Densities, Relative Permittivities, Excess Volumes, and Excess Molar Polarizations for Alkyl Ester (Methyl Propanoate, Methyl Butanoate, Ethyl Propanoate, and Ethyl Butanoate) + Hydrocarbons (*n*-Heptane, Benzene, Chlorobenzene, and 1,1,2,2-Tetrachloroethane) at 308.15 K and 318.15 K

Nandhibatla V. Sastry,* Alex George,† Nirmesh J. Jain,† and Pratap Bahadur†

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

New experimental values of density and relative permittivity for alkyl esters (methyl propanoate, methyl butanoate, ethyl propanoate, ethyl butanoate) + *n*-heptane, + benzene, + chlorobenzene, and + 1,1,2,2-tetrachloroethane are reported at 308.15 K and 318.15 K. The relative permittivities calcuated from the measured capacitances have an uncertainty of ±0.1%. The excess volumes and relative permittivity deviation are calculated from the density and relative permittivity data. The molar and excess molar polarizations are obtained from the combination of permittivity and density data for all the mixtures at both temperatures. The results are analyzed in terms of molecular interactions.

Introduction

Esters of both aliphatic and acrylic types are important industrial chemicals. The thermodynamic behavior of aliphatic alkyl alkanoates + aliphatic alkanes (Grolier et al., 1974; Jimenez et al., 1986; Garcia et al., 1995; Gonazalez et al., 1994; Ortega et al., 1991), + aromatic alkanes (Grolier et al., 1974; Qin et al., 1992; Katyal et al., 1990), and + chlorinated alkanes (Ortega et al., 1988) has been studied extensively by measurements of excess volumes and excess enthalpies. Detailed investigations on transport, dielectric, and acoustic properties of such mixtures are scarce in the literature. We are involved in a broad research program which encompasses studies of binary and ternary mixtures containing acrylic esters, alkanes, and alcohols. Various thermophysical properties, viz., viscosity, speeds of sound, density, relative permittivity, and molar polarizations, and related excess functions for acrylic esters + alkanes have been previously reported (Sastry and Dave, 1996a,b, 1997; Sastry and Valand, 1998). A knowledge of similar properties of individual binary mixtures of alkanes + either acrylic esters or + homologous aliphatic esters under identical conditions is highly desirable for ascertaining the role of unsaturation in the molecular interactions containing the latter components. Besides this physical consideration, this information is also useful in estimating the required group interaction parameters for developing group contribution methods for predicting the properties of mixtures.

As part of our ongoing work along these lines, we report densities, relative permittivity, excess volumes, and molar polarizations for 15 binary mixtures of alkyl alkanoate (methyl- and ethyl propanoate, methyl- and ethyl butanoate) + *n*-heptane, + benzene, + chlorobenzene, and + 1,1,2,2-tetrachloroethane at 308.15 K and 318.15 K.

* Corresponding author. Telefax: 0091-2692-36475. E-mail: sastry@pcbbs.net.
† Department of Chemistry, South Gujarat University, Surat 395 007, Gujarat, India.

Experimental Section

Materials. Methyl propanoate (MP) and methyl butanoate (MB) were Fluka chemicals. Ethyl propanoate (EP) and ethyl butanoate (EB) were Lancaster chemicals. These chemicals were used as such without any purification. Benzene and chlorobenzene were BDH AR chemicals and were used as received. *n*-Heptane was obtained from SD Fine Chemicals and was further purified by the standard procedure (Riddick et al., 1986). 1,1,2,2-Tetrachloroethane was a technical grade chemical from SD and was washed repeatedly with concentrated sulfuric acid, steam distilled, and fractionally distilled over a 20 plate column. The central portion boiling within 0.2 °C was stored over anhydrous calcium sulfate and was further dried over potassium carbonate for 1 day before use. The purity of all the chemicals was analyzed chromatographically and was found to be >99.8% on a mole basis.The measured densities, ρ, and relative permittivities, ϵ_r, of all the pure components were in reasonable agreement with the literature data, and such a comparison is given in Table 1.

The binary mixtures for each composition were prepared in hermetically sealed glass vials by mass measurements accurate to within ±0.02 mg on a Dhona single-pan balance, Dhona 100 DS. The uncertainty in the calculated mole fractions was about ±0.0001.

Methods. The densities were determined with a double-stem pycnometer with a bulb volume of about 11 cm^3. The pycnometer was calibrated with triple distilled water and double distilled cyclohexane, and the temperature during the measurements was maintained accurate to within ±0.01 °C. The relative permittivities of pure liquids and mixture components were measured with a universal dielectrometer type OH-301, Radelkis. The instrument in fact measures the capacitance in pF at a fixed frequency of 3 MHz. The capacitances of the static air and the dielectric liquids were measured in specially provided stainless steel measuring cells. The stray capacitance of the dielectric cells was ascertained by calibrating them with dioxane−water mixtures of varying compositions and

10.1021/je980174k CCC: $18.00
Published on Web 04/14/1999

Table 1. Densities (ρ) and Relative Permittivity (ϵ_r) for the Pure Components

	T = 308.15 K				T = 318.15 K			
	ρ/(g·cm^{-3})		ϵ_r		ρ/(g·cm^{-3})		ϵ	
	expt	lit.	expt	lit.	expt	lit.	expt	lit.
methyl propanoate	0.9093[a]	0.9093[a,b]	5.852	5.852[m]	0.8848		5.627	5.627[m]
methyl butanoate	0.8924[a]	0.89249[a,c]	5.288	5.290[m]	0.8737		5.066	5.066[m]
ethyl propanoate	0.8841[a]	0.88407[a,d]	5.580	5.582[m]	0.8624		5.361	5.360[m]
ethyl butanoate	0.8688		4.986	4.986[m]	0.8609		4.752	4.750[m]
n-heptane	0.6712	0.67101[e]	1.894	1.894[l]	0.6623	0.66232[f]	1.882	1.882[m]
benzene	0.8630	0.86304[g]	2.253	2.253[m]	0.8520	0.8522[h]	2.235	2.235[m]
chlorobenzene	1.0904	1.0904[i]	5.489	5.490[m]	1.0790	1.0795[j]	5.298	5.298[m]
1,1,2,2-tetrachloroethane	1.5745	1.5745[k]	7.096	7.098[m]	1.5642	1.5647[k]	7.063	7.063[m]

[a] Values at 298.15 K. [b] Chaar et al., 1995. [c] Fernandez et al., 1985. [d] Jimenez et al., 1986. [e] Romani et al., 1994. [f] Blanco et al., 1993. [g] Wieczorek and Zywocinski, 1983. [h] Aicart et al., 1980. [i] Extrapolated values from Timmermans (1965). [j] Matilla et al., 1993. [k] Prasad et al., 1990. [l] Sastry and Valand, 1996. [m] Extrapolated values from Lide (1994).

Table 2. Densities (ρ) and Excess Volumes (V^E) for Alkyl Alkanoate (1) + Hydrocarbons at 308.15 K

