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Measurement of Intermolecular Interactions of Hydroxamic Acids in DMSO

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Abstract. Apparent molar volumes of two hydroxamic acids, N-o-tolyl-4-methylbenzo- and N-p-tolyl-2-methylbenzo- have been calculated from experimental data of densities (ρ) in dimethyl sulfoxide at various temperatures (298.15 to 318.15 K). Results obtained have been discussed in terms of intermolecular interactions and a comprehensive discussion has been provided. The apparent molar volumes at infinite dilution and the slopes of Masson's equation are computed to interpret the solute-solvent interactions. The expansibility is also calculated. Structure breaking capacities of these molecules have been inferred from the sign of $[\partial V_{\phi}^{o} / \partial T]_{P}$, Both the compounds behave as structure breakers in DMSO.

Keywords: density, apparent molar volume, expansibility and hydroxamic acid.

1. Introduction

The volumetric behavior of non-electrolyte solution can provide useful information regarding solute-solvent and solute-solute interactions. In particulars relevance does the nature of the interactions of solvent with solute species, especially with ions possess non-polar groups that affect the structural properties of solvent. Therefore, the apparent and partial molar volumes, expansibilities and excess properties of solutes have proven to be very useful tools in elucidating the structural interactions occurring in solution and to study solute-solvent interactions[1-10]. N-aryl hydroxamic acids are derivatives of hydroxylamines represented by the general formula, R_2-CO-NR_1-OH, where R_1 and R_2 are phenyl or substituted phenyl groups. These are neutral, polyfunctional, non-electrolyte molecules and are recognized as compounds of pharmacological, toxicological and pathological importance[11-14]. The densities, apparent molar volumes, partial molar volumes, excess molar volumes of both the hydroxamic acids in DMSO are measured at different temperatures and the values have been used to understand molecular behavior and the nature of solute-solvent interactions. These studies are of great help in characterizing the structure and properties of solutions. The solution structure is of great importance in understanding the nature of action of bioactive molecules in the body system.

2. Experimental

2.1. Materials and Methods

Both hydroxamic acids namely, N-o-Tolyl-4-MBHA, N-p-Tolyl-2- MBHA were prepared in this laboratory [15]. These were purified by crystallization thrice with benzene,the purity of compound was ascertained by determining their melting points, and UV and IR spectra. The data obtained tally with reported values. DMSO was purchased from Marck. Hydroxamic acids solution of different concentrations were prepared by mass dilution technique, from stock solution (0.0207 to 0.2074) M 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 five temperatures. The pycnometer was calibrated at desired temperature with freshly prepared triple distilled water. The estimated 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}. Table 1 reports the densities (ρ_0) of DMSO and N-o-Tolyl-4-MBHA, N-p-Tolyl-2- MBHA.

3. Results

The experimental values of solutions densities are used to calculate the apparent molar volumes, V_ϕ, by means of the following expression[18],

$$V_\phi = 1000\ (\rho_0 - \rho\ )/c\rho\rho_0 + M_2/\rho \qquad (1)$$

where c, M_2, ρ and ρ_0 are the molarity, molar mass of solute, densities of the solution and solvent, respectively.

The apparent molar volume at infinite dilution (V^0_ϕ), is calculated graphically according to the following equation using a least-square treatment of the plot of,

$$V_\phi = V^0_\phi + S^*_V C^{1/2} \qquad (2)$$

where S^*_V is the experimental slope and c molality of the solute. The value of V^0_ϕ have been estimated by the least-square fitting of the plot of V_ϕ Versus $C^{1/2}$ using Masson's expression[19]. The temperature dependence of V^0_ϕ for the studied compounds can be expressed by the equation,

$$V^0_\phi = a + bT + cT^2$$

(3)

where a, b and c have been estimated by the least-square fitting of the V^0_ϕ at different temperatures in equation 3, and then the following equations are generated,

$$V^0_\phi = 2302.724\ (\pm1240.810) - 13.127(\pm8.060)\ T + 0.0194\ (\pm0.013)\ T^2 \qquad (4)$$

$$V^0_\phi = 1659.691\ (\pm1019.523) - 9.157\ (\pm6.622)\ T + 0.013\ (\pm0.010)\ T^2 \qquad (5)$$

The limiting apparent molar expansibilities can be obtained by differentiating eq 3 with respect to temperature,

$$\phi^0_E = (\partial V^0_\phi / \partial T)_P = b + 2cT \qquad (6)$$

where ϕ^0_E is apparent molar expansibilities at infinite dilution and p is the pressure.

