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Acoustic, volumetric, compressibility and refractivity properties and Flory's reduction parameters of some homologous series of alkyl alkanoates from 298.15 to 333.15 K

S.L. Oswal*, P. Oswal, P.S. Modi, J.P. Dave, R.L. Gardas

Department of Chemistry, South Gujarat University, Surat 395007, India

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Abstract

The speeds of sound u in, densities ρ and refractive indices n_D of some homologous series, such as *n*-alkyl ethanoates, *n*-alkyl propionates, methyl alkanoates, ethyl alkanoates, dialkyl malonates, and alkyl haloalkanoates, were measured in the temperature range from 298.15 to 333.15 K. Molar volume V, isentropic and isothermal compressibilities κ_S and κ_T, molar refraction R_m, Eykman's constant C_m, molecular radius r, Rao's molar function R, thermal expansion coefficient α, thermal pressure coefficient γ, and Flory's characteristic parameters $\tilde{v}$, P^*, V^*, and T^* have been calculated from the measured experimental data. Applicability of Rao theory and Flory–Patterson–Pandey (FPP) theory have been examined and discussed for these alkanoates.

Keywords: Alkyl alkanoate; Densities; Compressibilities; Molar refraction; Speed of sound

1. Introduction

In this laboratory, we are engaged in a systematic investigation of molecular interactions of binary mixtures containing alkyl alkanoates in variety of solvents employing thermodynamic, acoustic and transport properties [1–6]. An appropriate analysis of results can be achieved by applying modern Prigogine–Flory–Patterson (PFP) statistical theory of non-electrolyte liquid mixtures [7–9]. The PFP theory enables to estimate the free volume, internal pressure, interaction energy, molecular orientation, steric hindrance contributions to the changes in thermodynamic, and transport properties [9–15]. The estimation of these different contributions requires the knowledge of isobaric thermal expansion coefficient α, thermal pressure coefficient γ, internal pressure ($\pi = \gamma T$) [16], and specific volume v. Accuracy of these properties largely depends upon the accurate and precise measurements of densities, compressibilities and speeds of sound, over a wide range of temperature. With this view in mind, in this paper we report the measurements on densities ρ, speeds of sound u, isentropic compressibilities κ_S, and refractive indices n_D of homologous series of *n*-alkyl ethanoates, *n*-alkyl propionates, methyl alkanoates, ethyl alkanoates, dialkyl malonates, and alkyl haloalkanoates in the temperature range from 298.15 to 333.15 K. The results have been used to compute equation of state parameters and have been analysed in terms of the theories of Lorentz [17], Eykman [18], Rao [19], and Flory–Patterson–Pandey (FPP) [8,9,20,21].

2. Experimental

Methyl ethanoate (SRL extra pure, Bombay), ethyl ethanoate (BDH, AR), propyl ethanoate (Fluka AG), butyl ethanoate (Merck, Darmstade), pentyl ethanoate (BDH, Poole England), methyl propionate (Fluka AG), ethyl propionate (Fluka AG), ethyl butanoate (Fluka AG), ethyl isovalerate (Fluka AG) were kept over anhydrous K_2CO_3 for more than 72 h [22] and were fractionally distilled twice. The middle fraction of the distillate was used.

Dimethyl malonate (Riedel De Haen AG) and diethyl malonate (Riedel De Haen AG) were treated with sodium sulphate and then fractionally distilled. Ethyl chloroethanoate

* Corresponding author. Tel.: +91-261-222-7141; fax: +91-261-2227312.
E-mail address: oswalsl@satyam.net.in (S.L. Oswal).

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(Riedel De Haen AG), ethyl bromoethanoate (Merck Schuchardt), ethyl-2-bromopropionate (Fluka AG), ethyl-3-bromopropionate (Fluka AG), ethyl-2-bromobutanoate (Fluka AG), ethyl-4-bromobutanoate (Fluka AG), diethyl bromomalonate (Merck) were used as received after drying over molecular sieve 4 Å.

Decyl ethanoate and dodecyl ethanoate were prepared by dissolving decanol (Merck, Schuchardt, 97%), and dodecanol (Koch-Light), respectively, in excess acetic anhydride (AnalaR) in the presence of dry pyridine [23]. Each mixture was stirred for over 24 h. Excess pyridine and acetic anhydride were first removed by simple distillation. Alkanoates were distilled under reduced pressure and dried over anhydrous $MgSO_4$ before use. The middle fraction of the distillate was used. The purity of the liquid samples was checked by gas–liquid chromatography and it was better than 99.8 mol% with the exception of ethyl bromoethanoate (>99 mol%), ethyl-2-bromopropionate (>98 mol%), ethyl-3-bromopropionate (>98 mol%), ethyl-2-bromobutanoate (>98 mol%), ethyl-4-bromobutanoate (>98 mol%), diethyl bromomalonate (>98 mol%). Furthermore, the experimental densities, refractive indices, and speeds of sound compare well with the accepted literature values as shown in Table 1. Discrepancies in certain speed of sound values will be discussed in Section 4.2.

To ascertain the purity of the above liquid samples further some characteristic physical properties the densities ρ, the refractive indices n_D and speed of sound u were measured and were found to be in good agreement with literature data (Table 1).

Table 1
Comparison of densities ρ, refractive indices n_D and speeds of sound u ($m\,s^{-1}$) of pure liquids

Liquids	T (K)	ρ (g cm^{-3})		n_D		u ($m\,s^{-1}$)	
		Exp.	Literature	Exp.	Literature	Exp.	Literature
Methyl ethanoate	298.15	0.92780	0.9279 [22]	1.3597	1.3589 [22]	1155	1150.6 [31], 1159 [32]
	303.15	0.92083	0.9208 [24]	1.3567	1.3614 [22]	1132	1136 [33], 1144 [34]
Ethyl ethanoate	298.15	0.89471	0.8946 [25], 0.89451 [26]	1.3700	1.36979 [22]	1141	1140 [35], 1144 [36]
	303.15	0.88855	0.88851 [24]	1.3673	1.3672 [22]	1118	1119 [33], 1123 [37], 1128 [34]
Propyl ethanoate	298.15	0.88254	0.88303 [22]	1.3821	1.3828 [22]	1164	1172 [32]
	303.15	0.87703	0.87716 [24]	1.3794	1.3801 [22]	1144	1146 [33], 1150 [34]
Butyl ethanoate	298.15	0.87626	0.87636 [22]	1.3922	1.3918 [22]	1192	1190 [32], 1195 [38]
	303.15	0.87084	0.87129 [22]	1.3897	1.3827 [22]	1173	1170 [33], 1185 [34]
Pentyl ethanoate	298.15	0.87146	0.8719 [22]				
	303.15	0.86642	0.8672 [22]	1.4030	1.3974 [22]	1197	1197 [33]
Decyl ethanoate	298.15	0.86345	0.86347 [24]				
Dodecyl ethanoate	298.15	0.85893	0.86320 [24]				
Methyl propionate	298.15	0.91280	0.90932 [27]	1.3745	1.3742 [30]		
	308.15					1124	1130 [39]
Ethyl propionate	298.15	0.88493	0.8840 [22]	1.3823	1.3814 [22]	1156	1156.9 [40]
			0.88398 [28]		1.3817 [28]		
	303.15	0.87914	0.87903 [22]	1.3795	1.3790 [22]	1136	1141 [34]
	308.15					1114	1120 [39]
Ethyl butanoate	298.15	0.87432	0.87394 [22]	1.3903	1.3904 [22]		
	303.15	0.86883	0.86871 [24]	1.3876	1.3881 [22]	1151	1156 [34]
	308.15					1130	1138 [39]
Ethyl isovalerate	298.15	0.86135		1.3949	1.3944 [22]		
	303.15	0.85624	0.85582 [22]	1.3925	1.3926 [22]		
Ethyl chloroethanoate	293.15	1.15248	1.1585 [29]	1.4216	1.4215 [29]	1247	1249 [41]
Ethyl bromoethanoate	293.15	1.49886	1.5059 [29]	1.4506	1.4489 [29]		
Ethyl-2-bromopropionate	293.15	1.38945	1.3940 [29]	1.4459	1.4490 [29]		
Ethyl-3-bromopropionate	293.15	1.40744	1.4120 [29]	1.4524	1.4520 [29]		
Ethyl-2-bromobutanoate	293.15	1.32761	1.3280 [29]	1.4480	1.4470 [29]		
Ethyl-4-bromobutanoate	293.15	1.36267	1.3630 [29]	1.4565	1.4560 [29]		
Dimethyl malonate	293.15	1.16084	1.1582 [29]				
Diethyl malonate	303.15	1.04323	1.0446 [22]	1.4096	1.4097 [22]		
Diethyl bromomalonate	293.15			1.4521	1.4521 [22]		
	298.15	1.40606	1.4022 [29]				

The speeds of sound in the liquid alkanoates were measured with a single crystal multi-frequency ultrasonic interferometer (supplied by Mittal Enterprise, New Delhi). In the present work, a steel cell fitted with a quartz crystal of 2 MHz frequency was employed. The refractive index was measured using Research refractometer RL3 made in Poland. A water circulating thermostat with digital thermometer arrangement and with an accuracy of ±0.05 K, supplied by Gemini Scientific Instruments, Madras, was used for controlling the temperature for the speed of sound and refractive index measurements. The densities of liquid alkanoates were measured with an Anton Paar vibrating tube digital densimeter (model DMA 60/602) with an ultra-thermostat bath (Heto-Birkeroad) controlled to ±0.01 K. The details of the apparatus and procedure have been described in previous publications [1,2,42,43]. The values of speeds of sound, densities and refractive indices are accurate to $\pm 1\,\mathrm{m\,s^{-1}}$, $2 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$ and 0.0002, respectively. The isentropic compressibilities ($\kappa_S = 1/(u^2\rho)$) and molar volumes ($V = M/\rho$) are believed to be reliable within $1.0\,\mathrm{T\,Pa^{-1}}$ and $0.005\,\mathrm{cm^3\,mol^{-1}}$.

