

Dielectric behaviour of acrylic ester–organic solvent mixtures

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Abstract. Dielectric constants and refractive indices of fifteen binary mixtures containing methyl methacrylate (MMA), ethyl methacrylate (EMA) or butyl methacrylate (BMA), with hexane, heptane, carbon tetrachloride, chlorobenzene or *o*-dichlorobenzene are measured at 303.15 K. The excess dielectric constants, ϵ^E , excess molar polarizations, P_m^E and excess orientation polarizations, P_o^E were calculated from the measured properties of the pure and mixed components. An attempt was also made to provide qualitative interpretation of the complex molecular interactions involved based on the sign and magnitude of the excess dielectric function.

Keywords. Acrylic esters; dielectric constants; molar and orientation polarizations; molecular interactions.

1. Introduction

Production of acrylic esters of higher alkyl homologues is done either by direct esterification or by transesterification reactions with the corresponding alcohols in an inert solvent media. Both aliphatic and aromatic hydrocarbons are used as solvents. Thus, knowledge of the excess thermodynamic functions, viz excess volumes, excess compressibilities, excess viscosities and excess enthalpies, of binary mixtures with acrylic esters as one of the components is not only useful in understanding the molecular interactions but also in providing a vital feedback on the process parameters for designing an efficient industrial process for the ester interchange reactions. The densities, speed of sound and viscosities along with the derived excess quantities for several binary mixtures of MMA, EMA and BMA, with hexane, heptane, carbon tetrachloride, chlorobenzene or *o*-dichlorobenzene, were recently reported from our laboratory (Sastry and Dave 1996). In continuation of our earlier work on 15 such binary mixtures, this paper presents the static dielectric constants and the refractive indices for the same mixtures at 303.15 K. Several excess dielectric functions viz. excess dielectric constant, ϵ_o^E , excess molar polarization P_m^E and excess orientation polarization, P_o^E were derived.

2. Experimental

Materials: The acrylic esters, viz. MMA, EMA and BMA, and the organic solvents hexane, heptane, carbon tetrachloride, chlorobenzene and *o*-dichlorobenzene, were the same as those used in our earlier work (Sastry and Dave 1996a).

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Methods: The binary mixtures were prepared by weighing on a Mettler balance with an estimated mole fraction accuracy of ± 0.0001 units.

The static dielectric constants at 3 MHz were measured with a Universal Dielectrometer OH-301 of Radelkis (Hungary) make. Details of the calibrations of the dielectric cells and the estimations of dielectric constants of both pure and mixture components from the experimental measured capacitances were described elsewhere in detail (Sastry and Raj 1996). The measured dielectric constants were found to be accurate up to 0.001 units.

Refractive indices of the pure and mixture components were measured with an Abbe-type research refractometer. Water from a thermostatic bath maintained at 303.15 ± 0.01 K, was circulated through the dielectric cells and the refractometer inlets during the measurements. Values of the dielectric constants and refractive indices of the pure components are given in table 1 and are in close agreement with the corresponding literature data (Raetsch *et al* 1974; Riddick and Bunger 1986; Lide 1994; Oswal *et al* 1994).

3. Results and discussion

The data of the dielectric constants (ϵ), and refractive indices (n_D) of all the fifteen binary mixtures of acrylic ester–organic solvents at 303.15 K are also presented in table 1. The molar polarization, P_m , was evaluated by the Clausius–Mossoti relation,

$$P_m = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \left[\frac{x_1 M_1 + x_2 M_2}{\rho_{12}} \right], \quad (1)$$

the orientation polarization P^o from the relation described by Smyth (1995),

$$P^o = \frac{P_m - (x_1 R_{m(1)} + x_2 R_{m(2)})}{1 - \left[\frac{(\epsilon_{12} - 1)}{(\epsilon_{12} + 2)} \right]^2}, \quad (2)$$

and the molar refraction R_m by the Lorenz–Lorentz equation

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} \left[\frac{M}{\rho} \right] \quad (3)$$

where ϵ_{12} , x_1 , x_2 , $R_{m(1)}$, $R_{m(2)}$ and n_D are dielectric constants, mole fraction and refractive indices of the pure ester, organic solvents and their binary mixtures (subscripts 1, 2 and 12 respectively). M and ρ are the molecular weight and densities of the respective components. Thus, using (1)–(3), the P_m , P^o and R_m values were calculated for pure and mixture components.