x_1	ρ/(g·cm^{-3})	V^E/(cm^{-3}·mol^{-1})	x_1	ρ/(g·cm^{-3})	V^E/(cm^{-3}·mol^{-1})	x_1	ρ/(g·cm^{-3})	V^E/(cm^{-3}·mol^{-1})	x_1	ρ/(g·cm^{-3})	V^E/(cm^{-3}·mol^{-1})
MP + *n*-Heptane			MP + Benzene			MP + Chlorobenzene			MP + 1,1,2,2-Tetrachloroethane		
0.0447	0.6772	0.227	0.0415	0.8640	0.031	0.0485	1.0816	−0.044	0.0501	1.5444	−0.121
0.1083	0.6852	0.493	0.1037	0.8655	0.074	0.0993	1.0722	−0.077	0.1021	1.5128	−0.237
0.1932	0.6976	0.758	0.2041	0.8683	0.102	0.2038	1.0524	−0.111	0.2031	1.4499	−0.429
0.3018	0.7150	0.981	0.3026	0.8712	0.111	0.2614	1.0413	−0.119	0.3020	1.3865	−0.567
0.4146	0.7354	1.071	0.4053	0.8742	0.112	0.4087	1.0124	−0.113	0.3398	1.3618	−0.605
0.5227	0.7572	1.072	0.4569	0.8757	0.112	0.4556	1.0031	−0.114	0.5038	1.2516	−0.670
0.5693	0.7674	1.044	0.6013	0.8798	0.113	0.6041	0.9734	−0.103	0.6012	1.1838	−0.632
0.7002	0.7988	0.888	0.7026	0.8826	0.112	0.7011	0.9538	−0.099	0.6946	1.1143	−0.543
0.7986	0.8256	0.685	0.8018	0.8853	0.112	0.8064	0.9323	−0.087	0.7988	1.0416	−0.397
0.9016	0.8572	0.386	0.9039	0.8884	0.069	0.9054	0.9117	−0.059	0.9016	0.9655	−0.208
0.9509	0.8739	0.206	0.9674	0.8905	0.029	0.9486	0.9026	−0.038	0.9481	0.9308	−0.118
1.0000	0.8916										
MB + *n*-Heptane			MB + Benzene			MB + Chlorobenzene					
0.0525	0.6752	0.244	0.0519	0.8641	0.030	0.0851	1.0720	−0.093			
0.1560	0.6952	0.560	0.1011	0.8653	0.049	0.1025	1.0682	−0.106			
0.1959	0.7019	0.650	0.1924	0.8675	0.065	0.2257	1.0412	−0.137			
0.2969	0.7190	0.927	0.3006	0.8702	0.055	0.3019	1.0246	−0.127			
0.4989	0.7590	0.890	0.3979	0.8727	0.027	0.4004	1.0035	−0.109			
0.5971	0.7798	0.904	0.4927	0.8752	−0.012	0.5036	0.9819	−0.087			
0.7995	0.8279	0.678	0.6028	0.8779	−0.058	0.5911	0.9641	−0.078			
0.8524	0.8418	0.560	0.7012	0.8801	−0.090	0.6834	0.9457	−0.076			
0.9236	0.8617	0.337	0.7896	0.8818	−0.096	0.8223	0.9187	−0.072			
0.9531	0.8703	0.220	0.8998	0.8836	−0.076	0.8997	0.9039	−0.058			
0.9825	0.8793	0.091	0.9524	0.8843	−0.042	0.9522	0.8939	−0.034			
1.0000	0.8848		1.0000								
EP + *n*-Heptane			EP + Benzene			EP + Chlorobenzene			EP + 1,1,2,2-Tetracholroethane		
0.0514	0.6785	0.213	0.0521	0.8645	−0.073	0.0485	1.0807	−0.200	0.0486	1.5407	−0.226
0.0967	0.6851	0.389	0.0984	0.8655	−0.113	0.1020	1.0694	−0.345	0.0999	1.5041	−0.390
0.8165	0.7039	0.701	0.2018	0.8672	−0.151	0.1976	1.0480	−0.460	0.2025	1.4296	−0.563
0.3027	0.7184	0.850	0.3029	0.8686	−0.156	0.3070	1.0228	−0.463	0.2997	1.3587	−0.604
0.4024	0.7364	0.925	0.4009	0.8698	−0.157	0.3981	1.0020	−0.427	0.3983	1.2874	−0.595
0.5033	0.7483	0.948	0.4991	0.8709	−0.161	0.4981	0.9798	−0.393	0.5003	1.2142	−0.573
0.5880	0.7731	0.923	0.5982	0.8721	−0.166	0.6116	0.9556	−0.388	0.5986	1.1461	−0.559
0.7003	0.7976	0.811	0.7114	0.8732	−0.162	0.7034	0.9365	−0.391	0.7023	1.0751	−0.545
0.7994	0.8210	0.641	0.8042	0.8739	−0.136	0.7992	0.9169	−0.377	0.8010	1.0084	−0.490
0.9003	0.8468	0.372	0.8989	0.8744	−0.084	0.9000	0.8961	−0.277	0.9018	0.9407	−0.335
0.9484	0.8600	0.208	0.9200	0.8745	−0.069	0.9478	0.8860	−0.173	0.9510	0.9077	−0.202
1.0000	0.8747										
EB + *n*-Heptane			EB + Benzene			EB + Chlorobenzene			EB + 1,1,2,2-Tetrachloroethane		
0.0502	0.6793	0.181	0.0473	0.8640	−0.065	0.0537	1.0771	−0.185	0.0477	1.5358	−0.212
0.1025	0.6880	0.329	0.0990	0.8649	−0.119	0.0994	1.0656	−0.294	0.1018	1.4923	−0.413
0.2204	0.7084	0.560	0.1937	0.8661	−0.180	0.1869	1.0435	−0.412	0.2004	1.4129	−0.569
0.2998	0.7225	0.653	0.2987	0.8670	−0.210	0.3570	1.0066	−0.451	0.2603	1.3655	−0.590
0.3991	0.7412	0.719	0.4059	0.8677	−0.226	0.4049	0.9904	−0.443	0.3965	1.2620	−0.586
0.5188	0.7644	0.710	0.4998	0.8683	−0.236	0.4939	0.9702	−0.427	0.4979	1.1891	−0.583
0.6073	0.7823	0.656	0.5153	0.8687	−0.245	0.5929	0.9488	−0.415	0.6073	1.1144	−0.607
0.6954	0.8006	0.568	0.7021	0.8693	−0.249	0.6953	0.9278	−0.399	0.6955	1.0567	−0.630
0.8003	0.8232	0.419	0.7978	0.8695	−0.223	0.7941	0.9084	−0.366	0.8023	0.9893	−0.604
0.9011	0.8458	0.231	0.9030	0.8694	−0.151	0.9017	0.8877	−0.247	0.9007	0.9289	−0.436
0.9513	0.8574	0.120	0.9514	0.8692	−0.088	0.9369	0.8809	−0.171	0.9705	0.8866	−0.166
1.0000	0.8688										

dielectric strengths at each measuring temperature. The calibration constants of each cell were evaluated from a knowledge of the relative permittivity values of the calibrating mixtures in terms of the measured capacitance C_1 and stray capacitance C_2 with the following relation

$$C_1 = \frac{C'_3 - C_{air}}{\epsilon - 1} \quad (1)$$

where C_{air} = the measuring capacitance of the cell with air as dielectric and C'_3 = the overall capacitance of the cell when the measuring cell is filled with the calibrating liquid mixtures. The stray capacitance C_2 of the cell is ascertained from

$$C_2 = C_{air} - C_1 \quad (2)$$

Then the unknown relative permittivity of either pure liquids or binary mixtures was obtained with

Table 3. Densities (ρ) and Excess Volumes (V^E) for Alkyl Alkanoate (1) + Hydrocarbons at 318.15 K

x_1	ρ/(g·cm^{-3})	V^E/(cm^{-3}·mol^{-1})	x_1	ρ/(g·cm^{-3})	V^E/(cm^{-3}·mol^{-1})	x_1	ρ/(g·cm^{-3})	V^E/(cm^{-3}·mol^{-1})	x_1	ρ/(g·cm^{-3})	V^E/(cm^{-3}·mol^{-1})
MP + *n*-Heptane			MP + Benzene			MP + Chlorobenzene			MP + 1,1,2,2-Tetrachloroethane		
0.0447	0.6679	0.242	0.0415	0.8530	0.054	0.0485	1.0721	−0.026	0.0501	1.5339	−0.102
0.1083	0.6763	0.525	0.1037	0.8547	0.104	0.0993	1.0610	−0.046	0.1021	1.5021	−0.199
0.1932	0.6887	0.807	0.2041	0.8578	0.150	0.2038	1.0416	−0.068	0.2031	1.4390	−0.351
0.3018	0.7062	1.034	0.3026	0.8611	0.159	0.2614	1.0307	−0.073	0.3020	1.3756	−0.463
0.4146	0.7266	1.141	0.4053	0.8645	0.159	0.4087	1.0025	−0.073	0.3398	1.3509	−0.493
0.5227	0.7486	1.143	0.4569	0.8662	0.160	0.4556	0.9935	−0.072	0.5038	1.2412	−0.545
0.5693	0.7589	1.116	0.6013	0.8708	0.171	0.6041	0.9665	−0.071	0.6012	1.1739	−0.517
0.7002	07906	0.952	0.7026	0.8740	0.179	0.7011	0.9453	−0.061	0.6946	1.1081	−0.450
0.7986	0.8177	0.733	0.8018	0.8772	0.171	0.8064	0.9243	−0.052	0.7988	1.0332	−0.333
0.9016	0.8497	0.423	0.9039	0.8809	0.120	0.9054	0.9042	−0.033	0.9016	0.9580	−0.179
0.9509	0.8667	0.224	0.9674	0.8834	0.051	0.9486	0.8954	−0.019	0.9481	0.9254	−0.098
1.0000	0.8848										
MB + *n*-Heptane			MB + Benzene			MB + Chlorobenzene					
0.0525	0.6696	0.253	0.0519	0.8529	0.056	0.0851	1.0603	−0.066			
0.1560	0.6859	0.607	0.1011	0.8539	0.090	0.1025	1.0565	−0.079			
0.1959	0.6924	0.704	0.1924	0.8560	0.115	0.2257	1.0296	−0.120			
0.2969	0.7099	0.878	0.3006	0.8588	0.099	0.3019	1.0132	−0.126			
0.4989	0.7486	1.004	0.3979	0.8614	0.062	0.4004	0.9922	−0.119			
0.5971	0.7692	1.001	0.4927	0.8640	0.006	0.5036	0.9705	−0.087			
0.7995	0.8168	0.772	0.6028	0.8667	−0.049	0.5911	0.9525	−0.056			
0.8524	0.8307	0.639	0.7012	0.8689	−0.082	0.6834	0.9339	−0.023			
0.9236	0.8505	0.387	0.7896	0.8704	−0.092	0.8223	0.9068	0.011			
0.9531	0.8592	0.253	0.8998	0.8725	−0.066	0.8997	0.8921	0.023			
0.9825	0.8684	0.101	0.9524	0.8732	−0.042	0.9522	0.8824	0.013			
1.0000	0.8737		1.0000								
EP + *n*-Heptane			EP + Benzene			EP + Chlorobenzene			EP + 1,1,2,2-Tetrachloroethane		
0.0514	0.6694	0.257	0.0521	0.8536	−0.099	0.0485	1.0696	−0.237	0.0486	1.5304	−0.255
0.0967	0.6757	0.460	0.0984	0.8547	−0.156	0.1020	1.0583	−0.404	0.0999	1.4937	−0.443
0.2165	0.6940	0.810	0.2018	0.8564	−0.208	0.1976	1.0368	−0.530	0.2025	1.4187	−0.628
0.3027	0.7083	0.940	0.3029	0.8575	−0.205	0.3070	1.0114	−0.521	0.2997	1.3472	−0.664
0.4024	0.7262	0.988	0.4009	0.8585	−0.200	0.3981	0.9904	−0.475	0.3983	1.2754	−0.646
0.5033	0.7381	0.963	0.4991	0.8595	−0.201	0.4981	0.9680	−0.431	0.5003	1.2025	−0.627
0.5880	0.7626	0.933	0.5982	0.8605	−0.207	0.6116	0.9437	−0.430	0.5986	1.1338	−0.619
0.7003	0.7865	0.843	0.7114	0.8615	−0.204	0.7034	0.9247	−0.448	0.7023	1.0628	−0.613
0.7994	0.8091	0.732	0.8042	0.8666	−0.162	0.7992	0.9051	−0.444	0.8010	0.9963	−0.570
0.9003	0.8342	0.496	0.8989	0.8623	−0.098	0.9000	0.8842	−0.331	0.9018	0.9286	−0.398
0.9484	0.8473	0.301	0.9200	0.8623	−0.074	0.9478	0.8740	−0.211	0.9510	0.8955	−0.235
1.0000	0.8624										
EB + *n*-Heptane			EB + Benzene			EB + Chlorobenzene			EB + 1,1,2,2-Tetrachloroethane		
0.0502	0.6703	0.211	0.0473	0.8535	−0.094	0.0537	1.0662	−0.210	0.0477	1.5260	−0.247
0.1025	0.6789	0.387	0.0990	0.8547	−0.164	0.0994	1.0550	−0.331	0.1018	1.4823	−0.436
0.2204	0.6992	0.652	0.1937	0.8563	−0.232	0.1869	1.0333	−0.457	0.2004	1.4031	−0.599
0.2998	0.7134	0.736	0.2987	0.8575	−0.254	0.3570	0.9920	−0.482	0.2603	1.3558	−0.620
0.3991	0.7322	0.786	0.4059	0.8585	−0.257	0.4049	0.9809	−0.471	0.3965	1.2526	−0.612
0.5188	0.7556	0.765	0.4998	0.8593	−0.264	0.4939	0.9609	−0.450	0.4979	1.1800	−0.610
0.6073	0.7735	0.717	0.5153	0.8599	−0.274	0.5929	0.9399	−0.439	0.6073	1.1055	−0.646
0.6954	0.7920	0.615	0.7021	0.8610	−0.290	0.6953	0.9190	−0.417	0.6955	1.0481	−0.671
0.8003	0.8148	0.454	0.7978	0.8615	−0.276	0.7941	0.9001	−0.403	0.8023	0.9810	−0.641
0.9011	0.8376	0.250	0.9030	0.8616	−0.192	0.9017	0.8797	−0.279	0.9007	0.9208	−0.467
0.9513	0.8493	0.131	0.9514	0.8613	−0.114	0.9369	0.8730	−0.199	0.9705	0.8787	−0.179
1.0000	0.8609										

