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Thermochimica Acta 426 (2005) 141–149

thermochimica acta

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Speeds of sound, isentropic compressibilities, viscosities, and excess molar volumes of binary mixtures of alkanoates with tetra- and trichloromethanes at 303.15 K

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Received 19 May 2004; received in revised form 23 July 2004; accepted 29 July 2004
Available online 11 September 2004

Abstract

Speeds of sound u, isentropic compressibilities κ_S, viscosities η, excess isentropic compressibilities $\kappa_S{}^E$, excess molar volumes V^E, viscosity deviations $\Delta\eta$, and excess Gibbs energies of activation ΔG^{*E} of viscous flow have been investigated for six binary mixtures of diethyl malonate, diethyl bromomalonate, and ethyl chloroacetate with tetra- and trichloromethane at 303.15 K. The values of $\kappa_S{}^E$, V^E, $\Delta\eta$, and ΔG^{*E} are highly dependent on the type of components involved and the composition curves are unsymmetrical.

The results obtained for viscosity of binary mixtures were used to test the semi-empirical relations of Grunberg-Nissan, Tamura-Kurata, Hind-McLaughlin-Ubbelohde, Katti-Chaudhri, McAllister, Heric-Brewer and Auslaender. The experimental speeds of sound have been analyzed in terms of collision factor theory and free length theory of solutions.

Keywords: Alkanoate; Excess molar volume; Chloroalkane; Isentropic compressibility; Viscosity.

1. Introduction

As a part of our systematic studies on the thermodynamic, transport, and acoustic properties of liquid mixtures containing alkyl alkanoates, in the previous papers [1–4], the speeds of sound, isentropic compressibilities, viscosities and excess molar volumes for binary mixtures of methyl acetate, ethyl acetate, pentyl acetate and iso-pentyl acetate with chloroalkanes have been reported. The results were explained by considering specific interactions between acetate and chloroalkane. As an extension of our studies, in this paper we report speeds of sound, isentropic compressibilities, viscosities, and excess molar volumes for binary mixtures of diethyl malonate (DEM), diethyl bromomalonate (DEBrM), and ethyl chloroacetate (EClA) with tetrachloromethane (CCl_4) and trichloromethane ($CHCl_3$). The viscosity measurements will also provide a test of various empirical equations to correlate viscosity data of binary mixtures in terms of pure component properties.

2. Experimental

The speeds of sound u in pure liquids and in binary mixtures were measured with 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 viscosities η were measured with a modified suspended-level Ubbelohde viscometer [5]. The viscometer was designed so as to reduce surface tension effects to negligible value [6]. A water-circulating thermostat with an accuracy of ±0.02 K was used for controlling the temperature for the speed of sound and viscosity measurements. The densities ρ were measured with an Anton Paar vibrating-tube digital densimeter (model DMA 60/602)

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doi:10.1016/j.tca.2004.07.014

with a thermostated bath controlled to ±0.01 K. The details of the methods and techniques used to determine u, ρ and η have already been described elsewhere [7–9].

The mixtures were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. The error in u, η and ρ was estimated to be less than $\pm 1\ \mathrm{m\,s^{-1}}$, $\pm 2 \times 10^{-3}$ mPa s and $\pm 2 \times 10^{-2}\ \mathrm{kg\,m^{-3}}$, respectively. The isentropic compressibilities determined from the relation $\kappa_S = 1/(u^2\rho)$ are believed to be reliable to within 2 $\mathrm{TPa^{-1}}$.

Diethyl malonate (Riedel-Haenag, Seelze-Hannover >99% by GC), diethyl bromomalonate (Fluka AG, >98% by GC), and ethyl chloroacetate (Prosynth >98.5% by GC), were used after drying over molecular sieves. Tetrachloromethane (E. Merck, Bombay, AR >99%) was dried over anhydrous calcium chloride and was fractionally distilled. Trichloromethane (E. Merck, Bombay, AR >99%) was used after further purification by the standard procedure [10]. It was washed with NaOH solution and with distilled water. It was further treated three times with conc. H_2SO_4 and then with distilled water. It was dried over anhydrous calcium chloride and was fractionally distilled.

The purities of all the liquid samples were checked by gas liquid chromatography analysis at Gujarat Insecticide Ltd., Ankleshwar. The estimated purities of all the samples were better than 99.5% with the exception of diethyl bromomalonate (>98 mol%). Experimental densities and refractive indices of pure liquids are compared with literature values in Table 1.

3. Results

The results for the speeds of sound u, densities ρ, isentropic compressibilities κ_S, and viscosities η are given in Table 2. V^E for each mixture was calculated from equation

$$V^E = \sum \frac{x_i M_i}{\rho} - \sum \frac{x_i M_i}{\rho_i} \qquad (1)$$

$\kappa_S{}^E$ was calculated from the relation recommended by Benson and Kiyohara [17] and Douheret et al. [18]

$$\kappa_S^E = \kappa_S - \sum \phi_i \left\{ \kappa_{S,i} + \frac{TV_i(\alpha_i)^2}{C_{p,i}} \right\} - \frac{T\left(\sum x_i V_i\right)\left(\sum \phi_i \alpha_i\right)^2}{\sum x_i C_{p,i}} \qquad (2)$$

in which the V_i, α_i and $C_{p,i}$ are respectively, the molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component i and $\phi_i = x_i V_i/\Sigma x_j V_j$ is the volume fraction of i in the mixture, stated in terms of the unmixed components. The values of α_i and $C_{p,i}$ used for these calculations are listed in Table 1.