There exist differences of opinion in the literature, with regard to the calculation of the excess dielectric constants from the values of pure and mixture components. The values of the pure components for estimation of excess dielectric constants are evaluated either as mole fraction averages (Ritzoulis *et al* 1986; Sheshadri and Subramanyam 1990) or volume fraction averages (Jquelli *et al* 1986; Karla *et al* 1991). Even a dielectric fraction average is suggested (Oswal 1988). However, we have evaluated the pure values for all the dielectric functions as mole fraction averages. All the three excess dielectric functions, viz excess dielectric constant, ϵ^E , excess molar

Table 1. Dielectric constants and refractive indices of acrylic ester-organic solvent mixtures at 303.15 K.

x^*	ϵ	n_D	x	ϵ	n_D	x	ϵ	n_D	x	ϵ	n_D	x	ϵ	n_D
MMA-hexane														
0.0000	1.871	1.3695	0.0000	1.902	1.3830	0.0000	2.213	1.4540	0.0000	5.607	1.5224	0.0000	9.840	1.5460
0.0731	2.094	1.3682	0.0240	1.933	1.3810	0.0320	2.341	1.4524	0.0420	5.654	1.5201	0.0456	9.704	1.5425
0.1732	2.441	1.3702	0.1404	2.253	1.3812	0.0898	2.556	1.4499	0.1051	5.709	1.5123	0.1114	9.577	1.5335
0.2754	2.807	1.3721	0.2282	2.522	1.3818	0.1842	2.950	1.4469	0.2049	5.803	1.5067	0.2108	9.297	1.5262
0.3520	3.097	1.3769	0.3569	2.964	1.3840	0.2779	3.340	1.4425	0.3078	5.900	1.4945	0.3166	8.992	1.5173
0.4652	3.554	1.3801	0.4738	3.419	1.3862	0.3837	3.830	1.4379	0.4086	5.986	1.4858	0.4149	8.663	1.4998
0.5482	3.927	1.3849	0.5583	3.801	1.3899	0.4783	4.153	1.4322	0.5093	6.061	1.4779	0.5164	8.313	1.4862
0.6519	4.426	1.3889	0.6194	4.095	1.3930	0.5900	4.589	1.4300	0.6099	6.125	1.4665	0.6158	7.917	1.4778
0.7277	4.792	1.3935	0.7088	4.540	1.3958	0.6834	5.006	1.4245	0.7062	6.173	1.4527	0.7159	7.505	1.4603
0.8399	5.367	1.3968	0.8160	5.118	1.3995	0.7814	5.401	1.4201	0.8044	6.203	1.4467	0.8092	7.121	1.4475
0.9177	5.791	1.4011	0.9094	5.659	1.4021	0.8889	5.826	1.4158	0.9058	6.239	1.4346	0.9032	6.716	1.4382
0.9791	6.130	1.4047	0.9991	6.218	1.4042	0.9508	6.060	1.4069	0.9646	6.240	1.4203	0.9643	6.426	1.4265
1.0000	6.243	1.4085												
EMA-hexane														
0.0396	1.926	1.3785	0.0489	2.024	1.3871	0.0343	2.226	1.4515	0.0358	5.631	1.5149	0.0383	9.695	1.5432
0.2079	2.364	1.3850	0.2294	2.380	1.3909	0.1638	2.596	1.4475	0.1699	5.680	1.5000	0.1842	9.113	1.5162
0.4065	3.008	1.3919	0.4379	3.087	1.3960	0.3394	3.125	1.4398	0.3526	5.710	1.4785	0.3691	8.332	1.4965
0.5102	3.427	1.4045	0.5397	3.485	1.3983	0.4350	3.464	1.4330	0.4478	5.714	1.4682	0.4699	7.910	1.4820
0.7082	4.330	1.4070	0.7290	4.369	1.4042	0.6448	4.172	1.4250	0.6550	5.718	1.4470	0.6734	7.077	1.4549
0.8027	4.854	1.4095	0.8248	4.849	1.4070	0.7620	4.980	1.4210	0.7647	5.723	1.4170	0.7787	6.639	1.4355
0.9640	5.544	1.4120	0.9635	5.523	1.4111	0.9444	5.538	1.4165	0.9487	5.733	1.4122	0.9555	5.905	1.4211
1.0000	5.708	1.4122												
BMA-hexane														
0.0331	1.922	1.3809	0.0394	1.961	1.3871	0.0296	2.230	1.4514	0.0267	5.622	1.5165	0.0306	9.652	1.5369
0.1715	2.237	1.3895	0.1884	2.347	1.3940	0.1335	2.486	1.4495	0.1386	5.520	1.5006	0.1518	8.890	1.5175
0.3526	2.680	1.3910	0.3823	2.885	1.4023	0.2903	2.855	1.4420	0.2979	5.403	1.4807	0.3186	7.950	1.4962
0.4450	2.964	1.4180	0.4762	3.243	1.4067	0.3769	3.115	1.4375	0.3879	5.358	1.4729	0.4145	7.481	1.4860
0.6533	3.622	1.4200	0.6795	3.978	1.4149	0.5867	3.757	1.4320	0.5969	5.190	1.4523	0.6200	6.522	1.4638
0.7626	4.080	1.4209	0.7871	4.370	1.4167	0.7078	4.129	1.4300	0.7182	5.083	1.4413	0.7358	6.004	1.4495
0.9475	4.767	1.4219	0.9512	4.741	1.4211	0.9260	4.670	1.4250	0.9304	4.916	1.4270	0.9408	5.104	1.4362
1.0000	4.848	1.4225												