$$\epsilon_r = \frac{C_3'' - C_2}{C_1} \tag{3}$$

where C''_3 is the overall capacitance obtained with the liquids under examination. The temperature within the dielectric cells was maintained accurately to ±0.01 °C by circulating water from INSREF electronic digital temperature controllers. The values of the densities and relative permittivities are accurate to within ±0.0001 g·cm^{-3} and 0.001 units, respectively.

Results

The experimental densities along with the excess volumes, V^E, of all the binary mixtures at 308.15 K and 318.15 K are listed in Tables 2 and 3, respectively. V^E was calculated with the relation

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = \frac{x_1M_1 + x_2M_2}{\rho_{12}} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{4}$$

where x, M, and ρ are the mole fraction, molecular weight, and densities of pure ester (1), hydrocarbon (2), and the mixture (12). The relative permittivity, ϵ_r, and the relative permittivity deviation, $\delta\epsilon_r$, are listed in Table 4. The $\delta\epsilon_r$ values were calculated with the relation

$$\delta\epsilon_r = \epsilon_{r12} - (\phi_1\epsilon_{r1} + \phi_2\epsilon_{r2}) \tag{5}$$

where ϕ is the ideal-state volume fraction of pure components and was calculated from the individual pure molar volumes, V_i, with the relation

$$\phi_i = x_iV_i/(\sum x_iV_i) \tag{5a}$$

The excess molar polarizations, $P_m{}^E$, for all the mixtures was calculated with the relation

$$P_m{}^E/(\text{cm}^3\cdot\text{mol}^{-1}) = P_{m12} - (x_1P_{m1} + x_2P_{m2}) \tag{6}$$

P_m is the molar polarization, and the subscript numerals have the same notation as that described earlier. The molar polarizations for the binary mixture and respective pure components were calculated with the relations

$$P_{m,12} = \frac{\epsilon_{r12} - 1}{\epsilon_{r12} + 2}\frac{x_1M_1 + x_2M_2}{\rho_{12}} \tag{7}$$

$$P_{m,i} = \frac{\epsilon_{ri} - 1}{\epsilon_{ri} + 2}\frac{M_i}{\rho_i} \tag{8}$$

The $P_m{}^E$ values for all of the mixtures at both measuring

Table 4. Relative Permittivity and Relative Permittivity Deviations for Alkyl Alkanoate (1) + Hydrocarbon Mixtures at 308.15 K and 318.15 K

T = 308.15 K

ϕ_1	ϵ_r	$\delta\epsilon_r$	ϕ_1	ϵ_r	$\delta\epsilon_r$	ϕ_1	ϵ_r	$\delta\epsilon_r$
MP (1) + *n*-Heptane			MP (1) + Benzene			MP (1) + 1,1,2,2-Tetrachloroethane		
0.0300	1.823	−0.190	0.0451	2.296	−0.119	0.0466	6.957	−0.081
0.0744	1.779	−0.409	0.1122	2.389	−0.268	0.0954	6.826	−0.151
0.1368	1.806	−0.630	0.2187	2.591	−0.449	0.1911	6.593	−0.265
0.2225	1.951	−0.824	0.3215	2.846	−0.564	0.2863	6.425	−0.315
0.3192	2.201	−0.956	0.4266	3.157	−0.631	0.3230	6.294	−0.400
0.4202	2.530	−1.027	0.4788	3.331	−0.645	0.4898	6.105	−0.416
0.4666	2.702	−1.039	0.6222	3.861	−0.631	0.5829	5.937	−0.438
0.6072	3.305	−0.992	0.7206	4.292	−0.554	0.6783	5.845	−0.407
0.7241	3.919	−0.841	0.8154	4.754	−0.434	0.7863	5.786	−0.332
0.8585	4.769	−0.523	0.9113	5.286	−0.247	0.8947	5.783	−0.200
0.9276	5.273	−0.292	0.9701	5.652	−0.093	0.9442	5.802	−0.119
MB (1) + *n*-Heptane			MB (1) + Benzene					
0.0411	1.868	−0.166	0.0644	2.326	−0.094			
0.1251	1.936	−0.383	0.1255	2.471	−0.169			
0.1585	1.990	−0.442	0.2330	2.615	−0.280			
0.2462	2.172	−0.558	0.3541	2.867	−0.370			
0.4350	2.620	−0.750	0.4514	3.114	−0.416			
0.5340	2.876	−0.830	0.5533	3.367	−0.435			
0.7551	3.663	−0.794	0.6594	3.680	−0.422			
0.8170	3.979	−0.688	0.7496	3.980	−0.377			
0.9034	4.519	−0.441	0.8272	4.269	−0.308			
0.9402	4.790	−0.295	0.9196	4.663	−0.175			
0.9775	5.092	−0.120	0.9623	4.868	−0.091			
EP (1) + *n*-Heptane			EP (1) + Benzene			EP (1) + 1,1,2,2-Tetrachloroethane		
0.0407	1.947	−0.097	0.0662	2.409	−0.064	0.0530	7.114	0.098
0.0773	1.987	−0.192	0.1234	2.547	−0.117	0.1084	7.099	0.195
0.1777	2.098	−0.451	0.2459	2.857	−0.214	0.2176	7.034	0.268
0.2534	2.213	−0.615	0.3592	3.165	−0.283	0.3191	6.925	0.313
0.3450	2.412	−0.754	0.4633	3.472	−0.322	0.4203	6.785	0.326
0.4421	2.705	−0.819	0.5624	3.789	−0.335	0.5230	6.619	0.316
0.5275	3.023	−0.815	0.6576	4.122	−0.319	0.6203	6.447	0.291
0.6463	3.582	−0.694	0.7608	4.515	−0.269	0.7210	6.252	0.249
0.7571	4.171	−0.514	0.8412	4.849	−0.203	0.8152	5.993	0.204
0.8760	4.852	−0.271	0.9198	5.198	−0.115	0.9096	5.830	0.113
0.9350	5.198	−0.142	0.9369	5.277	−0.093	0.9552	5.709	0.061
EB (1) + *n*-Heptane			EB (1) + Benzene			EB (1) + 1,1,2,2-Tetrachloroethane		
0.0452	1.953	−0.081	0.0623	2.393	−0.047	0.0591	7.175	0.203
0.0928	2.028	−0.153	0.1397	2.543	−0.092	0.1245	7.232	0.399
0.2020	2.244	−0.275	0.2619	2.816	−0.153	0.2392	7.262	0.671
0.2769	2.419	−0.331	0.3862	3.111	−0.198	0.3062	7.231	0.781
0.3732	2.672	−0.376	0.5024	3.408	−0.218	0.4518	7.093	0.950
0.4912	3.020	−0.393	0.5961	3.666	−0.216	0.5543	6.930	1.004
0.5807	3.300	−0.390	0.6668	3.863	−0.212	0.6598	6.696	0.992
0.6715	3.640	−0.330	0.7769	4.198	−0.178	0.7413	6.454	0.922
0.7821	4.068	−0.244	0.8536	4.450	−0.136	0.8358	6.076	0.744
0.8908	4.506	−0.142	0.9323	4.727	−0.074	0.9192	5.611	0.455
0.9459	4.737	−0.082	0.9666	4.856	−0.039	0.9763	5.191	0.155

