

## THE STUDY ON VISCOSITY OF CINNAMIC AND MANDELIC ACIDS IN PURE AND MIXED SOLVENTS

SHAISTA JABEEN

*Department of Chemistry, University of Karachi, Karachi-75270, Pakistan*

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The viscosity values, coefficient A and B for cinnamic acid solutions and mandelic acid solutions in various compositions of methanol and water have been determined at 298 K, 303 K, 308 K and 313 K. The positive values of coefficient B calculated by Jones-Dole equation show that there is an increase with the increase of methanol content at different temperatures. The energy of activation, free energy of activation and entropy of activation, of acid solutions in pure solvents and in 54% aqueous methanol have also been determined at 298 K, 303 K and 313 K.

**Key words:** Viscosity, Viscosity coefficient, Activation parameters.

### Introduction

The variation of viscosity with temperature and solvent compositions have been employed to study the ion-solvent interaction by many workers [1 - 6].

The present work deals with the viscosities of cinnamic and mandelic acids in pure water, pure methanol and mixed solvents at various temperatures. The data have been interpreted in terms of Jones-Dole equation (1) which is expressed as :

$$\eta/\eta_0 = 1 + A \sqrt{C} + BC \dots\dots\dots (1)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the solution and solvent respectively, C is the molar concentration. A and B are the constants representing ion-ion and ion-solvent interactions respectively.

The effect of temperature on viscosity is given by the Andrade equation [7], given as:

$$\eta = A \exp. [E\eta/RT] \dots\dots\dots (2)$$

where  $E\eta$  is the activation energy for the viscous flow, A is the pre-exponential factor. Other symbols have the usual meanings.

The measurements on activation parameters have been reported by many workers [4 - 15]. This work involves the determination of activation energy, free energy and entropy of activation at various temperatures for cinnamic and mandelic acid solutions in mixed and pure solvents.

### Experimental

All the chemicals such as cinnamic acid, mandelic acid, methanol used were of E. Merck. Doubly distilled water was used for the preparation of various solutions.

The viscosity was measured by using an Ostwald Viscometer. By using a 10 ml capacity specific gravity bottle, the density measurements were made. For constant temperature maintenance 'HAAKE' thermostat (Model KT 33) with

an accuracy of  $\pm 0.01^\circ$  was used. Mixed aqueous solvents were prepared by weight in doubly distilled water and methanol. Each tabulated viscosity value\* is a mean of three readings and standard deviation was calculated.

### Results and Discussion

The viscosities of various solutions of cinnamic acid and mandelic acid in pure solvents and mixed solvents, at different temperatures are tabulated in Table 1-8. Results show that there is a regular increment in viscosity with the increase of concentration of the solutes at all tested temp. (298, 303, 308 and 313 K.)

The viscosities of the solutions are found to decrease with the rise of temperature at all concentrations ranging from  $1.2 \times 10^{-3}$  to  $3.5 \times 10^{-3}$  mol.dm<sup>-3</sup>.

Results also show that viscosities vary with the change of solvent composition. As the methanol content of the solvent is increased, the viscosity increases up to 25% w/w methanol solution and then decreases at 298 K. At 303, 308 and 313 K the viscosity increases up to 34% w/w methanol solution and after that it decreases. This increase in viscosity on the addition of methanol to water is due to the increase in the degree of solvent structuredness. As the alcohol content is increased further, the solvent structure is gradually destroyed. [16-19].

Solvent composition is given as : (a) 00.00% methanol, (b) 08.02% methanol, (c) 16.41% methanol, (d) 25.17% methanol, (e) 34.36% methanol, (f) 54.08% methanol, (g) 75.85% methanol, (h) 100.00% methanol.

At a lower temperature i.e. 298 K the viscosity is found to increase up to 25% w/w methanol content. This is due to the reason that structure making effect become saturated earlier at

\* This work is a part of M.Phil thesis.

TABLE 1. VISCOSITIES OF CINNAMIC ACID IN DIFFERENT SOLUTIONS AT 298 K.

