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THEORETICAL EVALUATION OF ACOUSTICAL STUDIES OF NON-LINEARITY PARAMETER (B/A) OF SODIUM DODECYL SULPHATE IN POLYVINYL ALCOHOL SOLUTION AT 303K

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ABSTRACT
The acoustical parameters of sodium dodecyl sulphate (SDS) in poly (vinyl alcohol) (PVA) solution was studied by ultrasonic velocity measurements. Ultrasonic velocity, density, viscosity in mixtures of sodium dodecyl sulphate in polyvinyl alcohol was measured over the entire range of composition. From the data, other related parameters, *viz*., adiabatic compressibility, intermolecular free length, surface tension were calculated theatrically. Ultrasonic velocities theoretically evaluated using Nomoto's Relation, Impedance Relation, Free Length Theory and it is compared with experimental values to check applicability of these equations to the systems studied. The present investigation comprises of theoretical evaluation of acoustic non-linearity parameter, B/A using Hartmann relation, Ballous empirical relation.
Keywords: Ultrasonic velocity, theoretical evaluation, non-linearity parameters, sodium dodecyl sulphate, polyvinyl alcohol solution.

INTRODUCTION

The study of propagation behavior of ultrasonic waves in liquid systems is now rather well established as an effective tool for examining certain physical properties of materials. The data obtained from ultrasonic propagation parameters i.e., ultrasonic velocity and its variation with different concentrations helps to understand the nature of molecular interaction. Several empirical and semi-empirical formulae have been developed correlating ultrasonic velocity with other molecular parameters and a brief account of theoretical aspects[1-3]. Therefore to get additional information on the nature and strength of molecular interactions, the related acoustical/ thermo dynamical parameters such as free length, adiabatic compressibility, free volume, internal pressure, acoustic impedance etc., and their excess parameters are calculated[4]. Ravichandran and Rathika Thiya kumari already studied the ultrasonic behavior and other thermo dynamical properties of binary solution of sodium dodecyl sulphate in poly vinyl alcohol in different concentrations at 303K.Several researchers[5-7] carried out ultrasonic investigations on liquid mixtures and correlated the experimental results of ultrasonic velocity with the theoretical relations of Nomoto, Vandeal and Vangeel and Rao's specific velocity and interpreted the results in terms of molecular interactions. In this work, the ultrasonic velocities of binary liquid mixture of sodium dodecyl sulphate (SDS) / poly (vinyl alcohol) (PVA) solution have been theoretically evaluated by using various theories and compared with the experimental values.

EXPERIMENTAL

Nomoto's Relation[8]

Nomoto established an empirical formula for ultrasonic velocity in binary liquid mixtures as-

$$U_{No} = \Sigma x_i R_i / \Sigma x_i V_m \quad (1)$$

Free Length Theory (U_{FLT}) [9]

Jacobson introduced the concept of determination of ultrasonic velocity in pure liquids and liquid mixtures known as Free Length Theory (FLT). Further, he related the ultrasonic velocity in pure liquid mixtures to the free length L_f by the relation-

$$UFLT = \frac{K_T}{L_{fmix}\ \rho^{1/2}}\ m/s \quad (2)$$

Impedance Dependent Relation (U_{IDR}) [10]

The impedance offered by a liquid to the propagation of ultrasonic wave is given by $Z_i = \rho_i U_i$. For a liquid mixture, the following empirical relation is-

$$U = \Sigma x_i Z_i / \Sigma\ x_i \rho_i\ m/s \quad (3)$$

Computation of non-linear parameter using B/A ratio

In the last few years[11], a number of theoretical methods have been proposed for estimating the non-linearity parameter (B/A) for pure liquids and liquid mixtures. This parameter has been further correlated with other thermo acoustical parameters, which are used to deduce the available volume and intermolecular free-length of liquid mixtures. Due to the increasing importance of B/A during recent years, an attempt has been made to evaluate B/A of binary mixtures using Hartmann relation and Ballou empirical relation. General formulation for non-linearity parameter in terms of the acoustical parameters of liquids has been made using the experiment for the sound velocity (U) and introducing the contribution due to acoustic parameters (K) and isothermal acoustic parameter (K").The expression for B/A has been expressed as[12]-

$$B/A = 2K+2\gamma K"$$

Computations of K and K" require only the knowledge of thermal expansion coefficient, α. Detailed method of calculation is given.

