) have been used to discuss the interactions of ions in the medium of different dielectric constants.

It has been found that the ultrasonic velocity of drugs Ampicillin, ciprofloxacin , and streptomycin found to increase with concentration .This indicate that the ultrasonic velocity data can be made to fit in the relation.

$(\mu - \mu_o) = fm$

Where μ is the velocity of solution and μ_o = is the velocity of solvent at different concentration m. It is observed that value of $(\mu - \mu_o)$ varies with concentration at each compression in same proportion .

The adiabatic compressibility β_0 was deduced from equation

$\beta_0 = \frac{1}{\mu d}$ where μ is ultrasonic velocity and density of solution.

It has been found that adiabatic compressibility decreases with increasing concentration in all three drugs i.e Ampicillin, ciprofloxacin , and streptomycin in aqueous acetonitrile and aqueous ethanol this is due to dispersion solvent molecule around ion supporting weak ion solvent interaction.

Thus the variation of adiabatic compressibility with concentration can be represented by the relation deduced by Bachem [6].

$\beta_0 = \beta_{0s} + Am + Bm^{3/2}$

Where β_0 is adiabatic compressibility of solution and β_{0s} is adiabatic compressibility of solvent A and B are intercepts and slopes of linear plots of $(\beta_0 - \beta_{0s})/m$ versus $\sqrt{m}$. A linear relation has been found in each case.

Apparent Molal Volume φ_v

Apparent Molal Volume φ_v was calculated from the equation

Apparent Molal Volume $\varphi_v = \frac{1000(d_{2-d})}{m d_2 d} + \frac{M}{d}$

φ_v is Apparent Molal Volume of solute , d_2 is density of solvent and d is the density of solution , m is molality and M molecular weight of solute .

The variation of φ_v against VM is found to be almost linear within concentration range studied at each composition. In general Apparent Molal Volume change with concentration and also with solvent composition . This indicates the applicability of Masson's equation.

$$\varphi_v = \varphi^0{}_v + S_v\sqrt{M}$$

Where $\varphi^0{}_v$ is partial molal volume at infinite solution and is measure of solute –solute interaction[8]. It is obtained from the linear plot of φ_v and S_v along with compressibility value of solvent and used in calculating Bachem's constant A and B the data shown in an agreement with those obtained β_s - $\beta^0{}_s/M$ vs VM plot.

Apparent Molal Compressibility :

Apparent Molal Compressibility of the system has been computed using relation

$$\Phi_k = \frac{1000(\beta s - \beta s_0)}{m d_0 d} + \beta_s \varphi_v$$

Where β_s and $\beta^0{}_s$ are the compressibility of solvent and solution respectively , m is the molality , d_0 is the density of the pure solvent and φ_v is Apparent Molal Volume. In limiting law for the Apparent Molal compressibility at concentration m as obtained by Gucker[9] from debye Huckel theory is found to be follow the relation

$$\Phi_k = \varphi^0{}_k + S_k\sqrt{M}$$

Where φ^0_k is apparent molal compressibility at infinite solution and is measure of solute –solvent interaction[8]. S_k is experimental slope which is measure of ion –solvent interaction. Gucker[10] and later Falkennagen and Bachem have shown that this relation is followed by all electrolytes . However , Krishnamurthy has reported a departure from such linear relationship while working on some alkali halides. In Present investigation , values of Φ_k are negative for all antibiotic that is streptomycin, Ampicilin, Ciprofloxicin at all concentration. It is found that variation of Φ_k plotted against $\sqrt{M}$ follows linear relationship exists within the concentration range in each of these cases at all compositions . The apparent molal compressibility's at infinite dilution φ^0_k obtained from the intercept of linear variation range and slope S_k for each evaluated .

Relative Viscosity:

The viscosity of antibiotic that is streptomycin, Ampicilin, Ciprofloxicin at all concentration from 0.001 to .01 was measured by Mansing Survismeter at 28^0 c . Uncertainty in the measurement of viscosity is found to be 0.01% . From the viscosity measurement relative viscosity was calculated using equation

$\eta/\eta_0 = \eta_r$

where η_r is relative viscosity , η and η_0 are viscosities of solution and solvent respectively.

