

Notes

Acoustical study of substituted azoles in N,N-dimethylformamide at different temperatures

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Received 19 October 2004; revised 22 March 2005

Ultrasonic velocity and density measurements of 2-(5-amino-[1,3,4]thiadiazol-2-yl)-phenol (L_1), 2-(5-mercapto-[1,3,4]oxadiazol-2-yl)-phenol (L_2), 2-(5-mercapto-[1,3,4]thiadiazol-2-yl)-phenol (L_3), 2-[1-(H-benzimidazol-2-yl)-5-phenyl-1H-pyrazol-3-yl]-4-methyl phenol (L_4) and 3-(2-hydroxy-5-methyl-phenyl-pyrazol-1-yl)-pyridin-4-yl-methanone (L_5) in N,N-dimethylformamide (DMF) have been carried out at 303, 308, 313, 318 and 323 K in the solute concentration of 1×10^{-2} mol dm⁻³. The experimental data have been used to calculate various acoustical parameters such as apparent molal volume (ϕ_v), apparent molal compressibility ($\phi_{k(s)}$), intermolecular free length (L_f), specific acoustic impedance (Z_s) and relative association (R_A). The results suggest the presence of molecular interactions. The effect of temperature variation on the strength of molecular interactions has been studied and the data have been quantitatively explained in terms of solute-solute and solute-solvent interactions.

IPC Code: Int.Cl.⁷ B01J19/10

Ultrasonic investigation has been the subject of exhaustive research and finds extensive application in characterizing physico-chemical behaviour and solute-solvent interactions in pure liquids^{1,2}, liquid mixtures³⁻⁶ and electrolytic solutions⁷⁻⁹ at various temperatures^{10,11}. Many workers¹²⁻¹⁸ have studied the solute-solvent interactions in aqueous and non-aqueous solutions^{19,20}. Recently Agrawal *et al.*²¹ have studied apparent molal volume and adiabatic compressibility of substituted thiadiazoles in ethanol-water, dioxane-water and acetone-water mixtures. In the present note an effort has been made to determine the acoustic parameters of substituted azoles in N, N-dimethylformamide in the temperature range 303-323 K in solute concentration of 1×10^{-2} mol dm⁻³ to study the strength of molecular interactions and predict the solution properties.

Experimental

All the chemicals used were of AR grade. The solvents were purified by standard procedures²². The

solutes used in the present investigation were synthesized by standard methods^{23,24}. Density measurements were made by a bicapillary pycnometer, the accuracy in density measurements was found to be ± 0.001 g/cc.

All the weighings were made on one pan digital balance (Adair Dutt-180). Ultrasonic sound velocity measurements were made by variable path single crystal interferometer (Mittal Enterprise, Model MX-3) at 1MHz with accuracy of $\pm 0.03\%$. The temperature was maintained with an accuracy of 0.1°C .

Results and discussion

The apparent molal volume has been determined from the relation

$$(\phi_v) = (1000(d_o - d_s))/m d_o d_s + M/d_s \quad \dots (1)$$

where d_o and d_s represent densities of solvent and solution respectively, m is the molality and M is the molecular weight of the solute. The apparent molal compressibility was deduced from Eq. (2)

$$(\phi_{k(s)}) = 1000(\beta_s d_o - \beta_o d_s)/m d_o d_s + \beta_s M/d_s \quad \dots (2)$$

where β_s and β_o are the adiabatic compressibilities of solution and solvent respectively.

Specific acoustic impedance (Z_s), relative association (R_A) and intermolecular free length (L_f) are the functions of ultrasonic velocity and are computed²⁵ using Eqs (3), (4) and (5).

$$Z_s = U_s d_s \quad \dots (3)$$

$$R_A = (d_s/d_o)(U_o/U_s)^{1/3} \quad \dots (4)$$

$$L_f = k \times \sqrt{\beta_s} \quad \dots (5)$$

where k is Jacobson's constant.

Temp	303	308	313	318	323 K
$k \times 10^4$	6.31	6.36	6.42	6.47	6.52

In the present study ultrasonic velocity and density have been used to compute the different thermodynamic parameters as listed in Table 1.

Table 1—Acoustic properties of L_1 , L_2 , L_3 , L_4 and L_5 in N,N-dimethylformamide at different temperatures in solute concentration of $1 \times 10^{-2} \text{ mol dm}^{-3}$