The experimental ρ data were used to calculate molar volume (V) and excess molar volume (V^E), by equations,

$$V = (x_1M_1 + x_2M_2) / \rho \qquad (7)$$

$$V^E = V - (x_1V_1 + x_2V_2) \qquad (8)$$

where x_1, V_1, and x_2, V_2 is mole fraction, molar volume of solvent and solute, respectively. The data are listed in Table 2.

4. Discussion

Volumetric properties are regarded as sensitive tools for understanding the molecular interactions in solutions. The experimental densities (ρ) and apparent molar volume V^0_ϕ N-o-Tolyl-4-MBHA, N-p-Tolyl-2-MBHA in DMSO at all five temperature are listed in table 2. The density increases with an increase in the concentration of the solution. This may be attributed to the shrinkage in the volume, which in turn is due to the presence of molecules. Large and positive values for V_ϕ suggests strong solute-solvent interactions. Apparent molar volume in both the cases increases with increasing concentration and temperature. The dependence of V_ϕ on molarity of both hydroxamic acids in DMSO over temperatures . The calculated values of V^0_ϕ and S^*_V are listed in Table 2. V^0_ϕ is regarded as resulting from solute-solvent interactions and it is independent of solute-solute interactions. The positive values indicate the presence of strong solute-solvent interactions. These interactions are weakened with a rise in temperature. The values of ϕ^0_E are listed in Table 2. Negative expansibility (i.e., decreasing volume with increasing temperature) is a characteristic property of aqueous solutions of hydrophobic solutes. Although the solvent in the present system is not water, it is still a slightly polar solvent due to the presence of S=O group. On the other hand, both the hydroxamic acids have a hydrophobic/hydrophilic balance. Therefore, the negative ϕ^0_E values originate from the highly hydrophobic characters of the solutes.

The excess molar volume depends mainly on two factors, (i) variation in inter molecular forces between two components into contact and (ii) variation in molecular packing as a consequence of differences in size and shape of molecules. The values of excess molar volume V^E are negative and large in magnitude for the entire range of concentration at all temperature, which indicates a decrease in the overall volume of the solution. Higher negative V^E values obtained for N-p-Tolyl-2-MBHA are attributed to the presence of strong specific interaction as shown in Figure 1.

5. Conclusions

Using density data, the apparent molar volumes, apparent molar volume at infinite dilution, expansibility and the excess molar volume have been computed. The behavior of V^E suggests the presence of solute-solvent interactions in the system. Positive V_ϕ, for both the hydroxamic acids suggest structure-breaking behavior of molecules in DMSO. Such parameters will be of further use in QSAR analysis.

6. Acknowledgements

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7. References

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TABLE 1. Properties of DMSO and Hydroxamic acids.

T/K	ρ_o/gcm^{-3}		Hdroxamic Acids	
	this work	lit.	N-o-Tolyl-4-MBHA	N-p-Tolyl-2- MBHA
298.15	1.0965	1.0955[a]	1.09793	1.09694
303.15	1.0903	1.0896[b]	1.09189	1.09090
308.15	1.0852	1.0855[a] 1.0847[b]	1.08685	1.08597
313.15	1.0802	1.0797[b]	1.08191	1.08109
318.15	1.0763	1.0757[a] 1.0748[b]	1.07815	1.07738

[a]ρ_o [16], [b]ρ_o [17],

TABLE 2. Densities (ρ), molar volume (V), apparent molar volume (V_ϕ), excess molar volume (V^E) of hydroxamic acids in DMSO at different temperatures.

M, solute (mol.kg^{-1})	ρ/ (g.cm^{-3})	V (cm^3.mol^{-1})	V_ϕ/(cm^3.mol^{-1})	V^E(cm^3.mol^{-1})	ρ/ (g.cm^{-3})	V (cm^3.mol^{-1})	V_ϕ/(cm^3.mol^{-1})	V^E(cm^3.mol^{-1})
	N-o-Tolyl-4-MBHA T = 298.15K				N-p-Tolyl-2-MBHA T = 298.15K			
0.0207	1.0988	71.3242	126.9166	-0.1498	1.0992	71.2981	110.8739	-0.1761
0.0414	1.1008	71.4141	132.8757	-0.2798	1.1018	71.3489	112.8066	-0.3452
0.0622	1.1027	71.5107	136.0352	-0.4037	1.1044	71.3997	113.2707	-0.5146
0.0829	1.1045	71.6143	138.4999	-0.5214	1.1069	71.4571	114.3718	-0.6778
0.1037	1.1061	71.7312	141.4988	-0.6265	1.1094	71.5146	114.9263	-0.8412
0.1244	1.1076	71.8552	144.0986	-0.7255	1.1118	71.5787	115.8776	-0.9985
0.1452	1.1090	71.9862	146.4743	-0.8183	1.1143	71.6364	115.9088	-1.1625
0.1659	1.1103	72.1243	148.7136	-0.9049	1.1165	71.7139	117.3748	-1.3075
0.1867	1.1116	72.2631	150.4126	-0.9919	1.1189	71.7784	117.5649	-1.4656
0.2074	1.1128	72.4089	152.1421	-1.0727	1.1212	71.8496	118.0687	-1.6176

