[Article]

Dielectric Relaxation Properties of Alcohols and Acrylic Esters

DHARMALINGAM K.[1,*]   RAMACHANDRAN K.[1]   SIVAGURUNATHAN P.[1]   KALAMSE G. M.[2]

(*[1]Department of Physics, Annamalai University, Annamalai Nagar-608002, Tamilnadu, India;*
[2]Postgraduate Department of Physics, Science College, Nanded-431605, Maharashtra, India)

Abstract: Dielectric relaxation of alcohols (1-propanol, 1-butanol, sec-butanol, tert-butanol, 1-pentanol, 1-heptanol, 1-octanol, and 1-decanol) with acrylic esters (methyl methacrylate, ethyl methacrylate, and butyl methacrylate) at 9.84 GHz were studied in *n*-heptane at 298 K. The result showed that 1:1 complex was predominant in these systems. The relaxation time showed a linear dependence with alkyl chain length of both alcohols and acrylic esters, but the dielectric constant showed a reverse trend. A comparative study of the free energy of activation for the dielectric relaxation and viscous flow suggested that a greater interference by neighboring atom was observed in the process of viscous flow than in dielectric relaxation, as the latter involved rotational form of motion, whereas the viscous flow involved both rotational and translational forms of motion.

Key Words: Dielectric relaxation;   Alcohols;   Acrylic esters;   Hydrogen bonding;   Solvent effects

Acrylic esters are industrially important chemicals, which are used as adhesives, paints, binders, and emulsifiers[1]. Alcohols play an important role in many chemical reactions because of their ability to undergo self-association with manifold internal structures and are widely used in industries and laboratories as reagents, solvents, and fuels. Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. The dielectric investigation of hydrogen-bonded compounds in non-polar solvent provides valuable information regarding complex formation of the compounds with the ions in solution. Recently our research group[2−9] has investigated the formation of complex of acrylic esters with proton donors (alcohols) in non-polar solvents using FTIR spectroscopic method. The study of the H bonds of the type O—H···O═C is of considerable importance as it is related to the study of biopolymers. Thus, the study and knowledge of the dielectric properties of the ternary mixtures of acrylic esters with polar associating liquids (alcohols) in non-polar solvents are believed to provide useful and vital process parameters for an efficient design of the transesterification processes of industrial interest. Considering both the industrial and scientific interests, an attempt has been made in the present work to study the hydrogen bonding between the free hydroxyl groups of alcohol and the carbonyl groups of ester using the dielectric method. This study is believed to provide better understanding of the nature of the molecular orientation processes.

1   Experimental

The alkyl (methyl, ethyl, and butyl) methacrylate monomers (>99% pure) used in this investigation were purchased from Aldrich, and were used without further purification. AR grade alcohols and benzene (>99.5% pure) were purified using standard methods[10]. The physical parameters of all the chemicals used in this work have been verified against their literature values.

The measurements of the dielectric constant (ε') and the 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 Aggarval *et al.*[11]. The values of ε' and ε'' thus obtained were accurate within ±1% and ±5%, respectively. The static dielectric constants (ε_0) were measured using the heterodyne beat method at 298 K using a commercial instrument, Dipolemeter DM 01, which was supplied by Wissenschaijftlich Technische Werkstatter, Germany, was operated at 220 V. The error in the measurement of ε_0 was less than ±0.5%. The refractive indices were measured using an Abbe′s refractometer with an accuracy of ±0.0005. The percentage of deviation in the measurement of the refractive index is about ±0.02% . The viscosities were measured using Oswald′s viscometer. The temperatures of all the measurements were maintained at (298.0±0.1) K using a water-circulating thermostat.

The proton donors (alcohols) and acceptors (methacrylates) under study were separately dissolved at the same molar concentration in the solvent benzene and their dielectric constants were measured separately. The two solutions were then mixed in different proportions but their total concentration was kept constant. And then, the resultant solution was subjected to the dielectric constant measurements. As the maximum deviation of the dielectric constant for all the systems studied occurs at an equimolar ratio of the solutes, it is presumed that the deviation is only attributed to the formation of 1:1 complexes.