Temp., K	303	308	313	318	323K
L_1					
$\beta_s (\text{bar}^{-1}) 10^{-6}$	45.8836	47.2571	48.7130	50.3019	52.6726
$Z_s (\text{kg m}^{-2} \text{s}^{-1}) 10^6$	1.4696	1.4438	1.4202	1.3958	1.3604
$\phi_v (\text{m}^3 \text{mol}^{-1}) 10^{-4}$	-7.5916	-3.0213	-3.4095	-5.5622	-5.6649
$\phi_{k(s)} (\text{m}^3 \text{mol}^{-1} \text{bar}^{-1}) 10^{-6}$	-0.3247	-0.3214	-0.2924	-0.2810	-0.2648
R_A	0.3280	0.3255	0.3570	0.3290	0.3300
$L_f (\text{\AA}) 10^2$	4.2742	4.3721	4.4808	4.5887	4.7319
L_2					
$\beta_s (\text{bar}^{-1}) 10^{-6}$	49.6977	50.1884	51.3079	52.8556	54.5739
$Z_s (\text{kg m}^{-2} \text{s}^{-1}) 10^6$	1.4060	1.3964	1.3780	1.3542	1.3224
$\phi_v (\text{m}^3 \text{mol}^{-1}) 10^{-4}$	1.1555	3.7856	5.0573	5.7133	16.2404
$\phi_{k(s)} (\text{m}^3 \text{mol}^{-1} \text{bar}^{-1}) 10^{-6}$	0.1043	0.0107	0.0156	0.0396	0.0501
R_A	0.3370	0.3320	0.3315	0.3318	0.3254
$L_f (\text{\AA}) 10^2$	4.4483	4.5056	4.5914	4.7038	4.8165
L_3					
$\beta_s (\text{bar}^{-1}) 10^{-6}$	48.0481	49.6182	51.0038	52.3893	54.2171
$Z_s (\text{kg m}^{-2} \text{s}^{-1}) 10^6$	1.4300	1.4056	1.3844	1.3621	1.3306
$\phi_v (\text{m}^3 \text{mol}^{-1}) 10^{-4}$	1.2353	2.0587	1.8760	2.9281	10.2942
$\phi_{k(s)} (\text{m}^3 \text{mol}^{-1} \text{bar}^{-1}) 10^{-6}$	-0.0634	-0.0561	-0.0318	-0.0231	-0.0195
R_A	0.3314	0.3311	0.3321	0.3317	0.3272
$L_f (\text{\AA}) 10^2$	4.3738	4.4799	4.5778	4.6830	4.8008
L_4					
$\beta_s (\text{bar}^{-1}) 10^{-6}$	50.1455	51.4581	52.4965	54.1599	56.6016
$Z_s (\text{kg m}^{-2} \text{s}^{-1}) 10^6$	1.4000	1.3784	1.3645	1.3408	1.3083
$\phi_v (\text{m}^3 \text{mol}^{-1}) 10^{-4}$	2.5122	6.4348	3.5873	2.7293	2.4037
$\phi_{k(s)} (\text{m}^3 \text{mol}^{-1} \text{bar}^{-1}) 10^{-6}$	0.1568	0.1544	0.1301	0.1583	0.1846
R_A	0.3387	0.3358	0.3369	0.3382	0.3389
$L_f (\text{\AA}) 10^2$	4.4683	4.5622	4.6443	4.7614	4.9052
L_5					
$\beta_s (\text{bar}^{-1}) 10^{-6}$	53.6026	55.2680	57.2195	58.8301	60.4549
$Z_s (\text{kg m}^{-2} \text{s}^{-1}) 10^6$	1.2850	1.2637	1.2380	1.2182	1.1984
$\phi_v (\text{m}^3 \text{mol}^{-1}) 10^{-2}$	1.1515	1.1691	1.2099	1.2148	1.2225
$\phi_{k(s)} (\text{m}^3 \text{mol}^{-1} \text{bar}^{-1}) 10^{-6}$	1.1136	1.1560	1.2868	1.3382	1.3084
R_A	0.2993	0.2985	0.2989	0.2992	0.2972
$L_f (\text{\AA}) 10^2$	4.6197	4.7281	4.8475	4.9625	5.0694

Experimental results reveal that ultrasonic velocity decreases linearly with the temperature. Decrease in ultrasonic velocity may be attributed to solute-solvent interactions. Values of apparent molal volume and apparent molal compressibility are presented in the Table 1.

It is observed that the value of β_s increases linearly with the temperature. This increase may be due to presence of solvent molecules around the ions. The ϕ_k values are positive for L_2 , L_3 , and L_5 and negative for L_1 and L_4 . The positive ϕ_k values are due to the compressibility of the solvent due to weak electrostatic forces in the vicinity of ions.

It could be seen from Table 1 that the intermolecular free length (L_f) increases linearly with

the temperature, which reveals that there is a weak solute solvent interaction. This may also imply that the increase in number of free ions, showing the occurrence of ionic dissociation due to weak ion-ion interactions.

The relative association (R_A) is influenced by two factors i) the breaking up of the solvent molecules on addition of electrolyte to it and ii) the solvation of ions that are simultaneously present. The former results in decrease and the latter in increase of R_A .

The specific acoustic impedance Z_s decreases with increase in temperature. The apparent molal volume ϕ_v increases with the temperature and is found to be positive showing that the interactions are insensitive to the solvent.

Acknowledgement

The authors are very much thankful to the Director, Govt. Vidarbha Institute of Science and Humanities, Amravati, for providing necessary facilities. One of the authors (DPG) is thankful to CSIR for the award of JRF.

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