$10^3 \times C/\text{mol. dm}^{-3}$	3.5	2.7	2.2	1.8	1.5	1.2	Solvent
$10^3 \times \eta/\text{Kg m}^{-1}\text{s}^{-1}$	0.9268	0.9166	0.9106	0.9035	0.8998	0.8985	(a)
	$\pm 0.004$	$\pm 0.003$	$\pm 0.003$	$\pm 0.005$	$\pm 0.002$	$\pm 0.003$	
	1.1350	1.1296	1.1245	1.1184	1.1145	1.1117	(b)
	$\pm 0.002$	$\pm 0.003$	$\pm 0.004$	$\pm 0.005$	$\pm 0.002$	$\pm 0.003$	
	1.2098	1.2010	1.1959	1.1906	1.1858	1.1824	(c)
	$\pm 0.002$	$\pm 0.002$	$\pm 0.004$	$\pm 0.004$	$\pm 0.003$	$\pm 0.002$	
	1.2475	1.2310	1.2242	1.2186	1.2121	1.2068	(d)
	$\pm 0.004$	$\pm 0.003$	$\pm 0.004$	$\pm 0.001$	$\pm 0.002$	$\pm 0.005$	
	1.2392	1.2281	1.2217	1.2145	1.2116	1.2073	(e)
	$\pm 0.003$	$\pm 0.001$	$\pm 0.001$	$\pm 0.001$	$\pm 0.002$	$\pm 0.004$	
	1.1863	1.1808	1.1737	1.1691	1.1656	1.1628	(f)
	$\pm 0.003$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	$\pm 0.001$	$\pm 0.004$	
	1.0989	1.0857	1.0716	1.0592	1.0452	1.0383	(g)
	$\pm 0.002$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	$\pm 0.001$	$\pm 0.003$	
	0.5962	0.5842	0.5746	0.5659	0.5571	0.5512	(h)
	$\pm 0.001$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	$\pm 0.001$	$\pm 0.002$	

TABLE 2. VISCOSITIES OF CINNAMIC ACID IN DIFFERENT SOLUTIONS AT 303 K.

$10^3 \times C/\text{mol. dm}^{-3}$	3.5	2.7	2.2	1.8	1.5	1.2	Solvent
$10^3 \times \eta/\text{Kg m}^{-1}\text{s}^{-1}$	0.8402	0.8335	0.8257	0.8201	0.8143	0.8093	(a)
	$\pm 0.003$	$\pm 0.004$	$\pm 0.004$	$\pm 0.004$	$\pm 0.003$	$\pm 0.002$	
	0.8894	0.8838	0.8794	0.8751	0.8680	0.8609	(b)
	$\pm 0.003$	$\pm 0.004$	$\pm 0.003$	$\pm 0.004$	$\pm 0.003$	$\pm 0.002$	
	0.9899	0.9843	0.9759	0.9703	0.9673	0.9616	(c)
	$\pm 0.002$	$\pm 0.004$	$\pm 0.002$	$\pm 0.002$	$\pm 0.003$	$\pm 0.002$	
	1.1077	1.1000	1.0943	1.0869	1.0808	1.0734	(d)
	$\pm 0.003$	$\pm 0.003$	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	$\pm 0.003$	
	1.1309	1.1205	1.1126	1.1077	1.1043	1.0992	(e)
	$\pm 0.003$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	
	1.0567	1.0502	1.0463	1.0421	1.0385	1.0346	(f)
	$\pm 0.003$	$\pm 0.001$	$\pm 0.002$	$\pm 0.003$	$\pm 0.001$	$\pm 0.000$	
	0.9037	0.8930	0.8847	0.8773	0.8723	0.8653	(g)
	$\pm 0.001$	$\pm 0.002$	$\pm 0.001$	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	
	0.5504	0.5449	0.5365	0.5310	0.5249	0.5190	(h)
	$\pm 0.001$	$\pm 0.002$	$\pm 0.001$	$\pm 0.002$	$\pm 0.001$	$\pm 0.001$	

TABLE 3. VISCOSITIES OF CINNAMIC ACID IN DIFFERENT SOLUTIONS AT 308 K.

