Computation of Thermoacoustic and Thermodynamic Properties of Aqueous Methyl Orange Solution from Density and Sonic Speed Data

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ABSTRACT: Density and ultrasonic speed data have been used to calculate a number of useful and important thermoacoustic and thermodynamic parameters such as thermal expansivities, α, isothermal compressibility, β_T, internal pressure, P_{int}, specific heat ratio, ϒ, surface tension, σ, Pseudo-Grüneisen parameter, Γ, non-linearity parameter, B/A, by empirical relations at T= (303, 308, 313 and 318) K temperatures in the range concentration from 0.05 to 1 molar. Solvation number, S_n, has been computed to support the conformational change in geometry of aqueous methyl orange solution. The calculated values highly support the change in orientation and abnormal behavior of methyl orange solution at varying concentrations and quite satisfactory results are obtained.

Keywords: Methyl orange; empirical relations; thermodynamic properties; ultrasonic speed; non-linearity parameter and internal pressure.

INTRODUCTION: The decolourization/fading of aqueous dye solutions by high intensity ultrasonic waves have been studied quite early by a number of workers.[1,2] The degradation of coloured chrome Azural S-Al complex has also been studied at 2MHz frequency of such high intensity ultrasonic waves.[3] But the propagation of low amplitude ultrasonic waves in aqueous dye solutions has so, far, not been studied. Hence the ultrasonic propagation parameters such as ultrasonic speed, absorption, relaxation etc could not be measured in such solutions. After an exhaustive literature survey we have come across two papers[4,5] dealing with the determination of ultrasonic speed, density, viscosity, surface tension of methyl orange[4] and 4-methyl-7-hydroxycoumarin.[5] The chemical structure of methyl orange is depicted in Figure 1. It is worthwhile to mention that these ultrasonic propagation parameters can be employed to determine a number of important and useful thermodynamic and transport properties of liquids and solutions.
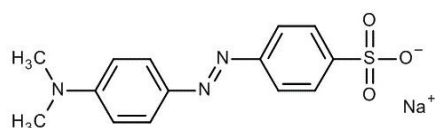

Figure 1: Structure of Methyl Orange.

With a proper theoretical formalism, the estimated properties will be helping in structural and physico-chemical studies of system. In order to achieve such goal, we have for the first time, taken such studies for dye solutions. The structure and nature of, and interactions occurring in liquids and solutions can be investigated from density and ultrasonic speed data. The experimental techniques involved in the measurements of density and ultrasonic speed are very simple, quick and quite precise. Such data can be employed to estimate a number of useful and important thermodynamic properties of liquids and solutions. There is only one thermodynamic property which can be directly determined from density and ultrasonic speed data, which is the adiabatic (isentropic) compressibility, β_s given by:

$$\beta_S = (u^2\rho)^{-1}$$

This property cannot be determined by any other method. In order to estimate other thermodynamic properties, some empirical relations based on dimensional analysis, have been developed during recent past.[6-11] In the present work we are using these equations for computing various thermodynamic and thermoacoustical properties of aqueous solutions of methyl orange. The experimental data of density (ρ) and ultrasonic

speed (u) have been taken from the recent paper of Thanuja et al.[4] The other paper[5] has quite limited data and hence ignored.

THEORETICAL FORMULATION: Based on the dimensional analysis[6-11] the following empirical relations between ρ-u and thermodynamic properties have been deduced:

Thermal expansivity:

$$\alpha = \frac{75.6 \times 10^{-3}}{T^{1/9} u^{1/2} \rho^{1/3}} \qquad (1)$$

Isothermal compressibility:

$$\beta_T = \frac{1.71 \times 10^{-3}}{T^{4/9} u^2 \rho^{4/3}} \qquad (2)$$

Internal pressure:

$$P_{int} = \frac{\alpha.T}{\beta_T} = 44.2 \times T^{4/3} u^{3/2} \rho \qquad (3)$$

Heat capacities ratio:

$$\gamma = \frac{17.1}{T^{4/9} \rho^{1/3}} \qquad (4)$$

Surface tension:

$$\sigma = T^{4/3} u^{3/2} \rho.10^{-4} \qquad (5)$$

One of the very important and useful parameter, known as pseudo-Grüneisen parameter (Γ), which has been studied by many workers[12-16] for investigating the internal structure and clustering phenomenon in liquids and solutions. Also, it is a dimensionless measure of change in entropy with volume or the thermal pressure and is usually investigated through the relations given below. Physical significance of this thermodynamic parameter has recently[13] been discussed and applied for liquids. This parameter is given by:

$$\Gamma = \frac{u^2 \alpha}{C_P} = \frac{\gamma - 1}{\alpha.T} \qquad (6)$$

The significance and importance of another thermodynamic parameter, called the Beyer's acoustic non-linearity parameter (B/A), has been discussed by several workers during recent years.[17-20]

