

Densities and Refractive Indices for *N*-Arylhydroxamic Acids in Dimethylsulphoxide at Various Temperatures

V. VERMA^{1,*} and R. PANDE²

¹Agriculture Processing and Food Engineering, Faculty of Agricultural Engineering, Indira Gandhi Krishi Vishwavidyalaya, Raipur-492 006, India ²School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur-492 010, India

*Corresponding author: E-mail: veenuverma88@gmail.com

(Received: 27 January 2012;	Accepted: 12 December 2012)	AJC-12517
	times (V^E) and molar refraction (R_M) of two isomeric obenzohydroxamic acid and <i>N</i> -phenyl-3-nitrobenzohydrox	· · ·

methylbenzohydroxamic acid, *N*-phenyl-2-nitrobenzohydroxamic acid and *N*-phenyl-3-nitrobenzohydroxamic acid have been calculated from experimental data of refractive indices (n) and densities (ρ) in dimethyl sulphoxide at various temperatures (298.15, 303.15, 308.15 and 313.15) K. Results obtained have been discussed in terms of intermolecular ineteractions and a comprehensive discussion has been provided. The apparent molar volume at infinite dilution and the slope of Masson's equation are computed, to interpret the solute-solvent interaction.

Key Words: Density, Molar refraction, Hydroxamic acid.

INTRODUCTION

Density values are often reported together with refractive index for non-electrolyte as proof of purity of the samples¹, The relation between refractive index and excess molar volumes has been studied for a long time, so it is common that these two properties are reported together.

N-aryl hydroxamic acids are *N*-acyl derivatives of hydroxamic acids represented by the general formula, R_2 -CO-NR₁-OH, where R_1 and R_2 are phenyl or substituted phenyl groups. It has been recognized as compounds of pharmacological, toxicological and pathological importance²⁻⁶.

Also the properties of dimethyl sulphoxide (DMSO) have been the subject of considerable interest because of its versatility as solvent and a plasticizer⁷. It is highly aprotic⁸ liquid which has the ability to participate in hydrogen bonding. The cryoprotectant effect of DMSO on biological and model membrane is widely recognized⁹⁻¹¹. Thus it is main purpose of the work to study the relation between density and refractive index.

To this end, the densities and refractive indices of three hydroxamic acids *i.e.*, *N*-phenyl-2-methylbenzohydroxamic acid (OMBHA), *N*-phenyl-2-nitrobenzohydroxamic acid (ONBHA) and *N*-phenyl-3-nitrobenzohydroxamic acid (MNBHA) have been measured under atmospheric pressure at various temperatures (298.15, 303.15, 308.15 and 313.15) K. The experimental values of ρ and n were used to calculate the excess properties (n^E, R^E_M, V^E), molar refraction (R_M),

polarizability (α) and apparent molar volume (V $_{\phi}$). These results have been used to understand the various types of interactions taking place in solutions of non-electrolyte and the temperature dependence of these interactions.

EXPERIMENTAL

All the three hydroxamic acids namely, N-phenyl-2methylbenzohydroxamic acid (I), N-phenyl-2-nitrobenzohydroxamic acid (II) and N-phenyl-3-nitrobenzohydroxamic acid (III), were prepared in this laboratory as reported in literature¹². These were purified by crystallization thrice with benzene and dried over phosphorus pentaoxide in vacuum desiccators for several hours. The melting point was determined on a tempo apparatus and is uncorrected. IR spectra were recorded with a FTIR 8400 Series Shimazdu (Japan) using KBr pellets. Elemental analysis was determined with a Vario-EL analysis apparatus. OMBHA (I), observed m.p. 81 °C and reported 81 °C in the literature, IR, cm⁻¹: 3050, 1620, 1340 and 915. Anal. (C14H13NO2) calcd. C, 73.99; N, 6.16; H, 5.77. Found: C, 74.10; N, 5.95; H, 6.10. ONBHA (II), observed m.p. 148 °C and reported 148 °C in the literature, IR, cm⁻¹: 3100, 1612, 1349 and 950. Anal. (C13H10N2O4) calcd. C, 60.46; N, 10.85; H, 3.90. Found: C, 60.80; N, 11.20; H, 3.70. and MNBHA (III), observed m.p. 117 °C and reported 117 °C in the literature, IR, cm⁻¹: 3100, 1650, 1340 and 880. Anal. (C₁₃H₁₀N₂O₄) calcd. C, 60.46; N, 10.85; H, 3.90. Found: C, 60.65; N, 10.80; H, 4.00. These were purified by crystallization

thrice with benzene and dried over phosphorus pentaoxide in vacuum desiccators for several hours. DMSO of analytical grade was used for preparing hydroxamic acids solution of varying concentration from (0.01 to 0.1 M) by mass dilution technique. Uncertainty in solution concentration was estimated to be \pm 0.001 units.

Densities of hydroxamic acids in DMSO were determined by using a 10 cm³ double armed pycnometer at four temperatures (298.15, 303.15, 308.15 and 313.15) K. The pycnometer was calibrated at desired temperature with freshly prepared triple distilled water. The estimate precision of density measurement of solution was $\pm 3 \times 10^{-5}$ g cm⁻³. The reproducibility of density measurement was $\pm 4 \times 10^{-5}$ g cm⁻³.

