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Solute-solvent interactions of N-Arylhydroxamic acids in DMSO at various temperatures

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Abstract
Densities (ρ) and refractive indices (n) for solutions of (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1) mol.L^{-1} N-Phenyl-2-bromobenzohydroxamic acid (PBBHA) and N-Phenyl-4-methylbenzohydroxamic acid (PMBHA) in dimethyl sulphoxide (DMSO) have been measured at temperatures (298.15, 303.15, 308.15 and 313.15) K under atmospheric pressure. Apparent molar volume (V_ϕ) and partial molar volume (V^0_ϕ) have been calculated from experimental values of densities. The refractive index data have been used to calculate molar refraction (R_M), polarizability (α) and thermal co-efficient of the refractive index (dn/dt) for the hydroxamic acids. These parameters have been used to discuss the solute-solvent interactions.

Keywords: Density, refractive index, apparent molar volume, dimethyl sulphoxide, hydrogen-bonding and hydroxamic acid.

1. Introduction
Hydroxamic acids were neutral, polyfunctional molecule with general molecular R–C(=O)N(R′)OH were introduced by H. Lossen in 1869. These have been recognized as compounds of pharmacological, toxicological and pathological importance [1-7]. These are versatile metal extractants and behave as non-electrolyte. Dimethyl sulphoxide, DMSO, is called 'super-solvent' due to its wide range of applicability as solvent in many chemical and biological processes. It has also been utilized as situ free radical scavenger for various cancer treatments [8] and as anti-inflammatory agent for arthritic condition [9]. The knowledge of volumetric behavior of electrolyte and non-electrolyte solutions can provide useful information regarding solute-solute and solute-solvent interactions. Molar volume and refractive index, their deviation from ideality and variation with temperature and composition of mixtures are useful for design engineering process, in chemical and biological industries [10-12] and to test the theories of solution [13]. Volumetric properties and refractive index of mixture represent together an important source of information for characterization of the interaction between components. In order to examine molecular interaction in hydroxamic acids with DMSO through volumetric and optical properties, we report here the densities (ρ) and refractive indices (n) of two hydroxamic acids, N- phenyl-2-bromobenzo- and N-phenyl-4-methylbenzo- with dimethyl sulphoxide (DMSO) as a function of their concentration at various temperatures (298.15, 303.15, 308.15 and 313.15) K. The experimental values of ρ and n were used to calculate apparent molar volume ($V\phi$), partial molar volume (V^0_ϕ), solute-solute interaction (S^*_V), molar refraction (R_M) and polarizability (α) of both the hydroxamic acids. These results have been used to understand molecular behavior and nature of solute-solvent interactions.

2. Experimental section
2.1 Materials and methods
N-Phenyl-2-bromobenzohydroxamic acid and N-Phenyl-4-methylbenzohydroxamic acid, were prepared in this laboratory following the procedure reported in literature [14]. The solute was purified by recrystallizing thrice with benzene and dried over phosphorus pentaoxide in vacuum desiccators for 24 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.

PBBHA, observed M. P. 113 °C and reported 113 °C in the literature [15], IR, cm^{-1}: 3100, 1640, 1320, and 1018. Anal. ($C_{13}H_{11}NBr$) Calcd C, 53.45 ; N, 3.43 ; H, 4.80. Found: C, 53.60 ; N, 3.60; H, 4.70. PMBHA, observed M. P. 115°C and reported 116 °C in the literature [16], IR, cm^{-1}: 3100, 1620, 1340 and 850. Anal. ($C_{13}H_{11}NO_2$) Calcd C, 73.99; N, 5.77; H, 6.16. Found: C, 74.10; N, 5.56; H, 5.95. 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 ±0.001 units.

2.2 Measurement of density

Densities of hydroxamic acids in DMSO were determined by using a 10 cm^3 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 ± 3 x 10^{-5}g cm^{-3}. The reproducibility of density measurement was ± 4 x 10^{-5}g cm^{-3}.

2.3 Measurement of refractive index

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 temperature [17]. The accuracy in the refractive index measurement was ±0.0001 unit. Temperature was controlled by circulating water around prisms of the refractometer form thermostatically controlled adequately stirred water bath (accuracy ±0.01 ^{0}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, $\rho 0$ and refractive Index, $n0$ along with literature values [18-23] of DMSO are given in Table 1.

