Densities, Viscosities, Refractive Indices, and Speeds of Sound in Methyl Acetoacetate + Methyl Acetate, + Ethyl Acetate, + *n*-Butyl Acetate, + Methyl Benzoate, and + Ethyl Benzoate at 298.15, 303.15, and 308.15 K[†]

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The densities, viscosities, refractive indices, and speeds of sound in binary mixtures of methyl acetoacetate with esters have been measured at 298.15, 303.15, and 308.15 K. The results are used to interpret the nature of thermodynamic interactions between the mixing components. The excess parameters have been fitted to a third-order polynomial to estimate the coefficients and standard errors.

Introduction

The study of molecular interactions in binary mixtures has been the subject of renewed interest in our laboratory in recent years (*1*, *2*). Accurate knowledge of thermodynamic excess properties of organic liquid mixtures has great relevance in theoretical and applied areas of research. In a previous study (*3*, *4*) from this laboratory, mixtures of methyl acetoacetate (MAA) with aromatic liquids as well as alcohols have been studied. In continuation of these studies, we now present the experimental data of the density, viscosity, refractive index, and speed of sound of mixtures of methyl acetoacetate with esters.

Methyl acetoacetate is a versatile organic solvent used in the preparation of antipyrene and a number of heterocycles. Furthermore, it is known to exhibit keto–enol tautomerism (*5*, *6*), the equilibrium of which is known to be affected by the presence of another solvent. The common esters such as methyl acetate, ethyl acetate, *n*-butyl acetate, methyl benzoate, and ethyl benzoate are the polar solvents used in a variety of engineering applications. To the best of our knowledge, we are not aware of any extensive study on the mixing properties of these mixtures. As a further contribution in this area, we now report the experimental densities, ρ, and viscosities, η, at 298.15, 303.15, and 308.15 K and refractive indices, n_D, and speeds of sound, u, at 298.15 K.

Experimental Section

Materials. Analar grade solvents were purified by the recommended methods (*7–9*). The purities of the solvents were ascertained by the constancy of their boiling temperatures during final distillations and also by comparing their densities and refractive indices at 298.15 K which agreed reasonably well with the corresponding literature values (Table I). The gas chromatographic tests using a flame ionization detector having a sensitivity better than 10^{-8} g of fatty acid/μL of solvent (Nucon series, 5700/5765 with fused silica columns) showed a purity of >99 mol %.

Mixtures were prepared by mixing the appropriate volumes of liquids in specially designed ground-glass stoppered bottles and weighed in a single-pan Mettler balance (Switzerland) to an accuracy of ±0.05 mg. Preferential evaporation of solvents from the mixtures was kept to a minimum as evidenced by a repeated measurement of the physical properties over an interval of 2–3 days during which time no changes in the physical properties were observed. The possible error in the mole fractions is estimated to be around ±0.0001.

Table I. Comparison of Literature Data at 298.15 K

liquid	ρ/(gm cm^{-3}) found	ρ/(gm cm^{-3}) lit.	η/(mPa s) found	η/(mPa s) lit.	n_D found	n_D lit.	ref
methyl acetoacetate	1.0720	1.0724	1.568	1.704[a]	1.4166	1.4186[a]	7
methyl acetate	0.9295	0.9274	0.388	0.361	1.3586	1.3588	13, 14
ethyl acetate	0.8941	0.8942	0.433	0.429	1.3702	1.3701	15, 16
n-butyl acetate	0.8758	0.8760	0.673	0.678	1.3909	1.3918	7, 15
methyl benzoate	1.0788[b]	1.0790[b]	1.656[b]	1.673[b]	1.5149	1.5146	7
ethyl benzoate	1.0377[b]	1.0372[b]	1.770[b]	1.751[b]	1.5027	1.5035	7

[a] Compared at 293.15 K. [b] Compared at 303.15 K.

Measurements. Densities, ρ, of pure liquids and their binary mixtures in the composition range 0.1–0.9 at 0.1 mole fraction intervals were measured by using a pycnometer having a bulb volume of about 10 cm^3 and a capillary having an internal diameter of 1 mm. For each measurement, sufficient time was allowed to attain thermal equilibrium in a thermostat: the evaporation losses remained insignificant during the time of actual measurement. The measured densities at 298.15, 303.15, and 308.15 K were considered significant to four figures. An average of triplicate measurements was taken into account, and these were reproducible within ±0.05%.

