

SHORT COMMUNICATION

DENSITIES AND ULTRASONIC SPEED OF 2-HYDROXY-5-METHYL-3-NITRO ACETOPHENONE IN *N,N*-DIMETHYLFORMAMIDE AT DIFFERENT TEMPERATURES

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ABSTRACT. Density, ultrasonic speed measurements have been made for 2-hydroxy-5-methyl-3-nitroacetophenone (HMNAP) ($0.06\text{-}0.21\text{ mol kg}^{-1}$) in *N,N*-dimethylformamide (DMF) at four equidistant temperatures: 298.15, 303.15, 308.15 and 313.15 K. These measurements have been used to evaluate some important thermodynamic and acoustic parameters, such as apparent molar volume, limiting apparent molar volume, adiabatic compressibility, apparent molar adiabatic compressibility, limiting apparent molar adiabatic compressibility. The apparent molar volume (V_ϕ) and apparent molar adiabatic compressibility ($K_{s,\phi}$), were computed using density data. These parameters, were used to discuss interactions between the ketonic (>CO) group and DMF molecule. The results are interpreted to gain insight in to the changes in molecular association equilibria and structural effects in these systems.

KEY WORDS: Density, Ultrasonic speed, Adiabatic compressibility, Acetophenone, Molecular interaction

INTRODUCTION

There is an increased interest in thermodynamic and transport properties of liquid solutions and liquid mixtures. These properties provide information about type and extent of molecular interactions, and can be used for the development of molecular models for describing the behavior of solutions [1-4]. They are also necessary for engineering calculations, research of mass transfer, heat transfer and fluid flow [5]. Ultrasonic waves have acquired the status of an important probe for the study of structure and properties of matter [6]. Ultrasonic speed measurements have widely used to study pure [7], binary [8] as well as ternary [9] liquid mixtures and solute of salts in binary solvent systems. The extension of physicochemical data is necessary not only for giving information about molecular features of pure organic solvents and their mixtures under different thermodynamic conditions [10-12], but also for evaluating and improving systematically new methods of prediction and estimation of properties which describe the volumetric and acoustic behavior of liquids. Among theories, it is very interesting those which provide a physical meaning to the parameters in their expression, allowing the understanding of molecular interactions and their organization in the fluid [13].

N,N-Dimethylformamide is a versatile solvent, used in the synthesis of pharmaceuticals, in agricultural chemistry, and as solvent for polymers. DMF has strong electron pair donating and accepting ability and it may work as an aprotic, protophilic solvent with large dipole moment, high dielectric constant ($\mu = 3.24$ Debye and $\epsilon = 36.71$ at 25 °C) [14] which enables to dissolve a wide range of both organic and inorganic compounds. Acetophenone and other aromatic ketones have industrial importance because they used in perfumery industries. To the best of our knowledge, there are only few reports on various acetophenones in different solvents [14a-14d].

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However, there are no reports on density and ultrasonic data of binary mixture of 2-hydroxy-5-methyl-3-nitroacetophenone [HMNAP] with DMF, which encouraged us to investigate effect of temperature on ultrasonic velocity and thermodynamic parameters of 2-hydroxy-5-methyl-3-nitroacetophenone in DMF. In the present paper, we report the densities (ρ), ultrasonic speed (u) of HMNAP ($0.06 - 0.21 \text{ mol kg}^{-1}$) in pure DMF at temperatures 298.15, 303.15, 308.15 and 313.15 K. Apparent molar volume (V_ϕ), limiting apparent molar volume, adiabatic compressibility (β_s), apparent molar adiabatic compressibility ($K_{s,\phi}$), limiting apparent molar adiabatic compressibility have been calculated. All these parameters are discussed in terms of solute-solvent interactions, occurring in solution.