The viscosity deviations from linear dependence on mole fraction were calculated by

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i \eta_i \qquad (3)$$

On the basis of the theory of absolute reaction rates [19], the excess Gibbs energy of activation ΔG^{*E} of viscous flow were calculated from

$$\Delta G^{*E} = RT\left[\ln \frac{\eta V}{\eta_2 V_2} - x_1 \ln \frac{\eta_1 V_1}{\eta_2 V_2}\right] \qquad (4)$$

where V is the molar volume of the mixture. V^E, $\kappa_S{}^E$, and ΔG^{*E} data are included in Table 2. The estimated accuracy of V^E, $\kappa_S{}^E$ and ΔG^{*E} is about $5 \times 10^{-9}\ \mathrm{m^3\,mol^{-1}}$, 2.0 $\mathrm{TPa^{-1}}$ and 15 $\mathrm{J\,mol^{-1}}$, respectively.

For compact and smooth representation, the values of u, κ_S, and η were fitted to a polynomial equation of the form

$$u \text{ or } \kappa_S \text{ or } \eta = \sum_{i=1}^{m} A_i x_1^{i-1} \qquad (5)$$

The values of $\kappa_S{}^E$, V^E, $\Delta\eta$, and ΔG^{*E} were smoothed to a Redlich–Kister polynomial regression of the type [20]

$$\psi^E = x_1 x_2 \sum_{i=1}^{m} B_i (1 - 2x_1)^{i-1} \qquad (6)$$

where $\psi^E = \kappa_S{}^E$, V^E, $\Delta\eta$ and ΔG^{*E}

Table 1
Densities, refractive indices, thermal expansion coefficient and isobaric heat capacity of pure liquids at 303.15 K

	ρ ($\mathrm{kg\,m^{-3}}$)		n_D		α ($\mathrm{kK^{-1}}$)	Cp ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
	Observed	Literature	Observed	Literature		
EClA	1139.18	1139.3 [11]	1.4170	1.4173 [11]	1.169 [12]	191.7 [12]
DEM	1043.23	1044.6 [10]	1.4096	1.4097 [10]	0.943 [11]	298.3 [11]
DEBrM	1406.06[a]	1402.2 [13][a]	1.4523[b]	1.4521 [13][b]	0.981 [11]	327 [14][c]
CCl_4	1574.82	1574.8 [10]	1.4541	1.45464 [10]	1.245 [15]	131.3 [16]
$CHCl_3$	1470.59	1470.6 [10]	1.4402	1.4400 [10]	1.265 [15]	117.0 [16]

[a] At 298.15 K.

[b] At 293.15 K.

[c] Values calculated using Missenard group contribution method [13].

Table 2
Density ρ (kg m^{-3}), speed of sound u (m s^{-1}), isentropic compressibility κ_S (TPa^{-1}), viscosity η (mPa s), excess molar volume V^E (10^{-9} m^3 mol^{-1}), excess isentropic compressibility $\kappa_S{}^E$ (TPa^{-1}), and excess Gibbs energy of activation ΔG^{*E} (J mol^{-1}) of viscous flow for binary mixtures at 303.15 K