$10^3 \times C/\text{mol. dm}^{-3}$	3.5	2.7	2.2	1.8	1.5	1.2	Solvent
$10^3 \times \eta/\text{Kg m}^{-1}\text{s}^{-1}$	0.7639	0.7584	0.7535	0.7442	0.7363	0.7318	(a)
	$\pm 0.003$	$\pm 0.004$	$\pm 0.003$	$\pm 0.000$	$\pm 0.003$	$\pm 0.002$	
	0.8010	0.7951	0.7922	0.7862	0.7831	0.7796	(b)
	$\pm 0.003$	$\pm 0.003$	$\pm 0.003$	$\pm 0.001$	$\pm 0.003$	$\pm 0.001$	
	0.9058	0.8979	0.8909	0.8890	0.8825	0.8757	(c)
	$\pm 0.001$	$\pm 0.003$	$\pm 0.000$	$\pm 0.002$	$\pm 0.002$	$\pm 0.000$	
	0.9620	0.9554	0.9473	0.9354	0.9288	0.9222	(d)
	$\pm 0.001$	$\pm 0.000$	$\pm 0.000$	$\pm 0.000$	$\pm 0.002$	$\pm 0.002$	
	1.0818	1.0748	1.0695	1.0681	1.0604	1.0565	(e)
	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	$\pm 0.003$	$\pm 0.000$	$\pm 0.001$	
	0.9891	0.9774	0.9702	0.9621	0.9541	0.9466	(f)
	$\pm 0.000$	$\pm 0.001$	$\pm 0.002$	$\pm 0.003$	$\pm 0.000$	$\pm 0.000$	
	0.8252	0.8158	0.8081	0.7992	0.7904	0.7843	(g)
	$\pm 0.000$	$\pm 0.001$	$\pm 0.002$	$\pm 0.003$	$\pm 0.004$	$\pm 0.002$	
	0.5368	0.5203	0.5132	0.5074	0.5015	0.4961	(h)
	$\pm 0.001$	$\pm 0.001$	$\pm 0.001$	$\pm 0.002$	$\pm 0.001$	$\pm 0.002$	



TABLE 4. VISCOSITIES OF CINNAMIC ACID IN DIFFERENT SOLUTIONS AT 313 K.

$10^3 \times C/\text{mol. dm}^{-3}$	3.5	2.7	2.2	1.8	1.5	1.2	Solvent
$10^3 \times \eta/\text{Kg m}^{-1}\text{s}^{-1}$	0.6936	0.6863	0.6809	0.6728	0.6674	0.6627	(a)
	$\pm 0.004$	$\pm 0.004$	$\pm 0.002$	$\pm 0.001$	$\pm 0.002$	$\pm 0.003$	
	0.7209	0.7156	0.7116	0.7078	0.7046	0.7004	(b)
	$\pm 0.004$	$\pm 0.003$	$\pm 0.004$	$\pm 0.000$	$\pm 0.004$	$\pm 0.004$	
	0.8104	0.8039	0.7999	0.7967	0.7920	0.7880	(c)
	$\pm 0.003$	$\pm 0.003$	$\pm 0.003$	$\pm 0.001$	$\pm 0.003$	$\pm 0.003$	
	0.8591	0.8515	0.8443	0.8380	0.8293	0.8231	(d)
	$\pm 0.000$	$\pm 0.003$	$\pm 0.002$	$\pm 0.001$	$\pm 0.004$	$\pm 0.003$	
	0.9441	0.9381	0.9337	0.9293	0.9256	0.9221	(e)
	$\pm 0.003$	$\pm 0.002$	$\pm 0.000$	$\pm 0.002$	$\pm 0.004$	$\pm 0.002$	
	0.9001	0.8913	0.8778	0.8670	0.8589	0.8508	(f)
	$\pm 0.003$	$\pm 0.002$	$\pm 0.000$	$\pm 0.003$	$\pm 0.000$	$\pm 0.002$	
	0.7594	0.7478	0.7390	0.7296	0.7234	0.7158	(g)
	$\pm 0.002$	$\pm 0.002$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	$\pm 0.001$	
	0.5044	0.4977	0.4897	0.4836	0.4752	0.4672	(h)
	$\pm 0.001$	$\pm 0.000$	$\pm 0.001$	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	

TABLE 5. VISCOSITIES OF MANDELIC ACID IN DIFFERENT SOLUTIONS AT 298 K.

$10^3 \times C/\text{mol. dm}^{-3}$	3.5	2.7	2.2	1.8	1.5	1.2	Solvent
$10^3 \times \eta/\text{Kg m}^{-1}\text{s}^{-1}$	0.9287	0.9235	0.9197	0.9136	0.9045	0.8994	(a)
	$\pm 0.002$	$\pm 0.004$	$\pm 0.003$	$\pm 0.000$	$\pm 0.002$	$\pm 0.003$	
	1.1441	1.1337	1.1272	1.1231	1.1175	1.1139	(b)
	$\pm 0.004$	$\pm 0.004$	$\pm 0.002$	$\pm 0.003$	$\pm 0.002$	$\pm 0.003$	
	1.2175	1.2092	1.2028	1.1960	1.1907	1.1845	(c)
	$\pm 0.005$	$\pm 0.001$	$\pm 0.004$	$\pm 0.003$	$\pm 0.001$	$\pm 0.003$	
	1.2515	1.2417	1.2309	1.2249	1.2136	1.2094	(d)
	$\pm 0.004$	$\pm 0.000$	$\pm 0.003$	$\pm 0.003$	$\pm 0.000$	$\pm 0.000$	
	1.2466	1.2375	1.2290	1.2233	1.2189	1.2146	(e)
	$\pm 0.004$	$\pm 0.002$	$\pm 0.003$	$\pm 0.001$	$\pm 0.000$	$\pm 0.001$	
	1.1933	1.1864	1.1822	1.1740	1.1658	1.1623	(f)
	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	$\pm 0.001$	$\pm 0.001$	$\pm 0.001$	
	1.1110	1.0948	1.0815	1.0696	1.0583	1.0480	(g)
	$\pm 0.003$	$\pm 0.003$	$\pm 0.003$	$\pm 0.000$	$\pm 0.002$	$\pm 0.001$	
	0.6089	0.5968	0.5869	0.5712	0.5663	0.5583	(h)
	$\pm 0.002$	$\pm 0.000$	$\pm 0.002$	$\pm 0.000$	$\pm 0.002$	$\pm 0.000$	

