

ACTIVATION PARAMETERS AND EXCESS THERMODYNAMIC FUNCTIONS OF HYDROXAMIC ACIDS IN ACETONE - WATER MIXTURE AT 303.15 K AND 313.15 K: A VISCOMETRIC APPROACH

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ABSTRACT. Experimental values of density and viscosity of N-arylsubstituted hydroxamic acids were evaluated at $T = 303.15$ K and 313.15 K in acetone-water mixture as a function of their concentration. The properties of solutes were obtained as an intercept of plots C vs η of solutions. Applying these data, viscosity- B -coefficients, activation parameters ($\Delta\mu_1^{0\neq}$) and ($\Delta\mu_2^{0\neq}$) and excess thermodynamic functions, viz., excess molar volume (V^E), excess viscosity (η^E) and excess molar free energy of activation of flow, (G^E) were calculated. The value of interaction parameter, d , of Grunberg and Nissan expression have also been calculated and reported. Analysis of these data suggests that specific interactions are present in the system.

KEY WORDS: Activation parameters, N-Arylsubstituted hydroxamic acids, Density, Viscosity, Viscosity- B -coefficients, Excess viscosity

INTRODUCTION

The thermodynamic and transport properties of molecules and their solutions are important to understand the molecular interactions. Hydroxamic acids behave like non-electrolytes and found in nature [1] and can be synthesised in laboratory [2]. All natural hydroxamic acids with ferric trihydroxamate center act as iron transfer agents and are designated as siderochromes [1]. Hydroxamic acids are host-spread in the tissues of plants and play an important role in the detoxification of toxic host plants [3, 4] and in iron acquisition of grasses [5, 6]. These are detected in rye, maize, rice and wheat seedlings [7, 8] and also reported to be active as herbicides [9] and pesticides [10]. Ferrichrome XV and XVI are found in Japanese sake [11] and account for part of its yellow colour. Hydroxamic acids are used as cultivator in corn seedlings to reduce water potential before, during and after germination [12]. Knowledge of transport properties of hydroxamic acids is important in all these applications to understand the molecular interactions. Very little work is done in this direction. Therefore, as an extension of our earlier work [13], the viscosity of two hydroxamic acids in acetone-water mixture 50 % (v/v) were obtained at 303.15 K and 313.15 K as a function of their concentration. Another equally important quantity which is often required to determine the viscosity, is the density, ρ . The density data were also measured under the same conditions. The other related useful parameters evaluated are, viscosity- B -coefficients, activation parameters, ($\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$) and excess thermodynamic properties, excess molar volume (V^E), excess viscosity (η^E) and excess molar free energy of activation of flow (G^E) of these molecules.

EXPERIMENTAL

Two hydroxamic acids (N-*p*-tolylbenzo, *p*-CH₃.C₆H₄NOHC₆H₅C=O and N-*o*-tolylbenzo, *o*-CH₃.C₆H₄NOH.C₆H₅C=O) were selected for the present investigation. These were synthesised in the laboratory following the method reported in literature [2] and were purified by crystallisation thrice with benzene. The purity of compounds was ascertained by determining their melting points, UV and IR spectra. The data obtained were tallied with reported values.

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Stock solution of 0.05 M was prepared by dissolving hydroxamic acid in 100 mL of 50 % (v/v) acetone-water mixed solvent. Mass dilution technique was applied to prepare the solution of different concentration ranged from 0.01 M to 0.05 M. Densities of hydroxamic acid solutions in mixed solvent were determined using 10 mL double armed pycnometer at temperatures 303.15 K and 313.15 K. The pycnometer was calibrated at these temperatures with distilled water and benzene. The estimated accuracy of density measurement of solution was $\pm 0.00003 \text{ g mL}^{-1}$.

Viscosities were measured by thermostated capillary viscometer of Ostwald-Sprengle type (MaHaRaNa, Instruments MFG-Company, Ajmer, India) with accuracy of $\pm 0.1 \text{ K}$. The viscometer was calibrated with triple distilled water. Viscosity values were determined using the relation,

$$\eta = \rho(Kt - L/t) \quad (1)$$

where, η is a viscosity, ρ is the density of the liquid, t is the flow time and K and L are constants for given viscometer. The flow time was measured with digital stop watch with accuracy of $\pm 0.01 \text{ s}$. The K and L were obtained by measuring the flow time of triple distilled water at temperatures 298.15 K, 303.15 K and 313.15 K. Linear regression analysis of a plot of η/t against t^2 for distilled water at three temperatures provided estimates of $K = 2.56 \times 10^{-5} \text{ cm}^2 \text{ s}^{-2}$ and $L = -0.12986 \text{ cm}^2$. Linear regression coefficient for distilled water was 0.97125. The value of parameters of pure acetone determined at three temperatures were $K = 1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-2}$ and $L = 0.1656 \text{ cm}^2$. Linear regression coefficient for pure acetone was 0.96822. The estimated accuracy of experimental viscosities was $\pm 0.1 \%$.