Refractive index was measured using thermostated Abbe's refractometer. The refractometer was calibrated by measuring the refractive indices of triply distilled water and toluene at known temperature¹³. The accuracy in the refractive index measurement was \pm 0.0001 unit. Temperature was controlled by circulating water around prisms of the refractometer from thermostatically controlled adequately stirred water bath (accuracy \pm 0.1 °C). The sample mixtures were directly injected into the prism assembly of the instrument by means of an airtight hypodermic syringe. An average three to four measurements were taken for each sample mixture at various temperatures (298.15, 303.15, 308.15 and 313.15) K. The experimental values of densities, ρ_0 and refractive index, η_0 of DMSO at 298.15, 303.15, 308.15 and 313.15 K are given in Table-1.

	TABLE-1 PROPERTIES OF DMSO										
		$\rho_{o}/g \text{ cm}^{-3}$		n _o							
T (K)	This work	L	This work	L							
298.15	1.0947	1.0955 ^a ; 1.09475 ^b	1.4720	1.4771 ^d ; 1.4765 ^e							
303.15	1.0907	1.0896°; 1.09076 ^b	1.4690	1.4752 ^d ; 1.4740 ^e							
308.15	1.0860	1.0855 ^a ; 1.08606 ^b	1.4680	1.4720 ^e							
		1.0847 ^c									
313.15	1.0804	1.08045 ^b ; 1.0797 ^c	1.4660	1.4492 ^d ; 1.4700 ^f							
${}^{a}\rho_{o}{}^{13}, {}^{b}\rho_{o}$	$^{14}, {}^{c}\rho_{o}^{15}, {}^{d}n_{o}^{1}$	$^{6}, {}^{e}n_{o}{}^{17}, {}^{f}n_{o}{}^{18}$									

RESULTS AND DISCUSSION

Tables 2 and 3 list the densities and refractive indices of three hydroxamic acids in DMSO at four temperatures (298.15, 303.15, 308.15 and 313.15) K.

From the density values, apparent molar volume, V_{ϕ} , is calculated using the following equation¹⁹,

 $V_{\phi} =$

$$1000 (\rho_0 - \rho) / c \rho_0 \rho + M / \rho$$
 (1)

where, ρ and ρ_0 are the densities of solution and solvent, respectively. M is the molar mass of hydroxamic acids and c is the concentration of hydroxamic acids. The V_{ϕ} values are presented in Table-4. The positive values of V_{ϕ} for all the hydroxamic acids indicate strong solute-solvent interactions. These interactions are strengthened with increasing concentration and temperature for *N*-phenyl-2-methylbenzo- (**I**), *N*phenyl-3-nitro- (**III**) and weakened for *N*-phenyl-2-nitrobenzohydroxamic acid (**II**).

The apparent molar volume, V_{ϕ} , of hydroxamic acids is plotted against the concentration, $C^{1/2}$, according to the Masson equation²⁰:

$$V_{\phi} = V_{\phi}^{0} + S_{V}^{*} C^{1/2}$$
(2)

where, intercept V_{ϕ}^{0} is the limiting apparent molar volume (same as partial molar volume at infinite dilution or standard partial molar volume), which is obtained by least-square fitting of V_{ϕ} values using the above equation (2). S_{V}^{*} is the experimental slope. The calculated V_{ϕ}^{0} and S_{V}^{*} values along with their standard errors are listed in Table-5. The positive values V_{f}^{0} for all the hydroxamic acids suggest strong solute-solvent interaction²¹. The S_{V}^{*} values becomes large and positive for *N*-phenyl-3-nitrobenzohydroxamic acid (**III**), suggest strong solute-solute interaction but opposite in case of N-phenyl-3methylbenzonydroxamic acid (**I**) and *N*-phenyl-2-nitrobenzohydroxamic acid (**II**) showing hydrophobic character²².

Form the measured values of refractive indices, molar refraction is calculated using the relation proposed by Lorentz-Lorenz,

$$R_{\rm M} = [(n^2 - 1/n^2 + 2)].V$$
(3)

In order to gain further information about specific interaction of any kind, the electronic polarizability of the system is computed. The molar refraction is related to the polarizability of molecules by Lorentz-Lorenz formula²³,