* x is the ester mole fraction

polarization, P_m^E and excess orientation polarization, P_o^E were evaluated from the relation,

$$A^E = A_{mix} - A_{id}, \quad (4)$$

where $A^E = \varepsilon^E, P_m^E$ or P_o^E , A_{mix} and A_{id} are the contributions of the respective functions of mixture and pure components. ε^E, P_m^E and P_o^E were also mathematically represented by the following equation,

$$Y^E = x(1-x) \sum_{i=0}^n a_i(2x-1)^i, \quad (5)$$

where $Y^E = \varepsilon^E, P_m^E$ ($\text{cm}^3 \text{mol}^{-1}$) and P_o^E ($\text{cm}^3 \text{mol}^{-1}$), x is the ester mole fraction and a_i are the coefficients. The values of the a_i were estimated by employing multiple regression analysis based on the least squares method. The estimated values of the coefficients along with the standard deviations, σ for all the three excess dielectric functions of the fifteen binary mixtures are presented in table 2.

Values of the excess dielectric constants (ε^E) for the MMA, EMA and BMA with organic solvents are graphically represented as a function of ester mole fraction in figure 1. The shapes and magnitudes of the curves are found to show a typical dependence on the alkyl chain length of the ester and the nature and type of organic solvent. ε^E values of MMA-hexane, MMA-heptane, EMA-hexane and EMA-heptane are negative. ε^E values for the acrylic ester-heptane mixtures are more negative than for the acrylic ester-hexane mixtures, while the ε^E vs x curves for BMA-hexane and BMA-heptane show sigmoidal trend with initial negative lobes followed by positive regions (figure 1c).

ε^E values for the mixtures containing nonpolar but highly polarizable carbon tetrachloride show an interesting trend. The ε^E curves for MMA and BMA containing mixtures are sigmoidal with initial negative values followed by positive regions. However, the same curves for EMA mixtures show a negative trend over the whole mole fraction range. The ε^E values for MMA- and EMA-chlorobenzene mixtures are positive over the whole range of ester mole fraction. The ε^E values of MMA-*o*-dichlorobenzene mixtures are more positive than those with chlorobenzene. However, an increase in the alkyl chain length of the ester is found to decrease the ε^E values in the *o*-dichlorobenzene mixtures and very large negative values are seen for the BMA-*o*-dichlorobenzene mixtures.

