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Volumetric Properties of N-phenyl-3-Nitrobenzohydroxamic Acid in DMSO at Various Temperatures

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Abstract: ***The refractive indices and densitics have been measured for N-phenyl-3-nitrobenzohydroxamic acid (PNBHA) in dimethylsulphoxide (DMSO) as a function of concentration at (298.15, 303.15, 308.15 and 313.15) K. Refractive index and density data have been used to evaluate the inolar refraction, polarizability, apparent molar volume and partial molar volume at infinite dilution. Furthermore, the deviation of refractive indices, moiar refractions and molar volumes have been calculated and reported. The knowledge of such parameters is help to understand the solute-solvent interactions.***

Keywords: refractive index, density, N-phenyl-3-nitrobenzohydroxamic acid, solute-solvent interactions, dimethylsulphoxide

1. Introduction

Hydroxamic acids were neutral, polyfunctional molecule with general molecular formula, R¸NOH.R¸C=O, introduced by H. Lossen in 1869. These have been recognized as compounds of pharmacological, toxicological and pathological important[1-7], These are versatile metal extractants and behave as non-electrolyte. Dimethylsulphoxide, DMSO, is called 'super-solvent' due to its wide range of applicability as solvent in many chemical and biological processes[8-9]. In order to characterize the molecular interaction in N-phenyl-3-nitrobenzohydroxamic acid with DMSO through optical and volumetric properties, we report here the refractive indices (n) and densities (p) of this molecule in dimethylsulphoxide as function of concentration at various temperatures, 298.15, 303.15, 308.15 and 313.15K. The experimental values of n and p were used to calculate the molar refraction polarizability, apparent molar volume and partial molar volume at infinite dilution, excess molar volume, deviations of refractive indices and molar refractions and the results have been used to understand molecular behavior and the nature of solute-solvent interactions.

2. Experimental

N-phenyl-2-methylbenzohydroxamic acid was pre- pared in the laboratory by the procedure reported in Literature[10]. The purification of solute is done by crystallization thrice with benzene and dried over phosphorus pentaoxide in vacuum desiccators for 24 hours. The purity of this compound was ascertained by deter mining the melting point and IR spectrum. The data obtained were tally with reported values. Elemental analysis was determined with a Vario-ELanalysis apparatus.

N-phenyl-3-nitrobenzohydroxamic acid observed M.P. of 81°C and reported M.P. of 81°C in the literature, IR, cm: 3050, 1620, 1340 and 915. Anal. ($C_{14}H_{13}NO_2$) Calcd C, 73.99; N, 6.16; 11, 5.77. Found: C, 74.10, N, 5.95, H, 6.10). Analytical grade DMSO was purchased from Merck. A 0.1 mol.L¹ stock solution of N-phenyl-2-methylbenzohydroxamic acid was prepared by disolving an appropriate amount in 100ml of DMSO Solutions of concentration varying from 0.01 to 0.09 were then prepared from the stock solution by stars dilution. Uncertainties were estimated to be ±0.001 mol L^{-1} units

Densities of N-phenyl-3-nitrobenzohydroxamic acid in DMSO was determined by using 10 cm^3 double armed pycnometer at four temperatures, 293.15, 303.15, 308.15 and 313.15 K. The pycnometer was calibrated at the desired temperature with freshly pre- pared triply distilled-water. The estimated precision of density measurement of solutions was ±3x$10^{-5}$$gcm^{-3}$The reproducibility of the density measurement was±4x$10^{-5}$$gcm^{-3}$. Refractive indices were measured with the help of a thermostated Abb's refractometer. The refractometer was calibrated by measuring the refractive indices of triply distilled water and toluene at known temperatures. The accuracy in the refractive index measurement was ±0.001 units. Temperature was controlled by circulating around prism of the refractometer from thermostatically controlled adequately stirred water (accuracy ±0.02). The sample mixture was directly injected into the prism assembly of the instrument by means of an airtight hypodermic syringe. An average of three to four measurements was taken for each sample mixture at various temperatures (298.15, 303.15, 308.15 and 313.15 K).

3. Results and Discussion

The data on the refractive indices (n) and densities (p) determined for N-phenyl-2-methylbenzohydroxamic acid in DMSO at four temperatures (298.15, 303.15, 308.15 and 313.15K) are listed in TABLE 1. The value of density decreases with increase in concentration and temperature. The

value of refractive index increase with increase in concentration and decreases with rise in temperatures.

