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Thermodynamics of Acrylic Esters Containing Binary Liquid Mixtures. I. Excess Volumes and Isentropic Compressibilities of Alkyl Methacrylates + *n*-Hexane, + *n*-Heptane, + Carbon Tetrachloride, + Chlorobenzene, and *o*-Dichlorobenzene at 303.15 K

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Excess volumes and isentropic compressibilities of 15 binary liquid mixtures containing methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA) and *n*-hexane, *n*-heptane, carbon tetrachloride, chlorobenzene, and *o*-dichlorobenzene are derived from the measured densities and speeds of sound at 303.15 K. The dependence of the excess volumes and the isentropic compressibilities both on the alkyl chain length and on the nature of the solvent shows the dominance of dispersing interactions in the mixtures of aliphatic hydrocarbons and specific interections in the chlorinated solvent mixtures. The speeds of sound of binary mixtures of MMA were found to be reasonably predicted by free length and collision factor theories. An attempt is also made to estimate the individual contributions of interactional, free volume and P^* effects to the overall excess volumes of binary mixtures containing MMA. The results indicate that the three factors are equally responsible for the observed values.

KEY WORDS: acrylic esters; excess volumes; excess isentropic compressibilities; molecular interactions; Prigogine–Flory–Patterson treatment.

1. INTRODUCTION

Acrylic esters are in general the most important industrial chemicals and are the precursors for the production of technically important polymers.

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The production of higher homologous acrylic esters is carried out through an ester interchange reaction with higher alcohols in an inert organic medium. In addition, the acrylic esters are also typical monomers empolyed in grafting processes. Measurements of density dependence of various thermodynamic properties *viz.*, viscosities, speeds of sound, and dielectric constants, etc., of binary mixtures of acrylic esters with polar and nonpolar solvents are very useful in designing an efficient industrial process for ester interchange reactions. The derivation of various excess functions from the measured properties of individual pure and of mixture components and the analysis of the latter in terms of application of several statistical theories of solutions give a better understanding of interactions present at molecular level.

A perusal of the literature reveals that the binary mixtures of alkyl alkanoates with other organic solvents [1–11] has attracted more attention for thermodynamic investigations than acrylic esters in spite of their high potential applications, especially in the production of polymers. The excess enthalpies and excess volumes of methyl methacrylate +*n*-hexane and +*n*-heptane mixtures has been reported by Luo et al. [12, 13]. Oswal et al. [21] have recently measured the viscosities of binary mixtures of methyl methacrylate–haloalkanes and –alkyl amines. We are interested in systematic measurements of various physical properties such as viscosities, speeds of sound, and dielectric constants of acrylic esters with a variety of polar and nonpolar solvents as a function of density. Our aim is to derive various excess thermodynamic functions and treat them through various statistical theories to gain an insight into the molecular interactions and relate them to the size, shape, and chemical nature of the component molecules.

This work is an extension of our earlier studies on binary mixtures of methyl methacrylate-alcohols [14, 15]. The present paper reports the measurements of densities and speeds of sound of several binary mixtures of methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA) with *n*-hexane, *n*-heptane, carbon tetrachloride, chlorobenzene, and *o*-dichlorobenzene at 303.15 K. The excess volumes and isentropic compressibilties were derived from experimental measurements, and in addition, the Prigogine–Flory–Patterson theory was employed to calculate the excess volumes of binary mixtures containing MMA.

2. EXPERIMENTS

MMA was a Fluka product (>99.9% pure on a mole basis). EMA and BMA were purchased from Merck (>99% pure on a mole basis).

Table I. Comparison of Densities and Sound Velocities of the Pure Components at 303.15 K

Liquid	Density (g $\cdot$ cm^{-3})		Sound velocity m $\cdot$ s^{-1})	
	Expt.	Lit	Expt.	Lit.
MMA	0.9317	0.9316 [20] 0.93171 [21] 0.93174 [22]	1178.8	—
EMA	0.9032	—	1196.0	—
BMA	0.8845	—	1196.4	—
n-Hexane	0.6502	0.6502 [23] 0.6506 [24]	1028.4	1028.6 [25]
n-Heptane	0.6756	0.6754 [23]	1122.8	—
Carbon Tetrachloride	1.5748	1.574[22] 1.5749 [27] 1.5748 [21]	905.8	906.0 [27]
Chorobenzene	1.0955	1.0955 [22] 1.0955 [26] 1.09469 [21]	1244.8	1245 [28]
o-Dichlorobenzene	1.2990	1.2992 [29] 1.29454 [28]	1268.0	1266.0 [30]

These chemicals were used without any further purifications. *n*-Hexane and *n*-heptane were BDH AnalaR-grade chemicals and were used as such. Carbon tetrachloride, chlorobenzene, and *o*-dichlorobenzene were from BDH chemicals and further purified by the standard procedures described by Riddick and Bunger [16]. The measured densities, speeds of sound, and refractive indices of the pure components were compared with the literature values. Such a comparison is presented in Table I. It can be seen from Table I that our values, in general, were in good agreement with the literature values.