TABLE-2
DENSITY, $\rho(g\ cm^{\cdot3})$ OF THE HYDROXAMIC ACIDS AT VARIOUS TEMPERATURES

N-phenyl-2-methylbenzohydroxamic acid											
Town (V)	C (mol dm ⁻³)										
Temp. (K)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	
298.15	1.1073	1.1113	1.1165	1.1201	1.1254	1.1284	1.1314	1.1354	1.1394	1.1430	
303.15	1.1004	1.1033	1.1073	1.1133	1.1172	1.1189	1.1212	1.1272	1.1303	1.1356	
308.15	1.0951	1.0971	1.1000	1.1059	1.1078	1.1109	1.1129	1.1171	1.1204	1.1273	
313.15	1.0871	1.0898	1.0917	1.0986	1.1003	1.1021	1.1054	1.1091	1.1137	1.1193	
	N-phenyl-2-nitrobenzohydroxamic acid										
298.15	1.0958	1.1013	1.1081	1.1150	1.1176	1.1239	1.1285	1.1356	1.1416	1.1599	
303.15	1.0905	1.0958	1.1021	1.1099	1.1121	1.1172	1.1219	1.1287	1.1348	1.1553	
308.15	1.0876	1.0921	1.0994	1.1061	1.1091	1.1130	1.1181	1.1251	1.1321	1.1536	
313.15	1.0808	1.0860	1.0932	1.0997	1.1028	1.1069	1.1126	1.1188	1.1286	1.1464	
			N-phenyl	-3-nitrobenz	ohydroxami	ic acid					
298.15	1.1579	1.1528	1.1469	1.1358	1.1201	1.1186	1.1124	1.1086	1.1020	1.0966	
303.15	1.1555	1.1505	1.1430	1.1321	1.1169	1.1136	1.1100	1.1036	1.0950	1.0907	
308.15	1.1519	1.1489	1.1411	1.1296	1.1140	1.1109	1.1065	1.1001	1.0903	1.0860	
313.15	1.1499	1.1466	1.1398	1.1279	1.1126	1.1090	1.1045	1.0982	1.0876	1.0817	