Volumetric properties

In present paper different volumetric properties are studied. From experimental values of densities, apparent molar volume (V_ϕ) have been calculated by using the following equation

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

where M, is the molar mass of hydroxamic acids, ρ_0 and ρ are the densities of solution and DMSO solvent, respectively. The apparent molar volumes V_ϕ values are reported in TABLE 2. The positive value of V_ϕ PNBHA in DMSO indicates strong solute-solvent interactions. These interactions are increases with rise in concentration at a particular temperature and are strengthened with a rise in temperature.

The partial molar volume V_ϕ^0 has been calculated by the equation [12],

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

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 value 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 4 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.

Refractive Properties

The molar refraction, R_M, was calculated from the measured refractive indices using the relation proposed by Lorentz-Lorenz [13]:

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

Where, V is the molar volume. The calculated values of R_M are shown in TABLE 4. Values of R_M increases with increasing concentration of the PNBHA. As R_M is directly proportional to polarizability, it is obtained by following the Lorentz- Lorenz equation[14].

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

where α is electronic polariziblity and N is Avogadro's number. The value of α are reported in TABLE 4. The values of polarizability increases with rise in concentration of solute indicate the presence of intermolecular interactions between the solute and solvent. The lower value of R_M, and α with rise in temerature of hydroxamic acid in DMSO is due to presence of polar, group on phenyl ring, which may higher the dispersive force.

Excess properties

The excess properties, Excess refractive index n^E and Excess molar Refraction R_M^E of the mixtures were the calculated using the following equation 5 and 6respectively are shown in TABLE 5:

$$n^E = n-(x_1n_1+x_2n_2) \quad (5)$$

$$R_M^E = R_M-(X_1R_{M1} + X_2R_{M2}) \quad (6)$$

Where, X_1, mole fraction of DMSO, X_2, mole fraction solute. The values strong intermolecular interactions via, hydrogen bonding between hydroxamic acids and DMSO. The Excess refractive index, n^E are positive throughout the concentration suggests that dispersion force is higher in solvent at lower concentration.

4. Conclusion

Hydroxamic acid functional group shows wide range of biological activity and molar refraction has been shown to be related to lipophilcity, molar volume and steric bulk. As hydroxamic acids are bioactive molecules, using refractive index and density data, apparent molar volume, molar refraction and excess properties has been computed. The behavior of these parameters suggests strong solute-solvent interaction in the system and N-phenyl-3-nitrolbenzobydroxamic acid acts as structure maker in DMSO through hydrogen bonding.

References

[1] Kehl, H. K.,Chemistry and Biology of Hydroxamic Acids, Karger, Basel, (1982).
[2] Bergeron, R. J. Synthesis and Solution Structure of Microbial Siderophores. *Chem. Rev.* **1984**, 84, 587-602.
[3] Hanessian, S.; Johnstone, S. Synthesis of Hydroxamic Esters via Alkoxyaminocarbonylation of β-Dicarbonyl Compounds *J. Org. Chem.* **1999**, 64, 5896-5903.
[4] Whittaker, M.; Floyd, C. D.; Brown, P.; Gearing, A. J. H. Design and Therapeutic Application of Matrix Metalloproteinase Inhibitors *Chem. Rev.* **1999,** 99, 2735-2776.
[5] Wada, C. K.; Holms, J. H.; Curtin, M. L.; Dai., Y.; Florjancic, A. S.; Garland.R. B.; Guo,Y.; Heyman, H. R.; Stacy, J. R.; Steinman, D. H.; Albert, D. H.; Bouska, J. J.; Elmore, I. N.; Goodfellow, C. L.; Marcotte, P. A.; Tapang, P.; Morgan, D. W.; Michaelides, M. R.; Davidsen, S. K. Phenoxyphenyl Sulfone *N*-Formylhydroxylamines (Retrohydroxamates) as Potent, Selective, Orally Bioavailable Matrix Metalloproteinase Inhibitors. *J. Med. Chem.* **2002,** *45*, 219-232.

