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SUPPLEMENTARY MATERIAL TO
Thermophysical properties of binary blends of cyclohexane with some esters

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TABLE S-I. Densities (ρ) and viscosities (η) of the pure liquids at 298.15, 308.15 and 313.15 K

Pure liquid	T / K	$\rho \times 10^{-3}$ / kg m^{-3}		η / mPa s	
		Exp.	Lit.	Exp.	Lit.
CH	298.15	0.77384	0.7737[1]	0.8927	0.8859[1]
			0.77392[2]		0.892[3]
			0.7739[3]		
			0.7740[4]		
	308.15	0.76433	0.76443[2]	0.7748	0.774[4]
	318.15	0.75473	0.75471[2]	0.6620	–
MA	298.15	0.92681	0.9268[5]	0.3809	0.384[5]
			0.9261[6]		0.3798[6]
	308.15	0.91524	0.9152[7,8]	0.3491	0.349[7]
	318.15	0.90225	0.9022[8]	0.3132	0.313[8]
EA	298.15	0.89455	0.8948[7]	0.4262	0.430[7]
			0.8945[8]		0.429[8]
			0.89444[9]		0.427[9]
	308.15	0.88267	0.8827[7]	0.3874	0.387[7]
			0.8821[8]		0.384[8]
			0.8826[10]		
	318.15	0.86994	0.8692[8]	0.3564	0.353[8]
			0.86997[9]		0.356[9]
			0.8696[10]		
MS	298.15	1.17931	1.179336[11]	1.5358	1.535[12]
			1.1782[12]		
	308.15	1.16931	1.169367[11]	1.4024	–
	318.15	1.15942	1.159405[11]	1.3027	–

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TABLE S-II. Densities (ρ), viscosities (η), excess molar volumes (V_m^E) and excess viscosities (η_E) for the binary blends of CH (1) with the three esters (2) at 298.15, 308.15 and 318.15 K; x_1 – mole fraction of CH

x_1	$\rho \times 10^{-3}$ / kg m^{-3}	η / mPa s	$V_m^E \times 10^6$ / m^3 mol^{-1}	η^E / mPa s
		CH (1) + MA (2) T = 298.15 K		
0	0.92681	0.3810	0	0
0.0754	0.90732	0.3938	0.380	–0.012
0.1551	0.88781	0.4094	0.800	–0.025
0.2393	0.86932	0.4285	1.160	–0.039
0.3286	0.85192	0.4517	1.440	–0.052
0.3700	0.84477	0.4641	1.510	–0.058
0.5241	0.82097	0.5242	1.630	–0.071
0.6314	0.80660	0.5808	1.600	–0.071
0.7460	0.79358	0.6568	1.389	–0.062
0.8686	0.78244	0.7579	0.900	–0.040
1	0.77384	0.8927	0	0
		T = 308.15 K		
0	0.91524	0.3491	0	0
0.0754	0.89370	0.3520	0.601	–0.019
0.1551	0.87433	0.3605	1.051	–0.034
0.2393	0.85607	0.3714	1.430	–0.051
0.3286	0.83895	0.3876	1.722	–0.066
0.3700	0.83151	0.3965	1.841	–0.072
0.5241	0.80796	0.4395	1.997	–0.091
0.6314	0.79386	0.4817	1.974	–0.096
0.7460	0.78118	0.5432	1.756	–0.090
0.8686	0.77086	0.6352	1.182	–0.062
1	0.76433	0.7748	0	0
		T = 318.15 K		
0	0.90225	0.3132	0	0
0.0754	0.87878	0.3057	0.840	–0.026
0.1551	0.85971	0.3094	1.320	–0.042
0.2393	0.84136	0.3155	1.771	–0.059
0.3286	0.82490	0.3228	2.050	–0.078
0.3700	0.81769	0.3297	2.171	–0.083
0.5241	0.79500	0.3556	2.310	–0.108
0.6314	0.78152	0.3889	2.260	–0.113
0.7460	0.76950	0.4386	2.000	–0.109
0.8686	0.75971	0.5201	1.390	–0.080
1	0.75473	0.6620	0	0
		CH (1) + EA (2) T = 298.15 K		
0	0.89455	0.4262	0	0
0.0914	0.88047	0.4475	0.227	–0.008
0.1845	0.86626	0.4640	0.480	–0.024
0.2795	0.85214	0.4872	0.737	–0.037
0.3764	0.83873	0.5162	0.919	–0.047
0.4200	0.83290	0.5284	0.987	–0.053