x_1	ρ	u	κ_S	η	V^E	$\kappa_S{}^E$	ΔG^{*E}
ECIA + CCl_4							
0.0000	1574.82	905	775	0.844			
0.0950	1530.01	933	750	0.853	−21.8	−8	−71
0.1992	1481.59	964	726	0.862	−30.9	−14	−152
0.2980	1436.61	994	704	0.862	−40.9	−18	−255
0.3972	1392.26	1025	683	0.870	−47.2	−20	−334
0.5000	1347.02	1058	663	0.891	−40.7	−21	−381
0.5978	1304.82	1089	646	0.928	−35.2	−18	−380
0.6984	1262.23	1123	628	0.967	−29.3	−16	−381
0.8044	1218.14	1158	612	1.021	−15.4	−10	−355
0.8978	1180.11	1191	597	1.113	−11.2	−6	−235
1.0000	1139.18	1227	583	1.275			
DEM + CCl_4							
0.1173	1480.36	949	750	0.857	183.2	−4	−137
0.2031	1419.02	982	730	0.877	287.7	−6	−215
0.2999	1356.61	1018	711	0.918	362.2	−6	−261
0.4623	1265.60	1080	677	1.002	360.1	−8	−326
0.5648	1215.59	1120	655	1.084	265.7	−10	−316
0.6579	1174.08	1154	639	1.167	147.1	−8	−307
0.7478	1136.91	1185	626	1.272	27.3	−6	−263
0.8311	1104.69	1216	612	1.388	−78.7	−5	−207
0.9189	1072.19	1247	599	1.544	−97.4	−3	−112
1.0000	1043.23	1274	590	1.721			
DEBrM + CCl_4							
0.1001	1552.35	944	722	1.012	−415.4	−23	121
0.1992	1531.61	980	679	1.207	−736.4	−36	224
0.3007	1512.21	1012	645	1.433	−1012.5	−41	298
0.4088	1492.99	1047	611	1.705	−1224.1	−46	346
0.4988	1478.09	1072	588	1.948	−1346.4	−44	351
0.5999	1462.10	1098	567	2.255	−1398.4	−41	342
0.6990	1446.77	1121	550	2.571	−1326.7	−35	298
0.8988	1415.72	1155	529	3.250	−683.4	−15	123
1.0000	1399.18	1166	525	3.614			
ECIA + $CHCl_3$							
0.0000	1470.59	967	727	0.512			
0.0989	1429.89	990	713	0.617	−81.1	1	249
0.1945	1392.15	1014	698	0.687	−118.1	1	306
0.2954	1354.22	1038	685	0.759	−131.5	4	330
0.3905	1320.14	1062	671	0.806	−120.1	4	266
0.5048	1281.24	1091	655	0.852	−80.7	5	145
0.6012	1250.32	1115	643	0.900	−46.1	7	61
0.6875	1223.93	1137	632	0.943	−9.2	7	−21
0.7658	1201.01	1159	619	0.989	25.9	6	−83
0.8992	1164.50	1198	598	1.114	47.4	2	−98
DEM + $CHCl_3$							
0.0968	1399.36	999	716	0.533	−50.5	2	−142
0.2004	1334.53	1031	704	0.568	−98.8	7	−260
0.3089	1276.40	1065	690	0.622	−129.2	10	−339
0.4122	1228.62	1097	676	0.692	−152.8	12	−377
0.5385	1178.25	1136	657	0.808	−179.9	12	−379
0.6125	1151.99	1159	646	0.891	−179.3	10	−364
0.7225	1116.70	1192	630	1.050	−159.8	8	−307
0.8156	1089.85	1220	616	1.226	−127.5	6	−226
0.9071	1065.78	1246	604	1.444	−82.5	4	−123
DEBrM + $CHCl_3$							
0.0980	1460.41	989	700	0.709	−191.7	0	407
0.1971	1450.47	1010	675	0.941	−286.8	1	682
0.2960	1441.28	1032	651	1.200	−315.2	2	839
0.4033	1432.36	1054	628	1.507	−303.5	3	900
0.5045	1424.91	1075	607	1.840	−267.2	3	904
0.5919	1419.12	1092	590	2.141	−219.6	3	844
0.6911	1413.32	1112	572	2.501	−165.4	2	724
0.7991	1407.82	1131	555	2.899	−110.9	2	528
0.8997	1403.21	1149	539	3.253	−50.6	1	279

The coefficients A_i of Eq. (5) and B_i of Eq. (6) and the standard deviations σ obtained from a least-squares fit with equal weights assigned to each point are given in Tables 3 and 4.

4. Correlating equations

Apart from expressing η as a polynomial fit, several semi-empirical relations have been proposed to estimate the dynamic viscosity η of liquid mixtures in terms of pure-component data [14,21]. We have examined equations proposed by Grunberg and Nissan [22], Tamura and Kurata [23], Hind, McLaughlin, and Ubbelohde [24], Katti and Chaudhri [25], McAllister [26], Heric and Brewer [27] and Auslaender [28].The Grunberg-Nissan phenomenological equation [22] reads

$$\eta = \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}) \tag{7}$$

where G_{12} is a parameter proportional to the interchange energy and has been regarded as an indicator for the non-ideal behavior of binary mixtures. The semi-empirical equation due to Tamura and Kurata [23] is

$$\eta = x_1\phi_1\eta_1 + x_2\phi_2\eta_2 + 2(x_1x_2\phi_1\phi_2)^{1/2}C \tag{8}$$

where C is an adjustable parameter.

Hind, McLaughlin, and Ubbelohde [24], have proposed the following equation

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2\eta_{12} \tag{9}$$

where η_{12} is attributed to unlike pair interactions. It is approximately equal to $0.5(\eta_1 + \eta_2)$, but this relation is not sufficiently accurate for prediction purposes. Katti and Chaudhri [25] derived the following equation:

$$\ln \eta V = x_1 \ln V_1\eta_1 + x_2 \ln V_2\eta_2 + \frac{x_1x_2W_{\text{vis}}}{RT} \tag{10}$$

where W_{vis} is an interaction term. All four above equations contain one adjustable parameter. The two-parameter McAllister equation [26] based on the Eyring's theory of absolute reaction rates [19] and the three-body interaction model is

Table 3
Coefficients A_i of Eq. (5) and standard deviations σ

Property	A_1	A_2	A_3	A_4	A_5	σ
EClA + CCl4						
u (m s^{-1})	944.2	194.8	12.1			0.3
κ_S (TPa^{-1})	774.8	−263.6	90.7	−19		0.5
η (mPa s)	0.8472	−0.0262	0.5322	−1.0753	0.9930	0.0083
DEM + CCl_4						
u (m s^{-1})	943.5	700.3	4.3	15.2		0.7
κ_S (TPa^{-1})	775.2	−217.9	−10.3	42.9		1.1
η (mPa s)	0.8443	−0.0143	1.0727	−1.0019	0.8200	0.0022
DEBrM + CCl_4						
u(m s^{-1})	943.7	811.6	42.6			0.4
κ_S (TPa^{-1})	774.7	−572	551.5	−384.2	155.3	0.9
η (mPa s)	0.8457	1.4836	1.6723	−0.3867		0.0031
EClA + $CHCl_3$						
u (m s^{-1})	801.7	322.4	27.2			0.4
κ_S (TPa^{-1})	727.3	−155.5	45.5	−34.8		0.9
η (mPa s)	0.5139	1.0730	−0.7962	−0.4318	0.9139	0.0044
DEM + $CHCl_3$						
u (m s^{-1})	801.8	802.7	59.3			0.4
κ_S (TPa^{-1})	726.8	−100.6	−73.3	37.4		0.5
η (mPa s)	0.5125	0.1173	0.8982	−0.6485	0.8416	0.0010
DEBrM + $CHCl_3$						
u (m s^{-1})	801.8	929.8	98.7	−32.7		0.4
κ_S (TPa^{-1})	726.9	−282.1	95	−14.8		0.3
η (mPa s)	0.5125	1.8689	1.3856	0.6601	−0.8162	0.0052

