Physical Sciences

ACTIVATION PARAMETERS OF BUTANE AND DECANE SULFONIC ACIDS (Na-SALT) IN PURE AND MIXED SOLVENTS AT DIFFERENT TEMPERATURES BY VISCOSITY MEASUREMENTS

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The viscosities of the various solutions of 1-Butane Sulfonic Acid (Na-Salt) and 1-Decane Sulfonic Acid (Na-Salt) in pure and mixed solvents have been measured at four temperatures 298, 303, 308 and 313 K. The measured data have been used to calculate viscosity coefficients of Jones-Dole equation. These coefficients have been found to be dependent on temperature and solvent composition. The positive values of B coefficients for butane and decane sulfonic acids (Na-salt) in pure and mixed solvents led to the conclusion that ion-solvent interaction is not so strong. Activation parameters such as energy of activation (E_η*), free energy change of activation (ΔG*) and entropy change of activation (ΔS*) have been evaluated at different temperatures in pure and mixed solvents.

Key words: Viscosity, Jones-Doles parameters, Activation parameters, Ion-ion and ion-solvent interactions.

Introduction

Studies on the variation of viscosity with temperature and solvent composition have been made by many workers. (Jones and Dole 1929; Gurney 1953; Fahimuddin and Farooqui 1984).

The present work deals with measurements of the viscosities of 1-butane sulfonic acid (Na-salt) and 1-decane sulfonic acid (Na-salt) in pure water, pure methanol and mixed solvents at various temperatures from 25 to 40°C. The data have been interpreted in terms of Jones-Dole equation (Jones and Dole 1929) which is expressed as:

$$\eta/\eta_o = 1 + A\sqrt{C} + BC \quad\quad\quad (1)$$

where η and η_o 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 as follows:

$$\eta = A\exp[E_\eta*/RT] \qu\quad\quad (2)$$

where E_η* is the activation energy for viscous flow, A is the pre-exponential factor and the other symbols have the usual meanings.

Measurements on activation parameters have been reported by many workers. (Nightingale and Benck 1959; Ganapathy and Ramanujam 1980; Fahimuddin *et al* 1995; Fahimuddin *et al* 1997; Afzal *et al* 1991). This present work involves the

determination of activation energy, change of (i) free energy and (ii) entropy of activation at various temperatures for 1-butane sulfonic acid (Na-salt) and 1-decane sulfonic acid (Na-salt) solutions in mixed and pure solvents.

Materials and Methods

1-Butane and decane sulfonic acids (Na-salt) of analar grade were used. Methanol and water were purified by distillation. Various mixture of solvents were prepared by weight in double distilled water and methanol.

The viscosity measurements were made by using an Ostwals viscometer and the density of the solutions by using a 10 ml capacity specific gravity bottle. To maintain the constant temperature throughout the work, the 'Haake' thermostat (Model KT 33) was used, with an accuracy of ±.0.1°C. Each tabulated viscosity value is a mean of three observations and standard deviations were calculated.

Results and Discussion

The viscosities of various solutions of butane sulfonic acid (Na-salt) and decane sulfonic acid (Na-salt) in pure solvents and mixed solvents, at the four different temperatures are tabulated in Tables 1-2 respectively.

Results show a regular increment in viscosity with the increase of concentration of the solutes at each temperature (298, 303, 308 and 313 K). At all concentrations ranging from 1.2×10^{-3} to 3.5×10^{-3} mol.dm^{-3}, the viscosities of the solutions are found to descrease with the rise of temperature. Results also show

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that viscosities vary with the change of solvent composition. As the methanol content of the solvent is increased, the viscosity increases upto 34% w/w methanol solution and after that, it decreases. This increase in viscosity on the addition of methanol to water is understood to be due to the increase in the degree of solvent structurenedness. As the alcohol content is increased further, the solvent structure is gradually destroyed . (Sandhu *et al* 1983; Herskovits *et al* 1973; Spink *et al* 1970; Arnett *et al* 1965). The values of A and B coefficients are determined from the intercept and slope of the lin-

ear plots of (η_{sp} / $\sqrt{C}$ vs $\sqrt{C}$). The regression method was applied for this purpose and the resulting 'A' and 'B' coefficients are summarized in Table 3.

