ABSORPTION STUDIES OF ANILINE AND ESTERS

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Abstract

Ultrasonic velocity (v), density (ρ), viscosity (η) for binary mixtures of Aniline with Methyl Acetate,Ethyl Acetate,Amyl Acetate have been measured at room temperature of about 300.15K over entire volume component percentage range. The Ultrasonic velocity (v) is measured with ultrasonic Pulse Echo Overlap (PEO) technique at a frequency of 2 MHz. The density (ρ) measurements have been carried out by 10ml specific gravity bottle. The Viscosity (η) measurements have been carried out by using Cannon-Fenske Viscometer with an accuracy of ±0.3%. Attenuation Coefficient (α) is measured using a cathode ray Oscilloscope (CRO) for a transmitted pulse and nth echo. Relaxation time (τ), Absorptivity (A) was computed using measured data of ultrasonic velocity, density, viscosity. Data of ultrasonic velocity (v), attenuation Coefficient (α), density (ρ) and viscosity (η) are useful in evaluating some useful thermodynamic properties like adiabatic compressibility (βs), internal pressure (πi), free volume (Vf) which can be utilized as a qualitative guide to predict the extent of complex formation in binary liquid mixtures. In Chemical industry, there exists a continuing need for reliable thermodynamic data of binary mixtures. This is particularly true for systems involved in industrial process with their objectives in mind, an attempt has been made to investigate the variations of ultrasonic velocity (v), attenuation Coefficient (α), density (ρ) and viscosity (η) in Aniline and Esters as a function of concentration and temperature. These systems have a scope for compellation through hydrogen bonding.

Key words: Ultrasonic Velocity (v), density (ρ), viscosity (η), Attenuation Coefficient (α), Absorptivity (A), Relaxation time (τ).

Introduction

Ultrasonic is a useful tool to know the nature of molecular interaction in pure, binary and ternary liquids. But no sufficient data is available in the binary mixture of Aniline in Methyl Acetate, Ethyl Acetate, Amyl Acetate. Ultrasonic method found extensive application in characterizing the various aspects of the physico-chemical behavior of liquid mixtures such

as molecular interaction and association .Molecular association and complex formation in liquid mixtures through ultrasonic velocity measurements have been studied by many researchers.

The propagation of ultrasonic waves in a substance has become a fundamental test to investigate its properties. Ultrasonic velocity measurements have been adequately employed to understand the nature of molecular interactions in pure liquids, binary and the ionic interactions in aqueous electrolytic solutions. In a material, scattering and absorption produced by various dynamical interactions which typically arise from enharmonic force between the atoms. When acoustic waves are propagated through a liquid, dissipation of acoustic energy that is associated with it changes the molecular structure of the medium with finite time, which is required for these changes to take place.

The pulse method is much suited to liquids than to gases, mainly because of the much greater absorption of sound by gases, because gases produce much greater damping of the transmitted pulse. The first effect means that the reflector must be of longer duration in order to allow for the greater build-up time of the transducer. These two requirements may be conflicting, because of standing waves that are to be avoided, the distance between transducer and reflector must exceed the length of the transmitted train of waves and might thus be such as to give excessive risk of attenuation for satisfactory measurements.

Ultrasonic absorption studies in liquid mixtures can help to determine the behavior in very fast reaction as has been reported by Larson,E.V.,Nugle,D.G.,and Adair.1971 . In many binary liquid mixtures, the characteristic feature is that there exists a prominent maximum in Viscosity, Ultrasonic Velocity and sound absorption at an intermediate concentration. Barfield and Schneider studied ultrasonic absorption in di ethyle amine and water and explained the excess absorption in this system by assuming a simple two-state model involving equilibrium between hydrogen bonds of like and unlike molecules.

Ultrasonic velocity of a liquid is related to binding forces between atoms and molecules. The sound velocity in liquid mixtures is known to be a quantity which depends on concentration in a variety of manners according to the nature of each component liquid. Accurate measurements of ultrasonic velocity deliver the information about the physical and chemical behavior of solutions and liquid mixtures.