The excess molar polarizations, P_m^E of the acrylic ester-organic solvent mixtures are plotted as a function of ester mole fraction in figure 2, for MMA, EMA and BMA containing mixtures. The P_m^E values for all the three esters, hexane and heptane are positive over the entire range of mole fractions. The P_m^E values of MMA-hexane mixtures are larger than for the MMA-heptane mixtures. However, in case of both EMA-heptane and BMA-heptane mixtures, the P_m^E values are more than that of same ester-hexane mixtures. Similarly the P_m^E values for all the three esters with chlorobenzene and *o*-dichlorobenzene are positive over the whole range of mole fractions. It is also seen P_m^E values for all the mixtures with *o*-dichlorobenzene are larger than those with chlorobenzene mixtures. P_m^E values for the MMA-carbon tetrachloride mixtures are large and positive over the whole mole fraction range. The increase in the carbon chain length of the alkyl group in the ester shows a diminishing effect on the P_m^E values. In fact the P_m^E vs x curves for EMA- and BMA-carbon tetrachloride mixtures are sigmoidal with initial negative lobes followed by positive regions.

Table 2. Least square coefficients of (5) for the representation of excess dielectric functions of acrylic esters-organic solvent mixtures at 303.15 K.

	ϵ^E ($\text{cm}^3 \text{ mol}^{-1}$)	P_m^E ($\text{cm}^3 \text{ mol}^{-1}$)	P_o^E ($\text{cm}^3 \text{ mol}^{-1}$)	ϵ^E ($\text{cm}^3 \text{ mol}^{-1}$)	P_m^E ($\text{cm}^3 \text{ mol}^{-1}$)	P_o^E ($\text{cm}^3 \text{ mol}^{-1}$)	ϵ^E ($\text{cm}^3 \text{ mol}^{-1}$)	P_m^E ($\text{cm}^3 \text{ mol}^{-1}$)	P_o^E ($\text{cm}^3 \text{ mol}^{-1}$)
	<i>MMA-hexane</i>			<i>EMA-hexane</i>			<i>BMA-hexane</i>		
a_0	-1.3632	32.9723	10.2303	-1.5882	16.2464	-8.2518	-1.0018	4.0949	-22.9935
a_1	-0.0699	-3.1740	-2.0018	0.8388	12.5264	26.5351	1.3264	-3.6008	28.8114
a_2	0.0586	-0.6255	1.0266	-0.0617	2.2006	-4.4124	1.2326	8.2097	25.6986
a_3	0.2344	-	4.4687	-	-	-	-	-	-
σ	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0005	0.0001
	<i>MMA-heptane</i>			<i>EMA-heptane</i>			<i>BMA-heptane</i>		
a_0	-2.0233	32.0432	4.3003	-1.9509	17.0380	-10.6699	-0.4105	15.8540	6.2273
a_1	-0.2897	-5.7419	-2.0069	0.2389	7.4000	19.3999	1.2189	8.2435	41.0405
a_2	-0.6631	-10.8304	-1.6043	0.7124	0.8598	-4.7179	-0.1683	2.7764	-25.8404
a_3	0.7019	21.873	14.3850	-	-	-	-	-	-
σ	0.0001	0.0008	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
	<i>MMA-carbon tetrachloride</i>			<i>EMA-carbon tetrachloride</i>			<i>BMA-carbon tetrachloride</i>		
a_0	0.1643	20.7762	3.9679	-1.2078	2.7824	-26.5931	-0.1292	-1.6763	-19.0487
a_1	0.2076	-5.6087	-1.3982	1.3310	5.5198	22.1964	0.7581	10.2971	17.9692
a_2	-	1.8546	-	0.7124	-3.4789	-	-0.3887	-4.8682	-14.3656
a_3	-	-	-	-	-	-	-	-	-
σ	0.0008	0.0006	0.0020	0.0005	0.0005	0.0070	0.0001	0.0005	0.0001
	<i>MMA-chlorobenzene</i>			<i>EMA-chlorobenzene</i>			<i>BMA-chlorobenzene</i>		
a_0	0.5273	2.5666	6.1812	0.1946	0.9022	3.2732	0.1322	2.5749	5.9522
a_1	0.1037	0.1822	1.5234	-0.0139	-1.1875	-4.4386	0.0180	-0.9402	-3.2478
a_2	-0.1170	-1.3077	-2.3210	0.4607	1.7836	-2.2227	0.0862	4.9876	12.4311
a_3	-	-	-	-	-	-	-	-	-
σ	0.0001	0.0001	0.0007	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
	<i>MMA-o-dichlorobenzene</i>			<i>EMA-o-dichlorobenzene</i>			<i>BMA-o-dichlorobenzene</i>		
a_0	1.2918	7.5646	6.0851	0.0462	8.3936	14.0358	-1.1565	15.6562	20.1728
a_1	0.2423	2.7705	2.2986	-0.0362	2.2593	0.8984	0.4029	4.9686	8.3732
a_2	-	0.2915	-2.1233	0.3368	1.1222	3.8531	0.2315	2.1759	-0.8912
σ	0.0006	0.0008	0.0001	0.0001	0.0005	0.0001	0.0001	0.0008	0.0001