2   Evaluation of the dielectric parameters

According to Higasi *et al.*[12], the relaxation time $\tau_{(1)}$ that

arising from the internal rotation of a polar group in a molecule is best described by

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

whereas the molecular relaxation time $\tau_{(2)}$ for the overall rotation is given by

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

and the most probable relaxation time $\tau_{(0)}$ is obtained by

$$\tau_{(0)}=\sqrt{\tau_{(1)}\tau_{(2)}} \qquad (3)$$

where ω is the angular frequency selected for the measurements, and a_0, a', a'', and a_{∞} are the slope values obtained from Eq.(4).

$$\varepsilon_0=\varepsilon_{01}+a_0w_2$$
$$\varepsilon'=\varepsilon_1+a'w_2$$
$$\varepsilon''=a''w_2 \qquad (4)$$
$$\varepsilon_{\infty}=\varepsilon_{1\infty}+a_{\infty}w_2$$

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

The molar free energies have been calculated using Eyring′s equation[13] as

$$\tau=(h/kT)\exp(\Delta F_{\tau}/RT) \qquad (5)$$
$$\eta=(Nh/V)\exp(\Delta F_{\eta}/RT) \qquad (6)$$

where h is the Plank′s constant, k is Boltzmann′s constant, N is Avogadro number, V is the molar volume, and ΔF_{τ} and ΔF_{η} are the molar free energies for the dielectric relaxation process and the viscous flow process, respectively.

3　Results and discussion

The systems selected were alcohols (1-propanol, 1-butanol, sec-butanol, tert-butanol, 1-pentanol, 1-heptanol, 1-octanol, and 1-decanol) with proton acceptors (methyl methacryrate (MMA), ethyl methacryrate (EMA), and butyl methacryrate (BMA)) using *n*-heptane as the solvent.

The following values are provided in Tables 1−6: the static dielectric constant (ε_0), the dielectric constant at angular frequency (ε_{∞}), the dielectric constant (ε'), the dielectric loss (ε''), the relaxation time τ_1 arising due to the individual rotation of the molecule, the relaxation time τ_2 arising due to the complete or overall rotation of the molecule, the most probable relaxation time τ_0, the activation energy ΔF_{τ} due to the dielectric relaxation process, and the activation energy ΔF_{η} due to the viscous flow of proton donors (1-propanol, 1-butanol, sec-butanol, tert-butanol, 1-pentanol, 1-heptanol, 1-octanol, and 1-decanol) with proton acceptors (MMA, EMA, and BMA) in *n*-heptane at 298 K. It can be seen from Tables 1−3 that for all the systems studied, the values of ε' and ε'' are found to decrease with the increase in the number of carbon atoms in the chain. This trend can 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[14].

It is also evident from Tables 4−6 that the values of τ_2 are significantly higher than the values of τ_1 and τ_0 for all the systems. The higher values of τ_2 indicate that the contribution of intermolecular or overall molecular relaxation is larger in comparison to the intramolecular or individual molecular relaxation

in the systems.

It is seen from Tables 4−6 that the values of the relaxation times (τ_1, τ_2, and τ_0) increase with the increasing chain length of both the alcohols and esters, and the increasing chain length hinders the rotation of the molecule. The increase in the relaxation time may be because of two effects: (i) increase in viscosity and, (ii) increase in molecular size with the increase[15–19] in the chain length.

