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Apparent molar volume and apparent molar adiabatic compressibility of 2-hydroxy-5-methyl acetophenone in *N,N*-dimethylformamide at different temperatures

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Abstract The speed of sound and density of 2-hydroxy-5-methyl acetophenone in dimethylformamide have been measured over the range of temperatures 25–40 °C. From the experimentally determined data, values of apparent molar volume (V_ϕ), adiabatic compressibility (β_s), apparent molar adiabatic compressibility ($K_{s,\phi}$) and their limiting values have been computed. Values at infinite dilution provide information regarding solute–solvent interaction. The density and velocity increases with increase in concentration and decreases with increase in temperature. These results have been analyzed in terms of molecular interactions between acetophenone and dimethylformamide.

Keywords Speed of sound · Adiabatic compressibility · Acetophenone · Molecular interactions

List of symbols

ρ	Density of solution, kg mol^{-3}
ρ^*	Density of solvent, kg mol^{-3}
u	Speed of sound, m s^{-1}
M	Molecular mass, kg mol^{-1}
T	Temperature, K
β_s	Adiabatic compressibility solution, Pa^{-1}
β_s^*	Adiabatic compressibility solvent, Pa^{-1}
V_ϕ	Apparent molar volume, m^3 mol^{-1}
V_ϕ^0	Partial molar volume, m^3 mol^{-1}
$K_{s,\phi}$	Apparent molar adiabatic compressibility, m^3 mol^{-1} Pa^{-1}
$K_{S,\phi}^0$	Partial molar adiabatic compressibility, m^3 mol^{-1} Pa^{-1}
S_v	Experimental slope, m^3 mol^{-2} kg
S_k	Experimental slope, m^3 mol^{-2} kg Pa^{-1}

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Introduction

The knowledge of thermodynamic properties of nonelectrolyte solution is essential in the chemical industry involving chemical separations, heat transfer, mass transfer, and fluid flow [1]. The thermodynamic properties of polar components with the carbonyl carbon group of ketones have been a significant interest area of research for years [2–5]. Acetophenone and other aromatic ketones have industrial importance because they used in perfumery [6]. Thermodynamic properties of non-electrolytic solution have proven to be a very useful tool in elucidating the structural interactions among the components. Ultrasonic studies on binary mixtures of some aromatic ketones and their excess thermodynamic studies have been studied by several workers [7–9]. Ultrasonic speed plays an important role in the investigation of intermolecular interactions.

DMF is an industrial solvent and it also an aprotic and unassociated [10] in its pure liquid state. It belongs to the so called supersovents, owing to its miscibility with almost all common polar and non-polar solvents *N,N*-dimethylformamide has a large dipole moment ($\mu = 3.8$ D) and high dielectric constant ($\epsilon = 36.76$) at 25 °C [11] therefore, it may works as an aprotic protophillic solvent which is widely used in the synthesis of pharmaceuticals, in agricultural chemistry, surface coating, and as a solvent for polymers.

A survey of the literature revealed that lot of work has been done on measurements on the densities, viscosities, and speed of sound for liquid mixtures at different temperatures [12–15] but to the best of our knowledge very scanty work have been done on acetophenone with pure solvents. Thus, in this article, we have synthesized ketone and measured the density, ultrasonic velocity, and other related parameters of ketone in pure DMF at varying temperature.

Table 1 Densities, speed of sound, apparent molar volume, adiabatic compressibility, and apparent molar adiabatic compressibility at 25–40 °C

