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J.D. Pandey, Rupali Sethi, Subhash Chandra Shrivastava & Ramakant

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ABSTRACT

The aim of the present study is to investigate the influence of temperature (293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K and change in physical properties (density, ultrasonic velocity and viscosity) measurement of seven types of honey samples taken from literature. The thermodynamic, thermophysical and thermoacoustical properties such as thermal expansion coefficient (α), isothermal compressibility (β_T), internal pressure (P_{int}), specific heat ratio (γ), pseudo-Grüneisen parameter (Γ) and solubility parameter (δ) were computed at different temperature and varying concentration. The results found were excellent. It predicts the quality of the types of honey with the exception of Baker's honey (Indian honey) which always show variation opposite to other six types owing to origin. The non-linearity parameter and internal pressure of seven types of honey samples the present study shows strong interactions among atoms and functional group due to prevalence of ion-ion, ion-dipole and dipole-dipole interactions.

Keywords: honey, ultrasonic velocity, viscosity, density, non-linearity parameter, internal pressure, solubility parameter.

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Estimation of Some Important and useful Thermodynamic, Thermophysical and Thermoacoustical Properties of Different Types of Honey Sample

J.D. Pandey^α, Rupali Sethi^α, Subhash Chandra Shrivastava^ρ & Ramakant^θ

ABSTRACT

The aim of the present study is to investigate the influence of temperature (293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K and change in physical properties (density, ultrasonic velocity and viscosity) measurement of seven types of honey samples taken from literature. The thermodynamic, thermophysical and thermoacoustical properties such as thermal expansion coefficient (α), isothermal compressibility (β_T), internal pressure (P_{int}), specific heat ratio (γ), pseudo-Grüneisen parameter (Γ) and solubility parameter (δ) were computed at different temperature and varying concentration. The results found were excellent. It predicts the quality of the types of honey with the exception of Baker's honey (Indian honey) which always show variation opposite to other six types owing to origin. The non-linearity parameter and internal pressure of seven types of honey samples the present study shows strong interactions among atoms and functional group due to prevalence of ion-ion, ion-dipole and dipole-dipole interactions.

The experimental data of surface tension (σ) confirm that temperature has minimal effect on the above properties and relevance of high viscosity of seven types of honey.

Keywords: honey, ultrasonic velocity, viscosity, density, non-linearity parameter, internal pressure, solubility parameter.

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I. INTRODUCTION

Honey produced by honey bees, *Apis mellifera* is produced globally in thousands of flavors and color depending on the blossoms visited by the honey bees. Single varietal honeys result when the honey bees gather nectar from the same type of flowers. Chemically honey contains fructose, glucose [1, 2, 3] and the amount and type of amino acids and organic acids vary by floral source which in turn determines the flavor of honey. The species of honey popular worldwide are Algerian honey [3], Australian honey [4], Millefiori honey [5], Israeli honey [6], Baker's honey (popularly known as Indian honey) [7], Romanian honey [8] and Spanish honey [9]. Raw honey is the best, as it is not adulterated.

Commercial honey has to be analyzed for its food and medicinal value (Figure 1) as more the medicinal value [11] more is its cost. Due to high anti-bacterial properties [12] New Zealand's Manuka [13], Malaysia's Tualang honey, Yemeni Sidr honey and European honeydew honey are 20 times costlier and kept as a treasure for treating burns, cuts, coughs, sore-throat, eye infection, insomnia, arthritis, diabetes [13, 14, 15], acid reflux, anticancer [13, 16, 17, 18] and other ailments.

- HONEY
- ANTI-MICRO-BIAL ACTIVITY
- ANTI-INFLAMMATORY ACTIVITY
- ANTIOXIDANT
- GASTROINTESTINAL TRACK DISORDER
- ANTI
- CANCER
- NEURO-
- LOGICAL DISORDER
- ANTI
- DIABETIC
- ANTI HYPER
- PIGMENTATION
- CARDIO-
- VASCULAR DISORDER
- WOUND CUT
- REPRODUCTIVE SYSTEM
- EYE DISORDER

Figure 1: Medicinal uses of Honey

Organic honey is also effective as it is certified by organic standard tests. Honey when mixed with a few spices act as medium for taking the medicine from the source to the place of infection and aids in its cure. It is a wonderful cosmetology base and is widely suggested by skin experts for cure of skin diseases. Pharmaceutical companies use it as a medium in some skin ointments.

1.1 Chemistry Involved in honey production

Bees harvest nectar, sucrose (Figure 2), a disaccharide which is stored in their honey stomachs and when mixed with enzymes break into smaller monosaccharide units namely glucose (Figure 3) and fructose (Figure 4).