Viscosities were measured with Cannon Fenske viscometers (sizes 75 and 100, ASTM D 445, supplied by Industrial Research Glassware Ltd., New Jersey). An electronic stopwatch with a precision of ±0.01 s was used for flow time measurements. Triplicate measurements of flow times were reproducible within ±0.05%. Computation of the kinematic viscosity, ν, was done by using the relation $\nu = At - B/t$, where t is the flow time in the viscometer; A and B are viscometer constants, determined by calibrating with water and pure benzene at the working temperatures. Absolute viscosities, η (mPa s), were then calculated by using the relation $\eta = \nu\rho$. The estimated error in the viscosity measurement is around ±0.05%.

Refractive indices for the sodium D line were measured with a thermostated Abbe refractometer (Bellingham and Stanley Ltd., London) with an error of less than ±0.0001 unit. However, these data were approximated to the fourth place (see Table II). Calibration checks of the refractometer

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[†] Based on the Ph.D. thesis of Mr. Raikar submitted to Karnatak University.

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Table II. Experimental Densities, Viscosities, Refractive Indices, and Speeds of Sound of Binary Mixtures

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})	x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
Methyl Acetoacetate (1) + Methyl Acetate (2)									
298.15 K									
0.0000	0.9295	0.388	1.3586	1167	0.5975	1.0276	0.915	1.3996	1314
0.0996	0.9496	0.448	1.3669	1196	0.6969	1.0396	1.044	1.4049	1333
0.1998	0.9678	0.520	1.3744	1222	0.7993	1.0514	1.202	1.4080	1353
0.3009	0.9847	0.596	1.3820	1246	0.9006	1.0620	1.373	1.4126	1368
0.3970	1.0001	0.688	1.3878	1269	1.0000	1.0720	1.568	1.4166	1383
0.4973	1.0139	0.798	1.3947	1292					
303.15 K									
0.0000	0.9230	0.371	1.3558		0.5975	1.0216	0.843	1.3974	
0.0996	0.9431	0.424	1.3645		0.6969	1.0340	0.963	1.4031	
0.1998	0.9622	0.489	1.3722		0.7993	1.0457	1.104	1.4056	
0.3009	0.9789	0.564	1.3801		0.9006	1.0565	1.257	1.4106	
0.3970	0.9936	0.643	1.3860		1.0000	1.0665	1.427	1.4138	
0.4973	1.0083	0.744	1.3928						
308.15 K									
0.0000	0.9164	0.352	1.3530		0.5975	1.0157	0.786	1.3958	
0.0996	0.9367	0.403	1.3624		0.6969	1.0283	0.913	1.4015	
0.1998	0.9552	0.463	1.3707		0.7993	1.0402	1.024	1.4042	
0.3009	0.9726	0.533	1.3784		0.9006	1.0510	1.155	1.4081	
0.3970	0.9875	0.603	1.3839		1.0000	1.0609	1.304	1.4115	
0.4973	1.0023	0.696	1.3915						
Methyl Acetoacetate (1) + Ethyl Acetate (2)									
298.15 K									
