

Densities, speeds of sound, isentropic compressibilities, refractive indexes, and viscosities of tetrahydrofuran with haloalkane or alkyl ethanoate at $T = 303.15$ K

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Received 23 May 2004; received in revised form 30 July 2004; accepted 2 August 2004

Available online 11 September 2004

Abstract

Isentropic compressibilities κ_S , excess isentropic compressibilities κ_S^E , excess molar volumes V^E , viscosity deviations $\Delta\eta$, and excess Gibbs energy of activation of viscous flow ΔG^{*E} for nine binary mixtures of C_4H_8O with CCl_4 , $CHCl_3$, $CHCl_2CHCl_2$, 1- $C_6H_{13}Cl$, 1- $C_6H_{13}Br$, $CH_3CO_2CH_3$, $CH_3CO_2C_2H_5$, $CH_3CO_2C_4H_9$, and $CH_3CO_2C_5H_{11}$ at 303.15 K have been derived from experimental densities ρ , speeds of sound u , refractive indexes n_D and viscosities η . The limiting values of excess partial molar volumes of C_4H_8O at infinite dilution $V_1^{E,\infty}$ in different solvents have been estimated. The results obtained for dynamic viscosity of binary mixtures were used to test the semi-empirical relations of Grunberg–Nissan, Tamura–Kurata, Hind–McLaughlin–Ubbelohde, Katti–Chaudhri, McAllister, Heric, and Auslaender. Finally, the experimental refractive indexes were compared with the predicted results for Lorentz–Lorenz, Dale–Gladstone, Eykman, Arago–Boit, Newton, Oster, Heller, and Wiener equations.

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Keywords: Isentropic compressibility; Excess molar volume; Refractive index; Speed of sound; Tetrahydrofuran; Viscosity

1. Introduction

As a part of our systematic studies on the thermodynamic, transport, and acoustic properties of liquid mixtures containing cyclic ethers, in previous papers [1–6] measurements of speeds sound, densities, and viscosities, and related excess functions for binary mixtures of *p*-dioxane and tetrahydrofuran with variety of solvents have been reported. As an extension of our studies in this paper we report densities ρ , speeds of sound u , isentropic compressibilities κ_S , refractive indexes n_D , viscosities η , and related excess properties for binary mixtures of tetrahydrofuran (C_4H_8O) with tetrachloromethane (CCl_4), trichloromethane ($CHCl_3$), 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$), 1-chlorohexane (1- $C_6H_{13}Cl$), 1-bromohexane (1- $C_6H_{13}Br$), methyl

ethanoate ($CH_3CO_2CH_3$), ethyl ethanoate ($CH_3CO_2C_2H_5$), *n*-butyl ethanoate ($CH_3CO_2C_4H_9$) and *n*-amyl ethanoate ($CH_3CO_2C_5H_{11}$). The results obtained for dynamic viscosity of binary mixtures were used to test the semi-empirical relations of Grunberg–Nissan [7], Tamura–Kurata [8], Hind–McLaughlin–Ubbelohde [9], Katti–Chaudhri [10], McAllister [11], Heric [12], and Auslaender [13]. Finally, the experimental refractive indexes were compared with the predicted results for Lorentz–Lorenz [14,15], Dale–Gladstone [14], Heller [14], Arago–Boit [15], Wiener [15]. Eykman [16], Newton [16], and Oster [16] equations.

2. Experimental

CCl_4 , $CHCl_3$, $CH_3CO_2CH_3$, $CH_3CO_2C_2H_5$, $CH_3CO_2C_4H_9$ and $CH_3CO_2C_5H_{11}$ from BDH of AR grade and $CHCl_2CHCl_2$ from Riedel Dehaenat Seeze-Hannover, 1-

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Table 1

Densities, refractive indexes, speeds of sound, isentropic compressibilities, thermal expansion coefficients and heat capacities for pure liquids at 303.15 K