3. Results

The experimental data on density ρ, refractive index n_D, speed of sound u, and isentropic compressibility κ_S for each pure liquid alkanoates: methyl ethanoate, ethyl ethanoate, propyl ethanoate, butyl ethanoate, pentyl ethanoate, decyl ethanoate, dodecyl ethanoate, methyl propionate, ethyl propionate, ethyl butanoate, ethyl isovalerate, ethyl chloroethanoate, ethyl bromoethanoate, ethyl-2-bromopropionate, ethyl-3-bromopropionate, ethyl-2-bromobutanonate, ethyl-4-bromobutanoate, dimethyl malonate, diethyl malonate and diethyl bromomalonate, in the temperature range of 298.15–333.15 K at intervals of 5 K were fitted to an equation of type (1)

$$Y = \sum_{i=1}^{m=3} A_i (T - 273.15)^{i-1} \tag{1}$$

The coefficients A_i and the standard deviations σ were obtained by the method of least squares. The standard deviation σ is defined by Eq. (2)

$$\sigma = \left[\frac{\sum (Y_{\mathrm{exp}} - Y_{\mathrm{cal}})^2}{n - m} \right]^{1/2} \tag{2}$$

where n is number of measurements and m number of coefficients in Eq. (1).

Thermal expansion coefficient α defined as $\alpha = V^{-1}(\mathrm{d}V/\mathrm{d}T)_P = -\rho^{-1}(\mathrm{d}\rho/\mathrm{d}T)_P$, has been calculated at each temperature from the experimental ρ, at different temperatures using coefficients from Eq. (1). The isothermal compressibility κ_T, heat capacities at constant volume C_V, the Rao's molar sound function R and thermal pressure coefficient γ were computed using the following relations

$$\kappa_T = \kappa_S + \frac{\alpha^2 V T}{C_P} \tag{3}$$

$$C_V = \left(\frac{k_S}{k_T} \right) C_P \tag{4}$$

$$R = u^{1/3} V \tag{5}$$

$$\gamma = \frac{\alpha}{\kappa_T} \tag{6}$$

For the purpose of calculation of κ_T and C_V at several temperatures, one also needs values of heat capacities at constant pressure C_P at different temperatures. We have used experimental C_P values wherever available otherwise computed from the heat capacity group parameters [44–46]. The estimated C_P values may be in error by 1%.

Table 2
Densities ρ ($\mathrm{g\,cm^{-3}}$), molar volumes V ($\mathrm{cm^3\,mol^{-1}}$), speeds of sound u ($\mathrm{m\,s^{-1}}$), isentropic and isothermal compressibilities, κ_S and κ_T ($\mathrm{T\,Pa^{-1}}$), isochoric and isobaric heat capacities, C_P and C_V ($\mathrm{J(mol\,K)^{-1}}$), and Rao's molar sound functions R ($(\mathrm{m\,s^{-1}})^{1/3}\,\mathrm{cm^3\,mol^{-1}}$) of pure liquids at different temperatures

T (K)	ρ	V	u	κ_S	κ_T	C_P	C_V	R
(1) Methyl ethanoate								
298.15	0.92780	79.844	1155	807	1183	143.9	98.3	837
303.15	0.92083	80.448	1132	847	1234	144.9	99.5	838
308.15	0.91383	81.064	1109	889	1288	146.1	100.9	839
313.15	0.90684	81.689	1086	934	1346	147.2	102.2	839
318.15	0.89990	82.319	1062	985	1409	148.4	103.8	839
323.15	0.89292	82.963	1039	1037	1474	149.6	105.2	840
328.15	0.88593	83.617	1015	1095	1545	150.9	107.0	840
(2) Ethyl ethanoate								
298.15	0.89471	98.474	1141	858	1191	167.7	120.8	1029
303.15	0.88855	99.157	1118	900	1245	168.9	122.1	1029
308.15	0.88240	99.848	1096	943	1300	170.2	123.4	1029
313.15	0.87611	100.565	1073	991	1361	171.5	124.9	1029
318.15	0.86992	101.281	1050	1042	1425	172.8	126.4	1029
323.15	0.86366	102.015	1026	1099	1496	174.2	128.1	1028
328.15	0.85744	102.755	1002	1161	1571	175.6	129.8	1028

Table 2 (*Continued*)

T (K)	ρ	V	u	κ_S	κ_T	C_P	C_V	R
(3) Propyl ethanoate								
298.15	0.88254	115.726	1164	836	1110	196.1	147.6	1217
303.15	0.87703	116.453	1144	871	1155	197.4	148.9	1217
308.15	0.87148	117.195	1123	909	1203	198.9	150.4	1218
313.15	0.86597	117.941	1102	950	1253	200.3	151.9	1218
318.15	0.86036	118.710	1080	996	1309	201.8	153.6	1217
323.15	0.85486	119.473	1059	1043	1366	203.4	155.3	1217
328.15	0.84923	120.265	1036	1097	1430	205.0	157.2	1216
(4) Butyl ethanoate								
298.15	0.87626	132.563	1192	803	1065	228.4	172.1	1405
303.15	0.87084	133.388	1173	834	1106	229.9	173.4	1406
308.15	0.86547	134.216	1153	869	1150	231.5	174.9	1407
313.15	0.86000	135.070	1132	907	1198	233.1	176.5	1407
318.15	0.85452	135.936	1111	948	1249	234.7	178.1	1407
323.15	0.84907	136.809	1090	991	1302	236.5	180.0	1407
328.15	0.84360	137.696	1068	1039	1360	238.2	181.9	1407
(5) Pentyl ethanoate								
298.15	0.87146	149.388	1221	769	995	260.1	201.1	1596
303.15	0.86642	150.257	1197	805	1038	261.7	203.1	1595
308.15	0.86144	151.126	1174	842	1081	263.5	205.2	1594
313.15	0.85645	152.007	1152	879	1126	265.2	207.2	1593
318.15	0.85137	152.914	1130	919	1173	267.1	209.4	1592
323.15	0.84637	153.817	1109	960	1222	268.9	211.4	1592
328.15	0.84134	154.736	1089	1002	1270	270.9	213.7	1591
(6) Decyl ethanoate								
298.15	0.86345	231.990	1290	695	842	412.6	341.0	2525
303.15	0.85941	233.081	1271	720	869	415.0	343.7	2524
308.15	0.85541	234.171	1251	746	899	417.5	346.6	2523
313.15	0.85137	235.282	1234	771	927	420.0	349.3	2523
318.15	0.84739	236.387	1215	799	958	422.7	352.4	2522
323.15	0.84332	237.528	1197	827	990	425.3	355.4	2522
328.15	0.83937	238.646	1178	858	1024	428.1	358.7	2520
(7) Dodecyl ethanoate								
298.15	0.85893	265.873	1330	658	790	483.6	402.9	2923
303.15	0.85564	266.895	1313	677	814	486.3	404.9	2922
308.15	0.85137	268.234	1296	699	840	489.1	407.1	2924
313.15	0.84739	269.493	1281	719	864	492.0	409.2	2926
318.15	0.84344	270.755	1264	742	891	494.9	411.7	2927
323.15	0.83978	271.936	1247	765	920	497.9	414.3	2926
328.15	0.83574	273.250	1231	789	949	501.0	416.8	2928
(8) Methyl propionate								
298.15	0.91280	96.523	1167	804	1101	172.7	126.1	1016
303.15	0.90671	97.171	1145	841	1147	173.9	127.5	1016
308.15	0.90061	97.829	1124	878	1194	175.2	128.9	1017
313.15	0.89451	98.496	1103	918	1243	176.5	130.4	1017
318.15	0.88842	99.172	1081	963	1297	177.8	132.0	1017
323.15	0.88232	99.857	1060	1008	1352	179.2	133.6	1018
328.15	0.87622	100.552	1039	1057	1411	180.6	135.3	1018
(9) Ethyl propionate								
298.15	0.88493	115.414	1156	845	1148	195.7	144.1	1211
303.15	0.87914	116.174	1136	881	1194	197.0	145.3	1212
308.15	0.87333	116.947	1114	922	1246	198.5	146.9	1212
313.15	0.86748	117.735	1093	964	1300	199.9	148.3	1212
318.15	0.86160	118.539	1072	1009	1356	201.5	150.0	1213
323.15	0.85569	119.357	1051	1057	1416	203.1	151.7	1213
328.15	0.84985	120.178	1030	1109	1479	204.7	153.4	1213
333.15	0.84396	121.016	1009	1163	1546	206.4	155.3	1213
(10) Ethyl butanoate								
298.15	0.87432	132.858	1172	832	1102	228.0	172.2	1400
303.15	0.86883	133.697	1151	868	1146	229.5	173.8	1401