In a material scattering and absorption produced by various dynamical interactions which typically arise from enharmonic force between the atoms, the presence of free charge

carriers, cycling to localized spin states and the presence of impurities. When acoustic waves are propagated through a liquid, dissipation of acoustic energy that is associated with changes in the molecular structure of the medium results from the finite time, which is required for these changes to take place which were reported by Denes,P. 1955.

Ultrasonic velocity has been a subject of active interest during the recent years. Nomoto and co researchers made successful attempt to evaluate the sound velocity in binary mixtures.

In the present communication we focus on the ultrasonic behavior of liquid mixtures at 300.15K temperature with Aniline as the base and few esters Methyl Acetate, Ethyl Acetate and Amyl Acetate as mixtures.

Methodology

During the past four decades the measurement of the Velocity and Attenuation of ultrasonic waves has been the basis of evolution of a wide variety of physical properties of gases, liquids and solids. The samples are taken for the present studies are of Analar reagent grade and procured from Sd.Fine Chemicals Limited, Bombay, India. The liquids are thoroughly distilled to remove the dissolved impurities using standard chemical procedures like steam distillation. Liquids practically are immiscible with water, volatile in steam and possessing a high boiling point.

By taking two liquids in separate burettes, Job's variation method of continuous variation has been used to prepare the mixtures of required proportions.

The ultrasonic velocity measurements are made with the help of microprocessor based ultrasonic Pulse Echo Overlap technique (model UX4400M) With built in time Velocity and thickness measuring feature with a frequency of 2MHz. supplied by Roop Telesonic Ultrasonic Ltd,Bombay,India. The internal circuit of (ULTRASONIX4400M) is designed with full solid state version. Further outstanding stability of operation is ensured by dynamic use of integrated circuit and PCB mounted gold switches. It has special memory features which enable one to enter testing procedures like angle and type of transducer for permanent storage and direct digital read out of Ultrasonic velocity up to an accuracy of ±1m/s.

The Pulse Echo Overlap (PEO) method is very versatile and highly accurate technique for measuring the velocity of the ultrasonic waves in materials of liquids and solids structures. A highly absolute accuracy is obtained from this system, since the method is capable of accurately measuring from any cycle of one echo to the corresponding cycle of the next echo. The PEO method is able to handle diffraction (beam spreading) and phase

correction properly, so that absolute accuracy of the PEO method may exceed the accuracy of most of the other methods. However, precision of some other methods is better than PEO method. The PEO method may operate either with transducer bonded to the specimen or directly with RF bursts. On the negative side, because of transducer effects, the leading cycles of successive echoes are attenuated and trailing cycles are burst up, so that great care has to be taken to obtain proper cycle for cycle match. The phase correction and identification of cycles are to be taken properly which is mentioned in Pulse Superposition technique.

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The densities of all the mixtures have been determined with 10ml. specific gravity bottle and mass (m) of a given volume of the liquid is determined by using a single pan opto-electrical balance. The results of the densities are accurate to ±0.5%.

The coefficient of absolute viscosity (η) has been determined using a Cannon- Fenske Viscometer. The results of viscosities are accurate to ± 0.3%.

The internal circuit of pulse echo overlap system is designed with fully solid state version, which allows immediate calculation of the ultrasonic wave velocity as given in the following equation.

$$v = 2l / t$$

Where l is the liquid length and t is the time interval.

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The longitudinal ultrasonic waves are passed through the binary mixture. They are reflected from the reflector face and received by the same transducer, which now acts as a receiver. The transmitted pulse and the received echoes are seen in the CRO screen. Once, the echo pattern is achieved on the screen on the CRO, the pattern is adjusted to a suitable height.

The transmitted pulse height is measured in mv/cm and noted as 'a_0' on the screen. The height of first echo is noted as 'a_1' and second echo as 'a_2' and so on. The path length is noted using the micrometer attached to the reflector and is noted as 2l.

∴ The attenuation coefficient (α) is calculated as

$$\alpha = 1/2l \ln \log_e (a_0/a_n) \text{ nepers/unit length.}$$

Where a_0 →amplitude of transmitted pulse.

a_n → amplitude of n^{th} echo.

