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Molecular Associations in Alcohol−Methyl Methacrylate Mixtures

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Molecular association between alcohols (1-propanol, 1-butanol, *sec*-butanol, *tert*-butanol, 1-pentanol, 1-heptanol, 1-octanol, and 1-decanol) with methyl methacrylate has been studied in *n*-heptane, CCl_4, and benzene at 298 K using FTIR spectroscopic and dielectric methods. The result obtained from both methods indicates only the existence of most likely 1:1 complex formation between the alcohol and the methyl methacrylate in these systems. The alkyl chain length of alcohol and the solvent used plays a significant role on the strength of hydrogen bond (O−H:O═C) determined on the basis of spectral and dielectric parameters.

Introduction

Methyl methacrylate (MMA) is an important monomer for a synthetic polymer poly(methyl methacrylate), which is an excellent substitute for glass and has a wider area of use in dental and industrial applications.[1] Alcohols play an important role in many chemical reactions due to the ability to undergo self-association with manifold internal structures and are in wide use in industry and science as reagents, solvents, and fuels.[2] The solvent effects play an important role in organic reactivity phenomena such as the chemical equilibrium, the rate of chemical reactions, the conversion of the polymerization, etc. The study of molecular association in ternary mixtures provides useful information about the behavior of different liquids and their functional groups. This information is very useful in the development of theories for the liquid state and predictive methods. Furthermore, the study of spectral and dielectric properties of liquid mixtures containing alcohol with acrylic ester in nonpolar solvent is expected to provide useful and vital process parameters for efficient design of transesterification processes of industrial interest.[3] Based on the above said important industrial applications of the mixtures of alcohols with MMA in nonpolar solvents, an attempt has been made in the present investigation to understand the influence of alkyl chain length of alcohol and solvent used on the strength of hydrogen bond formation between the alcohol and methyl methacrylate.

Experimental Section

Materials. All chemicals used were of analytical grade and were further purified by the methods described earlier.[4,5−14]

Methods. (a) FTIR Measurements. A Nicolet Avatar 360 FTIR spectrometer with a resolution of ± 1 cm^{-1} was used. Spectra were recorded at room temperature (298 K) in the region of 4000 to 400 cm^{-1}, and NaCl cell of path length 0.1 mm was used. The spectrometer possesses autoalign energy optimization and dynamically aligned interferometer. It is fitted with a KBr beam splitter, a DTGS-Detector and Everlgo mid-IR source. A baseline correction was made for the spectra recorded.

For ternary mixtures, the proton acceptor (MMA) concentration is fixed at 0.05 $mol \cdot L^{-1}$ and proton donor (alcohol) concentration varies from (0.03 to 0.15) $mol \cdot L^{-1}$. The free O−H band intensity and half-bandwidth increases with increasing alcohol concentration, but at the same time the reverse trend is observed for the carbonyl absorption band. This observation indicates that there is 1:1 complex formation between free hydroxyl group of alcohol and carbonyl group of MMA (i.e., O−H···O═C).[5−14]

(b) Calculation of the Equilibrium Constant and Free Energy Change. Utilizing the method of Nash,[15] the formation constant (*K*) for the 1:1 complex is determined by plotting a graph between $Y = [A]^{-1}$ and $X = (1 - (a/a_0))^{-1}$, where *a* and a_0 are the absorbances of the carbonyl band of MMA in the presence and absence of alcohol, respectively. The intercept of the graph in the ordinate yields the negative value of *K*. The free energy change ($\Delta G°$) of the systems was calculated using the following relation:[16]

$$\Delta G° = -RT \ln K \tag{1}$$

where *R*, *T*, and *K* represent the universal gas constant, absolute temperature, and formation constant of the relative systems, respectively.

(c) Dielectric Measurements. The measurement of dielectric constant (ϵ') and dielectric loss (ϵ'') were carried out in the X-band microwave frequency of 9.84 GHz. The experimental setup and the procedure employed were the same as reported by Aggarwal et al.[17] The temperature of all the measurements was maintained at 25 ± 0.1 °C using a water circulating thermostat.