RESULTS AND DISCUSSION

Viscosities of both the hydroxamic acids were calculated from equation (1). Measured densities and viscosities data in acetone-water 50 % (v/v) at 303.15 K and 313.15 K are shown in Figures 1-4, respectively. The viscosities of the solute were obtained as the intercept of the plots of concentration versus viscosity of solutions and indicated in Figure 3 and 4.

The Jones-Dole equation [14] was used to analyse the viscosities of given solutions,

$$\eta_r = \eta/\eta_1 = 1 + Ac^{1/2} + Bc \quad (2)$$

where η is viscosities of the solution and η_1 viscosities of the solvent. A is the coefficient and c is concentration. B is the function of solute-solvent interactions [15]. Hydroxamic acids are non-electrolyte molecules therefore, A -coefficient becomes zero. This reduces Jones-Dole equation to

$$\eta = \eta_1 (1 + Bc) \quad (3)$$

The B -coefficient obtained as slope of straight line has been recorded in Table 1. Einstein [16] proposed an equation,

$$\eta = \eta_1 (1 + 2.5v) \quad (4)$$

which describes the concentration dependence of the relative viscosity of solution of non-electrolyte. In this equation v is the aggregate volume (1 mL) of the solution. The coefficient of v is 2.5. The term 2.5 is taken to be valid for non-electrolyte and it is equivalent to the product in Bc the Jones-Dole equation. The value of Bc and 2.5 obtained are nearly of same magnitude as shown in the Table 1. For the present system these are positive indicating the solute-solvent interactions are strong.

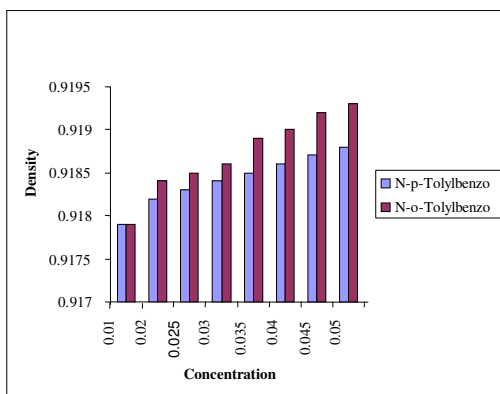


Figure 1. Densities (ρ) of hydroxamic acids in 50 % (v/v) acetone-water at 303.15 K.

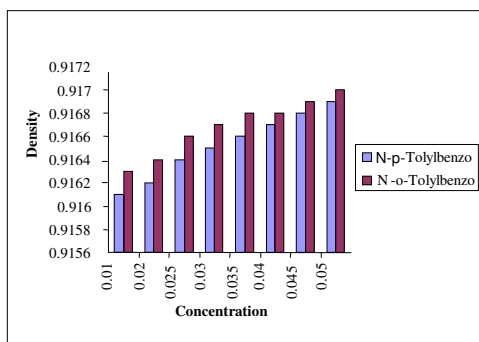


Figure 2. Densities (ρ) of hydroxamic acids in 50 % (v/v) acetone-water at 313.15 K.

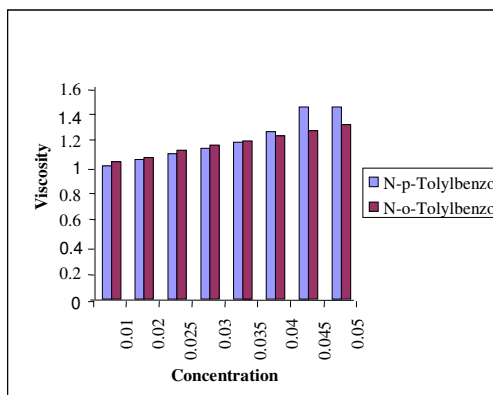


Figure 3. Viscosities (η) of hydroxamic acids in 50 % (v/v) acetone-water at 303.15 K.