Table 1: Properties of DMSO

	ρ_o/gcm^{-3}		n_o	
T/K	**this work**	**Lit.**	**this work**	**Lit.**
298.15	1.0947	1.0955[a] 1.09475[b]	1.4720	1.4771[d] 1.4765[e]
303.15	1.0907	1.0896[c] 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]ρ_o^{18}, [b]ρ_o^{19}, [c]ρ_o^{20}, [d] n_o^{21}, [e]n_o^{22}, [f]n_o^{23}

3. Results and discussions

Table 2 and 4 lists the densities (ρ) and refractive index (n) of both the hydroxamic acids in DMSO at four temperatures (298.15, 303.15, 308.15 and 313.15) K under atmospheric pressure. The densities and refractive index of the both hydroxamic acids solutions increase with increase in concentration in particular temperature but it decreases in rise temperature.

From experimental values of densities, apparent molar volume ($V\phi$) have been calculated by using the following equation [24],

$$V_\phi = 1000\,(\rho_o - \rho)/C\rho\rho_o + M/\rho \quad [1]$$

Where M, is the molar mass of hydroxamic acids, ρ and ρ_0 are the densities of solution and solvent, respectively. $V\phi$ values are included in Table 2. It is evident from Table 2 that $V\phi$ is a linear function of molarity of hydroxamic acids, shown in Fig. 1 and 2 respectively for both the hydroxamic acids.

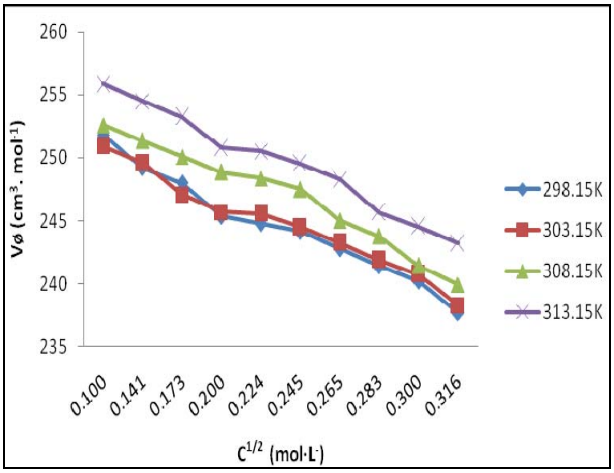

Fig 1: Plot of apparent molar volume Vø and square root of concentration of PBBHA.

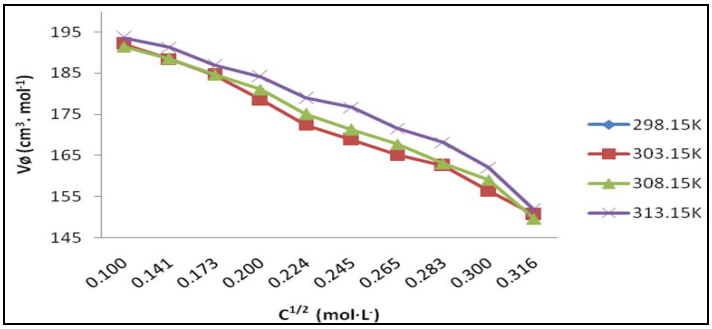

Fig 2: Plot of apparent molar volume Vø and square root of concentration of PMBHA.

Table 2: Density, ρ (g cm^{-3}) and apparent molar volume, Vø (cm^3. mol^{-1}) of PBBHA and PMBHA at various temperatures.

C/mol·L^{-1}	ρ				Vø			
	298.15	**303.15**	**308.15**	**313.15**	**298.15**	**303.15**	**308.15**	**313.15**
	N-phenyl-2-bromobenzohydroxamic acid							
0.01	1.1075	1.1034	1.0988	1.0915	251.8034	250.9209	252.5798	255.8643
0.02	1.1096	1.1045	1.0998	1.0926	249.2042	249.5572	251.338	254.4948
0.03	1.1106	1.1065	1.1008	1.0936	247.9671	247.0791	250.0967	253.2503
0.04	1.1127	1.1076	1.1018	1.0956	245.3706	245.7169	248.8558	250.7626
0.05	1.1132	1.1077	1.1022	1.0958	244.7527	245.5931	248.3596	250.514
0.06	1.1137	1.1086	1.1029	1.0966	244.1349	244.479	247.4914	249.5195
0.07	1.1148	1.1096	1.1049	1.0976	242.776	243.2415	245.0119	248.2767
0.08	1.1159	1.1107	1.1059	1.0997	241.4177	241.8808	243.7728	245.6685
0.09	1.1169	1.1116	1.1078	1.1006	240.1833	240.7679	241.4197	244.5512
0.10	1.1189	1.1136	1.1090	1.1017	237.7157	238.2959	239.9343	243.1862
	N-phenyl-4-methylbenzohydroxamic acid							
0.01	1.1083	1.1039	1.0986	1.0904	192.0816	191.4398	193.6323	197.5749
0.02	1.1114	1.1064	1.1006	1.0935	188.4101	188.475	191.2567	193.8845
0.03	1.1147	1.1096	1.1043	1.0975	184.5052	184.683	186.8653	189.1276
0.04	1.1197	1.1127	1.1066	1.1006	178.5955	181.0128	184.1379	185.4448
0.05	1.1249	1.1177	1.1110	1.1027	172.458	175.0998	178.9251	182.9518
0.06	1.1280	1.1209	1.1129	1.1058	168.8032	171.3197	176.6761	179.3931
0.07	1.1311	1.1239	1.1172	1.1097	165.1515	167.7789	171.5907	174.6527
0.08	1.1333	1.1279	1.1201	1.1118	162.5618	163.0623	168.1644	172.1662
0.09	1.1385	1.1313	1.1252	1.1166	156.4466	159.0572	162.1455	166.4881
0.10	1.1434	1.1393	1.1340	1.1251	150.6918	149.6476	151.7793	156.4516