In the systems described in this study it has been observed that the relaxation time of ternary mixtures (esters with alcohols in solvent) is considerably greater than that of the binary mixture (alcohols with solvent or esters with solvent). This result indi-

Table 1　Values of the static dielectric constant (ε_0), the dielectric constant at angular frequency (ε_{∞}), the dielectric constant (ε'), and the dielectric loss (ε'') for alcohols with methyl methacrylate (MMA) in *n*-heptane

Alcohol	Molar ratio of alcohol and ester	ε'	ε''	ε_0	ε_{∞}
1-propanol	1:3	2.3642	0.1556	2.4949	2.1157
	1:2	2.3763	0.1764	2.5583	2.1178
	1:1	2.3817	0.2075	2.6857	2.1194
	2:1	2.3765	0.1767	2.5591	2.1181
	3:1	2.3651	0.1563	2.4973	2.1164
1-butanol	1:3	2.3375	0.1374	2.4738	2.1174
	1:2	2.3406	0.1519	2.5165	2.1193
	1:1	2.3560	0.1846	2.6503	2.1216
	2:1	2.3411	0.1523	2.5186	2.1198
	3:1	2.3382	0.1381	2.4763	2.1185
sec-butanol	1:3	2.3288	0.1136	2.4313	2.1192
	1:2	2.3374	0.1317	2.4738	2.1209
	1:1	2.3482	0.1575	2.5686	2.1231
	2:1	2.3365	0.1324	2.4747	2.1211
	3:1	2.3293	0.1139	2.4331	2.1198
tert-butanol	1:3	2.3093	0.0927	2.3809	2.1209
	1:2	2.3196	0.1005	2.4118	2.1222
	1:1	2.3294	0.1309	2.4937	2.1241
	2:1	2.3189	0.1016	2.4132	2.1223
	3:1	2.3085	0.0913	2.3817	2.1216
1-pentanol	1:3	2.2693	0.1074	2.3865	2.1196
	1:2	2.2774	0.1206	2.4367	2.1218
	1:1	2.2875	0.1582	2.5529	2.1233
	2:1	2.2782	0.1215	2.4398	2.1224
	3:1	2.2695	0.1087	2.3892	2.1194
1-heptanol	1:3	2.2244	0.0825	2.3287	2.1215
	1:2	2.2387	0.1013	2.3906	2.1239
	1:1	2.2404	0.1194	2.4813	2.1254
	2:1	2.2395	0.1022	2.3927	2.1242
	3:1	2.2238	0.0836	2.3298	2.1207
1-octanol	1:3	2.1985	0.0655	2.3012	2.1224
	1:2	2.2124	0.0802	2.3534	2.1258
	1:1	2.2226	0.0975	2.4341	2.1277
	2:1	2.2125	0.0811	2.3556	2.1267
	3:1	2.1968	0.0648	2.2998	2.1221
1-decanol	1:3	2.1784	0.0435	2.2605	2.1276
	1:2	2.1865	0.0548	2.2986	2.1294
	1:1	2.1997	0.0793	2.3844	2.1302
	2:1	2.1859	0.0538	2.2967	2.1299
	3:1	2.1787	0.0429	2.2598	2.1288

Table 2 Values of the static dielectric constant (ε_0), the dielectric constant at angular frequency (ε_∞), the dielectric constant (ε'), and the dielectric loss (ε'') for alcohols with ethyl methacrylate (EMA) in *n*-heptane

