December 2009 Volume 4 Issue 2

Trade Science Inc.

Physical CHEMISTRY
An Indian Journal

Full Paper

PCAIJ, 4(2), 2009 [88-92]

Refractive indices, surface tension and excess properties of hydroxamic acids in acetone-water at 303.15K and 313.15K

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Received: 3rd December, 2009 ; Accepted: 13th December, 2009

ABSTRACT

The densities, ρ, refractive indices, n, and surface tensions, σ, of hydroxamic acids were measured as a function of their concentration in 50%(v/v) acetone-water at 303.15K and 313.15K. The experimental data are used to calculate parameters like apparent molar volume, partial molar volume at infinite dilution, molar refraction, polarizability and parachor. The deviation of refractive indices, molar refraction and surface tension are also calculated and reported. The data are discussed in terms solute-solvent interactions and hydroxamic acids acts as structure-maker in present system.

KEYWORDS

Hydroxamic acids;
Refractive index surface tension;
Density.

INTRODUCTION

Partial molar volumes provide useful information about various types of interactions occurring in solution[1,2]. Refractive indices and surface tensions are thermophysical properties that provide important information about intermolecular interactions in liquid mixtures. 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.

Hydroxamic acids, a group of weak organic acids of general formula ($R_1NOH{\cdot}R_2C{=}O$), fulfill a variety of roles in biology and medicine for example, as siderophores for iron(III),[3] as patent and selective inhibitors of enzymes such as peroxidases[4], ureases[5], and matrix metalloproteinases[6], and as hypotensive[7], anticancer, anti-tuberculous and anti-fungal agents[8].

This paper reports measurement of densities, refractive indices and surface tension of hydroxamic acids in 50%v/v acetone-water at 303.15K and 313.15K at atmospheric pressure. The experimental data have been used to calculate excess properties and results have been used to understand molecular behavior and nature of solute-solvent interactions.

EXPERIMENTAL

Two hydroxamic acids (N-p-tolylbenzo, p-$CH_3{\cdot}C_6H_4NOHC_6H_5C{=}O$, and N-o-tolylbenzo, o-$CH_3{\cdot}C_6H_4NOH.C_6H_5C{=}O$) were selected for the present investigation. These are synthesized in the laboratory following the method reported in literature[9] and were purified by crystallization thrice with ben-

zene. The purity of compounds was ascertained by determining their melting points, UV, and IR spectra. The data obtained were tally with reported values. Elemental analysis was determined with a Vario-EL analysis apparatus.

N-p-tolylbenzohydroxamic acid (1). Anal. ($C_{14}H_{13}NO_2$): Calcd.: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.50; H, 5.70; N, 5.99.

N-o-tolylbenzohydroxamic acid (2). Anal. ($C_{14}H_{13}NO_2$): Calcd.: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.60; H, 5.70; N, 6.05.

Stock solution of 0.05M was prepared by dissolving desired hydroxamic acid in 100ml of mixed solvent. Mass dilution technique was applied to prepare the solution of different concentration, ranges from 0.01M to 0.05M. Densities of hydroxamic acid solutions in mixed solvent were determined using 10 cm^3 doubled armed pycnometer at temperatures 303.15K 313.15K. The pycnometer was calibrated at these temperatures with distilled water and benzene. The estimated accuracy of density measurement of solution was ±0.0003 units.

Refractive indices were measured with the help of thermostated Abbe's refractometer. Calibration of the instrument was done by measuring the refractive indices of double distilled water and toluene at known temperatures[10]. The sample mixtures were directly injected into the prism assembly of the instrument by means of an air tight hydrodynamic springe. When the liquid mixtures attained constant temperature, the refractive index measurements were made. The error in refractive index measurements was less than ±0.0001 unit. The temperatures of the solutions were maintained at 303.15K and 313.15K in an electronically controlled thermostatic water bath attached with the refractomeres.