The A-Values. The negative values of A -coefficient do not have any significance (Seal *et al* 1979; Blokhra and Kumar 1983). In some cases a decrease in 'A'-values have been observed with the rise of temperature. This decrease is due to (i) greater thermal agitation at higher temperatures, and (ii) also due to reduction of attractive forces (Das and Das 1983).

Table 1

Viscosities of decane sulfonic acid (Na-salt) in different solutions

Viscosities 10^3 (Kgm^{-1} S^{-1})							
Composition of solvent (%)							
10^3 [Salt] (mol/dm^3) 0	8.02	16.41	25.17	34.36	54.08	75.85	100.00
Temperature:298 K							
3.5 0.945	1.158	1.230	1.264	1.273	1.20	1.128	0.623
2.7 0.940	1.153	1.227	1.258	1.269	1.198	1.123	0.616
2.2 0.937	1.146	1.219	1.257	1.260	1.190	1.114	0.603
1.8 0.921	1.132	1.211	1.239	1.255	1.186	1.110	0.597
1.5 0.917	1.12	1.208	1.220	1.246	1.179	1.107	0.577
1.2 0.904	1.125	1.196	1.217	1.240	1.169	1.107	0.558
Temperature:303 K							
3.5 0.876	0.920	1.066	1.141	1.199	1.088	0.939	0.635
2.7 0.873	0.911	1.061	1.136	1.191	1.082	0.933	0.610
2.2 0.869	0.907	1.057	1.122	1.181	1.077	0.924	0.604
1.8 0.840	0.900	1.046	1.117	1.167	1.073	0.919	0.581
1.5 0.832	0.892	1.032	1.103	1.153	1.062	0.913	0.556
1.2 0.829	0.883	1.011	1.100	1.141	1.059	0.903	0.533
Temperature:308 K							
3.5 0.797	0.837	0.930	0.983	1.112	1.027	0.863	0.568
2.7 0.782	0.831	0.930	0.977	1.106	1.018	0.860	0.556
2.2 0.781	0.826	0.925	0.964	1.098	1.011	0.851	0.543
1.8 0.779	0.820	0.917	0.956	1.090	1.009	0.854	0.536
1.5 0.763	0.816	0.902	0.944	1.089	1.006	0.826	0.512
1.2 0.754	0.809	0.894	0.936	1.081	1.004	0.812	0.505
Temperature:313 K							
3.5 0.714	0.757	0.851	0.884	0.996	0.912	0.788	0.534
2.7 0.705	0.750	0.848	0.878	0.991	0.910	0.781	0.526
2.2 0.700	0.747	0.841	0.871	0.983	0.908	0.779	0.517
1.8 0.695	0.740	0.836	0.869	0.979	0.901	0.773	0.502
1.5 0.683	0.731	0.826	0.861	0.970	0.893	0.769	0.483
1.2 0.673	0.728	0.822	0.854	0.967	0.888	0.761	0.478

Standard deviations are (0.001±0.004)