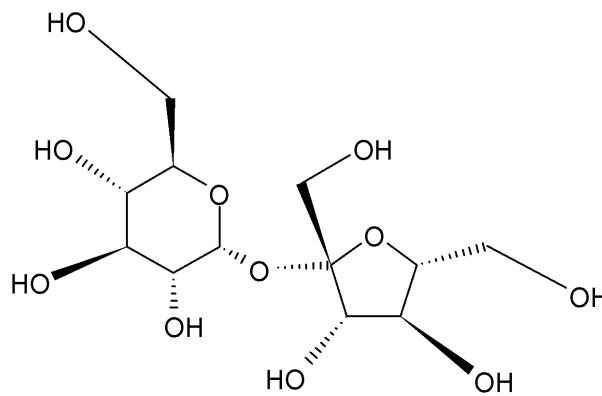


Figure 2: Structure of Sucrose (main content in nectar)

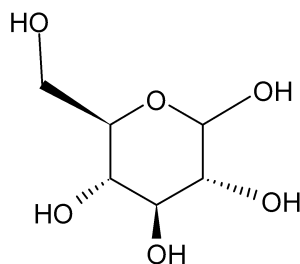


Figure 3: Structure of Glucose

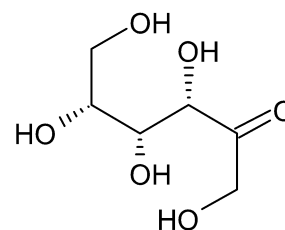


Figure 4: Structure of Fructose

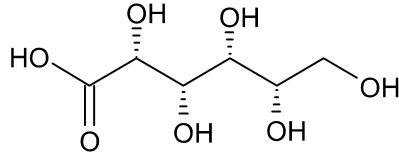


Figure 5: Structure of Gluconic acid

The nectar is deposited in the honeycomb and the bee fans it for fast evaporation of water till the water content falls to 17%. Since the water content is so low it draws water from surrounding i.e. dehydrates bacteria preventing it from spoilage. Apart from this gluconic acid (Figure 5), produced by bee secretion on glucose maintains a low pH of honey (pH = 3 — 4) and hydrogen peroxide (Figure 6) prevents bacterial growth responsible for its long shelf life.

Viscosity and surface tension are one of the most important properties of honey. The moisture content plays a key role in honey processing as it increases or decreases the viscosity of honey [20]. Apart from viscosity, water content is solely responsible for its storage conditions [21]. The rheological properties depend on temperature and composition. The presence of disaccharides along with monosaccharide increases the viscosity of honey.

In the present work, ultrasonic velocity, density data and viscosity measurements of seven types of honey done by M. Oroian [10] have been successfully used by us to predict the thermodynamic, thermophysical and thermoacoustical properties and also employed there property to study the nature of molecular interactions prevalent between them.

III. FORMULATION

Based on the dimensional analysis [22-25] following correlations between ρ - u thermodynamic properties are used:-

Isobaric thermal expansivity (Thermal expansion coefficient)

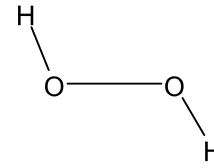


Figure 6: Structure of Hydrogen peroxide

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{75.6 \times 10^{-3}}{T^{3/10} u^{1/2} \rho^{1/4}} \quad (1)$$

Isothermal Compressibility

$$\beta_T = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1.71 \times 10^{-3}}{T^{1/9} \rho \cdot u^{3/2}} \quad (2)$$

Specific Heat Ratio

$$\gamma = \frac{C_p}{C_v} = \frac{\beta_T}{\beta_s} = \frac{17.1}{T^{4/9} \rho^{1/3}} \quad (3)$$

Internal Pressure

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

Pseudo-Grüneisen parameter

$$\Gamma = \frac{\gamma - 1}{\alpha \cdot T} \quad (5)$$

Solubility parameter

$$\delta = \sqrt{P_{int}} \quad (6)$$

Free length

$$L_f = k' (\beta_s)^{1/2} \quad (7)$$

where $k' = (93.875 + 0.375T) \times 10^{-8}$

Acoustic impedance

$$Z = \rho \cdot u \quad (8)$$

The thermoacoustic non-linear parameter, (B/A) [26-28] has been obtained from the following different equations:

Hartmann-Balizer [26]

$$\frac{B}{A} = 2 + \left[\frac{0.98 \times 10^4}{u} \right] \quad (9)$$

Ballou [27]