T = 318.15 K

ϕ_1	ϵ_r	$\delta\epsilon_r$	ϕ_1	ϵ_r	$\delta\epsilon_r$	ϕ_1	ϵ_r	$\delta\epsilon_r$
MP (1) + *n*-Heptane			MP (1) + Benzene			MP (1) + 1,1,2,2-Tetrachloroethane		
0.0299	1.889	−0.105	0.0449	2.315	−0.073	0.0467	6.936	−0.060
0.0740	1.897	−0.262	0.1116	2.421	−0.182	0.0955	6.813	−0.113
0.1361	1.920	−0.472	0.2166	2.619	−0.351	0.1913	6.669	−0.120
0.2215	2.003	−0.708	0.3203	2.836	−0.485	0.2865	6.416	−0.236
0.3179	2.195	−0.878	0.4268	3.109	−0.574	0.3232	6.296	−0.303
0.4189	2.510	−0.941	0.4792	3.264	−0.596	0.4851	6.049	−0.317
0.4652	2.690	−0.934	0.6210	3.773	−0.568	0.5832	5.889	−0.337
0.6059	3.285	−0.866	0.7180	4.195	−0.475	0.6785	5.769	−0.320
0.7230	3.981	−0.608	0.8146	4.661	−0.337	0.7865	5.669	−0.265
0.8578	4.771	−0.324	0.9108	5.159	−0.166	0.8948	5.616	−0.162
0.9273	5.189	−0.166	0.9699	5.470	−0.055	0.9443	5.611	−0.096
MB (1) + *n*-Heptane			MB (1) + Benzene					
0.0411	1.868	−0.145	0.0653	2.372	−0.077			
0.1250	1.943	−0.337	0.1254	2.495	−0.139			
0.1584	1.995	−0.391	0.2330	2.730	−0.230			
0.2468	2.164	−0.501	0.3540	3.030	−0.298			
0.4348	2.574	−0.692	0.4573	3.314	−0.327			
0.5338	2.813	−0.769	0.5533	3.605	−0.327			
0.7550	3.549	−0.737	0.6593	3.957	−0.297			
0.8169	3.853	−0.630	0.7495	4.281	−0.247			
0.9033	4.349	−0.409	0.8272	4.578	−0.186			
0.9401	4.601	−0.274	0.9196	4.950	−0.094			
0.9775	4.883	−0.111	0.9623	5.128	−0.046			
EP (1) + *n*-Heptane			EP (1) + Benzene			EP (1) + 1,1,2,2-Tetrachloroethane		
0.0407	1.941	−0.083	0.0663	2.407	−0.035	0.0534	7.025	0.053
0.0773	1.986	−0.165	0.1238	2.554	−0.068	0.1091	6.976	0.099
0.1778	2.112	−0.389	0.2462	2.868	−0.137	0.2189	6.856	0.166
0.2536	2.232	−0.532	0.3595	3.166	−0.193	0.3208	6.722	0.205
0.3451	2.428	−0.655	0.4636	3.453	−0.231	0.4221	6.571	0.226
0.4423	2.709	−0.712	0.5628	3.745	−0.249	0.5249	6.400	0.230
0.5277	3.016	−0.702	0.6579	4.050	−0.242	0.6220	6.224	0.220
0.6465	3.526	−0.605	0.7610	4.409	−0.205	0.7225	6.027	0.194
0.7572	4.069	−0.447	0.8414	4.711	−0.154	0.8163	5.827	0.153
0.8760	4.657	−0.273	0.9200	4.967	−0.091	0.9102	5.603	0.089
0.9350	5.012	−0.123	0.9370	5.096	−0.068	0.9555	5.485	0.048
EB (1) + *n*-Heptane			EB (1) + Benzene			EB (1) + 1,1,2,2-Tetrachloroethane		
0.0450	1.950	−0.004	0.0681	2.387	−0.019	0.0593	7.112	0.186
0.0924	2.027	−0.066	0.1394	2.545	−0.041	0.1247	7.125	0.350
0.2013	2.225	−0.187	0.2612	2.812	−0.080	0.2396	7.063	0.554
0.2754	2.380	−0.249	0.3867	3.091	−0.117	0.3067	6.978	0.624
0.3722	2.593	−0.320	0.5014	3.354	−0.143	0.4524	6.723	0.706
0.4902	2.932	−0.327	0.5954	3.581	−0.153	0.5549	6.496	0.715
0.5197	3.208	−0.313	0.6660	3.759	−0.152	0.6604	6.225	0.688
0.6706	3.513	−0.274	0.7762	4.059	−0.130	0.7417	5.984	0.635
0.7814	3.911	−0.201	0.8531	4.283	−0.099	0.8361	5.647	0.516
0.8904	4.324	−0.107	0.9320	4.529	−0.052	0.9194	5.259	0.321
0.9457	4.539	−0.054	0.9665	4.640	−0.028	0.9764	4.919	0.112

temperatures are given in Table 5. The excess volumes, relative permittivity deviations, and excess molar polarizations were mathematically represented by an equation of the form

$$Y^E = x_1(1 - x_1)\sum_{i=0}^{i=n} a_i(2x_1 - 1)^i \qquad (9)$$

where $Y^E = V^E/(\mathrm{cm^3 \cdot mol^{-1}})$, $\delta\epsilon_r$, and $P_m{}^E/(\mathrm{cm^3 \cdot mol^{-1}})$, x_1 is the ester mole fraction, and a_i are the coefficients. The values of the coefficients were estimated by a multiple regression analysis based on a least-squares method. The results of the analysis are summarized in Tables 6 and 7. The standard deviations, σ, between the experimental and calculated values were calculated with

$$\sigma = \left\{\frac{\sum(Y^E_{\mathrm{expt}} - Y^E_{\mathrm{calc}})^2}{p - n}\right\}^{1/2} \qquad (10)$$

where p is the number of experimental points and n is the number of coefficients of eq 9. The V^E, $\delta\epsilon_r$, and $P_m{}^E$ values for all of the binary mixtures are also graphically presented in Figures 1−3.

The excess volumes of all the ester + *n*-heptane mixtures were positive in the whole ester mole fraction range at both temperatures. A general decrease in V^E is noted for all the esters RCOOR′, when the chain length of either R or R′ is increased from propyl- to butyl- or ethyl- to butyl. The temperature coefficient of an equimolar mixture ($\partial V^E/\partial T$) for all of the *n*-heptane containing mixtures was positive. As far as we are aware, there are no direct literature data on excess volumes for these mixtures at our reported temperatures for a direct comparison of our values. Our $V^E{}_{0.5}$ values of 1.080, 0.940 $\mathrm{cm^3 \cdot mol^{-1}}$ for MP, MB + *n*-heptane were more than 1.003 and 0.744 $\mathrm{cm^3 \cdot mol^{-1}}$ for the same respective mixtures at 298.15 K (Postigo et al., 1995) and 0.825 and 0.529 $\mathrm{cm^3 \cdot mol^{-1}}$ for MP, MB + hexane mixtures at 298.15 K (Gonzalez et al., 1993). It is interesting to note that our previously reported $V^E{}_{0.5}$ values of 0.683 and 0294 $\mathrm{cm^3 \cdot mol^{-1}}$ at 303.15 K for *n*-heptane + methyl methacrylate (MMA) and + ethyl methacrylate (EMA) (Sastry and Dave, 1996a) are far less than corresponding V^E values of 0.940 and 0.710 $\mathrm{cm^3 \cdot mol^{-1}}$ at 298.15 K for MB + and EB + *n*-heptane mixtures. MB and EB are analogous with MMA and EMA with the only difference being the presence of unsaturation in the latter. Thus smaller V^E values for acrylic esters + *n*-heptane in comparison with

Table 5. Excess Molar Polarizations (P_m^E) for Alkyl Alkanoates + Hydrocarbons at 308.15 K and 318.15 K