The partial molar volume V_ϕ^0 has been calculated by the equation [25]

$$V_\phi = V_\phi^0 + S_V^* C^{1/2} \qquad [2]$$

Where V_ϕ^0 and S_V^* have been estimated by the least-square fittings of the apparent molar volume data in equation 2. The values of V_ϕ^0 and S_V^* are listed in Table 3. S^{*V} is the measure of solute-solute interactions and depends on charge, salt type and nature of the solvent. At infinite dilution, solute-solute interaction vanishes therefore, V_ϕ^0 provides information regarding solute-solvent interaction [12] Table 3 reveals values of V_ϕ^0 are large positive and greater than the values of S^{*V} thereby suggesting the presence of strong solute-solvent (hydroxamic acid- DMSO) interactions and weak solute-solute (hydroxamic acid- hydroxamic acid) interactions. The negative S^{*V} values shows hydrophobic character of solute [26].

Table 3: Partial molar volume, V_ϕ^0 and solute-solute interaction parameter, S_V^* of both the hydroxamic acids at various temperatures.

N-phenyl-2-bromobenzohydroxamic acid				
	298.15K	303.15K	308.15K	313.15K
V_ϕ^0	257.9807	256.876	259.7552	262.8209
S_V^*	-59.8549	-53.9558	-57.2781	-58.8042
N-phenyl-4-methylbenzohydroxamic acid				
	298.15K	303.15K	308.15K	313.15K
V_ϕ^0	215.1685	214.9187	216.8534	218.651
S_V^*	-192.265	-185.869	-179.527	-172.857

The refractive index data (*n*) have been utilized for calculating molar refraction (R_M) by using Lorentz-Lorenz equation,

$$R_M = [n^2 - 1/n^2 + 2].V \qquad [3]$$

Where *V* is molar volume of hydroxamic acids in DMSO. The data of *V* and R_M are presented in Table 4 respectively.

Table 4: Refractive indices, n, of PBBHA and PMBHA at various temperatures.

C/mol·L^{-1}	n							
	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
	N-phenyl-2-bromobenzohydroxamic acid				N-phenyl-4-methylbenzohydroxamic acid			
0.01	1.4722	1.4705	1.4695	1.468	1.4730	1.4720	1.4710	1.4690
0.02	1.4723	1.4708	1.4698	1.4682	1.4735	1.4723	1.4710	1.4695
0.03	1.4725	1.4712	1.4700	1.4685	1.4740	1.4728	1.4720	1.4705
0.04	1.4728	1.4718	1.4700	1.4689	1.4750	1.4730	1.4718	1.4708
0.05	1.4730	1.4720	1.4705	1.4690	1.4760	1.4735	1.4720	1.4708
0.06	1.4733	1.4725	1.4708	1.4693	1.4761	1.4741	1.4720	1.4710
0.07	1.4735	1.4728	1.4710	1.4695	1.4764	1.4742	1.4725	1.4714
0.08	1.474	1.4730	1.4715	1.4698	1.4765	1.4750	1.4730	1.4715
0.09	1.4743	1.4735	1.4725	1.4700	1.4770	1.4750	1.4735	1.4715
0.10	1.4753	1.4740	1.4730	1.4705	1.4775	1.4760	1.4745	1.4720

The molar refraction is related to the polarizability of the molecules by Lorentz-Lorenz formula [27],

$$R_M = \frac{4\pi\alpha N}{3} \quad [4]$$

Where α is electronic polarizablityand N is avogadro's number. The value of α are reported in Table 5. As evident from Table 5 shows that the R_M and α of N-Phenyl-2-bromobenzohydroxamic acid increases with concentrations but opposite trend in case of N-phenyl-4-methylbenzohydroxamic acid. It is assumed that the greater value of R_M and α for PBBHA than PMBHA arises from polarization of the phenyl ring when the substituent group is bromine atom rather than methyl group. This trend is slightly influenced by temperature for both PBBHA and a PMBHA decrease indicates the presence of intermolecular and intermolecular interactions between the molecules of solute and solvent.