Table 4
Coefficients B_i of Eq. (6) and standard deviations σ

System	Property	B_1	B_2		B_3	σ
EClA + CCl_4	$10^9 V^E$ (m^3 mol^{-1})	−161.8	81.1	−20.5		2.9
	$\kappa_S{}^E$ (TPa^{-1})	−79.3	17.6			0.6
	$\Delta\eta$ (mPa s)	−0.6547	0.3735	−0.2732	03289	0.0050
	ΔG^{*E} (J mol^{-1})	−1482.2	−722.0	−346.0	−606.5	13.5
DEM + CCl_4	$10^9 V^E$ (m^3 mol^{-1})	1326.6	−1584.8	−1587.1	−349.1	4.4
	$\kappa_S{}^E$ (TPa^{-1})	−35.5	−1			0.9
	$\Delta\eta$ (mPa s)	−1.0047	0.3250	−0.2051		0.0023
	ΔG^{*E} (J mol^{-1})	−1296.2	−106.4	−207.4		5.3
DEBrM + CCl_4	$10^9 V^E$ (m^3 mol^{-1})	−5388.4	−1849.5	−1046		5.0
	$\kappa_S{}^E$ (TPa^{-1})	−176	52.1	−52		1.1
	$\Delta\eta$ (mPa s)	−1.0908	−0.1876	0.0430		0.0027
	ΔG^{*E} (J mol^{-1})	1432.0	2.2	−105.2		3.1
EClA + $CHCl_3$	$10^9 V^E$ (m^3 mol^{-1})	−349.7	718.6	246.1	275.4	2.8
	$\kappa_S{}^E$ (TPa^{-1})	24.4	13.3	−11.6		1.0
	$\Delta\eta$ (mPa s)	−0.1567	0.6402	−0.2320	0.2208	0.0037
	ΔG^{*E} (J mol^{-1})	628.8	−1955.9	290.5	−706.9	13.1
DEM + $CHCl_3$	$10^9 V^E$ (m^3 mol^{-1})	−682.8	−226.5	−134.2		4.3
	$\kappa_S{}^E$ (TPa^{-1})	47.6	−19.3	−19.2	51.7	0.4
	$\Delta\eta$ (mPa s)	−1.3991	0.5229	−0.1958		0.0012
	ΔG^{*E} (J mol^{-1})	−1553.4	98.0	−9.1		3.6
DEBrM + $CHCl_3$	$10^9 V^E$ (m^3 mol^{-1})	−1067.4	880.9	−464.7	178.8	2.7
	$\kappa_S{}^E$ (TPa^{-1})	12.1	4.8	−9.1		0.3
	$\Delta\eta$ (mPa s)	−0.9421	−0.5388	0.1282	0.1946	0.0055
	ΔG^{*E} (J mol^{-1})	3623.7	−719.5	392.6	−349.3	5.9

Table 5
Values of the parameters in Eqs.(7)–(10) and standard percentage deviations σ (%) in correlating viscosity of binary mixtures at 303.15 K

Mixture	Eq. (7)		Eq. (8)		Eq. (9)		Eq. (10)	
	G_{12}	σ (%)	C	σ (%)	η_{12}	σ (%)	W_{vis}/RT	σ (%)
EClA + CCl_4	−0.60	3.31	0.69	4.82	0.71	4.51	−0.60	3.30
DEM + CCl_4	−0.65	0.41	0.64	4.83	0.74	2.61	−0.54	0.55
DEBrM + CCl_4	0.44	0.33	1.37	0.70	1.68	0.86	0.56	0.19
EClA + $CHCl_3$	0.25	6.80	0.73	7.19	0.79	6.66	0.29	6.76
DEM + $CHCl_3$	−0.81	0.63	0.18	11.89	0.38	5.55	−0.62	0.32
DEBrM + $CHCl_3$	1.22	2.25	1.15	1.14	1.61	2.64	1.48	2.66
σ (%)		2.29		5.11		3.81		2.30

$$\ln v = x_1^3 \ln v_1 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} + x_2^3 \ln v_2 - \ln\left(\frac{x_1 + x_2 M_2}{M_1}\right) + 3x_1^2 x_2 \ln\left(\frac{2}{3} + \frac{M_2}{3M_1}\right) + 3x_1 x_2^2 \ln\left(\frac{1}{3} + \frac{2M_2}{3M_1}\right) + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \quad (11)$$

where Z_{12} and Z_{21} are interaction parameters and M_i and v_i are the molecular mass and kinematic viscosity of pure component i. The two-parameter Heric and Brewer equation [27] is of the form:

$$\ln v = x_1 \ln v_1 + x_2 \ln v_2 + x_1 \ln M_1 + x_2 \ln M_2 + \ln(x_1 M_1 + x_2 M_2) + x_1 x_2[\alpha_{12} + \alpha_{21}(x_1 - x_2)] \quad (12)$$

where α_{12} and α_{21} are adjustable parameters.