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

Johnson et al [28]

$$\left(\frac{B}{A} \right) = \gamma (C_1 - 1) - (\gamma - 1)(\delta - 1) \quad (11)$$

where, $\gamma = C_p / C_v$, $C_1 =$ Moelwyn-Hughes parameter, $\delta =$ Anderson-Grüneisen parameter given respectively by

$$C_1 = \frac{13}{3} + (\alpha.T)^{-1} + \frac{4}{3}(\alpha.T) \quad (12)$$

$$\delta = \frac{10}{3} + 2(2\alpha.T)^{-1} + \frac{4}{3}\alpha.T + 1 \quad (13)$$

III. RESULTS AND DISCUSSION

The density (ρ), ultrasonic velocity (u) and viscosity (η) data of seven types of honey namely Australian honey [4], Millefiori honey [5], Israeli honey [6], Baker's honey (popularly known as Indian honey) [7], Romanian honey [8], Spanish honey [9] and Algerian honey [3] have been taken from the paper of Oroian [10] at seven different temperatures (293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K. The calculated values of thermal expansion coefficient (α), isothermal compressibility (β_T), heat capacities ratio (γ), internal pressure (P_{int}), pseudo-Grüneisen parameter (Γ), solubility parameter (δ), free length (L_f) and acoustic impedance (Z) of seven types of honey using empirical correlations (1-8) are reported in Table 1 at seven different temperatures mentioned earlier.

Table 1: Calculated values of Thermal expansivity (α), Isothermal Compressibility (β_T), Heat capacities ratio (γ) Internal pressure (P_{int}), pseudo-Grüneisen parameter (Γ), Solubility parameter (δ), Free Length (L_f) & Acoustic Impedance (Z) at different temperatures

$\alpha \times 10^{-7}$ K ⁻¹	$\beta_T \times 10^4$ TPa ⁻¹	Γ	$P_{int} \times 10^4$ atm	$\Gamma \times 10^3$	$\delta \times 10^7$ Pa ^{1/2}	$L_f \times 10^{-2}$ Nm	$Z \times 10^6$ kgm ⁻² s ⁻¹
T=293.15K							
1.014	1.845	1.228	4.188	7.675	6.557	4.505	6.958
1.012	1.841	1.228	4.197	7.678	6.564	4.500	6.970
1.010	1.836	1.227	4.209	7.674	6.574	4.493	6.987
1.007	1.829	1.227	4.225	7.688	6.586	4.485	7.006
1.003	1.817	1.226	4.253	7.671	6.608	4.470	7.045
0.993	1.795	1.224	4.306	7.698	6.649	4.442	7.112
0.988	1.783	1.223	4.334	7.708	6.671	4.428	7.148
T=298.15K							
1.015	1.851	1.220	4.261	7.285	6.614	4.520	6.926
1.013	1.846	1.220	4.274	7.280	6.624	4.514	6.943
1.011	1.842	1.220	4.283	7.282	6.632	4.509	6.955
1.009	1.838	1.219	4.293	7.285	6.639	4.504	6.967
1.004	1.824	1.218	4.325	7.286	6.663	4.487	7.008
0.995	1.803	1.216	4.376	7.292	6.703	4.461	7.073
0.990	1.791	1.216	4.405	7.300	6.725	4.446	7.109
T=303.15K							