The viscosity data can be analyzed from Jones-Dole equation

$\eta_r = 1 + A\sqrt{M} + BM$ here M is the concentration in gm/lit , B is the viscosity integration coefficient , A – represent the contribution from interionic electrostatic forces and B is the measure of order are disorder introduced by ion solvent structure . The intercept and slope of □/η_0 vs M gives the values of these constants.

Conclusion :

The present study was undertaken to assess the behavior of different drugs like Ampicilin, Ciprofloxicin , Streptomycin in aqueous 10% , 20% , 30% acetonitrile and aqueous 10% , 20% , 30% ethanol whether they are structure maker or structure breaker. **Ampicilin :** Increase in density values of ampicilin in aqueous acetonitrile and aqueous ethanol with increase in concentration results shrinkage in volume of solution

The increasing values of density and ultrasonic velocity reflect the presence of strong interaction among the molecules of ampicilin. Increase in ultrasound velocity indicate interaction between ion and solvent molecules suggesting structure promoting behavior of drug.

Increasing adiabatic compressibility with decreasing concentration may be due to dispersion of solvent molecules in supporting weak ion solvent interaction.

Apparent molal volume φ_v increases with decrease concentration indicate the existence of strong ion-solvent interaction.

Apparent molal compressibility φ_k increases with decrease concentration indicate the existence of weak electrostatic attractive force in the vicinity of ion causing electrostatic salvation of ions.

The negative values of Apparent molal compressibility φk Apparent molal volume φ_v indicate weak solute –solvent , ion –ion interaction. Negative values of φ^0_k , φ^0_v indicate weak solute- solvent , ion-solvent interaction.

Ciprofloxacin:

As drug concentration increases due to drug solvent interaction occurs with increase in density of solution .Density and Viscosity changes are showing indicative intermolecular interaction inn solution. Viscosity values in ciprofloxacin in aqueous ethanol an aqueous acetonitile show linear dependence over drug concentration. Density increases and becomes more stronger with increase in drug amount due to structural cause of change in density and existence and modification of solvent interaction. Overall result show drug solvent interaction with drug concentration.

Increasing adiabatic compressibility with decreasing concentration may be due to dispersion of solvent molecules in supporting weak ion solvent interaction.

Apparent molal volume φ_v increases with decrease concentration indicate the existence of strong ion-solvent interaction.

Apparent molal compressibility φ_k increases with decrease concentration indicate the existence of weak electrostatic attractive force in the vicinity of ion causing electrostatic salvation of ions

Streptomycin :

As drug concentration increases due to drug solvent interaction occurs with increase in density of solution .Density and Viscosity changes are showing indicative intermolecular interaction inn solution. Viscosity values in streptomycin in aqueous ethanol an aqueous acetonitile show linear dependence over drug concentration. Density increases and becomes more

stronger with increase in drug amount due to structural cause of change in density and existence and modification of solvent interaction. Overall result shows drug solvent interaction with drug concentration.

Increasing adiabatic compressibility with decreasing concentration may be due to dispersion of solvent molecules in supporting weak ion solvent interaction.

Apparent molal volume φ_v increases with decrease concentration indicate the existence of strong ion-solvent interaction.

Apparent molal compressibility φk increases with decrease concentration indicate the existence of weak electrostatic attractive

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BIO DATA

Name : **Suresh Gopalrao Kulkarni**

Designation : Associate Professor

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Qualification : M.Sc.(Merit III) (1988), M.Phil (Merit III)(1997)

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Date of Birth : 25th December 1963

Email : Sureshkulkarnirocks@gmail.com

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Experience : 29 years

Minor Research Project:

1) 2007-9 -- UGC Financial Assistance of Rs. 70000/

Thermodynamic studies of some acetophenone of some amino acids and some halogen substituted hydroxy acetophenone in different solvents.