Table 2

Viscosities of butane sulfonic acid (Na-salt) in different solutions

Viscosities 10^3 (Kg m^{-1} S^{-1})							
Composition of solvent (%)							
10^{-3} [Salt] (mol/dm3) 0	8.02	16.41	25.17	34.36	54.08	75.85	100.00
Temperature:298 K							
3.5 0.935	1.148	1.226	1.259	1.251	1.198	1.124	0.613
2.7 0.931	1.138	1.218	1.244	1.250	1.188	1.113	0.603
2.2 0.926	1.133	1.218	1.244	1.241	1.188	1.110	0.593
1.8 0.920	1.126	1.203	1.220	1.233	1.173	1.109	0.584
1.5 0.917	1.120	1.196	1.216	1.223	1.171	1.108	0.573
1.2 0.902	1.115	1.189	1.210	1.219	1.164	1.107	0.559
Temperature:303 K							
3.5 0.858	0.899	0.999	1.125	1.166	1.073	0.916	0.598
2.7 0.850	0.891	0.993	1.117	1.160	1.069	0.910	0.586
2.2 0.846	0.883	0.988	1.104	1.158	1.061	0.906	0.573
1.8 0.833	0.878	0.982	1.093	1.146	1.058	0.901	0.564
1.5 0.826	0.873	0.978	1.085	1.124	1.052	0.899	0.544
1.2 0.818	0.869	0.974	1.079	1.116	1.049	0.894	0.527
Temperature:308 K							
3.5 0.774	0.811	0.920	0.978	1.095	0.997	0.838	0.553
2.7 0.769	0.809	0.918	0.971	1.090	0.993	0.826	0.546
.2 0.761	0.801	0.910	0.967	1.087	0.983	0.819	0.539
1.8 0.753	0.798	0.906	0.951	1.078	0.979	0.811	0.521
1.5 0.746	0.793	0.897	0.946	1.072	0.970	0.802	0.518
1.2 0.738	0.789	0.883	0.934	1.068	0.96	0.793	0.496
Temperature:313 K							
3.5 0.695	0.737	0.837	0.864	0.968	0.901	0.772	0.516
2.7 0.692	0.732	0.833	0.859	0.961	0.899	0.769	0.512
2.2 0.668	0.729	0.826	0.854	0.958	0.893	0.762	0.506
1.8 0.682	0.724	0.811	0.847	0.953	0.887	0.758	0.498
1.5 0.674	0.717	0.806	0.843	0.950	0.882	0.753	0.485
1.2 0.667	0.708	0.796	0.839	0.948	0.877	0.748	0.474

Standard deviations are (0.001+0.004)

However, several of the A-values are found to increase with the increase of temperature. This may be due to the interpenetration effect, (cation-cation) and (cation-anion) (Jabeen 1994; Gopal and Singh 1970). which brings ions together.

From Table 3, it is observed that with the increase of methanol content, the 'A' values are found to vary irregularly with solvent composition. This may be due to different degrees of hydration of ions in different solvents (Fahimuddin 1995).

With some exceptions, the 'A'-values have been found to increase with the increase of organic solvent concentration, which is due to the decrease of dielectric constant of the medium and increase in the ion-ion interaction.

The B-Values. The values of 'B'-coefficients calculated are found to increase with the increase of methanol content at all temperatures with some exceptions. Some values are found to be negative which indicate structure breaking effect (Jabeen 1993).

Table 3
'A' and 'B' Coefficients of Jones-Dole equation at different temperatures

Temperature (mol/dm3)		Composition of solvent (%)							
		0	8.02	16.41	25.17	34.36	54.08	75.85	100.00
Decane sulfonic acid (Na-salt)									
298	'A' $(dm^3/mol)^{1/2}$	-14.47	-21.38	-9.49	-13.92	10.93	-10.38	-15.87	-15.02
	'B' (dm^3/mol)	16.46	19.38	8.39	11.83	07.91	9.30	14.41	28.29
303	'A' $(dm^3/mol)^{1/2}$	-0.03	1.34	1.76	0.43	0.96	1.67	2.15	1.34
	'B' (dm^3/mol)	31.27	3.87	6.89	14.51	11.97	1.41	-3.84	18.87
308	'A' $(dm^3/mol)^{1/2}$	1.27	1.37	1.33	-0.26	1.75	2.70	1.52	0.84
	'B' (dm^3/mol)	18.11	14.78	14.31	26.85	05.55	017.10	10.17	26.08
313	'A' $(dm^3/mol)^{1/2}$	3.44	1.07	2.15	2.65	3.33	3.21	3.15	-0.82
	'B' (dm^3/mol)	27.50	12.09	04.54	012.38	-20.43	-20.51	-17.13 Q	68.40
Butane sulfonic acid (Na-salt)									
298	'A' $(dm^3/mol)^{1/2}$	-0.01	-0.32	-0.10	-0.25	-0.13	-0.19	-0.23	-0.61
	'B' (dm^3/mol)	17.24	16.64	23.72	23.92	12.77	15.18	8.50	31.74
303	'A' $(dm^3/mol)^{1/2}$	-0.13	0.39	0.29	-0.50	0.69	2.64	3.36	-1.26
	'B' (dm^3/mol)	24.85	11.34	8.83	25.80	14.93	-16.69	-24.25	76.50
308	'A' $(dm^3/mol)^{1/2}$	-0.86	0.82	0.81	0.32	1.22	1.63	0.85	-0.14
	'B' (dm^3/mol)	58.75	4.90	10.58	17.19	-0.85	-1.29	17.02	40.85
313	'A' $(dm^3/mol)^{1/2}$	-0.11	1.07	0.42	1.76	2.17	2.55	2.30	-0.12
	'B' (dm^3/mol)	21.60	7.10	20.41	-4.31	-11.02	-13.65	-9.17	42.93

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 (Jabeen 1993). 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" (Mandal and Sanyal 1982). 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-coefficient may be always positive irrespective of how it interacts with the solvent (Mandal and Sanyal 1982).