TABLE 6. VISCOSITIES OF MANDELIC ACID IN DIFFERENT SOLUTIONS AT 303 K.

$10^3 \times C/\text{mol. dm}^{-3}$	3.5	2.7	2.2	1.8	1.5	1.2	Solvent
$10^3 \times \eta/\text{Kg m}^{-1}\text{s}^{-1}$	0.8545	0.8472	0.8413	0.8287	0.8254	0.8165	(a)
	$\pm 0.002$	$\pm 0.000$	$\pm 0.003$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	
	0.8974	0.8880	0.8830	0.8780	0.8743	0.8682	(b)
	$\pm 0.001$	$\pm 0.003$	$\pm 0.003$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	
	0.9968	0.9913	0.9843	0.9791	0.9759	0.9725	(c)
	$\pm 0.002$	$\pm 0.003$	$\pm 0.002$	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	
	1.1145	1.1056	1.0985	1.0918	1.0847	1.0763	(d)
	$\pm 0.002$	$\pm 0.002$	$\pm 0.004$	$\pm 0.004$	$\pm 0.001$	$\pm 0.004$	
	1.1655	1.1533	1.1426	1.1329	1.1229	1.1111	(e)
	$\pm 0.003$	$\pm 0.000$	$\pm 0.004$	$\pm 0.004$	$\pm 0.005$	$\pm 0.004$	
	1.0698	1.0633	1.0593	1.0540	1.0500	1.0473	(f)
	$\pm 0.003$	$\pm 0.002$	$\pm 0.004$	$\pm 0.004$	$\pm 0.004$	$\pm 0.003$	
	0.9135	0.9089	0.9057	0.9006	0.8957	0.8915	(g)
	$\pm 0.003$	$\pm 0.000$	$\pm 0.004$	$\pm 0.002$	$\pm 0.003$	$\pm 0.003$	
	0.5973	0.5779	0.5642	0.5484	0.5327	0.5214	(h)
	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	

TABLE 7. VISCOSITIES OF MANDELIC ACID IN DIFFERENT SOLUTIONS AT 308 K.

$10^3 \times C/\text{mol. dm}^{-3}$	3.5	2.7	2.2	1.8	1.5	1.2	Solvent
$10^3 \times \eta/\text{Kg m}^{-1}\text{s}^{-1}$	0.7709	0.7640	0.7585	0.7536	0.7432	0.7363	(a)
	$\pm 0.003$	$\pm 0.002$	$\pm 0.003$	$\pm 0.002$	$\pm 0.001$	$\pm 0.000$	
	0.8078	0.8018	0.7988	0.7941	0.7893	0.7858	(b)
	$\pm 0.003$	$\pm 0.002$	$\pm 0.003$	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	
	0.9184	0.9111	0.9041	0.8972	0.8904	0.8834	(c)
	$\pm 0.004$	$\pm 0.002$	$\pm 0.000$	$\pm 0.003$	$\pm 0.000$	$\pm 0.001$	
	0.9762	0.9637	0.9590	0.9424	0.9396	0.9325	(d)
	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	$\pm 0.001$	$\pm 0.002$	$\pm 0.004$	
	1.0905	1.0850	1.0803	1.0767	1.0732	1.0692	(e)
	$\pm 0.002$	$\pm 0.001$	$\pm 0.003$	$\pm 0.001$	$\pm 0.002$	$\pm 0.004$	
	0.9988	0.9922	0.9865	0.9798	0.9743	0.9686	(f)
	$\pm 0.004$	$\pm 0.000$	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	$\pm 0.003$	
	0.8375	0.8287	0.8147	0.8096	0.8011	0.7910	(g)
	$\pm 0.003$	$\pm 0.000$	$\pm 0.003$	$\pm 0.002$	$\pm 0.000$	$\pm 0.001$	
	0.5518	0.5381	0.5200	0.5074	0.5006	0.4924	(h)
	$\pm 0.001$	$\pm 0.002$	$\pm 0.001$	$\pm 0.000$	$\pm 0.001$	$\pm 0.002$	

TABLE 8. VISCOSITIES OF MANDELIC ACID IN DIFFERENT SOLUTIONS AT 313 K.

