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Viscosity Behaviour and Excess Thermodynamic Functions of Hydroxamic Acid in Benzene, Chlorobenzene and Toluene.

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ABSTRACT

Density and Viscosity of N-phenyl-2-chlorobenzene hydroxamic acid in Benzene, Chlorobenzene and Toluene have been determined at 30±°C. These data have been utilized to estimate the excess thermodynamic function, excess volume (V^E), excess viscosity (h^E) and excess Molar free energy of activation of Flow (G^{*E}). The parameter 'd' of Grunberg and Nissan expresssion has also been calculated. Analysis of these results suggests that specific interactions are present in the present systems.

Keywords : Hydroxamic acid, Grunberg and Nissan expression, Molar volume, Viscosity.

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INTRODUCTION

Hydroxamic acids are N-acyl derivatives of hydroxylamine. Extensive work has been carried out on their formation, reaction and structure. The field of hydroxamic acids is very vast ans lots of strenous work has been already done in different aspects of these versatile metal extractants. These reagents posses great importance in recent years becuase of their analytical [1-3], agricultural [4-6], biological [7-10], antioxidant [11] and technical applications [12-16].

Extensive work has been carried out on the viscosity of solutions of electrolytes in aqueous, non-aqueous and aqua-organic solvents [17-19]. Thus object of the present investigation is to measure the viscosity and density of hydroxamic acid in various organic solvents to understand the solute - solvent interactions. Thereafter, based on these data excess volume, excess viscosities, excess molar free energy of activation of flow and interaction strength term 'd' of Grunberg and Nissan expression are computed for these reagents.

EXPERIMENTAL

A stock solution of 0.05M of hydroxamic acid was prepared in organic solvents, viz, benzene, chlorobenzene and toluene. Further concentrations were obtained by using a Mass dilution technique.

Densities as a function of hydroxamic acid concentration were determined using a 10 cm**3** double armed Pycnometer and viscosities were measured by using viscometer an Ostwald sprengle type. Pyknometer and viscometer were calibrated with glass distilled water and benzene. All the solvents used were of analytical grade and the measurements were carried out in triplicate.

RESULTS AND DISCUSSION

Densities, viscosities and excess thermodynamic functions of hydroxamic acid, namely N-phenyl-2-chlorobenzohydroxamic acid was measured in benzene, chlorobenzne and toluene as a function of its concentrations at 30±1°C.Density (ρ) of this reagent was obtained [20] following the equation,

$$\rho \ \text{Solution} = \frac{\text{Wt. of Solution}}{\text{Wt. of Solvent}} \ \text{x} \ \rho \ \text{solvent} \qquad (1)$$

Viscosity (η) of this hydroxamic acids in benzene chlorobenzene and toluene was calculated [21] following the expression,

$$\frac{\eta_1}{\eta_2} = \quad \cdot \frac{\rho_1}{\rho_2} \qquad (2)$$

where, η_1, t_1 and ρ_1 are viscosity, time flow and density of solute and η_2, t_2 and ρ_2 are the same parameters of solvents.The data on densities and viscosities for the hydroxamic acids as a function of its concentraion in benzene, chlorobenzene and toluene is presented in Table 1. Viscosities of hydroxamic acids h were obtained as intercepts, by plotting the η_1 values against their concentrations. The data are presented in Table 1.

Table 1: Densities and Viscosities of N-Phenyl-2-Chlorobenzohydroxamic acid in Organic Solvents.

Solvent	Benzene		Chlorobenzene		Toluene	
Conc., M	ρ	η	ρ	η	ρ	η
0.01	0.8827	0.6403	1.0519	0.7634	0.9233	0.6509
0.02	0.8958	0.6540	1.0523	0.7641	0.9343	0.6612
0.03	0.8997	0.6578	1.0526	0.7695	0.9360	0.6627
0.04	0.9034	0.6645	1.0546	0.7765	0.9385	0.6702
0.05	0.9048	0.6664	1.0551	0.7951	0.9465	0.6785

Excess Viscosity (hE):

These were obtained [22] by applying the expression,

$$\eta^E = \eta_1 - (x_1\eta + x_2\eta_2) \tag{3}$$

where, h is viscosity of solute, x1 is the male fraction of solute and x2 is the mole fraction of solvent. The data are presented in Table 2.

Table 2: Excess Viscosities of N-Phenyl-2-Chlorobenzohydroxamic acid in Organic Solvents.

Solvent Conc., M	Benzene	Chlorobenzene	Toluene
0.01	0.0078	0.0131	0.0070
0.02	0.0245	0.0138	0.0173
0.03	0.0258	0.0192	0.0188
0.04	0.0321	0.0262	0.0263
0.05	0.0339	0.0448	0.0346

Excess Molar Volume (V_E):

From the measured values of densities, molar volume,V, of hydroxamic acid was first calculated [23] using the relation:

$$V = \frac{(X_1M_1 + X_2M_2)}{\rho} \tag{4}$$

where, M1 and M2 are the molecular weight of hydroxamic acid and solvent, respectively. Then, excess molar volume for these systems were obtained [24-26] by applying the equation:

$$V^E = V - (X_1V_1 + X_2V_2) \tag{5}$$

where, V_1 is molar volume of solute and V_2 is of solvent. The data on V and V_E are presented in Table 3.

