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Acoustical Properties of 3-α-Furyl Acrylic Acid in Protic and Aprotic Solvents

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Ultrasonic sound velocities of 3-α-furyl acrylic acid (FAA) solutions in different solvents such as dioxane, ethanol, acetone, benzene and toluene were measured at 30°C using single crystal interfermeter operating at frequency of 1 MHz using sound velocity (U), density (ρ) and viscosity (η) data of FAA solutions in above mentioned solvents. Various acoustical parameters such as adiabatic compressibility (β_{ad}), specific impedance (Z), apparent molar compressibility (ϕ_k), relative association (R_A), solvation number (S_n), intermolecular freepath (L_f), internal pressure (π), Rao's molar sound function (R), molar compressibility (W), the vander Waals constant (b) and the relaxation strength (r) have been calculated. Bachem's and Gucker's laws have been found to be applicable.

INTRODUCTION

Many thermodynamic properties of electrolyte solutions can be determined from sound velocity measurements[1–3]. These properties are more accurate measure of ion-ion and solvent interactions. Various aspects of physico-chemical behaviour of liquid mixtures such as molecular association, deassociation and complex formation can be characterized by isentropic compressibilities knowledge of acoustical properties of any solution provides information about the interactions occuring in the solution[4, 5]. Viscosity, apparent molar volume and ultrasonic velocity data of solutions provides solute-solute and solute-solvent interactions. Present paper describes the evaluation of acoustical parameters on 3-α-furyl acrylic acid (FAA) in protic and aprotic solvents at 30°C.

EXPERIMENTAL

3-α-Furyl acrylic acid (FAA) was synthesized from furfural, malonic acid and pyridine as catalyst[6] and recrystallized from hot water and benzene till m.p. 139–140°C obtained. Solvents used for the study were purified and redistilled prior to use, solutions of different molarities were prepared by dissolving accurately known weights of FAA in each solvent. The density, viscosity and sound velocity measurements were made by using pyknometer, Ubbelhode suspended level viscometer and a single Crystal Mittal Enterprise Multifrequency Interferrometer (M-81) operating at a frequency of 1 MHz at 30°C, respectively.

RESULTS AND DISCUSSION

Different acoustical parameters such as adiabatic compressibility (β_{ad}), specific acoustic impedance (Z), apparent molar compressibility (ϕ_k), relative association (R_A), solvation number[7] (S_n), intermolecular free length[8] (L_f), internal pressure[9] (II), Rao's molar sound function[10] (R), molar compressibility[11] (W), the van der Waals' constant[12] (b) and the relaxation strength[13](r) have been calculated at 30°C using ultrasonic sound velocity (U), density (ρ) and viscosity (η) data (Table-1) of FAA solutions in different profic and aprotic solvents according to following equations:

$$\beta_{ad} = \frac{1}{U^2\rho} \tag{1}$$

$$Z = U\rho \tag{2}$$

$$\phi_k = (\rho_0\beta_{ad} - \rho\beta^0_{ad})\frac{1000}{c\rho_0} + \frac{\beta^0_{ad}M_2}{\rho_0} \tag{3}$$

$$R_A = \rho/\rho_0(U_0/U)^{1/3} \tag{4}$$

where U, U_0 and ρ, ρ_0 are ultrasonic velocities and densities of solution and solvent, respectively; β^0_{ad}, C and M_2 are adiabatic compressibility of pure solvent, concentration (mol/lit) and molecular weight of the solute, respectively;

$$S_n = (m_2/M_1(1 - \beta_{ad}/\beta^0_{ad})([Wo - x]/x) \tag{5}$$

$$L_f = K\beta^{1/2}_{ad} \tag{6}$$

K is Jacobson constant (6.0816×10^4 at 30°C);

$$\pi = bRT\left(\frac{k\eta}{U}\right)^{1/2}\frac{\rho^{2/3}}{M^{7/6}} \tag{7}$$

b = 2 (packing factory); R is gas constant (JK^{-1} mol^{-1}) and k is the constant (4.28×10^9);

$$R = \left(\frac{M}{\rho}\right)U^{1/3} \tag{8}$$

$$W = \left(\frac{M}{\rho}\right)\beta^{-1/7}_{ad} \tag{9}$$

M is the average weight of the solution

$$b = \left(\frac{m}{\rho}\right)\left[1 - \frac{RT}{MU^2}\left(\sqrt{\frac{1 + MU^2}{3RT}} - 1\right)\right] \tag{10}$$