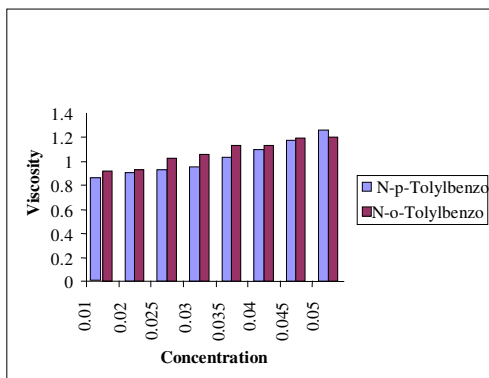


Figure 4. Viscosities (η) of hydroxamic acids in 50 % (v/v) acetone-water at 313.15 K.

Table 1. Value of B_c , 2.5 v and B -coefficient of hydroxamic acids in 50 % (v/v) acetone-water.

Conc. (M)	B_c		2.5 v		B	
	303.15 K	313.15 K	303.15 K	313.15 K	303.15 K	313.15 K
N-p-Tolylbenzohydroxamic acid						
0.0000	–	–	–	–	10.9734	13.4602
0.0100	0.0144	0.8933	0.0144	0.8933		
0.0200	0.0599	0.1561	0.0599	0.1561		
0.0250	0.1057	0.1896	0.1057	0.1896		
0.0300	0.1452	0.2220	0.1452	0.2220		
0.0350	0.1939	0.3261	0.1939	0.3261		
0.0400	0.2698	0.4072	0.2698	0.4072		
0.0450	0.3552	0.5072	0.3552	0.5072		
0.0500	0.4551	0.6225	0.4551	0.6225		
N-o-Tolylbenzohydroxamic acid						
0.0000	–	–	–	–	7.2835	9.3836
0.0100	0.0404	0.18672	0.0404	0.18672		
0.0200	0.0772	0.25352	0.0772	0.25352		
0.0250	0.1257	0.30990	0.1257	0.30990		
0.0300	0.1653	0.35131	0.1653	0.35131		
0.0350	0.2003	0.40693	0.2003	0.40693		
0.0400	0.2389	0.45852	0.2389	0.45852		
0.0450	0.2784	0.51300	0.2784	0.51300		
0.0500	0.3219	0.54369	0.3219	0.54369		

Activation parameter

The viscosity data have also been analyzed on the basis of a transition state theory of relative viscosity as suggested by Feakins *et al.* [17]. The viscosity B -coefficient is expressed by equation,

$$B = (V_1^0 - V_2^0)/1000 + V_1^0 [\Delta\mu_1^{0\ddagger} - \Delta\mu_2^{0\ddagger}] RT/1000 \quad (5)$$

where, V_1^0 and V_2^0 are the partial molar volume of the mixed solvent and solute, respectively. The values of partial molar volume are obtained by the relation

$$V = (X_1^0 M_1^0 + X_2^0 M_2^0)/\rho \quad (6)$$

where $X_1^0 M_1^0$ and $X_2^0 M_2^0$ are the mole fraction and molecular weight of mixed solvent and solute, respectively. The values of V are given in Table 4.

$\Delta\mu_2^{0\neq}$ is the contribution per mole of solute to the Gibb's free energy change of activation of viscous flow of the solution. $\Delta\mu_2^{0\neq}$ and $\Delta\mu_1^{0\neq}$ were calculated from the following expressions,

$$\Delta\mu_1^{0\neq} = RT \ln (\eta V_2^0/hN) \quad (7)$$

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + (RT/V_2^0) [1000 B - (V_1^0 - \bar{V}_2^0)] \quad (8)$$

where R is the gas constant, T is temperature, h is Planck's constant and N is Avogadro's number, respectively. The values of $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ are listed in Table 2.

Table 2. Activation parameter of hydroxamic acids in 50 % (v/v) acetone-water.

Conc. (M)	$\Delta\mu_1^{0\neq}$ (kJ.mol ⁻¹)		$\Delta\mu_2^{0\neq}$ (10 ³ kJ.mol ⁻¹)	
	303.15 K	313.15 K	303.15 K	313.15 K
N- <i>p</i> -Tolylbenzohydroxamic acid				
0.0000	–	–	–	–
0.0100	36.8362	37.5363	16.6982	28.6927
0.0200	37.0305	38.0361	14.9849	19.6715
0.0250	37.1274	38.0875	14.4016	19.3682
0.0300	37.1908	38.1468	14.0942	18.8722
0.0350	37.2471	38.3707	13.9670	18.3450
0.0400	37.3294	38.3896	13.7682	17.8725
0.0450	37.3947	38.4669	13.6298	17.5847
0.0500	37.4991	38.5655	13.5058	17.3641
N- <i>o</i> -Tolylbenzohydroxamic acid				
0.0000	–	–	–	–
0.0100	34.3665	34.8506	11.2711	23.3519
0.0200	36.9948	38.0419	10.5868	14.8932
0.0250	37.0872	38.1394	10.2047	14.1985
0.0300	37.1563	38.2253	09.8901	13.6472
0.0350	37.2140	38.3191	09.6670	13.0433
0.0400	37.3589	38.3892	09.4588	12.7358
0.0450	38.8224	38.4457	09.4124	12.4360
0.0500	38.8607	38.6481	09.4124	12.4366