$10^3 \times C/\text{mol. dm}^{-3}$	3.5	2.7	2.2	1.8	1.5	1.2	Solvent
$10^3 \times \eta/\text{Kg m}^{-1}\text{s}^{-1}$	0.6932	0.6865	0.6797	0.6743	0.6715	0.6662	(a)
	$\pm 0.003$	$\pm 0.003$	$\pm 0.001$	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	
	0.7350	0.7284	0.7228	0.7145	0.7110	0.7076	(b)
	$\pm 0.003$	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	$\pm 0.003$	$\pm 0.002$	
	0.8348	0.8241	0.8149	0.8089	0.8032	0.7963	(c)
	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	$\pm 0.001$	$\pm 0.003$	$\pm 0.000$	
	0.8614	0.8559	0.8519	0.8466	0.8426	0.8381	(d)
	$\pm 0.001$	$\pm 0.000$	$\pm 0.003$	$\pm 0.003$	$\pm 0.000$	$\pm 0.000$	
	0.9678	0.9644	0.9611	0.9568	0.9529	0.9495	(e)
	$\pm 0.002$	$\pm 0.001$	$\pm 0.001$	$\pm 0.002$	$\pm 0.004$	$\pm 0.003$	
	0.9003	0.8946	0.8893	0.8844	0.8810	0.8761	(f)
	$\pm 0.004$	$\pm 0.002$	$\pm 0.000$	$\pm 0.002$	$\pm 0.003$	$\pm 0.003$	
	0.7702	0.7622	0.7598	0.7549	0.7517	0.7482	(g)
	$\pm 0.000$	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	$\pm 0.003$	$\pm 0.002$	
	0.5153	0.5040	0.4974	0.4891	0.4795	0.4725	(h)
	$\pm 0.000$	$\pm 0.001$	$\pm 0.001$	$\pm 0.000$	$\pm 0.002$	$\pm 0.002$	

lower temperature, i.e. 298 K. The solvent is in a more ordered form at lower temperature as compared to the higher temperatures. As the alcohol content is further increased, the ordered solvent structure is gradually destroyed and viscosity decreases.

The values of A and B co-efficient are determined from the intercept and slope of the linear plots of  $\eta_{sp}\sqrt{C}$  vs  $\sqrt{C}$ . Regression method was applied for these linear plots. Plots of  $\eta_{sp}\sqrt{C}$  vs  $\sqrt{C}$  for cinnamic acid and mandelic acid are shown in Fig. 1 (representative plots). A and B co-efficients of different solutions at different temperatures are summarized in Table 9, 10 respectively.

The negative values of coefficient A do not have any significance [20,21]. Data shows that there is a decrease in A values with the rise in temperature in some cases. This

decrease is due to greater thermal agitation at higher temperatures, and also due to reduction of attractive forces [22]. This behaviour is commonly expected. However, several A values are found to increase with the increase of temperature. This may be due to the interpenetration effect (cation-cation) [23,24] and (cation anion) [24] which brings ions together.

From Table 9 and 10 it was concluded that with the increase of methanol content the A values are found irregularly varied with solvent composition. This may be due to different degrees of hydration of ions in different solvents [6]. With some exceptions, A values have been found to increase with the increase of organic solvent concentration. This is due to the decrease of dielectric constant of the medium and increase in the ion-ion interaction.



TABLE 9. A AND B CO-EFFICIENTS OF JONES-DOLE EQUATION FOR CINNAMIC ACID AT DIFFERENT TEMPERATURES.