Surface tension of solutions were determined from the drop number method using modified stalagnometer at 303.15K and 313.15K. The stalagnometer was calibrated with distilled water and the correction factor was employed. The accuracy of the surface tension measurement was ±0.1mN.m^{-1}.

TABLE 1 : Densities, ρ, and refractive index, n, of hydroxamic acids in 50%v/v Acetone + water at 303.15K and 313.15K

Concentration ($mol.L^{-1}$)	$\rho\times10^{-3}$ ($Kg.m^{-1}$)		n	
	303.15K	313.15K	303.15K	313.15K
N-p-Tolylbenzohydroxamic acid				
0.000	0.9172	0.9151	1.3580	1.3570
0.010	0.91 79	0.9161	1.3610	1.3590
0.020	0.91 82	0.91 62	1.3640	1.3620
0.025	0.91 83	0.91 64	1.3650	1.3620
0.030	0.9184	0.91 65	1.3670	1.3650
0.035	0.9185	0.9166	1.3680	1.3670
0.040	0.91 86	0.91 67	1.3710	1.3680
0.045	0.91 87	0.91 68	1.3720	1.3690
0.050	0.91 88	0.91 69	1.3750	1.3700
N-o-Tolylbenzohydroxamic acid				
0.000	0.9172	0.9151	1.3580	1.3570
0.010	0.9178	0.9162	1.3750	1.3670
0.020	0.9183	0.9164	1.3760	1.3710
0.025	0.9185	0.9165	1.3770	1.3720
0.030	0.9186	0.9167	1.3790	1.3730
0.035	0.9187	0.9168	1.3800	1.3740
0.040	0.9188	0.9169	1.3820	1.3780
0.045	0.9190	0.9170	1.3830	1.3780
0.050	0.9193	0.9171	1.3840	1.3790

TABLE 2 : Apparent molar volume, ϕ_v, limiting apparent molar volume, V_ϕ°, and experimental slope, S_v^*, hydroxamic acids in 50%v/v acetone + water at 303.15K and 313.15K

Concentration ($mol.L^{-1}$)	$\phi v\times10^{-6}$ ($m^3.mol^{-1}$)		$V_\phi^\circ\times10^{-6}$ ($m^3.mol^{-1}$)		$S_v^*\times10^{-6}$ ($m^{3.}mol^{-3/2}.dm^{-3/2}$)	
	303.15K	313.15K	303.15K	313.15K	303.15K	313.15K
N-p-Tolylbenzohydroxamic acid						
0.000	164.158	128.504				
0.010	187.857	182.162				
0.020	194.956	185.700				
0.025	199.683	192.039	135.117	89.315	351.820	557.238
0.030	203.053	196.560				
0.035	205.574	199.944				
0.040	207.530	202.571				
0.045	209.089	204.668				
N-o-Tolylbenzohydroxamic acid						
0.000	176.055	155.537				
0.010	181.896	193.199				
0.020	185.418	200.715				
0.025	191.727	202.888	154.710	122.319	207.435	443.980
0.030	196.227	206.851				
0.035	199.600	209.816				
0.040	199.116	213.950				
0.045	197.116	215.170				

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TABLE 3 : Molecular refraction, Rm, polarazibility, α, surface tension, γ, and parachor, P, of hydroxamic acids in 50%v/v acetone + water at 303.15K and 313.15K