TABLE S-II. Continued

x_1	$\rho \times 10^{-3}$ / kg m^{-3}	η / mPa s	$V_m^E \times 10^6$ / m^3 mol^{-1}	η^E / mPa s
		CH (1) + EA (2)	$T = 298.15$ K	
0.5759	0.81413	0.5909	1.025	–0.061
0.6787	0.80289	0.6462	0.941	–0.058
0.7836	0.79243	0.7107	0.746	–0.050
0.8907	0.78304	0.7925	0.395	–0.031
1	0.77384	0.8927	0	0
		$T = 308.15$ K		
0	0.88267	0.3874	0	0
0.0914	0.86805	0.3981	0.325	–0.015
0.1845	0.85376	0.4108	0.627	–0.029
0.2795	0.83972	0.4277	0.914	–0.042
0.3764	0.82515	0.4456	1.283	–0.057
0.4200	0.82079	0.4560	1.182	–0.062
0.5759	0.80223	0.5029	1.248	–0.075
0.6787	0.79137	0.5436	1.145	–0.076
0.7836	0.78153	0.6009	0.896	–0.066
0.8907	0.77239	0.6752	0.534	–0.043
1	0.76433	0.7748	0	0
		$T = 318.15$ K		
0	0.86994	0.3564	0	0
0.0914	0.85474	0.3592	0.443	–0.018
0.1845	0.84042	0.3635	0.802	–0.036
0.2795	0.82682	0.3725	1.086	–0.051
0.3764	0.81389	0.3834	1.297	–0.066
0.4200	0.80830	0.3882	1.374	–0.074
0.5759	0.79017	0.4202	1.455	–0.089
0.6787	0.77936	0.4487	1.389	–0.094
0.7836	0.76955	0.4913	1.175	–0.088
0.8907	0.76152	0.5586	0.690	–0.060
1	0.75473	0.6620	0	0
		CH (1) + MS (2)	$T = 298.15$ K	
0	1.17931	1.5358	0	0
0.1168	1.13610	1.4367	0.281	–0.005
0.2294	1.09741	1.3549	0.060	–0.001
0.3379	1.06052	1.2856	–0.370	0.007
0.4425	1.02285	1.2236	–0.719	0.016
0.4878	1.00603	1.1969	–0.873	0.018
0.6411	0.94605	1.1096	–1.281	0.025
0.7353	0.90552	1.0554	–1.309	0.025
0.8265	0.86273	1.0015	–1.052	0.021
0.9146	0.81950	0.9473	–0.707	0.012
1	0.77384	0.8927	0	0
		$T = 308.15$ K		
0	1.16931	1.4024	0	0
0.1168	1.12552	1.3008	0.342	–0.008

TABLE S-II. Continued

x_1	$\rho \times 10^{-3}$ / kg m^{-3}	η / mPa s	$V_m^E \times 10^6$ / m^3 mol^{-1}	η^E / mPa s
		T = 308.15 K		
0.2294	1.08606	1.2194	0.200	–0.004
0.3379	1.04900	1.1489	–0.221	0.001
0.4425	1.01121	1.0892	–0.559	0.011
0.4878	0.99471	1.0639	–0.752	0.014
0.6411	0.93462	0.9777	–1.141	0.019
0.7353	0.89413	0.9256	–1.159	0.019
0.8265	0.85231	0.8744	–1.002	0.016
0.9146	0.80851	0.8249	–0.547	0.010
1	0.76433	0.7748	0	0
		T = 318.15 K		
0	1.15942	1.3027	0	0
0.1168	1.11418	1.1942	0.502	–0.009
0.2294	1.07371	1.1084	0.469	–0.007
0.3379	1.03673	1.0344	0.028	–0.002
0.4425	0.99954	0.9721	–0.388	0.007
0.4878	0.98303	0.9471	–0.583	0.011
0.6411	0.92305	0.8612	–0.982	0.017
0.7353	0.88228	0.8087	–0.948	0.017
0.8265	0.84081	0.7571	–0.812	0.013
0.9146	0.79715	0.7086	–0.337	0.007
1	0.75473	0.6620	0	0

TABLE S-III. Molar volumes ($V_{m,1}^*$ and $V_{m,2}^*$), partial molar volumes at infinite dilution ($\overline{V}_{m,1}^0$ and $\overline{V}_{m,2}^0$) and excess partial molar volumes at infinite dilution ($\overline{V}_{m,1}^{0,E}$ and $\overline{V}_{m,2}^{0,E}$) for each component in the binary blends at 298.15 K; the molar volumes are given in cm^3 mol^{-1}

Parameter	CH (1) +		
	MA (2)	EA (2)	MS (2)
$V_{m,1}^*$	108.76	108.76	108.76
$\overline{V}_{m,1}^0$	112.95	111.05	114.21
$V_{m,2}^*$	79.93	98.50	129.02
$\overline{V}_{m,2}^0$	87.92	102.41	119.03
$\overline{V}_{m,1}^{0,E}$	4.19	2.29	5.45
$V_{m,2}$	7.99	3.91	–9.98

TABLE S-IV. Free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation of viscous flow for the binary blends; x_1-mole fraction of CH

x_1	ΔG^* / kJ mol^{-1}			ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1}mol^{-1}	R^2
	298.15 K	308.15 K	318.15 K			
		CH (1) + MA (2)				
0.0000	10.745	10.914	11.019	6.657	–13.744	0.9928
0.0754	10.905	11.022	11.051	8.711	–7.406	0.9920
0.1551	11.082	11.167	11.170	9.761	–4.472	0.9944