The densities of pure and mixture components were measured by a bicapillary pycnometer which was precalibrated with triple-distilled water and double-distilled benzene. The pycnometer was placed vertically in an electronically controlled water bath maintained at a measuring temperature accurate up to ± 0.05 K. The values of the densities so estimated were accurate to ± 0.0001 U.

Speeds of sound were measured with an ultrasonic interferometer (Mittal Enterprises, New Delhi), operating at a fixed frequency of 2 MHz. The temperature of the double-jacketed measuring cell was maintained by circulating water from a thermostatic bath maintained at the measuring temperature as described earlier. The measured speeds of sound were found to be accurate to $\pm 0.15\%$.

3. RESULTS

The densities, speeds of sound, excess volumes, V^E (cm^3 mol^{-1}), and excess isentropic compressibilities, K_S^E (TPa^{-1}), for various binary mixtures of acrylic esters with organic solvents at 303.15 K are presented in Tables II and III. The excess volume, V^E, and isentropic compressibilities, K_S^E, were calculated from the following relations:

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \tag{1}$$

$$K_S^E = K_{S12} - (x_1 K_{S1} + x_2 K_{S2}) \tag{2}$$

where x, M, and ρ are the mole fraction, molecular weight, and density of pure components 1 and 2 and mixture components 12, respectively. The compressibilites were calculated by the following equation:

$$K_S = 1/v^2\rho \tag{3}$$

where K_S is in TPa^{-1}, v is the speed of sound in m $\cdot$ s^{-1}, and ρ is the density in kg $\cdot$ m^{-3}.

The derived excess functions were fitted through an empirical equation of the form

$$Y^E = x(1-x) \sum_{i=0}^{i=n} a_i(2x-1)^i \tag{4}$$

where Y^E = either V^E (cm$^3 \cdot$ mol^{-1}) or K_S^E (Tpa)$^{-1}$, x is the mole fraction of ester, and a_i is the polynomial coefficient. The values of the coefficients a_i in Eq. (4) were evaluated by regression analysis based on the method of least squares, with an equal weightage to all points. The values of the a_i together with the standard deviations, σ, are presented in Table IV. The standard deviations, σ, were calculated from

$$\sigma = \left[\frac{(Y_{\text{exp}}^E - Y_{\text{fitt}}^E)^2}{p-n}\right]^{1/2} \tag{5}$$

where Y_{exp}^E and Y_{fitt}^E are experimental and fitted excess functions, p is the number of experimental points, and n is the number of coefficients used in Eq. (4) for the best smoothing of the data.

The experimentally observed excess volumes along with the fitted values are plotted as a function of ester mole fraction in Figs. 1–3. The magnitude of the excess volumes and their dependence on both the alkyl

Table II. Densities oand Excess Volumes of Binary Mixtures of Acrylic Esters at 303.15 K