Alcohol	Molar ratio of alcohol and ester	ε'	ε''	ε_0	ε_∞
1-propanol	1:3	2.3057	0.1356	2.4468	2.1172
	1:2	2.3193	0.1574	2.4985	2.1196
	1:1	2.3208	0.1825	2.6124	2.1217
	2:1	2.3179	0.1583	2.4997	2.1178
	3:1	2.3044	0.1368	2.4479	2.1181
1-butanol	1:3	2.2536	0.1122	2.3907	2.1198
	1:2	2.2697	0.1344	2.4548	2.1209
	1:1	2.2828	0.1629	2.5678	2.1226
	2:1	2.2691	0.1341	2.4562	2.1217
	3:1	2.2503	0.1105	2.3871	2.1192
sec-butanol	1:3	2.2395	0.0853	2.3338	2.1209
	1:2	2.2498	0.1008	2.3791	2.1227
	1:1	2.2586	0.1204	2.4555	2.1246
	2:1	2.2495	0.1004	2.3797	2.1238
	3:1	2.2397	0.0862	2.3357	2.1216
tert-butanol	1:3	2.2142	0.0538	2.2673	2.1221
	1:2	2.2294	0.0701	2.3088	2.1241
	1:1	2.2384	0.0838	2.3525	2.1262
	2:1	2.2295	0.0696	2.3097	2.1253
	3:1	2.2123	0.0519	2.2642	2.1236
1-pentanol	1:3	2.2131	0.0807	2.3283	2.1214
	1:2	2.2297	0.1005	2.3897	2.1231
	1:1	2.2429	0.1268	2.4754	2.1255
	2:1	2.2292	0.1008	2.3899	2.1226
	3:1	2.2128	0.0812	2.3305	2.1223
1-heptanol	1:3	2.1855	0.0602	2.2876	2.1218
	1:2	2.1999	0.0801	2.3459	2.1235
	1:1	2.2215	0.1013	2.4353	2.1358
	2:1	2.1996	0.0802	2.3465	2.1233
	3:1	2.1860	0.0601	2.2889	2.1225
1-octanol	1:3	2.1688	0.0411	2.2425	2.1244
	1:2	2.1795	0.0578	2.2946	2.1257
	1:1	2.1878	0.0728	2.3545	2.1279
	2:1	2.1791	0.0577	2.2951	2.1259
	3:1	2.1685	0.0407	2.2426	2.1246
1-decanol	1:3	2.1531	0.0213	2.1962	2.1249
	1:2	2.1645	0.0372	2.2481	2.1264
	1:1	2.1733	0.0505	2.2984	2.1283
	2:1	2.1649	0.0379	2.2503	2.1265
	3:1	2.1534	0.0211	2.1973	2.1256

Table 3 Values of the static dielectric constant (ε_0), the dielectric constant at angular frequency (ε_∞), the dielectric constant (ε'), and the dielectric loss (ε'') for alcohols with butyl methacrylate (BMA) in *n*-heptane
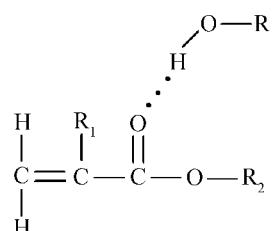
Alcohol	Molar ratio of alcohol and ester	ε'	ε''	ε_0	ε_∞
1-propanol	1:3	2.2585	0.1152	2.4078	2.1197
	1:2	2.2676	0.1315	2.4587	2.1209
	1:1	2.2794	0.1608	2.5579	2.1227
	2:1	2.2672	0.1316	2.4594	2.1215
	3:1	2.2584	0.1161	2.4093	2.1192
1-butanol	1:3	2.2294	0.0911	2.3619	2.1206
	1:2	2.2392	0.1107	2.4114	2.1223
	1:1	2.2445	0.1383	2.5015	2.1241
	2:1	2.2398	0.1116	2.4222	2.1234
	3:1	2.2282	0.0905	2.3609	2.1209
sec-butanol	1:3	2.1947	0.0485	2.2572	2.1228
	1:2	2.2076	0.0653	2.3027	2.1242
	1:1	2.2284	0.0976	2.4022	2.1265
	2:1	2.2058	0.0622	2.2977	2.1254
	3:1	2.1931	0.0467	2.2538	2.1239
tert-butanol	1:3	2.1572	0.0137	2.1729	2.1247
	1:2	2.1778	0.0303	2.2164	2.1263
	1:1	2.1985	0.0521	2.2843	2.1281
	2:1	2.1753	0.0285	2.2121	2.1272
	3:1	2.1545	0.0115	2.1678	2.1258
1-pentanol	1:3	2.1965	0.0704	2.3057	2.1225
	1:2	2.2114	0.0902	2.3612	2.1248
	1:1	2.2277	0.1195	2.4591	2.1263
	2:1	2.2106	0.0907	2.3648	2.1239
	3:1	2.1979	0.0718	2.3104	2.1236
1-heptanol	1:3	2.1685	0.0416	2.2424	2.1247
	1:2	2.1805	0.0623	2.3048	2.1256
	1:1	2.1953	0.0884	2.3961	2.1278
	2:1	2.1789	0.0615	2.3022	2.1252
	3:1	2.1669	0.0403	2.2398	2.1245
1-octanol	1:3	2.1535	0.0209	2.1935	2.1259
	1:2	2.1656	0.0404	2.2478	2.1274
	1:1	2.1815	0.0688	2.3454	2.1297
	2:1	2.1659	0.0406	2.2496	2.1277
	3:1	2.1531	0.0219	2.1956	2.1252
1-decanol	1:3	2.1419	0.0014	2.1449	2.1276
	1:2	2.1514	0.0153	2.1865	2.1293
	1:1	2.1678	0.0474	2.2912	2.1307
	2:1	2.1507	0.0155	2.1868	2.1286
	3:1	2.1416	0.0012	2.1442	2.1274