Theory

According to the method of Higasi et al.,[18] the individual relaxation time $\tau_{(1)}$ is described by

$$\tau_{(1)} = a''/\omega(a' - a_\infty) \tag{2}$$

while the overall dielectric relaxation $\tau_{(2)}$ is given by

$$\tau_{(2)} = (a_0 - a')a''/\omega a'' \tag{3}$$

and the most probable relaxation time is given by

$$\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}} \tag{4}$$

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Table 1. Infrared Data for Alcohols with MMA in Nonpolar Solvents at 298 K

alcohol	ν_{OH} free/cm^{-1}			$\nu_{C=O}$/cm^{-1}		
	n-heptane	CCl_4	benzene	*n*-heptane	CCl_4	benzene
1-propanol	3648	3637	3608	1731	1726	1724
1-butanol	3648	3637	3608	1731	1726	1724
sec-butanol	3635	3630	3606	1731	1726	1724
tert-butanol	3620	3615	3603	1731	1726	1724
1-pentanol	3648	3637	3608	1731	1726	1724
1-heptanol	3648	3637	3608	1731	1726	1724
1-octanol	3648	3637	3608	1731	1726	1724
1-decanol	3648	3637	3608	1731	1726	1724

Table 2. Formation Constant (K) and Free Energy Change ($\Delta G°$) for Alcohols with MMA in Different Solvent Systems at 298 K

alcohol	K/L·mol^{-1}			$-(\Delta G°)$/k·cal·mol^{-1}		
	n-heptane	CCl_4	benzene	*n*-heptane	CCl_4	benzene
1-propanol	0.70	4.59	9.5	−0.21	0.89	1.34
1-butanol	1.21	5.42	10.3	0.11	1.00	1.39
sec-butanol	0.9	4.20	9.8	−0.06	0.85	1.35
tert-butanol	0.2	2.81	8.4	−0.95	0.61	1.26
1-pentanol	1.71	6.07	11.6	0.32	1.06	1.46
1-heptanol	3.57	8.12	13.56	0.75	1.24	1.54
1-octanol	4.13	9.30	14.28	0.84	1.32	1.57
1-decanol	6.17	11.15	15.63	1.07	1.42	1.62

where ω is the angular frequency; a_0, a', a'', and a_∞ are defined by the following:

$$\epsilon_0 = \epsilon_{01} + a_0 w_2$$

$$\epsilon' = \epsilon'_1 + a' w_2$$

$$\epsilon'' = a'' w_2$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty \mathrm{w}_2 \tag{5}$$

in which subscript 1 refers to the pure solvent, 2 refers to the solute, 0 refers to the static frequency, and ∞ refers to the infinite or optical frequency measurements, and w_2 is the weight fraction of the solute.

The molar free energy of activation, for both dielectric relaxation ΔF_τ as well as the viscous flow processes ΔF_η have been evaluated using the equations given by Eyring and coworkers.[19]

$$\tau = (h/kT)\,\exp(\Delta F_\tau/\mathrm{RT}) \tag{6}$$

$$\eta = (Nh/V)\,\exp(\Delta F_\eta/RT) \tag{7}$$

where h is Plank's constant, k is Boltzmann constant, N is Avogadro's number, and V is the molar volume.

Results and Discussion

FTIR Studies. The observed infrared spectral data (The frequency of the free monomeric O−H ν_{OH} "free" and the carbonyl absorption $\nu_{C=O}$ bands) of alcohols (1-propanol, 1-butanol, *sec*-butanol, *tert*-butanol, 1-pentanol, 1-heptanol, 1-octanol, and 1-decanol) with MM in *n*-heptane, CCl_4, and benzene are provided in Table 1. The frequency of the free monomeric O−H band of alcohol decreases in the order: 1-butanol > *sec*-butanol > *tert*-butanol. Richards[20] and Barrow[21] have reported that these frequency shifts must arise from inductive or mesomeric shifts in the molecule. The frequency falls on passing to secondary alcohols and tertiary alcohols because of the increasing numbers of methyl groups available to take part in the effect (Table 1). Hydroxyl frequencies seem thus to decrease with increasing positive charge on the oxygen atom.[22]