x	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	x	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	x	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	x	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	x	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})
MMA + *n*-hexane			MMA + *n*-heptane			MMA + carbon tetrachloride			MMA + chlorobenzene			MMA + *o*-dichlorobenzene		
0.0731	0.664	0.1400	0.0240	0.6794	0.1481	0.0320	1.5520	0.0148	0.0354	1.0894	0.0043	0.0456	1.2835	−0.0388
0.1732	0.6892	0.3595	0.1404	0.7004	0.4683	0.0898	1.5113	0.0351	0.0942	1.0793	0.0125	0.114	1.2606	−0.0600
0.2754	0.7137	0.5143	0.2282	0.7173	0.6753	0.1842	1.4460	0.0583	0.1956	1.0620	0.0281	0.2108	1.2256	−0.0832
0.3520	0.7330	0.5770	0.3569	0.7449	0.7444	0.2779	1.3825	0.0742	0.2938	1.0454	0.0435	0.3166	1.1878	−0.0950
0.4652	0.7628	0.6384	0.4738	0.7723	0.7371	0.3837	1.3123	0.0844	0.3901	1.0295	0.0351	0.4149	1.1522	−0.0960
0.5482	0.7859	0.6277	0.5583	0.7938	0.6679	0.4783	1.25609	0.0806	0.4907	1.0132	0.0089	0.5164	1.1150	−0.9120
0.6519	0.8163	0.5612	0.6194	0.8102	0.6040	0.5900	1.1800	0.0592	0.5914	0.9972	−0.0359	0.6158	1.0782	−0.0874
0.7277	0.8398	0.4600	0.7088	0.8354	0.5189	0.6834	1.1217	0.0537	0.6922	0.9809	−0.0362	0.7159	1.0407	−0.0776
0.8399	0.8760	0.3277	0.8160	0.8684	0.3331	0.7814	1.0616	0.0486	0.7951	0.9644	−0.0352	0.8092	1.0054	−0.0687
0.9177	0.9025	0.2049	0.9094	0.8991	0.2032	0.8889	0.9970	0.0335	0.8949	0.9485	−0.0297	0.9032	0.9697	−0.0487
0.9791	0.9243	0.0886	0.9991	0.9312	0.0210	0.9508	0.9604	0.0214	0.9580	0.9384	−0.006	0.9643	0.9458	−0.0361
EMA + *n*-hexane			EMA + *n*-heptane			EMA + carbon tetrachloride			EMA + chlorobenzene			EMA + *o*-dichlorobenzene		
0.03396	0.6596	0.0344	0.0489	0.6847	0.0975	0.0343	1.5448	0.0316	0.0358	1.0872	−0.0094	0.0383	1.2828	−0.0579
0.2079	0.6999	0.1777	0.2294	0.7204	0.2495	0.1638	1.4376	0.1004	0.1699	1.0574	−0.0582	0.1842	1.2206	−0.1237
0.4065	0.7485	0.2882	0.4379	0.7647	0.3103	0.3394	1.3050	0.1500	0.3526	1.0193	−0.1032	0.3691	1.1442	−0.1659
0.5102	0.7744	0.3136	0.5397	0.7875	0.3200	0.4350	1.2377	0.1744	0.4478	1.0066	−0.1280	0.4699	1.1037	−0.1731
0.7082	0.8252	0.2589	0.7290	0.8326	0.2336	0.6448	1.1022	0.1647	0.6550	0.9618	−0.1162	0.6734	1.0244	−0.1616
0.8027	0.8461	0.1919	0.8248	0.8566	0.1805	0.7620	1.0326	0.1396	0.7647	0.9425	−0.1053	0.7787	0.9843	−0.1267
0.9640	0.8933	0.0518	0.9635	0.8931	0.0588	0.9444	0.9321	0.0443	0.9487	0.9117	−0.0553	0.9555	0.9196	−0.0759
BMA + *n*-hexane			BMA + *n*-heptane			BMA + carbon tetrachloride			BMA + chlorobenzene			BMA + *o*-dichlorobenzene		
0.0331	0.695	0.0085	0.0394	0.6845	0.0319	0.0296	1.5411	0.0454	0.0267	1.0868	−0.0015	0.0306	1.2819	−0.0617
0.1715	0.6970	0.0444	0.1884	0.7172	0.0800	0.1335	1.4527	0.1831	0.1386	1.0544	−0.1414	0.1518	1.2173	−0.2296
0.3526	0.7433	0.0217	0.3823	0.7588	0.1304	0.2903	1.2940	0.2748	0.2979	1.0136	−0.2713	0.3186	1.1373	−0.4216
0.4450	0.7660	−0.0521	0.4762	0.7787	0.1248	0.3769	1.2275	0.2901	0.3879	0.9932	−0.3475	0.4145	1.0949	−0.4540
0.6533	0.8139	−0.1311	0.6795	0.8205	0.1180	0.5867	1.0891	0.2858	0.5969	0.9505	−0.3453	0.6200	1.0126	−0.3338
0.7626	0.8373	−0.1193	0.7871	0.8422	0.1020	0.7078	10213	0.2276	0.7182	0.9286	−0.2796	0.7358	0.9690	−0.1332
0.9475	0.8746	−0.0600	0.9512	0.8748	0.0488	0.9260	0.9160	0.0796	0.9304	0.8947	−0.1003	0.9408	0.9025	−0.0733

Table III. Speeds of Sound and Excess Isentropic Compressibilities of Binary Mixtures of Acrylic Esters (x) + Organic Solvents at 303.15 K