TABLE S-IV. Continued

x_1	ΔG^* / kJ mol^{-1}			ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1}mol^{-1}	R^2
	298.15 K	308.15 K	318.15 K			
			CH (1) + MA (2)			
0.2393	11.275	11.326	11.308	10.771	−1.727	0.9967
0.3286	11.485	11.517	11.452	11.961	1.547	0.9947
0.3700	11.586	11.612	11.545	12.182	1.951	0.9955
0.5241	12.008	12.000	11.872	14.015	6.667	0.9942
0.6314	12.340	12.315	12.190	14.553	7.372	0.9963
0.7460	12.720	12.701	12.587	14.692	6.562	0.9968
0.8686	13.148	13.174	13.112	13.670	1.705	0.9966
1.0000	13.620	13.746	13.809	10.793	−9.515	0.9974
			CH (1) + EA (2)			
0.0000	11.541	11.717	11.915	5.956	−18.719	0.9990
0.0914	11.691	11.820	11.972	7.501	−14.039	0.9992
0.1845	11.811	11.932	12.037	8.429	−11.351	0.9997
0.2795	11.962	12.067	12.134	9.389	−8.648	0.9987
0.3764	12.134	12.206	12.240	10.536	−5.378	0.9990
0.4200	12.204	12.273	12.286	10.967	−4.179	0.9979
0.5759	12.520	12.564	12.537	12.253	−0.933	0.9973
0.6787	12.765	12.787	12.735	13.198	1.414	0.9975
0.7836	13.021	13.063	12.995	13.384	1.161	0.9947
0.8907	13.308	13.379	13.350	12.676	−2.174	0.9950
1.0000	13.620	13.746	13.809	10.793	−9.515	0.9974
			CH (1) + MS (2)			
0.0000	15.387	15.693	16.029	5.825	−32.054	0.9977
0.1168	15.182	15.460	15.763	6.526	−29.021	0.9990
0.2294	14.987	15.247	15.519	7.060	−26.583	0.9997
0.3379	14.804	15.041	15.282	7.679	−23.896	0.9999
0.4425	14.631	14.853	15.065	8.162	−21.702	0.9999
0.4878	14.554	14.770	14.973	8.316	−20.928	0.9998
0.6411	14.292	14.478	14.645	9.019	−17.694	0.9996
0.7353	14.126	14.296	14.438	9.469	−15.634	0.9993
0.8265	13.961	14.112	14.225	10.010	−13.271	0.9988
0.9146	13.790	13.933	14.021	10.349	−11.573	0.9978
1.0000	13.620	13.746	13.809	10.793	−9.515	0.9974

TABLE S-V. Ultrasonic speeds (u), isentropic compressibilities (κ_s), intermolecular free lengths (L_f), free volumes (V_f), excess isentropic compressibilities (κ_s^E), excess intermolecular free lengths (L_f^E) and excess free volumes (V_f^E) for the binary blends at 298.15 K; x_1 – mole fraction of CH

x_1	u / m s^{-1}	κ_s / TPa^{-1}	L_f / Å	$V_f \times 10^6$ m^3 mol^{-1}	κ_s^E TPa^{-1}	L_f^E / Å	$V_f^E \times 10^6$ m^3 mol^{-1}
			CH (1) + MA (2)				
0	1148.5	8.180	0.5883	0.378	0	0	0
0.0754	1146.9	8.379	0.5954	0.363	0.189	0.0070	0.003
0.1551	1152.2	8.484	0.5991	0.351	0.285	0.0106	0.009