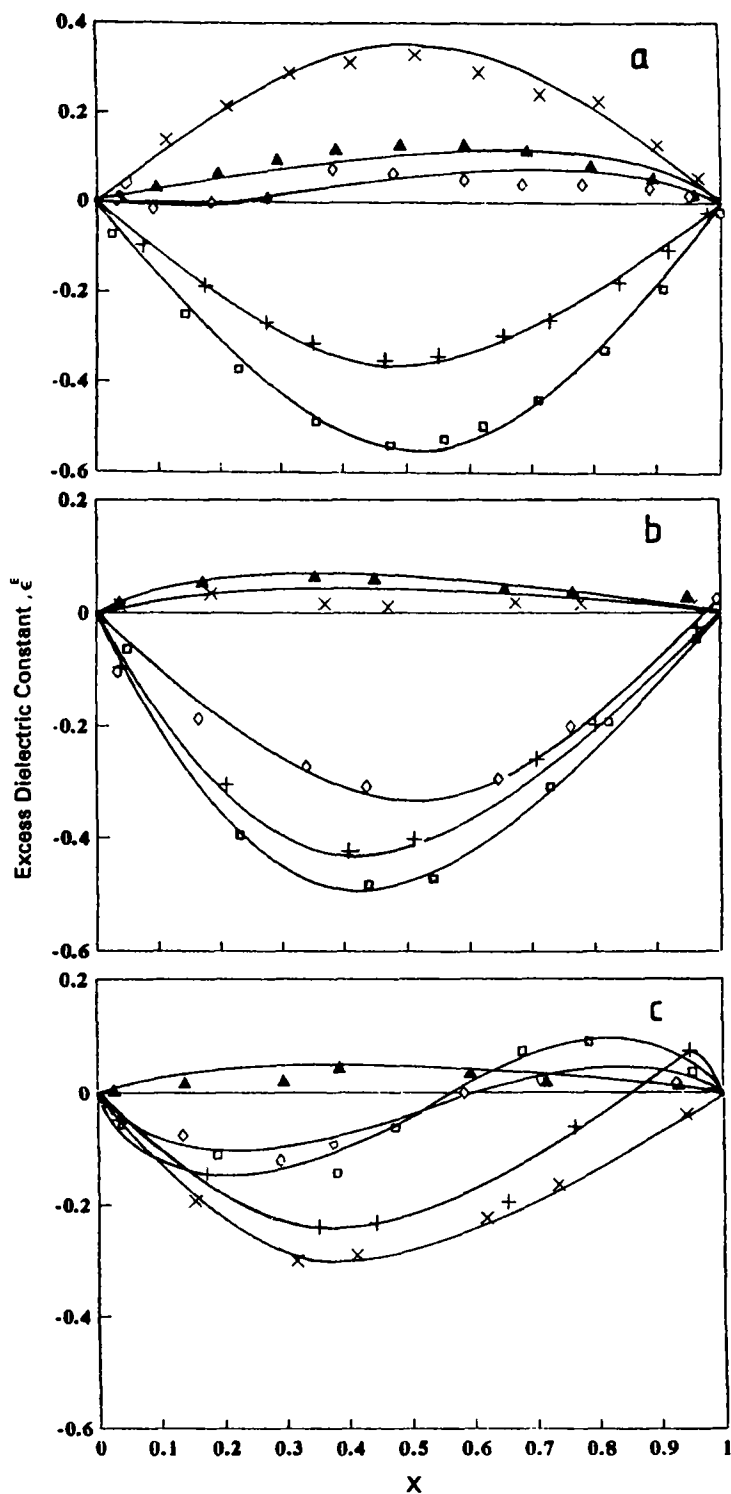


Figure 1. Excess dielectric constants as a function of ester mole fraction at 303.15 K (a) MMA, (b) EMA and (c) BMA with hexane (+), heptane (■), carbon tetrachloride (◇), chlorobenzene (▲), and *o*-dichlorobenzene (×). (—) Fitted values as per (5) using the coefficients from table 2.

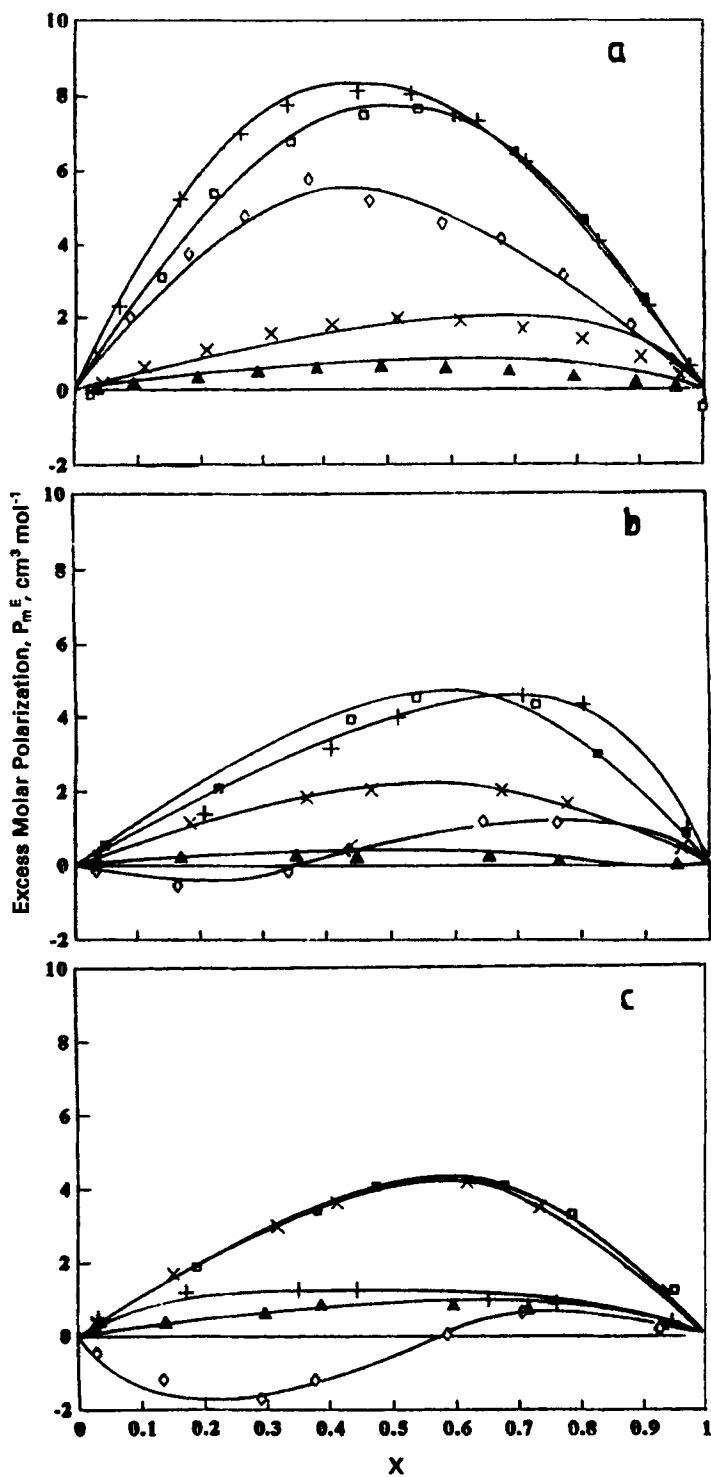


Figure 2. Excess molar polarizations as a function of ester mole fraction at 303-15 K. (a) to (c) and symbols as in figure 1.