Liquids	ρ (kg m ⁻³)	n_D	u (m s ⁻¹)	η (mPa s)	α° (kK ⁻¹)	C°_p (J mol ⁻¹ K ⁻¹)
C ₄ H ₈ O	876.70	1.4028	1255	0.4383		
	876.7 ^a	1.4028 ^c	1254 ^b	0.438 ^c	1.243 ^b	125.9 ^b
CCl ₄	1574.82	1.4555	905	0.8441		
	1574.80 ^c	1.4547 ^c	905 ^d	0.845 ^c	1.245 ^c	131.3 ^c
CHCl ₃	1470.59	1.4410	967	0.5100		
	1470.60 ^c	1.4400 ^c	967.5 ^d	0.514 ^c	1.265 ^c	117.0 ^e
CHCl ₂ CHCl ₂	1578.60	1.4881	1135	1.4570		
1-C ₆ H ₁₃ Cl	1578.60 ^c	1.4886 ^c	1134.7 ^f		0.964 ^g	169.8 ^c
	868.78	1.4168	1184	0.6544		
1-C ₆ H ₁₃ Br	873.47 ⁿ	1.4197 ⁿ				
	873.33 ^{n,h}	1.4179 ^{n,i}			1.131 ^g	213.7 ^j
	1162.67	1.4441	1075	0.9030		
	1169.62 ⁿ	1.4464 ⁿ				
CH ₃ CO ₂ CH ₃	1174.40 ^{n,h}	1.4478 ^{n,i}			1.254 ^g	220.0 ^j
	920.83	1.3567	1136	0.3430		
CH ₃ CO ₂ C ₂ H ₅	920.8 ^k	1.3564 ^c	1136 ^l		1.516 ^m	144.9 ^m
	888.55	1.3664	1117	0.4043		
CH ₃ CO ₂ C ₄ H ₉	888.51 ^k	1.36717 ^c	1119 ^l	0.400 ^c	1.392 ^m	168.9 ^m
	870.80	1.3896	1172	0.6453		
CH ₃ CO ₂ C ₅ H ₁₁	871.29 ^c	1.3894 ^c	1170 ^l	0.6444 ^c	1.243 ^m	229.9 ^m
	867.20	1.3961	1197	0.7573		
	867.2 ^c	1.3974 ^c	1197 ^l		1.156 ^m	261.7 ^m

^a Ref. [20].^b Ref. [21].^c Ref. [17].^d Ref. [22].^e Ref. [23].^f Ref. [24].^g Ref. [25].^h Ref. [26].ⁱ Ref. [27].^j Values calculated using Missenard group contribution method [28].^k Ref. [29].^l Ref. [30].^m Ref. [31].ⁿ At 298.15 K.

C₆H₁₃Cl and 1-C₆H₁₃Br from Merck, Bombay were used after further purification by standard procedures [17]. C₄H₈O (Merck, AR) was refluxed for several hours over sodium metal pieces till free from peroxide and finally fractionally distilled over sodium [17]. Immediately before use all liquid samples were dried over molecular sieve 0.4 nm (Fluka) and fractionally distilled twice. The purity of liquid samples tested by gas–liquid chromatography was better than 99.8 mol% for all samples.

The speeds of sound 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 frequencies was employed. The refractive indexes were measured using research refractometer RL₃ made in Poland. The viscosities were measured with a modified suspended-level Ubbelohde viscometer. A water-circulating thermostat with an accuracy of ± 0.02 K was used for controlling the temperature for the speed of sound, refractive index and viscosity measurements. The densities were measured with an Anton Paar vibrating tube digital densimeter (model DMA 60/602)

with a thermostated bath controlled to ± 0.01 K. The details of the apparatus and procedure have been described in previous publications [18,19].

Mixtures were prepared by in all cases by mass using an electronic Mettler (AE 163, Switzerland) balance accurate to 0.1 mg. The possible error in the mole fraction is estimated to be $\pm 1 \times 10^{-4}$. The errors in values of ρ , u , n_D , and η were estimated to be < 0.02 kg m⁻³, 1 m s⁻¹, 0.0002 units, and 0.002 mPa s, respectively. The isentropic compressibilities determined from the relation $\kappa_S = 1/(u^2 \rho)$ are believed to be reliable to ± 1 TPa⁻¹. The experimentally measured physical properties ρ , n_D , u , and η of the pure components agree with the literature data, as shown in Table 1.

3. Results and discussion

The experimental densities ρ , speeds of sound u , isentropic compressibilities κ_S , refractive indexes n_D , and viscosities η for binary mixtures at 303.15 K are given in Table 2. No published work on the speeds of sound, isentropic

Table 2

Densities, speeds of sound, isentropic compressibilities, refractive indexes, and viscosities for tetrahydrofuran binary mixtures at 303.15 K