TABLE S-V. Continued

x_1	u / m s^{-1}	κ_s / TPa^{-1}	L_f / Å	$V_f \times 10^6$ m^3 mol^{-1}	κ_s^E TPa^{-1}	L_f^E / Å	$V_f^E \times 10^6$ m^3 mol^{-1}
			CH (1) + MA (2)				
0.2393	1160.6	8.540	0.6011	0.337	0.332	0.0124	0.015
0.3286	1171.8	8.549	0.6014	0.321	0.334	0.0126	0.020
0.3700	1177.0	8.545	0.6012	0.313	0.327	0.0124	0.021
0.5241	1197.8	8.490	0.5993	0.276	0.265	0.0102	0.020
0.6314	1212.7	8.430	0.5972	0.246	0.202	0.0079	0.015
0.7460	1226.9	8.371	0.5951	0.213	0.142	0.0056	0.008
0.8686	1240.2	8.309	0.5929	0.178	0.080	0.0032	0.003
1	1253.3	8.227	0.5899	0.145	0	0	0
			CH (1) + EA (2)				
0	1144.3	8.537	0.6010	0.411	0	0	0
0.0914	1154.5	8.521	0.6004	0.385	0.013	0.0004	−0.002
0.1845	1165.2	8.503	0.5997	0.367	0.024	0.0008	0.005
0.2795	1176.3	8.481	0.5990	0.344	0.032	0.0011	0.007
0.3764	1187.5	8.455	0.5981	0.318	0.036	0.0012	0.007
0.4200	1192.2	8.447	0.5978	0.308	0.042	0.0015	0.008
0.5759	1209.2	8.401	0.5961	0.263	0.044	0.0015	0.005
0.6787	1220.1	8.367	0.5949	0.231	0.041	0.0014	0.001
0.7836	1231.0	8.328	0.5935	0.202	0.034	0.0012	−0.001
0.8907	1241.5	8.286	0.5920	0.172	0.025	0.0009	−0.002
1	1253.3	8.227	0.5899	0.145	0	0	0
			CH (1) + MS (2)				
0	1410.9	4.260	0.4245	0.187	0	0	0
0.1168	1356.0	4.787	0.4500	0.179	0.056	0.0062	−0.002
0.2294	1325.7	5.185	0.4683	0.174	−0.004	0.0059	−0.003
0.3379	1305.2	5.535	0.4839	0.170	−0.098	0.0035	−0.003
0.4425	1292.5	5.852	0.4976	0.165	−0.209	−0.0001	−0.003
0.4878	1286.7	6.004	0.5040	0.163	−0.243	−0.0012	−0.003
0.6411	1268.4	6.570	0.5272	0.156	−0.297	−0.0034	−0.004
0.7353	1258.7	6.970	0.5430	0.152	−0.271	−0.0031	−0.004
0.8265	1252.8	7.385	0.5590	0.149	−0.209	−0.0023	−0.004
0.9146	1249.3	7.818	0.5751	0.146	−0.105	−0.0007	−0.003
1	1253.3	8.227	0.5899	0.145	0	0	0

TABLE S-VI. Refractive indices (n_D), molar refractions (R_m) and excess molar refractions (R_m^E) for the binary blends at 298.15 K; x_1 – mole fraction of CH

x_1	n_D	$R_m \times 10^6$ / m^3 mol^{-1}	$R_m^E \times 10^6$ / m^3 mol^{-1}
		CH (1) + MA (2)	
0.0000	1.3604	17.658	0
0.0754	1.3659	18.472	0.055
0.1551	1.3717	19.352	0.132
0.2393	1.3776	20.270	0.201
0.3286	1.3836	21.224	0.256
0.3700	1.3862	21.649	0.264

TABLE S-VI. Continued

x_1	n_D	$R_m \times 10^6$ / m^3 mol^{-1}	$R_m^E \times 10^6$ / m^3 mol^{-1}
CH (1) + MA (2)			
0.5241	1.3958	23.223	0.286
0.6314	1.4022	24.303	0.285
0.7460	1.4089	25.425	0.253
0.8686	1.4158	26.567	0.160
1.0000	1.4234	27.730	0
CH (1) + EA (2)			
0.0000	1.3712	22.343	0
0.0914	1.3753	22.831	–0.004
0.1845	1.3799	23.362	0.025
0.2795	1.3849	23.925	0.076
0.3764	1.3898	24.475	0.104
0.4200	1.3920	24.721	0.115
0.5759	1.4000	25.566	0.120
0.6787	1.4054	26.110	0.110
0.7836	1.4109	26.642	0.077
0.8907	1.4172	27.190	0.048
1.0000	1.4234	27.730	0
CH (1) + MS (2)			
0.0000	1.5352	40.179	0
0.1168	1.5247	38.882	0.157
0.2294	1.5136	37.439	0.116
0.3379	1.5028	35.999	0.026
0.4425	1.4920	34.627	–0.043
0.4878	1.4872	34.032	–0.074
0.6411	1.4700	32.024	–0.174
0.7353	1.4585	30.820	–0.205
0.8265	1.4470	29.728	–0.162
0.9146	1.4354	28.680	–0.113
1.0000	1.4234	27.730	0

Model correlation of excess molar volumes

Prigogine–Flory–Paterson theory (PFP). The PFP theory[13,14] is a modified version of the Flory statistical theory.[15–18] It has been successfully applied to predict, estimate and analyze the excess thermodynamic functions of liquid blends with non-polar as well as polar liquids. This theory considers the excess molar volumes of binary blends to be a sum of three contributions: *i*) the interaction contribution (V_{int}^E) that is proportional to the interaction parameter, $\chi_{1,2}$; *ii*) the free volume contribution that arises from the dependence of the reduced volume upon the reduced temperature; *iii*) the internal pressure contribution (V_{p*}^E) that depends on both the differences of the characteristic pressures and on the differences of reduced volumes of the components. The relation for V_m^E in terms of the three contributions is as follows:[19,20]

$$\frac{V_m^E}{x_1 V_1^* + x_2 V_2^*} = \underbrace{\frac{(\tilde{v}^{1/3}-1)\tilde{v}^{2/3}\psi_1\theta_2}{[(4/3)\tilde{v}^{-1/3}-1]p_1^*}\chi_{1,2}}_{(\chi_{1,2}\ \text{contribution})} - \underbrace{\frac{(\tilde{v}_1-\tilde{v}_2)^2[(14/9)\tilde{v}^{-1/3}-1]\psi_1\psi_2}{[(4/3)\tilde{v}^{-1/3}-1]\tilde{v}}}_{(\tilde{v}\ \text{contribution})} +$$