Table 2 (*Continued*)

T (K)	ρ	V	u	κ_S	κ_T	C_P	C_V	R
308.15	0.86340	134.538	1130	907	1193	231.2	175.7	1401
313.15	0.85798	135.388	1109	947	1242	232.7	177.4	1401
318.15	0.85246	136.264	1088	990	1294	234.4	179.4	1401
323.15	0.84703	137.138	1068	1035	1347	236.1	181.3	1401
328.15	0.84154	138.033	1047	1084	1406	237.8	183.3	1401
(11) Ethyl isovalerate								
298.15	0.86135	151.142	1158	865	1095	271.2	214.3	1587
303.15	0.85624	152.044	1138	901	1138	272.7	216.0	1587
308.15	0.85114	152.955	1118	939	1183	274.3	217.9	1587
313.15	0.84618	153.851	1097	982	1231	276.2	220.2	1586
318.15	0.84111	154.779	1076	1026	1283	278.2	222.6	1586
323.15	0.83598	155.729	1055	1074	1337	280.6	225.4	1585
328.15	0.83095	156.671	1034	1125	1394	283.2	228.5	1584
(12) Ethyl chloroethanoate								
298.15	1.14583	106.955	1247	561	787	190.6	135.8	1151
303.15	1.13918	107.579	1227	583	815	191.7	137.1	1151
308.15	1.13253	108.211	1207	606	844	192.8	138.4	1152
313.15	1.12590	108.848	1188	629	873	194.0	139.8	1152
318.15	1.11924	109.496	1169	653	903	195.2	141.2	1153
323.15	1.11262	110.147	1150	679	935	196.4	142.6	1154
328.15	1.10604	110.803	1131	706	969	197.7	144.2	1154
(13) Ethyl bromoacetate								
298.15	1.49886	111.425	1124	528	725	198.2	144.3	1158
303.15	1.49090	112.020	1106	548	751	199.3	145.5	1158
308.15	1.48276	112.635	1089	568	777	200.4	146.7	1158
313.15	1.47443	113.271	1072	590	804	201.6	147.9	1159
318.15	1.46641	113.890	1055	612	832	202.8	149.3	1159
323.15	1.45823	114.529	1040	634	859	204.1	150.5	1160
328.15	1.45018	115.165	1023	658	890	205.4	152.0	1160
(14) Ethyl-2-bromopropionate								
298.15	1.38226	130.970	1080	620	802	231.3	178.8	1343
303.15	1.37507	131.655	1064	642	829	232.8	180.3	1344
308.15	1.36778	132.357	1048	665	857	234.3	181.9	1344
313.15	1.36069	133.046	1032	690	887	235.9	183.5	1344
318.15	1.35362	133.741	1017	714	916	237.5	185.1	1344
323.15	1.34627	134.472	1000	742	950	239.2	186.9	1344
328.15	1.33912	135.190	985	769	982	241.0	188.8	1345
333.15	1.33190	135.922	969	799	1018	242.3	190.2	1345
(15) Ethyl-3-bromopropionate								
298.15	1.40316	129.020	1154	535	706	221.2	167.6	1353
303.15	1.39622	129.661	1138	553	729	222.4	168.7	1353
308.15	1.38925	130.311	1120	573	754	223.7	170.2	1353
313.15	1.38226	130.970	1103	594	779	225.1	171.7	1353
318.15	1.37531	131.632	1085	617	807	226.4	173.2	1352
323.15	1.36834	132.303	1068	640	835	227.9	174.8	1352
328.15	1.36138	132.979	1051	664	864	229.3	176.4	1352
333.15	1.35440	133.664	1035	689	893	230.9	178.1	1352
(16) Ethyl-2-bromobutanoate								
298.15	1.32106	147.656	1101	624	791	259.5	204.8	1524
303.15	1.31455	148.387	1085	646	817	261.1	206.4	1524
308.15	1.30796	149.135	1068	670	845	262.8	208.3	1524
313.15	1.30141	149.885	1051	695	875	264.6	210.2	1523
318.15	1.29486	150.643	1035	720	905	266.4	212.2	1523
323.15	1.28832	151.408	1018	748	937	268.2	214.2	1523
328.15	1.28177	152.182	1002	777	970	270.1	216.3	1522
333.15	1.27522	152.963	985	808	1005	272.1	218.7	1521
(17) Ethyl-4-bromobutanoate								
298.15	1.35633	143.816	1179	530	680	249.4	194.4	1519
303.15	1.34990	144.501	1162	548	702	250.8	195.9	1519
308.15	1.34365	145.173	1148	564	722	252.2	197.1	1520

Table 2 (*Continued*)

T (K)	ρ	V	u	κ_S	κ_T	C_P	C_V	R
313.15	1.33730	145.863	1132	583	745	253.7	198.6	1520
318.15	1.33096	146.557	1117	602	768	255.3	200.2	1520
323.15	1.32462	147.259	1101	622	792	256.8	201.7	1520
328.15	1.31827	147.968	1085	644	818	258.5	203.5	1520
333.15	1.31192	148.684	1069	667	845	260.2	205.3	1520
(18) Dimethyl malonate								
298.15	1.15427	114.460	1388	449	583	233.7	180	1276
303.15	1.14870	115.015	1364	467	605	235.2	181.7	1275
308.15	1.14315	115.574	1341	486	627	236.9	183.5	1274
313.15	1.13761	116.136	1320	504	650	238.5	185.1	1273
318.15	1.13207	116.705	1302	521	670	240.3	186.8	1274
323.15	1.12657	117.275	1284	538	691	242.1	188.4	1274
328.15	1.12087	117.871	1269	554	711	243.9	190.0	1276
(19) Diethyl malonate								
298.15	1.04814	152.815	1291	572	707	296.5	239.9	1663
303.15	1.04323	153.534	1274	590	729	298.3	241.6	1664
308.15	1.03829	154.264	1256	610	753	300.2	243.3	1664
313.15	1.03337	154.999	1238	631	777	304.3	247.1	1664
318.15	1.02843	155.743	1220	653	803	306.4	249.1	1664
323.15	1.02342	156.506	1201	677	831	308.6	251.3	1663
328.15	1.01849	157.263	1182	702	861	310.9	253.6	1662
(20) Diethyl bromomalonate								
298.15	1.40606	171.466	1184	507	657	325.0	250.9	1813
303.15	1.39918	172.309	1166	525	679	327.0	253.0	1813
308.15	1.39235	173.154	1149	544	701	329.0	255.1	1813
313.15	1.38543	174.019	1133	562	723	331.1	257.2	1814
318.15	1.37859	174.882	1117	581	746	333.3	259.4	1814
323.15	1.37175	175.754	1102	600	770	335.6	261.6	1815
328.15	1.36484	176.644	1088	618	792	337.9	263.8	1816

Molar refraction R_m, Eykman's constant C_m, and molecular radius $r(R_m)$ have been evaluated from the experimental refractive index n_D and molar volume V through following relations

$$R_m = \frac{(n_D^2 - 1)V}{n_D^2 + 2} \tag{7}$$

$$C_m = \frac{n_D^2 - 1}{(n_D + 0.4)\rho} \tag{8}$$

$$r(R_m) = \left(\frac{3R_m}{4\pi N}\right)^{1/3} \tag{9}$$

Table 2 summarises the values of density ρ, molar volume V, speed of sound u, isentropic and isothermal compressibilities κ_S and κ_T, heat capacities at constant pressure and at constant volume C_P and C_V, and the Rao's molar sound function R for investigated 20 different alkanoates, in the temperature range of 298.15–333.15 K at intervals of 5 K. The values of refractive index n_D, molar refraction R_m, Eykman's constant C_m and molecular radius $r(R_m)$ for each of the liquids at different temperatures are recorded in Table 3. The coefficients A_i of Eq. (1) and the standard deviations σ obtained by the method of least squares using computer programming for ρ, n_D, u, and κ_S are listed in Tables 4–7.

