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Study of the Refractive Parameters of N-Phenyl-2-Nitrobenzohydroxamic 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 M) N-Phenyl-2-nitrobenzohydroxamic acid (PNBHA) in dimethylsulphoxide (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), polarizibility (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 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. Properties such as 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 N Phenyl-2-nitrobenzohydroxamic acid with dimethylsulphoxide (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_ϕ), partial molar volume (V^0_ϕ), solute-solute interaction (S^*_V), molar refraction (R_M) and polarizibility (α) of both the hydroxamic acids. These results have been used to understand molecular behavior and nature of solute-solvent interactions.

2. Materials and Methods

N Phenyl-2-nitrobenzohydroxamic acid was prepared in this laboratory following the procedure reported in literature. [14] The solute was purified by recrystalling thrice with benzene and dried over phosphorus pentaoxide in vaccum dessicator 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. PNBHA, observed m.p. 148°C and reported 148°C in the literature, IR, cm^{-1}: 3100, 1612, 1349, and 950. Anal. ($C_{13}H_{11}NO_2$) Calcd C, 60.47 ; N, 10.85 ; H, 3.90. Found: C, 60.80 ; N, 11.20; H, 3.70. 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 ±0.001 units.

Measurement of Density, ρ. Densities of hydroxamic acid 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 ± 0.03$kg.m^{-3}$. The reproducibility of density measurement was ± 0.04 kg. m^{-3}.

Measurement of Refractive Index, n. 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.[15] 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, ρ_0 and refractive Index, η_0 of DMSO at 298.15, 303.15, 308.15 and 313.15K 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[16], [b] ρ_o[17], [c] ρ_o[18], [d] n_o[19], [e] n_o[20], [f] n_o[21]

3. Results and Discussions

Table 2 and 3 lists the densities (ρ) and refractive index (n) of 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 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_ϕ) have been calculated by using the following equation [21],

$$V_\phi = 1000\,(\rho_0 - \rho)/C\rho_0 + M/\rho_0 \qquad (1)$$

where M, is the molar mass of hydroxamic acids, ρ and ρ_0 are the densities of solution and solvent, respectively. V_ϕ values are included in Table 4. It is evident from Table 4 that V_ϕ is a linear function of molality of hydroxamic acids.

Table 2: Density, ρ (g cm^{-3}) of the hydroxamic acids at various temperatures.

N-phenyl-2-nitrobenzohydroxamic acid				
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K
0.01	1.0958	1.0905	1.0876	1.0808
0.02	1.1013	1.0958	1.0921	1.0860
0.03	1.1081	1.1021	1.0994	1.0932
0.04	1.1150	1.1099	1.1061	1.0997
0.05	1.1176	1.1121	1.1091	1.1028
0.06	1.1239	1.1172	1.1130	1.1069
0.07	1.1285	1.1219	1.1181	1.1126
0.08	1.1356	1.1287	1.1251	1.1188
0.09	1.1416	1.1348	1.1321	1.1286
0.10	1.1599	1.1553	1.1536	1.1464

Table 3: Refractive indices, n, of the hydroxamic acids at various temperatures.

N-phenyl-2-nitrobenzohydroxamic acid				
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K
0.01	1.4743	1.4725	1.4714	1.4695
0.02	1.4745	1.4730	1.4715	1.4700
0.03	1.4750	1.4733	1.4720	1.4705
0.04	1.4755	1.4740	1.4723	1.4705
0.05	1.4760	1.4743	1.4725	1.4710
0.06	1.4768	1.4748	1.4730	1.4715
0.07	1.4770	1.4750	1.4735	1.4720
0.08	1.4773	1.4755	1.4740	1.4725
0.09	1.4775	1.4760	1.4750	1.4730
0.10	1.4777	1.4765	1.4755	1.4735

Table 4: Apparent molar volume, V_ϕ (cm^3. mol^{-1}) of the hydroxamic acids at various temperatures

N-phenyl-2-nitrobenzohydroxamic acid				
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K
0.01	235.4861	236.6988	237.4813	238.8552
0.02	235.2455	236.5006	237.3754	238.6644
0.03	235.1252	236.4020	237.2529	238.5397
0.04	235.0650	236.3186	237.2031	238.4919
0.05	235.1056	236.3717	237.2440	238.5272
0.06	235.0770	236.3621	237.2566	238.5355
0.07	235.0791	236.3608	237.2492	238.5201
0.08	235.0517	236.3354	237.2227	238.5025
0.09	235.0416	236.3232	237.2015	238.4520
0.10	234.9212	236.1816	237.0511	238.3374

The partial molar volume V_ϕ^0 has been calculated by the equation [22],

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

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 5. 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 5 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.