The less complicated three-parameter Auslaender equation [28] has the form:

$$x_1(x_1 + B_{12}x_2)(\eta - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta - \eta_2) = 0 \quad (13)$$

where B_{12}, A_{21} and B_{21} are the parameters representing binary 12 interactions. The correlating ability of each of Eqs. (7)–(13), was tested by calculating the standard percentage deviations σ (%) between the experimental and the calculated viscosity as:

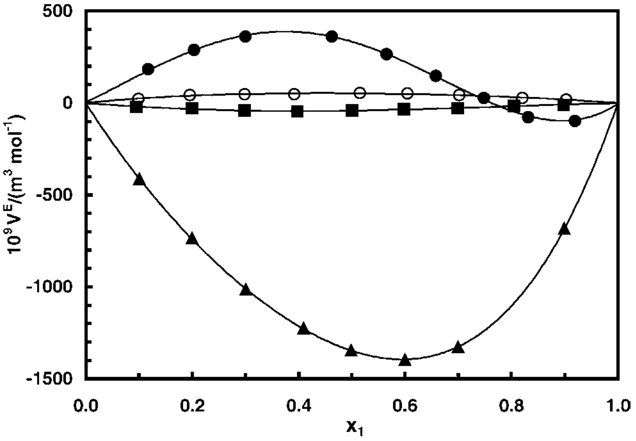

Fig. 1. Excess molar volumes for alkanoate + tetrachloromethane at 303.15 K. Experimental points: EClA (■), DEM (●), DEBrM (▲), EA (○) [1].

$$\sigma(\%) = \left[\frac{1}{n-k}\sum\left\{\frac{100(\eta_{exp} - \eta_{cal})}{\eta_{exp}}\right\}^2\right]^{1/2} \quad (14)$$

where n represents the number of data points and k is the number of numerical coefficients in the respective equation. The results of the correlating Eqs. (7)–(13) are compiled in Tables 5 and 6. The values of the different parameters and the percentage standard deviations σ (%) listed in Tables 5 and 6 were obtained from the experimental viscosity data using the method of least squares.

Table 6
Values of the parameters in Eqs. (11)–(13) and standard percentage deviations ((%) in correlating viscosities of binary mixtures at 303.15 K

Mixtures	Eq. (11)			Eq. (12)			Eq. (13)			
	Z_{12}	Z_{21}	α (%)	α_{12}	α_{21}	σ (%)	B_{12}	A_{21}	B_{21}	σ (%)
EClA + CCl_4	0.62	0.64	1.09	−0.60	−0.42	1.09	−0.12	−0.69	−8.35	0.41
DEM + CCl_4	0.93	0.66	0.44	−0.54	−0.04	0.44	0.02	1.02	2.70	0.25
DEBrM + CCl_4	1.81	1.06	0.21	0.56	0.00	0.21	0.55	0.99	1.32	0.14
EClA + $CHCl_3$	0.61	0.76	0.73	0.28	−0.91	0.73	2.56	1.53	1.90	0.66
DEM + $CHCl_3$	0.8	0.46	0.17	−0.62	0.04	0.17	0.22	1.71	1.65	0.17
DEBrM + $CHCl_3$	1.84	1.18	0.86	1.48	−0.35	0.86	0.76	1.27	0.88	0.31
σ (%)		0.58			0.58				0.32	

5. Discussion

5.1. Alkanoate + tetrachloromethane

The dependence of V^E, $\kappa_S{}^E$, $\Delta\eta$ and ΔG^{*E} on composition x_1, is shown in Figs. 1–4. Previously published results of ethyl acetate (EA) + CCl_4 [1,2,29] are also included in Figs. 1–4 for the purpose of comparison with EClA + CCl_4. It can be seen from Figs. 1–4 that the values of V^E, $\kappa_S{}^E$, $\Delta\eta$, and ΔG^{*E} for alkanoate + CCl_4 mixtures are highly dependent on the type of components involved and curves are unsymmetrical. The values of V^E for EClA + CCl_4 are very small negative whereas for DEBrM + CCl_4, the V^E are very large negative. For mixture DEM + CCl_4, the values of V^E change sign from positive to negative at $x_1 = 0.78$ of DEM. The values of $\kappa_S{}^E$ are negative for all the three binary mixtures. The order of magnitude of $\kappa_S{}^E$ for CCl_4 mixtures is DEM > EClA > DEBrM. The viscosity deviations $\Delta\eta$ (Fig. 3) are large and negative for all the three mixtures whereas ΔG^{*E} (Fig. 4) are negative for EClA + CCl_4 and DEM + CCl_4 but positive for DEBrM + CCl_4. It appears from the sign and magnitude of V^E and $\kappa_S{}^E$ that specific interactions O · · · Cl exits between alkanoate and CCl_4 molecules [1,2,30–33]. The exaltation of polarization supported the specific interactions between alkanoate and tetrachlorometnane [34]. This graded behaviour is consistent with the present viscosity results.