HMAP					
Molality (m) mol/kg	Density $\rho \times 10^3$ kg/m	Ultrasonic velocity u/ms	Apparent molar volume $V_\phi \times 10^{-6}$ m^3/mol	Adiabatic compressibility $\beta_s \times 10^{-10}$/Pa	Apparent molar adiabatic compressibility $K_{s,\phi} \times 10^{-13}$ m^3/mol/Pa
$T = 25$ °C					
0.06	0.9512	1427.03	35.448	5.1625	2.444
0.09	0.9513	1429.09	75.013	5.1471	1.712
0.12	0.9519	1432.01	90.103	5.1229	1.242
0.15	0.9523	1435.32	100.626	5.0972	0.956
0.18	0.9532	1438.45	104.480	5.0702	0.740
0.21	0.9550	1440.28	102.347	5.0478	0.584
$T = 30$ °C					
0.06	0.9463	1425.21	38.764	5.2025	1.220
0.09	0.9471	1427.22	68.688	5.1835	0.810
0.12	0.9477	1428.25	85.485	5.1727	0.687
0.15	0.9482	1430.32	96.286	5.1551	0.567
0.18	0.9497	1431.35	97.130	5.1395	0.466
0.21	0.9499	1432.48	104.754	5.1303	0.463
$T = 35$ °C					
0.06	0.9425	1416.02	21.298	5.2915	−2.519
0.09	0.9433	1417.04	57.101	5.2794	−1.597
0.12	0.9443	1419.07	72.901	5.2586	−1.226
0.15	0.9447	1421.09	87.101	5.2415	−0.953
0.18	0.9450	1423.01	97.305	5.2258	−0.759
0.21	0.9458	1424.10	101.709	5.2134	−0.620
$T = 40$ °C					
0.06	0.9378	1407.30	20.704	5.3841	−7.217
0.09	0.9386	1409.24	56.401	5.3645	−4.818
0.12	0.9401	1413.21	68.601	5.3263	−3.817
0.15	0.9403	1415.09	85.000	5.3108	−3.005
0.18	0.9404	1417.03	96.833	5.2958	−2.458
0.21	0.9407	1418.01	104.147	5.2868	−2.042

Table 2 Limiting values of V_ϕ, $K_{s,\phi}$ with slopes for HMAP in *N,N*-dimethylformamide at various temperature

HMAP				
Temp.	$V^0_\phi \times 10^{-6}$/m^3/mol	$K^0_{S,\phi} \times 10^{-13}$/m^3/mol/Pa	$S_V \times 10^{-6}$/m^3/mol kg	$S_K \times 10^{-13}$/m^3/mol kg/Pa
25 °C	28.944	2.8866	412.78	−11.903
30 °C	27.07	1.3369	405.79	−4.702
35 °C	3.8762	−2.8587	511.30	11.701
40 °C	0.6017	−8.2344	528.49	32.161

Experimental

High-purity analytical reagent grade sample of DMF was procured from S.D's. Fine Chemicals Mumbai, India and further purified prior to their used by an appropriate method [16]. The estimated purity was better than 99.8%. Our experimental values are in agreement with those reported in literature values [17–20]. The acetophenone 2-hydroxy-5-methylacetophenones (HMAP) was prepared by simple fries migration reaction and recrystallized from acetic acid. Purity was further checked by m.p. and T.L.C.

Density measurements were performed with a precalibrated bicapillary pyknometer. Accuracy of the density measurements was up to ± 0.0001 g cm^3. Ultrasonic velocity was measured with a variable path ultrasonic interferometer (Mittal Enterprises, M-81, New Delhi) at 2 MHz. The uncertainty in measured ultrasonic values was ± 0.1 ms^{-1}. The temperature of the test solution during the measurements was maintained with electronically controlled thermostatic water bath (Yorco-YSI413) with an uncertainty of ± 0.01 K.

Results and discussion

The experimental data of density, speed of sound at the range of temperature (25–40)°C for HMAP, in *N,N*-dimethylformamide (DMF) system are listed in Table 1. The apparent molar volumes, V_ϕ and apparent molar adiabatic compressibility, $K_{s,\phi}$ of HMAP, at different concentrations were calculated from the following relations [21].

$$V_\phi = \frac{\rho * - \rho}{m \cdot \rho \cdot \rho *} + \frac{M}{\rho} \quad (1)$$

$$K_{s,\phi} = \frac{\beta_s - \beta_s^*}{m \cdot \rho *} + V_\phi \beta_s \quad (2)$$

where, ρ^* and ρ are density of solvent and solution, respectively, m (mol kg^{-1}) is molality; M is the molecular mass of solute. β_s and β_s^* indicates the adiabatic compressibilities of the solution and solvent. Adiabatic compressibility calculated by using Laplace-Newton equation which is depends on density of solution and ultrasonic velocity (u).

$$\beta_s = \frac{1}{\rho u^2} \quad (3)$$

The variation of apparent molar volume, V_ϕ and apparent molar adiabatic compressibility, $K_{s,\phi}$ with molar concentration can be adequately represented by the Masson's equation.