x	v $(\mathrm{m \cdot s^{-1}})$	K_s^E $(\mathrm{TPa})^{-1}$	x	v $(\mathrm{m \cdot s^{-1}})$	K_s^E $(\mathrm{TPa})^{-1}$	x	v $(\mathrm{m \cdot s^{-1}})$	K_s^E $(\mathrm{TPa})^{-1}$	x	v $(\mathrm{m \cdot s^{-1}})$	K_s^E $(\mathrm{TPa})^{-1}$	x	v $(\mathrm{m \cdot s^{-1}})$	K_s^E $(\mathrm{TPa})^{-1}$
MMA + *n*-hexane			MMA + *n*-heptane			MMA + carbon tetrachloride			MMA + chlorobenzene			MMA + *o*-dichlorobenzene		
0.0731	1035.2	−4.2	0.0240	1125.1	−1.6	0.0320	909.8	4.5	0.0354	1244.0	−2.4	0.0456	1269.6	−8.8
0.1732	1045.2	−8.0	0.1404	1133.5	−6.4	0.0898	918.4	10.7	0.0942	1241.3	−5.1	0.1114	1264.6	−15.5
0.2754	1056.5	−11.0	0.2282	1140.4	−10.5	0.1842	933.6	19.8	0.1956	1238.1	−10.7	0.2108	1254.0	−21.8
0.3520	1065.6	−12.8	0.3569	1149.4	−17.6	0.2779	951.6	24.3	0.2938	1236.1	−16.9	0.3166	1243.5	−27.3
0.4652	1180.4	−13.8	0.4738	1160.1	−21.7	0.3837	976.9	25.1	0.3901	1232.6	21.3	0.4149	1232.4	−29.2
0.5482	1091.9	−13.1	0.5583	1165.1	−21.8	0.4783	1001.1	24.5	0.4907	1224.3	20.6	0.5164	1222.5	−30.3
0.6519	1108.1	−11.9	0.6194	1168.5	−21.4	0.5900	1033.4	20.5	0.5914	1215.3	18.5	0.6158	1212.7	−28.9
0.7277	1221.2	−10.7	0.7088	1170.2	−17.2	0.6834	1062.9	16.2	0.6922	1205.8	−14.8	0.7159	1203.6	25.7
0.8399	1143.0	−7.7	0.8160	1172.4	11.8	0.7814	1096.3	11.0	0.7951	1199.2	−13.8	0.8092	1196.2	−21.3
0.9177	1159.3	−4.0	0.9094	1177.5	−6.5	0.8889	1136.0	4.7	0.8949	1187.4	−5.3	0.9032	1188.4	14.2
0.9791	1174.0	−0.9	0.9991	1178.9	−0.1	0.9508	1159.5	2.0	0.9580	1181.8	−1.4	0.9643	1181.6	−4.6
EMA + *n*-hexane			EMA + *n*-heptane			EMA + carbon tetrachloride			EMA + chlorobenzene			EMA + *o*-dichlorobenzene		
0.0396	1029.3	3.8	0.0489	1122.7	4.1	0.0343	911.6	5.0	0.0358	1242.4	0.2	0.0383	1267.1	−4.6
0.2079	1037.0	15.8	0.2294	1125.6	13.3	0.1638	937.6	17.3	0.1699	1236.4	−1.9	0.1842	1253.7	−12.1
0.4065	1056.2	20.0	0.4379	1132.7	20.3	0.3394	980.1	25.7	0.3526	1228.2	−4.0	0.3691	1235.1	−14.9
0.5102	1070.6	19.5	0.5397	1140.1	18.2	0.4350	1006.5	23.6	0.4478	1222.3	−3.0	0.4699	1225.7	−14.4
0.7082	1108.9	13.0	0.7290	1158.6	12.2	0.6448	1070.4	17.9	0.6550	1212.9	−3.2	0.6734	1208.7	−9.4
0.8027	1135.7	8.2	0.8248	1171.0	7.2	0.7620	1109.3	13.0	0.7647	1207.2	−2.5	0.7787	1202.9	−6.7
0.9640	1182.7	1.7	0.9635	1189.9	2.1	0.9444	1175.2	2.8	0.9487	1199.1	−1.7	0.9555	1197.8	−3.0
BMA + *n*-hexane			BMA + *n*-heptane			BMA + carbon tetrachloride			BMA + chlorobenzene			BMA + *o*-dichlorobenzene		
0.0331	1430.1	−2.1	0.0394	1123.9	−2.4	0.0296	915.9	−0.4	0.0267	1245.0	−1.0	0.0306	1270.2	−4.9
0.1715	1334.1	−6.2	0.1884	1144.2	−5.9	0.1335	949.9	−2.5	0.1386	1244.2	−3.8	0.1518	1263.8	−11.7
0.3526	1210.4	−9.6	0.3823	1135.8	−5.7	0.2903	998.7	−3.8	0.2979	1239.1	−6.3	0.3186	1251.6	−16.7
0.4450	1148.7	−9.9	0.4762	1140.4	−3.6	0.3769	1024.3	−3.4	0.3879	1234.7	−6.6	0.4145	1243.5	−17.0
0.6533	1011.1	−9.1	0.6795	1161.0	−3.0	0.5867	1085.3	−3.8	0.5969	1223.7	−5.9	0.6200	1227.2	−15.9
0.7626	940.4	−7.2	0.7871	1172.3	−2.6	0.7078	1119.1	−3.4	0.7182	1216.2	−5.3	0.7358	1218.3	−12.4
0.9475	822.7	−2.1	0.9512	1189.4	−0.4	0.9260	1177.9	−1.8	0.9304	1201.8	−2.1	0.9408	1201.6	−4.0

Table IV. Least-Squares Coefficients of Eq. (4) and Standard Deviations σ as Calculated by Eq. (5) for the Excess Functions of Acrylic Esters + Organic Solvent Mixtures at 303.15 K

	V^E (cm$^3\cdot$mol^{-1})					K_s^E (TPa)$^{-1}$				
	a_0	a_1	a_2	a_3	σ	a_0	a_1	a_2	a_3	σ
MMA +										
n-Hexane	2.4418	−0.9870	0.2750	2.4270	0.0004	−54.4838	−3.6056	−2.0733	14.5296	0.05
n-Heptane	2.7312	−1.6336	1.4901	—	0.0001	−85.1464	−47.7673	40.9840	73.9789	0.05
Carbon tetrachloride	0.2851	−0.0461	0.1872	—	0.0001	96.4280	−55.5820	−6.2730	—	0.07
Chlorobenzene	0.0090	−0.2659	−0.0746	—	0.0001	−84.1464	−7.5270	37.5649	25.7468	0.05
o-Dichlorobenzene	−0.3107	0.0085	−0.6357	—	0.0001	−117.39	−24.7144	−62.664	64.1170	0.10
EMA +										
n-Hexane	1.1847	0.2567	—	—	0.004	76.8931	−30.4608	−3.5477	—	0.05
n-Heptane	1.1763	−0.2535	0.7855	—	0.0001	72.2374	−18.1668	−2.0294	—	0.05
Carbon tetrachloride	0.6774	−0.0071	0.2527	—	0.0001	92.6099	−50.9724	9.5913	—	0.05
Chlorobenzene	−0.4676	−0.3696	−0.2754	—	0.0001	−13.3347	−10.6685	−8.2417	—	0.05
o-Dichlorobenzene	−0.5486	−0.0901	−1.2470	—	0.0002	−48.1305	30.1625	−54.399	—	0.05
BMA +										
n-Hexane	−0.3151	−0.8339	—	—	0.020	−38.2954	8.3660	−16.801	—	0.05
n-Heptane	0.4586	0.0130	0.6827		0.0001	−16.6220	25.6220	−23.353	—	0.05
Carbon tetrachloride	1.2749	−0.2757	—	—	0.020	−14.0762	0.4614	−17.506	—	0.05
Chlorobenzene	−1.5361	−0.4802	0.7677	—	0.010	−25.7383	2.5103	−11.215	—	0.05
o-Dichlorobenzene	−1.5368	0.5845	—	—	0.006	−61.0753	34.0562	−61.517	—	0.05