Table 5: Molar Refraction, R_M (cm^3. mol^{-1}) and Polarizability, α (cm^3. mol^{-1}) of PBBHA and PMBHA at various temperatures

C/mol·L^{-1}	R_M				α			
	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
	N-phenyl-2-bromobenzohydroxamic acid							
0.01	19.7999	19.8114	19.8589	19.9372	0.7845	0.7849	0.7868	0.7899
0.02	19.8042	19.8409	19.8904	19.9636	0.7847	0.7861	0.7881	0.7910
0.03	19.8318	19.8578	19.9184	19.9954	0.7858	0.7868	0.7892	0.7922
0.04	19.8433	19.8983	19.9391	20.0126	0.7862	0.7884	0.7900	0.7929
0.05	19.8800	19.9425	19.9891	20.0520	0.7877	0.7901	0.7920	0.7945
0.06	19.9204	19.9832	20.0264	20.0878	0.7893	0.7918	0.7935	0.7959
0.07	19.9464	20.0148	20.0362	20.1163	0.7903	0.7930	0.7939	0.7970
0.08	19.9833	20.0411	20.0754	20.1280	0.7918	0.7940	0.7954	0.7975
0.09	20.0148	20.0820	20.1163	20.1584	0.7930	0.7957	0.7970	0.7987
0.10	20.0535	20.1027	20.1519	20.1962	0.7945	0.7965	0.7984	0.8002
N-phenyl-4-methylbenzohydroxamic acid								
0.01	19.8023	19.8459	19.9056	19.9822	0.7846	0.7863	0.7887	0.7917
0.02	19.7914	19.8386	19.8963	19.9709	0.7842	0.7860	0.7883	0.7913
0.03	19.7770	19.8258	19.8924	19.9614	0.7836	0.7855	0.7882	0.7909
0.04	19.7503	19.8041	19.8706	19.9430	0.7825	0.7847	0.7873	0.7902
0.05	19.7202	19.7594	19.8253	19.9318	0.7813	0.7829	0.7855	0.7897
0.06	19.6953	19.7504	19.8180	19.9116	0.7804	0.7825	0.7852	0.7889
0.07	19.6776	19.7271	19.7856	19.8806	0.7796	0.7816	0.7839	0.7877
0.08	19.6687	19.7112	19.7783	19.8732	0.7793	0.7810	0.7836	0.7874
0.09	19.6214	19.6775	19.7319	19.8135	0.7774	0.7796	0.7818	0.7850
0.10	19.5796	19.5988	19.6385	19.7063	0.7758	0.7765	0.7781	0.7808

The temperature gradient, *dn/dt*, can be determined by using the relationship of Murphy and Alpert [28] as

$$\frac{dn}{dT} = -\frac{3n(n^2-1)\gamma}{2(2n^2-1)} \quad [5]$$

$$\frac{dn}{dT} = -3.3356 \times 10^{-4}\ \frac{n(n^2-1)}{2n^2-1}$$

$$\frac{dn}{dT} = -2.9482 \times 10^{-4}\ \frac{n(n^2-1)}{2n^2-1} \quad [6]$$

Where γ is the co-efficient of thermal expansivity, independent of wavelength, dn/dT = –2.6x10^{-4} and dn/dT =– 2.3x10^{-4} for PBBHA and PMBHA, as extracted from the negative slope of plot of n vs T, we can determine the unknown γ in equation 5 to be as follows.

γ=3.3356 x10^{-4}; 2.9482x10^{-4} for N-phenyl-2-bromobenzo- and N-phenyl-4-methylbenzohydroxamic acids respectively. The *dn/dt* is negative value suggest the structure making of both the hydroxamic acid in DMSO though H-bonding.

4. Conclusions

Using density and refractive indices data, the apparent molar volumes, apparent molar volume at infinite dilution, molar refraction properties have been computed. Greater the value of molar refraction and polarizability of PBBHA than PMBHA, arises from polarization of phenyl group when substitution group is Br rather than non-polar CH_3 group. Negative S_V^* values of PBBHA and PMBHA shows hydrophobic character. Positive V_ϕ, for both the hydroxamic acids suggest structure-maker with DMSO through hydrogen bonding.

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