x_1	ρ (kg m ⁻³)	u (m s ⁻¹)	κ_S TPa ⁻¹	n_D	η (mPa s)
C₄H₈O + CCl₄					
0.1068	1513.72	932	761	1.4519	0.8152
0.2017	1457.18	955	753	1.4486	0.7880
0.3004	1395.97	982	743	1.4451	0.7580
0.3960	1334.07	1008	738	1.4409	0.7210
0.5030	1261.58	1042	730	1.4357	0.6782
0.6000	1192.83	1074	727	1.4304	0.6359
0.6923	1124.71	1109	723	1.4247	0.5916
0.7949	1045.62	1152	721	1.4182	0.5453
0.8889	969.98	1196	721	1.4116	0.4962
C₄H₈O + CHCl₃					
0.1023	1410.89	986	729	1.4380	0.5307
0.2085	1349.01	1006	733	1.4346	0.5467
0.3045	1292.84	1024	738	1.4315	0.5566
0.4278	1220.11	1051	742	1.4273	0.5590
0.5003	1176.98	1070	742	1.4251	0.5580
0.6047	1114.67	1102	739	1.4210	0.5445
0.6976	1058.96	1133	736	1.4168	0.5245
0.8077	992.59	1174	731	1.4121	0.4955
0.8921	941.69	1208	728	1.4079	0.4676
C₄H₈O + CHCl₂CHCl₂					
0.1023	1523.21	1138	507	1.4830	1.3889
0.2128	1460.02	1143	524	1.4760	1.3071
0.3093	1401.59	1149	540	1.4701	1.2270
0.4056	1340.18	1157	557	1.4639	1.1362
0.5093	1270.31	1168	577	1.4556	1.0289
0.6032	1203.28	1180	597	1.4472	0.9116
0.7046	1126.91	1195	621	1.4368	0.7860
0.8008	1050.12	1212	648	1.4268	0.6647
0.8973	968.58	1231	681	1.4160	0.5519
C₄H₈O + 1-C₆H₁₃Cl					
0.1039	869.11	1195	806	1.4161	0.6407
0.3050	870.03	1216	777	1.4142	0.6046
0.5025	871.36	1233	755	1.4122	0.5698
0.7336	873.79	1247	736	1.4088	0.5114
0.9013	875.66	1252	729	1.4053	0.4711
C₄H₈O + 1-C₆H₁₃Br					
0.0976	1146.32	1087	738	1.4420	0.8602
0.3008	1107.30	1119	721	1.4368	0.7753
0.4975	1061.20	1154	708	1.4307	0.6995
0.6960	1002.92	1194	699	1.4223	0.6258
0.9000	924.62	1235	709	1.4105	0.5054
C₄H₈O + CH₃CO₂CH₃					
0.1028	915.90	1151	824	1.3649	0.3512
0.3022	906.64	1178	795	1.3748	0.3672
0.5035	897.56	1204	769	1.3847	0.3841
0.6930	889.35	1226	748	1.3927	0.4035
0.8918	881.07	1246	731	1.4008	0.4251
C₄H₈O + CH₃CO₂C₂H₅					
0.0995	887.39	1129	884	1.3707	0.4078
0.2035	886.11	1141	867	1.3750	0.4082
0.3016	884.98	1153	850	1.3785	0.4085
0.3923	883.95	1165	834	1.3821	0.4091
0.4868	882.82	1177	818	1.3858	0.4111
0.5955	881.45	1192	799	1.3892	0.4147
0.6973	880.21	1206	781	1.3921	0.4184
0.8120	878.89	1224	760	1.3964	0.4236
0.9000	877.84	1238	743	1.3995	0.4287

Table 2 (Continued)

x_1	ρ (kg m ⁻³)	u (m s ⁻¹)	κ_S TPa ⁻¹	n_D	η (mPa s)
C₄H₈O + CH₃CO₂C₄H₉					
0.1033	871.17	1177	829	1.3911	0.6261
0.1989	871.58	1182	821	1.3924	0.6085
0.3041	872.04	1188	812	1.3941	0.5892
0.3995	872.51	1194	804	1.3954	0.5762
0.4967	873.01	1201	794	1.3970	0.5573
0.6013	873.59	1210	782	1.3979	0.5346
0.6979	874.18	1219	770	1.3991	0.5107
0.7978	874.96	1229	757	1.4005	0.4893
0.8999	875.79	1241	741	1.4018	0.4644
C₄H₈O + CH₃CO₂C₅H₁₁					
0.1067	867.69	1198	803	1.3967	0.7426
0.2980	868.75	1203	795	1.3978	0.7005
0.4997	870.25	1212	782	1.3992	0.6373
0.6997	872.25	1224	765	1.4005	0.5686
0.9027	875.00	1242	741	1.4021	0.4829

compressibilities and refractive indexes was found for the present mixtures with which to compare our results.

The values of u and κ_S were fitted to a polynomial equation of the form

$$u \text{ or } \kappa_S = \sum_{i=1}^m A_i X_1^{i-1} \quad (1)$$

The values of coefficients A_i of Eq. (1) and the corresponding standard deviations σ obtained by the method of least squares are given in Table 3.

Table 4 compares the experimental refractive indexes for binary mixtures with the predicted results for Lorentz–Lorenz [14,15], Dale–Gladstone [14], Eykman [16], Arago–Boit [15], Newton [16], Oster [16], Heller [14], and Wiener [15] equations. In Table 4, the root-mean-square deviations of the calculated values are presented. The Lorentz–Lorenz relationship is most suitable for C₄H₈O + CCl₄ and C₄H₈O + CHCl₃. For the remaining mixtures, similar deviations are obtained by using all the equations except Arago–Boit. Highest deviations for the calculated refractive indexes are obtained by using Arago–Boit equation.

Tables 5 and 6 show parameters calculated and the standard deviations between experimental values obtained for viscosities and the predicted results using semi-empirical relations of Grunberg–Nissan [7], Tamura–Kurata [8], Hind–McLaughlin–Ubbelohde [9], Katti–Chaudhri [10], McAllister [11], Heric [12], and Auslaender [13]. As observed, the best accuracy is given for the three-parameter Auslaender equation.