	P_m^E/(cm³·mol⁻¹)			P_m^E/(cm³·mol⁻¹)			P_m^E/(cm³·mol⁻¹)	
x_1	308.15 K	318.15 K	x_1	308.15 K	318.15 K	x_1	308.15 K	318.15 K
MP (1) + *n*-Heptane			MP (1) + Benzene			MP (1) + 1,1,2,2-Tetrachloroethane		
0.0447	−3.9	−1.4	0.0415	−0.7	−0.1	0.0501	−0.3	−0.3
0.1083	−7.5	−3.5	0.1037	−1.3	−0.5	0.1021	−0.7	−0.5
0.1932	−9.8	−6.1	0.2041	−1.7	−0.9	0.2031	−1.2	−0.6
0.3018	−9.9	−8.0	0.3026	−1.6	−1.2	0.3020	−1.5	−1.1
0.4146	−8.4	−7.8	0.4053	−1.3	−1.2	0.3398	−1.6	−1.4
0.5227	−6.4	−6.4	0.4569	−1.1	−1.1	0.5038	−2.0	−1.6
0.5693	−5.5	−4.9	0.6013	−0.7	−0.6	0.6012	−2.2	−1.7
0.7002	−3.2	−2.5	0.7026	−0.4	−0.2	0.6946	−2.1	−1.6
0.7986	−1.6	0.1	0.8018	−0.2	0.2	0.7988	−1.7	−1.4
0.9016	−0.4	0.7	0.9039	−0.06	0.3	0.9016	−1.0	−0.9
0.9509	−0.1	0.5	0.9674	−0.02	0.1	0.9481	−0.6	−0.6
MB (1) + *n*-Heptane			MB (1) + Benzene					
0.0525	−2.5	−2.8	0.0519	−0.2	−0.1			
0.1560	−4.6	−5.2	0.1011	−0.3	−0.1			
0.1959	−4.6	−5.4	0.1924	−0.4	−0.1			
0.2969	−4.4	−4.9	0.3006	−0.4	−0.1			
0.4989	−4.2	−4.3	0.3979	−0.3	0.2			
0.5971	−4.3	−4.4	0.4927	−0.3	0.4			
0.7995	−3.4	−3.4	0.6028	−0.3	0.5			
0.8524	−3.2	−2.6	0.7012	−0.3	0.5			
0.9236	−1.5	−1.4	0.7896	−0.3	0.5			
0.9531	−0.9	−0.9	0.8998	−0.6	0.3			
0.9825	−0.3	−0.3	0.9524	−0.1	0.2			
EP (1) + *n*-Heptane			EP (1) + Benzene			EP (1) + 1,1,2,2-Tetrachloroethane		
0.0514	−0.7	−0.4	0.0521	0.4	0.7	0.0486	0.3	0.1
0.0967	−1.6	−1.1	0.0984	0.6	1.1	0.0999	0.5	0.3
0.8165	−3.9	−3.0	0.2018	1.0	1.7	0.2025	0.8	0.6
0.3027	−4.9	−3.8	0.3029	1.2	1.9	0.2997	1.2	0.9
0.4024	−5.0	−3.9	0.4009	1.3	1.8	0.3983	1.4	1.1
0.5033	−4.0	−3.1	0.4991	1.3	1.7	0.5003	1.5	1.2
0.5880	−2.8	−2.0	0.5982	1.2	1.5	0.5986	1.4	1.2
0.7003	−0.8	−0.4	0.7114	0.9	1.2	0.7023	1.3	1.1
0.7994	0.4	0.7	0.8042	0.7	0.8	0.8010	0.7	0.9
0.9003	0.8	0.6	0.8989	0.4	0.5	0.9018	0.6	0.5
0.9484	0.5	0.6	0.9200	0.3	0.4	0.9510	0.3	0.3
EB (1) + *n*-Heptane			EB (1) + Benzene			EB (1) + 1,1,2,2-Tetrachloroethane		
0.0502	−0.6	−0.2	0.0473	0.3	0.6	0.0477	0.8	0.8
0.1025	−0.9	−0.3	0.0990	0.5	1.0	0.1018	1.6	2.6
0.2204	−0.7	−0.3	0.1937	0.9	1.5	0.2004	3.0	1.3
0.2998	−0.2	0.1	0.2987	1.1	1.7	0.2603	3.6	3.1
0.3991	0.4	0.3	0.4059	1.2	1.7	0.3965	4.9	4.1
0.5188	1.0	0.8	0.4998	1.1	1.4	0.4979	5.5	4.5
0.6073	1.1	1.2	0.5153	1.0	1.2	0.6073	5.8	4.6
0.6954	1.5	1.4	0.7021	0.7	0.8	0.6955	5.7	4.5
0.8003	1.4	1.4	0.7978	0.4	0.3	0.8023	4.9	3.9
0.9011	0.8	0.9	0.9030	0.2	0.2	0.9007	3.3	2.0
0.9513	0.3	0.5	0.9514	0.03	0.1	0.9705	1.2	0.9

Table 6. Coefficients a_i of Equation 9 for the Least-Squares Representation of Excess Volumes of Alkyl Alkanoates + Hydrocarbons at 308.15 K and 318.15 K[a]

	308.15 K					318.15 K				
	a_0	a_1	a_2	a_3	σ	a_0	a_1	a_2	A_3	σ
MP +										
n-heptane	4.3213	−0.4938	0.6573		0.003	4.6005	−0.4692	−0.7678		0.003
benzene	0.4553	0.0272	0.4862		0.004	0.6486	0.1298	0.9649		0.001
chlorobenzene	−0.4348	0.1101	−0.5204		0.001	−0.2802	0.0776	−0.2652		0.002
1,1,2,2-tetrachloroethane	−2.6673	0.1036	0.2457		0.005	−2.1807	0.0913	0.1396		0.001
MB +										
n-heptane	3.7324	−0.2545	1.4336	0.4379	0.008	4.0381	0.3027	1.6538		0.002
benzene	−0.0593	−0.8549	−0.1254		0.001	−0.0988	−1.0813	0.3229		0.003
chlorobenzene	−0.3522	0.3216	−0.8453		0.001	−0.3532	0.6437	0.0607		0.003
EP +										
n-heptane	3.8351	−0.1308	0.6446		0.007	3.8839	−0.8057	2.2997	1.5818	0.008
benzene	0.6460	−0.1229	−0.7055	0.5243	0.001	−0.8263	−0.0959	−0.8792	0.8161	0.004
chlorobenzene	−1.5816	0.4407	−2.8858		0.002	−1.7246	0.4555	−3.6743		0.002
1,1,2,2-tetrachloroethane	−2.2926	0.3676	−2.7702		0.002	−2.5000	0.2706	−3.4278		0.002
EB +										
n-heptane	2.8434	−0.6247	0.4039		0.006	3.1109	−0.8646	0.6347		0.007
benzene	−0.9480	−0.2398	−0.8912		0.002	−1.0554	−0.2139	−1.4909		0.001
chlorobenzene	−1.7047	0.3150	−2.0715		0.003	−1.7952	0.3525	−2.5314		0.006
1,1,2,2-tetrachloroethane	−2.3753	−0.3274	−3.4546		0.009	−2.4595	−0.2728	−3.9759		0.004

[a] MP = methyl propanoate, MB = methyl butanoate, EP = ethyl propanoate, and EB = ethyl butanoate.

alkyl esters + *n*-heptane mixtures indicate that there exist a close packing and high degree of alignment of dipoles in the pure acrylic esters.

The excess volumes were small and positive in MP + benzene, small positive−negative in MB + benzene, and small negative over the whole mole fraction range in EP +, EB + benzene mixtures at both temperatures. The $(\partial V^E/\partial T)_{0.5}$ was positive for MP + and MB + benzene mixtures and negative for EP + and EB + benzene. The value $V^E_{0.5}$ of −0.162 cm³·mol⁻¹ for EP + benzene at 308.15 K is less than the literature reported equimolar excess volume of 0.1173 cm³·mol⁻¹ for ethyl ethanoate + benzene at 298.15 K (Grolier et al., 1974). A further diminishing effect in the excess volumes was noted in all four esters + chlorobenzene mixtures at both temperatures. The V^E values become more negative with an increase in the chain length of R′ in the

Table 7. Coefficients a_i of Equation 9 for the Least-Squares Representation of Relative Permittivity Deviation and Excess Molar Polarizations of Alkyl Alkanoates + Hydrocarbons at 308.15 K and 318.15 K[a]

	308.15 K					318.15 K				
	a_0	a_1	a_2	a_3	σ	a_0	a_1	a_2	a_3	σ
				$\delta\epsilon_r$						
MP +										
n-heptane	−4.006	−1.012	−1.570		0.001	−3.789	−0.638	0.968		0.006
benzene	−2.593	0.031	−0.433		0.003	−2.403	0.024	0.734		0.001
1,1,2,2-tetrachloroethane	−1.701	−0.396	0.403		0.008	−1.260	−0.444	−0.368		0.008
MB +										
n-heptane	−3.008	−1.792	−2.406		0.001	−2.796	−1.765	−2.089		0.009
benzene	−1.737	−0.051	−0.266		0.001	−1.302	0.305	0.019		0.001
EP +										
n-heptane	−3.272	−0.505	1.026		0.003	−2.845	−0.454	0.912		0.001
benzene	−1.338	0.029	0.077		0.001	−0.995	−0.108	0.228		0.002
1,1,2,2-tetrachloroethane	1.269	−0.381	0.482		0.009	0.920	−0.061	0.207		0.001
EB +										
n-heptane	−1.571	−0.075	−0.240		0.009	−1.392	−0.380	0.832		0.009
benzene	−0.879	0.113	−0.085		0.002	−0.611	−0.090	0.124		0.002
1,1,2,2-tetrachloroethane	4.019	0.456	1.087		0.002	2.856	−0.153	1.344		0.001
				P_m^E/(cm^3·mol^{-1})						
MP +										
n-heptane	−27.45	46.35	−22.99		0.10	−26.81	27.69	19.49		0.2
benzene	−4.74	9.02	−12.28	−16.92	0.20	−4.00	7.33	4.98	−4.48	0.2
1,1,2,2-tetrachloroethane	−8.26	−2.90	−1.52		0.10	−6.02	−3.24	−3.23		0.2
MB +										
n-heptane	−17.70	1.56	−25.52	−24.21	0.10	−17.23	−4.73	−23.64	27.38	0.2
benzene	−1.23	0.79	−2.40		0.10	1.41	3.12	−0.50		0.2
EP +										
n-heptane	−16.50	17.14	18.10		0.40	−11.20	12.77	18.58		0.6
benzene	5.02	−1.78	1.11		0.10	6.8	−5.12	2.55		0.1
1,1,2,2-tetrachloroethane	5.59	0.19	0.67		0.10	4.76	0.53	−0.51	2.03	0.1
EB +										
n-heptane	4.02	11.0	−7.81		0.20	3.22	8.64	0.23	−0.37	0.1
benzene	4.46	−2.73	−0.93		0.10	5.51	−5.94	2.22		0.1
1,1,2,2-tetrachloroethane	21.73	11.85	8.88		0.10	16.99	8.02	5.08		0.3

[a] MP = methyl propanoate, MB = methyl butanoate, EP = ethyl propanoate, and EB = ethyl butanoate.