EXPERIMENTAL

The 2-hydroxy-5-methyl-3-nitroacetophenone (HMNAP) used in this study was prepared in our laboratory by Fries migration of *p*-cresyl acetate, using anhydrous aluminium chloride in the absence of solvent (Figure 1). The compound was recrystallized before use. The purity of synthesized compound was checked by thin layer chromatography (TLC), which indicates the presence of only one compound it was further confirmed by its m.p. The purity of chemical products was verified by measuring density and ultrasonic speed ($\rho = 0.9399$, $u = 1438.0$ at 303.15 K) which were in good agreement with literature values [15-17]. The solvent N,N-dimethylformamide (DMF) (S.D's. Fine Chemicals) used in the present study was of analytical grade and further purified according to the standard procedure [18]. The estimated purity was better than 99.8%. The densities of pure liquid and solutions were measured by using a double arm pycnometer made of borosil glass having a bulb capacity of 10 mL was used to measure the density. Uncertainty in the density values was $\pm 1 \cdot 10^{-4} \text{ g cm}^{-3}$. The ultrasonic speed is measured with a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, M-81, New Delhi) operating at 2 MHz which was calibrated with benzene and water [19]. The uncertainty in measured ultrasonic values was $\pm 0.1 \text{ ms}^{-1}$. The temperature stability of the test solution during the measurements was maintained with electronically controlled thermostatic water bath (Yorco-YSI413) with circulating thermostated water around the cell with a circulating pump with an uncertainty of $\pm 0.01 \text{ K}$. Several maxima were allowed to pass and their number n (10) was counted in order to minimize the uncertainty of the measurements. All maxima were recorded with the highest swing of the needle on the micrometer scale. The total distance, d , moved by the reflector is given by

$$d = n\lambda / 2 \quad (1)$$

where λ is the wavelength.

The frequency of crystal ν being accurately known (2 MHz), the ultrasonic speed, u , is calculated by using the relation

$$U = \lambda \nu \quad (2)$$

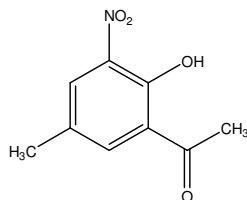


Figure 1. 2-Hydroxy-5-methyl-3-nitroacetophenone (HMNAP).

RESULTS AND DISCUSSION

The experimental values of densities and ultrasonic speed of 2-hydroxy-5-methyl-3-nitroacetophenone in *N,N*-dimethylformamide as a function of acetophenone concentration and temperature are reported in Table 1.

Table 1. Densities, ultrasonic speed, apparent molar volume, adiabatic compressibility, and apparent molar isentropic compressibility of HNMAP in DMF at 298.15–313.15 K.

Molality	Density	Ultrasonic speed	Apparent molar volume	Adiabatic compressibility	Apparent molar Adiabatic compressibility
(<i>m</i>) Mol.kg ⁻¹	$\rho \times 10^{-3}$ kg · m ⁻³	<i>U</i> ms ⁻¹	$V_{\phi} \times 10^6$ m ³ mol ⁻¹	$\beta_s \times 10^{10}$ Pa ⁻¹	$K_{\phi,s} \times 10^{13}$ m ³ mol ⁻¹ Pa ⁻¹
T = 298.15 K					
0.03	952.3	1456.000	-79.32	4.953	-3.251
0.06	953.8	1452.7	35.99	4.968	-0.993
0.09	956.1	1449.5	63.50	4.978	-0.345
0.12	957.8	1445.8	83.40	4.995	0.065
0.15	958.7	1442.2	101.10	5.015	0.372
0.18	959.2	1440.8	114.99	5.022	0.505
0.21	959.3	1436.8	127.30	5.049	0.718
T = 303.15 K					
0.03	947.8	1448.0	-88.62	5.032	-4.45
0.06	947.9	1440.0	57.30	5.087	-0.733
0.09	949.8	1438.4	83.10	5.089	-0.245
0.12	951.9	1435.8	94.40	5.096	0.048
0.15	953.2	1432.0	107.20	5.116	0.343
0.18	955.4	1425.0	109.44	5.154	0.619
0.21	957.1	1418.8	113.92	5.190	0.820
T = 308.15 K					
0.03	943.7	1438.9	-113.16	5.118	-12.02
0.06	945.7	1431.1	10.00	5.163	-4.867
0.09	947.9	1429.2	48.00	5.165	-3.015
0.12	949.3	1427.2	74.30	5.175	-1.998
0.15	949.7	1422.2	98.00	5.206	-1.154
0.18	949.9	1419.9	114.59	5.222	-0.693
0.21	950.1	1412.5	126.63	5.276	-0.165
T = 313.15 K					
0.03	940.2	1430.9	-160.93	5.194	-22.28
0.06	940.3	1425.8	21.95	5.231	-9.950
0.09	942.9	1422.3	51.02	5.243	-6.308
0.12	944.8	1418.6	72.30	5.260	-4.398
0.15	945.9	1416.6	90.40	5.268	-3.290
0.18	946.7	1398.4	105.05	5.402	-1.770
0.21	947.0	1374.8	117.90	5.586	-0.400