	T = 303.15K				T = 303.15K			
0.0207	1.0928	71.7169	119.3997	-0.1639	1.0931	71.6972	107.2341	-0.1839
0.0414	1.0950	71.7947	125.2157	-0.3085	1.0958	71.7419	108.9870	-0.3615
0.0622	1.0970	71.8858	129.6889	-0.4403	1.0984	71.7933	110.7414	-0.5328
0.0829	1.0989	71.9837	132.8171	-0.5659	1.1009	71.8513	112.4977	-0.6978
0.1037	1.1006	72.0953	136.2270	-0.67868	1.1034	71.9095	113.4448	-0.8630
0.1244	1.1022	72.2138	139.1043	-0.7853	1.1059	71.9677	113.9878	-1.0286
0.1452	1.1037	72.3395	141.6809	-0.8857	1.1084	72.0260	114.3005	-1.1943
0.1659	1.1052	72.4655	143.5601	-0.9864	1.1106	72.1044	115.9933	-1.3409
0.1867	1.1065	72.6055	145.8885	-1.0744	1.1130	72.1696	116.3500	-1.5008
0.2074	1.1078	72.7461	147.7125	-1.1628	1.1153	72.2416	116.9909	-1.6545
	T = 308.15K				T = 308.15K			
0.0207	1.0878	72.0477	115.3879	-0.1721	1.0881	72.0277	103.1102	-0.1922
0.0414	1.0901	72.1194	121.2562	-0.3246	1.0909	72.0662	104.8813	-0.3781
0.0622	1.0922	72.2046	125.7674	-0.4643	1.0936	72.1114	106.6531	-0.5575
0.0829	1.0942	72.2968	128.9202	-0.5976	1.0962	72.1633	108.4260	-0.7305
0.1037	1.0960	72.4026	132.3558	-0.7180	1.0987	72.2219	110.2006	-0.8973
0.1244	1.0977	72.5154	135.2529	-0.8322	1.1012	72.2806	111.2949	-1.0643
0.1452	1.0993	72.6354	137.8458	-0.9402	1.1037	72.3395	112.0009	-1.2316
0.1659	1.1008	72.7625	140.2518	-1.0419	1.1060	72.4118	113.4891	-1.3860
0.1867	1.1022	72.8968	142.5363	-1.1374	1.1084	72.4776	114.1339	-1.5473
0.2074	1.1035	73.0385	144.7387	-1.2266	1.1108	72.5435	114.5981	-1.7089
	T = 313.15K				T = 313.15K			
0.0207	1.0829	72.3747	111.2959	-0.1805	1.0832	72.3546	98.9068	-0.2007
0.0414	1.0853	72.4404	117.2169	-0.3411	1.0861	72.3867	100.6969	-0.3948
0.0622	1.0875	72.5196	121.7667	-0.4888	1.0888	72.4323	103.8624	-0.5758
0.0829	1.0895	72.6126	125.9801	-0.6234	1.0915	72.4779	105.3089	-0.7570
0.1037	1.0914	72.7126	129.2359	-0.7517	1.0940	72.5371	107.7194	-0.9252
0.1244	1.0932	72.8196	132.0164	-0.8738	1.0966	72.5895	108.5491	-1.1003
0.1452	1.0948	72.9405	135.1229	-0.9828	1.0990	72.6556	110.2454	-1.2625
0.1659	1.0963	73.0687	137.9179	-1.0855	1.1013	72.7286	111.9687	-1.4183
0.1867	1.0978	73.1973	140.0441	-1.1887	1.1036	72.8017	113.2516	-1.5744
0.2074	1.0993	73.3264	141.7022	-1.2922	1.1061	72.8614	113.3990	-1.7440
	T = 318.15K				T = 318.15K			
0.0207	1.0791	72.6303	107.1332	-0.1884	1.0794	72.6101	94.6568	-0.2088
0.0414	1.0816	72.6897	113.0962	-0.3568	1.0823	72.6424	98.5409	-0.4043
0.0622	1.0838	72.7696	119.0647	-0.5053	1.0851	72.6816	101.0380	-0.5933
0.0829	1.0859	72.8564	122.9585	-0.6475	1.0878	72.7275	103.1887	-0.7758
0.1037	1.0878	72.9570	126.8606	-0.7766	1.0903	72.7871	106.0327	-0.9452