V^E for each mixture was calculated from equation

$$V^E = \frac{\sum(x_i M_i)}{\rho} - \frac{\sum(x_i M_i)}{\rho_i} \quad (2)$$

Table 3
Coefficients A_i of Eq. (1), and standard deviations σ

Property	A_1	A_2	A_3	A_4	A_5	σ
$C_4H_8O + CCl_4$						
u ($m s^{-1}$)	905.1	247.5	-10.0	112.3		0.5
κ_S (TPa^{-1})	774.9	-154.8	224.1	-247.8	127.6	0.7
$C_4H_8O + CHCl_3$						
u ($m s^{-1}$)	967.0	197.5	-141.3	406.6	-175.0	0.6
κ_S (TPa^{-1})	727.1	-8.7	277.9	-548.7	276.8	0.9
$C_4H_8O + CHCl_2CHCl_2$						
u ($m s^{-1}$)	1135.0	20.0	74.7	25.1	0.2	
κ_S (TPa^{-1})	490.9	142.6	74.8	-112.4	128.1	0.3
$C_4H_8O + 1-C_6H_{13}Cl$						
u ($m s^{-1}$)	1183.7	117.0	-31.5	-14.7	0.7	
κ_S (TPa^{-1})	821.5	-170.4	73.0		0.7	
$C_4H_8O + 1-C_6H_{13}Br$						
u ($m s^{-1}$)	1074.9	115.8	112.4	-48.2		0.4
κ_S (TPa^{-1})	743.8	-45.8	-145.1	170.8		0.7
$C_4H_8O + CH_3CO_2CH_3$						
u ($m s^{-1}$)	1135.7	151.7	-31.9			0.5
κ_S (TPa^{-1})	841.1	-173.2	55.9			0.1
$C_4H_8O + CH_3CO_2C_2H_5$						
u ($m s^{-1}$)	1117.0	117.3	3.7	16.9		0.3
κ_S (TPa^{-1})	902.0	-181.7	25.4	-21.8		0.4
$C_4H_8O + CH_3CO_2C_4H_9$						
u ($m s^{-1}$)	1172.0	46.7	12.6	23.6		0.2
κ_S (TPa^{-1})	836.0	-68.2	-23.6	-198		0.4
$C_4H_8O + CH_3CO_2C_5H_{11}$						
u ($m s^{-1}$)	1196.6	15.5	13.4	28.9		0.8
κ_S (TPa^{-1})	804.5	-18.0	-40.4	-21.7		0.9

κ_S^E was calculated from the relation recommended by Benson and Kiyohara [32]

$$\kappa_S^E = \kappa_S - \sum \phi_i \left\{ \frac{\kappa_{S,i}^0 + TV(\alpha_i^0)^2}{C_{P,i}^0} \right\} - \frac{T(\sum X_i V_i^0)(\sum \phi_i \alpha_i^0)^2}{\sum X_i C_{P,i}^0} \quad (3)$$

in which the V_i^0 , α_i^0 and $C_{P,i}^0$ are respectively, the molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component i and $\phi_i = x_i V_i / \sum x_j V_j$ is the volume fraction of i in the mixture, stated in terms of the unmixed components.

The viscosity deviations from a linear dependence on mole fraction $\Delta\eta$ are calculated from

$$\Delta\eta = \eta - \sum_i x_i \eta_i \quad (4)$$

where η and η_i represents the viscosities of the mixture and of the pure component i . On the basis of the theory of absolute reaction rates [33], the excess Gibbs energy of activation ΔG^{*E} of viscous flow may be calculated from

$$\frac{\Delta G^{*H}}{RT} = \ln \frac{\eta V}{\eta_1 V_1} - X_1 \ln \frac{\eta_1 V_1}{\eta_2 V_2} \quad (5)$$

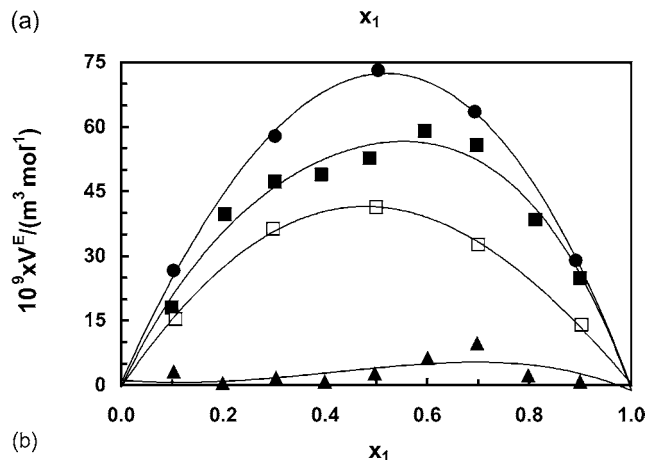
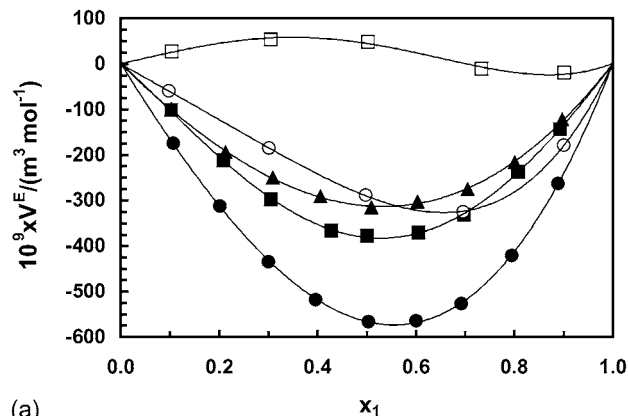