The apparent molar volume V_ϕ and apparent molar adiabatic compressibility $K_{\phi,s}$ of HMNAP in DMF at different temperature are calculated from the following relations [20] respectively;

$$V_\phi = M/\rho - \{1000 (\rho - \rho_0)/m\rho\rho_0\} \quad (3)$$

$$K_{\phi,s} = M\beta_s/\rho - \{1000 (\beta_{s,0}\rho - \beta_s\rho_0)/m\rho\rho_0\} \quad (4)$$

where, ρ_0 and ρ are density of solvent and solution, respectively, m (mol kg^{-1}) is molality, M is the molecular mass of solute. $\beta_{s,0}$ and β_s are the coefficients of adiabatic compressibilities of pure solvent and solution, respectively.

The coefficient of adiabatic compressibility (β_s) was determined from the speed of sound, u and density, ρ data by using Eq. (5)

$$\beta_s = 1/u^2\rho \quad (5)$$

From the (V_ϕ), V_ϕ and $K_{\phi,s}$ data, V_ϕ versus m curves was drawn and the plot was found to be linear in the concentration range studied, as represented by (6)

$$Y_\phi = Y_\phi^0 + S_Q m_s \quad (6)$$

where Y_ϕ^0 (denotes V_ϕ^0 or K_ϕ^0) is the limiting value of apparent partial molar property (equal to the infinite dilution partial molar property) and S_Q (S_Q denotes S_v or S_k) is the experimental or limiting slope indicative of solute-solute interactions. The uncertainties in the limiting values of V_ϕ and $K_{\phi,s}$ are $\pm 0.02 \times 10^{-6}$ ($\text{m}^3 \text{mol}^{-1}$) and $\pm 0.02 \times 10^{-13}$ ($\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$), respectively.

It is observed from Table 1 that the values of density, (ρ) are found to increase with the increase in concentration of HMNAP while the values of ultrasonic speed (u) exhibits the decreasing trend with concentration and temperature. The increase in the value of density suggests the molecular interaction exists between solute and solvent molecules. The increase in density is attributed to the presence of strong intermolecular attraction such as dipole-dipole attraction and hydrogen bonding. An increase in concentration allows for a closer approach of solvent and solute molecules, and stronger association between solute and solvent molecules. This leads to decrease in the volume and an increase in the density of the solution.

