Ultrasonic Speed and Related Acoustical Parameters of 1,1'-Binaphthalene-2,2'-diyl Diacetate Solutions at 308.15 K

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Abstract: The density (ρ), viscosity (η) and ultrasonic speed (U) (2MHz) of chloroform, THF, ethyl alcohol, ethyl acetate, 1,4-dioxane and 1,1'-binaphthalene-2,2'-diyl diacetate (DBNA) solutions have been determined at 308.15 K. Various acoustical parameters namely specific acoustical impedance (Z), adiabatic compressibility (κ_a), Van der Waals constant (b), intermolecular path length (L_f), internal pressure (π), Rao's molar sound function (R), relaxation time (τ), classical absorption coefficient ($(\alpha f^2)_{cl}$) and solvation number (S_n) have been derived from ρ , η and U data and correlated with concentration (C). A fairly good to excellent correlation has been observed between a particular parameter and C . Linear increase of Z , R , b , $(\alpha f^2)_{cl}$ and τ (except EA) ($R^2 = 0.90 - 0.999$) and linear decrease of κ_s , π and L_f ($R^2 = 0.947 - 0.995$) with C supported existence of powerful molecular interactions in the solutions and further supported by nonlinear increase of S_n with C . A fairly constant Gibbs free energy of activation has been observed in all the solvent systems studied.

Keywords: Ultrasonic speed, Acoustical parameters, Solvation number, Gibbs free energy of activation

Introduction

Novel materials with controlled stereochemistry have found numerous applications. 2,2'-Substituted 1,1'-binaphthyl systems have been found extensively useful because of their stable conformation¹. (*R*) or (*S*) - BINOLS have often been used as the starting materials for obtaining chiral binaphthyl compounds, leading to a variety of binaphthyl derivatives, which can exhibit remarkably stable chiral configuration as well as high chiral induction in many asymmetric processes².

The measurement of speed of sound in liquid mixtures and solutions has also been found to be important tool to study the physicochemical properties of the mixtures and solutions³. The density, viscosity and speed of sound provide important information about molecular packing, molecular interactions and their strength influenced by the size, shape and the chemical nature of component molecules^{4,6}. The measurements of physical properties such as density(ρ), refractive index (n), coefficient of viscosity(η), ultrasonic velocity (U), molar sound velocity or Rao's number(R), molar volume (v_f), adiabatic compressibility (β), characteristic acoustic impedance(Z), inter molecular or free length(L_f), free volume (V_f), available volume(V_a) play an important role in sound transmission in different organic solvents and solutions.

To our knowledge no work has been reported on acoustical properties of BINOL derivatives except our recent publication⁷. In present work an effort has been made to understand molecular interactions in 1,1'-binaphthalene-2,2'-diyl diacetate (DBNA) solutions at 308.15 K.

Experimental

Solvents used in the present study were purified prior to their use⁸. 1,1'-Bi-2-naphthol (DBN) was synthesized by free radical coupling reaction of 0.05 mol 2-naphthol (in 300 mL water) using FeCl_3 (14 g in 30 mL water) as a catalyst at 60 °C for 15-20 min. DBN was crystallized at least three times from toluene and methanol-water systems (yield 55.9% and mp 218 °C). DBNA was synthesized by condensing 0.055 mol DBN in 60 mL of 10% sodium hydroxide and 18.4 mL acetic anhydride at 0-5 °C for 30 min. The separated product was filtered, washed well with water and dried at room temperature. DBNA was crystallized three times from methanol-water. The yield was 98.6% and mp 56 °C. Stock solutions of DBNA were prepared in selected solvents. From stock solutions, a series of solutions were prepared. The density (ρ), viscosity (η) and ultrasonic speed (U) measurements of pure solvents and solutions were carried out at 35 °C using specific gravity bottle, Ubbelohde suspended level viscometer and Mittal Enterprise Interferometer (New Delhi, Model No F-81) operating at 2 MHz, respectively. The ρ , η and U measurements were accurate to $\pm 0.0001 \text{ g cm}^{-3}$, $\pm 0.01 \text{ mPa s}$ and $\pm 0.15\%$, respectively.

Results and Discussion

The experimental data on ρ , η and U of pure solvents:

Chloroform (CF), tetrahydrofuran (THF), ethyl alcohol (EtOH), ethyl acetate (EA), 1,4-dioxane (DO) and DBNA solutions at 308.15 K are summarized in Table 1. The observed trends in ρ , η and U are $\text{CF} > \text{DO} > \text{EA} > \text{THF} > \text{EtOH}$; $\text{DO} > \text{EtOH} > \text{CF} > \text{EA} > \text{THF}$ and $\text{DO} > \text{THF} > \text{EtOH} > \text{EA} > \text{CF}$, respectively. From Table 1, it is observed that ρ (decreased in CF), η (decreased in EA) and U increased linearly with increasing concentration (C). The observed variation in ρ with C is little, while it is considerable for η and U . Linear variation of ρ , η and U with C confirmed existence of powerful molecular interactions in the solutions. Variation in ρ and U with C is not as appreciable as η because molecular motion is much more affected by solvent-solute interactions^{9,10}. Because of molecular interactions the structure of the solute is modified and hence physical properties change accordingly. The density, viscosity and ultrasonic speed are inherent structural properties of the materials. The least squares equations along with regression coefficients (R^2) are summarized in Table 2 from which it is observed that a fairly good to excellent correlation is found between said parameters and C (0.904 - 0.999).