Solvent	298K		303K		308K		313K	
	A	B	A	B	A	B	A	B
	(dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1/2</sup>	dm <sup>3</sup> mol <sup>-1</sup>	(dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1/2</sup>	dm <sup>3</sup> mol <sup>-1</sup>	(dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1/2</sup>	dm <sup>3</sup> mol <sup>-1</sup>	(dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1/2</sup>	dm <sup>3</sup> mol <sup>-1</sup>
a	-0.5853	20.5487	-0.4322	22.8182	-0.4396	25.7748	-0.4926	25.1001
b	-0.3049	13.1225	0.1204	13.6628	0.2956	9.4690	0.6613	6.1006
c	-0.3093	13.6749	-0.3424	17.1550	-0.0786	20.9532	0.5056	6.5661
d	-0.4304	18.9920	-0.3496	18.2156	-0.8252	29.4532	0.6313	13.8466
e	-0.6117	18.1147	0.2666	9.7999	0.2981	12.7231	1.2843	-2.7224
f	0.0152	8.2287	2.1016	-12.7460	0.4978	15.2514	0.0086	32.8396
g	-1.3108	41.4352	1.3641	5.8019	0.3294	21.2242	-0.4052	32.1620
h	-1.6108	54.6160	-0.6438	35.1242	-0.9306	45.1134	-0.6554	44.0995

TABLE 10. A AND B CO-EFFICIENTS OF JONES-DOLE EQUATION FOR MANDELIC ACID AT DIFFERENT TEMPERATURES.

Solvent	298K		303K		308K		313K	
	A	B	A	B	A	B	A	B
	(dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1/2</sup>	dm <sup>3</sup> mol <sup>-1</sup>	(dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1/2</sup>	dm <sup>3</sup> mol <sup>-1</sup>	(dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1/2</sup>	dm <sup>3</sup> mol <sup>-1</sup>	(dm <sup>3</sup> mol <sup>-1</sup> ) <sup>1/2</sup>	dm <sup>3</sup> mol <sup>-1</sup>
a	-0.3995	19.5395	-0.1328	23.1200	-0.1101	22.8949	-0.2223	20.7388
b	-0.1943	12.3345	0.4390	10.0359	0.6603	5.8422	0.6751	12.4569
c	-0.2984	15.7550	0.2324	9.0898	0.6133	11.9539	0.4486	17.1655
d	-0.4149	20.7202	-0.2942	19.051	-0.4246	26.2103	1.8328	-6.6517
e	-0.3511	15.6311	0.5046	15.7666	1.4086	-6.0211	2.7713	-20.3174
f	-0.2274	15.1026	2.6271	-17.9237	1.8716	-5.3811	2.5056	-13.8095
g	-0.8498	36.4527	2.8580	14.6082	0.6583	20.3415	2.3619	-11.9686
h	-1.3107	56.6518	-2.4312	93.5960	-2.4018	81.8996	-0.4890	47.3499

The values of B-coefficient calculated are found to increase with the increase of methanol content at all temperatures with some exceptions. Some values are found negative indicating structure breaking effect [25].

At all temperatures the B values are found higher in pure methanol than in pure water. Methanol is generally considered as less structured than water [25]. The solutes have a much better structure promoting effect on methanol.

A solute with a positive B coefficient is expected to have a structure making effect, and a less positive or negative value indicates structure breaking effect [26,27]. As our solutes are very large and may show an "obstruction effect" which means a bending of the streamlines around a large solute particle. In such a case the B co-efficient may be always positive irrespective of how it interacts with the solvent [26].

Data shows that some irregular variation of B values with the composition of mixed solvents is present. This can not be explained on the basis of dielectric constant of the medium but may be due to the different degree of hydrolysis in different solvents [5].

According to the Stokes equation [28], the coefficient B can be discussed in terms of various viscosity effects at different solvent compositions and at different temperatures [29, 30]. The equation is given as:

$$\eta_E + \eta_A + \eta_D = \eta^0 B \dots\dots\dots (3)$$

where  $\eta_E$  and  $\eta_A$  are the viscosity increment due to the size and shape of the ion and the orientation of solvent molecules around the ions respectively.  $\eta_D$  is the viscosity decrement as a result of distortion of solvent structure by the ions. When coefficient B increases with temperature, this indicates that the viscosity decreases due to solvent structure ( $\eta_D$ ) is small and B value is positive [30, 31]. when coefficient B decreases, this indicates that solvent distortion ( $\eta_D$ ) is large,  $\eta_E$  and  $\eta_A$  are small. This is due to the competition between the ionic field and the bulk structure [30].

In mixed solvents, the values of coefficient B are found smaller as compared to that in aqueous solvent with a few exceptions. This effect may be due to the formation of mixed solvent clusters which are more strongly bonded with each other and are bulkier than those of water and are therefore, unable to interact with the ions for lack of proper orientation around the ions. Water and methanol being mutually associated show least tendency to orient around the ions. Thus  $\eta_E + \eta_A$  term is small and  $\eta_D$  is of considerable magnitude due to the significant distortion in the molecules of solvent present in the vicinity of ionic field. Hence small B-values have been observed in mixed solvent [29].