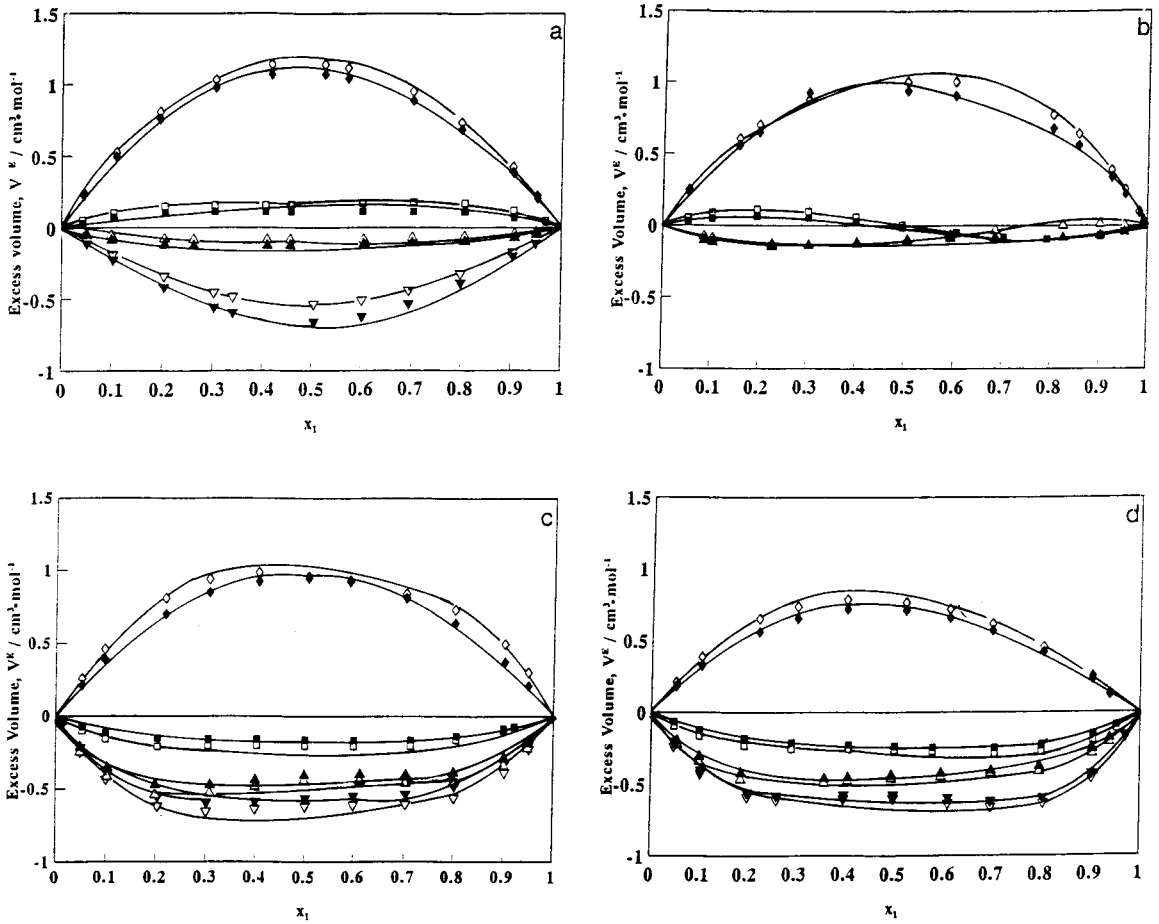

Figure 1. Excess volumes for ester + hydrocarbons; (a) methyl proponoate, (b) methyl butanoate, (c) ethyl propanoate, and (d) ethyl butanoate at 308.15 K (♦) *n*-heptane, (■) benzene, (▲) chlorobenzene, (▼) 1,1,2,2-tetrachloroethane and at 318.15 K (◊) *n*-heptane, (□) benzene, (△) chlorobenzene, (▽) 1,1,2,2-tetrachloroethane; (—) calculated values from eq 9 and coefficients from Table 6.

ester. The $V^E_{0.5}$ values of −0.088 and −0.426 cm^3·mol^{-1} at 308.15 K for MB + and EB + chlorobenzene mixtures are largely more negative than our previously reported 0.001 and −0.117 cm^3·mol^{-1} at 303.15 K for corresponding acrylic

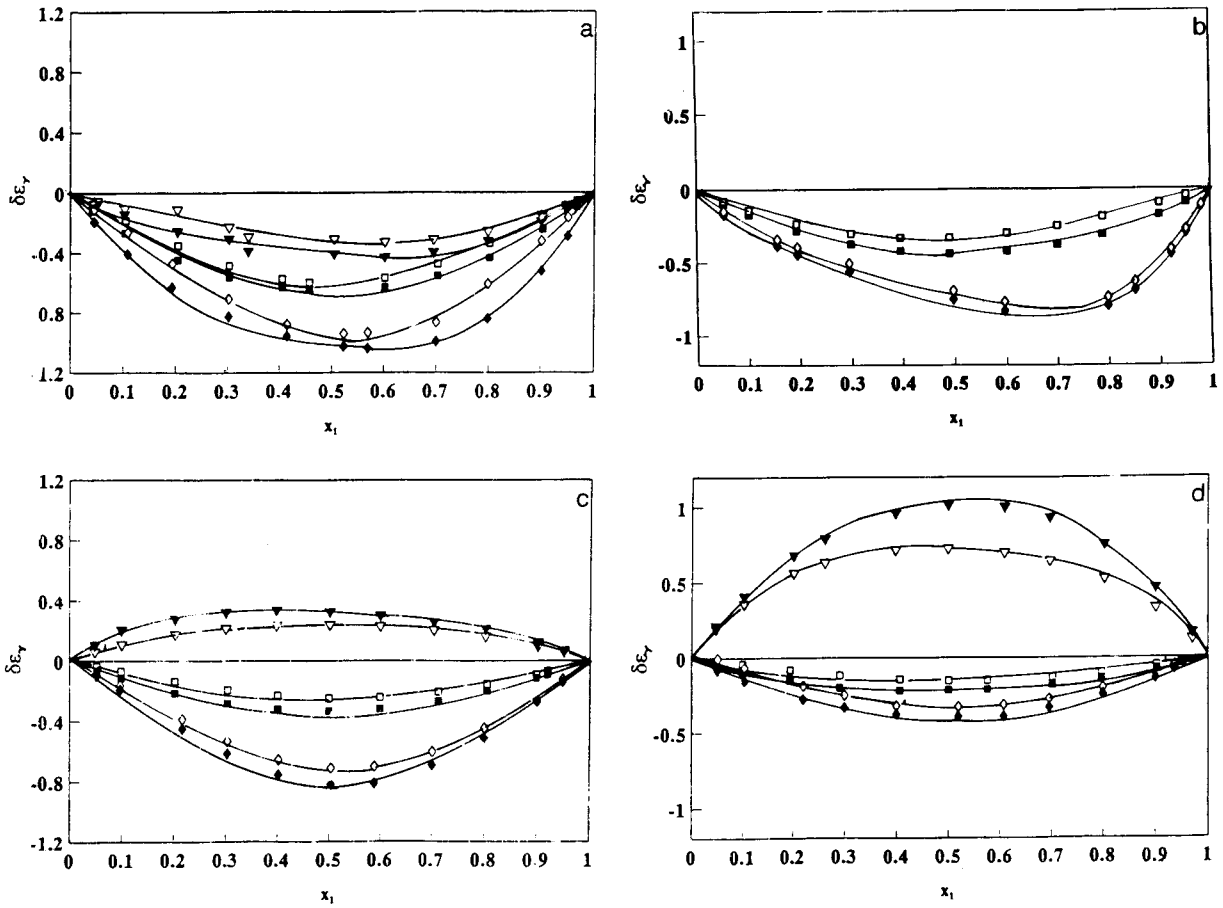

Figure 2. Relative permittivity deviation for ester + hydrocarbons: (a) methyl proponoate, (b) methyl butanoate, (c) ethyl propanoate, and (d) ethyl butanoate at 308.15 K (♦) *n*-heptane, (■) benzene, (▼) 1,1,2,2-tetrachloroethane and at 318.15 K (◊) *n*-heptane, (□) benzene, (▽) 1,1,2,2-tetrachloroethane; (—) calculated values from eq 9 and coefficients from Table 7.

esters, viz., MMA + and EMA + chlorobenzene mixtures. The presence of π electrons in the acrylic esters is thus expected to weaken the specific interactions in the later mixtures because of possible repulsion between the π electrons of the aromatic ring. The excess volumes of all of the mixtures containing 1,1,2,2-tetrachloroethane were negative over the whole mole fraction range at both temperatures except for a few positive points in the MB rich regions at 318.15 K. The general trend in the $V^E_{0.5}$ values of the mixtures in the individual esters can be summarized as follows: *n*-heptane > benzene > chlorobenzene > 1,1,2,2-tetrachloroethane.