0.0000	0.8941	0.433	1.3702	1145	0.5934	1.0059	0.916	1.3998	1288
0.1006	0.9141	0.488	1.3754	1168	0.6964	1.0233	1.051	1.4040	1310
0.1979	0.9332	0.551	1.3806	1194	0.7983	1.0402	1.195	1.4084	1335
0.2962	0.9520	0.624	1.3858	1214	0.9006	1.0566	1.376	1.4126	1358
0.3988	0.9710	0.711	1.3909	1237	1.0000	1.0720	1.568	1.4166	1383
0.4978	0.9890	0.810	1.3957	1265					
303.15 K									
0.0000	0.8875	0.410	1.3671		0.5934	1.0001	0.849	1.3981	
0.1006	0.9079	0.462	1.3729		0.6964	1.0178	0.970	1.4023	
0.1979	0.9273	0.519	1.3783		0.7983	1.0345	1.099	1.4062	
0.2962	0.9460	0.587	1.3832		0.9006	1.0510	1.258	1.4104	
0.3988	0.9654	0.666	1.3886		1.0000	1.0665	1.427	1.4138	
0.4978	0.9835	0.755	1.3933						
308.15 K									
0.0000	0.8814	0.390	1.3643		0.5934	0.9947	0.792	1.3958	
0.1006	0.9018	0.438	1.3705		0.6964	1.0120	0.900	1.3998	
0.1979	0.9212	0.491	1.3759		0.7983	1.0289	1.015	1.4040	
0.2962	0.9403	0.553	1.3809		0.9006	1.0456	1.155	1.4084	
0.3988	0.9595	0.629	1.3859		1.0000	1.0609	1.304	1.4115	
0.4978	0.9775	0.706	1.3910						
Methyl Acetoacetate (1) + *n*-Butyl Acetate (2)									
298.15 K									
0.0000	0.8758	0.673	1.3909	1195	0.6004	0.9837	1.055	1.4053	1287
0.1019	0.8925	0.719	1.3948	1205	0.7005	1.0047	1.163	1.4080	1309
0.2013	0.9091	0.768	1.3964	1221	0.8087	1.0279	1.289	1.4109	1336
0.3015	0.9267	0.826	1.3996	1235	0.8989	1.0483	1.407	1.4133	1358
0.4035	0.9457	0.895	1.4002	1250	1.0000	1.0720	1.568	1.4166	1383
0.5006	0.9641	0.969	1.4027	1269					
303.15 K									
0.0000	0.8704	0.630	1.3883		0.6004	0.9782	0.973	1.4032	
0.1019	0.8871	0.672	1.3926		0.7005	0.9993	1.068	1.4054	
0.2013	0.9039	0.716	1.3936		0.8087	1.0226	1.181	1.4089	
0.3015	0.9215	0.768	1.3967		0.8989	1.0430	1.284	1.4112	
0.4035	0.9400	0.830	1.3980		1.0000	1.0665	1.427	1.4138	
0.5006	0.9586	0.896	1.4004						
308.15 K									
0.0000	0.8652	0.592	1.3859		0.6004	0.9729	0.901	1.4011	
0.1019	0.8819	0.629	1.3902		0.7005	0.9939	0.987	1.4034	
0.2013	0.8985	0.669	1.3935		0.8087	1.0170	1.085	1.4065	
0.3015	0.9160	0.717	1.3947		0.8989	1.0373	1.179	1.4090	
0.4035	0.9347	0.774	1.3955		1.0000	1.0609	1.304	1.4115	
0.5006	0.9532	0.832	1.3979						
Methyl Acetoacetate (1) + Methyl Benzoate (2)									
298.15 K									
0.0000	1.0836	1.825	1.5149	1406	0.5986	1.0755	1.615	1.4595	1386
0.0981	1.0823	1.775	1.5061	1399	0.6984	1.0743	1.598	1.4490	1384
0.1935	1.0809	1.732	1.4977	1398	0.7980	1.0735	1.583	1.4388	1382
0.2966	1.0793	1.703	1.4884	1396	0.8977	1.0726	1.569	1.4276	1380
0.4001	1.0778	1.667	1.4788	1390	1.0000	1.0720	1.568	1.4166	1383
0.4987	1.0766	1.639	1.4695	1388					

Table II (Continued)