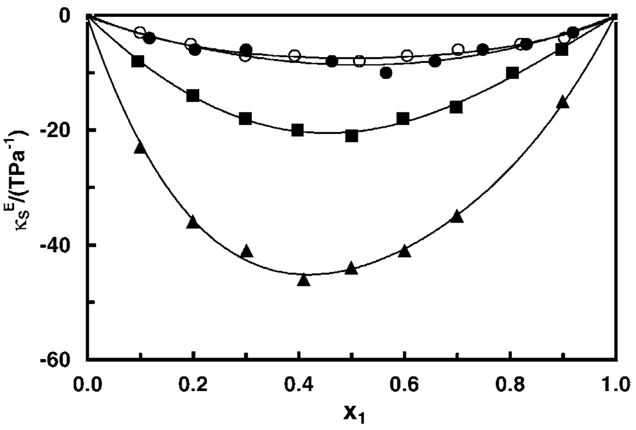

Fig. 2. Excess isentropic compressibility for alkanoate + tetrachloromethane at 303.15 K. Experimental points: EClA (■), DEM (●), DEBrM (▲), EA (○) [29].

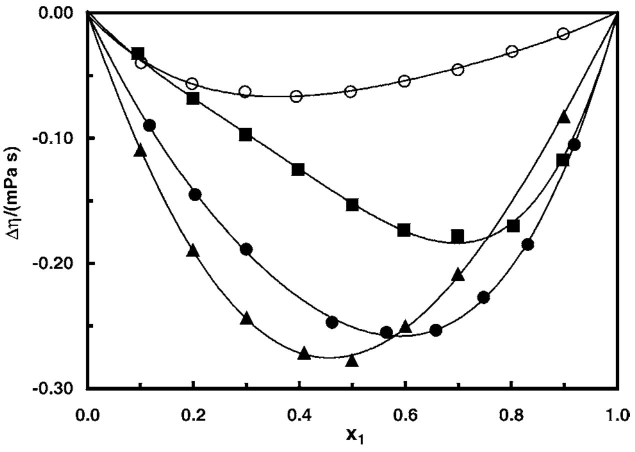

Fig. 3. Viscosity deviations in for alkanoate + tetrachloromethane at 303.15 K. Experimental points: EClA (■), DEM (●), DEBrM (▲), EA (○) [2].

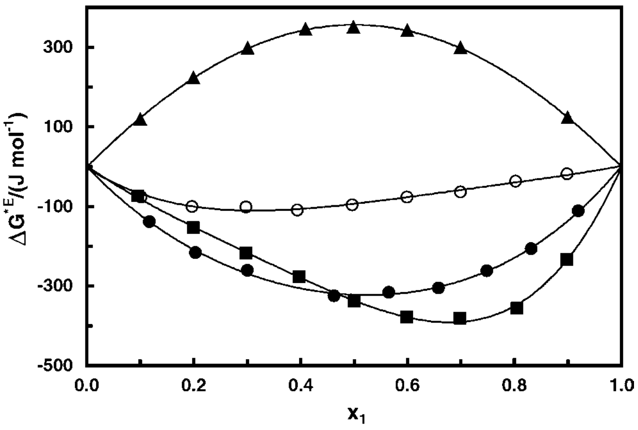

Fig. 4. Excess Gibbs energy of activation of viscous flow for alkanoate + tetrachloromethane at 303.15 K. Experimental points: EClA (■), DEM (●), DEBrM (▲), EA (○) [2].

A comparison of V^E and $\kappa_S{}^E$ of EClA + CCl_4 with EA + CCl_4 [1,29] in Figs. 1 and 2 shows that both the functions are smaller for the former mixture. This is indicative of stronger Cl · · · O interactions in former mixture compared to later. Similarly, V^E and $\kappa_S{}^E$ for DEBrM + CCl_4 are very large and negative, while that for DEM + CCl_4, $\kappa_S{}^E$ are small negative and V^E are positive in alkanoate poor region. Thus, there is a pronounced influence on the strength of specific interactions by introducing the Br atom into DEM molecule.

5.2. Alkanoate + trichloromethane

The dependence of V^E, $\kappa_S{}^E$, $\Delta\eta$ and ΔG^{*E} on composition is shown in Figs. 5–8. Previously published results of ethyl acetate (EA) + $CHCl_3$ [1,2,29] are also included in Figs. 5–8 for the purpose of comparison with EClA + $CHCl_3$. The V^E for $CHCl_3$ mixtures are unsymmetrical and negative except for EClA + $CHCl_3$, where they are positive at higher mole fraction of EClA. Contrary to the CCl_4 mixtures, the $\kappa_S{}^E$ for $CHCl_3$ mixtures are generally positive except for DEBrM + $CHCl_3$ which has small negative values at low concentration region of DEBrM. The $\Delta\eta$ for mixtures DEM + $CHCl_3$ and DEBrM + $CHCl_3$ are large and negative over the entire range of composition. For the mixture EClA + $CHCl_3$, $\Delta\eta$ versus x_1 curve is sigmoid, having positive deviations when composition of EClA is low otherwise deviations are negative. The ΔG^{*E} are negative for DEM + $CHCl_3$ and large and positive for DEBrM + $CHCl_3$. Mixture EClA + $CHCl_3$ have both positive as well as negative values of ΔG^{*E}. The similar behaviour was also observed for *p*-dioxane + $CHCl_3$ and acetone + $CHCl_3$ [30,35] systems. Such behaviour is attributed to