Table 3. Values of Dielectric Constant (ϵ') and Dielectric Loss (ϵ'') for Alcohols with MMA in Nonpolar Solvents at 298 K

alcohols	molar ratio ester:alc	ϵ'			ϵ''		
		C_6H_{14}	CCl_4	C_6H_6	C_6H_{14}	CCl_4	C_6H_6
1-propanol	0:1	2.1954	2.4076	2.5053	0.0842	0.1115	0.1325
	1:3	2.3642	2.5927	2.6653	0.1556	0.2634	0.2846
	1:2	2.3763	2.6165	2.6847	0.1764	0.2848	0.3064
	1:1	2.3817	2.6208	2.6911	0.2075	0.3179	0.3359
	2:1	2.3765	2.6141	2.6841	0.1767	0.2897	0.3097
	3:1	2.3651	2.5914	2.6614	0.1563	0.2646	0.2846
	1:0	2.0944	2.3696	2.4389	0.0323	0.0625	0.0723
1-butanol	0:1	2.1716	2.3807	2.4648	0.0774	0.0958	0.1257
	1:3	2.3375	2.5543	2.6115	0.1374	0.2359	0.2637
	1:2	2.3406	2.5646	2.6204	0.1519	0.2638	0.2843
	1:1	2.356	2.5801	2.6303	0.1846	0.2905	0.3285
	2:1	2.3411	2.5643	2.6211	0.1523	0.2619	0.2846
	3:1	2.3382	2.5526	2.6123	0.1381	0.2348	0.2645
	1:0	2.0944	2.3696	2.4389	0.0323	0.0625	0.0723
sec-butanol	0:1	2.1687	2.3698	2.4595	0.0605	0.0705	0.1008
	1:3	2.3288	2.5341	2.5997	0.1136	0.2028	0.2304
	1:2	2.3374	2.5496	2.6085	0.1317	0.2291	0.2506
	1:1	2.3482	2.5579	2.6104	0.1575	0.2518	0.2768
	2:1	2.3365	2.5462	2.6098	0.1324	0.2296	0.2511
	3:1	2.3293	2.5354	2.5997	0.1139	0.2043	0.2302
	1:0	2.0944	2.3696	2.4389	0.0323	0.0625	0.0723
tert-butanol	0:1	2.1585	2.3488	2.4229	0.0407	0.0487	0.0574
	1:3	2.3093	2.5292	2.5874	0.0927	0.1725	0.1812
	1:2	2.3196	2.5186	2.5997	0.1005	0.1813	0.2054
	1:1	2.3294	2.5324	2.6005	0.1309	0.2036	0.2349
	2:1	2.3189	2.5192	2.5993	0.1016	0.1821	0.2057
	3:1	2.3085	2.5284	2.5849	0.0913	0.1733	0.1833
	1:0	2.0944	2.3696	2.4389	0.0323	0.0625	0.0723
1-pentanol	0:1	2.1659	2.3689	2.4482	0.0663	0.0864	0.1075
	1:3	2.2693	2.5212	2.5803	0.1074	0.2125	0.2497
	1:2	2.2774	2.5412	2.5904	0.1206	0.2422	0.2689
	1:1	2.2875	2.5554	2.6019	0.1582	0.2709	0.3087
	2:1	2.2782	2.5418	2.5901	0.1215	0.2435	0.2693
	3:1	2.2695	2.5215	2.5809	0.1087	0.2117	0.2502
	1:0	2.0944	2.3696	2.4389	0.0323	0.0625	0.0723
1-heptanol	0:1	2.1248	2.3442	2.4106	0.0396	0.0653	0.0829
	1:3	2.2244	2.4775	2.5217	0.0825	0.1822	0.2138
	1:2	2.2387	2.4946	2.5372	0.1013	0.2044	0.2349
	1:1	2.2404	2.5108	2.5405	0.1194	0.2306	0.2692
	2:1	2.2395	2.4957	2.5377	0.1022	0.2026	0.2354
	3:1	2.2238	2.4793	2.5221	0.0836	0.1835	0.2143
	1:0	2.0944	2.3696	2.4389	0.0323	0.0625	0.0723
1-octanol	0:1	2.1052	2.3273	2.3854	0.0179	0.0429	0.0602
	1:3	2.1985	2.4489	2.4859	0.0655	0.1504	0.1827
	1:2	2.2124	2.4607	2.4984	0.0802	0.1711	0.2039
	1:1	2.2226	2.4874	2.5096	0.0975	0.2019	0.2375
	2:1	2.2125	2.4623	2.4989	0.0811	0.1735	0.2042
	3:1	2.1968	2.4491	2.4861	0.0648	0.1516	0.1834
	1:0	2.0944	2.3696	2.4389	0.0323	0.0625	0.0723
1-decanol	0:1	2.0968	2.3133	2.3518	0.0009	0.0234	0.0245
	1:3	2.1784	2.4296	2.4402	0.0435	0.1289	0.1486
	1:2	2.1865	2.4469	2.4537	0.0548	0.1574	0.1728
	1:1	2.1997	2.4603	2.4704	0.0793	0.1723	0.2075
	2:1	2.1859	2.4462	2.4541	0.0538	0.1568	0.1732
	3:1	2.1787	2.4274	2.4408	0.0429	0.1263	0.1491
	1:0	2.0944	2.3696	2.4389	0.0323	0.0625	0.0723