R is the gas constant (erg deg^{-1} $mole^{-1}$);

and

$$r = 1 - (U/U_\alpha)^2 \tag{11}$$

where $U_\alpha = 1.6 \times 10^5$ cm/sec

TABLE-1
SOUND VELOCITY, DENSITY AND VISCOSITY DATA OF FURYL ACRYLIC ACID IN VARIOUS SOLVENT SYSTEMS AT 30°C

Concentration moles/litre	$V \cdot 10^{-5}$ cm sec^{-1}	ρ g cm^{-3}	$\eta \cdot 10^{3}$ poise	$V \cdot 10^{-5}$ cm sec^{-1}	ρ g cm^{-3}	$\eta \cdot 10^{3}$ poise
	Dioxane			Acetone		
0.01	1.3332	1.0284	10.1753	1.1560	0.7868	2.8769
0.02	1.3553	1.0281	9.8794	1.1543	0.7867	2.8808
0.04	1.3373	1.0291	10.1403	1.1590	0.7869	2.8495
0.06	1.3398	1.0314	10.2190	1.1561	0.7889	4.1673
0.08	1.3374	1.0291	10.2800	1.1563	0.7899	4.2069
0.10	1.3395	1.0302	10.5483	1.1562	0.7902	4.1892
0.20	1.3454	1.0341	10.9194	1.1617	0.7969	4.3134
	Ethyl alcohol			Benzene		
0.01	1.1391	0.7887	9.3946	1.2540	0.8699	4.9824
0.02	1.1435	0.7890	9.5871	1.2510	0.8713	4.9550
0.04	1.1390	0.7895	9.4447	1.2520	0.8713	5.1915
0.06	1.1417	0.7904	9.2260	1.2510	0.8720	5.1602
0.08	1.1434	0.7910	9.4986	1.2510	0.8724	5.2217
0.10	1.1407	0.7907	9.2297	1.2500	0.8735	5.1690
0.20	1.1456	0.7969	9.3856	1.2500	0.8771	5.3670
	Toluene					
0.01	1.2920	0.8622	4.6809			
0.02	1.2950	0.8637	4.8531			
0.04	1.2980	0.8638	4.8959			
0.06	1.2980	0.8649	4.7895			
0.08	1.2970	0.8657	4.8761			
0.10	1.2970	0.8665	4.8806			

and are presented in Tables 2 and 3. It has been found graphically (not shown here) that the variation of above mentioned parameters vary almost linearly with concentration (*cf.* Table-2). The values of Z, ϕ_k, R_A, R, W and b increased linearly with concentration in all solvent systems studied. In case of U it is increased in dioxane, acetone and ethanol systems, and decreased in benzene and toluene systems while the values of S_n increased in case of dioxane and ethanol systems but decreased in acetone, benzene and toluene systems. The values of β, L_f, π (except dioxane) and r are decreased linearly with concentration. From Table-2 and 3, it is evident that sudden variation in U and β implies the absence of complex formation which is again supported by linear variation of R, W and b parameters. Again low values of R_A signifier the weak association between the solvent and solute.