Hartmann and Balizer obtained the following relation for B/A as-

$$B/A = 2 + \frac{0.98\times10^4}{U}$$ Where U is in ms^{-1} (4)

Empirical relation proposed by Ballou is given [11-12] by

$$B/A = -0.5 + \frac{1.2\times10^4}{U} \quad (5)$$

RESULTS AND DISCUSSION

Theoretical data on ultrasonic velocity, density and other acoustical properties of 0.25N of SDS in polyvinyl alcohol solutions at 303K were reported in Tables-1 and 2. The variations of ultrasonic velocity were found increased with mole fraction of SDS. The variations of relative viscosity were found linear. The variations in viscosity were due to the structural changes. Variation in ultrasonic velocity in any solution generally indicates molecular association in it. This is due to the interaction between solute solvent molecules. Interaction is weaker at minimum velocity [13-15].The variation of Ultrasonic velocity was found to be non-linear. The decreasing minimum velocity of Ultrasonic velocity indicates the weakening of molecular association at a mole fraction of 0.9997 of SDS. In the lower region of SDS, the linear change of velocity indicates the miscibility of the solution. For higher concentration, ultrasonic velocity is found to be increased with mole fraction of SDS. The ultrasonic velocity increases up to 0.9993 mole fraction of SDS starts to decrease rapidly up to 0.9997 and suddenly it increases and attains constant values for three velocities and then starts to increase. Likewise, for lower concentration, the ultrasonic velocity falls up to 0.9974 mole fraction of SDS and from 0.9985 mole fraction of SDS it starts to increase and reaches a peak at the mole fraction 0.9996 and then falls off gradually. It can be seen from Table-1 that the theoretical values of ultrasonic velocity computed by various theories show deviation from experimental values. These theories generally fail to predict accurately the ultrasonic velocities where strong interactions are supposed to exist. An important reason for deviation from experimental values of ultrasonic velocity is that the molecular association effects are not taken into account in these theories. When two liquids are mixed, the interaction between the molecules of the two liquids takes place because of the presence of various forces like dispersive force, charge transfer, hydrogen bonding dipole-dipole and dipole-induced dipole interactions. Hence the observed deviation shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture. Similar kinds of results were obtained by earlier workers. Higher deviations are observed in some intermediate concentration

range. This suggests the existence of strong tendency for the association between component molecules as a result of Hydrogen bonding.[16-19]

Ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules and is used to understand the intermolecular interactions in the present investigation, ultrasonic velocity found to be increased with mole fraction of SDS where L_f is decreased. Change in velocity depends on the intermolecular free length or decrease in intermolecular free length causing increase in velocity[15-16].

The increase in concentration of SDS weakens the molecular forces and hence the change in velocity is obtained at 70: 30 and then from 30: 70 concentrations it maintains constant. When the salts are dissolved in water, the ions are disintegrated and are strongly bonded with water molecules. The smaller ions, induces higher order in the water structure. The increase in structural order of water may cause more collision and hence decrease in value of β is obtained with increase in velocity.[20-21]

The B/A values for the liquids have been interpreted as the quantity representing the magnitude of the hardness of liquids. The interaction between the components of the binary mixtures is stronger at higher concentration, while it is weaker at lower concentration of salts.[22-23] The behavior of binary liquid mixtures can be explained in terms of – (i.) physical forces -dispersion (ii.) chemical forces – dipole-dipole interaction. The former factor increases the intermolecular free length as described by Jacobson. This is turn, causes negative deviation in sound speed and positive deviation in compressibility.

Table-1: Comparison of Experimental and Theoretical Velocities of Sodium Dodecyl Sulphate (SDS) in Poly Vinyl Alcohol Solution at higher Concentrations

Mole Fraction of SDS $(X_1)\times10^{-3}$	Experimental Ultrasonic Velocity (U) (m/s)	Theoretical values of Ultrasonic velocity (U) m/s			Deviation in Ultrasonic velocity (%)		
		Nomoto's relation	Impedance Relation	Free length Theory	Nomoto's relation	Impedance Relation	Free length Theory
0.0000	1534	1533.66	1535.22	1533.61	0.0034	-0.0122	-0.0011
0.9971	1506	1506.12	1503.26	1505.33	-0.0012	0.0274	0.0067
0.9987	1531	1531.23	1534.35	1530.50	-0.0023	-0.0335	0.0045
0.9993	1540	1540.02	1543.82	1539.53	-0.0002	-0.0382	0.0047
0.9995	1516	1516.03	1518.56	1515.60	-0.0003	-0.0256	0.0040
0.9997	1505	1504.56	1507.78	1505.27	0.0044	-0.0278	-0.0027
0.9998	1508	1509.35	1512.55	1507.33	-0.0135	-0.0455	0.0067
0.9999	1510	1510.56	1514.33	1511.66	-0.0056	-0.0433	-0.0166
0.9999	1531	1531.92	1533.40	1530.64	-0.0092	-0.0240	0.0036
0.9999	1499	1499.86	1497.20	1498.50	-0.0086	0.0180	0.0050
1.0000	1504	1505.30	1506.11	1504.22	-0.0130	-0.0211	-0.0022