Fig. 1. (a) Excess molar volumes for tetrahydrofuran + haloalkane at 303.15 K. Experimental points: CCl_4 (●), $CHCl_3$ (■), $CHCl_2CHCl_2$ (▲), $1-C_6H_{13}Cl$ (□), $1-C_6H_{13}Br$ (○). (b) Excess molar volumes for tetrahydrofuran + alkyl ethanoate at 303.15 K. Experimental points: $CH_3CO_2CH_3$ (●), $CH_3CO_2C_2H_5$ (■), $CH_3CO_2C_4H_9$ (▲), $CH_3CO_2C_5H_{11}$ (□).

where V is the molar volume of the mixture and V_i the molar volume of the pure component i . The estimated accuracy in the values of V^E , κ_S^E , $\Delta\eta$, and ΔG^{*E} is within $5 \times 10^{-9} m^3 mol^{-1}$, $1 TPa^{-1}$, $0.002 mPa s$, and $15 J mol^{-1}$.

The values of V^E , κ_S^E , and ΔG^{*E} for the mixture were smoothed to a Redlich–Kister polynomial regression of the type

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

where $\psi^E = V^E$, κ_S^E , and ΔG^{*E}

The values of coefficients B_i of Eq. (6) and the corresponding standard deviations σ are given in Table 7. The limiting values of excess partial molar volumes of cyclic ethers $V_1^{E,\infty}$ at infinite dilution in different solvents provide additional information regarding molecular interactions [34]. The values of $V_1^{E,\infty}$ were evaluated from coefficients B_i of Eq. (6) as to the V^E results, as $\sum_{i=1}^m B_i$. The values of $V_1^{E,\infty}$ of tetrahydrofuran are also compared with p -dioxane at infinite dilution in various solvents in Table 8.

Fig. 1 shows that the values of V^E for the mixtures $C_4H_8O + CH_3CO_2CH_3$, $C_4H_8O + CH_3CO_2C_2H_5$ and $C_4H_8O +$

Table 4

Standard deviations of the experimental refractive index results from predicted for the Lorentz–Lorenz (L–L), Dale–Gladstone (G–D), Eykman (Eyk), Arago–Boit (A–B), Newton (Nw), Oster (Os), Heller (He), and Wiener (Wi) equations

L–L	G–D	Eyk	A–B	Nw	Os	He	Wi
C₄H₈O + CCl₄							
0.0037	0.0035	0.0036	0.0035	0.0033	0.0034	0.0037	0.0036
0.0011 ^a	0.0013 ^a	0.0012 ^a	0.0037 ^a	0.0014 ^a	0.0013 ^a		
C₄H₈O + CHCl₃							
0.0025	0.0024	0.0024	0.0024	0.0023	0.0024	0.0025	0.0024
0.0008 ^a	0.0009 ^a	0.0008 ^a	0.0027 ^a	0.0010 ^a	0.0009 ^a		
C₄H₈O + CHCl₂CHCl₂							
0.0046	0.0041	0.0042	0.0041	0.0036	0.0038	0.0046	0.0043
0.0031 ^a	0.0028 ^a	0.0029 ^a	0.0040 ^a	0.0025 ^a	0.0026 ^a		
C₄H₈O + 1-C₆H₁₃Cl							
0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
0.0006 ^a	0.0005 ^a	0.0005 ^a	0.0008 ^a	0.0005 ^a	0.0005 ^a		
C₄H₈O + 1-C₆H₁₃Br							
0.0014	0.0013	0.0013	0.0013	0.0012	0.0012	0.0014	0.0013
0.0003 ^a	0.0003 ^a	0.0003 ^a	0.0019 ^a	0.0004 ^a	0.0003 ^a		
C₄H₈O + CH₃CO₂CH₃							
0.0029	0.0030	0.0030	0.0037	0.0030	0.0030	0.0029	0.0030
0.0029 ^a	0.0029 ^a	0.0028 ^a	0.0029 ^a	0.0029 ^a	0.0029 ^a		
C₄H₈O + CH₃CO₂C₂H₅							
0.0024	0.0023	0.0023	0.0023	0.0022	0.0023	0.0024	0.0023
0.0026 ^a	0.0025 ^a	0.0025 ^a	0.0030 ^a	0.0024 ^a	0.0024 ^a		
C₄H₈O + CH₃CO₂C₄H₉							
0.0017	0.0016	0.0016	0.0016	0.0016	0.0016	0.0017	0.0016
0.0017 ^a	0.0017 ^a	0.0017 ^a	0.0017 ^a	0.0016 ^a	0.0016 ^a		
C₄H₈O + CH₃CO₂C₅H₁₁							
0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
0.0006 ^a	0.0006 ^a	0.0006 ^a	0.0009 ^a	0.0006 ^a	0.0006 ^a		

^a Non additivity on mixing.