Table 3
Refractive index n_D, molar refraction R_m ($cm^3\,mol^{-1}$), Eykman's constant C_m ($cm^3\,g^{-1}$), van der Waals volume V_{vdW} ($cm^3\,mol^{-1}$) and molecular radius r(Sch) and $r(R_m)$ (Å)

T (K)	n_D	R_m	C_m	V_{vdW}	r(Sch)	$r(R_m)$
(1) Methyl ethanoate						
298.15	1.3597	17.61	0.520	73.47	1.938	1.911
303.15	1.3567	17.61	0.520	73.91	1.942	1.911
308.15	1.3538	17.61	0.520	74.36	1.946	1.911
313.15	1.3510	17.62	0.520	74.81	1.950	1.912
318.15	1.3484	17.64	0.520	75.27	1.954	1.912
323.15	1.3459	17.66	0.521	75.73	1.958	1.913
328.15	1.3436	17.69	0.521	76.20	1.962	1.914
(2) Ethyl ethanoate						
298.15	1.3700	22.27	0.554	91.15	2.083	2.067
303.15	1.3673	22.28	0.554	91.64	2.086	2.067
308.15	1.3647	22.29	0.554	92.13	2.090	2.067
313.15	1.3621	22.31	0.554	92.65	2.094	2.068
318.15	1.3597	22.34	0.554	93.16	2.098	2.069
323.15	1.3573	22.36	0.555	93.67	2.102	2.070
328.15	1.3550	22.39	0.556	94.19	2.105	2.071
(3) Propyl ethanoate						
298.15	1.3821	26.94	0.579	107.81	2.202	2.202
303.15	1.3794	26.94	0.578	108.34	2.206	2.202
308.15	1.3767	26.94	0.578	108.88	2.210	2.202
313.15	1.3741	26.94	0.578	109.42	2.213	2.202
318.15	1.3716	26.95	0.578	109.96	2.217	2.202
323.15	1.3691	26.96	0.578	110.51	2.221	2.203
328.15	1.3668	26.99	0.579	111.07	2.224	2.203

Table 3 (*Continued*)

T (K)	n_D	R_m	C_m	V_{vdW}	r(Sch)	$r(R_m)$
(4) Butyl ethanoate						
298.15	1.3922	31.58	0.597	124.08	2.308	2.322
303.15	1.3897	31.60	0.598	124.70	2.312	2.322
308.15	1.3872	31.61	0.598	125.31	2.316	2.323
313.15	1.3848	31.64	0.598	125.93	2.319	2.323
318.15	1.3824	31.66	0.598	126.57	2.323	2.324
323.15	1.3801	31.70	0.599	127.20	2.327	2.325
328.15	1.3779	31.74	0.599	127.84	2.331	2.326
(5) Pentyl ethanoate						
298.15	1.4050	36.61	0.619	140.50	2.406	2.439
303.15	1.4030	36.67	0.620	141.13	2.409	2.440
308.15	1.4004	36.67	0.620	141.76	2.413	2.440
313.15	1.3980	36.69	0.620	142.40	2.416	2.441
318.15	1.3956	36.71	0.620	143.06	2.420	2.441
323.15	1.3931	36.72	0.620	143.72	2.424	2.442
328.15	1.3905	36.72	0.620	144.39	2.428	2.442
(6) Decyl ethanoate						
298.15	1.4286	59.76	0.659	221.20	2.799	2.872
303.15	1.4263	59.76	0.659	222.04	2.802	2.872
308.15	1.4241	59.77	0.659	222.87	2.806	2.872
313.15	1.4218	59.76	0.659	223.73	2.809	2.872
318.15	1.4194	59.75	0.658	224.56	2.813	2.872
323.15	1.4168	59.71	0.657	225.43	2.816	2.871
328.15	1.4144	59.69	0.657	226.27	2.820	2.871
(7) Dodecyl ethanoate						
298.15	1.4330	69.10	0.669	254.51	2.933	3.014
303.15	1.4304	69.00	0.668	255.28	2.936	3.013
308.15	1.4278	68.98	0.667	256.35	2.940	3.013
313.15	1.4253	68.95	0.667	257.35	2.943	3.012
318.15	1.4226	68.89	0.666	258.33	2.947	3.011
323.15	1.4200	68.82	0.665	259.23	2.951	3.010
328.15	1.4174	68.77	0.664	260.27	2.955	3.010
(8) Methyl propionate						
298.15	1.3745	22.07	0.549	89.49	2.070	2.060
303.15	1.3719	22.08	0.549	89.96	2.073	2.061
308.15	1.3693	22.09	0.549	90.44	2.077	2.061
313.15	1.3667	22.10	0.549	90.93	2.081	2.061
318.15	1.3364	20.59	0.509	91.41	2.085	2.013
323.15	1.3615	22.12	0.549	91.91	2.088	2.062
328.15	1.3589	22.13	0.549	92.41	2.092	2.062
(9) Ethyl propionate						
298.15	1.3857	27.09	0.582	107.42	2.200	2.206
303.15	1.3823	27.06	0.581	107.97	2.204	2.205
308.15	1.3791	27.03	0.580	108.53	2.207	2.205
313.15	1.3759	27.01	0.580	109.11	2.211	2.204
318.15	1.3728	26.99	0.579	109.69	2.215	2.204
323.15	1.3697	26.98	0.579	110.28	2.219	2.203
328.15	1.3667	26.97	0.578	110.87	2.223	2.203
333.15	1.3636	26.95	0.577	111.47	2.227	2.202
(10) Ethyl butanoate						
298.15	1.3903	31.52	0.596	124.26	2.309	2.320
303.15	1.3876	31.52	0.596	124.88	2.313	2.320
308.15	1.3850	31.53	0.596	125.49	2.317	2.321
313.15	1.3825	31.54	0.596	126.11	2.321	2.321
318.15	1.3801	31.57	0.596	126.75	2.325	2.322
323.15	1.3778	31.60	0.597	127.39	2.328	2.322
328.15	1.3756	31.64	0.597	128.04	2.332	2.323
(11) Ethyl isovalerate						
298.15	1.3949	36.23	0.612	141.85	2.413	2.431
303.15	1.3925	36.25	0.612	142.52	2.417	2.431

Table 3 (*Continued*)

T (K)	n_D	R_m	C_m	V_{vdW}	r(Sch)	$r(R_m)$
308.15	1.3900	36.26	0.612	143.19	2.421	2.431
313.15	1.3876	36.27	0.612	143.84	2.425	2.432
318.15	1.3852	36.29	0.612	144.51	2.428	2.432
323.15	1.3828	36.31	0.612	145.20	2.432	2.432
328.15	1.3803	36.32	0.612	145.87	2.436	2.433
(12) Ethyl chloroethanoate						
298.15	1.4193	27.03	0.487	100.34	2.150	2.204
303.15	1.4170	27.05	0.487	100.81	2.154	2.205
308.15	1.4148	27.09	0.487	101.28	2.157	2.206
313.15	1.4125	27.11	0.488	101.76	2.160	2.207
318.15	1.4103	27.15	0.488	102.24	2.164	2.208
323.15	1.4081	27.18	0.489	102.73	2.167	2.209
328.15	1.4059	27.21	0.489	103.22	2.171	2.209
(13) Ethyl bromoacetate						
298.15				104.86	2.182	
303.15	1.4460	29.87	0.396	105.29	2.185	2.279
308.15				105.75	2.188	
313.15				106.23	2.192	
318.15				106.69	2.195	
323.15	1.4367	29.99	0.397	107.17	2.198	2.282
328.15				107.64	2.201	
(14) Ethyl-2-bromopropionate						
298.15	1.4435	34.76	0.425	123.43	2.304	2.397
303.15	1.4411	34.77	0.425	123.94	2.307	2.398
308.15	1.4387	34.79	0.425	124.47	2.310	2.398
313.15	1.4364	34.81	0.426	124.98	2.314	2.399
318.15	1.4340	34.83	0.426	125.49	2.317	2.399
323.15	1.4316	34.85	0.426	126.03	2.320	2.399
328.15	1.4292	34.87	0.426	126.56	2.323	2.400
333.15	1.4268	34.88	0.426	127.09	2.327	2.400
(15) Ethyl-3-bromopropionate						
298.15	1.4524	34.83	0.427	121.92	2.295	2.399
303.15	1.4500	34.84	0.427	122.40	2.298	2.399
308.15	1.4475	34.85	0.427	122.88	2.301	2.399
313.15	1.4451	34.86	0.427	123.37	2.304	2.400
318.15	1.4430	34.90	0.427	123.85	2.307	2.400
323.15	1.4410	34.94	0.427	124.35	2.310	2.401
328.15	1.4388	34.96	0.427	124.84	2.313	2.402
333.15	1.4367	35.00	0.428	125.35	2.316	2.403
(16) Ethyl-2-bromobutanoate						
298.15	1.4457	39.35	0.447	139.60	2.401	2.499
303.15	1.4434	39.37	0.447	140.14	2.404	2.499
308.15	1.4411	39.39	0.447	140.70	2.407	2.499
313.15	1.4388	39.41	0.447	141.25	2.410	2.500
318.15	1.4366	39.44	0.447	141.81	2.413	2.500
323.15	1.4343	39.45	0.447	142.37	2.416	2.501
328.15	1.4320	39.47	0.447	142.94	2.420	2.501
333.15	1.4290	39.43	0.447	143.51	2.423	2.500
(17) Ethyl-4-bromobutanoate						
298.15	1.4542	38.96	0.443	136.35	2.382	2.490
303.15	1.4519	38.97	0.443	136.87	2.385	2.491
308.15	1.4496	38.98	0.443	137.38	2.388	2.491
313.15	1.4473	39.00	0.443	137.90	2.391	2.491
318.15	1.4450	39.01	0.443	138.42	2.394	2.491
323.15	1.4427	39.02	0.443	138.94	2.397	2.491
328.15	1.4403	39.02	0.443	139.47	2.400	2.492
333.15	1.4380	39.03	0.443	140.00	2.403	2.492
(18) Dimethyl malonate						
298.15	1.4106	28.40	0.474	108.34	2.206	2.241
303.15	1.4095	28.47	0.475	108.74	2.209	2.243