The relative permittivity, $\delta\epsilon_r$, values as shown in Figure 2 are negative over the whole ester mole fraction range at both temperatures except for EP + and EB + 1,1,2,2-tetrachloroethane mixtures in which positive values were noted. The relative permittivity values for all four pure esters and chlorobenzene were close to each other, and hence the mixture permittivity values could not be measured. The negative magnitude of $\delta\epsilon_r$ was less when the alkyl chain length of R or R′ in the ester RCOOR′ was raised from propyl to butyl or from ethyl to propyl, respectively. At the same time positive $\delta\epsilon_r$ values were larger in the case of EB + 1,1,2,2-tetrachloroethane mixtures than corresponding mixtures with ethyl propanoate. There is a general decrease in the negative or positive magnitude of $\delta\epsilon_r$ with the rise in the temperature. The general trend in the variation of $\delta\epsilon_{r\ 0.5}$ values for all four esters follow the order *n*-heptane < benzene < 1,1,2,2-tetrachloroethane.

The excess molar polarizations (P_m^E) values show a distinct variation for individual methyl or ethyl esters. The P_m^E values for all four mixtures containing either methyl propanoate or methyl butanoate were negative except for slight positive values for ester rich regions of MP + *n*-heptane and + benzene mixtures. It is interesting to note that the P_m^E values for MP + and MB + *n*-heptane mixtures fall sharply in the ester lean regions by a factor of about 4−8, at both temperatures. The values for EP + or EB + *n*-heptane mixtures were negative−positive at both temperatures; otherwise positive values were always noted for EP + and EB + benzene and 1,1,2,2-tetrachloroethane mixtures, respectively. The negative $(P_m^E)_{0.5}$ value of −0.310 $cm^3 \cdot mol^{-1}$ for MB + benzene at 308.15 K is in strong contrast to our previously reported large positive $(P_m^E)_{0.5}$ value of 3.891 $cm^3 \cdot mol^{-1}$ for MMA + benzene mixture at the same temperature (Sastry et al., 1998). There is a general decrease in P_m^E values either to the negative or positive side with the rise in the temperature, while no definite trend in the temperature coefficient of $(P_m^E/\partial T)_{0.5}$ values was noted.

Discussion

A qualitative analysis of results can be made from the experimental values of V^E, $\delta\epsilon_r$, and P_m^E in the binary mixtures of MP +, MB +, EP +, and EB + *n*-heptane, benzene, chlorobenzene, and 1,1,2,2-tetrachloroethane. The excess volumes show a constant decrease with the rise in the chain length of either R or R′ in the ester RCOOR′ + *n*-heptane and + benzene mixtures. This is in strong contrast to the usual increase in excess volumes with the

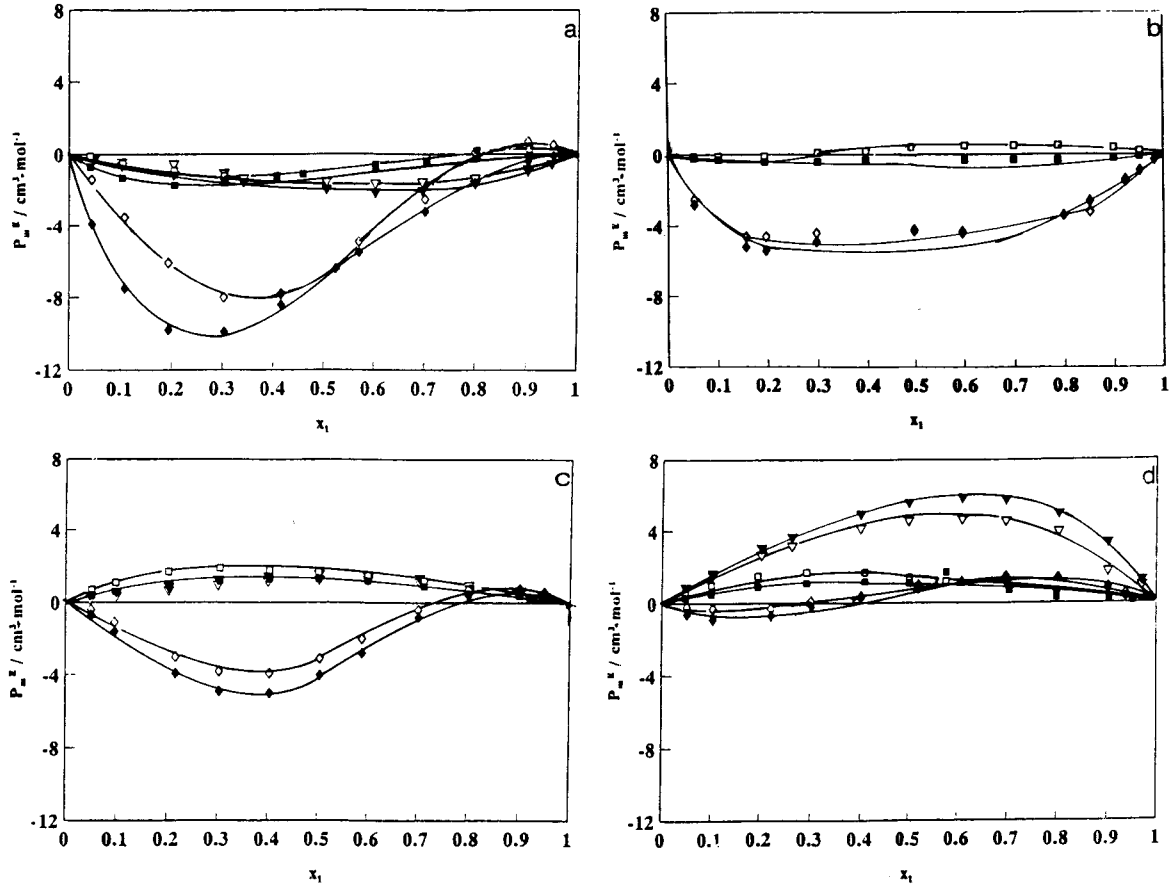

Figure 3. Excess molar polarization for ester + hydrocarbons: (a) methyl proponoate, (b) methyl butanoate, (c) ethyl propanoate, and (d) ethyl butanoate at 308.15 K (♦) *n*-heptane, (■) benzene, (▼) 1,1,2,2-tetrachloroethane and at 318.15 K (◊) *n*-heptane, (□) benzene, (▽) 1,1,2,2-tetrachloroethane; (—) calculated values from eq 9 and coefficients from Table 7.

rise in alkyl chain length of *n*-alkanes for a given ester, e.g., methyl acrylate + alkanes (*n*-pentane to *n*-dodecane) (Sastry and Valand, 1998), methyl methacrylate + alkanes (*n*-hexane and *n*-heptane) (Sastry and Dave, 1997), alkyl ethanoates + alkanes (hexane to hexadecane) (Grolier et al., 1974), and methyl esters (ethanoate to tetradecanoate) + odd *n*-alkanes (pentane to tridecane) (Postigo et al., 1995). This indicates that the $-CH_2-$ group in the presence of a $-COO-$ group contribute differently to V^E values than *n*-alkanes. The increase in the $-CH_2-$ chain length in an ester generally dilutes the dipolar association in the pure ester species, and hence lower alkyl esters such as methyl esters (methanoate and ethanoate) always show large positive volumes upon mixing with *n*-alkanes (higher than C_6). The large positive excess volumes can be mainly attributed to the disruption in the dipolar association in esters by alkanes upon mixing. The largely diminished or even negative V^E values, on the other hand, for MP +, MB +, EP +, and EB + benzene mixtures indicate the presence of specific $n-\pi$ interactions between the lone pair of electrons and π electrons of the aromatic ring and probably overbalance the structure disruption effects. Such specific interactions are further strengthened by additional Cl···O type forces between the Cl− group of chlorobenzene or 1,1,2,2-tetrachlorethane and the O− of ester molecules. These effects result in the large negative excess volumes observed in the present study for this type of mixture.