TABLE-2
VARIOUS ACOUSTICAL PARAMETERS OF FURYL ACRYLIC ACID IN VARIOUS SOLVENT SYSTEMS AT 30°C

Concentration moles/litre	$\beta \times 10^{11}$	$Z \times 10^{-5}$	$\phi_k \times 10^8$	R_A	E_n	$L_f A^0$
			Dioxane			
0.01	5.471	1.3711	−2.9670	1.0064	1.2759	0.4498
0.02	5.455	1.3728	−1.8338	1.0054	2.3351	0.4492
0.04	5.434	1.3762	−1.2062	1.0061	2.2666	0.4483
0.06	5.401	1.3819	−1.3131	1.0077	2.6784	0.4469
0.08	5.433	1.3763	−0.2461	1.0061	1.1615	0.4483
0.10	5.410	1.3799	−0.3379	1.0066	1.4034	0.4473
0.20	5.342	1.3913	−0.2438	1.0089	1.3961	0.4445
			Acetone			
0.01	9.511	0.9095	−12.7517	1.0016	16.1498	0.5931
0.02	9.540	0.9081	−4.0177	1.0019	6.0314	0.5940
0.04	9.460	0.9120	−3.2235	1.0008	5.8080	0.5915
0.06	9.484	0.9120	−1.5935	1.0107	3.3089	0.5923
0.08	9.469	0.9134	−1.1126	1.0234	2.7378	0.5918
0.10	9.467	0.9136	−0.6083	1.0130	2.2111	0.5917
0.20	9.230	0.9257	−1.0534	1.0303	2.7080	0.5843
			Ethyl Alcohol			
0.01	9.769	0.8986	−1.5610	1.0049	−1.2278	0.6011
0.02	9.693	0.9022	−3.7854	1.0037	6.0407	0.5988
0.04	9.763	0.8992	+0.5593	1.0057	−0.0436	0.6009
0.06	9.706	0.9024	−0.1920	1.0060	1.6256	0.5992
0.08	9.670	0.9044	−0.2585	1.0063	1.9974	0.5980
0.10	9.719	0.9020	+0.6634	1.0067	0.7439	0.5996
0.20	9.562	0.9129	+0.0138	1.0131	1.7089	0.5947
			Benzene			
0.01	7.3100	1.0909	−5.2345	0.9990	9.2979	0.5199
0.02	7.3336	1.0899	−1.4457	1.0014	2.8622	0.5208
0.04	7.3219	1.0911	−0.0012	1.0012	1.8676	0.5204
0.06	7.3277	1.0909	+0.1007	1.0022	1.0966	0.5206
0.08	7.3294	1.0914	+0.2844	1.0027	0.8820	0.5205
0.10	7.3268	1.0919	+0.3922	1.0042	0.6683	0.5206
0.20	7.2968	1.0964	+0.4784	1.0084	0.5477	0.5495
			Toluene			
0.01	6.9480	1.1140	7.8209	1.0013	−8.9271	0.5069
0.02	6.9039	1.1185	1.6576	1.0023	−1.4615	0.5053
0.04	6.8713	1.1212	0.5445	1.0016	+0.3762	0.5041
0.06	6.8625	1.2260	0.4371	1.0029	+0.4487	0.5038
0.08	6.8668	1.1228	0.5771	1.0041	+0.2632	0.5040
0.10	6.8604	1.1238	0.5541	1.0050	+0.2963	0.5037