Concentration ($mol.L^{-1}$)	$Rm\times10^{-6}$ (m^3mol^{-1})		$\alpha\times10^{-24}$ ($m.mol^{-1}$)		$\gamma\times10^{3}$ ($N.m^{-1}$)		P ($mol.dm^{-3}$)	
	303.15K	313.15K	303.15K	313.15K	303.15K	313.15K	303.15K	313.15K
N-p-Tolylbenzohydroxamic acid2.5470								
0.000	6.263	6.208	2.483	2.461	44.616	44.051	73.166	72.650
0.010	6.310	6.268	2.501	2.484	44.471	43.892	73.210	72.739
0.020	6.341	6.288	2.513	2.492	44.151	43.933	73.156	71.965
0.025	6.383	6.324	2.530	2.506	43.527	41.793	72.999	71.955
0.030	6.421	6.362	2.545	2.521	42.922	41.651	72.795	71.970
0.035	6.453	6.384	2.558	2.530	41.749	41.432	72.343	71.952
0.040	6.475	6.404	2.567	2.538	41.329	40.815	72.327	71.733
0.045	6.503	6.429	2.578	2.547	39.333	38.005	71.423	70.539
N-o-Tolylbenzohydroxamic acid								
0.000	6.483	6.332	2.570	2.510	41.856	40.791	72.033	71.290
0.010	6.512	6.408	2.581	2.539	41.738	40.258	72.135	71.198
0.020	6.535	6.434	2.590	2.550	41.320	39.222	72.029	70.805
0.025	6.572	6.447	2.605	2.556	40.773	38.977	71.866	70.724
0.030	6.592	6.459	2.613	2.560	40.639	38.629	71.807	70.677
0.035	6.630	6.479	2.628	2.568	39.475	38.484	71.337	70.672
0.040	6.653	6.543	2.637	2.593	39.468	38.127	71.484	70.527
0.045	6.671	6.563	2.644	2.602	39.227	37.892	71.400	70.494

RESULT AND DISCUSSION

The measured values of densities and refractive indices of two hydroxamic acids in acetone + water (50% v/v) mixed solvent as a function of concentration at 303.15K and 313.15K are listed in TABLE 1.

The experimental values of densities were used to calculate the apparent molar volumes using the following expression[11]

$$V\phi = 1000\ (\rho_o - \rho)/C\rho\rho_o + M_2/\rho \qquad (1)$$

Where, C in the morality, ρ_1 and ρ are densities of mixed solvents and solution, respectively. M_2 is molecular weight of nonelectrolyte. The resulting values of $V\phi$ of solute are reported in TABLE 2. It is observed that this apparent molar $V\phi$ of the hydroxamic acid solution increases with the concentration of the solute. The magnitude of positive values of $V\phi$ of the hydroxamic acid indicates greater solute-solvent interactions. These interactions are strengthened with concentration at a particular temperature.

The apparent molar volume at infinite dilution of solute was calculated using a least squares treatment of the plot of $V\phi$ versus $C^{1/2}$ using the following Masson's expression[12].

$$V\phi = V_\phi^\circ + S_v^* C^{1/2} \qquad (2)$$

where V_ϕ° is the apparent molar volume at infinite dilution and S_v^* is the experimental slope. The calculated values of V_ϕ° and S_v^* are listed in TABLE 2. is also regarded for solute –solvent interaction as it is the apparent molar volume at infinite dilution, by definition and is independent of solute-solute interaction. The positive values indicate the presence of strong solute-solvent interactions. These interactions are weakened with rise in temperature.

The experimental refractive indices presented in (TABLE 1) show an increasing trend with increase in concentration of hydroxamic acids in the mixed solvent. This indicates that the refractive index is directly related to the interactions in the solutions.

The molar refraction, Rm, of hydroxamic acid solution were calculated from the values of refractive indices, using the relation proposed by Lorentz-Lorentz,

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

The molar refraction is related to the polarizability

TABLE 4 : Excess refractive index, n^E, excess molar refraction, R_m^E, and excess surface tension of hydroxamic acids in 50%v/v acetone + water at 303.15K and 313.15K