REFRACTIVE INDICES, n, OF HYDROXAMIC ACIDS AT VARIOUS TEMPERATURES N-phenyl-2-methylbenzohydroxamic acid C (mol dm ⁻³) C (mol dm ⁻³) O.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.10 298.15 1.4720 1.4730 1.4745 1.4746 1.4749 1.4750 1.4754 1.4757 1.4757 1.4760 303.15 1.4710 1.4715 1.4718 1.4720 1.4725 1.4727 1.4735 1.4735 1.4745 308.15 1.4669 1.4690 1.4691 1.4692 1.4692 1.4694 1.4695 1.4700 1.4700 1.4720 313.15 1.4670 1.4673 1.4676 1.4677 1.4680 1.4685 1.4690 1.4700 303.15 1.4743 1.4745 1.4750 1.4755 1.4700 1.4773 1.4700 1.4700 1.4700 1.4700 1.4700 1.4700 1.4700 1.4700 1.4700 1		TABLE-3										
$\frac{C (mol dm^3)}{0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.10}{0.08 0.09 0.10 0.05 0.06 0.07 0.08 0.09 0.10}$ $\frac{298.15 1.4720 1.4730 1.4745 1.4746 1.4749 1.4750 1.4754 1.4757 1.4757 1.4757 1.4760}{0.303.15 1.4710 1.4715 1.4718 1.4720 1.4725 1.4725 1.4727 1.4735 1.4735 1.4745 1.4745 0.4692 0.4692 1.4694 1.4695 1.4700 1.4700 1.4720 0.4720 0.313.15 1.4670 1.4673 1.4673 1.4676 1.4677 1.4677 1.4680 1.4685 1.4690 1.4700 1.4720 0.4720 0.4725 0.4697 1.4677 1.4680 1.4685 1.4690 1.4700 1.4700 1.4700 1.4700 1.4773 0.4775 0.4775 0.4775 0.4765 0.4755 0.4760 0.4755 0.4760 0.4755 0.4755 0.4755 0.4755 0.4755 0.4760 0.4755 0.$		REFRACTIVE INDICES, n, OF HYDROXAMIC ACIDS AT VARIOUS TEMPERATURES										
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		N-phenyl-2-methylbenzohydroxamic acid										
1 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.10 298.15 1.4720 1.4730 1.4745 1.4746 1.4749 1.4750 1.4754 1.4757 1.4757 1.4757 1.4757 1.4757 1.4757 1.4750 303.15 1.4710 1.4715 1.4718 1.4720 1.4725 1.4725 1.4727 1.4735 1.4735 1.4745 308.15 1.4689 1.4690 1.4691 1.4692 1.4692 1.4694 1.4695 1.4700 1.4700 1.4700 313.15 1.4670 1.4673 1.4676 1.4677 1.4677 1.4680 1.4685 1.4690 1.4700 298.15 1.4743 1.4745 1.4750 1.4755 1.4760 1.4773 1.4775 1.4760 1.4775 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 <td>Tama (V)</td> <td colspan="8">C (mol dm⁻³)</td> <td></td>	Tama (V)	C (mol dm ⁻³)										
303.15 1.4710 1.4715 1.4718 1.4720 1.4725 1.4725 1.4727 1.4735 1.4735 1.4745 308.15 1.4689 1.4690 1.4691 1.4692 1.4692 1.4694 1.4695 1.4700 1.4700 1.4720 313.15 1.4670 1.4673 1.4673 1.4676 1.4677 1.4677 1.4680 1.4685 1.4690 1.4700 <i>N</i> -phenyl-2-nitrobenzohydroxamic acid <i>N</i> -phenyl-2-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4750 1.4755 1.4760 1.4768 1.4770 1.4773 1.4775 1.4760 303.15 1.4714 1.4715 1.4720 1.4743 1.4748 1.4750 1.4755 1.4760 1.4753 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 <	Temp. (K)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	
308.15 1.4689 1.4690 1.4691 1.4692 1.4692 1.4694 1.4695 1.4700 1.4700 1.4720 313.15 1.4670 1.4673 1.4673 1.4676 1.4677 1.4677 1.4680 1.4685 1.4690 1.4700 1.4700 N-phenyl-2-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4750 1.4755 1.4760 1.4768 1.4770 1.4773 1.4775 1.4777 303.15 1.4725 1.4730 1.4733 1.4740 1.4743 1.4748 1.4750 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 <	298.15	1.4720	1.4730	1.4745	1.4746	1.4749	1.4750	1.4754	1.4757	1.4757	1.4760	
313.15 1.4670 1.4673 1.4673 1.4676 1.4677 1.4677 1.4680 1.4685 1.4690 1.4700 N-phenyl-2-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4750 1.4755 1.4760 1.4768 1.4770 1.4773 1.4775 1.4777 303.15 1.4725 1.4730 1.4733 1.4740 1.4743 1.4748 1.4750 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4750 1.4750 1.4750 1.4755 1.4730 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4755 1.4760 1.4769 1.4751 1.4751 1.4760 1.4769 1.4751 1.4743 1.47	303.15	1.4710	1.4715	1.4718	1.4720	1.4725	1.4725	1.4727	1.4735	1.4735	1.4745	
N-phenyl-2-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4750 1.4755 1.4760 1.4768 1.4770 1.4773 1.4775 1.4777 303.15 1.4725 1.4730 1.4733 1.4740 1.4743 1.4748 1.4750 1.4755 1.4760 1.4765 308.15 1.4714 1.4715 1.4720 1.4723 1.4725 1.4730 1.4755 1.4760 1.4755 313.15 1.4695 1.4700 1.4705 1.4705 1.4710 1.4715 1.4720 1.4755 313.15 1.4695 1.4700 1.4705 1.4705 1.4710 1.4715 1.4720 1.4735 N-phenyl-3-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4748 1.4749 1.4751 1.4746 1.4769 303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4750 1.4753 1.4757	308.15	1.4689	1.4690	1.4691	1.4692	1.4692	1.4694	1.4695	1.4700	1.4700	1.4720	
298.15 1.4743 1.4745 1.4750 1.4760 1.4768 1.4770 1.4773 1.4775 1.4777 303.15 1.4725 1.4730 1.4733 1.4740 1.4743 1.4768 1.4750 1.4755 1.4760 1.4768 303.15 1.4725 1.4730 1.4733 1.4740 1.4743 1.4748 1.4750 1.4755 1.4760 1.4765 308.15 1.4714 1.4715 1.4720 1.4723 1.4725 1.4730 1.4755 1.4760 1.4755 313.15 1.4695 1.4700 1.4705 1.4705 1.4710 1.4715 1.4720 1.4735 N-phenyl-3-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4748 1.4749 1.4751 1.4757 1.4760 1.4764 1.4769 303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4750 1.4753 1.4757	313.15	1.4670	1.4673	1.4673	1.4676	1.4677	1.4677	1.4680	1.4685	1.4690	1.4700	
303.15 1.4725 1.4730 1.4733 1.4740 1.4743 1.4748 1.4750 1.4755 1.4760 1.4765 308.15 1.4714 1.4715 1.4720 1.4723 1.4725 1.4730 1.4735 1.4740 1.4755 1.4760 1.4765 313.15 1.4695 1.4700 1.4705 1.4705 1.4710 1.4715 1.4720 1.4755 M-phenyl-3-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4748 1.4749 1.4751 1.4757 1.4760 1.4764 1.4769 303.15 1.4743 1.4745 1.4748 1.4749 1.4751 1.4757 1.4760 1.4764 1.4769 303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4760 1.4764 1.4769 303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4750 1.4753 1.4757 </td <td></td> <td></td> <td></td> <td>N-phenyl</td> <td>-2-nitrobenz</td> <td>ohydroxami</td> <td>c acid</td> <td></td> <td></td> <td></td> <td></td>				N-phenyl	-2-nitrobenz	ohydroxami	c acid					
308.15 1.4714 1.4715 1.4720 1.4723 1.4725 1.4730 1.4735 1.4740 1.4750 1.4755 313.15 1.4695 1.4700 1.4705 1.4705 1.4710 1.4715 1.4720 1.4725 1.4730 1.4755 N-phenyl-3-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4748 1.4749 1.4751 1.4754 1.4757 1.4760 1.4764 1.4769 303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4750 1.4753 1.4757	298.15	1.4743	1.4745	1.4750	1.4755	1.4760	1.4768	1.4770	1.4773	1.4775	1.4777	
313.15 1.4695 1.4700 1.4705 1.4705 1.4710 1.4715 1.4720 1.4725 1.4730 1.4735 N-phenyl-3-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4748 1.4749 1.4751 1.4754 1.4757 1.4760 1.4764 1.4769 303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4750 1.4753 1.4757	303.15	1.4725	1.4730	1.4733	1.4740	1.4743	1.4748	1.4750	1.4755	1.4760	1.4765	
N-phenyl-3-nitrobenzohydroxamic acid 298.15 1.4743 1.4745 1.4748 1.4749 1.4751 1.4754 1.4757 1.4760 1.4764 1.4769 303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4750 1.4753 1.4757	308.15	1.4714	1.4715	1.4720	1.4723	1.4725	1.4730	1.4735	1.4740	1.4750	1.4755	
298.15 1.4743 1.4745 1.4748 1.4749 1.4751 1.4754 1.4757 1.4760 1.4764 1.4769 303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4750 1.4753 1.4757	313.15	1.4695	1.4700	1.4705	1.4705	1.4710	1.4715	1.4720	1.4725	1.4730	1.4735	
303.15 1.4725 1.4728 1.4731 1.4736 1.4739 1.4743 1.4747 1.4750 1.4753 1.4757				N-phenyl	-3-nitrobenz	ohydroxami	c acid					
	298.15	1.4743	1.4745	1.4748	1.4749	1.4751	1.4754	1.4757	1.4760	1.4764	1.4769	
308 15 1 4706 1 4710 1 4713 1 4717 1 4720 1 4725 1 4720 1 4734 1 4730 1 4742	303.15	1.4725	1.4728	1.4731	1.4736	1.4739	1.4743	1.4747	1.4750	1.4753	1.4757	
500.15 1.4700 1.4710 1.4715 1.4717 1.4720 1.4725 1.4727 1.4734 1.4737 1.4742	308.15	1.4706	1.4710	1.4713	1.4717	1.4720	1.4725	1.4729	1.4734	1.4739	1.4742	
313.15 1.4690 1.4694 1.4697 1.4700 1.4706 1.4710 1.4713 1.4717 1.4720 1.4725	313.15	1.4690	1.4694	1.4697	1.4700	1.4706	1.4710	1.4713	1.4717	1.4720	1.4725	