[6] Kolasa, T.; Stewart, A. O.; Brooks,C. D. W. Asymmetric Synthesis of (R)-N-3-butyn-2-yl-N-Hydroxyurea, a Key Intermediate for 5-Lipoxygenase Inhibitors. *Tetrahedron: Asymmetry* **1996**, *7*,729-736.
[7] Kerdesky,F. A. J.; Schmidt, S. P.; Holms, J. H.; Dyer, R. D.; Carter, G. W.; Brooks,_D. W. Synthesis and 5-Lipoxygenase Inhibitory Activity of 5-Hydroperoxy-6,8,11,14-Eicosatetraenoic Acid Analogs. *J. Med. Chem.* **1987,** *30* , 1177-1186.
[8] Salim, A. Removing Oxygen-Derived Free Radicals Delays Hepatic Metastases and Prolongs Survival in Colonic Cancer. *Oncology* **1992** , *49*, 58-62.
[9] Jacob, S.W.; Rosenbaum, E. E.; Wood, D.C. "Dimethylsulphoxide" Mercel Dekker, New York, (1971).
[10] Aminabhavi, T. M.; Raiker S. K.; Balundgi, R.H. Volumetric, Acoustic, Optical, and Viscometric Properties of Binary Mixtures of 2-Methoxyethanol with Aliphatic Alcohols (C1-C8). *Ind. Eng. Chem. Res.* **1993**, *32*, 931-936.
[11] Ali, A.; Soghra, H. Molecular Interaction Study in Binary Mixtures of Dimethylsulphoxide with 1,2-Dichloroethane and 1,1,2,2-Tetrachloroethane at 303 K, *Ind. J. Phys.* **2002**, *76(B)*, 23-28.
[12] Comeli, F.; Ottani, S.; Francesconi, R.; Coastellari. C. Ultrasonic velocity, Viscosity, Density and Excess Properties of Binary Mixture of Dimethyl Sulphoxide with Propanoic acid and *n*-Butyric acid. *J. Chem.Eng.Data* **2002**, *47*, 93-97.
[13] Koltz, I.; Rosenberg, R.M. Chemical Thermodynamics, Basic Theory and Methods, 3rd ed; W.A. Benzanin: CA, 1972.
[14] Masson, D.O. Solute Molecular Volume in relation to Solvation and Ionization. *Philos* . *Mag* **1929**, *8*, 218-235.

Author Profile

Dr. (Mrs.) Veenu Chandraker is a dedicated Lecturer at the Government Polytechnic, Mahasamund, with extensive experience in teaching and research in the field of Chemistry. She has previously served as an Assistant Professor (Contractual) at Government MVPG College, Mahasamund, and NIT Raipur. A recipient of prestigious accolades such as the Young Scientist Award (2011) from the Chhattisgarh Council of Science and Technology and the Student Research Convention Award (2009) from Pt. Ravishankar Shukla University, Dr. Chandraker has made significant contributions to scientific research. Her work includes impactful studies on the nutritional value and processing of millet, published in esteemed international journals like the Journal of Applicable Chemistry and the Emirates Journal of Food and Agriculture. With a rich research background spanning roles at Pt. Ravishankar Shukla University and Indira Gandhi Agricultural University, she continues to inspire through her academic and professional endeavors.

Table 1: Density, ρ (g cm^{-3}) and Refractive indices, n, of the hydroxamic acids at various temperatures.

	ρ (g cm^{-3})				n,			
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0.01	1.1579	1.1555	1.1519	1.1499	1.4743	1.4725	1.4706	1.4690
0.02	1.1528	1.1505	1.1489	1.1466	1.4745	1.4728	1.4710	1.4694
0.03	1.1469	1.1430	1.1411	1.1398	1.4748	1.4731	1.4713	1.4697
0.04	1.1358	1.1321	1.1296	1.1279	1.4749	1.4736	1.4717	1.4700
0.05	1.1201	1.1169	1.1140	1.1126	1.4751	1.4739	1.4720	1.4706
0.06	1.1186	1.1136	1.1109	1.1090	1.4754	1.4743	1.4725	1.4710
0.07	1.1124	1.1100	1.1065	1.1045	1.4757	1.4747	1.4729	1.4713
0.08	1.1086	1.1036	1.1001	1.0982	1.4760	1.4750	1.4734	1.4717
0.09	1.1020	1.0950	1.0903	1.0876	1.4764	1.4753	1.4739	1.4720
0.10	1.0966	1.0907	1.0860	1.0817	1.4769	1.4757	1.4742	1.4725

Table 2: Molar volume, V (cm^3. mol^{-1}) and apparent molar volumes V_ϕ of the hydroxamic acids at various temperatures.