$$Y = Y^0 + S_v m \quad (4)$$

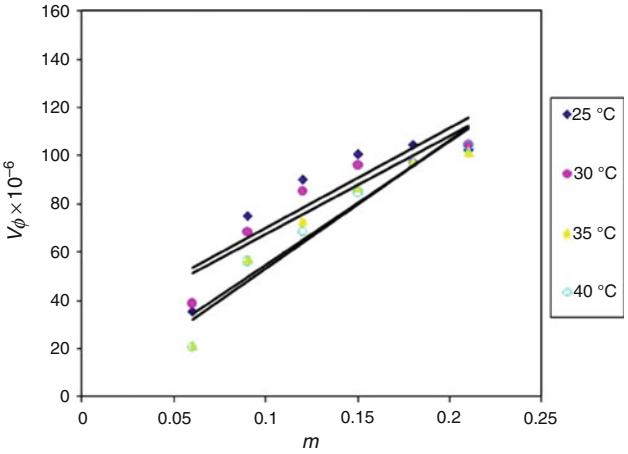

Fig. 1 Apparent molar volume (V_ϕ) for HMAP + DMF

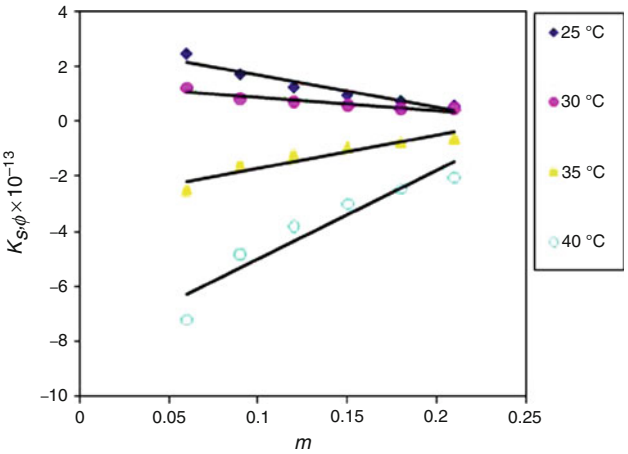

Fig. 2 Apparent molar adiabatic compressability ($K_{s,\phi}$) for HMAP + DMF

where Y represents V_ϕ and $K_{s,\phi}$, Y^0 is the value at infinite dilution and S_v and S_k experimental slope, m is the molality. The limiting values of apparent molar volumes and compressibility have been listed in Table 2. These properties are important because they solely reflect the interactions between the HMAP molecule and solvent. The carbonyl group of ketone is a considerably proton acceptor, it was interesting to see how this difference was reflected in the properties of DMF and ketone. When DMF and ketone was mixed, the main changes that occurred in association equilibria are evidently the rupture of the C=O–H–C hydrogen bonded chain between DMF molecules and mainly arise from the breaking of strong self association interactions and dipole–dipole interactions.

The results of density, ρ, ultrasonic speed, u, indicate association amongst the molecules and greater solute–solvent interaction as it increases linearly with increase concentration of solute. The pronounced increase or decrease

in the values of these parameters with composition of solution indicates the presence of interactions between the components molecules in the system.

Adiabatic compressibility (β_s) decreases with concentration and increases with temperature as given in Table 1. The apparent molar volume found to be a linear function of molality over the studied concentration range. The positive values of V_ϕ, in Table 1 indicate the presence of strong solute–solvent interactions. The plots of V_ϕ against molality were found to be linear over the concentration range studied (Fig. 1). The positive $K_{s,\phi}$, values indicate that the solute are loosely attached to solvent molecules and are more compressible. Further, apparent molar adiabatic compressibility found to be negative at 35 and 40 °C (Fig. 2). The negative values of $K_{s,\phi}$ is may be due to electrostatic effect, which leads to decrease in compressibility of the solution. The partial molar volume V_ϕ^0 has been obtained by fitting V_ϕ values in Masson's equation using least square method are given in Table 2. The positive values of V_ϕ^0 indicates the strong solute–solvent interaction. The partial molar compressibility $K_{S,\phi}^0$ is a measure of the protection against compression, which the solute molecules impart to solvent. The experimental S_v values are given in Table 2. S_v values are positive and increasing values of the limiting compressibility suggest that solute–solvent interactions are relatively stronger.

Conclusions

The density and speed of sound data are reported for the HMAP in *N,N*-dimethylformamide at varying temperatures (25–40) °C. Densities and speed of sound values are increases linearly with increase in concentrations this suggest that the HMAP in DMF shows structure maker behavior. The positive values of apparent molar volume V_ϕ, shows the presence of strong solute–solvent interaction. The negative values of apparent molar adiabatic compressibility, $K_{s,\phi}$,at higher temperature indicates the loss of structural compressibility of solvent molecules. The limiting positive values of apparent molar volume, V_ϕ^0, show strong interaction.

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