The absorptivity is measured by dividing α by the square of the frequency (2MHZ) of the ultrasonic wave propagated into the liquid media, i.e

$$\text{Absorptivity, } A = \alpha/f^2$$

Where f is the frequency of the ultrasonic wave propagated.

Results and discussion

Ultrasonic velocity measurements were made in Aniline-Methyl Acetate, Aniline-Ethyl Acetate, Aniline-Amyl Acetate. Ultrasonic velocity decreases in Aniline-Methyl Acetate, Aniline-Ethyl Acetate, Aniline-Amyl Acetate. Ultrasonic velocity is larger in Aniline-Amyl Acetate the reason being that Amyl Acetate is more alcoholic. Aniline is a basic component and possesses less number of H^+ ions which causes for freer movement of Ultrasonic waves through the medium. Therefore Ultrasonic velocity increases with respect to the increase in Aniline concentration. The observed variation in the ultrasonic velocity and other calculated parameters are shown in Tables 1, 2, 3. The density values decrease with respect to the increase in Ester concentration in all the systems. The density values are lesser in Aniline-Amyl Acetate system and larger in Aniline-Methyl Acetate system. The order of densities is Amyl Acetate < Ethyl Acetate < Methyl Acetate. The viscosity values decrease with respect to increase in ester concentration in all the systems these were reported by K.Sathi Reddy and D. Linga Reddy.2008.

The attenuation coefficient is a quantity that characterizes how easily a material or medium can be penetrated by a beam of light, sound, particles, or other energy or matter . A large attenuation coefficient means that the beam is quickly "attenuated" (weakened) as it passes through the medium, and a small attenuation coefficient means that the medium is

relatively transparent to the beam . The ultrasonic waves are passed through the specimen under study. They are reflected from the opposite face and received by the same transducer, which now acts as a receiver. The amplitude pulse noted as a_o and the amplitude of the n^{th} echo pulse as a_n.

The ultrasonic velocity is found to decrease with increase in Aniline volume concentration. The variation of velocity density and viscosity are shown in Fig. 1, 2, 3. These results are in tune with Van Dael,W.,Van Itterbeek,1966. The curves of absorptivity and attenuation coefficient show a decrease in the value at a concentration 10% of Ester as shown in the Fig.4, 5, 6. The reason may be thought as the ester concentration is less only the Aniline is showing its effect.

A perusal of attenuation coefficient (α) obtained for various binary mixtures of the Aniline with Esters reveals the following factors.

(i) Attenuation coefficients (α) of binary mixture of Aniline with Methyl acetate lower compared to binary mixture of Ethyl acetate and Amyl acetate with Aniline. This means the chain length of the Esters is deciding even attenuation coefficients (α) as observed with ultrasonic velocities (v).

(ii) Attenuation coefficients (α) for Amyl acetate is higher than Methyl acetate and Ethyl acetate similar composition of Amyl acetate with Aniline. Generally it can be said that, higher the chain length of the Esters, the higher will be the attenuation coefficient (α).

Some of the standardized values of Ultrasonic velocity (**v**) and attenuation coefficient (α) of few International standard samples are:

- Ultrasonic velocity (v) of Ethyl acetate at 27^0C **(Expt.)** = 1103m/s
- Ultrasonic velocity (v) of Ethyl acetate at 27^0C (Lit.) = 1108m/s
- Attenuation coefficient (α) of Ethyl acetate at 27^0C **(Expt.)** = 0.69nep/cm
- Attenuation coefficient (α) of Ethyl acetate at 27^0C (Lit.) = 0.70 nep/cm
- Ultrasonic velocity (v) of Methyl acetate at 27^0C **(Expt.)** = 1120m/s
- Ultrasonic velocity (v) of Methyl acetate at 27^0C (Lit.) = 1126m/s
- Attenuation coefficient (α) of Methyl acetate at 27^0C **(Expt.)** = 0. 68nep/cm
- Attenuation coefficient (α) of Methyl acetate at 27^0C (Lit.) = 0.67nep/cm

Conclusion

Absorption studies are carried out apart from ultrasonic studies on Methyl Acetate, Ethyl Acetate, and Amyl Acetate with Aniline over entire volume component percentage range. It is found that Ultrasonic velocity increases with increase in Ester concentration. The density values decrease with respect to the increase in Ester concentration in all the systems. The Attenuation Coefficient and Absorptivity decrease as the concentration of the Esters increase.