Table 3: Molar Volumes and Excess Volumes of N-Phenyl-2-Chlorobenzohydroxamic acid in Organic Solvents.

Solvent Conc., M	Benzene		Chlorobenzene		Toluene	
	V	V^E	V	V^E	V	V^E
0.01	184.4397	61.5761	171.1474	38.9352	183.9326	55.2413
0.02	183.769	58.2686	171.0823	38.8701	181.7670	53.0757
0.03	180.9547	58.0911	171.0336	38.8214	181.4369	52.7456
0.04	180.6823	57.6491	170.7092	38.4970	180.9536	52.2623
0.05	179.9347	57.0711	170.6283	38.4161	163.7340	50.7328

Excess Moalr Free Energy of Activation of Flow (G^{*E}):

The excess Molar free energy of activation of flow is obtained using the equation,

$$G^{*E} = RT \left[\mathit{ln}\ \eta_1 V - X_1\ \mathit{ln}\ \eta V_1 - X_2\ \mathit{ln}\ \eta_2 V_2 \right] \tag{6}$$

where R is gas constant (1.98 cal. mol-**1**) and T is absolute temperature (303 K). G^{*E} values computed for the hydroxamic acid in benzene, chlorobenzene and toluene is given in Table 4.

Table 4: Excess Gibbs Free Energies of Activation of Flow of N-Phenyl-2-Chlorobenzohydroxamic acid in Organic Solvents.

Solvent Conc., M	Benzene	Chlorobenzene	Toluene
0.01	274.95	154.18	235.92
0.02	276.03	176.08	237.76
0.03	279.63	180.16	237.99
0.04	283.01	184.48	243.16
0.05	284.07	198.40	245.44

**Interaction Parameter (d):**

$$\mathit{ln}\ \eta_1 = X_1\ \mathit{ln}\ \eta + X_2\ \mathit{ln}\ \eta_2 + X_1 X_2 d \tag{7}$$

The impact of solute on viscosity is explained by Grunberg and Nissan [27]. They proposed an equation, where, parameter, d, is regarded as a measure of the strength of interaction between solute & solvent [28-30]. The values of d for these systems are calulated and present in Table 5.

Table 5: Excess Gibbs Free Energies of Activation of Flow of N-Phenyl-2-Chlorobenzohydroxamic acid in Organic Solvents.

Solvent Conc., M	Benzene	Chlorobenzene	Toluene
0.01	0.0488	0.0688	0.0428
0.02	0.1264	0.0724	0.1056
0.03	0.1568	0.1004	0.1144
0.04	0.1968	0.1368	0.1596
0.05	0.2088	0.2316	0.2088

Figure 1: Plots of Viscosity versus Concentration for N-Phenyl-2-Chlorobenzohydroxamic Acid.

◆ Benzene ■ Chlorobenzene △ Toluene
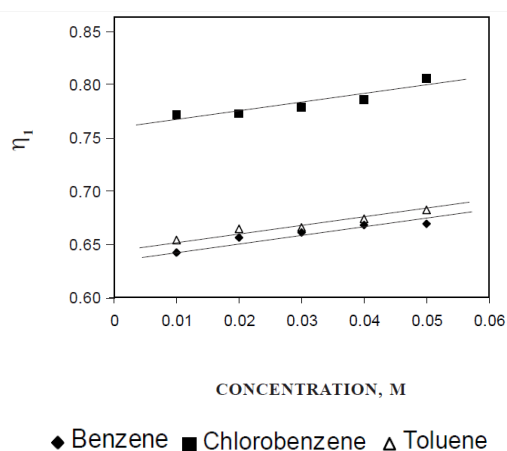
CONCLUSION

It is concluded from the data that the values of excess viscosities for these systems are positive and increases with increase in concentration of hydroxamic acid, where excess volume for these systems decreases with increase in concentration of hydroxamic acid in solution. A marked decrease in V^E in the sovent is observed in the order of their increasing polarizability, which is in the order, benzene > toluene > chlorobenzene. Greater the polarizability, greater will be the contraction in volume. G^{*E} values are also positive for all these systems and increases with increase in solute concentration. The maximum value of G^{*E} obtained for N-phenyl-2-chlorobenzohydroxamic acid is 284.07 cal. mal**-1** in benzene shows that it is a weakly interactive system. The values of η^E and d are greater than zero but the magnitude is less. This supports the formation of intermolecular complexes between solute and solvent and also suggest that weak specific interactions are present in these systems.

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