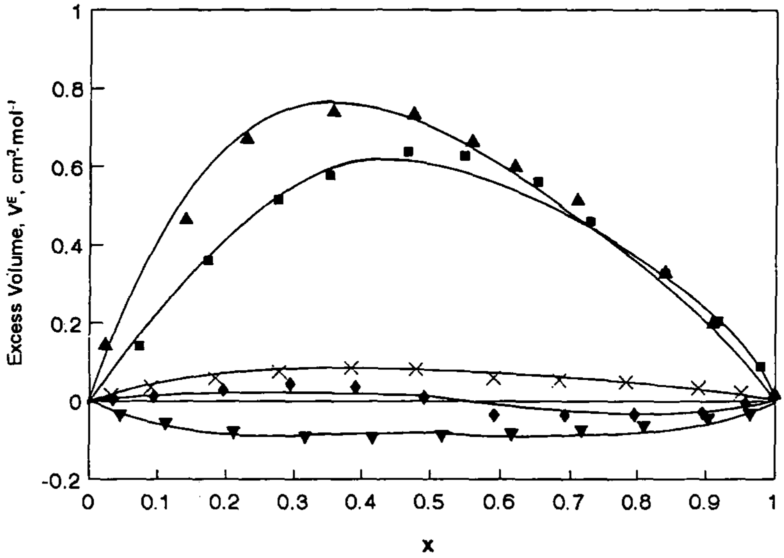

Fig. 1. Excess volumes of methyl methacrylate + organic solvetn mixtures at 303.15 K. (■) *n*-Hexane; (▲) *n*-heptane; (×) carbon tetrachloride; (◆) chlorobenzene; (▼) *o*-dichlorobenzene; (——) calculated from Eq. (4) and coefficients from Table IV.

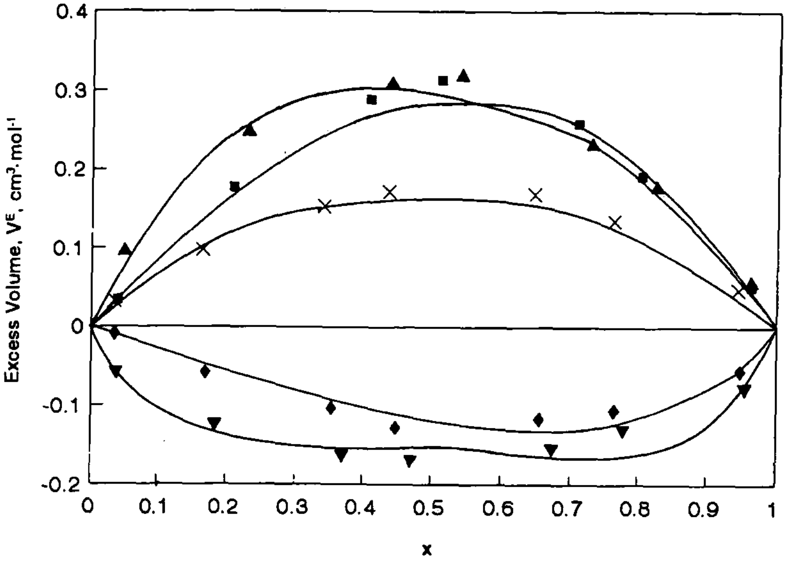

Fig. 2. Excess volumes of ethyl methacrylate + organic solvent mixtures at 303.15 K. Symbols are the same as in Fig. 1.

