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Studies on Acoustical Properties of Diclofanac Sodium Methanol-Water System at 30°C

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Ultrasonic velocity measurements of diclofanac sodium in methanol-water (90 and 70% v/v) mixtures were carried out at 30°C using a single crystal multifrequency interferometer operating at 3 MHz. Various acoustical parameters like β_{ad}, Z, L_f, R, R_A, r, b, π, ϕ_k and S_n were evaluated using U, ρ and η data at 30°C at different concentrations and interpreted in terms of ion-solvent and ion-ion interactions. The drug has structure-breaking tendency at low concentrations (< 0.02–0.01 M) and structure-making tendency at higher concentrations. The solvation is maximum at about 0.04, 0.06 and 0.08 M for pure methanol, 90% and 70% methanol solutions.

INTRODUCTION

The sound velocity is a useful tool for studying ion-solvent interactions and in determining several thermodynamic properties. In recent years, ultrasonic velocity measurements in aqueous and nonaqueous electrolytic solutions is a subject of investigation of ion-ion and ion-solvent interactions[1–6]. With a view to study the interactions occurring in aqueous methanol solutions, an ultrasonic study on diclofanac sodium solutions were investigated at 30°C.

EXPERIMENTAL

Diclofanac sodium is a well-known anti-inflammatory drug. Diclofanac sodium was recrystallized from methanol. Methanol used in the study was fractionally distilled and double distilled water was used for the preparation of 90% and 70% methanol-water (v/v) mixtures. The drug is not completely soluble in other methanol-water mixtures. Solutions of different molarities were prepared by dissolving accurate weights of the drug in a given mixture as well as in pure methanol. Ultrasonic velocity (U), viscosity (η) and density (ρ) of these solutions were measured at 30 ± 0.1°C, using M-82 multifrequency interferometer operating at 3 MHz, suspended level Ubbelohde viscometer and by specific gravity bottle, with an accuracy of ±0.06%, ±0.01% and 0.0001 g/mL, respectively.

RESULTS AND DISCUSSION

Various acoustical parameters like adiabatic compressibility (β_{ad}), acoustic impedance (Z), apparent molar compressibility (ϕ_k), intermolecular free length (L_f), Rao's molar sound function (R), relaxation strength (r), van der Waals constant (b), internal pressure (π), relative association (R_A) and solvation number (S_n) were calculated using U, ρ and η data with the help of standard equations

presented in our earlier papers[7, 8]. The variation of these parameters with concentration (C) is reported in Tables 1 and 2.

TABLE-1
VARIATION OF U, Z, β_{ad}, R_A AND R WITH CONCENTRATION AT 30°C

Conc (M)	$U \times 10^{-5}$ cm/sec	$Z \times 10^{-5}$ g/cm^2	$\beta_{ad} \times 10^{11}$ cm^2/dyne	R_A	R
			Pure MeOH		
0.00	1.0973	0.8654	10.5306	—	1942.416
0.005	1.1001	0.8733	10.4094	1.0056	1966.167
0.01	1.0978	0.8700	10.4698	1.0047	2002.756
0.02	1.1010	0.8749	10.3819	1.0063	2068.246
0.04	1.0972	0.8750	10.4167	1.0112	2194.741
0.06	1.1046	0.8822	10.2614	1.0104	2332.786
0.08	1.1100	0.8923	10.0961	1.0154	2454.092
0.10	1.1135	0.8995	9.9835	1.0192	2576.341
0.15	1.1211	0.9127	9.7731	1.0248	2887.857
0.20	1.1322	0.9306	9.4915	1.0313	3186.161
			90% MeOH		
0.00	1.1851	0.9692	8.7065	—	1837.921
0.005	1.1758	0.9609	8.8510	1.0019	1867.969
0.01	1.1779	0.9639	8.9076	1.0026	1899.975
0.02	1.1790	0.9664	8.7764	1.0041	1963.893
0.04	1.1810	0.9726	8.7064	1.0081	2087.551
0.06	1.1865	0.9796	8.6039	1.0091	2216.580
0.08	1.1906	0.9876	8.5046	1.0128	2337.519
0.10	1.1958	0.9954	8.4014	1.0148	2460.923
0.15	1.2078	1.0135	8.1695	1.0196	2765.062
0.20	1.2194	1.0327	7.9410	1.0258	3055.447
			70% MeOH		
0.00	1.3476	1.1705	6.3399	—	1640.974
0.005	1.3496	1.1713	6.3261	0.9988	1674.428
0.01	1.3524	1.1772	6.2812	1.0010	1701.852
0.02	1.3557	1.1803	6.2493	1.0004	1765.369
0.04	1.3533	1.1819	6.2520	1.0041	1882.697
0.06	1.3494	1.1854	6.2517	1.0110	1991.209
0.08	1.3436	1.1865	6.2729	1.0178	2097.217
0.10	1.3476	1.1927	6.2216	1.0190	2214.323
0.15	1.3593	1.2134	6.0628	1.0225	2494.380
0.20	1.3628	1.2205	6.0122	1.0272	2781.891

TABLE-2
VARIATION OF r, L_f, b, π, S_n and ϕ_k WITH CONCENTRATION AT 30°C.