cates that a hydrogen bond is formed between the hydrogen atom in the O—H group of alcohol and the oxygen atom in the C=O group of ester[15,16,20,21], which is shown in Fig.1.

It is seen from Tables 4–6 that 1-butanol has a greater relaxation time than sec-butanol and tert-butanol which indicates that the solute-solute interaction is of the order of 1-butanol > sec-butanol>tert-butanol. Compared with the tert-butyl alcohol, a large difference was observed in the relaxation time values of this molecule because of the large difference in the two mechanisms viz., the end-over-end rotation and the OH group rotation. The increase in the relaxation time may be due to the increase in the effective radius of the rotating unit. The value of the relax-

Fig.1 Hydrogen bonding interaction between alcohols and esters

R=C$_3$H$_7$ (1-propanol), C$_4$H$_9$ (1-butanol), s-C$_4$H$_9$ (sec-butanol), t-C$_4$H$_9$ (tert-butanol), C$_5$H$_{11}$ (1-pentanol), C$_7$H$_{15}$ (1-heptanol), C$_8$H$_{17}$ (1-octanol), C$_{10}$H$_{21}$ (1-decanol); R$_1$=CH$_3$; R$_2$=CH$_3$ (MMA), C$_2$H$_5$ (EMA), C$_4$H$_9$ (BMA)

Table 4　Values of the dielectric relaxation time and the activation energies (ΔF_τ and ΔF_η) for alcohols with methyl methacrylate (MMA) in *n*-heptane at 298 K