Table 5: Partial molar volume, V_{ϕ}^{0} and solute-solute interaction parameter, S_V^* of hydroxamic acids at various temperatures.

N-phenyl-2-nitrobenzohydroxamic acid				
	298.15K	303.15K	308.15K	313.15K
V_{ϕ}^{0}	274.1146 (± 0.1387)	274.3388 (± 0.1728)	274.7856 (± 0.1773)	277.7446 (± 0.1509)
S_V^*	-1.8940 (± 0.5916)	-1.6724 (± 0.7368)	-1.3638 (± 0.7559)	-1.6975 (± 0.6437)

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

$$R_M = [(n^2 - 1 / n^2 + 2)] V \quad (3)$$

where V is molar volume of hydroxamic acids in DMSO. The data of V and R_M are presented in Table 6 and Table 7 respectively.

Table 6: Molar volume, V (cm^3. mol^{-1}) of the hydroxamic acids at various temperatures.

N-phenyl-2-nitrobenzohydroxamic acid				
C/mol·dm^{-3}	298.15K	303.15 K	308.15 K	313.15 K
0.01	71.4200	71.7624	71.9534	72.4109
0.02	71.1779	71.5357	71.7788	72.1833
0.03	70.8525	71.2414	71.4192	71.8262
0.04	70.5300	70.8537	71.0954	71.5139
0.05	70.4765	70.8292	71.0217	71.4288
0.06	70.1915	70.6166	70.8863	71.2801
0.07	70.0172	70.4319	70.6720	71.0273
0.08	69.6855	70.1139	70.3436	70.7430
0.09	69.4253	69.8455	70.0145	70.2348
0.10	68.4215	68.7000	68.7998	69.2382

The molar refraction is related to the polarizibility of the molecules by Lorentz-Lorenz formula [23],

$$R_M = \frac{4\pi\alpha N}{3} \quad (4)$$

where α is electronic polariziblity and N is avogadro's number. The value of α are reported in Table 8. As evident from Table 7 and Table 8 shows, that the R_M and α of N-Phenyl-2-nitro benzohydroxamic acid decreases with concentrations. It is assumed that the greater value of R_M and α for PNBBHA arises from polarization of the phenyl ring when the substituent group is nitro atom. This trend is slightly influenced by temperature indicates the presence of intermolecular interactions between the molecules of solute and solvent.

Table 7: Molar Refraction, R_M (cm^3. mol^{-1}) f the hydroxamic acids at various temperatures

N-phenyl-2-nitrobenzohydroxamic acid				
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K
0.01	20.0825	20.1132	20.1265	20.1843
0.02	20.0217	20.0678	20.0813	20.1393
0.03	19.9481	19.9961	19.9988	20.0580
0.04	19.8752	19.9125	19.9190	19.9707
0.05	19.8780	19.9164	19.9056	19.9652
0.06	19.8261	19.8745	19.8856	19.9417
0.07	19.7840	19.8297	19.8435	19.8891
0.08	19.7009	19.7580	19.7692	19.8275
0.09	19.6343	19.7001	19.7122	19.7029
0.10	19.3574	19.3944	19.3877	19.4409

Table 8: Polarizibility, α (cm^3. mol^{-1}) of both the hydroxamic acids at various temperatures.

N-phenyl-2-nitrobenzohydroxamic acid				
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K
0.01	0.7957	0.7969	0.7974	0.7997
0.02	0.7933	0.7951	0.7956	0.7979
0.03	0.7904	0.7923	0.7924	0.7947
0.04	0.7875	0.7889	0.7892	0.7913
0.05	0.7876	0.7891	0.7887	0.7910
0.06	0.7855	0.7874	0.7879	0.7901
0.07	0.7839	0.7857	0.7862	0.7880
0.08	0.7806	0.7828	0.7833	0.7856
0.09	0.7779	0.7805	0.7810	0.7806
0.10	0.7670	0.7684	0.7682	0.7703

4. Conclusion

From density and refractive index behavior of N--phenyl-2-nitroobenzohydroxamic acid in DMSO reveals that the positive V^0_{ϕ} values for hydroxamic acids suggest strong solute-solvent and interaction becomes stronger with rise in temperature. The molar refraction and polarizibility of N-phenyl-2-nitroobenzohydroxamic acid shows greater solute-solvent interaction, it may due to substitution of polar nitro group. This hydroxamic acid act as structure maker with DMSO through hydrogen bonding.

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