1.016	1.859	1.213	4.332	6.922	6.669	4.537	6.889
1.015	1.856	1.213	4.337	6.918	6.673	4.534	6.897
1.014	1.853	1.213	4.344	6.917	6.679	4.531	6.906
1.011	1.845	1.212	4.363	6.907	6.693	4.521	6.930
1.006	1.832	1.210	4.396	6.895	6.718	4.504	6.974
0.997	1.811	1.209	4.445	6.906	6.755	4.479	7.033
0.992	1.797	1.207	4.480	6.897	6.782	4.461	7.080
T=308.15K							
1.374	2.518	1.206	3.262	4.856	5.787	5.290	5.614
1.018	1.865	1.205	4.404	6.544	6.724	4.553	6.860
1.016	1.861	1.205	4.414	6.547	6.732	4.548	6.872
1.014	1.855	1.204	4.427	6.541	6.742	4.541	6.889
1.012	1.847	1.203	4.447	6.520	6.757	4.531	6.916
0.908	1.357	1.089	6.052	3.184	7.882	3.884	9.384
0.996	1.811	1.201	4.536	6.537	6.824	4.486	7.023
T=313.15K							
1.020	1.874	1.199	4.471	6.214	6.775	4.572	6.820
1.019	1.871	1.198	4.477	6.210	6.779	4.569	6.828
1.017	1.866	1.198	4.489	6.216	6.789	4.562	6.843
1.014	1.860	1.197	4.504	6.212	6.800	4.555	6.861
1.011	1.850	1.196	4.527	6.207	6.818	4.543	6.890
1.001	1.826	1.194	4.586	6.190	6.862	4.514	6.963
0.997	1.817	1.194	4.611	6.199	6.880	4.502	6.991
T=318.15K							
1.022	1.882	1.192	4.538	5.891	6.826	4.590	6.785
1.018	1.875	1.191	4.555	5.902	6.839	4.581	6.803
1.018	1.872	1.191	4.562	5.898	6.843	4.578	6.811
1.016	1.869	1.191	4.569	5.895	6.849	4.574	6.820
1.012	1.860	1.190	4.593	5.914	6.867	4.563	6.846
1.006	1.843	1.189	4.634	5.895	6.897	4.542	6.896
1.001	1.828	1.187	4.671	5.859	6.925	4.524	6.945
T=323.15K							
1.023	1.888	1.185	4.610	5.589	6.880	4.606	6.753
1.020	1.883	1.184	4.623	5.594	6.889	4.599	6.767
1.019	1.880	1.184	4.631	5.591	6.895	4.596	6.776
1.017	1.874	1.184	4.644	5.585	6.905	4.589	6.793
1.015	1.866	1.182	4.665	5.563	6.921	4.579	6.820
1.008	1.848	1.180	4.710	5.536	6.954	4.557	6.876
0.997	1.826	1.180	4.766	5.579	6.995	4.530	6.934

Table 1 indicates that with change in temperature from 293.15 to 328.15 K the value of thermal expansion coefficient (α) increases slightly showing that the fluidity of honey is minutely affected till 303.15 K but at 308.15 K there is a sharp increase in value if thermal expansion coefficient (α) indicating that Baker's honey fluidity increases manifolds, due to lesser interaction between the honey molecules & larger intermolecular space (voids). These two factors make the baker's honey less viscous at 313.15 K & 318.15 K. There is again a fall in the value of

thermal expansion coefficient (α), thereby decreasing the viscosity.

In the case of isothermal compressibility (β_T) similar trend is obtained which means that Baker's honey is most compressible with temperature rise making it stickier and most crystalline with adverse temperature range. The heat capacity ratio (γ) is constantly decreasing throwing light on the fact that specific heat at constant volume (C_v) is decreasing constantly at elevated temperatures. The internal pressure (P_{int})

values are high with regular rise with temperature till 303.15 K with the exception of Baker's honey at which it falls sharply and then rise constantly showing less repulsion between atoms of honey. Lesser repulsion is attributed to the fact of existence of a strong intermolecular hydrogen bonding.

In the case of pseudo-Grüneisen parameter (Γ) the value is falling constantly till 308.15 K then rising, reverse of thermal expansion coefficient (α) as they are inversely proportional to each other.

Solubility parameter (δ) is very high in all type of honey with increase in value till 303.15 K then falling at 308.15 K (Baker's honey) and again

increasing makes it miscible in water easily and far more soluble.

Free length (L_f) values constantly increase and at its peak at 308.15 K indicating more mobility. The acoustic impedance is decreasing constantly i.e. the existence to flow of Honey is decreases constantly till 308.15 K then a sharp increase is shown marked by less resistance and more viscous flow.

Table 2 indicates the calculated values of non-linearity parameter (B/A), from equation (9-13), internal Pressure (P_{int}) and surface tension (σ) at seven different temperatures.

Table 2: Calculated values of non-linearity parameter (B/A), internal pressure (P_{int}) and surface tension (σ) at 293.15 K – 323.15 K temperature range