Alcohol	Molar ratio of alcohol and ester	Relaxation time			ΔF_τ	ΔF_η
		τ_1	τ_2	τ_0	(kJ·mol^{-1})	(kJ·mol^{-1})
		ps	ps	ps		
1-propanol	1:3	11.18	14.18	12.59	11.09	13.08
	1:2	12.16	17.42	14.55	11.60	13.35
	1:1	14.08	24.74	18.67	12.47	14.13
	2:1	12.18	17.45	14.58	11.61	13.37
	3:1	11.22	14.28	12.66	11.11	13.10
1-butanol	1:3	11.23	16.75	13.72	11.51	13.21
	1:2	12.34	19.55	15.54	11.89	13.56
	1:1	14.11	26.92	19.49	12.68	14.35
	2:1	12.38	19.68	15.61	11.91	13.58
	3:1	11.31	16.89	13.82	11.53	13.26
sec-butanol	1:3	9.78	15.24	12.21	11.27	12.94
	1:2	10.96	17.49	13.84	11.61	13.37
	1:1	12.57	23.63	17.23	12.36	14.08
	2:1	11.07	17.63	13.97	11.63	13.40
	3:1	9.81	15.39	12.29	11.30	13.01
tert-butanol	1:3	8.95	13.04	10.80	10.89	12.57
	1:2	9.23	15.49	11.96	11.31	13.16
	1:1	11.52	21.19	15.63	12.09	13.89
	2:1	9.37	15.67	12.12	11.34	13.18
	3:1	8.89	13.54	10.97	10.98	12.62
1-pentanol	1:3	13.32	18.43	15.66	11.74	13.46
	1:2	14.33	22.30	17.88	12.22	13.95
	1:1	17.73	28.33	22.41	12.81	14.51
	2:1	14.42	22.46	17.99	12.23	13.98
	3:1	13.44	18.60	15.81	11.77	13.69
1-heptanol	1:3	15.58	21.35	18.24	12.11	13.84
	1:2	16.89	25.32	20.68	12.53	14.26
	1:1	19.86	34.07	26.01	13.27	14.95
	2:1	16.95	25.31	20.72	12.53	14.28
	3:1	15.76	21.41	18.37	12.12	13.87
1-octanol	1:3	17.67	26.48	21.63	12.64	14.33
	1:2	18.53	29.69	23.45	12.93	14.62
	1:1	20.23	36.63	27.22	13.45	15.18
	2:1	18.94	29.80	23.76	12.93	14.66
	3:1	17.88	26.84	21.91	12.68	14.36
1-decanol	1:3	19.69	31.87	25.05	13.10	14.89
	1:2	21.22	34.54	27.08	13.30	15.07
	1:1	23.91	39.33	30.67	13.62	15.36
	2:1	21.38	34.78	27.27	13.32	15.11
	3:1	19.90	31.92	25.21	13.10	15.92

Table 5　Values of the dielectric relaxation time and the activation energies (ΔF_τ and ΔF_η) for alcohols with ethyl methacrylate (EMA) in *n*-heptane at 298 K

Alcohol	Molar ratio of alcohol and ester	Relaxation time			ΔF_τ	ΔF_η
		τ_1	τ_2	τ_0	(kJ·mol^{-1})	(kJ·mol^{-1})
		ps	ps	ps		
1-propanol	1:3	13.08	17.57	15.16	11.63	13.35
	1:2	14.27	19.22	16.57	11.85	13.53
	1:1	16.60	26.98	21.17	12.69	14.36
	2:1	14.33	19.39	16.67	11.87	13.55
	3:1	13.37	17.71	15.39	11.65	13.38
1-butanol	1:3	15.75	20.63	18.03	12.02	13.72
	1:2	16.77	23.26	19.75	12.32	14.08
	1:1	18.75	29.54	23.54	12.91	14.69
	2:1	16.91	23.56	19.96	12.35	14.13
	3:1	15.87	20.91	18.21	12.06	13.75
sec-butanol	1:3	13.70	18.67	16.00	11.78	13.46
	1:2	14.98	21.66	18.02	12.14	13.82
	1:1	16.87	27.62	21.59	12.75	14.41
	2:1	15.11	21.90	18.19	12.17	13.85
	3:1	13.92	18.81	16.18	11.79	13.49
tert-butanol	1:3	11.56	16.67	13.88	11.50	13.28
	1:2	12.89	19.13	15.70	11.84	13.54
	1:1	14.34	22.99	18.16	12.29	13.93
	2:1	12.96	19.46	15.88	11.88	13.57
	3:1	11.65	16.89	14.03	11.53	13.32
1-pentanol	1:3	17.43	24.11	20.50	12.41	14.15
	1:2	18.23	26.88	22.14	12.68	14.39
	1:1	20.61	30.96	25.26	13.03	14.76
	2:1	18.28	26.92	22.19	12.68	14.41
	3:1	17.81	24.48	20.88	12.45	14.18
1-heptanol	1:3	20.25	28.64	24.08	12.84	14.53
	1:2	21.50	30.78	25.73	13.01	14.78
	1:1	23.69	35.64	29.06	13.38	15.07
	2:1	21.56	30.93	25.83	13.03	14.81
	3:1	20.30	28.91	24.22	12.86	14.56
1-octanol	1:3	22.46	30.28	26.08	12.97	14.69
	1:2	24.22	33.63	28.54	13.23	14.92
	1:1	26.49	38.67	32.01	13.58	15.28
	2:1	24.54	33.95	28.86	13.26	14.95
	3:1	22.61	30.74	26.36	13.01	14.72
1-decanol	1:3	24.47	34.17	28.91	13.27	14.96
	1:2	25.54	37.95	31.13	13.53	15.28
	1:1	27.07	41.83	33.65	13.77	15.46
	2:1	25.70	38.05	31.27	13.54	15.33
	3:1	24.92	35.13	29.59	13.34	15.08