The activation entropy and enthalpy contributions due to solute were evaluated following the equations,

$$-d(\Delta\mu_2^{0\neq})/dT = \Delta S_2^{0\neq} \quad (9)$$

and

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T \Delta S_2^{0\neq} \quad (10)$$

The value of solvent and solute activation parameters are given in Table 3. According to Feakins model, the greater the value of $\Delta\mu_2^{0\neq}$ the greater is the structure ability of the solute. The values, $\Delta\mu_2^{0\neq}$ are very large as compared to those of $\Delta\mu_1^{0\neq}$, which suggests that the formation of

transition state is accompanied by breaking and distortion of inter molecular bonds. The values of $\Delta H_2^{0\ddagger}$ and $\Delta S_2^{0\ddagger}$ given in Table 4 are negative indicating that the attainment of transition state of viscous flow is accompanied by bond breaking.

Table 3. Activation parameter of hydroxamic acids in 50 % (v/v) acetone-water.

Conc. (M)	$\Delta H_2^{0\ddagger}$ (10^4 kJ.mol ⁻¹)		$\Delta S_2^{0\ddagger}$ (10^2 kJ.mol ⁻¹ K ⁻¹)	
	303.15 K	313.15 K	303.15 K	313.15 K
N- <i>p</i> -Tolylbenzohydroxamic acid				
0.0000	–	–	–	–
0.0100	– 48.9259	– 89.5620	–16.6982	–28.6927
0.0200	– 43.9134	– 59.6295	–14.9849	–19.6715
0.0250	– 42.2164	– 58.6890	–14.4016	–19.3682
0.0300	– 41.3044	– 57.2042	–14.0942	–18.8722
0.0350	– 40.9230	– 55.5972	–13.9670	–18.3450
0.0400	– 40.3366	– 54.1727	–13.7682	–17.8725
0.0450	– 39.9261	– 53.2933	–13.6298	–17.5847
0.0500	– 39.5747	– 52.2626	–13.5058	–17.3641
N- <i>o</i> -Tolylbenzohydroxamic acid				
0.0000	–	–	–	–
0.0100	– 33.0373	– 70.7854	– 11.2711	– 23.3513
0.0200	– 31.0146	– 43.6445	– 10.5868	– 14.8932
0.0250	– 29.9009	– 43.0161	– 10.2047	– 14.1985
0.0300	– 28.9925	– 41.3489	– 09.8901	– 13.6472
0.0350	– 28.3175	– 38.2264	– 09.6670	– 13.0483
0.0400	– 27.9363	– 38.5904	– 09.5380	– 12.6031
0.0450	– 27.7018	– 36.9366	– 09.4585	– 12.6031
0.0500	– 27.5852	– 36.4379	– 09.4124	– 12.4360

Table 4. Molar volume (V) of hydroxamic acids in 50 % (v/v) acetone-water.

Conc. (M)	V (mL mol ⁻¹)	
	303.15 K	313.15 K
N- <i>p</i> -Tolylbenzohydroxamic acid		
0.0000	28.2666	28.1857
0.0100	28.3181	28.2096
0.0200	28.3595	28.2699
0.0250	28.3878	28.2861
0.0300	28.4239	28.3085
0.0350	28.4430	28.3324
0.0400	28.4691	28.3687
0.0450	28.4989	28.3839
0.0500	28.5291	28.4095
N- <i>o</i> -Tolylbenzohydroxamic acid		
0.0000	28.2666	28.1857
0.0100	28.3254	28.2089
0.0200	28.3850	28.2655
0.0250	28.4154	28.2931
0.0300	28.4461	28.3049
0.0350	28.4600	28.3500
0.0400	28.4912	28.3746
0.0450	28.5208	28.3824
0.0500	28.5308	28.4129

Excess properties

The excess molar volume (V^E) for these solutions were obtained by the given expression,

$$V^E = V - (X_1V_1 + X_2V_2) \quad (11)$$

where, V , V_1 and V_2 are the molar volume of solution, mixed solvent and solute, respectively. It is well known that negative excess molar volume arises due to increased interaction between the unlike molecules [18]. The molar volumes for mixed solvent are 28.266 and 28.185, respectively. The molar volumes of solution are given in Table 4. The molar volume of solutes are 247.37, 239.86 for *N-p*-tolylbenzohydroxamic acid and 247.86, 240.80 for *N-o*-tolylbenzohydroxamic acid at 303.15 K and 313.15 K, respectively.