Table 3 (*Continued*)

T (K)	n_D	R_m	C_m	V_{vdW}	r(Sch)	$r(R_m)$
308.15	1.4081	28.52	0.475	109.15	2.211	2.244
313.15	1.4065	28.56	0.476	109.56	2.214	2.245
318.15	1.4047	28.59	0.476	109.99	2.217	2.246
323.15	1.4027	28.60	0.476	110.41	2.220	2.246
328.15	1.4004	28.60	0.476	110.87	2.223	2.246
(19) Diethyl malonate						
298.15	1.4118	38.01	0.523	144.96	2.431	2.470
303.15	1.4096	38.01	0.523	145.50	2.434	2.470
308.15	1.4074	38.01	0.523	146.05	2.437	2.470
313.15	1.4052	38.01	0.522	146.60	2.440	2.470
318.15	1.4031	38.01	0.522	147.15	2.443	2.470
323.15	1.4009	38.02	0.522	147.71	2.446	2.470
328.15	1.3988	38.02	0.522	148.27	2.449	2.470
(20) Diethyl bromomalonate						
298.15	1.4500	46.08	0.424	163.31	2.529	2.634
303.15	1.4477	46.10	0.424	163.96	2.533	2.634
308.15	1.4455	46.13	0.424	164.61	2.536	2.634
313.15	1.4433	46.16	0.424	165.28	2.540	2.635
318.15	1.4411	46.19	0.424	165.95	2.543	2.636
323.15	1.4390	46.23	0.424	166.62	2.546	2.636
328.15	1.4370	46.28	0.425	167.32	2.550	2.637

Table 4
Coefficients and standard deviations of Eq. (1) for density ρ (g cm^{-3}) of liquid alkanoates

Liquids	A_1	$A_2 \times 10^3$	$A_3 \times 10^6$	$\sigma \times 10^5$
Methyl ethanoate	0.96275	−1.39924	0.04762	1.6
Ethyl ethanoate	0.92538	−1.21860	−0.30952	3.2
Propyl ethanoate	0.90993	−1.08898	−0.26190	2.8
Butyl ethanoate	0.90305	−1.06355	−0.31905	2.4
Pentyl ethanoate	0.89639	−0.99502	−0.10952	2.5
Decyl ethanoate	0.88367	−0.81152	0.10476	2.5
Dodecyl ethanoate	0.87822	−0.75576	0.30476	23.8
Methyl propionate	0.94327	−1.21821	−0.01429	0.3
Ethyl propionate	0.91379	−1.14643	−0.29524	2.6
Ethyl butanoate	0.90147	−1.08438	−0.09524	2.7
Ethyl isovalerate	0.88666	−1.01364	0.01429	4.7
Ethyl chloroethanoate	1.17930	−1.34376	0.20952	1.6
Ethyl bromoethanoate	1.53958	−1.62550	−0.01429	9.8
Ethyl-2-bromopropionate	1.41804	−1.42989	−0.09286	7.2
Ethyl-3-bromopropionate	1.43797	−1.39131	−0.02381	1.2
Ethyl-2-bromobutanoate	1.35386	−1.31194	0.02143	1.6
Ethyl-4-bromobutanoate	1.38792	−1.26389	−0.04524	3.4
Dimethyl malonate	1.18176	−1.09576	−0.19048	4.8
Diethyl malonate	1.07254	−0.97012	−0.23333	2.0
Diethyl bromomalonate	1.44037	−1.37190	−0.01905	2.5

4. Discussion

4.1. Density and molar volume

Densities of alkyl ethanoate from methyl to dodecyl, of methyl alkanoate from ethanoate to butanoate, of ethyl alkanoate from ethanoate to butanoate, of dialkyl malonate from dimethyl to diethyl decrease with the increase of alkyl chain length. This behaviour is due to the strong dipole–dipole interaction in lower member of series. Increase of molar volume V by increase of one –CH_2– group in the homologous series is not constant. Say, for example, the increase of molar volume per –CH_2– group in alkyl ethanoate series at 303.15 K from methyl to ethyl, from ethyl to propyl, from propyl to butyl, from butyl to pentyl, from decyl to dodecyl is 18.58, 17.25, 16.85, 16.99 cm^3 mol^{-1}, respectively. The contribution of –CH_2– to molar volume for higher member of series becomes constant. Similar behaviour of molar volume is observed for alkanol homologous series from methanol to octanol [47] and for alkane series [48]. As the

Table 5
Coefficients and standard deviations of Eq. (1) for refractive index of liquid alkanoates

Liquids	A_1	$A_2 \times 10^3$	$A_3 \times 10^6$	$\sigma \times 10^5$
Methyl ethanoate	1.37703	−0.76262	2.80952	2.4
Ethyl ethanoate	1.38473	−0.62952	1.61905	2.4
Propyl ethanoate	1.39700	−0.63333	1.52381	3.1
Butyl ethanoate	1.40580	−0.57310	1.19048	2.4
Pentyl ethanoate	1.41561	−0.39119	−1.19048	11.6
Decyl ethanoate	1.43864	−0.37071	−1.28571	6.8
Dodecyl ethanoate	1.44573	−0.50476	−0.19048	4.1
Methyl propionate	1.38704	−0.49571	−0.28571	8.5
Ethyl propionate	1.40286	−0.71357	1.00000	5.1
Ethyl butanoate	1.40530	−0.65000	2.00000	0.0
Ethyl isovalerate	1.40704	−0.48571	0.00000	3.8
Ethyl chloroethanoate	1.43091	−0.47310	0.33333	2.4
Ethyl-2-bromopropione	1.45521	−0.46631	−0.11905	2.8
Ethyl-3-bromopropione	1.46641	−0.60833	1.95238	9.6
Ethyl-2-bromobutanoate	1.45554	−0.36869	−1.16667	18.5
Ethyl-4-bromobutanoate	1.46548	−0.44667	−0.19048	2.3
Dimethyl malonate	1.41296	0.01810	−4.47619	2.4
Diethyl malonate	1.42310	−0.46024	0.33333	2.4
Diethyl bromomalonate	1.46217	−0.51048	0.95238	3.1

Table 6
Coefficients and standard deviations of Eq. (1) for speed of sound u (m s^{-1}) of liquid alkanoates

Liquids	A_1	A_2	$A_3 \times 10^3$	σ
Methyl ethanoate	1267.0	−4.40	−0.33	0.24
Ethyl ethanoate	1246.4	−4.05	−0.71	0.33
Propyl ethanoate	1259.6	−3.62	−0.81	0.36
Butyl ethanoate	1282.7	−3.38	−0.95	0.31
Pentyl ethanoate	1350.6	−5.54	1.43	0.19
Decyl ethanoate	1407.6	−4.10	0.52	0.70
Dodecyl ethanoate	1412.7	−3.33	0.05	0.59
Methyl propionate	1275.4	−4.38	0.14	0.33
Ethyl propionate	1262.0	−4.23	0.02	0.38
Ethyl butanoate	1277.9	−4.27	0.12	0.28
Ethyl isovalerate	1255.1	−3.76	−0.48	0.24
Ethyl chloroethanoate	1349.9	−4.24	0.48	0.24
Ethyl bromoethanoate	1217.4	−3.92	0.71	0.50
Ethyl-2-bromopropione	1158.9	−3.16	0.00	0.31
Ethyl-3-bromopropione	1243.4	−3.60	0.19	0.62
Ethyl-2-bromobutanoate	1184.5	−3.34	0.02	0.34
Ethyl-4-bromobutyrat	1253.2	−2.94	−0.21	0.62
Dimethyl malonate	1537.1	−6.87	3.62	0.41
Diethyl malonate	1372.1	−3.06	−0.71	0.19
Diethyl bromomalonate	1283.6	−4.34	1.43	0.19