ation time for sec-butyl alcohol is greater than that of tert-butyl alcohol. This may be because of the fact that the CH_3 is group attached to the same carbon atom to which the OH group is attached. This increases the size of the molecule and may hinder to the group rotation, which may lead to an increase in the relaxation time. This can be attributed to the increase in the effective radius of the rotating unit and the inner friction experienced by these molecules and can be explained on the basis of mutual and averaged mutual viscosities of the compounds[16].

It has been found that two opposing effects, namely, specific interactions between the C=O group of ester and the —OH group of alcohol, and nonspecific dispersion interactions, i.e.,

the rupture of the intermolecular hydrogen bonds in alcohols, are possibly operative in these mixtures. The relative sizes of both ester and alcohol molecules determine the predominance of a particular type of interaction over the other.

It is evident from the data obtained in this study that the value of the 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, faces greater interference from neighboring atom than dielectric relaxation, which involves only, rotational form of motion[15].

Table 6 Values of the dieletric relaxation time and the activation energies (ΔF_τ and ΔF_η) for alcohols with butyl methacrylate (BMA) in *n*-heptane at 298 K

Alcohol	Molar ratio of alcohol and ester	Relaxation time			ΔF_τ (kJ·mol^{-1})	ΔF_η (kJ·mol^{-1})
		τ_1 ps	τ_2 ps	τ_0 ps		
1-propanol	1:3	15.53	21.88	18.43	12.17	13.86
	1:2	16.67	24.54	20.23	12.45	14.18
	1:1	18.96	29.25	23.55	12.89	14.59
	2:1	16.81	24.66	20.36	12.47	14.21
	3:1	15.60	21.95	18.50	12.18	13.88
1-butanol	1:3	16.14	24.56	19.91	12.46	14.12
	1:2	18.08	26.27	21.79	12.62	14.36
	1:1	21.85	31.38	26.18	13.06	14.73
	2:1	18.31	27.60	22.48	12.74	14.49
	3:1	16.29	24.76	20.08	12.48	14.15
sec-butanol	1:3	14.02	21.76	17.47	12.16	13.83
	1:2	15.77	24.59	19.70	12.46	14.15
	1:1	18.64	30.07	23.68	12.96	14.67
	2:1	15.70	24.95	19.79	12.49	14.19
	3:1	14.16	21.95	17.63	12.18	13.86
tert-butanol	1:3	12.18	19.35	15.35	11.86	13.51
	1:2	13.46	21.51	17.02	12.13	13.86
	1:1	15.46	27.81	20.74	12.76	14.41
	2:1	13.91	21.80	17.41	12.16	13.89
	3:1	12.78	19.53	15.80	11.89	13.55
1-pentanol	1:3	19.65	26.19	22.69	12.61	14.36
	1:2	20.84	28.04	24.17	12.78	14.41
	1:1	22.96	32.70	27.40	13.16	14.88
	2:1	20.92	28.71	24.51	12.84	14.54
	3:1	19.94	26.46	22.97	12.64	14.38
1-heptanol	1:3	23.18	30.00	26.37	12.95	14.62
	1:2	25.41	33.69	29.26	13.24	14.95
	1:1	27.64	38.36	32.56	13.56	15.22
	2:1	25.83	33.85	29.57	13.25	14.99
	3:1	23.55	30.55	26.82	13.00	14.68
1-octanol	1:3	25.03	32.32	28.44	13.14	14.81
	1:2	27.62	34.36	30.80	13.29	14.98
	1:1	30.33	40.23	34.93	13.68	15.36
	2:1	27.76	34.81	31.08	13.32	15.02
	3:1	25.68	32.77	29.01	13.17	14.85
1-decanol	1:3	29.55	36.18	32.70	13.42	15.14
	1:2	30.04	38.74	34.11	13.58	15.22
	1:1	33.92	43.96	38.61	13.90	15.63
	2:1	30.43	39.33	34.60	13.62	15.36
	3:1	28.95	36.59	32.54	13.44	15.17