TABLE-4

APPARENT MOLAR VOLUME, V⁰_{\$\phi\$} (cm³. mol⁻¹) OF BOTH THE HYDROXAMIC ACIDS AT VARIOUS TEMPERATURES

N-phenyl-2-methylbenzohydroxamic acid										
Temp. (K)	C (mol dm ⁻³)									
Temp. (K)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
298.15	193.24	188.49	182.38	178.11	171.92	168.37	164.82	160.10	155.39	151.22
303.15	195.62	192.08	187.37	180.31	175.69	173.65	170.92	163.89	160.25	154.01
308.15	197.70	195.36	191.84	184.82	182.65	178.96	176.63	171.66	167.73	159.53
313.15	201.38	198.16	195.90	187.75	185.67	183.53	179.64	175.23	169.88	163.26
			N-phenyl	-2-nitrobenz	ohydroxami	ic acid				
298.15	235.26	228.56	220.27	212.00	208.82	201.22	195.72	187.18	179.99	158.11
303.15	235.71	229.32	221.67	212.22	209.58	203.40	197.73	189.51	182.21	157.73
308.15	235.13	229.72	220.88	212.66	209.10	204.38	198.18	189.79	181.35	155.60
313.15	237.69	231.35	222.61	214.65	210.89	205.95	199.06	191.55	179.75	158.39
			N-phenyl	-3-nitrobenz	ohydroxami	ic acid				
298.15	160.52	166.53	173.63	186.88	205.78	207.64	215.12	219.73	227.67	234.22
303.15	157.46	163.46	172.40	185.44	203.76	207.78	212.13	219.86	230.22	235.45
308.15	157.61	161.23	170.53	184.40	203.20	206.95	212.21	219.97	231.84	237.09
313.15	154.20	158.18	166.28	180.61	199.02	203.44	208.81	216.44	229.37	236.54

TABLE-5 PARTIAL MOLAR VOLUME, V⁰_♦ AND SOLUTE-SOLUTE INTERACTION PARAMETER, S^{*}_V OF THE HYDROXAMIC ACIDS AT VARIOUS TEMPERATURES

N-phenyl-2-methylbenzohydroxamic acid												
	298.15 K	303.15 K	308.15 K	313.15 K								
V^0_{ϕ}	215.7253	218.3021	218.7563	222.3683								
S [*] v	-197.264	-191.044	-169.436	-170.583								
	N-phenyl-2-nitrobenzohydroxamic acid											
V^{0}_{ϕ}	274.1146	274.3388	274.7856	277.7446								
S [*] v	-317.79	-313.473	-316.484	-322.929								
	N-phenyl-3-nitrobenzohydroxamic acid											
V^0_{ϕ}	117.6816	112.0569	109.0075	104.0639								
S [*] v	365.3631	386.0596	398.3157	406.0243								

$$R_{\rm M} = \frac{4\pi\alpha N}{3} \tag{4}$$

where, α is the electronic polarizability and N is Avogadro's number. The value of R_M and a are shown in Tables 6 and 7 for both hydroxamic acids. As inspection from Tables 6 and 7, the value of a for *N*-phenyl-3-nitrobenzohydroxamic acid (**III**) increases with concentration but apposite in case of *N*-phenyl-2-nitrobenzohydroxamic acid (**II**) and *N*-phenyl-2-

methylbenzohydroxamic acid (I). This trend is slightly influence by temperature and the obvious decrease with temperature for N-phenyl-3-nitrobenzohydroxamic acids (III) but opposite in case of rest two hydroxamic acids, indicates the presence of intermolecular interaction between the molecules of solute and solvent.