Our data shows that some irregular variation of 'B' values with the composition of mixed solvents is present. This cannot be explained on the basis of dielectric constant of the medium, but may well be due to the different degrees of hydrolysis in different solvents (Ganepathy and Ramanujam 1980).

According to the Stokes equation (Stokes and Mills 1965), the coefficient 'B' can be discussed in terms of various viscosity effects at different solvent compositions and at different temperatures (Iqbal et al 1976; Misra and Das 1978). The equation is given as:

$$\eta^E + \eta^A + \eta^D = \eta^B_0 \qquad \qquad (3)$$

where η^E and η^A are the viscosity increments due to the size and shape of the ion and the orientation of solvent molecules around the ions, respectively. η^D is the viscosity decrement as a result of distortion of solvent structure by the ions. When the coefficient 'B' increases with temperature, this indicates that the viscosity decrease due to solvent structure (η^D) is small and 'B' value is positive (Misra and Das 1978; Das 1981).

When coefficient B decreases, this indicates that solvent distortion (η^D) is large, whereas η^E and η^A are small. This effect is due to the competition between the ionic field and the bulk structure (Misra and Das 1978).

In mixed solvents, the values of coefficient 'B' are found smaller as compared to those 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 the $\eta^E + \eta^A$ term is small and η^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 solvents (Iqbal et al 1976). Because our solutes are of high molecular weights,

Table 4

Activation parameters in different solvent composition at different temperatures

Temp (K) (KJ/mol)	Decane sulfonic acid Solvent		Butanie sulfonic acid (Na-salt)		(Na-salt)	
	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
			(J/Kmol)			
(in pure solvent)						
298	9.16	25.00	9.17	17.6	9.16	20.38
303	9.05	25.00	9.05	17.76	9.05	20.44
313	8.84	24.00	8.84	17.87	8.84	20.45
$E\eta^*$ (KJ/mol) 16.63			14.43		15.24	
(in 54.08% methanol)						
298	10.91	26.10	10.92	22.01	10.91	11.18
303	10.71	26.40	10.72	22.30	10.71	11.65
313	10.63	25.80	10.62	21.87	10.63	11.56
E_η^* (KJ/mol) 18.71			17.47		14.24	
(in pure methanol)						
298	9.97	0.04	9.97	-3.20	9.97	-2.66
303	9.98	0.01	9.98	-3.18	9.98	-2.65
313	10.04	-2.20	10.04	-3.28	10.04	-2.77
E_η^* (KJ/mol) 9.97			9.01		9.17	

the high 'B'-values show that the ion-solvent interaction is not so strong (Ganepathy and Ramanjam 1980; Das et al 1983).

Energies of activation. The relationship between viscosity and energy of activation is given by the following expression:

$$\eta = A \exp [E_\eta^*/RT] \qquad \qquad (4)$$

where E_η^* is the energy of activation. When a graph was plotted between lnη vs 1/T (reciprocal of the absolute temperature), a straight line relation was obtained whose slope gives the value of Eη^*. The values of Eη^* obtained in such a way are given in Table 4. Plots of lnη vs 1/T for decane sulfonic acid (Na-salt) and butane sulfonic acid (Na-salt) are shown in Figs 1 and 2 respectively.

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 (Ganapathy and Ramanujam 1980; Fahimuddin et al 1995). From Table 4, it was conslused that the values of activation energy are found the highest in pure water and then decreases as the alcohol content increases.