4 Conclusions

The hydrogen bonded complexes of alcohols (1-propanol, 1-butanol, sec-butanol, tert-butanol, 1-pentanol, 1-heptanol, 1-octanol, and 1-decanol) and acrylic esters (methyl methacrylate, ethyl methacrylate, and butyl methacrylate) have been studied in a dilute solution of *n*-heptane using the dielectric method. Based on this study, it can be concluded that the primary alcohols have relatively more tendency to form complexes than secondary and tertiary alcohols. The alkyl-chain length of alcohols and esters plays an important role in determining the dielectric properties of the systems studied.

References

1 Schildknecht, C. E. Vinyl and related polymers. New York: Wiley, 1977
2 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Z. Phys. Chem.*, **2005, 219:** 1385
3 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Spectrochim. Acta,* **2006, 64A:** 127
4 Dharmalingam, K.; Ramachandran, K. *Phys. Chem. Liq.,* **2006, 44:** 77
5 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Z. Phys. Chem.,* **2005, 219:** 1635
6 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Indian J. Pure Appl. Phys.,* **2005, 43:** 905
7 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Indian J. Phys.,* **2005, 79:** 1403
8 Dharmalingam, K.; Ramachandran, K.; Sivagurunathan, P. *Main Group Chemistry,* **2005, 4:** 241
9 Dharmalingam, K.; Ramachandran, K.; Sivagurunathan, P. *Z. Phys. Chem.,* **2006, 220:** 127
10 Vogal, A. I. Text book of practical organic chemistry. London: Longman, 1957
11 Aggarval, C.; Arya, R.; Gandhi, J. M.; Sisodia, M. L. *J. Mol. Liq.,* **1990, 44:** 161
12 Higasi, K.; Koga, Y.; Nagamura, M. *Bull. Chem. Soc. Japan,* **1971, 44:** 988
13 Glasstone, S.; Laider, K.; Eyrings, H. The theory of rate processes. New York: McGraw-Hill, 1941
14 Abd-El-Messieh, S. L.; Mohamed, M. G.; Mazrouaa, A. M.; Soliman, A. *J. Appl. Polym. Sci.,* **2002, 85:** 271
15 Kalaivani, T.; Kumar, S.; Krishnan, S. *Indian J. Chem.,* **2004, 43A:** 291
16 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K.; Kalamse, G. M. *Main Group Chemistry,* **2005, 4:** 227
17 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K.; Undre, B. P.; Khirade, P. W.; Mehrotra, S. C. *Main Group Chemistry,* **2005, 4:** 235
18 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K.; Undre, B. P.; Khirade, P. W.; Mehrotra, S. C. *Physica B,* **2007, 387:** 203
19 Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K.; Undre, B. P.; Khirade, P. W.; Mehrotra, S. C. *Phil. Mag. Letts.,* **2006, 86:** 291
20 Singh, A.; Singh, M. C. *J. Mol. Liq.,* **1983, 25:** 81
21 Saxena, S. K.; Saxena, M. C. *Indian J. Pure Appl. Phys.,* **1981, 19:** 550