Table1. Ultrasonic velocity (v), density (ρ), viscosity (η), Relaxation Time (τ), Attenuation Coefficient(α), Absorptivity (A) of Binary mixture of Aniline in Methyl Acetate at 300.15 K

Volume Component Percentage		**Ultrasonic Velocity (V)m/s**	**Density (ρ) 10^{-3} Kgm^{-3}**	**Viscosity (η) poise**	**Relaxation Time(τ) 10^{-8} sec**	**Attenuation Coefficient (α)**	**Absorptivity (A) 10^{-13}**
Aniline	**Methyl Acetate**						
90	10	1502	1.0182	0.025	1.4511	0.5531	1.3827
80	20	1439	1.0068	0.0178	1.1383	0.6192	1.548
70	30	1407	1.0053	0.0151	1.011	0.6247	1.56175
60	40	1370	0.9962	0.0117	0.8343	0.6347	1.58675
50	50	1327	0.9858	0.0098	0.7556	0.6491	1.62275
40	60	1285	0.9784	0.0084	0.6932	0.6568	1.6427
30	70	1240	0.9718	0.0072	0.7002	0.6642	1.6605
20	80	1200	0.9521	0.0066	0.6418	0.6715	1.67875
10	90	1150	0.945	0.0053	0.5654	0.6821	1.70525

Table2. Ultrasonic velocity (v), density (ρ), viscosity (η), Relaxation Time (τ), Attenuation Coefficient(α), Absorptivity(A) of Binary mixture of Aniline in Ethyl Acetate at 300.15 K

Volume Component Percentage		**Ultrasonic Velocity (V)m/s**	**Density (ρ) 10^{-3} Kgm^{-3}**	**Viscosity (η) poise**	**Relaxation Time(τ) 10^{-8} sec**	**Attenuation Coefficient (α)**	**Absorptivity (A) 10^{-13}**
Aniline	**Ethyl Acetate**						
90	10	1502	1.0095	0.0248	1.4519	0.5531	1.3827
80	20	1457	1.0017	0.0194	1.2164	0.6247	1.56175
70	30	1412	0.9905	0.0166	1.1207	0.6347	1.58675
60	40	1373	0.9879	0.0137	0.9808	0.6491	1.62275
50	50	1329	0.9835	0.0111	0.8504	0.6568	1.642
40	60	1288	0.9717	0.0095	0.7857	0.6642	1.6605
30	70	1244	0.9489	0.0081	0.7354	0.6715	1.67875
20	80	1203	0.9289	0.007	0.6942	0.6821	1.70525
10	90	1153	0.9243	0.0059	0.6402	0.6977	1.74425

Table3. Ultrasonic velocity (v), density (ρ),viscosity(η), Relaxation Time(τ), Attenuation Coefficient(α), Absorptivity(A) of Binary mixture of Aniline in Amyl Acetate at 300.15 K

Volume Component Percentage		**Ultrasonic Velocity (V)m/s**	**Density (ρ) 10^{-3} Kgm^{-3}**	**Viscosity (η) poise**	**Relaxation Time(τ) 10^{-8} sec**	**Attenuation Coefficient (α)**	**Absorptivity (A) 10^{-13}**
Aniline	**Amyl Acetate**						
90	10	1504	1.0142	0.0249	1.4471	0.5531	1.3827
80	20	1460	1.0097	0.0186	1.1522	0.6491	1.62275
70	30	1417	0.9781	0.0160	1.0862	0.6568	1.642
60	40	1390	0.9641	0.0106	0.7587	0.6642	1.6605
50	50	1348	0.9520	0.0089	0.6859	0.6821	1.70525
40	60	1301	0.9423	0.0080	0.6687	0.6821	1.70525
30	70	1278	0.9208	0.0072	0.6383	0.6977	1.74425
20	80	1240	0.9023	0.0064	0.6150	0.7083	1.77075
10	90	1203	0.8906	0.0052	0.5379	0.7153	1.78825