Free Energy and Entropy of Activation. The free energy change of activation for viscous flow (ΔG^*) is given by the following expression (Nightingale and Benck 1959).
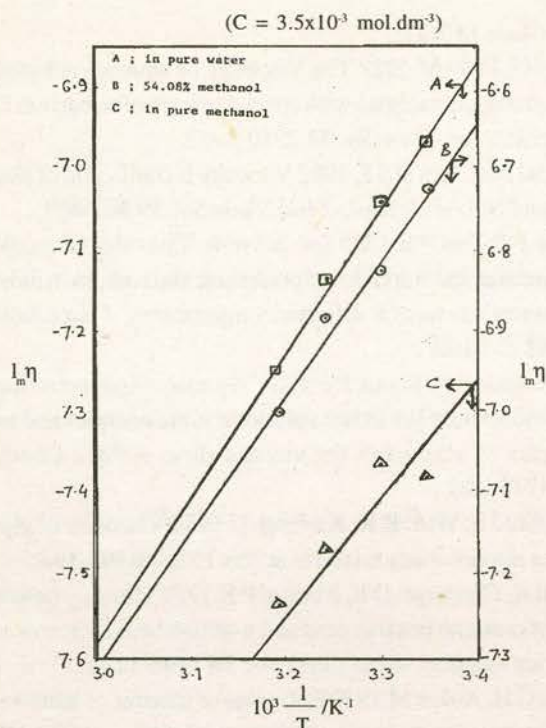
Fig 1. Plots of ln η vs 1/T for decane sulfonic acid (Na-salt_ 3.5×10^{-3} mol.dm^{-3} in different solvents. (a) Pure water (b) 54.08% methanol, (c) Pure methanol.
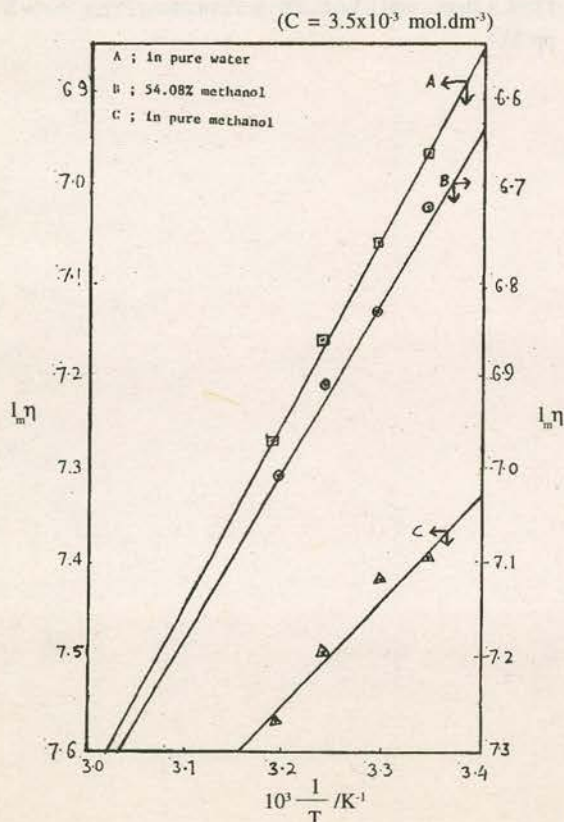

Fig 2. Plots of ln η vs 1/T for butane sulfonic acid (Na-salt_ 3.5×10^{-3} mol.dm^{-3} in different solvents. (a) Pure water, (b) 54.8% (c) Pure methanol.

$$\Delta G^* = RT \ In \frac{\eta v}{hN} \quad \dots (5)$$

Where h is the Planck's constant, N is the Avogadro's number and V is the volume of one mole of solution particles. The values of ΔG^* control the rate of flow in fluid process. The flow process is governed by the ability of a molecule to move into the prepared hole and the readiness with which the holes are prepared in the liquid.

The entropy of activation is given by

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

The energy of activation does not differ appreciably from activation enthalpy (ΔH^*).

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

The values of free energy change of activation and entropy of activation were calculated and are tabulated in Table 4. Data show that in some cases the values of Eη and ΔS^* are found lesser than that of the pure solvent indicating that the solvent structure is broken by the presence of the solutes. In some cases these values are found higher which are attributed to the excess of energy necessary to break the hydrogen bonds in solution. When these values are found equal to that of the solvent, the hydrogen bond breaking of the solvent is not significantly effected by these solutes.

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