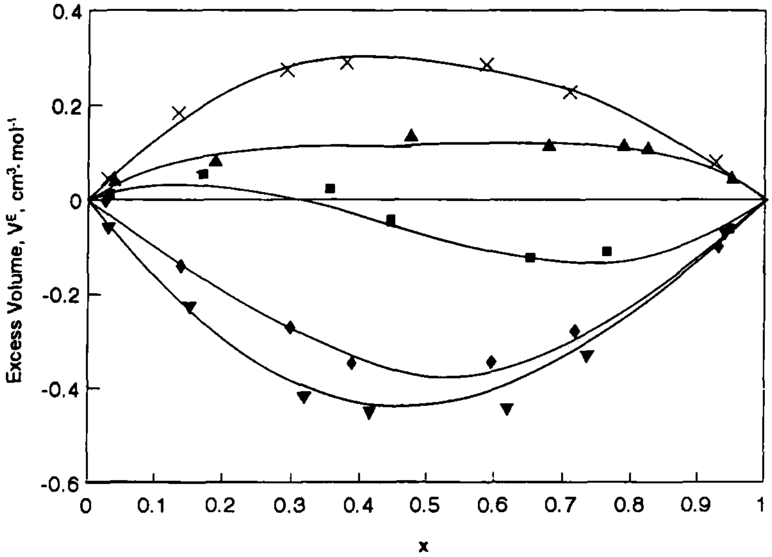

Fig. 3. Excess volumes of butyl methacrylate + organic solvent mixtures at 303.15 K. Symbols are the same as in Fig. 1.

chain length of the ester and the solvent type show a definite trend. It can be seen from the figures that the excess volumes of binary mixtures of both MMA + and EMA + nonpolar solvents, *viz.*, *n*-hexane and *n*-heptane, are positive over the entire range of mole fraction, however, the V^E values in BMA + *n*-hexane mixtures are found to be sigmoidal, with slight initial positive values followed by a negative trend. However, the excess volumes of BMA + *n*-heptane mixtures are positive.

The excess volumes of the all three acrylic esters with carbon tetrachloride, which itself is nonpolar but highly polarizable, were found to be positive in the entire range of mole fraction. The V^E values of the acrylic esters with the polar aromatic solvents, *viz.*, chlorobenzene and *o*-dichlorobenzene, were found to be negative with the exception of the mixtures of MMA + chlorobenzene, in which the shape of the curve was observed to be sigmoidal.

A comparison of the magnitudes and sign of the K_S^E values from Table III at an ester mol fraction of 0.5 of the mixtures offered further insight into the balance of forces present. It was observed that there was a general decrease in the K_S^E values for the acrylic esters + alkane mixtures, with heptane < hexane, while a similar decrease was observed in acrylic esters + chlorinated hydrocarbons in the manner dichlorobenzene < chlorobenzene < carbon tetrachloride. However, it may be noticed that the

Table V. Sound Velocities of Binary Mixtures of MMA(x) + Organic Solvents as Derived from FLT and CFT Calculations at 303.15 K

x	v_{FLT} $(m \cdot s^{-1})$	v_{CFT} $(m \cdot s^{-1})$
	MMA + *n*-hexane	
0.0731	1046.2	1039.0
0.1732	1059.4	1051.7
0.2754	1076.5	165.9
0.3520	1088.7	1076.6
0.4652	1105.9	1092.8
0.5482	1118.5	1105.3
0.6519	1133.9	1121.8
0.7277	1145.4	1133.6
0.8399	1159.9	1152.0
0.9177	1169.6	1165.1
0.9791	1157.0	1168.8
	MMA + chlorobenzene	
0.0354	1236.7	1242.2
0.0942	1225.2	1238.6
0.1956	1209.4	1231.3
0.2938	1197.7	1224.8
0.3901	1190.1	1218.4
0.4907	1185.1	1212.2
0.5914	1182.8	1206.0
0.6922	1180.1	1199.3
0.7951	1178.8	1192.5
0.8949	1178.3	1185.9
0.9580	1178.6	1181.6
	MMA + *n*-heptane	
0.0240	1121.3	1123.7
0.1404	1104.4	1127.5
0.2282	1129.2	1130.6
0.3569	1138.9	1136.9
0.4738	1147.6	1143.4
0.5583	1154.1	1148.1
0.6194	1159.1	1152.1
0.7088	1164.3	1157.5
0.8160	1171.3	1165.4
0.9094	1174.7	1171.5
0.9991	1178.2	1178.5

Table V. *(Continued)*

x	ν_{FLT} $(m \cdot s^{-1})$	ν_{CFT} $(m \cdot s^{-1})$
	MMA + *o*-dichlorobenzene	
0.0456	1174.7	1264.4
0.1114	1178.2	1258.7
0.2108	1211.1	1250.1
0.3166	1192.6	1240.9
0.4149	1180.3	1231.9
0.5164	1171.9	1223.2
0.6158	1167.7	1214.1
0.7159	1166.6	1204.9
0.8092	1168.5	1196.4
0.9032	1172.6	1188.9
0.9643	1176.8	1182.1
	MMA + carbon tetrachloride	
0.0320	911.9	914.3
0.0898	923.3	929.9
0.1842	943.2	955.5
0.2779	964.2	980.9
0.3837	989.6	1009.6
0.4783	1013.9	1035.6
0.5900	1045.0	1066.4
0.6834	1072.2	1068.9
0.7814	1102.5	1118.7
0.8889	1172.0	1147.9
0.9508	1160.3	1165.2

K_S^E values in the case of all the mixtures with chlorobenzene and *o*-dichlorobenzene were found to be negative over the entire range of ester mole fractions. The K_S^E values of all the mixtures containing butyl methacrylate (BMA) were also found to be negative over the entire range of compositions.