From the Table 1, it is evident that *n*-heptane has a higher monomeric OH absorption frequency than CCl_4 and benzene for all the systems. This is due to the specific solute−solvent association that exists for CCl_4 and benzene systems. No such association is possible in the *n*-heptane systems.[5−10] This result fully confirms the Bellamy and Williams[23] results that the solvent shifts of stretching vibrations frequency are primarily due to local association effects with solvent molecules.

The formation constant K and the free energy change $\Delta G°$ values for all the systems are provided in Table 2. The K and

Table 4. Values of Dielectric Relaxation Time and Activation Energies (ΔF_τ and ΔF_η) for Alcohols with MMA in Nonpolar Solvents at 298 K

		relaxation time/ps														
	molar ratio	$\tau_{(1)}$			$\tau_{(2)}$			$\tau_{(0)}$			ΔF_τ/kJ·mol^{-1}			ΔF_η/kJ·mol^{-1}		
alcohol	ester:alc	C_6H_{14}	CCl_4	C_6H_6	C_6H_{14}	CCl_4	C_6H_6	C_6H_{14}	CCl_4	C_6H_6	C_6H_{14}	CCl_4	C_6H_6	C_6H_{14}	CCl_4	C_6H_6
1-propanol	0:1	8.97	13.73	11.39	12.45	17.72	15.36	10.57	15.60	13.22	10.77	11.65	11.29	12.52	13.32	12.98
	1:3	11.18	15.65	13.76	14.18	19.39	17.25	12.59	17.42	15.41	11.09	11.87	11.58	13.08	13.54	13.24
	1:2	12.16	16.06	14.18	17.42	23.47	20.48	14.55	19.42	17.04	11.60	12.34	12.01	13.35	14.03	13.65
	1:1	14.08	18.27	16.01	24.74	28.46	27.38	18.67	22.80	20.94	12.47	12.82	12.72	14.13	14.56	14.26
	2:1	12.18	16.47	14.42	17.45	23.14	20.01	14.58	19.52	16.99	11.61	12.31	11.95	13.37	14.00	13.60
	3:1	11.22	15.84	13.83	14.28	19.36	17.41	12.66	17.52	15.51	11.11	11.87	11.60	13.10	13.58	13.27
	1:0	5.42	8.87	7.83	8.52	12.91	10.88	6.80	10.70	9.23	9.83	10.84	10.46	11.56	12.57	12.19
1-butanol	0:1	10.33	15.63	13.84	14.12	19.60	17.14	12.08	17.50	15.40	11.08	11.90	11.56	12.95	13.65	13.26
	1:3	11.23	17.33	15.27	16.75	21.50	19.83	13.72	19.30	17.40	11.51	12.13	11.93	13.21	13.82	13.67
	1:2	12.34	18.67	16.25	19.55	25.53	22.18	15.54	21.83	18.98	11.89	12.55	12.20	13.56	14.29	13.94
	1:1	14.11	20.05	18.48	26.92	30.21	29.55	19.49	24.62	23.37	12.68	12.97	12.91	14.35	14.75	14.59