$$+ \underbrace{\frac{(\tilde{v}_1-\tilde{v}_2)(p_1^*-p_2^*)\psi_1\psi_2}{(p_1^*\psi_2+p_2^*\psi_1)}}_{(p^*\ \text{contribution})} \tag{S-1}$$

where ψ_1 and ψ_2 stand for the molecular contact energy fractions of liquids 1 and 2 in a blend; θ_2 is the molecular site fraction of liquid 2 in a mixture and the other symbols have their usual significance.[13,14] Various characteristic and reduced parameters of the pure liquid components, such as the reduced volume ($\tilde{v}$), reduced temperature ($\tilde{T}$), characteristic volume (V^*), characteristic pressure (p^*) and characteristic temperature (T^*) for each liquid component (needed for the V_m^E correlation) were calculated using the Flory formalism[15–18] and are listed in Table S-VII.

TABLE S-VII. Isobaric molar heat capacities (C_P), expansion coefficient (α), isothermal compressibility (κ_T) and the Flory parameters for the pure liquids at 298.15 K

Liquid	C_p [a]	$\tilde{v}$	$\tilde{T}$	V^* / cm^3 mol^{-1}	P^* / Pa	T^* / K	α / kK^{-1}	κ_T / TPa^{-1}
CH	155.01	1.2939	0.0636	84.09	539.84	4686.95	1.2348	1141.8
MA	141.93	1.3107	0.0658	60.98	609.89	4530.98	1.3250	1112.8
EA	170.66	1.3199	0.0670	74.62	605.88	4452.90	1.3756	1179.3
MS	249.06	1.2147	0.0517	106.22	692.34	5769.79	0.8433	535.8

[a]Values adapted from Ref. 21 were multiplied with molecular weight for unit conversion

The interaction contributions to V_m^E were obtained from Eq. (3) using a computer program, as detailed elsewhere.[22] The optimized $\chi_{1,2}$ values, the calculated and experimental V_m^E values, their deviation (ΔV_m^E) and the different contributions to the V_m^E values at near equimolar ($x_1 \approx 0.5$) composition at 298.15 K are given in Table S-VIII.

TABLE S-VIII. Interaction parameters ($\chi_{1,2}$), calculated and experimental values of excess molar volumes ($V_{m,exp}^E$ and $V_{m,PFP}^E$), their deviations (ΔV_m^E) and different PFP contributions at 298.15 K. The excess molar volumes and their deviations are for equimolar composition ($x_1 \approx 0.5$)

CH (1) +	$\chi_{1,2}$ J mol^{-1}	$V_{m,exp}^E \times 10^6$ m^3 mol^{-1}	$V_{m,PFP}^E \times 10^6$ m^3 mol^{-1}	$\Delta V_m^E \times 10^6$ m^3 mol^{-1}	PFP contributions$\times 10^3$		
					int[a]	fv[b]	ip[c]
MA (2)	76.254	1.630	1.630	0.000	0.0219	0.0001	0.0005
EA (2)	46.868	1.025	0.991	0.034	0.0123	0.0002	0.0007
MS (2)	–13.482	–0.870	–0.870	0.000	–0.0022	0.0022	–0.0047

[a]Interaction contribution; [b]free volume contribution; [c]internal pressure contribution

Peng–Robinson equation of state (PR-EOS). Cubic equations of state are powerful tools for predicting the thermodynamic properties and phase equilibria of hydrocarbon systems. These equations are widely applied in industrial process design for their relatively simple mathematical structure and computational efficiency in the calculation of the volume and other related thermodynamic parameters, such as fugacity coefficient, *etc*. These equations can conveniently be extended to mixtures using different mixing rules. Herein, the classical cubic PR-EOS equation of state was used for correlating the excess molar volumes ($V_{m,PR-EOS}^{E}$) of the blends studied at 298.15 K. The two parameter PR-EOS is given by:[23]

$$p = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{S-2}$$

For a pure component the energy a and co-volume b parameters were obtained from the relations:

$$a = a(T) = a(T_c)\left[1 + \xi\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{S-3}$$

$$b = b(T) = b(T_c) \tag{S-4}$$

$$a(T_c) = 0.45724\frac{R^2 T_c^2}{p_c} \tag{S-5}$$

$$b(T_c) = 0.07780\frac{RT_c}{p_c} \tag{S-6}$$

where T_c and p_c are the critical temperature and pressure of a pure component. The parameter ξ in terms of the acentric factor (ω) is defined by:

$$\xi = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{S-7}$$

The acentric factor (ω) for each pure liquid was calculated from the relation:[24]

$$\omega = \frac{3T_{br}}{7(1-T_{br})}\log p_c - 1 \tag{S-8}$$

where $T_{br} = T_b / T_c$ and T_b is the boiling point of a pure liquid. The T_b, T_c and p_c values were taken from the literature.[21] For a binary blend, the energy a and co-volume b parameters are given by:[24]

$$a(T) = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j \sqrt{a_i a_j}(1-k_{ij}) \tag{S-9}$$

$$b(T) = \sum_{i=1}^{2} x_i b_i \tag{S-10}$$

where k_{ij} is an empirically determined binary interaction coefficient characterizing the binaries formed by component i and component j, whereby $k_{ij} = 0$ for $i = j$. The different parameters related to Eq. (4) can be conveniently expressed in terms of compressibility factor ($Z = PV/RT$) as follows:

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \qquad \text{(S-11)}$$

where $B = pb/RT$ and $A = ap/(RT)^2$. Thus, from knowledge of the compressibility factors (Z) of the pure components and their blends, the corresponding excess molar volumes ($V_{m, PR-EOS}^E$) of the studied binary blends can be calculated. The values of the interaction coefficient (k_{ij}) were found to be 0.1358, 0.0882 and 0.0524, respectively, for the blends CH + MA, CH + EA and CH + MS. A comparison between the experimental excess molar volumes (V_m^E) and the calculated excess molar volumes ($V_{m, PFP}^E$ and $V_{m, PR-EOS}^E$) as a function of the mole fraction of CH (x_1) for the studied blends at 298.15 K is depicted in Fig. S-1. The overall performance of these models (PFP and PR-EOS) was judged by the absolute maximum percentage average deviations (PD_{max}).[25] For the blends with the alkyl esters, PD_{max} values for both the models were 10 % but were above 100 % for the blend with MS. Thus, it is evident that the calculated excess molar volumes ($V_{m, PFP}^E$) agree reasonably with the experimental excess molar volumes (V_m^E) for the binary blends with alkyl esters but not with MS. This is most probably due to strong dipole-induced dipole interactions and increased intermolecular compactness in the blend CH + MS.
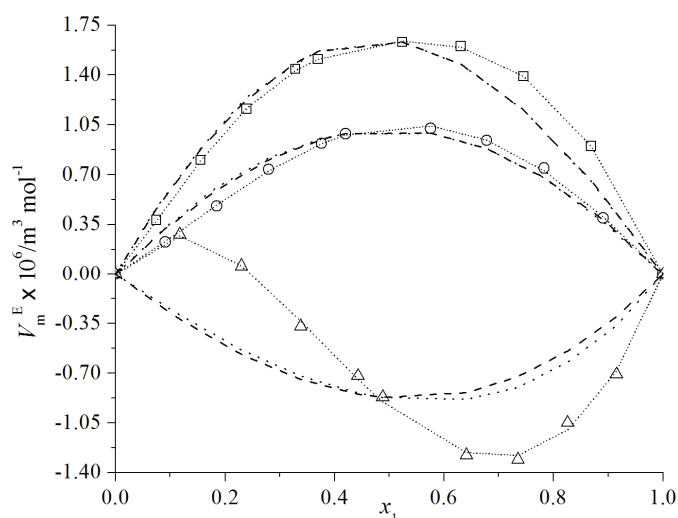

Fig. S-1. A comparison between the excess molar volumes (V_m^E) against mole fraction of CH (x_1) for the binary blends of CH (1) + some esters (2) at $T = 298.15$ K. The graphical points represent experimental V_m^E values: □, MA; ○, EA; Δ, MS. Dashed lines: PR-EOS; dotted lines: PFP; short-dotted lines: Redlich–Kister polynomial.

Viscosity correlation models

Mehrotra *et al.*[26] reviewed the practical implications of several empirical or semi-empirical viscosity models for the viscosities of liquid blends. These models can simulate the viscosity of liquids or liquid blends. However, such models that apply the corresponding state principle based on the van der Waals hypothesis[27] are limited. Therefore, the experimental viscosities of the studied binaries were correlated with the PR-EOS[20,28] and the Bloomfield–Dewan model (BF).[20,23]

PR-EOS. In terms of the ΔG^{*E} and η can also be expressed by the relation:[29]

$$\eta = \frac{(\eta V)^{\text{id}}}{V_{\text{m}}} \exp\left(\frac{\Delta G^{*E}}{RT} \right) \tag{S-12}$$

where V_{m} and $(\eta V)^{\text{id}}$ are the molar volume and kinematic viscosity of an ideal mixture, respectively. $(\eta V)^{\text{id}}$ is defined as follows:

$$(\eta V)^{\text{id}} = \exp\left[\sum_{i=1}^{2} x_i \ln(\eta_i V_i) \right] \tag{S-13}$$