The measured speed of sound data on acrylic ester + organic solvents mixtures were further analysed by applying the free length theory (FLT) and collision factor theory (CFT) for the MMA + organic solvent systems. The pertinent relations that were used to caculate the speeds of sound through FLT and CFT have been described in detail in the literature [34–36]. The calculated speeds of sound are included in Table V. The standard deviation, $\sigma(\%)$, between the experimental and the predicted speeds of sound for MMA + hexane, + *n*-heptane + carbon tetrachloride,

+chlorobenzene, and +dichlorobenzene were 1.24, 2.59, 0.32, 0.59, and 0.83 for FLT calculations and 0.22, 2.57, 0.25, 0.44, and 0.83 for CFT calculations, respectively. The smaller percentage values of the deviation through CFT calculations indicate the suitability of the later for predicting the speeds of sound of such mixtures.

4. DISCUSSION

The volumetric behavior of acrylic esters +aliphatic alkanes (*n*-hexane and *n*-heptane) was found to follow the same order as in the case of other aliphatic alkyl alkanoate +alkane binary mixtures [1, 10]. The equimolar excess volumes of MMA +*n*-hexane and +*n*-heptane mixtures were found to be large and positive. Such large V^E values can be attributed to the disordering of the ester structures by unlike alkane molecules. The decrease in V^E $(x=0.5)$ values for a given mixture with an increase in the alkyl chain length of the ester species can be attributed to the well-known dilution in the dipolar interactions in the higher alkyl esters. The observed negative V^E $(x=0.5)=-0.0622$ for BMA +*n*-hexane mixtures indicates the domination of packing effects in the form of interisitial accommodation of smaller hexane molecules into loose BMA structures. To our knowledge, there are no literature V^E values for comparison of our data with similar binary mixtures with EMA and BMA. However, our observed V^E $(x=0.5)$ at 303.15 K for MMA +*n*-hexane and +*n*-heptane mixture, *viz*., 0.6288 and 0.7260 $cm^3 \cdot mol^{-1}$, are comparable with the 0.5750 and 0.7685 $cm^3 \cdot mol^{-1}$ values for the same mixtures at equimolar fractions and at 298.15 K as reported by Luo et al. [12]. The decrease in the V^E values with increased alkyl chain length is also comparable with the alkyl acetate *n*-heptane mixtures at 298.15 K as reported by Grolier et al. [1]. Our V^E $(x=0.5)$ value of 0.6288 for MMA +*n*-hexane mixtures is higher than the V^E $(x=0.5)$ of 0.5285 for methyl butanoate +*n*-hexane mixtures at 298.15 K reported by Gonzalez et al. [10]. Methyl butanoate has a molecular structure identical to that of MMA, the only difference being the presence of unsaturation in the later. The higher V^E $(x=0.5)$ value in MMA +*n*-hexane mixtures thus indicates closer packing in MMA molecules, which in turn may be disrupted by unlike *n*-hexane molecules. The literature reported higher positive excess enthalpies for MMA +*n*-hexane and MMA +*n*-heptane mixtures [12] as well as for methyl butanoate +*n*-hexane mixtures [10] at 298.15 K, further support the notion of domination of dispersing interactions in these mixtures.

The V^E $(x=0.5)$ for various acrylic esters +chlorobenzene and +*o*-dichlorobenzene mixtures were found to be either too small or negative. The negative V^E values may be attributed to the balance of several forces, *viz.*, (i) n–π interactions between the lone pair of electrons of ester group and π electrons of the aromatic ring, (ii) specific interactions of O——Cl type, (iii) packing interactions through interstitial accommodation, and (iv) dispersing structure-breaking interactions. The interactions of types (i)–(iii) are of the structure-making type and are expected to be dominant in the EMA and BMA mixtures.

It can be seen from Table III that the excess isentropic compressibilities are found to be negative for all mixtures except EMA +n-hexane, EMA +n-heptane, MMA +carbon tetrachloride, and EMA +carbon tetrachloridre. The negative excess compressibilities in the case of MMA +n-hexane and +n-heptane mixtures were rather unexpected considering the high positive excess volumes of these mixtures.

Hence it is thought worthwhile to apply the Prigogine–Flory–Patterson (PFP) treatment to predict the equimolar excess volumes of MMA–organic solvent mixtures. The PFP treatment considers the excess thermodynamic properties of binary mixtures to be sum of the contributions from an interactional term, $V^{\mathrm{E}}(\chi_{12})$, which is proportional to the Flory χ_{12} parameter, P^* contribution, $V^{\mathrm{E}}(P^*)$, which arises due to the differences in the internal pressures and reduced volumes of the pure components and the free volume contribution, V^{E} (f.v.), which orginates from the difference in the degrees of thermal expansion between the components. The appropriate relations used for above calculations are the same as described by Van and Patterson [17] and Letcher and Dexter [18]. The relation used to calculate the excess volume of a binary mixture through PFP is summarized as

$$\frac{V^{\mathrm{E}}}{x_1 V_1^* + x_2 V_2^*} = \frac{(\tilde{v}^{1/3}-1)\,\tilde{v}^{2/3}\Psi_1\theta_2\chi_{12}}{[(4/3\tilde{v}^{-1/3}-1]\,P_1^*} \quad \text{(interactional term)}$$