There are several methods of determination of B/A, but there are several limitations. In the present case of methyl orange solutions, the only possible three formulae can be employed. These are:

Hartmann- Balizer[20]

$$\frac{B}{A} = 2 + [\frac{0.98 \times 10^4}{u}] \qquad (7)$$

Ballou[21]

$$\frac{B}{A} = -0.5 + [\frac{1.2 \times 10^4}{u}] \qquad (8)$$

Internal pressure, P_{int}, is related to B/A as:

$$P_{int} = \frac{\rho u^2}{1 + B/A} \qquad (9)$$

The apparent molar volume (ϕ_v), apparent molar compressibility (ϕ_k) and solvation number (S_n) are obtained respectively using eqs (10), (11) and (12):

$$\phi_V = \left(\frac{M_2}{\rho}\right) + \left\{n_1 M_1 (\rho_0 - \rho) m.\rho.\rho_0\right\} \quad (10)$$

$$\phi_{ks} = \left(\frac{M_2 \beta_s}{\rho}\right) + \left\{\frac{n_1 M_1 (\beta_s \rho_0 - \beta_s^0 \rho)}{m.\rho.\rho_0}\right\} \quad (11)$$

$$S_n = \frac{n_1}{n_2}\left[1 - \frac{K_s}{K_{si}}\right] \qquad (12)$$

RESULTS AND DISCUSSION: Computation of various thermodynamic and thermoacoustical properties of aqueous methyl orange solution have been done using the experimental data of density, ρ, and ultrasonic speed, u, at four different temperatures 303, 308, 313 and 318K and varying concentrations (0.05 - 2.0) mole %. The experimental values of density and ultrasonic velocity were taken from the paper of Thanuja et al.[4] The calculated values of α, β_T, P_{int}, Υ, σ and Γ from empiricial equations (1) to (6) are recorded in Table 1.

The thermoacoustic non-linearity parameter, B/A, and the internal pressure, P_{int}, have been calculated from two different methods namely Hartmann-Balizer[20] and Ballou[21] using equations (7), (8) and (9) are enlisted in Table 2.

Table 3 focuses on the calculated values of apparent molar volume (ϕ_v), apparent molar isentropic compressibility (ϕ_{ks}) and most important of all the solvation number at all temperatures considered above using equations (10), (11) and (12).

Table 1: Estimated values of thermal expansivity (α), isothermal compressibility (β$_T$), internal pressure (P$_{int}$), specific heat ratio (ϒ), surface tension (σ), pseudo-Grüneisen parameter (Γ) at T= (303, 308, 313 and 318) K.

| Conc.	T	αx10³	β$_T$x10¹⁷	P$_{int}$	ϒ	σ	Γ
(mole%)	K	K⁻¹	atm⁻¹	atm		Nm⁻¹	
0.05	**303**	**0.9984**	**52.713**	**459214**	**1.308**	**43.411**	**1.018**
	308	0.9906	51.081	477068	1.2997	44.447	0.982
	313	0.9875	50.436	488003	1.2908	44.872	0.941
	318	0.9888	50.713	492935	1.2829	44.689	0.9
Ideal	303	1.0422	62.59	430265	1.3503	38.164	1.109
0.1	**303**	**0.9867**	**50.275**	**476107**	**1.3084**	**44.98**	**1.031**
	308	0.9953	52.062	470596	1.3001	43.817	0.979
	313	0.9644	45.879	525531	1.2928	48.176	0.97
	318	0.9681	46.595	526869	1.2849	47.619	0.925
Ideal	303	1.0435	62.884	429762	1.3519	38.031	1.113
0.5	**303**	**0.9641**	**45.832**	**510631**	**1.3088**	**48.212**	**1.057**
	308	0.9707	47.093	507678	1.3005	47.241	1.005
	313	0.9942	51.817	478800	1.2916	43.972	0.937
	318	0.9833	49.578	501684	1.2833	45.454	0.906
Ideal	303	1.0423	62.598	430253	1.3503	38.161	1.109
1	**303**	**0.9899**	**50.922**	**472139**	**1.3092**	**44.551**	**1.031**
	308	0.9892	50.781	479764	1.3005	44.643	0.986
	313	0.986	50.125	491172	1.292	45.081	0.946
	318	0.9808	49.08	505804	1.2837	45.799	0.91
Ideal	303	1.0423	62.602	430271	1.3504	38.159	1.11
2	**303**	**1.007**	**54.553**	**448914**	**1.31**	**42.308**	**1.016**
	308	0.9972	52.446	468868	1.3013	43.576	0.981
	313	0.9901	50.983	485551	1.2928	44.511	0.945
	318	0.9887	50.684	494356	1.2845	44.708	0.905
Ideal	303	1.0422	62.587	430271	1.3503	38.166	1.109

Table 2: Calculated values of non-linearity parameter (B/A) and internal pressure (P$_{int}$) at T= (303, 308, 313 and 318) K.