Table 7
Coefficients and standard deviations of Eq. (1) for isentropic compressibility κ_S ($T\,Pa^{-1}$) of liquid alkanoates

Liquids	A_1	A_2	$A_3 \times 10^3$	σ
Methyl ethanoate	667.7	3.78	7.24	0.77
Ethyl ethanoate	723.1	3.34	8.38	1.10
Propyl ethanoate	717.7	2.96	7.14	0.76
Butyl ethanoate	692.0	2.87	6.24	0.45
Pentyl ethanoate	612.0	5.62	2.67	0.45
Decyl ethanoate	590.6	3.65	2.19	0.75
Dodecyl ethanoate	572.1	3.00	1.71	0.60
Methyl propionate	666.1	4.22	5.24	0.82
Ethyl propionate	704.9	4.15	5.81	0.53
Ethyl butanoate	688.9	4.53	4.81	0.52
Ethyl isovalerate	731.6	3.83	6.05	0.45
Ethyl chloroethanoate	468.4	3.21	2.00	0.46
Ethyl bromoethanoate	439.4	3.19	1.43	0.38
Ethyl-2-bromopropionate	529.4	3.02	2.45	0.59
Ethyl-3-bromopropionate	456.5	2.58	2.17	0.47
Ethyl-2-bromobutanoate	535.2	2.85	2.81	0.49
Ethyl-4-bromobutanoate	465.0	2.10	2.10	0.66
Dimethyl malonate	346.4	4.35	−1.05	0.36
Diethyl malonate	500.9	2.16	2.71	0.19
Diethyl bromomalonate	415.3	3.64	0.10	0.36

chain length increases, the shielding effect of hydrocarbon chain preventing dipole interaction increases. This may be the reason for such volumetric behaviour of alkanoates.

4.2. Speed of sound and compressibility

For most liquids, the speeds of sound obtained in the present work are in good agreement with the recent data reported in the literature [31–33,35–38,40,41]. For methyl ethanoate our *u*-value at 298.15 K lies in between the values reported in the literature [31,32]. However, the speed of sound values of Pancholy and Mathur [34], for several alkyl ethanoates are consistently 5–10% higher than the present values as well as with those reported by other investigators [33,37]. Also, the values of speed of sound in methyl propionate, ethyl propionate and ethyl butanoate at 308.15 K reported by Sastry et al. [39] are higher by 5–6% than the present experimental values. Speed of sound and compressibility data for ethyl isovalerate, dimethyl malonate, diethyl malonate, diethyl bromomalonate, ethyl bromoethanoate, ethyl-2-bromopropionate, ethyl-3-bromopropionate, ethyl-2-bromobutanoate, ethyl-4-bromo butanoate have been determined for first time in present work.

The values of speed of sound linearly decrease with the increase in temperature. A careful analysis of the Table 2 shows that the values of speed of sound for various homologous series (methyl alkanoate, ethyl alkanoate, *n*-alkyl ethanoate, dialkyl malonate) increase with the increase of chain length. Only the first member, such as methyl ethanoate, methyl propionate and dimethyl malonate of their respective series is exception to it. Lagemann et al. [33,49,50] also observed similar trend for *n*-alkyl ethanoate and alkanones. The high values of speeds of sound in methyl ethanoate, methyl propionate and dimethyl malonate then the next member in the homologous series were explained considering relatively large dipole–dipole interaction in these pure liquids then the higher member of each respective homologous series. As the chain length in the alkanoate increases, due to its shielding effect, there is an internal dilution of dipole–dipole interaction.

In general it is observed that chloro- or bromo-derivatives of alkyl alkanoates have lower speed of sound *u* than the corresponding parent alkanoates. The position of bromine also affects the value of speed of sound in isomers of bromo alkanoates. Larger the distance between the substituted Br and –C–O– group large is the speed of sound, that is to say that speed of sound in ethyl-3-bromopropionate > ethyl-2-bromopropionate, and ethyl-4-bromobutanoate > ethyl-2-bromo butanoate. Forgoing analysis reveals that speed of sound in liquids largely depends on the structure, size and shape and molecular associations.

Isentropic and isothermal compressibilities κ_S and κ_T of investigated alkanoates increase with the temperature but not linearly. The compressibilities decrease with the increase in the alkyl chain length of all the homologues series investigated in this work, only exception is the first member methyl ethanoate, methyl propionate and dimethyl malonate of their respective homologous series. The substituted chloro- and bromo-alkanoates have lower values of isentropic compressibilities than the corresponding unsubstituted alkanoate. Similar trend was found by Lagemann et al. [49,50].

4.3. The molar refraction and Eykman's constant

Refractive index increases with the chain length in the homologous series from methyl ethanoate to pentyl ethanoate, from ethyl ethanoate to ethyl butanoate and from dimethyl malonate to diethyl malonate while it decreases with increase in temperature. The molar refraction R_m is constant at all temperature as expected (Table 3). The variation of R_m with chain length is shown in Fig. 1. Value of molar refraction for $–CH_2–$ group estimated from the data of methyl ethanoate to dodecyl ethanoate, from ethyl ethanoate to ethyl butanoate and from dimethyl malonate to diethyl malonate is constant having an average value of $4.650 \pm 0.110\,cm^3\,mol^{-1}$. From quoted value [51] of molar refraction of C and H also, it comes out to be $4.63\,cm^3\,mol^{-1}$. This value is also in close agreement with the value of $4.644 \pm 0.041\,cm^3\,mol^{-1}$ for alkanol series; reported by Sjoblom et al. [52]. Substitution of chlorine or bromine in alkanoates increases the molar refraction. Considering the molar refraction of $H = 1.100$, the values of molar refraction for Cl– and Br– are 5.854 and $8.48\,cm^3\,mol^{-1}$, respectively. The reported values are 5.907 and $8.815\,cm^3\,mol^{-1}$ for Cl– and Br–, respectively.

The values of $r(R_m)$ summarised in Table 3 which reveals that $r(R_m)$ increases with the increase in molecular weight of the alkanoate. $r(R_m)$ also increases with the substitution of chlorine or bromine in the alkanoate. The values

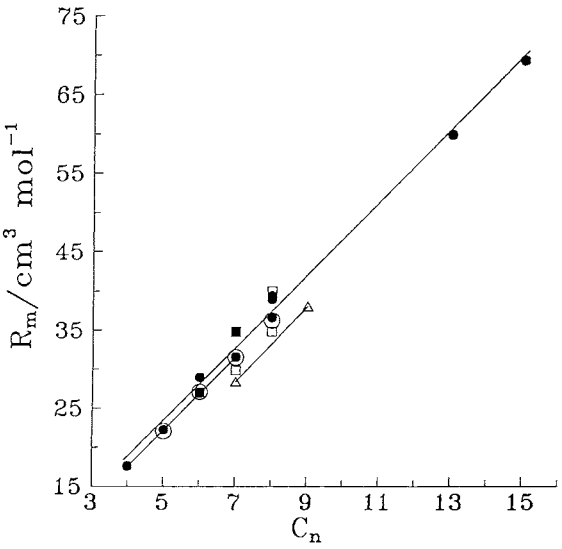

Fig. 1. Variation of molar refraction with chain length of alkanoates. Experimental points: (●) alkyl ethanoate, (○) ethyl alkanoate, (△) dialkyl malonate, (□) halo alkanoate.

of Eykman's constant C_m calculated by Eq. (8) are constant and independent of temperature for all the alkanoates in present investigation. They increase with the increase in chain length of alkanoate. Substitution of chloro or bromo in alkanoate decreases its value. The decrease is greater for the bromo than the chloro substitution.

4.4. van der Waals volume and molecular radius

Molecular radius can be obtained from molar refraction R_m as well as from van der Waals constant 'b' using the Schaaffs's collision factor theory [53]. Schaaffs applying hard sphere model deduced an expression for van der Waals (vdW) constant 'b' relating speed of sound and heat capacity ratio γ^*. The vdW equation of state for 1 mol of fluid is

$$\left(\frac{P - a\rho^2}{M^2}\right)\left(\frac{M}{\rho - b}\right) = RT \tag{10}$$

It is assumed that vdW constants 'a' and 'b' are function of density and temperature. The speed of sound at constant temperature u_T is given by

$$u_T^2 = \left(\frac{dP}{d\rho}\right)_T \tag{11}$$

From Eqs. (10) and (11) and eliminating 'a' and replacing isothermal speed of sound 'u_T' by '$u\gamma^*$', one obtains

$$b = \frac{M}{\rho}\left\{1 - \frac{\gamma^* RT}{Mu^2}\left[\left(1 + \frac{Mu^2}{3\gamma^* RT}\right) - 1\right]\right\} \tag{12}$$

The actual volume of molecules per mole B is obtained by the relations (12) and (13),

$$B = \frac{b}{4} \tag{13}$$

where γ^* is specific heat ratio. Radius as per Schaaffs theory r(Sch) can be computed as

$$r(\text{Sch}) = \left(\frac{3B}{4\pi N}\right)^{1/3} \tag{14}$$

where N is the Avogadro's number.