	2:1	12.38	18.51	16.26	19.68	25.97	22.15	15.61	21.93	18.98	11.91	12.59	12.20	13.58	14.32	13.96
	3:1	11.31	17.41	15.33	16.89	21.65	19.86	13.82	19.41	17.45	11.53	12.14	11.93	13.26	13.85	13.69
	1:0	5.42	8.87	7.83	8.52	12.91	10.88	6.80	10.70	9.23	9.83	10.84	10.46	11.56	12.57	12.19
sec-butanol	0:1	8.77	13.42	11.78	12.11	17.63	15.45	10.31	15.38	13.49	10.70	11.63	11.31	12.49	13.36	13.05
	1:3	9.78	15.26	13.93	15.24	19.88	17.26	12.21	17.42	15.51	11.27	11.93	11.58	12.94	13.45	13.35
	1:2	10.96	16.19	14.98	17.49	23.70	20.48	13.84	19.58	17.52	11.61	12.37	12.01	13.37	13.98	13.59
	1:1	12.57	18.37	16.71	23.63	28.27	26.23	17.23	22.79	20.94	12.36	12.80	12.62	14.08	14.43	14.28
	2:1	11.07	16.49	14.98	17.63	23.88	20.50	13.97	19.84	17.53	11.63	12.39	12.01	13.40	13.98	13.62
	3:1	9.81	15.33	13.96	15.39	19.94	17.36	12.29	17.48	15.57	11.30	11.94	11.60	13.01	13.49	13.38
	1:0	5.42	8.87	7.83	8.52	12.91	10.88	6.80	10.70	9.23	9.83	10.84	10.46	11.56	12.57	12.19
tert-butanol	0:1	6.57	12.75	9.23	10.79	15.60	13.24	8.42	14.10	11.05	10.42	11.33	10.92	12.13	13.02	12.67
	1:3	8.95	13.43	11.51	13.04	17.85	15.79	10.80	15.48	13.48	10.89	11.66	11.36	12.57	13.27	13.16
	1:2	9.23	14.99	12.70	15.49	21.98	17.82	11.96	18.15	15.04	11.31	12.18	11.66	13.16	13.74	13.38
	1:1	11.52	16.75	14.76	21.19	25.35	24.18	15.63	20.61	18.89	12.09	12.53	12.42	13.89	14.28	14.01
	2:1	9.37	14.99	12.80	15.67	21.75	17.97	12.12	18.06	15.17	11.34	12.15	11.68	13.18	13.70	13.42
	3:1	8.89	13.62	11.78	13.54	17.98	15.90	10.97	15.65	13.68	10.98	11.68	11.38	12.62	13.31	13.19
	1:0	5.42	8.87	7.83	8.52	12.91	10.88	6.80	10.70	9.23	9.83	10.84	10.46	11.56	12.57	12.19
1-pentanol	0:1	11.92	17.90	14.23	16.25	21.87	19.70	13.92	19.79	16.74	11.43	12.17	11.91	13.26	13.89	13.66
	1:3	13.32	19.41	16.36	18.43	23.86	21.88	15.66	21.52	18.92	11.74	12.38	12.17	13.46	14.01	13.91
	1:2	14.33	20.39	17.28	22.30	27.18	24.01	17.88	23.54	20.37	12.22	12.71	12.40	13.95	14.46	14.23
	1:1	17.73	22.07	19.25	28.33	32.17	31.54	22.41	26.64	24.64	12.81	13.12	13.07	14.51	14.89	14.86
	2:1	14.42	20.38	17.36	22.46	27.09	24.03	17.99	23.49	20.43	12.23	12.70	12.40	13.98	14.43	14.25
	3:1	13.44	19.42	16.39	18.60	23.98	21.81	15.81	21.58	18.91	11.77	12.40	12.16	13.69	14.05	13.89