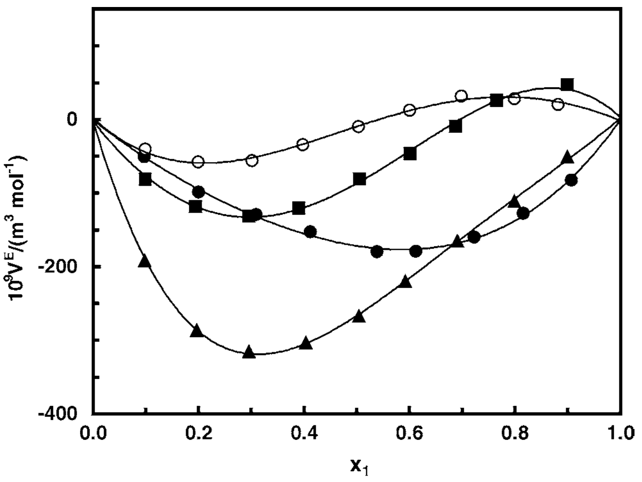

Fig. 5. Excess molar volumes for alkanoate + trichloromethane at 303.15 K. Experimental points: EClA (■), DEM (●), DEBrM (▲), EA (○) [1].

the formation of H-bond between unlike molecules. Comparison of excess functions for EClA + $CHCl_3$ and EA + $CHCl_3$ [1,29] in Figs. 5 and 6 indicates that V^E for EClA mixture are more negative and $\kappa_S{}^E$ are less positive than those for EA mixture, which again suggests that interactions between EClA and $CHCl_3$ are stronger than those between EA and $CHCl_3$. Very large and positive values of ΔG^{*E} for EClA + $CHCl_3$ also support strong specific interactions between unlike molecules leading to complex formation through H-bonding.

5.3. Correlating equations

The values of σ (%) are in the range from 0.33 to 6.80%, 0.70 to 11.89%, 0.86 to 6.66%, and 0.19 to 6.76% for the single-parameter Grunberg-Nissan, Tamura-Kurata, Hind-McLaughlin-Ubbelohde, and Katti-Chaudhri equations, respectively; from 0.17 to 1.09% for the two-parameter McAllister equation and Heric equation; and from 0.17 to 0.66% for the three-parameter Auslaender equation. The average percentage standard deviations σ (%) for Grunberg-Nissan, Tamura-Kurata, Hind-McLaughlin-Ubbelohde Katti-Chaudhri, McAllister, Heric equation and Auslaender equations are 2.29, 5.11, 3.81, 2.30, 0.58, 0.58 and 0.32, respectively. Thus, the best accuracy is given by the three-parameter Auslaender equation.

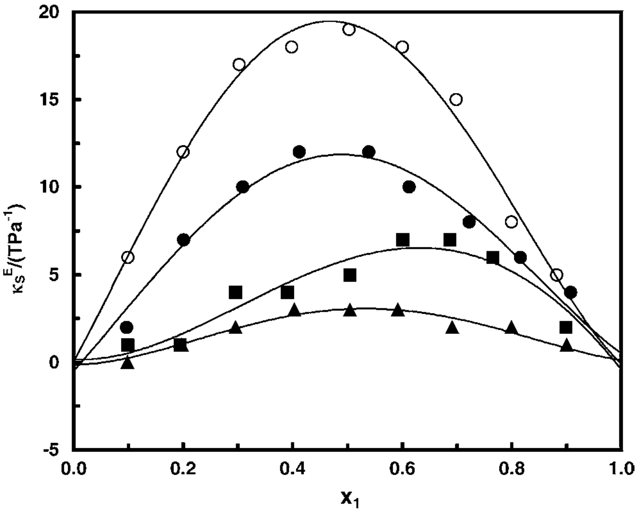

Fig. 6. Excess isentropic compressibility for alkanoate + trichloromethane at 303.15 K. Experimental points: EClA (■), DEM (●), DEBrM (▲), EA (○) [29].

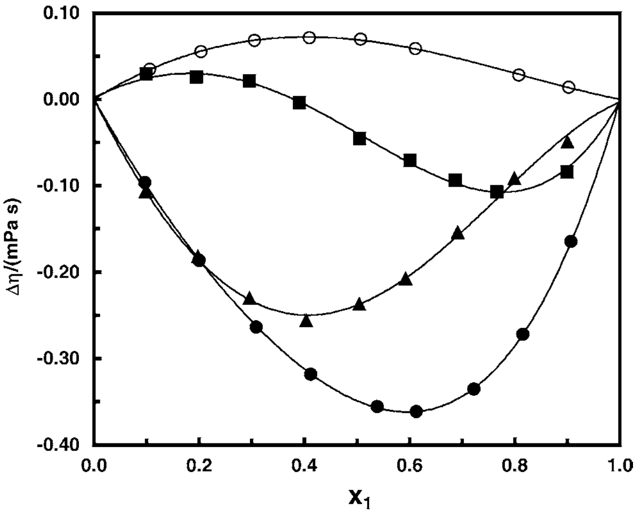

Fig. 7. Viscosity deviations in for alkanoate + trichloromethane at 303.15 K. Experimental points: EClA (■), DEM (●), DEBrM (▲), EA (○) [2].