ΔG^{*E} for a binary blend can also be expressed as:

$$\frac{\Delta G^{*E}}{RT} = \frac{G^{*E}}{RT} + \frac{1}{2} \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j g_{ij} = \frac{G^{*E}}{RT} + x_1 x_2 g_{12} \tag{S-14}$$

where g_{12} is binary interaction parameter ($g_{ii} = 0$ and $g_{ij} = g_{ji}$). The parameter g_{12} is evaluated from a comparison of the experimental viscosities with those obtained from Eq. (S-12). The value of G^{*E}/RT can be obtained from the relation:

$$\frac{G^{*E}}{RT} = \sum_{i=1}^{2} x_i (\ln \phi_i - \ln \phi_i^0) \tag{S-15}$$

where φ_i^0 and φ_i stand for the fugacity coefficients of the ith component in the pure state and in the mixture, respectively. As per the PR-EOS, the fugacity coefficient for a pure component is given by:

$$\ln \phi = (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln\left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \tag{S-16}$$

and fugacity coefficient for the ith component in a binary blend is given by:

$$\ln \phi_i = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - $$

$$-\frac{A}{2\sqrt{2}B}\left(\frac{2}{a} \sum_{j=1}^{2} x_j (a_i a_j)^{\frac{1}{2}} (1 - k_{ij}) - \frac{b_i}{b} \right) \ln\left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \tag{S-17}$$

where the values of k_{ij} used were calculated earlier from Eq. (S-9). Hence, from Eqs. (S-12)–(S-17), one obtains:

$$\eta = \frac{(\eta V)^{\text{id}}}{V_{\text{m}}} \exp\left[\sum_{i=1}^{2} x_i (\ln \phi_i - \ln \phi_i^0) + \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j g_{ij}\right] \tag{S-18}$$

The binary interaction parameters (g_{12}) were obtained from non-linear regression with minimum standard deviations (σ) for the blends using a C-program.[20] The binary interaction parameters (g_{12}) were found to be –0.409, –0.338 and –0.829 for the blends CH + MA, CH + EA and CH + MS, respectively. The absolute maximum percentage average deviations (PD_{max})[25] when comparing the experimental viscosities and those calculated from this model for the blends CH + MA, CH + EA and CH + MS were found to be 0.32, 0.41 and 0.19, respectively. Therefore, this model can reasonably well describe the viscosity behavior of the studied binary blends.

BD model. Combining two semi-empirical theories of liquid viscosities, *viz.*, the absolute reaction rate[30] and the free volume theory,[31] Bloomfield and Dewan[28] developed the following expression for viscosity deviation ($\Delta \ln \eta$) of blends:

$$\Delta \ln \eta = f(\tilde{v}) - \frac{\Delta G^{\text{R}}}{RT} \tag{S-19}$$

where

$$\Delta \ln \eta = \ln \eta - \sum_{i=1}^{2}(x_i \eta_i) \tag{S-20}$$

and

$$f(\tilde{v}) = \frac{1}{\tilde{v}-1} - \sum_{i=1}^{2}\frac{x_i}{\tilde{v}_i - 1} \tag{S-21}$$

The residual free energy of mixing (ΔG^{R}) is given by the relation:

$$\Delta G^{\text{R}} = \Delta G^{\text{E}} + RT\sum_{i=1}^{2} x_i \ln(x_i / \varphi_i) \tag{S-22}$$

where ϕ_i is the segment fraction of the ith component in a binary blend.[15–18] Based on the Flory statistical thermodynamic theory for liquid mixtures,[15–18] the excess energy ΔG^{E} can be obtained from the relation:

$$\Delta G^{\text{E}} = \sum_{i=1}^{2} x_i P_i^* V_i^*[(1/\tilde{v}_i - 1/\tilde{v}) + 3\tilde{T}_i \ln\{(\tilde{v}_i^{1/3} - 1)/(\tilde{v}^{1/3} - 1)\}] +$$
$$+(x_1 \theta_2 V_1^* \chi_{12})/\tilde{v} \tag{S-23}$$

where the $\chi_{1,2}$ values used were calculated a priori from Eq. (S-1). The absolute maximum percentage average deviations (PD_{max})[25] when comparing the experimental viscosities and those calculated from BD model for the blends CH + MA, CH + EA and CH + MS were found to be 50, 34 and 34 %, respectively. A comparison between the experimental viscosities and the calculated viscosities from these two viscosity models are depicted in Fig. S-2. It is evident that the BD model badly predicted the viscosities for all the studied blends as compared to the PR-EOS model.
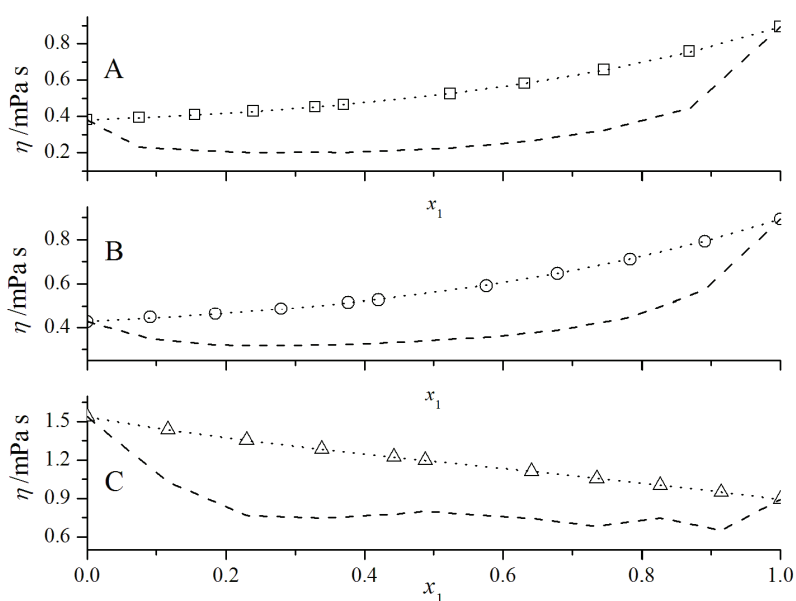
Fig. S-2. A comparison between the viscosities (η) obtained from various models against mole fraction of CH (x_1) for the binary blends of CH (1) with A, MA (2); B, EA (2) and C, MS (2) at T = 298.15 K. The graphical points represent experimental η values: □, MA; ○, EA; △, MS. Dashed lines - BF; dotted lines - PR-EOS.