Table-2: Comparison of Experimental and Theoretical Velocities of Sodium Dodecyl Sulphate (SDS) in Poly (vinyl Alcohol) Solution at lower Concentrations

Mole Fraction of SDS(X_1) $\times10^{-3}$	Experimental Ultrasonic Velocity(U) (m/s)	Theoretical values of Ultrasonic Velocity (U) (m/s)			Deviation in Ultrasonic velocity (%)		
		Nomoto's relation	Impedence Relation	Free length Theory	Nomoto's relation	Impedence Relation	Free length Theory
0.9943	1536	1536.3	1536.2	1536.4	-0.0033	0.00	00
0.9974	1532	1532.6	1533.2	1532.2	-0.0056	-0.01	00
0.9985	1537	1538.4	1538.4	1537.5	-0.0136	-0.01	00
0.9990	1537	1538.7	1541.1	1537.3	-0.0166	-0.04	00

0.9994	1540	1541.8	1542.3	1540.5	-0.0175	-0.02	00
0.9996	1540	1541.9	1541.2	1541.3	-0.0185	-0.01	-0.01
0.9997	1538	1538.6	1538.4	1538.7	-0.0055	0.00	00
0.9998	1535	1534.6	1536.5	1535.7	0.0044	-0.01	00
0.9999	1536	1538.2	1538.3	1536.3	-0.0222	-0.02	00
1.0000	1522	1521.6	1522.5	1522.3	0.0044	0.00	00

On the other hand, the latter factor decreases the intermolecular path lengths leading to a positive deviation in sound speed and negative deviation in compressibility. Theoretical values of ultrasonic speed calculated form Nomoto's and impedance relations are almost shows some error and free length theory shows minimum percentage error in theoretical ultrasonic speed [24-27].

Table-3: Theoretical values of U, ρ, β_{ad}, Z, σ and L_f acoustic impedance, surface tension, molecular free length of Sodium Dodecyl Sulphate (SDS) in Polyvinyl alcohol solution of higher concentration using free length theory

Mole Fraction of PVA $\times 10^{-3}$	Mole Fraction of SDS (X_1)	velocity (U)ms^{-1}	Density (ρ) kgm^{-3}	Adiabatic compressibility (β_{ad})10^{-10} $Kg^{-1}ms^2$	Acoustic impedance (Z) $kgm^{-2}s^{-1}$	Surface tension σ $\left(Kgm^{-2}s^{-1}\right)$	free length (L_f) 10^{-11}m
1	0	1533.61	1090	3.9049	1670479	41205	4.1004
2.8717	0.9971	1505.33	1094	4.0302	1647357	40278	4.1656
1.2783	0.9987	1530.50	1095	3.8958	1676144	41324	4.0956
0.7461	0.9993	1539.53	1096	3.8457	1688493	41757	4.0692
0.4797	0.9995	1515.60	1097	3.9672	1662650	40784	4.1329
0.3199	0.9997	1505.27	1098	4.0222	1651944	40374	4.1615
0.2133	0.9998	1507.33	1101	3.9967	1659444	40595	4.1483
0.1371	0.9999	1511.66	1103	3.9731	1666386	40801	4.1360
0.0799	0.9999	1530.64	1105	3.8621	1691390	41692	4.0778
0.0355	0.9999	1498.50	1111	4.0039	1666135	40640	4.1520
0	1	1504.22	1117	3.9585	1679648	41038	4.1284

Table-4: Theoretical Values of Ultrasonic Velocity, Density, Adiabatic compressibility, Acoustic Impedance, Surface Tension, Free Length of Sodium Dodecyl Sulphate (SDS) in Poly Vinyl Alcohol Solution of Lower Concentration Using Free Length Theory