$$-\frac{(\tilde{v}_1-\tilde{v}_2)^2\{(14/9\tilde{v}^{-1/3})-1)\}\;\Psi_1\Psi_2}{[(4/3\tilde{v}^{1/3})-1]\,\tilde{v}} \quad \text{(free volume term)}$$

$$+\frac{(\tilde{v}_1-\tilde{v}_2)(P_1^*-P_2^*)\;\Psi_1\Psi_2}{P_2^*\Psi_1+P_1^*\Psi_2} \quad (P^*\ \text{effect})$$

where $\tilde{v}_i$ and P_i^* are the reduced volume and characteristic pressure of components 1 and 2, respectively. The terms θ_2 and Ψ_i are the site fraction and contact energy fraction of the a respective components. The term χ_{12} is the interaction term representing binary contacts and, in general, is evaluated from a fit to experimental excess enthalpies. However, because of the non-availability of H^{E} values for the present mixtures, we have calculated the value of χ_{12} from the respective fit to the experimental V^{E} ($x = 0.5$) data. The reduced, characteristic parameters and the site and segment fractions

Table VI. Physcochemical Data and Characteristic Parameters of Pure Liquids at 303.15 K

Liquid	α (K^{-1})	C_p $(J{\cdot}K^{-1}{\cdot}mol^{-1})^a$	$\tilde{v}$	V^* $(cm^3{\cdot}mol^{-1})$	P^* $(J{\cdot}cm^{-3})$	$\tilde{T}$
MMA	1.2888×10^{-3}	194.54	1.3079	82.16	635.99	0.06544
n-Hexane	1.4040×10^{-3}	197.34	1.3292	99.71	405.27	0.06808
n-Heptane	1.2660×10^{-3}	226.28	1.3038	113.81	437.21	0.06491
Carbon tetrachloride	1.2410×10^{-3}	129.61	1.2990	75.20	563.88	0.06429
Chlorobenzene	0.9850×10^{-3}	152.31	1.2480	82.33	590.56	0.05704
O-Dichlorobenzene	0.5312×10^{-3}	223.28	1.1452	98.82	404.43	0.03859

[a] C_p values are interpolated from the Refs. 16, 31, 32, and 33.

of the individual pure components needed for these calculations were derived from the Flory formalism [19] and are summarized in Table VI.

The individual contributions along with the calculated and experimental equimolar excess volumes, V^E_{cal} and V^E_{exp}, are given in Table VII. The V^E_{cal} and V^E_{exp} in the case of all the mixtures were observed to have the same sign and found to have values closer to each other. This indicates that the PFP treatment represents a reasonable approximation in predicting the excess volumes of these mixtures. It is evident also from the Table VII that the individual contributions to the excess volumes provide no definite trend but offer interesting insight into the dominant factor.

The $V^E(\chi_{12})$ value for the MMA +*n*-hexane and MMA +*n*-heptane mixtures was found to be close to the experimental V^E value and, at the same time, was found to be slightly higher in the former and lower in the later mixture. These over- and underestimations are balanced, however, by the combined contributions of V^E(f.v.) and $V^E(P^*)$. Similar trends were observed in MMA +carbon tetrachloride and +chlorobenzene mixtures.

Table VII. Interactional, Free Volume, and P^* Contributions to the Equimolar Excess Volumes of MMA–Organic Solvent Mixtures at 303.15 K

MMA +	χ^{12} $(J{\cdot}cm^{-3})^a$	$V^E(\chi_{12})$ $(cm^3{\cdot}mol^{-1})$	V^E (f.v.) $(cm^3{\cdot}mol^{-1})$	$V^E(P^*)$ $(cm^3{\cdot}mol^{-1})$	V^E_{cal} $(cm^3{\cdot}mol^{-1})$	V^E_{exp} $(cm^3{\cdot}mol^{-1})$	δ^b
n-Hexane	37.35	0.8730	−0.0149	−0.2172	0.6409	0.6288	−0.0121
n-Heptane	29.70	0.6795	−0.00003	0.0374	0.7169	0.7266	0.0097
Carbon tetrachloride	2.92	0.0495	−0.0023	0.0209	0.0681	0.0757	0.0076
Chlorobenzene	1.19	0.0194	−0.1093	0.0912	0.0013	0.0007	0.0006
o-Dichlorobenzene	−63.29	−0.8449	−0.8873	1.6585	−0.0737	−0.0969	−0.0232

[a] Calculated from a fit to experimental $V^E_{0.5}$ data.

[b] $\delta = V^E_{exp} - V^E_{cal}$.

The $V^E(\chi_{12})$ and $V^E(\text{f.v.})$ values were found to be large and negative in the case of MMA + *o*-dichlorobenzene mixtures and were equally balanced by high positive $V^E(P^*)$ values. These observations and the balance of the various factors emphasize the complex nature of interactions in the acrylic ester + organic solvent mixtures. The different factors, *viz.*, interactional, free volume, and P^* effects, are supposed to play an equal role in the final value of the observed experimental excess volumes.

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