6. Application of CFT and FLT

The speed of sound u from the Schaaffs' collision factor theory (CFT) [36] and the Jacobson's intermolecular free

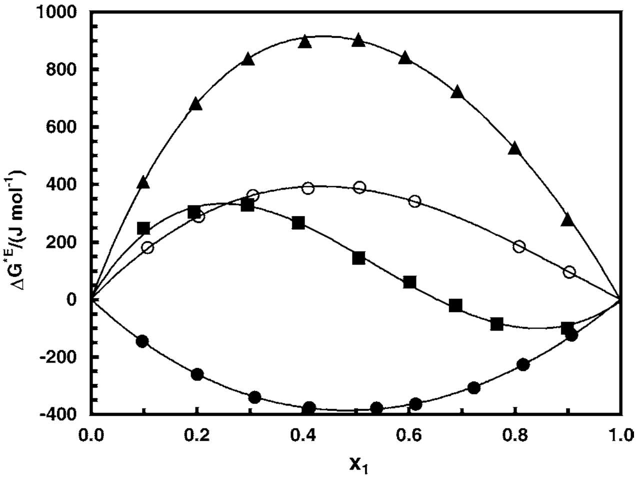

Fig. 8. Excess Gibbs energy of activation of viscous flow for alkanoate + trichloromethane at 303.15 K, Experimental points: EClA (■), DEM (●), DEBrM (▲), EA (○) [2].

Table 7
Properties of pure components for the CFT and the FLT

Liquid	$10^6 V$ ($m^3 mol^{-1}$)	$10^6 B$ ($m^3 mol^{-1}$)	S_S	γ	T_c (K)	10^6Va ($m^3 mol^{-1}$)	$10^4 Y$ ($m^2 mol^{-1}$)
EClA	107.54	25.19	3.27	1.40	610.0	20.03	80.51
DEM	153.42	36.31	3.35	1.28	505.0	36.90	97.44
DEBrM	171.34	40.75	3.14	1.31	531.0	38.41	106.39
CCl_4	97.91	22.68	2.44	1.45	556.6	20.58	74.14
$CHCl_3$	81.29	18.75	2.63	1.48	536.6	17.96	64.90

Table 8
Comparison of equimolar experimental speeds of sound with theCFT and the FLT at 303.15 K along with standard percentage deviations

Mixture	u_{expt} ($m\,s^{-1}$)	u_{CFT} ($m\,s^{-1}$)	σ (%)	u_{FLT} ($m\,s^{-1}$)	σ (%)
EClA + CCl_4	1057	1064	0.6	1052	0.3
DEM + CCl_4	1091	1084	0.5	1065	2.0
DEBrM + CCl_4	1085	1061	1.8	1087	0.4
EClA + $CHCl_3$	1089	1098	0.7	1104	1.2
DEM + $CHCl_3$	1122	1123	0.1	1112	0.8
DEBrM + $CHCl_3$	1088	1088	0.1	1074	1.0

length theory (FLT) [37] have also been estimated for the present binary mixtures. The pertinent relations in these calculations and their theoretical basis have been outlined several times [36–41]. Only brief mention will be made here. In terms of the CFT [38,39] the speed of sound u in pure liquid and mixture is related to

$$u = u_\infty S_S r_f \tag{15}$$

where u_∞ = 1600 m s^{-1}, S_S = collision factor and $r_f = B/V$, space filling factor. B is actual volume of the molecules per mole and V molar volume. For binary mixtures S_S and B are related to pure component values through

$$S_S = \sum_i x_i S_{S,i} \tag{16}$$

$$B = \sum_i x_i B_i \tag{17}$$

The speed of sound u in the binary mixture according to FLT [37] is given by:

$$u = \frac{k}{(L_f \rho^{1/2})} \tag{18}$$

The free length of the mixture L_f is obtained by

$$L_f = \frac{(V - \sum_i x_i V_{0,i})}{\sum_i x_i Y_i} \tag{19}$$

where $V_{0,i}$ = molar volume of pure component i at 0 K, and Y_i = surface area per mole for pure component i. For spherical molecules the surface area per mole of the pure liquid is given by Eq. (20)

$$Y_i = (36\pi N V_{0,i}^2)^{1/3} \tag{20}$$

The molar volume of pure component i at absolute zero temperature $V_{0,i}$ is obtained by Sugden's formula

$$V_{0,i} = V_i \left(\frac{1-T}{T_{c,i}}\right)^{0.3} \tag{21}$$

where T_c critical temperature. The value of k for the individual mixture has been taken as $k = \Sigma_i\, x_i k_i$, where the values of k_i for both the components in the mixture were obtained from Eq. (18).

Values of molar volume V, actual volume B, collision factor S_S, ratio of principle heat capacities γ, critical temperature T_c, available free volume V_a, and surface area Y for pure components employed in and evaluated from the CFT and the FLT are listed in Table 7. The theoretical speeds of sound u for the binary mixture over the entire range of compositions were estimated. The theoretical u at equimolar composition is compared with experimental results in Table 8. The values of the standard percentage deviation σ (%) for each individual mixture are also included in this Table. The study of Table 8 reveals that the values of σ (%) in estimating u from the CFT are in the range from 0.1 to 1.8 and from the FLT are from 0.3 to 3.0 for present mixtures. The average values standard percentage deviation σ (%) for CFT and FLT are 0.6 and 1.2, respectively.

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