Hartmann		Ballou		Johnson		
B/A	P_{int} atm	B/A	P_{int} atm	$B/A \times 10^4$	$P_{int} \times 10^{-3}$ atm	$\sigma \times 10^{-3}$ Nm ⁻¹
T=293.15K						
3.952	6.961	1.850	12.093	3.364	1.025	3.275
3.950	6.982	1.848	12.136	3.370	1.026	3.282
3.948	7.009	1.846	12.188	3.377	1.027	3.292
3.944	7.048	1.841	12.266	3.387	1.029	3.304
3.941	7.107	1.836	12.379	3.402	1.032	3.326
3.929	7.234	1.822	12.634	3.436	1.038	3.367
3.924	7.301	1.815	12.768	3.454	1.041	3.390
T=298.15K						
3.954	6.919	1.853	12.016	3.305	1.037	3.277
3.952	6.946	1.850	12.067	3.312	1.039	3.286
3.950	6.967	1.848	12.110	3.317	1.040	3.294
3.948	6.989	1.846	12.153	3.323	1.041	3.301
3.943	7.059	1.839	12.292	3.341	1.044	3.325
3.933	7.174	1.827	12.519	3.371	1.050	3.364
3.927	7.241	1.820	12.652	3.388	1.053	3.387
T=303.15K						
3.956	6.873	1.855	11.930	3.247	1.049	3.276
3.955	6.884	1.854	11.952	3.250	1.050	3.280
3.954	6.899	1.853	11.981	3.253	1.051	3.285
3.951	6.937	1.850	12.055	3.263	1.053	3.299
3.946	7.006	1.843	12.187	3.279	1.057	3.324
3.937	7.115	1.832	12.404	3.308	1.062	3.361
3.931	7.191	1.825	12.554	3.326	1.066	3.388
T=308.15K						
4.393	4.207	2.390	6.692	2.363	0.960	2.427
3.960	6.825	1.860	11.836	3.188	1.062	3.276
3.958	6.846	1.858	11.879	3.194	1.063	3.284

3.956	6.873	1.855	11.930	3.200	1.064	3.293
3.954	6.909	1.853	11.998	3.208	1.067	3.308
3.943	9.453	1.839	16.460	3.576	1.306	4.502
3.937	7.105	1.832	12.387	3.258	1.076	3.374
T=313.15K						
3.963	6.772	1.863	11.738	3.132	1.073	3.273
3.962	6.784	1.862	11.760	3.134	1.074	3.277
3.959	6.812	1.859	11.815	3.142	1.075	3.286
3.957	6.841	1.856	11.873	3.149	1.077	3.297
3.953	6.889	1.851	11.966	3.161	1.080	3.314
3.944	7.009	1.840	12.200	3.189	1.086	3.358
3.939	7.062	1.834	12.307	3.203	1.089	3.375
T=318.15K						
3.966	6.722	1.867	11.642	3.077	1.085	3.270
3.962	6.759	1.862	11.717	3.087	1.087	3.282
3.961	6.770	1.861	11.739	3.089	1.087	3.287
3.960	6.785	1.860	11.767	3.093	1.088	3.292
3.954	6.839	1.853	11.876	3.108	1.090	3.309
3.948	6.918	1.846	12.030	3.126	1.095	3.339
3.944	6.987	1.841	12.160	3.141	1.100	3.366
T=323.15K						
3.968	6.681	1.870	11.566	3.026	1.097	3.270
3.965	6.708	1.866	11.621	3.033	1.098	3.280
3.964	6.723	1.865	11.649	3.037	1.099	3.285
3.962	6.749	1.862	11.699	3.043	1.101	3.295
3.960	6.785	1.860	11.767	3.050	1.103	3.309
3.954	6.869	1.853	11.929	3.069	1.109	3.341
3.941	6.995	1.836	12.184	3.103	1.114	3.381

Table 2 focuses on non-linearity parameter (B/A) and internal pressure (P_{int}) by Hartmann, Ballou and Johnson methods. By Hartmann and Ballou methods, B/A decreases constantly with viscosity & internal pressure is increasing showing more interaction between the atoms of honey making it stronger in interaction intensity. In Johnson method the B/A and P_{int} are constantly increasing indicating the role of specific heat capacity ratio (γ) in seven types of honey undertaken in our study.

The temperature change results in an increase in B/A value & decrease in internal pressure as the intermolecular spaces increases and interaction decreases.

The surface tension (σ) increases with viscosity increase making the outer layer less susceptible to interaction. The cohesive force becomes far more than adhesive force creating tension into the outermost layer. This does not allow bacteria to

incubate on honey. Killing the bacteria at the surface & in turn the shelf life of honey is enhanced with increasing surface tension.

The temperature rise has no impact on the surface tension of honey or very minimal change is observed which can be omitted.

VI. CONCLUSIONS

The uniqueness is in the fact that Baker's honey has a characteristic feature which is an exception in all properties discussed in our study due to the types of honey bee present in Indian climate conditions.

Rests of the honey varieties are less susceptible to climate change. The quality of honey is affected by change in density, viscosity, ultrasonic velocity and surface tension effect. Our aim is to establish that thermodynamic and thermoacoustical properties support the experimental findings as

honey is a thick fluid and shows all characteristics of liquid state. We have incorporated relevant structure for better understanding of the work.

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