Table 5

Values of parameters in Grunberg–Nissan (G_{12}), Tamura–Kurata (C), Hind–McLaughlin–Ubbelohde (η_{12}), Katti–Chaudhri (W_{vis}/RT) equations, and standard percentage deviations $\sigma(\%)$ in correlating viscosity of binary mixtures at 303.15 K

Mixture	G_{12}	$\sigma(\%)$	C	$\sigma(\%)$	η_{12}	$\sigma(\%)$	W_{vis}/RT	$\sigma(\%)$
C ₄ H ₈ O + CCl ₄	0.45	0.66	0.70	0.51	0.72	0.36	0.44	0.60
CHCl ₃	0.62	0.72	0.63	0.97	0.63	0.98	0.60	0.71
CHCl ₂ CHCl ₂	1.01	1.62	1.04	2.59	1.10	2.20	1.03	1.62
1-C ₆ H ₁₃ Cl	0.26	0.81	0.59	0.38	0.60	0.49	0.40	0.96
1-C ₆ H ₁₃ Br	0.46	2.65	0.69	1.34	0.73	1.63	0.60	2.78
CH ₃ CO ₂ CH ₃	−0.03	0.15	0.38	0.18	0.38	0.17	−0.03	0.14
CH ₃ CO ₂ C ₂ H ₅	−0.09	0.46	0.41	0.42	0.40	0.49	−0.07	0.45
CH ₃ CO ₂ C ₄ H ₉	0.17	0.54	0.56	0.30	0.57	0.38	0.28	0.68
CH ₃ CO ₂ C ₅ H ₁₁	0.43	0.62	0.67	1.13	0.68	0.44	0.62	0.88
Average ($\sigma(\%)$)		0.92		0.87		0.79		0.98

CH₃CO₂C₅H₁₁ are small and positive, while for C₄H₈O + CCl₄, C₄H₈O + CHCl₃, C₄H₈O + CHCl₂CHCl₂, and C₄H₈O + 1-C₆H₁₃Br are negative. For C₄H₈O + 1-C₆H₁₃Cl, the values of V^E are both small positive and small negative. The V^E for C₄H₈O + CCl₄, C₄H₈O + CHCl₃, C₄H₈O + CHCl₂CHCl₂ and C₄H₈O + CH₃CO₂C₂H₅ mixtures have been reported in the literature [35–38]. The present V^E values for C₄H₈O + CCl₄, C₄H₈O + CHCl₃ and C₄H₈O + CH₃CO₂C₂H₅ are in reasonable agreement with literature values. However, equimolar literature V^E $-617 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ [38]

for C₄H₈O + CHCl₂CHCl₂ is quite different than the present value $-313.2 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$. The values of κ_S^E (Fig. 2) for the mixtures C₄H₈O + CCl₄, C₄H₈O + CHCl₂CHCl₂, C₄H₈O + 1-C₆H₁₃Cl, C₄H₈O + 1-C₆H₁₃Br, C₄H₈O + CH₃CO₂CH₃ and C₄H₈O + CH₃CO₂C₂H₅ are negative, while for C₄H₈O + CH₃CO₂C₅H₁₁ C₄H₈O + CHCl₃ are positive. For C₄H₈O + CH₃CO₂C₄H₉ the values of V^E and κ_S^E are almost zero. The $\Delta\eta$ and ΔG^{*E} in Figs. 3 and 4 show positive values for the binary mixtures C₄H₈O + CCl₄, C₄H₈O + CHCl₃, C₄H₈O + CHCl₂CHCl₂, C₄H₈O + 1-C₆H₁₃Cl, C₄H₈O + 1-C₆H₁₃Br,

Table 6

Values of the parameters in McAllister (Z_{12} and Z_{21}), Heric (α_{12} and α_{21}), Auslaender (B_{12} , A_{21} , and B_{21}) equations and standard percentage deviations σ (%) in correlating viscosities of binary mixtures at 303.15 K