Conc (M)	r	L_f (Å)	b cm^3	π atmos.	S_n	$\phi_k \times 10^8$ cm^5/dyne/mol
			Pure MeOH			
0.00	0.5297	0.6241	36.6749	1079.121	—	—
0.005	0.5273	0.6205	37.1185	1084.538	1.73	-33.619
0.01	0.5292	0.6223	37.8513	1083.240	6.93	-6.908
0.02	0.5265	0.6197	39.1002	1052.234	5.68	-7.128
0.04	0.5298	0.6207	41.6147	988.795	14.89	-1.539
0.06	0.5234	0.6161	44.2346	925.993	9.51	-2.466
0.08	0.5187	0.6111	46.5536	860.225	7.87	-3.723
0.10	0.5156	0.6077	48.9095	844.170	7.84	-3.775
0.15	0.5090	0.6013	54.9226	742.090	8.60	-3.065
0.20	0.4993	0.5925	60.6225	807.604	8.45	-3.166
			90% MeOH			
0.00	0.4514	0.5675	33.9392	1275.169	—	—
0.005	0.4599	0.5722	34.5874	1269.769	-1.22	33.615
0.01	0.4580	0.5707	35.1826	1255.546	-3.48	12.990
0.02	0.4570	0.5697	36.3965	1212.105	-10.07	5.885
0.04	0.4552	0.5675	38.7493	1111.475	—	1.880
0.06	0.4501	0.5641	41.1699	1061.910	20.92	0.296
0.08	0.4463	0.5609	43.4514	981.086	14.22	-0.688
0.10	0.4414	0.5574	45.7654	939.509	11.79	-1.217
0.15	0.4302	0.5497	51.4686	833.975	10.16	-1.704
0.20	0.4192	0.5420	56.9020	753.415	9.60	-1.988
			70% MeOH			
0.00	0.2906	0.4842	29.1783	1740.211	—	—
0.005	0.2885	0.4837	29.7788	1728.758	9.61	0.4990
0.01	0.2856	0.4820	30.2666	1656.123	4.53	-4.932
0.02	0.2821	0.4808	31.4103	1697.641	5.89	-2.977
0.04	0.2846	0.4809	33.5837	1586.345	12.19	-0.754
0.06	0.2887	0.4809	35.6151	1447.816	18.25	-0.355
0.08	0.2948	0.4817	37.6217	1305.999	32.10	0.157
0.10	0.2906	0.4797	39.7558	1291.957	22.84	-0.068
0.15	0.2782	0.4735	44.8413	1132.256	14.77	-0.700
0.20	0.2745	0.4716	50.1333	1027.805	16.92	-0.302

It is observed graphically that U varied nonlinearly with increasing C. U increased initially, decreased to minimum and then increased linearly with

increasing C. The minimum in U shifted towards higher concentration as methanol content decreased in the mixture and U increased with decreasing methanol content at all concentrations. The minima are observed at about 0.04, 0.06 and 0.08 M respectively for pure methanol, 90% and 70% methanol solutions.

A nonlinear increase in U and Z; and decrease in β_{ad}, L_f, r, π and S_n with C suggest the increase of intermolecular forces with the addition of the salt-forming aggregates of solvent molecules around solute ions[9–12], supports the strong ion-solvent interactions due to which structural arrangement is affected[10]. The increase in β_{ad}, L_f and r with C indicates presence of strong ion-ion interactions in the solutions. The ion-solvent interactions were further supported by linear variation of R and b with C. On examining S_n values, it is evident that at low concentrations, the drug behaves as structure-breaker and at higher concentrations it acts as structure-maker.

From Table-2, it is clear that ϕ_k decreases with C for 90% and it increases for pure methanol while it decreases, reaches minimum and then increases in case of 70% methanol solutions. ϕ_k remains almost constant above 0.08 M drug concentration. The negative ϕ_k values are interpreted in terms of loss of compressibility of solvent due to strong electrostrictive solvation of ions. The positive values of ϕ_k are interpreted in terms of loose attachment of solvent molecules to ions[5, 6, 13].

The decrease in solvation of ions with concentration is reflected in decrease of R_A values (Table-1) while increase in R_A values with C indicates predominant solvation of ions over breaking up of the solvent aggregates: water-water, methanol-methanol, water-methanol on the addition of the drug.

In conclusion, ion-solvent and ion-ion interactions exist in pure as well as nonaqueous system. The drug has structure-making and breaking tendency at high and low concentrations, respectively.

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