Table 1. Density (ρ), viscosity (η) and ultrasonic speed (U) data of DBNA at 308.15 K

Conc., %	ρ , kg/m ³				
	CF	THF	EtOH	EA	DO
0.925	1464	877.3	784.6	888.5	1015
1.85	1463	879.8	790.2	891.5	1018
3.7	1461	886.5	796.1	897.4	1023
5.55	1458	892.3	804.6	904.2	1026
7.4	1458	899.2	812.2	910.9	1029
	η , mPas				
	CF	THF	EtOH	EA	DO
0.925	0.547	0.446	0.946	0.477	1.026
1.85	0.564	0.45	0.987	0.458	1.04
3.7	0.569	0.473	1.035	0.46	1.133
5.55	0.587	0.499	1.088	0.423	1.166
7.4	0.604	0.532	1.142	0.415	1.24
	U, ms ⁻¹				
	CF	THF	EtOH	EA	DO
0.925	957.6	1233	1119	1099	1294
1.85	958.8	1237	1125	1102	1296
3.7	961.2	1238	1134	1109	1298
5.55	968.4	1245	1142	1113	1307
7.4	970.8	1250	1148	1122	1310

Various acoustical parameters namely specific acoustical impedance (Z), adiabatic compressibility (κ_a), Rao's molar sound function (R), Van der Waals constant (b), intermolecular free path length (L_f), internal pressure (π), relaxation time (τ), classical absorption coefficient $(\alpha f^2)_{cl}$ and solvation number (S_n) were derived using ρ , η and U data according to our recent publications^{7,11,12} and correlated with C. The least squares equations along with regression coefficients are summarized in Table 2. A fairly good to excellent correlation is observed between a given parameter and C.

Table 2. Least square equations and correlation coefficients for DBNA at 35 °C

Parameter	Correlation equations and regression coefficients				
	CHCl ₃	THF	EtOH	EA	DO
ρ , kg/m ³	-1.007C + 1464. R ² = 0.929	3.390C + 873.8 R ² = 0.998	4.161C + 781.3 R ² = 0.995	3.460C + 885.0 R ² = 0.999	2.202C + 1013. R ² = 0.979
η , m. Pas	3.460C + 885.0 R ² = 0.999	0.022C + 0.413 R ² = 0.944	0.049C + 0.891 R ² = 0.997	-0.015C + 0.494 R ² = 0.906	0.055C + 0.954 R ² = 0.961
U, m.s ⁻¹	3.6C + 952.5 R ² = 0.929	4.24C + 1228 R ² = 0.958	7.48C + 1111. R ² = 0.997	5.84C + 1091. R ² = 0.973	4.32C + 1288. R ² = 0.926
Z, 10 ⁻⁶ kg m ⁻² s ⁻¹	0.003C + 1.396 R ² = 0.882	0.010C + 1.068 R ² = 0.980	0.013C + 0.862 R ² = 0.997	0.011C + 0.961 R ² = 0.983	0.009C + 1.302 R ² = 0.976
κ_a 10 ¹⁰ , Pa ⁻¹	-0.046C + 7.515 R ² = 0.909	-0.096C + 7.614 R ² = 0.98	-0.213C + 10.40 R ² = 0.998	-0.152C + 9.509 R ² = 0.983	-0.059C + 5.956 R ² = 0.968
R. 10 ⁴ , m ^{10/3} s ^{-1/3} mol ⁻¹	0.214C + 7.883 R ² = 0.986	0.612C + 8.448 R ² = 0.990	0.811C + 5.615 R ² = 0.989	0.538C + 9.913 R ² = 0.990	0.459C + 9.154 R ² = 0.986
π , 10 ⁻⁸ , Pa	-0.062C + 3.855 R ² = 0.953	-0.169C + 3.885 R ² = 0.994	-0.705C + 9.274 R ² = 0.990	-0.216C + 3.526 R ² = 0.993	-0.130C + 5.027 R ² = 0.979
b, 10 ⁵ m ³	0.203C + 7.884 R ² = 0.988	0.553C + 7.763 R ² = 0.990	0.749C + 5.339 R ² = 0.989	0.497C + 9.463 R ² = 0.988	0.407C + 8.289 R ² = 0.987
L_f , 10 ¹¹ , m	-0.037C + 5.778 R ² = 0.979	-0.037C + 5.778 R ² = 0.979	-0.071C + 6.757 R ² = 0.998	-0.053C + 6.458 R ² = 0.982	-0.025C + 5.110 R ² = 0.967
$(\alpha f^2)_{cl}$, 10 ¹⁴ s ² m ⁻¹	0.009C + 1.118 R ² = 0.903	0.013C + 0.692 R ² = 0.969	0.026C + 2.246 R ² = 0.991	-0.032C + 1.087 R ² = 0.968	0.028C + 1.197 R ² = 0.945
τ , 10 ¹³ , s	0.098C + 5.348 R ² = 0.965	0.153C + 4.223 R ² = 0.931	0.034C + 1.247 R ² = 0.997	-0.282C + 6.242 R ² = 0.958	0.337C + 7.616 R ² = 0.944