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})	x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
303.15 K									
0.0000	1.0788	1.656	1.5127		0.5986	1.0703	1.469	1.4574	
0.0981	1.0774	1.609	1.5039		0.6984	1.0691	1.453	1.4464	
0.1935	1.0759	1.573	1.4951		0.7980	1.0680	1.440	1.4364	
0.2966	1.0744	1.548	1.4861		0.8977	1.0673	1.429	1.4255	
0.4001	1.0728	1.515	1.4766		1.0000	1.0665	1.427	1.4138	
0.4987	1.0715	1.490	1.4673						
308.15 K									
0.0000	1.0740	1.510	1.5096		0.5986	1.0650	1.343	1.4546	
0.0981	1.0724	1.467	1.5016		0.6984	1.0638	1.329	1.4443	
0.1935	1.0709	1.435	1.4929		0.7980	1.0627	1.316	1.4342	
0.2966	1.0693	1.413	1.4838		0.8977	1.0619	1.306	1.4233	
0.4001	1.0676	1.382	1.4741		1.0000	1.0609	1.304	1.4115	
0.4987	1.0664	1.362	1.4647						
Methyl Acetoacetate (1) + Ethyl Benzoate (2)									
298.15 K									
0.0000	1.0425	1.954	1.5027	1374	0.5978	1.0559	1.653	1.4554	1372
0.0992	1.0440	1.834	1.4958	1372	0.6966	1.0591	1.633	1.4467	1373
0.2023	1.0460	1.796	1.4879	1371	0.7979	1.0628	1.598	1.4368	1376
0.3004	1.0478	1.757	1.4803	1370	0.8986	1.0670	1.583	1.4269	1380
0.3990	1.0502	1.729	1.4729	1367	1.0000	1.0720	1.568	1.4166	1383
0.4991	1.0531	1.700	1.4642	1368					
303.15 K									
0.0000	1.0377	1.770	1.5000		0.5978	1.0506	1.501	1.4535	
0.0992	1.0391	1.661	1.4933		0.6966	1.0538	1.484	1.4448	
0.2023	1.0411	1.627	1.4855		0.7979	1.0575	1.452	1.4352	
0.3004	1.0431	1.593	1.4784		0.8986	1.0618	1.440	1.4244	
0.3990	1.0452	1.571	1.4707		1.0000	1.0665	1.427	1.4138	
0.4991	1.0477	1.543	1.4622						
308.15 K									
0.0000	1.0330	1.610	1.4973		0.5978	1.0455	1.373	1.4512	
0.0992	1.0350	1.514	1.4906		0.6966	1.0487	1.356	1.4425	
0.2023	1.0362	1.484	1.4831		0.7979	1.0522	1.328	1.4329	
0.3004	1.0380	1.453	1.4758		0.8986	1.0562	1.316	1.4227	
0.3990	1.0402	1.434	1.4684		1.0000	1.0609	1.304	1.4115	
0.4991	1.0427	1.408	1.4597						

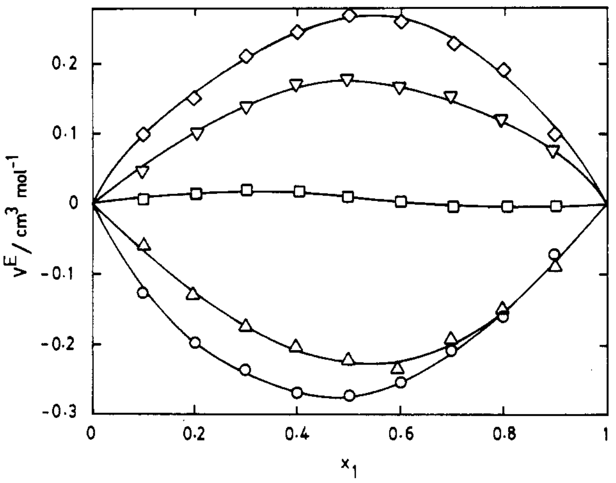

Figure 1. Excess molar volume versus mole fraction at 298.15 K for mixtures of MAA with (○) methyl acetate, (△) ethyl acetate, (□) *n*-butyl acetate, (▽) methyl benzoate, and (◇) ethyl benzoate.

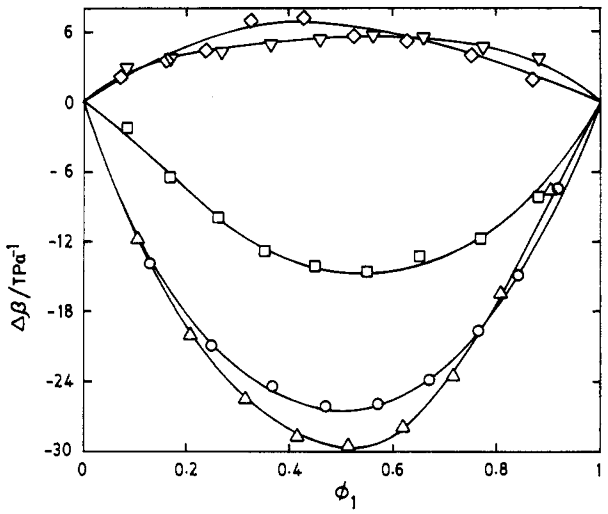

Figure 2. Changes in isentropic compressibility versus volume fraction at 298.15 K for the same binary mixtures given in Figure 1.

were done routinely with the help of the glass piece of known refractive index supplied with the instrument.