Concentration (mol.L^{-1})	n^E		$R_m^E \times 10^{-6}$ (m^{3}mol^{-1})		$\gamma^E \times 10^3$ (N.m^{-1})	
	303.15K	313.15K	303.15K	313.15K	303.15K	313.15K
N-p-Tolylbenzohydroxamic acid						
0.000	0.0040	0.0047	0.0110	0.0654	- 0.4629	-0.3611
0.010	0.0070	0.0071	0.0578	0.1253	-0.6084	-0.4276
0.020	0.0080	0.0080	0.0880	0.1448	-0.9283	-2.3873
0.025	0.0099	0.0100	0.1305	0.1805	-1.5527	-2.5278
0.030	0.0110	0.0120	0.1093	0.2188	-2.0885	-2.6697
0.035	0.0132	0.0133	0.2005	0.2141	-3.3278	-2.8858
0.040	0.0146	0.0142	0.2231	0.2609	-3.7564	-3.5043
0.045	0.0182	0.0151	0.2513	0.2829	-5.7390	-6.5316
N-o-Tolylbenzohydroxamic acid						
0.000	0.0144	0.0127	0.2305	0.1893	-3.1961	-3.5272
0.010	0.1900	0.0160	0.2597	0.2647	-3.3339	-4.0598
0.020	0.0201	0.0171	0.2821	0.2915	-3.7623	-5.0942
0.025	0.0220	0.0180	0.3197	0.3046	-4.3136	-5.3395
0.030	0.0229	0.0179	0.3399	0.3157	-4.4365	-6.4602
0.035	0.0236	0.0190	0.3441	0.3364	-5.6007	-6.5839
0.040	0.0243	0.0227	0.4045	0.4003	-5.6025	-6.9430
0.045	0.0284	0.0241	0.4161	0.4202	-5.8481	-7.1817

of the molecules by the Lorentz-Lorentz formula[13]

$$Rm = (4\pi\alpha N)/3 \quad (4)$$

Where, N is the Avogadro's number and α is the molecular polarizability. The value of Rm is directly proportional to the molecular polarizability and is found to increase in concentration of hydroxamic acids in mixed solvent at temperature 303.15K and 313.15K.

Surface tension was determined using relation,

$$\gamma = n_1 / n \times \rho / \rho_1 \times \gamma_1 \quad (5)$$

Where, n_1 and n are number of drops of mixed solvent and hydroxamic acid solution. γ_1 and γ are the surface tension of mixed solvent and solution respectively.

Parachor is a physico-chemical parameter which is calculated from the given expression,

$$P=V X \gamma^{1/4} \quad (6)$$

The value of γ and P are listed in TABLE 3.

The refractive index values have been used to calculate[14] excess refractive indices using,

$$n^E= n-(x_1n_1+x_2n_2) \quad (7)$$

Where n, n_1 and n_2 are the refractive indices of solution, mixed solvent and solute respectively. The values of n^E presented in TABLE 4. As evidenced from the calculations, the excess refractive index of both hydroxamic acids increases with an increase of concentration and decrease with an increase of temperature.

The excess molar refraction,

$$R_m^E = Rm-(x_1Rm_1+ x_2Rm_2) \quad (8)$$

and gives more information then excess refractive indices about the mixture process because it takes into account the electronic perturbation of molecular orbital during the liquid mixture process and R_m^E is positive for all systems analyzed indicating that the depression forces are higher in mixture than in the pure liquids. The data on R_m^E are reported in TABLE 4.

Excess surface tension γ^E is calculated from following expression,

$$\gamma^E = \gamma - (x_1\gamma_1 - x_2\gamma_2) \quad (9)$$

Where, x_1 and x_2 are mole fraction of solute and solvent. γ_1 and γ_2 are surface tension of solute and solvent. The values are listed in TABLE 4.

CONCLUSION

The large positive values of Vϕ and () suggests strong solute- solvent interactions with increase of concentration at particular temperature and is weakened with increase of temperature. The positive value of surface tension suggests solute-solvent interaction. The interaction weakened with increase in concentration and temperatures.

Refractive index is an important physico-chemical parameter the solvation processes. The excess refractive indices that by hydroxamic acids as structure maker in 50% acetone: water mixture. Molar refraction has been shown to be related to lipophilicity, molar volume and sphere bulk. As hydroxamic acids are bio-active molecule this parameter will be use in QSAR studies.

ACKNOWLEDGEMENTS

The Author Ram Prakash Rajwade is grateful to University Grant Commission, New Delhi, India for providing financial assistance.

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