	1:0	5.42	8.87	7.83	8.52	12.91	10.88	6.80	10.70	9.23	9.83	10.84	10.46	11.56	12.57	12.19
1-heptanol	0:1	13.93	20.57	16.11	20.08	25.68	22.39	16.73	22.98	18.99	11.96	12.57	12.23	13.68	14.21	13.98
	1:3	15.58	22.84	18.24	21.35	27.16	24.85	18.24	24.90	21.29	12.11	12.70	12.48	13.84	14.42	14.18
	1:2	16.89	23.58	19.12	25.32	32.49	28.14	20.68	27.68	23.19	12.53	13.15	12.79	14.26	14.81	14.46
	1:1	19.86	25.03	21.80	34.07	36.74	37.16	26.01	30.32	28.46	13.27	13.45	13.48	14.95	15.07	15.19
	2:1	16.95	23.27	19.16	25.31	32.26	28.16	20.72	27.40	23.23	12.53	13.13	12.79	14.28	14.78	14.48
	3:1	15.76	22.78	18.28	21.41	27.29	24.85	18.37	24.94	21.31	12.12	12.72	12.48	13.87	14.46	14.23
	1:0	5.42	8.87	7.83	8.52	12.91	10.88	6.80	10.70	9.23	9.83	10.84	10.46	11.56	12.57	12.19
1-octanol	0:1	16.89	22.43	17.65	23.96	28.89	26.79	20.12	25.46	21.74	12.39	12.86	12.67	14.04	14.58	14.35
	1:3	17.67	24.51	19.31	26.48	30.75	29.62	21.63	27.46	23.91	12.64	13.01	12.92	14.33	14.84	14.59
	1:2	18.53	25.87	20.28	29.69	35.81	32.07	23.45	30.43	25.50	12.93	13.39	13.12	14.62	15.02	14.87
	1:1	20.23	26.43	22.58	36.63	40.51	39.59	27.22	32.72	29.90	13.45	13.70	13.64	15.18	15.46	15.42
	2:1	18.94	25.97	20.39	29.80	35.29	32.04	23.76	30.28	25.56	12.93	13.35	13.11	14.66	14.98	14.85
	3:1	17.88	24.54	19.40	26.84	30.75	29.56	21.91	27.47	23.95	12.68	13.01	12.91	14.36	14.86	14.56
	1:0	5.42	8.87	7.83	8.52	12.91	10.88	6.80	10.70	9.23	9.83	10.84	10.46	11.56	12.57	12.19
1-decanol	0:1	19.00	25.83	20.28	28.14	31.68	29.50	23.12	28.60	24.46	12.79	13.09	12.91	14.51	14.84	14.69
	1:3	19.69	26.35	22.50	31.87	33.79	35.76	25.05	29.84	28.37	13.10	13.25	13.39	14.89	14.96	15.08
	1:2	21.22	27.51	23.96	34.54	37.39	38.67	27.08	32.07	30.44	13.30	13.50	13.58	15.07	15.27	15.26
	1:1	23.91	29.60	25.71	39.33	45.68	42.56	30.67	36.77	33.08	13.62	13.99	13.82	15.36	15.68	15.53
	2:1	21.38	27.24	23.99	34.78	37.90	38.58	27.27	32.13	30.42	13.32	13.53	13.57	15.11	15.32	15.23
	3:1	19.90	26.20	22.68	31.92	33.85	36.30	25.21	29.78	28.69	13.10	13.25	13.42	15.92	14.99	15.12
	1:0	5.42	8.87	7.83	8.52	12.91	10.88	6.80	10.70	9.23	9.83	10.84	10.46	11.56	12.57	12.19