Furthermore the refractive indices and densities experimental data, refractive index deviations defined on a mole fraction basis²⁴ n^E and excess volume V^E, have been calculated as follows:

$$n^{E} = n - (x_{1}n_{1} + x_{2}n_{2})$$
(5)
$$V^{E} = V - (x_{1}V_{1} + x_{2}V_{2})$$
(6)

where, x_1 , n_1V_1 and x_2 , n_2 , V_2 is mole fraction, refractive index and molar volume of solvent and solute, respectively. n and V is the refractive index and molar volume of hydroxamic solutions. The values of V, n^E and V^E are listed in Tables 8-10. According to Nakata and Sakurai the sign of n^E is apposite to that of V^E , if the behaviour of refractive index is not linear between n_1 and n_2 . This rule is truly fulfilled for compound (**II**) and (**III**) but not for (**I**) hydroxamic acids. The *N*-phenyl-2-methylbenzohydroxmic acid (**I**) shows negative n^E and V^E values, indicates the heteromolecular interactions in the liquid mixtures and is attributed to charge transfer, dipole-dipole, dipole-induced dipole interactions and hydrogen bonding between the hydroxamic acids and DMSO. Compound (II) and (III) show positive n^E and negative V^E over the whole range of composition.

We can remark that the effect of the temperature is not significant, the n^E value being bigger if the temperature increases for all the hydroxamic acids and V^E values become smaller, when temperature increases.

N-phenyl-2-methylbenzohydroxamic acid											
Temp. (K)	C (mol dm ⁻³)										
Temp. (K)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	
298.15	19.7839	19.7748	19.7628	19.7288	19.6730	19.6499	19.6373	19.6039	19.5600	19.5348	
303.15	19.8733	19.8645	19.8306	19.7577	19.7325	19.7282	19.7208	19.6702	19.6420	19.6106	
308.15	19.8926	19.8873	19.8640	19.7872	19.7806	19.7581	19.7524	19.7212	19.6875	19.6614	
313.15	19.9687	19.9575	19.9500	19.8630	19.8619	19.8563	19.8347	19.8125	19.7760	19.7385	
			N-phenyl	-2-nitrobenz	ohydroxami	ic acid					
298.15	20.0825	20.0217	19.9481	19.8752	19.8780	19.8261	19.7840	19.7009	19.6343	19.3574	
303.15	20.1132	20.0678	19.9961	19.9125	19.9164	19.8745	19.8297	19.7580	19.7001	19.3944	
308.15	20.1265	20.0813	19.9988	19.9190	19.9056	19.8856	19.8435	19.7692	19.7122	19.3877	
313.15	20.1843	20.1393	20.0580	19.9707	19.9652	19.9417	19.8891	19.8275	19.7029	19.4409	
			N-phenyl	-3-nitrobenz	ohydroxami	ic acid					
298.15	19.0036	19.1236	19.2637	19.4866	19.8009	19.8713	20.0266	20.1401	20.3098	20.4635	
303.15	18.9809	19.1043	19.2704	19.5051	19.8154	19.9220	20.0345	20.1958	20.4004	20.5311	
308.15	18.9739	19.0678	19.2390	19.4821	19.7997	19.9059	20.0323	20.2019	20.4379	20.5660	
313.15	18.9515	19.0505	19.2049	19.4508	19.7733	19.8861	20.0104	20.1744	20.4198	20.5859	

TABLE-7

N-phenyl-2-methylbenzohydroxamic acid										
Temp. (K)	C (mol dm ⁻³)									
Temp. (K)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
298.15	0.7839	0.7835	0.7830	0.7817	0.7795	0.7785	0.7780	0.7767	0.7750	0.7740
303.15	0.7874	0.7870	0.7857	0.7828	0.7818	0.7816	0.7814	0.7793	0.7782	0.7770
308.15	0.7882	0.7880	0.7870	0.7840	0.7837	0.7828	0.7826	0.7814	0.7800	0.7790
313.15	0.7912	0.7907	0.7904	0.7870	0.7869	0.7867	0.7859	0.7850	0.7835	0.7821
			N-phenyl	-2-nitrobenz	ohydroxami	ic acid				
298.15	0.7957	0.7933	0.7904	0.7875	0.7876	0.7855	0.7839	0.7806	0.7779	0.7670
303.15	0.7969	0.7951	0.7923	0.7889	0.7891	0.7874	0.7857	0.7828	0.7805	0.7684
308.15	0.7974	0.7956	0.7924	0.7892	0.7913	0.7879	0.7862	0.7833	0.7810	0.7682
313.15	0.7997	0.7979	0.7947	0.7887	0.7910	0.7901	0.7880	0.7856	0.7806	0.7703
			N-phenyl	-3-nitrobenz	ohydroxami	ic acid				
298.15	0.7529	0.7577	0.7632	0.7721	0.7845	0.7873	0.7935	0.7980	0.8047	0.8108
303.15	0.7520	0.7569	0.7635	0.7728	0.7851	0.7893	0.7938	0.8002	0.8083	0.8135
308.15	0.7518	0.7555	0.7623	0.7719	0.7845	0.7887	0.7937	0.8004	0.8098	0.8148
313.15	0.7509	0.7548	0.7609	0.7707	0.7834	0.7879	0.7928	0.7993	0.8090	0.8156