Mole Fraction of PVA $\times 10^{-3}$	Mole Fraction of SDS(X_1) $\times 10^{-3}$	velocity (U) ms^{-1}	Density (ρ) kgm^{-3}	Adiabatic compressibility (β_{ad}) 10^{-10} $Kg^{-1}ms^2$	Acoustic impedance (Z) $kgm^{-2}s^{-1}$	Surface tension σ $\left(Kgm^{-2}s^{-1}\right)$	free length (L_f) 10^{-11} m
1	0	1536	1063	3.9976	1630703	40237	4.1487
5.727	0.9943	1532	1071	3.9571	1644907	40618	4.1277
2.553	0.9974	1537	1075	3.9617	1647596	40628	4.1301
1.491	0.9985	1537	1079	3.9225	1658660	40967	4.1096
0.959	0.9990	1540	1082	3.9124	1662808	41072	4.1043
0.630	0.9994	1541	1087	3.8801	1673514	41374	4.0873
0.4264	0.9996	1538	1093	3.8537	1684214	41649	4.0734
0.2742	0.9997	1535	1097	3.8537	1686935	41682	4.0734
0.1599	0.9998	1536	1099	3.8618	1687352	41644	4.0777
0.0711	0.9999	1522	1101	3.8506	1691106	41751	4.0718
0	1	1536	1104	3.9103	1680517	41301	4.1032

Table-5: Computation of non-linearity (B/A) parameter of Sodium Dodecyl Sulphate (SDS) in Poly-(vinyl Alcohol) Solution by Hartmann and Ballizer equation

Mole Fraction of SDS $(X_1)\times10^{-3}$	B/A values by Hartman and ballizer			
	From experimental velocity	From Nomoto's relation	From Impedance Relation	From Free length Theory
0	8.388	8.389	8.383	8.390
0.9971	8.507	8.507	8.519	8.510
0.9987	8.401	8.400	8.387	8.403
0.9993	8.363	8.362	8.348	8.366
0.9995	8.464	8.464	8.453	8.466
0.9997	8.511	8.514	8.499	8.510
0.9998	8.498	8.492	8.479	8.502
0.9999	8.490	8.488	8.472	8.483
0.9999	8.401	8.397	8.391	8.403
0.9999	8.537	8.534	8.456	8.539
1	8.515	8.510	8.506	8.515

Tables-5 and 6 shows the variations of the B/A values calculated from Hartmann and Ballou relation and it shows decreased trend with increase in concentration. This data of velocity and densities were taken for computing the various quantities employed in the equation for B/A. The B/A values for the liquids have been interpreted as the quantity representing the magnitude of the hardness of liquids. The B/A values are concenerned with interactions between the components of the binary systems. A close examination of data presented in Tables-5 and 6 reveal that the values of B/A calculated using (4) and (5) shows a decreasing trend with concentration of SDS. It is evident from eq.(4) and (5), that Ballous and Hartmann relations depend mainly on the ultrasonic velocity.

The interaction between the components of the binary mixtures is stronger at higher concentration, while it is weaker at lower concentration of salts and the accuracy of both the methods limits the usefulness of direct application of these methods to liquid mixture investigation [28-29].

Table-6: Computation of non-linearity (B/A) parameter of Sodium Dodecyl Sulphate (SDS) in Poly (vinyl Alcohol) Solution by Ballou empricial relation

Mole Fraction of SDS$(X_1)\times10^{-3}$	B/A values by Ballou empirical relation			
	From experimental velocity	From Nomoto's relation	From Impedance Relation	From Free length Theory
0.9943	7.313	7.310	7.312	7.311
0.9974	7.333	7.332	7.331	7.330
0.9985	7.307	7.303	7.302	7.300
0.9990	7.307	7.298	7.299	7.298
0.9994	7.292	7.288	7.287	7.283
0.9996	7.292	7.286	7.286	7.282
0.9997	7.302	7.300	7.301	7.300
0.9998	7.318	7.321	7.320	7.322
0.9999	7.313	7.303	7.301	7.303
1	7.384	7.385	7.387	7.387

CONCLUSIONS

Hence, it concluded that, Ultrasonic velocities predicted using NOM, IMP and FLT were compared with experimentally measured velocity values at 303K for the binary mixtures of sodium dodecyl sulphate (SDS) in poly(vinyl alcohol) (PVA) solution. It may be concluded that FLT relation is best suited for all the binary mixtures under study. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of intermolecular interactions in the systems studied. In conclusion, the concentration, nature of solvent, nature of the solute and nature of the substituent and its position play an important role in determining the interactions occurring in the solutions. Further study may give more details about complex ion formation. On the basis of the discussion, it can be concluded that the variation of computed values of B/A will depends on the ultrasonic sound wave in a given medium which helps in the interpretation of the magnitude of the hardness of the liquid in terms of the non-linearity parameter.

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