Speeds of sound were measured by using a variable-path single-crystal interferometer (Mittal Enterprises, New Delhi, Model M-84). A crystal-controlled high-frequency generator was used to excite the transducer at a frequency of 1 MHz. The frequency was measured with an accuracy of 1 in 10^6 by using a digital frequency meter. The current variations across the transducer were observed on a microammeter. The interferometer cell was filled with the test liquid and was connected to the output terminal of the high-frequency generator through a shielded cable. Water was then circulated around the measuring cell from a thermostat maintained at the desired constant temperature. The other experimental details were given earlier (*3*). Our value of u (1255 m s^{-1}) at 308.15 K for benzene compares well with the data (1255 m s^{-1}) of Nath and Dixit (*10*). Similarly, u at 298.15 K for benzene (1301 m s^{-1}) and toluene (1306 m s^{-1}) agree closely with the literature values of 1301 and 1306 m s^{-1}, respectively, of Nath and Tripathi (*11*). The isentropic compressibilities were calculated as $\beta = 1/u^2\rho$. The average uncertainty in β is around ±0.01%.

In all the property measurements, thermostats (Toshniwal, Model GL-15, and INSREF 016 AP) were maintained constant

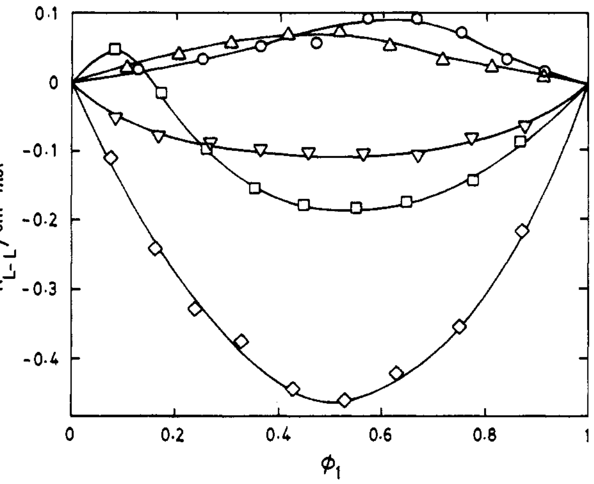

Figure 3. Excess molar refraction versus volume fraction at 298.15 K for the same mixtures of Figure 1.

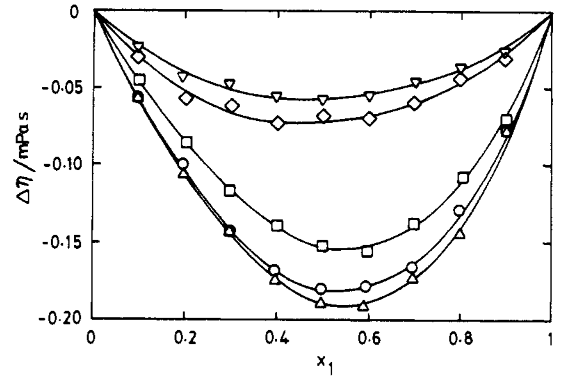

Figure 4. Dependence of $\Delta\eta$ on mole fraction at 298.15 K for the same binary mixtures given in Figure 1.

to ±0.01 K at the desired temperatures as checked by a calibrated (1968 temperature scale) thermometer. The results compiled in Table II are the averages of three measurements at each point.

Results and Discussion

Using the experimental results of ρ, n_D, η, and β of the binary mixtures (Table II), the various excess quantities, viz., excess volume, V^E, excess refraction, R^E, changes in isentropic compressibility, $\Delta\beta$, and changes in viscosity, $\Delta\eta$, have been calculated as

$$V^E = V_m - V_1x_1 - V_2x_2 \tag{1}$$

$$R^E = R_m - R_1\phi_1 - R_2\phi_2 \tag{2}$$

$$\Delta\beta = \beta_m - \beta_1\phi_1 - \beta_2\phi_2 \tag{3}$$

$$\Delta\eta = \eta_m - \eta_1x_1 - \eta_2x_2 \tag{4}$$

where V_i, R_i, β_i, and η_i are, respectively, the molar volume, molar refraction, isentropic compressibility, and viscosity of the ith component of the mixture. The subscript m for these symbols represents the mixture properties. The terms x_i and ϕ_i refer to the mole fraction and volume fraction, respectively. In eq 2, the molar refractivity, R_i, is obtained from the Lorentz–Lorenz rule (*1*). The volume fraction, ϕ_i, of the ith component is related to the mole fraction as