	V (cm^3. mol^{-1})				V_ϕ ($cm^3 mol^{-1}$)			
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0.01	67.5829	67.7223	67.9320	68.0503	229.8165	230.7379	231.5596	232.4516
0.02	67.9851	68.1256	68.2184	68.3556	232.8927	233.9918	234.7586	235.8576
0.03	68.4460	68.6806	68.7931	68.8720	233.9455	235.1511	235.9705	237.0992
0.04	69.2258	69.4541	69.6119	69.7157	234.5888	235.8088	236.6637	237.8394
0.05	70.3167	70.5210	70.7080	70.7939	235.0596	236.2832	237.1541	238.3455
0.06	70.5286	70.8490	71.0229	71.1458	235.1579	236.4176	237.2891	238.5036
0.07	71.0415	71.1976	71.4221	71.5516	235.2889	236.5172	237.4020	238.6267
0.08	71.4057	71.7322	71.9614	72.0856	235.3599	236.6238	237.5102	238.7406
0.09	71.9554	72.4196	72.7365	72.9225	235.4430	236.7287	237.6289	238.8740
0.10	72.4349	72.8313	73.1525	73.4489	235.4988	236.7737	237.6736	238.9366

Table 3: Apparent molar volume at infinite dilution, ϕ_v^0 (cm^3mol^{-1}) and experimental slope S_v^* (cm^3mol^{-1}) of the hydroxamic acids at various temperatures.

ϕ_V^0 (cm^3mol^{-1})				S_V^* (cm^3mol^{-1})			
298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
229.3282	230.2196	230.957	231.8086	22.1515	23.5172	24.0524	25.4534

Table 4: Molar refraction, R_M and Polarizability,α, of the hydroxamic acids at various temperatures.

	R_M				α			
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0.01	19.0036	18.9809	18.9739	18.9515	0.7529	0.7520	0.7518	0.7509
0.02	19.1236	19.1043	19.0678	19.0505	0.7577	0.7569	0.7555	0.7548
0.03	19.2637	19.2704	19.2390	19.2049	0.7632	0.7635	0.7623	0.7609
0.04	19.4866	19.5051	19.4821	19.4508	0.7721	0.7728	0.7719	0.7707
0.05	19.8009	19.8154	19.7997	19.7733	0.7845	0.7851	0.7845	0.7834
0.06	19.8713	19.9220	19.9059	19.8861	0.7873	0.7893	0.7887	0.7879
0.07	20.0266	20.0345	20.0323	20.0104	0.7935	0.7938	0.7937	0.7928
0.08	20.1401	20.1958	20.2019	20.1744	0.7980	0.8002	0.8004	0.7993
0.09	20.3098	20.4004	20.4379	20.4198	0.8047	0.8083	0.8098	0.8090
0.10	20.4635	20.5311	20.5660	20.5859	0.8108	0.8135	0.8148	0.8156

Table 5: Excess refractive index n^E and Excess molar Refraction R_M^E of the hydroxamic acids at various temperatures.

	n^E				R_M^E (cm^3mol^{-1})			
C/mol·dm^{-3}	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0.01	0.0003	0.0005	0.0006	0.0010	-1.1038	-1.1266	-1.1360	-1.1925
0.02	0.0005	0.0008	0.0010	0.0014	-1.0127	-1.0320	-1.0709	-1.1222
0.03	0.0008	0.0011	0.0013	0.0017	-0.9019	-0.8952	-0.9291	-0.9971
0.04	0.0009	0.0016	0.0017	0.0020	-0.7091	-0.6908	-0.7162	-0.7813
0.05	0.0011	0.0019	0.0020	0.0026	-0.4264	-0.4119	-0.4301	-0.4903
0.06	0.0014	0.0023	0.0025	0.0030	-0.3862	-0.3359	-0.3543	-0.4080
0.07	0.0017	0.0027	0.0029	0.0033	-0.2621	-0.2542	-0.2589	-0.3146
0.08	0.0020	0.0030	0.0034	0.0037	-0.1798	-0.1246	-0.1211	-0.1822
0.09	0.0024	0.0033	0.0039	0.0040	-0.0424	0.0471	0.0818	0.0298
0.10	0.0029	0.0037	0.0042	0.0045	0.0790	0.1457	0.1776	0.1632