Mixture	Z_{12}	Z_{21}	σ (%)	α_{12}	α_{21}	σ (%)	B_{12}	A_{21}	B_{21}	σ (%)
C ₄ H ₈ O + CCl ₄	0.57	0.56	0.22	0.44	0.08	0.22	0.54	0.93	1.44	0.26
CHCl ₃	0.52	0.47	0.77	0.60	-0.04	0.77	-3.06	1.05	3.85	0.40
CHCl ₂ CHCl ₂	0.85	0.92	0.42	1.03	0.20	0.42	2.31	3.76	0.25	0.59
1-C ₆ H ₁₃ Cl	0.66	0.70	0.55	0.40	0.11	0.55	-0.27	-0.46	-3.47	0.43
1-C ₆ H ₁₃ Br	0.73	0.68	0.84	0.60	0.34	0.84	1.43	1.46	1.10	0.37
CH ₃ CO ₂ CH ₃	0.45	0.41	0.13	-0.03	-0.01	0.13	-0.02	-0.04	-35.04	0.12
CH ₃ CO ₂ C ₂ H ₅	0.46	0.47	0.17	-0.07	-0.06	0.17	-0.32	-1.02	-3.32	0.13
CH ₃ CO ₂ C ₄ H ₉	0.63	0.68	0.19	0.28	0.09	0.19	-0.05	-0.08	-16.45	0.22
CH ₃ CO ₂ C ₅ H ₁₁	0.73	0.83	0.51	0.62	0.10	0.51	0.14	0.47	3.15	0.29
Average (σ %)			0.42			0.42				0.31

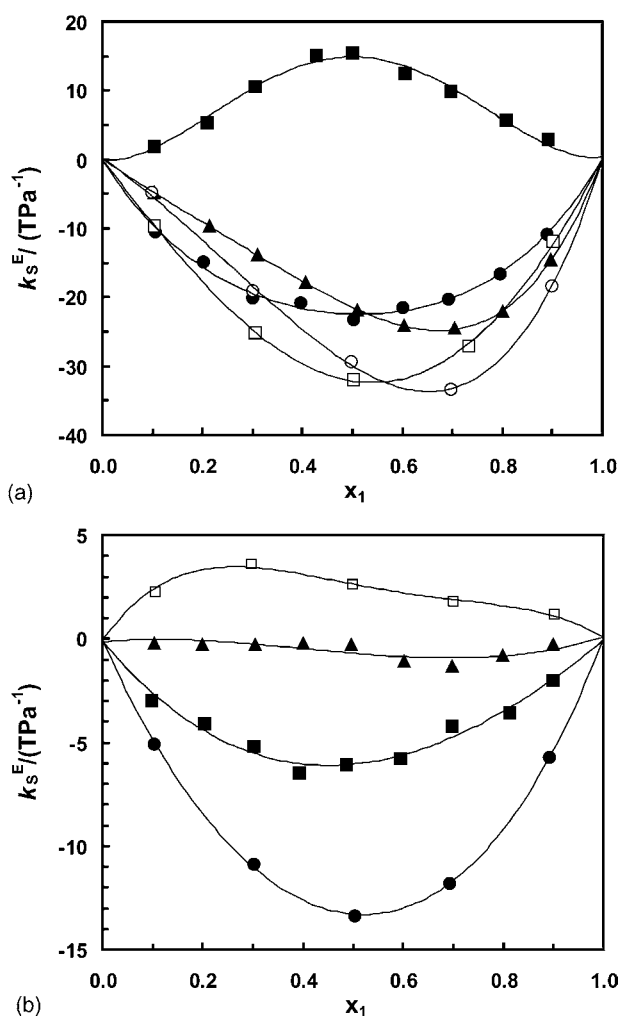


Fig. 2. (a) Excess isentropic compressibility for tetrahydrofuran + haloalkane at 303.15 K. Experimental points: CCl₄ (●), CHCl₃ (■), CHCl₂CHCl₂ (▲), 1-C₆H₁₃Cl (□), 1-C₆H₁₃Br (○). (b) Excess isentropic compressibility for tetrahydrofuran + alkyl ethanoate at 303.15 K. Experimental points: CH₃CO₂CH₃ (●), CH₃CO₂C₂H₅ (■), CH₃CO₂C₄H₉ (▲), CH₃CO₂C₅H₁₁ (□).