TABLE-8

N-phenyl-2-methylbenzohydroxamic acid											
Temp. (K)	C (mol dm ⁻³)										
Temp. (K)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	
298.15	70.6518	70.4911	70.2577	70.1239	69.8880	69.7930	69.6983	69.5419	69.3862	69.2594	
303.15	71.1002	71.0039	70.8441	70.5580	70.4041	70.3888	70.3368	70.0548	69.9543	69.7164	
308.15	71.4427	71.4106	71.3137	71.0251	71.0013	70.8948	70.8613	70.6847	70.5640	70.2143	
313.15	71.9667	71.8865	71.8593	71.5067	71.4896	71.4692	71.3523	71.2072	71.0110	70.7467	
N-phenyl-2-nitrobenzohydroxamic acid											
298.15	71.4200	71.1779	70.8525	70.5300	70.4765	70.1915	70.0172	69.6855	69.4253	68.4215	
303.15	71.7624	71.5357	71.2414	70.8537	70.8292	70.6166	70.4319	70.1139	69.8455	68.7000	
308.15	71.9534	71.7788	71.4192	71.0954	71.0217	70.8863	70.6720	70.3436	70.0145	68.7998	
313.15	72.4109	72.1833	71.8262	71.5139	71.4288	71.2801	71.0273	70.7430	70.2348	69.2382	
N-phenyl-3-nitrobenzohydroxamic acid											
298.15	67.5829	67.9851	68.4460	69.2258	70.3167	70.5286	71.0415	71.4057	71.9554	72.4349	
303.15	67.7223	68.1256	68.6806	69.4541	70.5210	70.8490	71.1976	71.7322	72.4196	72.8313	
308.15	67.9320	68.2184	68.7931	69.6119	70.7080	71.0229	71.4221	71.9614	72.7365	73.1525	
313.15	68.0503	68.3556	68.8720	69.7157	70.7939	71.1458	71.5516	72.0856	72.9225	73.4489	

EXCI	TABLE-9 EXCESS MOLAR VOLUME V ^E (cm ³ mol ⁻¹) OF HYDROXAMIC ACIDS AT VARIOUS TEMPERATURES										
	N-phenyl-2-methylbenzohydroxamic acid										
Tama (V)	C (mol dm ⁻³)										
Temp. (K)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	
298.15	-0.7621	-1.0173	-1.3443	-1.5717	-1.9002	-2.0882	-2.2757	-2.5241	-2.7713	-2.9895	
303.15	-0.7012	-0.8935	-1.1487	-1.5291	-1.7775	-1.8879	-2.0348	-2.4089	-2.6029	-2.9322	
308.15	-0.6305	-0.7591	-0.9518	-1.3346	-1.4532	-1.6534	-1.7805	-2.0489	-2.2612	-2.6989	
313.15	-0.4948	-0.6736	-0.7993	-1.2486	-1.3638	-1.4821	-1.6960	-1.9374	-2.2289	-2.5871	
	N-phenyl-2-nitrobenzohydroxamic acid										
298.15	-0.0175	-0.3772	-0.8190	-1.2568	-1.4269	-1.8259	-2.1146	-2.5580	-2.9299	-4.0322	
303.15	-0.0624	-0.4080	-0.8200	-1.3238	-1.4662	-1.7947	-2.0949	-2.5260	-2.9072	-4.1500	
308.15	-0.1429	-0.4372	-0.9150	-1.3560	-1.5480	-1.5348	-2.1310	-2.5731	-3.0149	-4.3263	
313.15	-0.0736	-0.4222	-0.8990	-1.3301	-1.8007	-1.8022	-2.1719	-2.5719	-3.1915	-4.2894	
	N-phenyl-3-nitrobenzohydroxamic acid										
298.15	-10.6441	-10.3400	-9.9786	-9.3015	-8.3178	-8.2086	-7.8020	-7.5440	-7.1038	-6.7344	
303.15	-4.0846	-3.7844	-3.3342	-2.6685	-1.7140	-1.4950	-1.2565	-0.8353	-0.2650	0.0317	
308.15	-4.1462	-3.9628	-3.4932	-2.7827	-1.7995	-1.5937	-1.3055	-0.8800	-0.2236	0.0768	
313.15	-4.4146	-4.2123	-3.8010	-3.0658	-2.1004	-1.8579	-1.5632	-1.1431	-0.4258	-0.0168	