Conc.	T	B/A	P$_{int}$	B/A	P$_{int}$
(mole %)	K	Hartmann	atm	Ballou	atm
0.05	**303**	**8.4763**	**265310**	**2.9302**	**639704**
	308	8.3869	274644	2.8206	674768
	313	8.3653	276893	2.7942	683454
	318	8.3935	272877	2.8288	669471
Ideal	303	8.6216	227192	3.1081	532109
0.1	**303**	**8.3209**	**282901**	**2.7399**	**705066**
	308	8.444	267921	2.8906	650349
	313	8.0524	315403	2.4111	837025
	318	8.1097	306714	2.4813	802597
Ideal	303	8.6216	226396	3.1081	530245
0.5	**303**	**8.0315**	**320369**	**2.3855**	**854642**
	308	8.125	306639	2.5	799451
	313	8.444	267431	2.8906	649160
	318	8.3177	281484	2.7359	702039
Ideal	303	8.6216	227171	3.1081	532063
1	**303**	**8.3537**	**278499**	**2.7801**	**689139**
	308	8.3603	277218	2.7882	684990
	313	8.334	279801	2.7559	695342
	318	8.2821	285518	2.6923	717760
Ideal	303	8.6212	227177	3.1076	532116
2	**303**	**8.5684**	**254285**	**3.0429**	**601818**
	308	8.4559	265869	2.9051	643772
	313	8.3802	273904	2.8125	673908
	318	8.3761	273878	2.8074	674445
Ideal	303	8.6216	227201	3.1081	532131

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Table 3: Calculated values of apparent molar volume (Φ_v) apparent molar isentropic compressibility (Φ_{ks}) and solvation number (S_n).

Conc.	T	Φ_v	Φ_{ks}	S_n
Mol %	K	$m^3\,mol^{-1}$	m^2N^{-1}	
0.05	**303**	**119.61**	**7245.4**	**-0.025**
	308	125.42	7362.3	-0.025
	313	127.36	7429.4	-0.025
	318	133.21	7472.7	-0.025
	303	332.06	9685.7	-0.021
0.1	**303**	**209.96**	**4074.9**	**-0.026**
	308	213.28	4354	-0.024
	313	218.85	3827.9	-0.028
	318	222.22	4041.5	-0.026
	303	334.72	5740.8	-0.02
0.5	**303**	**281.14**	**1574.7**	**-0.028**
	308	282.46	1771.1	-0.025
	313	282.9	1823.8	-0.024
	318	283.79	1756.3	-0.025
	303	328.46	2359.3	-0.02
1	**303**	**290.26**	**1477.9**	**-0.025**
	308	290.97	1464	-0.025
	313	291.69	1455.6	-0.025
	318	292.41	1436.6	-0.026
	303	328.3	1939.5	-0.02
2	**303**	**295.22**	**1396.9**	**-0.023**
	308	295.86	1353.6	-0.024
	313	296.49	1342.2	-0.024
	318	297.13	1345.5	-0.024
	303	328.09	1729	-0.02

There is a sharp fall in density (ρ), ultrasonic speed (u), thermal expansivities (α), isothermal compressibility (β_T), internal pressure (P_{int}) owing to the stereochemistry of methyl orange. Methyl orange exhibits geometrical isomerism at N=N (azo group). The structure can be represented as Figure 2 syn (Z) and Figure 3 anti (E) 2D forms. Figure 4 and Figure 5 represents syn (Z) and anti (E) 3D form.
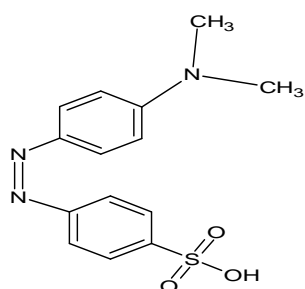
Figure 2: Syn form (2D).