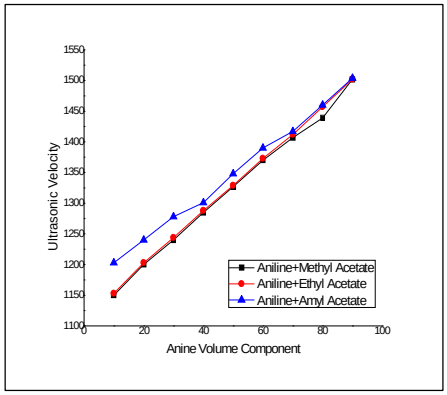

Fig.1.Aniline volume component vs Ultrasonic velocity

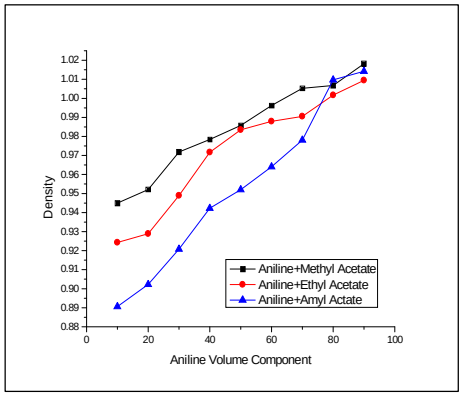

Fig.2.Aniline volume component vs Density

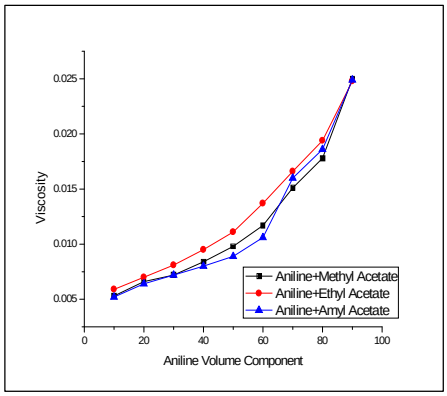

Fig.3.Aniline volume component vs Viscosity

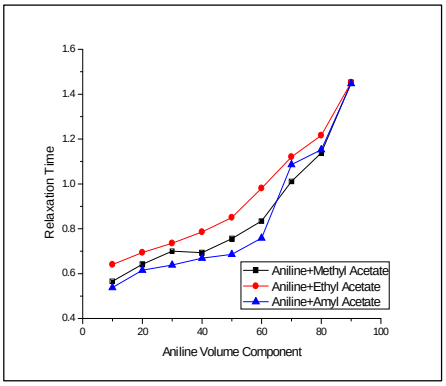

Fig.4.Aniline volume component vs Relaxation Time

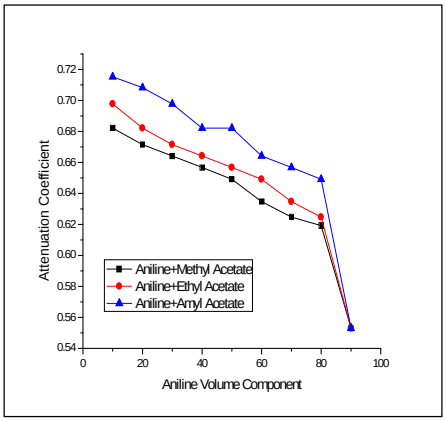

Fig.5.Aniline volume component vs Attenuation Coefficient

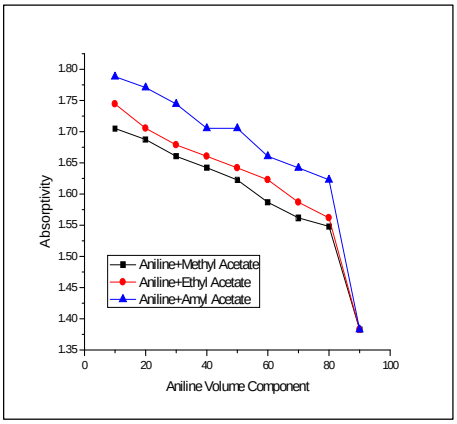

Fig.6.Aniline volume component vs Absorptivity

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