Because our solutes are of high molecular weights, high B-values show that the ion-solvent interaction is not so strong [5,22].

TABLE 11. ACTIVATION PARAMETERS IN DIFFERENT SOLVENTS AT DIFFERENT TEMPERATURES (C = 3.5 x 10<sup>-3</sup> mol. dm<sup>-3</sup>).

Temp. K	Solvent		Cinnamic acid		Mandelic acid	
	$\Delta G^*$ K J mol <sup>-1</sup>	$\Delta S^*$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^*$ K J mol <sup>-1</sup>	$\Delta S^*$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^*$ K J mol <sup>-1</sup>	$\Delta S^*$ J K <sup>-1</sup> mol <sup>-1</sup>
IN DISTILLED WATER						
298	9.1662	25.000	9.1672	20.3886	9.1672	25.0389
303	9.0467	25.000	9.0477	20.4465	9.0477	25.0199
313	8.8355	24.900	8.8366	20.4678	8.8366	24.8951
$\Delta E^*$ KJ mol <sup>-1</sup>	16.6288		15.2430		16.6288	
IN 54.08% METHANOL						
298	10.9135	26.100	10.9144	9.8752	10.9145	14.5251
303	10.7139	26.400	10.7149	10.3709	10.7149	14.9442
313	10.6266	25.800	10.6276	10.3185	10.6277	14.7453
$\Delta E^*$ KJ mol <sup>-1</sup>	18.7074		13.8573		15.2430	

The relationship between viscosity and energy of activation is given by the following expression [7].

$$\eta = A \exp [E^*\eta / RT] \dots\dots\dots (4)$$

where E $\eta$  is the energy of activation. When a graph was plotted between ln  $\eta$  vs 1/T (reciprocal of the absolute temperature), a stright line relation was obtained whose slope gives the value of E $\eta$ . The values of E $\eta$  obtained in such a way are given in Table 11. Plots of ln  $\eta$  vs 1/T for cinnamic and mandelic acid are shown in Fig. 2,3 respectively.

E $\eta$ , the energy of activation can be related to the work needed to form a hole in the liquid. The holes are necessary for a liquid to flow [5,6]. From Table 11, it was concluded that the values of activation energy are found the highest in pure water and then decreases as the alcohol content increases.

The free energy of activation for viscous flow ( $\Delta G^*$ ) is given by the following expression [4, 8].

$$\Delta G^* = RT \ln \frac{\eta V}{hN} \dots\dots\dots (5)$$

where h is the Planck's constant, N is the Avogadro's number and V is the volume of one mole of solution particles [4].

The entropy of activation is given by

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \dots\dots\dots (6)$$

The energy of activation does not differ appreciably from activation enthalpy ( $\Delta H^*$ ) [9]

Thus 
$$\Delta S^* = \frac{\Delta E^*\eta - \Delta G^*}{T} \dots\dots\dots (7)$$

The values of free energy of activation and entropy of activation were calculated and are tabulated in Table 11. Data shows that in some cases the values of  $\Delta E^*\eta$  and  $\Delta S^*$  are found

lesser than that of the pure solvent indicating that the solvent structure is broken by the presence of the solutes [10, 12]. In some cases these values are found higher which are attributed to the excess of energy necessary to break the hydrogen bonds in solution [10, 12].

When these values are found equal to that of the solvent indicating that the hydrogen bond breaking of the solvent is not significantly effected by these solutes.

The values of  $\Delta G^*$  control the rate of flow in fluid process [9]. The flow process is governed by the ability of molecule