$$\phi_i = x_iV_i/\sum_{i=1}^{2}x_iV_i \tag{5}$$

Table III. Estimated Parameters of Excess Functions

function	temp/K	a_0	a_1	a_2	a_3	σ
Methyl Acetoacetate (1) + Methyl Acetate (2)						
V^E/(cm^3 mol^{-1})	298.15	−1.097	−0.187	−0.219	−0.071	0.019
	303.15	−1.157	−0.264	−0.272	−0.307	0.021
	308.15	−1.181	−0.117	−0.076	−0.361	0.010
$\Delta\eta$/(mPa s)	298.15	−0.721	0.102	−0.051	0.065	0.003
	303.15	−0.626	0.113	−0.041	−0.038	0.003
	308.15	−0.524	−0.062	0.064	0.124	0.006
$\Delta\beta$/TPa^{-1}	298.15	−106.9	4.384	−25.076	−44.5	0.422
R^E_{L-L}/(cm^3 mol^{-1})	298.15	0.331	−0.425	0.752	−0.647	0.026
	303.15	0.510	−0.450	0.620	−0.354	0.034
	308.15	0.722	−0.498	0.886	−0.256	0.033
Methyl Acetoacetate (1) + Ethyl Acetate (2)						
V^E/(cm^3 mol^{-1})	298.15	−0.906	0.125	0.018	0.257	0.008
	303.15	−1.094	−0.018	−0.088	0.331	0.012
	308.15	−1.165	−0.079	0.281	0.161	0.015
$\Delta\eta$/(mPa s)	298.15	−0.756	0.168	−0.040	−0.007	0.003
	303.15	−0.649	0.140	−0.034	−0.004	0.002
	308.15	−0.554	0.120	−0.042	−0.022	0.002
$\Delta\beta$/TPa^{-1})	298.15	−118.320	5.107	−50.247	4.558	2.181
R^E_{L-L}/(cm^3 mol^{-1})	298.15	0.249	0.145	−0.161	−0.356	0.008
	303.15	0.389	−0.161	0.263	0.164	0.010
	308.15	0.409	0.140	0.353	0.533	0.010
Methyl Acetoacetate (1) + *n*-Butyl Acetate (2)						
V^E/(cm^3 mol^{-1})	298.15	0.042	0.148	−0.126	−0.089	0.018
	303.15	0.046	0.078	−0.009	−0.614	0.014
	308.15	−0.010	0.278	−0.543	−0.425	0.012
$\Delta\eta$/(mPa s)	298.15	−0.608	0.126	−0.023	0.052	0.002
	303.15	−0.530	0.110	−0.023	0.048	0.002
	308.15	−0.461	0.095	−0.027	0.035	0.002
$\Delta\beta$/TPa^{-1}	298.15	−59.042	4.252	39.549	−3.751	1.616
R^E_{L-L}/(cm^3 mol^{-1})	298.15	−0.748	0.095	1.037	1.293	0.038
	303.15	−0.666	−0.017	0.909	1.636	0.037
	308.15	−0.638	0.024	1.584	2.641	0.042
Methyl Acetoacetate (1) + Methyl Benzoate (2)						
V^E/(cm^3 mol^{-1})	298.15	0.705	−0.074	−0.214	−0.182	0.008
	303.15	0.702	−0.156	−0.098	−0.124	0.008
	308.15	0.722	−0.082	−0.015	−0.318	0.007
$\Delta\eta$/(mPa s)	298.15	−0.225	−0.007	−0.077	−0.013	0.003
	303.15	−0.198	0.003	−0.076	−0.042	0.003
	308.15	−0.175	−0.007	−0.072	−0.034	0.003
$\Delta\beta$/TPa^{-1}	298.15	21.901	−4.707	4.538	34.275	0.775
R^E_{L-L}/(cm^3 mol^{-1})	298.15	−0.444	0.059	−0.103	−0.594	0.006
	303.15	−0.407	0.067	−0.516	−0.411	0.017
	308.15	−0.335	0.113	−0.170	0.283	0.011
Methyl Acetoacetate (1) + Ethyl Benzoate (2)						
V^E/(cm^3 mol^{-1})	298.15	1.048	0.064	−0.361	0.305	0.016
	303.15	1.089	−0.220	0.265	0.022	0.008
	308.15	1.117	0.255	−1.294	−0.911	0.017
$\Delta\eta$/(mPa s)	298.15	−0.293	−0.071	−0.060	0.087	0.005
	303.15	−0.260	−0.029	−0.066	−0.001	0.005
	308.15	−0.229	−0.029	−0.033	−0.010	0.005
$\Delta\beta$/TPa^{-1}	298.15	24.237	−0.616	−13.630	−40.484	0.351
R^E_{L-L}/(cm^3 mol^{-1})	298.15	−1.747	−0.270	0.447	0.058	0.029
	303.15	−1.580	−0.223	0.071	0.111	0.029
	308.15	−1.515	−0.214	0.060	0.642	0.025