The excess viscosity (η^E) have been evaluated from the observed viscosity of the solution and that of its pure components using the relation,

$$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2) \quad (12)$$

where, η , η_1 and η_2 are the viscosities of solution, mixed solvent and solute, respectively. The data are listed in Table 5.

Table 5. Excess viscosity (η^E) and excess molar volume (V^E) of hydroxamic acid.

Conc. (M)	V^E		η^E	
	303.15 K	313.15 K	303.15 K	313.15 K
N- <i>p</i> -Tolylbenzohydroxamic acid				
0.0000	–	–	–	–
0.0100	–0.0020	–0.0419	0.0062	0.1973
0.0200	–0.0030	–0.0441	0.0253	0.2494
0.0250	–0.0033	–0.0500	0.0437	0.2755
0.0300	–0.0028	–0.0584	0.0589	0.3000
0.0350	–0.0044	–0.0639	0.0770	0.3819
0.0400	–0.0014	–0.0678	0.1038	0.4453
0.0450	–0.0047	–0.0691	0.1321	0.5235
0.0500	–0.0050	–0.0872	0.1630	0.6148
N- <i>o</i> -Tolylbenzohydroxamic acid				
0.0000	–	–	–	–
0.0100	–0.0020	–0.0380	0.0443	0.1457
0.0200	–0.0070	–0.0430	0.0769	0.1978
0.0250	–0.0110	–0.0260	0.1291	0.2417
0.0300	–0.0130	–0.0630	0.1647	0.2740
0.0350	–0.0240	–0.0470	0.1996	0.3174
0.0400	–0.0260	–0.0580	0.2381	0.3577
0.0450	–0.0280	–0.0760	0.2773	0.4139
0.0500	–0.0460	–0.0140	0.3208	0.4261

The impact of solute on viscosity is understood in terms of the parameter d , regarded as a measure of the strength of interaction between components of solution. It has been estimated using relationship proposed by Gruenberg and Nissan [19],

$$\ln \eta = X \ln \eta_1 + X \ln \eta_2 + X_1X_2 d \quad (13)$$

where d is the parameter proportional to W/RT , W is the interchange energy or a measure of interactions. It is observed that values of d and η^E are positive suggesting complex formation involving mixed solvent.

The extra thermodynamic property, excess Gibb's free energy of activation of flow (G^E) for the solution have been computed from the Eyring equation [20],

$$G^E = RT [\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)] \quad (14)$$

The positive value of G^E indicates the presence of strong interactions between the solute and mixed solvent accompanied by the complex formation. The values of d and G^E are reported in Table 6. The value of G^E increases with increase in concentration of solute and also increases with increase in temperature suggesting the interaction becomes more and more stronger.

Table 6. Interaction parameters of Gurnberg and Nissan (d) and excess Gibb's free energy (G^E).

Conc. (M)	d		G^E (10^3)	
	303.15 K	313.15 K	303.15 K	313.15 K
N- <i>p</i> -Tolylbenzohydroxamic acid				
0.0000	–	–	–	–
0.0100	22.1078	131.8771	4.5736	27.5121
0.0200	44.7251	111.6700	18.3281	46.7035
0.0250	61.6903	106.7472	31.5397	55.9291
0.0300	69.1444	102.0938	42.3982	64.2686
0.0350	77.5062	109.2391	47.1601	90.9439
0.0400	91.9945	132.2163	74.9108	110.2748
0.0450	103.3392	137.5965	95.3500	132.3668
0.0500	114.0383	149.9408	117.7206	156.5710
N- <i>o</i> -Tolylbenzohydroxamic acid				
0.0000	–	–	–	–
0.0100	61.5145	263.6711	12.3233	54.5905
0.0200	57.2972	174.3782	23.1925	72.2237
0.0250	93.6509	165.9143	38.8381	86.3540
0.0300	77.9236	156.1452	47.7337	96.3672
0.0350	73.4618	149.5809	57.0112	109.3788
0.0400	93.4673	145.2054	66.9843	121.1746
0.0450	83.2692	148.1073	76.8529	136.6061
0.0500	85.2568	134.9908	87.3567	139.3960

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