The molecular radius $r(R_m)$ and r(Sch) obtained from molar refraction R_m and speed of sound u data are compared in Table 3. The comparison shows that the agreement between these two sets of values is within 1% and can be said satisfactory. The van der Waals molecular radius r(Sch) computed from speed of sound data at several temperatures is slightly temperature dependent. The increase in radius per degree is found to be approximately 8×10^{-4} Å. This difference is very small and can be considered negligible considering approximations involved in the Schaaffs theory.

4.5. Rao's molar sound function

As expected from the Rao's theory, the values of R (Table 2) computed from Eq. (5) for each of the 20 investigated liquids are independent of temperature in the range from 298.15 to 328.15 or 333.15 K. Further, for a homologous series, a plot of R versus molecular weight is a straight line as can be seen from Fig. 2. The value of R obtained for $-CH_2-$ group by analysis of the data on alkanoates is 190 $(m\,s^{-1})^{1/3}\,cm^3\,mol^{-1}$, in good agreement with the literature value, which is in the range of 188–193 $(m\,s^{-1})^{1/3}\,cm^3\,mol^{-1}$ [49,50,53]. It is clear that this approach can provide an approximate guide as to the Rao's molar sound function, other factors occurring with the liquid will ultimately determine the observed values.

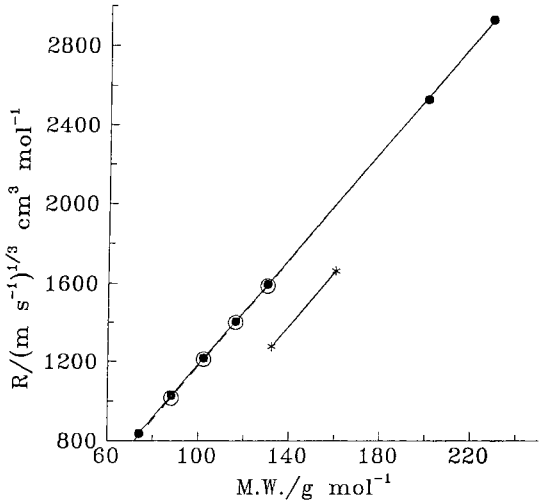

Fig. 2. Variation of Rao's molar sound function with molecular weight of alkanoates. Experimental points: (●) alkyl ethanoate, (○) ethyl alkanoate, (∗) dialkyl malonate.

5. Flory–Patterson–Pandey theory

5.1. Equation of state and Flory's characteristic parameters

Flory et al. [8], Flory [20] and Abe and Flory [54] developed the statistical theory of non-electrolyte solutions, which relates the excess properties of the mixture to the measurable macroscopic properties of the pure liquid components. The strong point in favour of the Flory theory was its ability to predict all excess functions in terms of a single interaction parameter in addition to its simplicity in development. To use the Flory theory the required equation of state-parameters of pure liquids are the specific volume v, the thermal expansion coefficient α and the thermal pressure coefficient γ. The reduced equation of state in Flory's notation is given by

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3}-1)} - \frac{1}{\tilde{v}\tilde{T}} \tag{15}$$

$$\tilde{v} = \frac{V}{V^*} \tag{16}$$

$$\tilde{T} = \frac{T}{T^*} \tag{17}$$

$$\tilde{P} = \frac{P}{P^*} \tag{18}$$

where $\tilde{v}$, $\tilde{T}$ and $\tilde{P}$ are reduced volume, reduced temperature and reduced pressure, respectively, and V^*, T^* and P^* are characteristics reduction parameters for each of the pure components. In Flory's treatment, the reduced equation of state take the form (19) in the limit of zero pressure

$$\tilde{T} = \frac{\tilde{v}^{1/3}-1}{\tilde{v}^{4/3}} \tag{19}$$

The values of reduced volume $\tilde{v}$ and characteristic reduction parameters V^*, T^* and P^* for pure component liquids in the limit of zero pressure can be obtained from following expressions

$$\tilde{v} = \left[\frac{1+4\alpha T/3}{1+\alpha T}\right]^3 \tag{20}$$

$$V^* = \frac{V}{\tilde{v}} \tag{21}$$

$$T^* = \frac{T}{\tilde{T}} = \frac{T\tilde{v}^{4/3}}{\tilde{v}^{1/3}-1} \tag{22}$$

and

$$P^* = \gamma T \tilde{v}^2 \tag{23}$$

The Flory's parameters $\tilde{v}$, V^*, T^*, and P^* for each of the investigated liquids at 298.15, 303.15, 313.15, 323.15 K were calculated, which are summarised in Table 7 along with the values of α and γ.

5.2. PFP's method for the theoretical evaluation of speed of sound

Theoretically, speed of sound can be estimated applying Flory theory, using Pandey's approach [21]. Pandey extended the Flory theory through the work of Patterson and Rastogi [55] to calculate the speed of sound in pure liquids. Extending the corresponding state theory to deal with the surface tension σ, following equation for characteristic surface tension σ^* can be written [55],

$$\sigma^* = (kP^{*2}T^*)^{1/3} \tag{24}$$

where k is Boltzman's constant.

The reduced surface tension equation can be derived for van der Waals liquids starting from the work of Prigogine and Saraga [56], which is,

$$\tilde{\sigma}(\tilde{v}) = \frac{M}{\tilde{v}^{5/3}} - \left(\frac{\tilde{v}^{1/3}-1}{\tilde{v}^2}\right)\ln\left(\frac{\tilde{v}^{1/3}-0.5}{\tilde{v}^{1/3}-1}\right) \tag{25}$$

where the most suitable value of M is 0.29 [55].

The surface tension can now be obtained as

$$\sigma = \sigma^*\tilde{\sigma}(\tilde{v}) \tag{26}$$

The speed of sound u_{th} can be estimated using Auerbach's relation [57]

$$u_{\text{th}} = \left(\frac{10^4\sigma}{6.3\rho}\right)^{2/3} \tag{27}$$

The speeds of sound in each liquid at 298.15, 303.15, 313.15, and 323.15 K were calculated from Eq. (27) and compared with experimental values in Tables 8 and 9. The percentage deviation from experimental values has also been included in Table 9. The values of deviations observed in experimental values of speed of sound and that predicted from the Flory–Patterson–Pandey theory (Table 9), are up to 13%. For pure alkanoates methyl ethanoate, ethyl ethanoate, propyl ethanoate, butyl ethanoate, pentyl ethanoate, decyl ethanoate, dodecyl ethanoate, methyl propionate, ethyl propionate, ethyl butanoate, ethyl isovalerate, dimethyl malonate and diethyl malonate, the predicted speeds of sounds are higher than the experimental values while for ethyl chloroethanoate, ethyl bromoethanoate, ethyl-2-bromopropionate, ethyl-3-bromopropionate, ethyl-2-bromobutanoate, ethyl-4-bromobutanoate, diethyl bromomalonate opposite is the case. Baring few alkanoates, dimethyl malonate, diethyl malonate, ethyl chloroethanoate, ethyl-2-bromopropionate, ethyl-3-bromopropionate, ethyl-2-bromobutanoate, ethyl-4-bromobutanoate, diethyl bromomalonate, it appears that the agreement between the experimental speed of sound and that predicted by the FPP theory is poor. However, as the Flory's statistical theory [8,20] is based on sound theoretical basis and is basically developed for non-polar liquids, it requires modification to apply this theory for the alkanoates, which have dipole moment around 2D.