TABLE-3
VARIOUS ACOUSTICAL PARAMETERS OF FURYL ACRYLIC ACID IN VARIOUS SOLVENT SYSTEMS AT 30°C

Concentration moles/litre	π	R	W	b	r
			Dioxane		
0.01	498.75	4379.90	2507.13	80.6933	0.3057
0.02	490.53	4386.97	2510.79	80.7849	0.3035
0.04	496.04	4391.54	2513.54	80.8377	0.3014
0.06	497.42	4390.64	2513.65	80.7810	0.2988
0.08	497.75	4404.31	2520.85	81.0766	0.3013
0.10	503.28	4408.53	2523.48	81.1213	0.2991
0.20	507.94	4430.10	2536.69	81.4306	0.2929
			Acetone		
0.01	386.98	3602.07	1997.94	68.2898	0.4780
0.02	385.79	3611.81	2003.45	68.5083	0.4795
0.04	380.58	3637.85	2017.58	68.9372	0.4753
0.06	458.41	3647.24	2023.75	69.1748	0.4779
0.08	457.76	3664.50	2033.67	69.5107	0.4777
0.10	453.78	3684.76	2045.04	69.9088	0.4778
0.20	446.80	3765.78	2094.27	71.4113	0.4728
			Ethyl Alcohol		
0.01	923.42	2839.08	1576.45	53.6733	0.4931
0.02	926.35	2854.92	1584.97	53.9230	0.4892
0.04	912.31	2874.34	1596.21	54.3628	0.4932
0.06	892.31	2898.14	1609.50	54.7916	0.4908
0.08	896.23	2922.15	1622.89	55.2375	0.4893
0.10	875.52	2945.96	1636.23	55.7378	0.4917
0.20	844.48	3048.97	1694.96	57.6983	0.4870
			Benzene		
0.01	370.76	4494.31	2519.08	83.9828	0.3857
0.02	369.97	4489.79	2517.40	83.9580	0.3887
0.04	377.32	4502.46	2524.41	84.1822	0.3877
0.06	375.32	4511.15	2529.67	84.3697	0.3887
0.08	376.45	4521.55	2535.66	84.5700	0.3887
0.10	373.82	4526.94	2539.24	84.6962	0.3896
0.20	375.95	4570.10	2564.95	85.5340	0.3896
			Toluene		
0.01	290.45	5399.31	3018.19	100.4679	0.3479
0.02	295.43	5399.06	3018.46	100.3993	0.3449
0.04	295.77	5412.56	3025.73	100.5889	0.3419
0.06	292.16	5415.56	3027.96	100.6491	0.3419
0.08	294.46	5419.02	3030.40	100.7399	0.3429
0.10	294.16	5423.82	3033.49	100.8337	0.3429

The change in ultrasonic sound velocity in solution depends on the intermolecular free length on mixing. On the basis of a model for sound propagation proposed by Eyring and Kinacaid[14], ultrasonic velocity increases with decrease of free length and vice-versa. Intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in liquids and their solutions. In the present investigation, L_f decreases linearly with increasing concentration of FAA and hence an increase of U suggests a structure promoting tendency of the added electrolyte.

Decrease of β_{ad} with increasing concentration of FAA might be due to aggregation of solvent molecules around solute molecules indicating strong, solvent-solute interactions[15]. Similarly, increasing trend of b and decreasing trend of r with concentration supports the solvent solute interactions. Some type of behaviour is also observed in many solutions. Internal pressure is a measure of cohesive forces occurring in a liquid and is sensitive to change of temperature, concentration and external pressure. It is observed that π decreases with increase in concentration of FAA in all cases except dioxane system, indicates decrease of cohesive forces with increase in concentration. The increase in π with concentration in dioxane system probably may be due to predominant H-bonding.

In the present case adiabatic compressibilities of solutions are fitted to Bachem's relation[16].

$$\beta_{ad} = \beta^0_{ad} + AC + BC^{3/2} \quad (12)$$

In order to evaluate the constants A and B and are reported in Table-4. Similarly partial molar compressibilities ϕ_k of solutions are fitted to Gucker's[17] relation.

$$\phi_k = \phi^0_k + S_k\sqrt{C} \quad (13)$$

In order to evaluate the partial molar compressibility at infinite dilution ϕ^0_k and S_k. The values of ϕ^0_k and S_k are also reported in Table-4. The negative values of ϕ^0_k may be due to loss of compressibility of solvent due to strong electrostrictive force in the vicinity of solute causing electrostrictive solvation of ions[18]. The positive values of S_k implies that solute-solute interaction increases with concentration, which is also evident from decrease of S_n with increasing concentration of FAA in acetone, benzene and toluene systems. The positive values of S_n suggest appraciable solvation of the solute which behaves as structure promotor while negative values of S_n indicates the structure breaking tendency of FAA in a particular solvent[19], for a given concentration.

TABLE-4
BACHEM'S CONSTANTS A AND B, ϕ^0_k AND S_k VALUES OF FURYL ACRYLIC ACID IN VARIOUS SOLVENTS AT 30°C

Solvent	$A \times 10^{11}$	$B \times 10^{11}$	$\phi^0_k \times 10^8$	$S_k \times 10^8$
Dioxane	–1.8	3.33	–3.9	8.25
Acetone	–3.8	13.00	–1.8	1.56
Ethyl alcohol	–4.3	5.67	–2.0	4.50
Benzene	–2.2	5.00	–0.8	2.67
Toluene	–1.0	2.29	–0.5	4.00

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