$\Delta G°$ values for 1-propanol with MMA are found to be lesser than those for all other primary alcohols with MMA, which reveal that the proton-donating ability of 1-propanol is lesser than that of all other primary alcohols. This result may suggest that the higher chain alcohols have a higher proton-donating ability than that of lower chain alcohols or that the proton-donating ability of alcohol increases with an increasing number of carbons in the alkyl chain length.[11−13]

It is evident from Table 2 that the primary alcohol (1-butanol) has higher K values than that for the secondary alcohol (*sec*-butanol) and tertiary alcohol (*tert*-butanol) for all the solvents studied. It may be may be due to the lowering of the electrostatic energy in the order primary > secondary > tertiary. From other chemical consideration, it is known that the proton-donor character of alcohols diminishes as we pass from primary to tertiary through secondary alcohols.[10,14]

The K values for the mixtures of alcohols with MMA in benzene are higher than that in n-heptane. This may be due to solute−solvent interactions that exist between the OH group of alcohol and the π-electron of benzene that will promote the proton-donating ability of alcohols, which gives rise to the higher K values in benzene. No such interaction is possible in the *n*-heptane systems, which gives rise to the lower *K* values in *n*-heptane.[5−10]

Dielectric Studies. The values of dielectric constant (ϵ'), dielectric loss (ϵ''), relaxation time $\tau_{(1)}$ due the individual rotation of the molecule, relaxation time $\tau_{(2)}$ due the whole or overall rotation of the molecule, the most probable relaxation time $\tau_{(0)}$, activation energy ΔF_τ due to dielectric relaxation process, and activation energy ΔF_η due to viscous flow of proton donors (1-propanol, 1-butanol, *sec*-butanol, *tert*-butanol, 1-pentanol, 1-heptanol, 1-octanol, and 1-decanol) with proton acceptor (MMA) in *n*-heptane, CCl_4, and benzene at 298 K have been provided in Tables 3 and 4. A perusal of Table 3 shows that it is noticed that the value of ϵ' and ϵ'' is found to be decreased by increasing the number of carbon atoms in the chain for all the systems studied. This trend could be attributed to the decrease in the number of dipoles in the complex, which may lead to a decrease in the molar volume of the rotated molecule.[24,25]

It is also evident from Table 4 that the values of $\tau_{(2)}$ are significantly higher than $\tau_{(1)}$ and $\tau_{(0)}$ for all the systems. Higher values of $\tau_{(2)}$ indicate that the contribution of intermolecular or overall molecular relaxation is larger in comparison to intramolecular or individual molecular relaxation in the systems.[25]

In the present systems studied, it has been observed that the relaxation time of ternary mixtures (alcohols with esters in solvent) is much greater than the binary mixture (alcohols with solvent or esters with solvent). This result indicates that there is a hydrogen bond formation between the hydrogen atom in the O−H group of alcohol and the oxygen atom in the C═O group of ester.

It is seen from Table 4 that the value of relaxation times ($\tau_{(1)}$, $\tau_{(2)}$, and $\tau_{(0)}$) increases with increasing chain length of both the alcohols and esters and offers hindrance to the rotation of the molecule. The increase in relaxation time may be due to two effects: (i) the increase of viscosity as the chain length increases and (ii) the increase of molecular size as the chain length increases.[25]

From the Table 4, the value relaxation time is greatest for 1-butanol and least for *tert*-butanol. This indicates that solute−solute association is on the order of 1-butanol > *sec*-butanol > *tert*-butanol. A large difference in relaxation time values in this molecule is due to the large difference in the two mechanisms (viz., the end-over-end rotation and the O−H group rotation as compared to *tert*-butyl alcohol). The increase in relaxation time may be due to the increase in effective radius of the rotating unit. The value of relaxation time for *sec*-butyl alcohol is greater than that of *tert*-butyl alcohol. This may be due to the fact that the CH_3 group attached to the same carbon atom as which the O−H group is attached. This increases the size of the molecule and may cause hindrance to the group rotation, which may give rise to increased relaxation time.[26]

From the Table 4, it is seen that the values of relaxation time in CCl_4 are higher than benzene and *n*-heptane, which shows direct proportionality with the nature of solvent used. Carbon tetrachloride is a symmetrical and a nonpolar molecule. But each chlorine atom in this molecule is highly polarizable due to its three lone pairs of electrons; therefore, it can function as an electron donor. There is, therefore, a possibility of association between the solute and the carbon tetrachloride molecule. The potential hydrogen-bonding nature of the carbon tetrachloride molecule may therefore contribute to increasing the relaxation time.[27]

It is evident from our data that the value of molar free energy of activation for viscous flow is greater than the free energy of activation for all the systems studied. This is in agreement with the fact that the process of viscous flow, which involves both rotational and translational forms of motion, faced greater interference from neighbors than dielectric relaxation, which takes place by rotation only.[25,28,29]

By a critical examination of Table 4, it is noticed that the energy value parameters ΔF_τ and ΔF_η are somewhat larger in CCl_4 solution. One may say from this that CCl_4 hinders the rotation of the solute dipoles in this solution much more effectively than benzene and *n*-heptane. Similar conclusions were also drawn by Madan.[30]

Conclusions

Comparative studies of molecular association between alcohols (1-propanol, 1-butanol, *sec*-butanol, *tert*-butanol, 1-pentanol, 1-heptanol, 1-octanol, and 1-decanol) have been studied in dilute solution of *n*-heptane, carbon tetrachloride, and benzene using FTIR spectroscopic and dielectric methods at 298 K. Both the methods support the following conclusions:

(i) only the existence of most likely the 1:1 complex formation between the alcohol and methyl methacrylate;

(ii) the proton-donating ability or tendency of complex formation of alcohols increases with alkyl chain length;

(iii) the primary alcohols have relatively more tendency of complex formation than the secondary and tertiary alcohols;

(iv) finally, the nature of solvents plays an important role in the determination of hydrogen bonding (O−H:O═C) of the above systems studied.

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