The excess orientation polarizations, P_o^E , for MMA, EMA and BMA–organic solvents are represented graphically as a function of ester mole fraction in figure 3. The curves show positive trends in MMA–hexane and –heptane mixtures and are sigmoidal with negative–positive lobes for EMA– and BMA–hexane and –heptane mixtures. P_o^E values are positive in the entire ester mole fraction range in all the mixtures containing both chlorobenzene and *o*-dichlorobenzene components. Larger positive values are observed in ester–dichlorobenzene than in the ester–chlorobenzene mixtures. The trend in P_o^E vs x curves in the mixtures containing carbon tetrachloride show all positive values in MMA, and all negative values in EMA–, and BMA–containing mixtures.

The types of interactions that can be expected in the acrylic ester–organic solvent mixtures and (i) dilution in the dipolar interactions (ii) n – π interactions between the lone pair of electrons of ester group and the π electrons of aromatic ring, (iii) specific interactions of the O–Cl type, and (iv) packing interactions through interstitial accommodation of smaller unlike molecules. The net balance of these forces is expected to be reflected in the signs and magnitudes of the excess functions. The dependence of the various dielectric functions on the ester mole fraction of present mixtures, as described in the earlier section, shows the complex nature of the interactions between the acrylic ester and the organic solvents. Though there are no earlier reports in the literature on the dielectric properties of these mixtures for a direct comparison, an attempt is made to give a reasonable interpretation by comparing the equimolar excess dielectric functions. Table 3 summarises the equimolar excess dielectric functions of all the fifteen mixtures.

It can be seen from table 3 that the $\epsilon_{0.5}^E$ values for the binary mixtures of all the three esters with aliphatic hydrocarbons, viz. hexane and heptane, are negative. The negative excess dielectric constants indicate the changed alignment of dipoles in the ester species due to the dipole–dipole type dispersing interactions. However, the P_m^E values for the same mixtures are large and positive. The positive and large excess volumes for these mixtures (Sastry and Dave 1996a) and also their negative viscosity deviations (Sastry and Dave 1996b) which are further complimented by the present negative $\epsilon_{0.5}^E$ values support the presence of weaker dipole–dipole dispersing interactions. The assumption of dominance of structure-breaking dispersing interactions in the acrylic ester–alkane systems is supported by the literature reports of positive excess enthalpies for MMA–hexane, –heptane mixtures at 298.15 K (Luo *et al* 1986). The volumetric behaviour of several alkyl alkanooates–alkane binary mixtures are also interpreted on similar lines (Grolier *et al* 1974; Gonzalez *et al* 1993, 1994).

The $\epsilon_{0.5}^E$ values go from the positive to the negative side with increase in the alkyl chain length of the ester species in the binary mixtures with carbon tetrachloride, which itself is nonpolar but is highly polarizable. Trends in the P_m^E values also show similar patterns.

The positive $\epsilon_{0.5}^E$ and P_m^E values for the acrylic ester–chlorobenzene and *o*-dichlorobenzene mixtures in general suggest the possibility of O–Cl type and n – π interactions. The presence of such specific interactions is also indicated from our earlier reported negative excess volumes and isentropic compressibilities of the same mixtures (Sastry and Dave 1996a). Raetsch *et al* (1974) and Oswal and Rathnam (1987) have also attributed positive excess dielectric constants to the presence of specific interactions between methyl methacrylate–aromatic hydrocarbon and ethyl acetate–aromatic hydrocarbon mixtures respectively. Similarly, the positive excess orientation