It is also be seen that the sound velocity increases or decreases depending on the structure and properties of solute. Therefore, the solutes that increase the ultrasonic velocity are structure maker while those decreases the sound velocities are structure breakers. The decrease in ultrasonic velocity indicates that the interaction between solute and solvent is becoming less dominant. This is due to the replacement of strong intermolecular attraction between solvent molecules by weaker intermolecular interactions. This indicates that the solvent-solvent interaction is replaced by solute-solvent interaction. It is evident that the values of adiabatic compressibility β_s increase with an increase in concentration and temperature. This indicates that the solute/solvent interaction is replaced by comparatively stronger interaction between solute molecules, releasing the solvent molecules. The increase in adiabatic compressibility also indicates a change in the conformation/orientation of the solute molecules in solution, leading to weaker inter-molecular interaction. This is attributed to the steric requirement of arranging an increasing number of large molecules. In this situation, the steric factor takes predominance over intermolecular interactions. An increase in adiabatic compressibility indicates a change in the orientation of the solvent molecules around the HMNAP (solute) molecule undergoing conformational change, which results in weakening of the solute/solvent interactions. The formation of weaker intermolecular interaction leads to an increase in adiabatic compressibility. It also indicates the associating tendency of the solute molecules in solution. In acetophenone, the carbonyl group is highly polar in nature and carrying negative charge on its oxygen atom.

Hence, one would expect a strong interaction with *N,N*-dimethylformamide. DMF is actually a electron pairs donors from its nitrogen atom and this also favors because of the presence of two electrons repelling $-\text{CH}_3$ groups. This makes the lone pair at nitrogen more perceptible towards donation [21], whereas ketones are electron acceptors [22]. Hence electron donor-acceptor complex between the vacant 2p orbital of the oxygen atom of carbonyl group of ketone and lone pair electrons on nitrogen in DMF is of sensitive towards various types of molecular interactions occurring in solution [23, 24].

The plots of V_ϕ against molality were found to be linear over a studied concentration range (Figure 2). Apparent molar isentropic compressibility is found to be negative. The negative values of $K_{\phi,s}$ indicate the loss of structural compressibility of solvent molecules. Table 2 shows that the values of S_v and S_K are positive at all temperature suggesting interactions are sensitive in this system.

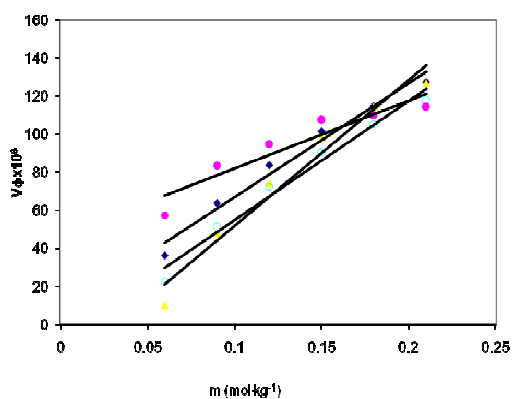


Figure 2. Apparent molar volume for HMNAP + DMF at (298.15, 303.15, 308.15, and 313.15 K).

Table 2. Limiting values of V_ϕ^0 , $K_{\phi,s}^0$ along with slopes for HMNAP in *N,N*-dimethylformamide at various temperatures.

Temp. K	$V_\phi^0 \times 10^6$ $\text{m}^3 \text{mol}^{-1}$	$K_{\phi,s}^0 \times 10^{13}$ $\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$	$S_v \times 10^6$ $\text{m}^3 \text{L}^{1/2} \text{mol}^{-3/2}$	$S_K \times 10^{13}$ $\text{m}^3 \text{mol}^{-2} \text{kg} \cdot \text{Pa}^{-1}$
298.15	6.88	-1.4131	598.76	10.865
303.15	46.02	-1.2279	357.06	10.147
308.15	-25.12	-6.009	768.19	29.830
313.15	-8.41	-12.385	628.51	59.498

CONCLUSIONS

In the present investigation density and sound velocity of HMNAP in *N,N*-dimethylformamide at 298.15, 303.15, 308.15 and 313.15 K have been reported. From the experimental data the values of apparent molar volumes and adiabatic compressibility for solution are evaluated. The positive values of (V_ϕ) increase regularly with addition of solute, indicating that solute-solvent interaction increases with concentration. The negative values of apparent molar adiabatic compressibility ($K_{\phi,s}$) imply that loss of compressibility of the solvent molecules. Values of limiting apparent molar volume move from positive to negative with temperature suggesting stronger to weaker interactions.

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