Prediction of ultrasonic speed of sound

Ultrasonic speeds of sound for the three blends were theoretically predicted with empirical theories, such as the Flory theory (FL), the collision factor theory (CFT), the Nomoto relation (NOM), the Impedance dependence relation (IDR), the Ideal mixture relation (IMR) and the Junjie relation (JUN). Details of these theoretical models are given in some previous articles[32,33] and references therein. The goodness of fitting of the experimental speeds of sound to these models was judged by the absolute maximum percentage average deviations (PD_{max}),[25] given in Table S-IX and Fig. S-3, from which it is evident that that the relative predictive capability of these models follows the orders: FL > IDR ≈ IMR > CFT

> JN > NOM for CH + M); NOM > JN > IMR > FL > IDR > CFT (for CH + EA) and JN > FL > IMR > NOM > CFT > IDR (for CH + MS). It is also evident that the FL theory, amongst all the theories tested, could reasonably well predict the speeds of sound of the studied blends, except for the blend containing EA.

TABLE S-IX. Absolute maximum percentage average deviations (PD_{max}) for ultrasonic speeds of sound from different empirical theories

Blend	FL	IDR	IMR	CFT	JN	NOM
CH (1) + MA (2)	0.38	049	0.54	0.76	0.88	1.05
CH (1) + EA (2)	1.98	0.35	0.28	0.80	0.13	0.02
CH (1) + MS (2)	1.49	3.74	1.77	3.69	0.48	3.36
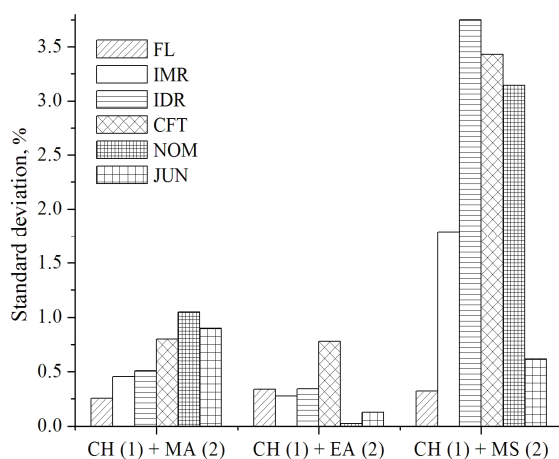
Fig. S-3. Standard deviations for theoretical prediction of ultrasonic speeds by different empirical relations at $T = 298.15$ K for the studied binary blends. Models: FL, Flory theory; IMR, ideal mixing relation; IDR, impedance dependence relation; CFT, collision factor theory; NOM, Nomoto relation; JUN, Junjie relation.
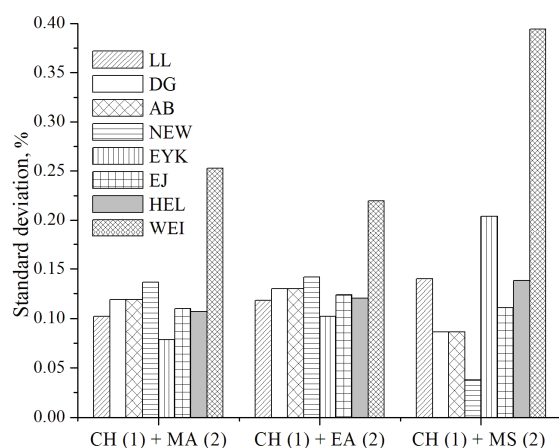

Fig. S-4. Standard deviations for theoretical prediction of refractive indices by various models at $T = 298.15$ K for the studied binary blends. Models: LL, Lorentz–Lorenz; DG, Gladstone––Dale; AB, Arago–Biot; NEW, Newton; EYK, Eykman; EJ, Eyring–John; HEL, Heller; WEI, Weiner.

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