Z , R , b , $(\alpha/f^2)_{Cl}$ and τ (except EA) ($R^2 = 0.90 - 0.999$) increased linearly, while κ_a , π and L_f ($R^2 = 0.947 - 0.995$) decreased linearly with C . Linear increase or decrease of the said parameters further confirmed the existence of powerful molecular interactions in the solutions. Variation of U in the solution depends on intermolecular free path length^{9,10}.

When ultrasonic waves are incident on the solution, the molecules get perturbed. Since the medium has some elasticity and hence perturbed molecules regain their equilibrium positions. When a solute is added to a solvent, its molecules attract certain solvent molecules towards them. This phenomenon is known as compression. Every solvent has a limit for compression and is known as limiting compressibility. Generally κ_s decreases with C . The decrease of κ_s may be due to the aggregation of solvent molecules around solute molecules supporting strong solvent-solute interactions.

According to Jacobson's intermolecular free length theory for liquids, the molecules of the liquid are assumed to be spherical and the average value of the distance that the ultrasonic waves travel between the two molecules is called the intermolecular free path length. Decrease of L_f with C further supported solvent-solute interactions. Due to solvent-solute interactions, structural arrangement is considerably changed.

The dispersion of U in the system gives information about the characteristic time of the relaxation process that causes the dispersion. According to Eyring rate process theory¹³, variation of τ with temperature (T) can be given by

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\frac{\Delta G^*}{RT}}$$

Where k is the Boltzmann constant, h is the Planck's constant, R is the gas constant, T is the temperature and ΔG^* is the Gibbs free energy of activation. Observed τ is due to structural relaxation processes. Rearrangement of the molecules is a cooperative process involving the movement of many molecules around a hole in the system¹⁴. According to above equation, the value of ΔG^* was calculated at different concentrations (Table 3) and extrapolated to infinite dilution ($R^2 = 0.933 - 0.992$). The least squares intrinsic values of ΔG^* for CF, THF, EtOH, EA and DO systems are 3.195, 2.620, -0.518, 3 490 and 4.148 kJ mol⁻¹, respectively. Linear variation of ΔG^* with C indicates that the condensation in the phase and absorption due to rearrangement of molecules are independent of C and are characteristic physical properties of the solute only.

Table 3. Variation of ΔG^* with concentration for different solvent systems at 35 °C

Conc, %	ΔG^* , Jmol ⁻¹				
	CF	THF	EtOH	EA	DO
0.925	3200.16	2693.79	-494.55	3424.49	4206.19
1.85	3274.09	2694.37	-433.44	3296.90	4229.97
3.7	3288.25	2795.78	-371.84	3257.99	4424.38
5.55	3333.88	2890.13	-304.27	3005.18	4456.64
7.4	3394.50	3011.28	-233.02	2894.92	4593.32
For CF: $\Delta G^* = 26.33C + 3195$, $R^2 = 0.933$					
For THF: $\Delta G^* = 50.69C + 2620$, $R^2 = 0.978$					
For EtOH: $\Delta G^* = 38.80C - 518.1$, $R^2 = 0.992$					
For EA: $\Delta G^* = -80.85C + 3490$, $R^2 = 0.959$					
For DO: $\Delta G^* = 60.18C + 4148$, $R^2 = 0.958$					

Depending on the nature of the solvent and solute molecular interactions may lead to contraction or expansion. Internal pressure of a solution is sensitive to molecular interactions namely solvent-solute interactions, quantum mechanical dispersion forces and dielectric forces, which play an important role in transport properties of the solutions. Decrease of π with C suggested decrease of cohesive forces. Presence of molecular interactions in solutions is further supported by nonlinear increase of solvation number (S_n) (Figure 1). S_n decreased linearly with C in THF and increased nonlinearly with C in CF and EtOH, while it decreased nonlinearly with C in DO and EA. Molecular interactions are influenced by the nature and structure of the solute, pressure, concentration, nature of the substituent, *etc.* The presence of polar substituent in the solute molecules lead to enhanced molecular interactions. Solvation causes compressibility of the molecules. Thus solvation is a measure of structure forming or breaking tendency of the solutes. The dipole-dipole interactions of the opposite type favor the structure formation; while of the same type disrupt the structure formed previously. In the present case positive values of S_n indicated predominant dipole-dipole interactions of the opposite type. In conclusion, derived acoustical parameters suggested the presence of strong molecular interactions in the solutions. DBNA possesses structure forming tendency in all the solvent systems.

Figure 1. Plots of S_n against concentration for DBNA solutions at 308.15 K

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