0.1244	1.0896	73.0647	130.0761	-0.8994	1.0930	72.8331	106.4536	-1.1281
0.1452	1.0913	73.1796	132.9023	-1.0158	1.0954	72.8997	108.4592	-1.2914
0.1659	1.0928	73.3087	136.0129	-1.1192	1.0977	72.9731	110.4175	-1.4483
0.1867	1.0943	73.4381	138.3842	-1.2229	1.1001	73.0399	111.4205	-1.6122
0.2074	1.0957	73.5750	140.6597	-1.3203	1.1025	73.1069	112.1709	-1.7764

TABLE 3 Apparent molar volume at infinite dilution (V^0_f), experimental slop (S^*_V) and apparent molar expansibilities at infinite dilution (ϕ^0_E), of hydroxamic acids in DMSO at different temperatures.

T/K	V^0_ϕ ($cm^3.mol^{-1}$)	S^*_V ($cm^3.mol^{-3/2}.dm^{-3/2}$)	ϕ^0_E ($cm^3.mol^{-1}$)
		N-o-Tolyl-4-MBHA	
298.15	115.866 (±0.403)	80.036 (±1.195)	-4.8435
303.15	106.701 (±0.335)	90.932 (±0.990)	-3.8624
308.15	102.088 (±0.165)	93.759 (±0.494)	-2.8812
313.15	97.132 (±0.328)	99.181 (±0.971)	-1.9001
318.15	91.538 (±0.362)	108.696 (±1.073)	-0.9189
		N-p-Tolyl-2-MBHA	
298.15	107.803 (±0.314)	22.559 (±0.930)	-4.8435
303.15	102.882 (±0.407)	31.425 (±1.206)	-3.8624
308.15	97.259 (±0.350)	38.994 (±1.038)	-2.8812
313.15	91.262 (±0.522)	49.835 (±1.546)	-1.9001
318.15	86.848 (±0.497)	56.822 (±1.471)	-0.9189

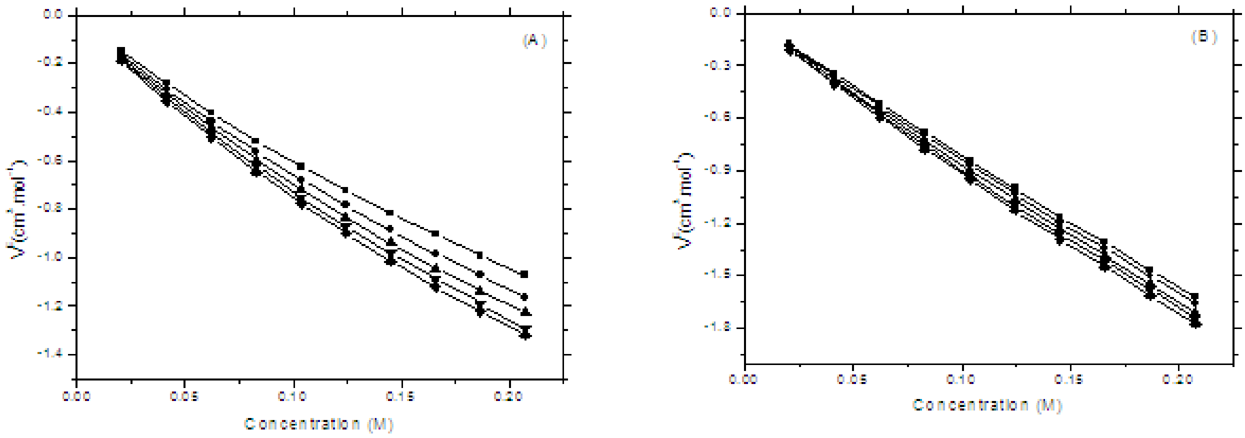

Figure 1. Plots of Excess Molar Volume, (V .. vs concentration of (A) N-o-Tolyl-4-MBHA in DMSO, (B) N-p-Tolyl-2- MBHA in DMSO,at (▪), 298.15 K; (●), 303.15 K; (7), 308.15 K; (▼), 313.15 K; and (■), 318.15 K.