The above observations are also expected to be reflected in the signs and magnitudes of $\delta\epsilon_r$ and P_m^E and in their variation with the alkyl chain length of the ester for a given set of mixtures. The disruption in the dipolar association decreases the degree of alignment of dipoles in the presence of *n*-heptane as evidenced by the large and negative $\delta\epsilon_r$ values for ester + *n*-heptane mixtures at both temperatures. The trend in the variation in $\delta\epsilon_r$ with the alkyl chain length of the ester resembles the same pattern as that observed for excess volumes. The fact that the $\delta\epsilon_r$ values for any given ester progressively increase when *n*-heptane is replaced with benzene and 1,1,2,2-tetrachloroethane (even become largely negative for EP + and EB + 1,1,2,2-tetrachloroethane mixtures) corroborates earlier observation that specific interactions overbalance the net forces in either aromatic hydrocarbon + or chlorinated hydrocarbon + ester mixtures. The change in the degree of alignment in the dipoles of esters has an effect on the molar polarization as well. Large and negative P_m^E values for MP + and EP + *n*-heptane further give evidence of dominance of structure disruption effects. The presence of specific interactions however reinforces the polarization effects as reflected in either a decrease in negative P_m^E values for MP +, MB + benzene or 1,1,2,2-tetracholroethane mixtures or even positive values for EP +, EB + benzene and 1,1,2,2-tetrachloroethane mixtures. A similar qualitative trend in the signs and magnitudes of P_m^E values has also been reported for methyl acrylate + aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene) (Sastry et al., 1998), methyl acrylate + alkanes (pentane to dodecane) (Sastry and Valand, 1998), and ethyl acetate + aromatic hydrocarbons (toluene, ethylbenzene, and *o*- and *m*-xylenes) (Oswal and Rathnam, 1987).

Acknowledgment

A.G. and N.J.J. thank Prof. Dr. H. C. Trivedi, Head, Department of Chemistry, Sardar Patel University for permitting us to use the laboratory facilities.

Literature Cited

Aicart, E.; Tardajos, G.; Diaz Pena, M. Thermodynamics of Cyclohexane + Benzene at Various Temperatures. *J. Chem. Thermodyn.* **1980**, *12*, 1085−1091.

Blanco. A. M.; Ortega, J.; Garcia, B.; Leal, J. M. Studies on Densities and Viscosities of Binary Mixtures of Alkyl Benzoate in *n*-Heptane. *Thermochim. Acta* **1993**, *22*, 127−136.

Chaar, M.; Ortega, J.; Placido, J.; Gonzalez, E. Excess Volumes of Binary Liquid Mixtures of Methyl *n*-Alknoates (C_3−C_{16}) + Alkan-1-ols (C_2−C_{10}) at 298.15 K. *Int. Electron J. Phys. Chem. Data* **1995**, *1*, 191−208.

Fernandez, J.; Pintos, M.; Baluja, M. C.; Jimenez, E.; Paz Andrade, M. I. Excess Enthalpies of Some Ester−Alcohol Binary Mixtures. *J. Chem. Eng. Data* **1985**, *30*, 318−320.

Garcia, P. H.; Postigo, M. A.; Ortega, J. Thermodynamic Properties of (a Methyl Ester + an Alkane) VIII. {x $CH_3(CH_2)_{u-1}CO_2CH_3$ + (1−x)$CH_3(CH_2)_{v-3}$ CH_3} with u = 4 to 16 and v = 5 to 12. *J. Chem Thermodyn.* **1995**, *27*, 1249−1260.

Gonzalez, E.; Ortega, J. Thermodynamic Properties of (a Methyl Ester + an Alkane) VI. {x$CH_3(CH_2)_{u-1}CO_2CH_3$ (u = 1 to 6) + (1−x)CH_3-$(CH_2)CH_3$. *J. Chem. Thermodyn.* **1994**, *26*, 41−47.

Gonzalez, E.; Ortega, J.; Matos, J. S.; Tardajos, G. Thermodynamic Properties of (a Methyl Ester + an Alkane) II. H_mE and V_mE for {x$CH_3(CH_2)_{u-1}CO_2CH_3$ (u = 1 to 6) + (1−x)$CH_3(CH_2)CH_3$. *J. Chem. Thermodyn.* **1993**, *25*, 561−568.

Grolier, J.-P. E.; Ballet, D.; Viallard, D. Thermodynamics of Ester Containing Mixtures. Excess Enthalpies, Excess Volumes for Alkyl Acetates + Alkanes, + Benzene, + Toluene and + Ethylbenzene. *J. Chem. Thermodyn.* **1974**, *6*, 895−908.

Jimenez, E.; Romani, L.; Paz Andrade, M. I.; Roux-Desgranges, G.; Grolier, J.-P. E. Molar Excess Heat Capacities and Volumes for Mixtures of Alkanoates with Cyclohexane at 25 °C. *J. Solution Chem.* **1986**, *15*, 879−890.

Katyal, R. C.; Sethi, B. P. S., Raju, K. S. N. Enthalpies of Mixing of Binary Systems of Alkyl Esters with o-, m- and p- Xylene at 298.15 K. *Ind. J. Technol.* **1990**, *28*, 191−196.

Lide, D. R., Ed. *Handbook of Physics and Chemistry*, 75th ed.; CRC Press: Boca Raton, FL, 1994.

Matilla, A. D.; Tardajos G.; Aicart, E. Thermodynamic Mixing Properties of Chlorobenzene + an Alkanol. *J. Chem. Thermodyn.* **1993**, *25*, 201−207.

Ortega, J.; Matos, J. S.; Paz Andrade, M. I.; Fernandez, J.; Pias, L. Analysis of Excess Enthalpies of Ester + 1-Chloroalkanes with Two Group Contribution Models. *Fluid Phase Equilib.* **1988**, *43*, 295−316.

Ortega, J.; Legido, J. L.; Fernandez, J.; Pias, L.; Paz Andrade, M. I.; Measurements and Analysis of Excess Enthalpies of Ester + Alkane using UNIFAC Model. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 128−135.

Oswal, S. L.; Rathnam, M. V. Study of Dielectric Constant, Refractive Indexes of Binary Mixtures of Ethyl Acetate with Toluene, Ethylbenzene, o- and p-Xylene and Dioxane. *Ind. J. Chem.* **1987**, *26A*, 29−32.

Postigo, M. A.; Garcia, P. H.; Ortega, J.; Trdajos, G. Excess Molar Volumes of Binary Mixtures Containing a Methyl Ester (Ethanoate to Tetradecanoate) with Odd Alkanes at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 283−289.

Prasad, G. S.; Rao, M. V.; Prasad, D. H. L. Density and Viscosity of Ethanol + 1,2-Dichloroethane, Ethanol + 1,1,1-Trichloroethane and Ethanol + 1,1,2,2-Tetrachloroethane Binary Mixtures. *J. Chem. Eng. Data* **1990**, *35*, 122−124.

Qin, A.; Hoffman, D. E.; Munk, P. Excess Volumes of Selected Alkyl Esters and Ketones with Aromatic Hydrocarbons. *J. Chem. Eng. Data* **1992**, *37*, 66−70.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Organic Solvents, 4th ed.; Wiley-Interscience: New York, 1986; Vol II.

Romani, L.; Peleteiro, J.; Iglesias, T. P.; Carballo, E., Escudero, R.; Legido, J. L. Temperature Dependence of the Volumetric Properties of Binary Mixtures Containing Alcohols (1-Propanol, 1-Pentanol, 1-Heptanol + *n*-Heptane). *J. Chem. Eng. Data* **1994**, *39*, 19−22.

Sastry, N. V.; Dave, P. N. Thermodynamics of Methyl Methacrylate + Organic Solvents I. Excess Volumes and Isentropic Compressibilities of Methyl Methacrylate + *n*-Hexane, + *n*-Heptane, + Carbon Tetrachloride, + Chlorobenzene and + o-Dichlorobenzene at 303.15 K. *Int. J. Thermophys.* **1996a**, *17*, 1289−1304.

Sastry, N. V.; Dave, P. N. Thermodynamics of Methyl Methacrylate + Organic Solvents II. Viscosities of Methyl Methacrylate + *n*-Hexane, + *n*-Heptane, + Carbon Tetrachloride, + Chlorobenzene and + o-Dichlorobenzene at 303.15 K. *Thermochim. Acta* **1996b**, *286*, 119−130.

Sastry, N. V.; Dave, P. N. Thermodynamics of Methyl Methacrylate + Organic Solvents III. Excess Dielectric Functions for Methyl Methacrylate + *n*-Hexane, + *n*-Heptane, + Carbon Tetrachloride, + Chlorobenzene and + o-Dichlorobenzene at 303.15 K. *Proc. Ind. Acad. Sci.* (*Chem. Sci.*) **1997**, *109*, 211−220.

Sastry, N. V.; Valand, M. K. Densities, Speeds of Sound, Viscosities, and Relative Permittivity for 1-Propanol + 1-Butanol + Hexane and + Heptane at 298.15 K and 308.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1421−1425.

Sastry, N. V.; Valand, M. K. Excess Volumes and Relative Permittivity Increments for {xCH_2:$CHCO_2CH_3$ + (1−x)C_nH_{2n+2} (n = 5, 6, 7, 10, 12)} at 298.15 K and 308.15 K. *J. Chem. Thermodyn.* **1998**, *30*, 929−938.

Sastry, N. V.; Patel, S. R.; Patel, M. C. Excess Volumes, Relative Permittivty Deviation and Excess Molar Polarization for {xCH_2:CCH_3COOCH_3 + (1−x)C_6H_6, + C_7H_8, o-C_8H_{10}, m-C_8H_{10}, p-C_8H_{10} and C_8H_{10}} at 298.15 K and 308.15 K. *J. Chem. Thermodyn.*, in press.

Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1965.

Wieczorek, S. A.; Zywocinski, A. Determination of the Excess Molar Volumes of Cyclohexane + Benzene between 293.15 and 308.15 K by Use of a Continuous Dilution Dilatometer. *J. Chem. Thermodyn.* **1983**, *15*, 327−331.

Received for review July 31, 1998. Accepted December 8, 1998.

JE980174K