The parameters Y ($=V^E$, R^E, $\Delta\beta$, and $\Delta\eta$) are fitted to the Redlich–Kister-type relation (*12*) shown below:

$$Y = C_1C_2\sum_{i=0}^{3}a_i(C_2-C_1)^i \tag{6}$$

where C_1 and C_2 are the mole or volume fractions and a_i's represent the coefficients to be evaluated. For fitting the results of V^E and $\Delta\eta$ we have used mole fractions, x_i, for C_i, while for R^E and $\Delta\beta$ results, the volume fractions, ϕ_i, are used. A third-order fit of the Redlich–Kister relation in almost all cases reproduced insignificant differences between the calculated and observed quantities. The back-calculated values of the excess quantities are used to draw the smooth curves given in Figures 1–4. Different symbols in these figures represent the observed points. The estimated parameters, a_i's, of eq 6 and the standard deviations, σ, are compiled in Table III.

The dependence of the excess molar volume on the mole fraction at 298.15 K is displayed in Figure 1. It is found that mixtures of MAA with methyl acetate or ethyl acetate have negative values of V^E, suggesting specific interactions between the mixing components. For mixtures of MAA with methyl benzoate or ethyl benzoate, positive values of V^E are observed. This suggests the presence of dispersion-type interactions. However, with the MAA + *n*-butyl acetate mixture, we find that the V^E values are close to zero, suggesting their nearly ideal behavior. It is further observed that V^E results of the binary mixtures with MAA vary according to the sequence methyl acetate < ethyl acetate < *n*-butyl acetate < methyl benzoate < ethyl benzoate. The same sequence also holds good at higher temperatures, viz., 303.15 and 308.15 K. The above sequence is in accordance with the molecular size differences between the components of the mixture.

The results of $\Delta\beta$ as displayed in Figure 2 are somewhat different in that, for MAA + *n*-butyl acetate, the values of $\Delta\beta$ are negative over the entire range of mixture composition. Also, $\Delta\beta$ values for the MAA + ethyl acetate mixture are smaller than those observed for the MAA + methyl acetate mixture. However, the values of $\Delta\beta$ for both these mixtures are negative. For mixtures of MAA with methyl benzoate or ethyl benzoate, the positive $\Delta\beta$ values are more or less identical as seen in Figure 2.

The dependence of R^E_{L-L} on the mole fraction is shown in Figure 3 wherein it is observed that R^E_{L-L} is positive for mixtures of MAA with methyl acetate or ethyl acetate. This observation is opposite to that observed for V^E or $\Delta\beta$ as discussed before. The values of R^E_{L-L} are negative for MAA + methyl benzoate and MAA + ethyl benzoate mixtures. However, MAA + *n*-butyl acetate shows a sign inversion as displayed in Figure 3.

The results of $\Delta\eta$ at 298.15 K are shown in Figure 4. It is observed that $\Delta\eta$ values for all the mixtures are negative in the entire mole fraction range and vary according to the sequence ethyl acetate < methyl acetate < *n*-butyl acetate < ethyl benzoate < methyl benzoate. This sequence is also true at higher temperatures.

In conclusion, we are not aware of any data on the systems investigated here, and hence, no comparisons could be made. It is further realized that such binary data on ester–ester interactions will have some relevance in polymer-processing industries because the esters are known to act as plasticizing agents for many industrial plastics.

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