2) Minor Research Project:

2014-16 -- UGC Financial Assistance of Rs. 480000/

To study the effect of addition of Antibiotic drugs on aqueous Alcohol and aqueous acetonitrile solvent

Paper published:

Ultrasonic, volumetric and viscometric studies of some substituted acetophenones in HF –Water, DNF-water and Dioxane –water co-solvents at 303.15 K (*Indian Journal of Chemistry –vol.39 A . November 2000. Pp 1214-1217*)

University Work:

1) Member of Syllabus framing committee B.Sc. II Physical chemistry (2016-17)

2) Member of Syllabus framing committee B.Sc. II Skill Enhanced Course : Food Processing and Food Adulteration

3) Member of Syllabus framing committee Career Oriented Course: Certificate course in 'Food Processing and Food Technology'.

4) Member of University Selection committee.

5) Chairman of University Examination Flying squad (2013-14)

6) Member of University Examination Flying squad (2014-15)

7) Worked as Chief Superintendent at college.

8) Worked as Joint Chief Superintendent a) MDM Aurad S. b) Shri Bhagatsingh Mahavidyalaya Killari c) Shivaji mahavidyalaya , Udgir, d) Shivaji mahavidyalaya ,Renapur e) Yogeshwari mahavidyalaya ,Ambajogai, f) Bidve Engineering college Latur.

9) University Approved PG Teacher.

10)PG Guest Lecture at Dyanand Science college Latur, Lal Bhadur Shastri Mahvidaylaya, Dharmabad , Mahatma Gandhi mahavidyalaya Ahemadpur , Shivaji mahavidyalaya , Omerga.

11) External practical Examiner for PG (Chemistry)

12) External practical Examiner For all UG classes. (Chemistry)

13) University Paper Setter, Moderator, Examiner of all UG Classes (Physical Chemistry)

College Work:

1) Coordinator of Admission Committee :

2) Coordinator of Criterion II of IQAC Teaching Learning and Evaluation 2007-2017

3) In-charge Professor of Student Council (2013-14)

4) Member of Student Council –Principal nominated .(2014 -16)

5) Coordinator of ' smart village –Bhangar Chincholi '

6) Coordinator of Internal University Examination.

7) Coordinators of parent meet. (2007 -2016).

8) Coordinator of Alumni Meet. (2007 -2017)

9) Coordinator of Remedial classes (2009-16)

10) Coordinator of NSS (2009-12)

11) Coordinator of NSS – 'Jagar Janivancha' (2012-13)

12) Coordinator of Career oriented Course –Food Processing and Food Technology

13) Coordinator of Meal committee for University Youth Festival 2013-14

14) Organizing committee Member of Different conferences/seminars/workshops organized by college

15) Coordinator of District level seminar competition in chemistry.

16) Organized quiz competitions, seminar competitions, GK Examination for UG classes.

Social Awareness:

17) Coordinator of NSS (2009-12)

18) Coordinator of NSS – 'Jagar Janivancha' (2012-13)

19) Donated Blood Five times

20) Actively engaged tree plantation programmers, different rallies.

21) Financial assistance of Rs .6000/ prof. Panchal

22) Financial assistance of Rs .2100/year to Matoshri Vradhashram latur.

23) Financial assistance of Rs .1500/ Ku. Haswale for uniform and admission fee.

24) Financial assistance of Rs .1000/ towords Prime Ministers Relief fund

25) Financial assistance of Rs 1000/ to Swadhar Kendra Budhoda.

26) 'Swachata Abhiyan ' Nilkanteshwar Temple , Shivaji Chawk , Bus Stand. Renuka devi temple Kharosa.

27) Cash Prize of Rs. 1ooo/year and certificate for meritorious student in Chemistry B.Sc III.

Awards:

Best NSS Coordinator (District level) 2010-11

College received award for " Jagar –Janivacha' Second Cash prize of Rs.200000/ and memento from SRTMU Nanded.