TABLE-10

EXCESS REFRACTIVE INDEX (cm3 mol-1) OF HYDROXAMIC ACIDS AT VARIOUS TEMPERATURES

Temp. (K)	C (mol dm ⁻³)										
	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	
298.15	-0.0020	-0.0010	0.0005	0.0006	0.0009	0.0010	0.0014	0.0017	0.0017	0.0020	
303.15	-0.0010	-0.0005	-0.0002	0.0000	0.0005	0.0005	0.0007	0.0015	0.0015	0.0025	
308.15	-0.0011	-0.0010	-0.0009	-0.0008	-0.0008	-0.0006	-0.0005	0.0000	0.0000	0.0020	
313.15	-0.0010	-0.0007	-0.0007	-0.0004	-0.0003	-0.0003	0.0000	0.0005	0.0010	0.0020	
N-phenyl-2-nitrobenzohydroxamic acid											
298.15	0.0003	0.0005	0.0010	0.0015	0.0020	0.0028	0.0030	0.0033	0.0035	0.0037	
303.15	0.0005	0.0010	0.0013	0.0020	0.0023	0.0028	0.0030	0.0035	0.0040	0.0045	
308.15	0.0014	0.0015	0.0020	0.0023	0.0025	0.0030	0.0035	0.0040	0.0050	0.0055	
313.15	0.0015	0.0020	0.0025	0.0025	0.0030	0.0035	0.0040	0.0045	0.0050	0.0055	
N-phenyl-3-nitrobenzohydroxamic acid											
298.15	0.0003	0.0005	0.0008	0.0009	0.0011	0.0014	0.0017	0.0020	0.0024	0.0029	
303.15	0.0005	0.0008	0.0011	0.0016	0.0019	0.0023	0.0027	0.0030	0.0033	0.0037	
308.15	0.0006	0.0010	0.0013	0.0017	0.0020	0.0025	0.0029	0.0034	0.0039	0.0042	
313.15	0.0010	0.0014	0.0017	0.0020	0.0026	0.0030	0.0033	0.0037	0.0040	0.0045	

Conclusion

From density and refractive index studies of hydroxamic acids. It is revealed that: (a) Greater the value of R_M and a for *N*-phenyl-2-nitrobenzohydroxamic acid (II) and *N*-phenyl-3nitrobenzohydroxamic acid (III), arises from polarization of phenyl ring when substitution group is NO₂ rather than nonpolar CH₃ group; (b) Negative S^{*}_V values of *N*-phenyl-2methylbenzohydroxamic acid (I) and *N*-phenyl-2-nitrobenzohydroxamic acid (II) shows hydrophobic character; (c) Positive V_{ϕ}, for all the hydroxamic acids suggest structure-maker with DMSO.

REFERENCES

- 1. S.C.P Hwa and W.T. Ziegler, J. Phys. Chem., 70, 2572 (1966).
- H.K. Kehl, Chemistry and Biology of Hydroxamic Acids, Karger, Basel, (1982).
- R.D. Wagh, H.S. Mahajan and S.G. Kaskhedikar, Asian J. Chem., 19, 4188 (2007).
- 4. S. Hanessian and S. Johnstone, J. Org. Chem., 64, 5896 (1999).
- M. Whittaker, C.D. Floyd, P. Brown and A.J.H. Gearing, *Chem. Rev.*, 99, 2735 (1999).
- T. Kolasa, A.O. Stewart and C.D.W. Brooks, *Tetrahedron:Asym.*, 7, 729 (1996).
- F.A.J. Kerdesky, S.P. Schmidt, J.H. Holms, R.D. Dyer, G.W. Carter and D.W. Brooks, *J. Med. Chem.*, **30**, 1177 (1987).

- 8. R.K. Dewan, S.P. Gupta and S.K. Mehta, J. Soln. Chem., 18, 13 (1989).
- A. Galmes, J. Besalduch, J. Bergay, A. Novo, M. Morey, J.M. Gureria and M.A. Duran, *Transfusion*, **39**, 70 (1999).
- T.T. Anchrodoguy, C.A. Cecchini and J.H. Crowe, *Cryobiology*, 28, 467 (1991).
- 11. T.J. Reid, G. Esteban, M. Clear and M. Gorogias, *Transfusion*, **39**, 616 (1999).
- 12. R. Pande and S.G. Tandon, J. Chem. Eng. Data, 24, 72 (1979).
- J.A. Riddick, W.B. Bunger and T. Sakano, Organic Solvent, Techniques of Chemistry, Wiley Interscience, New York, Vol I, edn. 4 (1986).
- 14. P.G. Sears, W.D. Sieqfried and D.E. Sunds, *J. Chem. Eng. Data*, **9**, 261 (1964).
- 15. Bhanupriya, R.P. Rajwade and R. Pande, *J. Eng. Chem. Data*, **53**, 1458 (2008).
- M.A. Saleh, S. Akhtar, M.S. Ahmed and M.H. Uddin, *Phys. Chem. Liq.*, 40, 621 (2002).
- 17. J.F. Casteel and P.G. Sears, J. Chem. Eng. Data, 19, 196 (1974).
- 18. S.A. Markarian and A.M. Erzyan, J. Chem. Eng. Data, 52, 1704 (2007).
- I. Koltz and R.M. Rosenberg, Chemical Thermodynamics, Basic Theory and Methods, W.A. Benzanin: CA, edn 3 (1972).
- 20. D.O. Masson, Philos. Mag., 8, 218 (1929).
- P. Brocos, A. Pineiro, R. Bravo and A. Amigo, *Phys. Chem. Chem. Phys.*, 5, 550 (2003).
- A. Ali, S. Sabir, A.K. Nain, S. Hyder, S. Ahmad and R. Patel, J. Indian Chem. Soc., 83, 581 (2006).
- 23. H. Lorentz, Ann. Phys., 9, 64; L.V. Lorenz, Ann. Phys., 11, 70 (1980).
- 24. Y.Y. Fialkov, Russ. J. Phys. Chem., 41, 398 (1967).