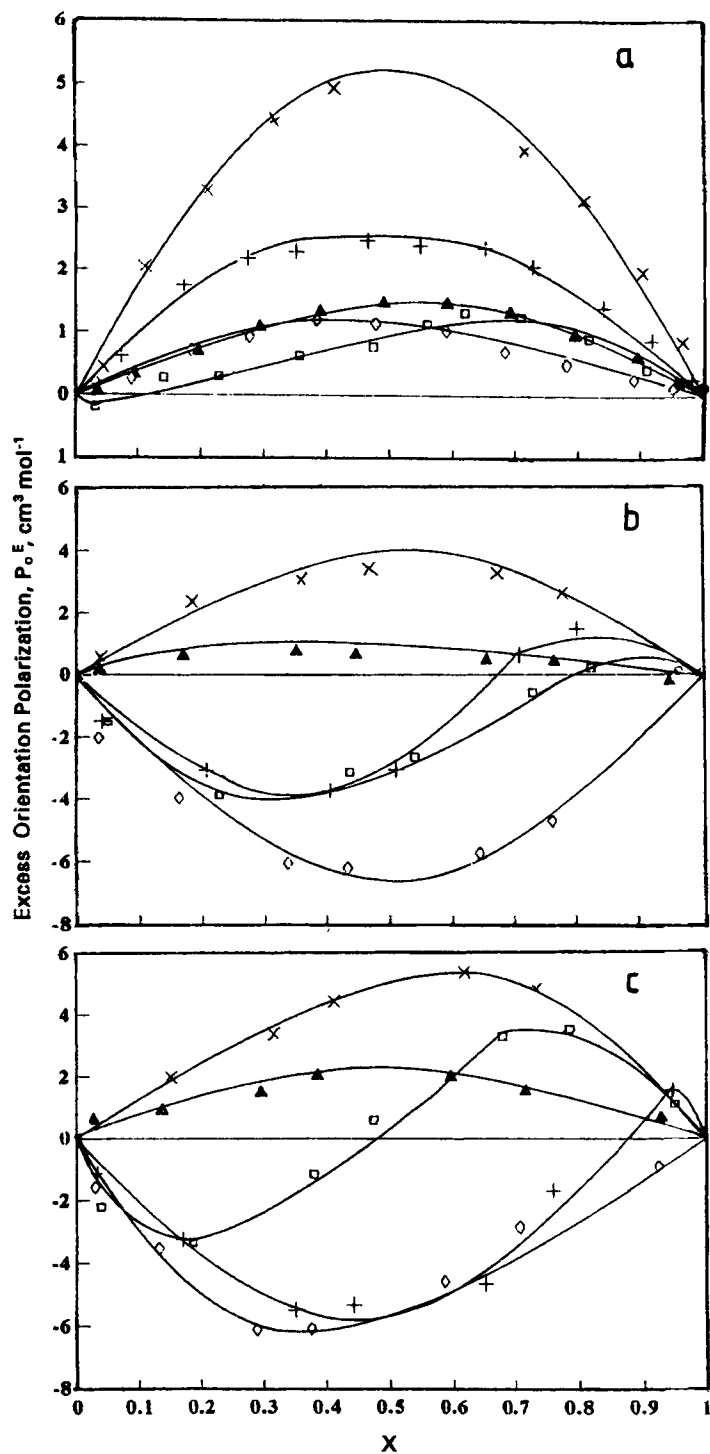


Figure 3. Excess orientation polarizations as a function of ester mole fraction at 303-15K. (a) to (c) and symbols as in figure 1.

Table 3. Equimolar excess dielectric functions of acrylic ester + organic solvent mixtures at 303·15 K

Organic solvent	Acrylic ester								
	MMA			EMA			BMA		
	ϵ^E	P_m^E	P_o^E	ϵ^E	P_m^E	P_o^E	ϵ^E	P_m^E	P_o^E
Hexane	-0.339	8.19	2.56	-0.395	4.05	-2.4	-0.227	1.25	-5.28
Heptane	-0.531	7.64	1.04	-0.471	4.36	-2.7	-0.048	4.05	0.86
Carbon tetra- chloride	0.051	5.27	1.08	-0.310	0.65	-6.5	-0.048	-0.51	-5.48
Chloro- benzene	0.129	0.61	1.92	0.061	0.28	0.75	0.035	0.84	1.97
<i>o</i> -Dichloro- benzene	0.324	1.90	5.08	0.019	2.12	3.59	-0.278	3.94	6.23

polarizations, P_o^E can be ascribed to the decreased degree of alignment of dipoles due to the specific interactions and negative P_o^E values which indicate, in general, the increased degree of alignment of the dipoles.

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