Table 8
Thermal expansion coefficient α ($k\,K^{-1}$), thermal pressure coefficient γ ($J\,cm^{-3}\,K^{-1}$), reduced volume $\tilde{v}$ and characteristic reduction parameters V^* ($cm^3\,mol^{-1}$), T^* (K) and P^* ($J\,cm^{-3}$)

T (K)	α	γ	$\tilde{v}$	V^*	T^*	P^*
(1) Methyl ethanoate						
298.15	1.506	1.273	1.3430	59.45	4276	684
303.15	1.516	1.228	1.3491	59.63	4305	677
313.15	1.539	1.143	1.3617	59.99	4360	663
323.15	1.562	1.059	1.3743	60.37	4416	646
(2) Ethyl ethanoate						
298.15	1.379	1.157	1.3206	74.57	4447	601
303.15	1.392	1.118	1.3271	74.72	4469	596
313.15	1.419	1.043	1.3403	75.03	4512	586
323.15	1.447	0.967	1.3537	75.36	4556	572
(3) Propyl ethanoate						
298.15	1.249	1.124	1.2966	89.25	4660	563
303.15	1.260	1.091	1.3026	89.40	4681	561
313.15	1.282	1.022	1.3147	89.71	4723	553
323.15	1.305	0.955	1.3269	90.04	4765	543
(4) Butyl ethanoate						
298.15	1.232	1.156	1.2934	102.49	4692	576
303.15	1.243	1.124	1.2994	102.65	4711	575
313.15	1.266	1.057	1.3116	102.98	4751	569
323.15	1.290	0.991	1.3240	103.33	4790	561
(5) Pentyl ethanoate						
298.15	1.148	1.153	1.2773	116.96	4861	561
303.15	1.156	1.114	1.2826	117.15	4883	555
313.15	1.172	1.041	1.2932	117.54	4930	544
323.15	1.189	0.973	1.3040	117.95	4975	534
(6) Decyl ethanoate						
298.15	0.934	1.109	1.2340	188.00	5435	503
303.15	0.937	1.077	1.2379	188.28	5464	500
313.15	0.943	1.017	1.2457	188.87	5523	494
323.15	0.950	0.959	1.2538	189.45	5579	487
(7) Dodecyl ethanoate						
298.15	0.897	1.135	1.2262	216.83	5563	508
303.15	0.905	1.112	1.2311	216.79	5573	510
313.15	0.921	1.065	1.2410	217.16	5596	513
323.15	0.936	1.017	1.2507	217.43	5625	514
(8) Methyl propionate						
298.15	1.336	1.213	1.3128	73.53	4513	623
303.15	1.345	1.172	1.3185	73.70	4539	617
313.15	1.363	1.096	1.3300	74.06	4593	607
323.15	1.382	1.022	1.3416	74.43	4646	594
(9) Ethyl propionate						
298.15	1.312	1.143	1.3084	88.21	4552	583
303.15	1.324	1.108	1.3146	88.37	4572	580
313.15	1.349	1.037	1.3274	88.70	4614	572
323.15	1.374	0.970	1.3401	89.07	4658	562
(10) Ethyl butanoate						
298.15	1.246	1.130	1.2961	102.51	4666	566
303.15	1.255	1.094	1.3017	102.71	4690	562
313.15	1.273	1.024	1.3130	103.12	4738	552
323.15	1.291	0.958	1.3242	103.56	4788	542
(11) Ethyl isovalerate						
298.15	1.176	1.073	1.2827	117.83	4801	526
303.15	1.183	1.039	1.2879	118.06	4827	522
313.15	1.197	0.972	1.2982	118.51	4879	512
323.15	1.211	0.905	1.3085	119.02	4932	500
(12) Ethyl chloroethanoate						
298.15	1.164	1.477	1.2804	83.53	4826	722
303.15	1.169	1.433	1.2851	83.71	4856	717
313.15	1.179	1.350	1.2946	84.08	4915	708
323.15	1.189	1.271	1.3040	84.47	4975	698
(13) Ethyl bromoacetate						
298.15	1.085	1.496	1.2649	88.09	5005	713
303.15	1.091	1.452	1.2697	88.23	5031	709
313.15	1.103	1.371	1.2793	88.54	5082	702
323.15	1.116	1.298	1.2892	88.84	5131	697
(14) Ethyl-2-bromopropionate						
298.15	1.038	1.294	1.2554	104.32	5125	608
303.15	1.044	1.259	1.2602	104.47	5149	606
313.15	1.056	1.191	1.2697	104.79	5197	600
323.15	1.069	1.125	1.2794	105.11	5244	594
(15) Ethyl-3-bromopropionate						
298.15	0.992	1.405	1.2461	103.54	5254	650
303.15	0.998	1.369	1.2507	103.67	5276	649
313.15	1.008	1.293	1.2596	103.98	5326	642
323.15	1.019	1.220	1.2687	104.28	5375	634
(16) Ethyl-2-bromobutanoate						
298.15	0.992	1.253	1.2461	118.50	5254	580
303.15	0.997	1.220	1.2505	118.66	5279	578
313.15	1.007	1.150	1.2594	119.01	5329	571
323.15	1.017	1.085	1.2683	119.38	5380	563
(17) Ethyl-4-bromobutanoate						
298.15	0.934	1.373	1.2340	116.54	5435	623
303.15	0.938	1.336	1.2381	116.71	5461	620
313.15	0.948	1.272	1.2468	116.99	5507	619
323.15	0.958	1.208	1.2555	117.29	5554	615
(18) Dimethyl malonate						
298.15	0.9581	1.641	1.2390	92.38	5357	751
303.15	0.964	1.592	1.2436	92.48	5378	746
313.15	0.977	1.503	1.2530	92.68	5417	738
323.15	0.990	1.431	1.2625	92.89	5457	737
(19) Diethyl malonate						
298.15	0.937	1.325	1.2346	123.77	5425	602
303.15	0.943	1.293	1.2392	123.90	5444	601
313.15	0.957	1.231	1.2488	124.12	5478	601
323.15	0.971	1.167	1.2584	124.37	5514	597
(20) Diethyl bromomalonate						
298.15	0.976	1.485	1.2428	137.97	5302	683
303.15	0.981	1.444	1.2472	138.16	5326	680
313.15	0.991	1.369	1.2560	138.55	5375	676
323.15	1.002	1.301	1.2651	138.93	5422	672

Table 9
Comparison of experimental and Flory theory speeds of sound ($m\,s^{-1}$) at different temperatures for alkanoates

T (K)	$u_{exp.}$	U_{Fl}	Dev. (%)	T (K)	$u_{exp.}$	u_{Fl}	Dev (%)
(1) Methyl ethanoate							
298.15	1155	1159	0	303.15	1132	1149	−1
313.15	1086	1127	−3	323.15	1039	1103	−6
(2) Ethyl ethanoate							
298.15	1141	1180	−3	303.15	1118	1168	−4
313.15	1073	1144	−6	323.15	1026	1117	−8

Table 9 (*Continued*)

T (K)	$u_{exp.}$	U_{Fl}	Dev. (%)	T (K)	$u_{exp.}$	u_{Fl}	Dev (%)
(3) Propyl ethanoate							
298.15	1164	1224	−5	303.15	1144	1214	−6
313.15	1102	1191	−8	323.15	1059	1166	−10
(4) Butyl ethanoate							
298.15	1192	1252	−5	303.15	1173	1243	−5
313.15	1132	1220	−7	323.15	1090	1196	−9
(5) Pentyl ethanoate							
298.15	1221	1293	−5	303.15	1197	1279	−6
313.15	1152	1254	−8	323.15	1109	1230	−10
(6) Decyl ethanoate							
298.15	1290	1391	−7	303.15	1271	1382	−8
313.15	1234	1363	−10	323.15	1197	1343	−12
(7) Dodecyl ethanoate							
298.15	1330	1434	−7	303.15	1313	1425	−8
313.15	1281	1409	−10	323.15	1247	1391	−11
(8) Methyl propionate							
298.15	1167	1204	−3	303.15	1145	1193	−4
313.15	1103	1172	−6	323.15	1060	1150	−8
(9) Ethyl propionate							
298.15	1156	1206	−4	303.15	1136	1196	−5
313.15	1093	1172	−7	323.15	1051	1149	−9
(10) Ethyl butanoate							
298.15	1172	1236	−5	303.15	1151	1225	−6
313.15	1109	1203	−8	323.15	1068	1180	−10
(11) Ethyl isovalerate							
298.15	1158	1249	−7	303.15	1138	1239	−8
313.15	1097	1216	−10	323.15	1055	1192	−13
(12) Ethyl chloroethanoate							
298.15	1247	1195	4	303.15	1227	1187	3
313.15	1188	1170	1	323.15	1150	1154	0
(13) Ethyl bromoacetate							
298.15	1124	1034	7	303.15	1106	1027	7
313.15	1072	1012	5	323.15	1040	998	3
(14) Ethyl-2-bromopropionate							
298.15	1080	1043	3	303.15	1064	1035	2
313.15	1032	1021	1	323.15	1000	1005	0
(15) Ethyl-3-bromopropionate							
298.15	1154	1091	5	303.15	1138	1084	4
313.15	1103	1068	3	323.15	1068	1052	1
(16) Ethyl-2-bromobutanoate							
298.15	1101	1079	1	303.15	1085	1072	1
313.15	1051	1056	0	323.15	1018	1040	−2
(17) Ethyl-4-bromobutanoate							
298.15	1179	1132	3	303.15	1162	1125	3
313.15	1132	1112	1	323.15	1101	1098	0
(18) Dimethyl malonate							
298.15	1388	1351	2	303.15	1364	1339	1
313.15	1320	1317	0	323.15	1284	1301	−1
(19) Diethyl malonate							
298.15	1291	1321	−2	303.15	1274	1313	−3
313.15	1238	1296	−4	323.15	1201	1277	−6
(20) Diethyl bromomalonate							
298.15	1184	1124	5	303.15	1166	1116	4
313.15	1133	1102	2	323.15	1102	1088	1

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