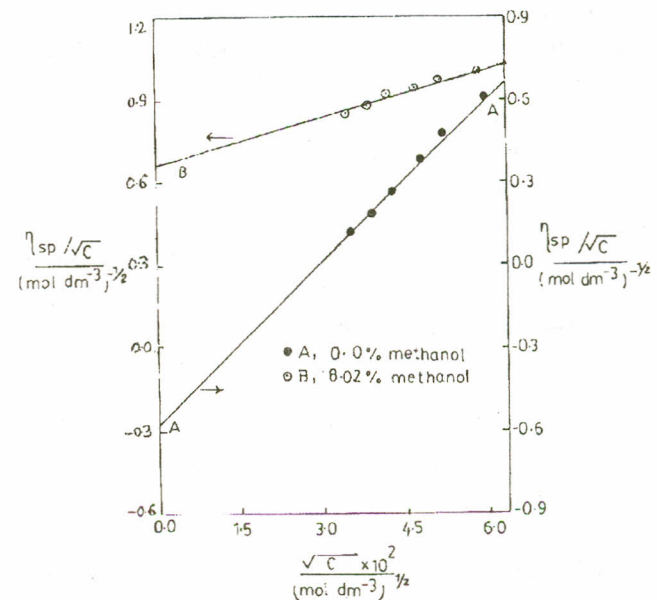


Fig. 1. Plots of  $\eta_{sp}/\sqrt{C}$  vs  $\sqrt{C}$  for cinnamic acid at 298 K, mandelic acid at 308 K. (A) 0% methanol, (B) 8.02% methanol.



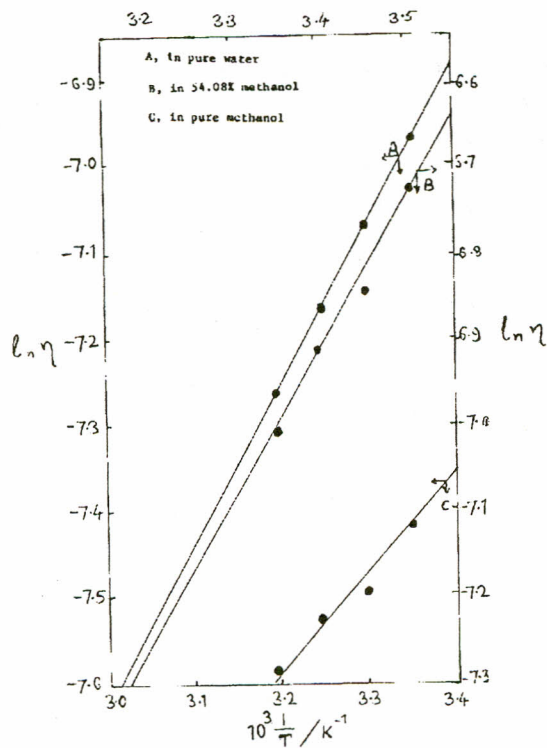


Fig. 2. Plots of  $\ln \eta$  vs  $1/T$  for cinnamic acid ( $3.5 \times 10^{-3} \text{ mol.dm}^{-3}$ ) in different solvents., (A) pure water, (B) 54.08% methanol, (C) pure methanol.

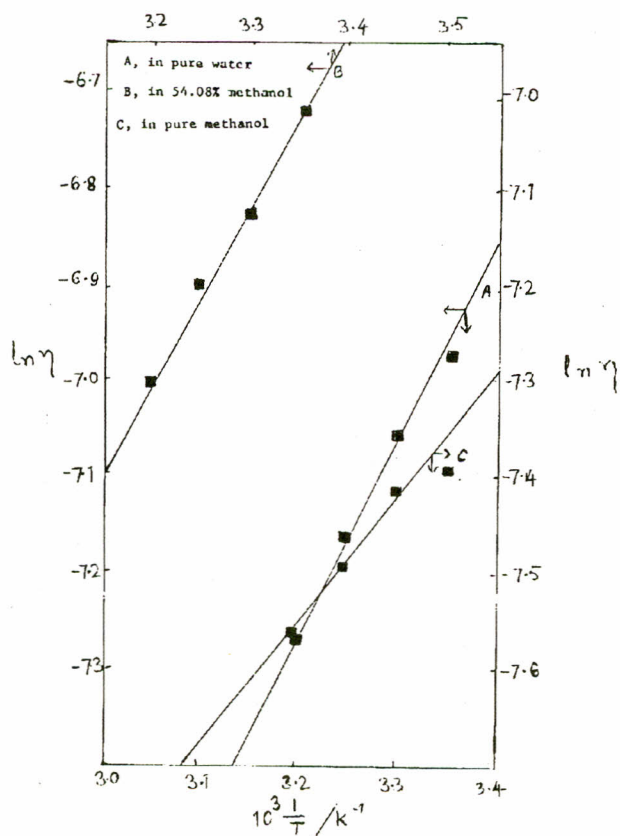


Fig. 3. Plots of  $\ln \eta$  vs  $1/T$  for mandelic acid ( $3.5 \times 10^{-3} \text{ mol.dm}^{-3}$ ) in different solvents., (A) pure water, (B) 54.08% methanol (C) pure methanol.

to move into the prepared hole and the readiness with which the holes are prepared in the liquid.

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