Here dark grey balls represents carbon atom, light grey are the hydrogen atoms, blue is nitrogen, yellow is sulphur atom and red balls are the oxygen atoms. At low concentration less molecules of methyl orange are available in water so it prefers the anti conformer where the two nitrogen atoms are more available for hydrogen bonding therefore denser. But as the methyl orange moiety increases equal number of molecules in

syn as well as (in equilibrium) anti form exists. In syn form the lone pair on nitrogen is less available for hydrogen bonding due to steric hindrance and hence less density at higher mole fraction.
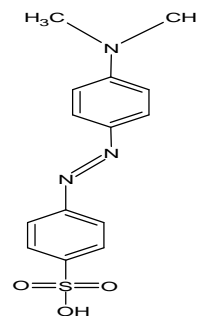
Figure 3: Anti form (2D).
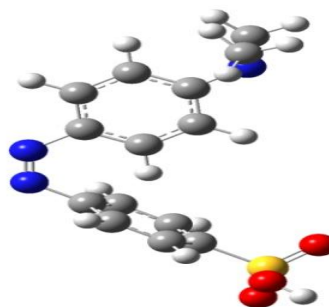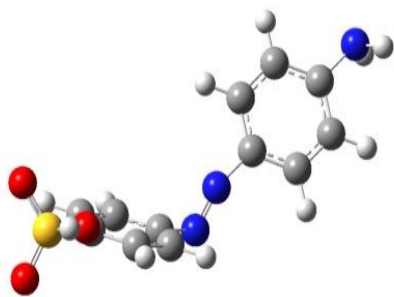

Figure 4: Syn Form (3D).

Figure 5: Anti Form (3D).

Increase in molar concentration decreases the values of α and β_T as they are inversely proportional to density, density increases in region of low concentration and low temperatures (303, 308K) and apparently increases in region of high concentration and temperatures (313 and 318K) due to breakdown of hydrogen bonds, releasing the dipoles of water leading to formation of intermolecular hydrogen bonds. Similarly P_{int} increases with concentration till 0.5 then decreases till 2 % showing close interaction between solute-solvent in region of low concentration, which apparently decreases abruptly with increase in solute volume or solute molecules in solvent leading to an increase in the volume of solution. At high concentration, the solute-solvent interactions present are dominated by solute-solute interaction. Similar is the trend with temperature in case of P_{int}.

Heat capacity ratio, ϒ, increases with concentration as the number of interacting molecule increases, the bulky group in methyl orange increases with concentration thereby more association with solvent (water) molecules and reverse trend is with temperature as rise in temperature keeps the molecules in excited state predominantly. With increase in concentration of methyl orange the Γ value increases till 0.5 mol% then there is a sharp decrease from 1to 2 mol% indicating large clustering and more compact lattice structure during interaction till 0.5 mol% followed by sudden decrease, this abnormal behavior is due to sharp decrease in density due to sudden increase in the volume of the solution with the addition of methyl orange. The rise in temperature at each concentration decreases the value continuously predicting that as the temperature increases continuously the interaction between the solute and solvent decreases due to increased intermolecular distance and breaking or lengthening of hydrogen bonds prevalent between them.

The non-linearity parameter, B/A values as calculated by Hartmann and Ballou relations, show a marked decrease with concentration till 0.5% and apparent increase till 2% concentration indicative of more number of interacting molecules in the system. The temperature rise decreases the value of B/A at each concentration as the ultrasonic speed increases with increasing intermolecular distance and volume in the same order. Deviation from ideal behavior is noticed in solution with a concentration of 0.1%. At elevated temperature breaking of hydrogen bonds becomes more feasible.

Apparent molar volume and apparent molar compressibility are increasing with temperature as well as concentration. An attempt has also been made to deduce the values of ϕ_v^0, S_v, ϕ_k^0, S_k using Masson's equations $\phi_v = \phi_v^0 + S_{v,m}$ and $\phi_k = \phi_k^0 + S_{k,m}$. Here ϕ_v^0 and ϕ_k^0 measure the solute-solvent interaction, whereas S_v and S_k the experimental slopes, measure the solute-solute interaction. Unfortunately, in the present case of methyl orange solution, the ϕ_v versus ϕ_k plots are found to be non-linear, hence cannot be used to determine ϕ_v^0, S_v, ϕ_k^0, S_k. In addition, the solvation number is negative indicates that the ion is likely to dissolve in solvent but with increasing temperature and concentration the negative value increases showing less interaction with water molecules.

CONCLUSION: A remarkable property of methyl orange dye has come into being owing to its sharp fall in density and ultrasonic speed at a high concentration due its stereochemistry. The change in conformation on varying concentration is responsible for its abnormal behavior. The solvation number parameter supports its uniqueness. The above is depicted well with the help of self explanatory diagrams drawn with the help of software, ACD LAB Chem Sketch for 2D conformation and Gauss View software for 3D conformation. The solvation number parameter supports the above explanation. This is a stepping milestone in our explanation of the interaction parameters with the help of software and its successful implementation justifying the uniqueness of methyl orange in solution chemistry.

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