Table 7

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

Mixture	Property	B_1	B_2	B_3	B_4	σ
C ₄ H ₈ O + CCl ₄	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	-2260.4	530.2			2.5
	κ_S^E (TPa^{-1})	-89.1	2.4	-31.9		0.7
	ΔG^{*E} (J mol^{-1})	1090.1	-198.1	47.1		5.4
CHCl ₃	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	-1529.1	225.9	358.1		3.3
	κ_S^E (TPa^{-1})	58.4	-3.7	-57.5		1.0
	ΔG^{*E} (J mol^{-1})	1611.9	-117.9	-400.5	443.1	4.6
CHCl ₂ CHCl ₂	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	-1252.6	163.0	55.8		3.3
	κ_S^E (TPa^{-1})	-86.0	67.3	-30.3		0.1
	ΔG^{*E} (J mol^{-1})	2640.7	-512.9	-207.0		2.8
1-C ₆ H ₁₃ Cl	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	170.2	326.8	-216.2		6.3
	κ_S^E (TPa^{-1})	-129.5	20.6	16.8		0.6
	ΔG^{*E} (J mol^{-1})	926.6	-267.8	231.7		12.6
1-C ₆ H ₁₃ Br	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	-1164.4	820.4	-263.2		2.1
	κ_S^E (TPa^{-1})	-120.6	91.4	-13.9		0.8
	ΔG^{*E} (J mol^{-1})	1399.6	-869.4	355.6		0.3
CH ₃ CO ₂ CH ₃	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	290.8	-12.3			1.6
	κ_S^E (TPa^{-1})	-53.0	2.9	-6.6		0.2
	ΔG^{*E} (J mol^{-1})	-82.3	35.2	33.3		2.4
CH ₃ CO ₂ C ₂ H ₅	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	229.2	-36.1	26.0		3.6
	κ_S^E (TPa^{-1})	-25.0	-5.2			0.4
	ΔG^{*E} (J mol^{-1})	-179.9	149.4			4.5
CH ₃ CO ₂ C ₄ H ₉	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	16.0	-2.7	3.8		3.2
	κ_S^E (TPa^{-1})	-2.9	2.2			0.3
	ΔG^{*E} (J mol^{-1})	727.6	-213.8	-66.5		3.3
CH ₃ CO ₂ C ₅ H ₁₁	$10^9 V^E$ ($\text{m}^3 \text{mol}^{-1}$)	163.1	5.8			1.3
	κ_S^E (TPa^{-1})	10.6	7.6	13.3		0.3
	ΔG^{*E} (J mol^{-1})	1495.8	-239.0	180.3		6.3

Table 8

The limiting values of excess partial molar volumes of C₄H₈O at infinite dilution $V_1^{E,\infty}$ in different solvents at 303.15 K

Solvent	$10^6 \times V_1^{E,\infty}$ ($\text{m}^3 \text{mol}^{-1}$)	Solvent	$10^6 \times V_1^{E,\infty}$ ($\text{m}^3 \text{mol}^{-1}$)
CCl ₄	-1.73, -1.93 ^a	CH ₃ CO ₂ CH ₃	0.28
CHCl ₃	-0.95	CH ₃ CO ₂ C ₂ H ₅	0.22
CHCl ₂ CHCl ₂	-1.03	CH ₃ CO ₂ C ₄ H ₉	0.02
1-C ₆ H ₁₃ Cl	0.28	CH ₃ CO ₂ C ₅ H ₁₁	0.17
1-C ₆ H ₁₃ Br	-0.61		

^a Ref. [35].

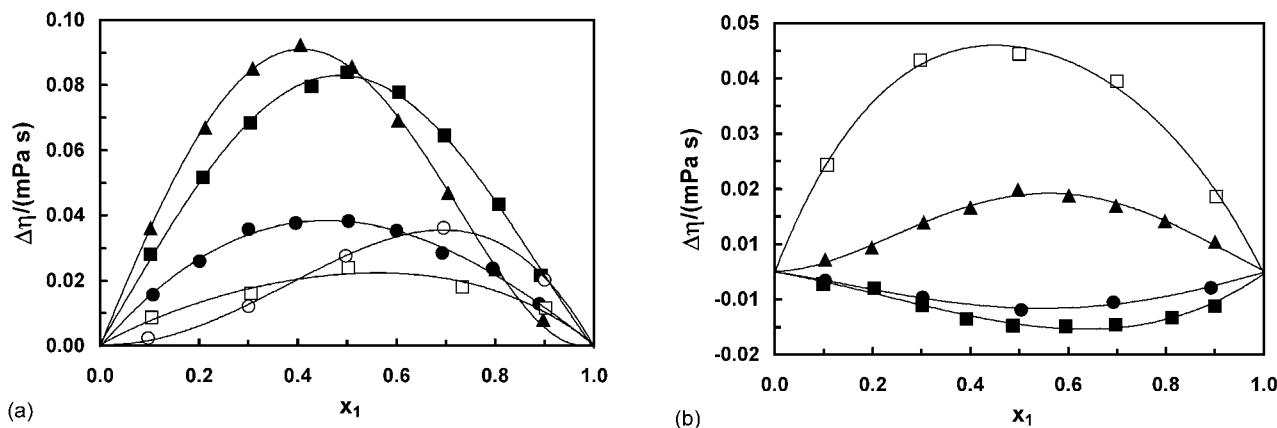


Fig. 3. (a) Viscosity deviations in for tetrahydrofuran + haloalkane at 303.15 K. Experimental points: CCl_4 (●), CHCl_3 (■), $\text{CHCl}_2\text{CHCl}_2$ (▲), $1\text{-C}_6\text{H}_{13}\text{Cl}$ (□), $1\text{-C}_6\text{H}_{13}\text{Br}$ (○). (b) Viscosity deviations in for tetrahydrofuran + alkyl ethanoate at 303.15 K. Experimental points: $\text{CH}_3\text{CO}_2\text{CH}_3$ (●), $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ (■), $\text{CH}_3\text{CO}_2\text{C}_4\text{H}_9$ (▲), $\text{CH}_3\text{CO}_2\text{C}_5\text{H}_{11}$ (□).

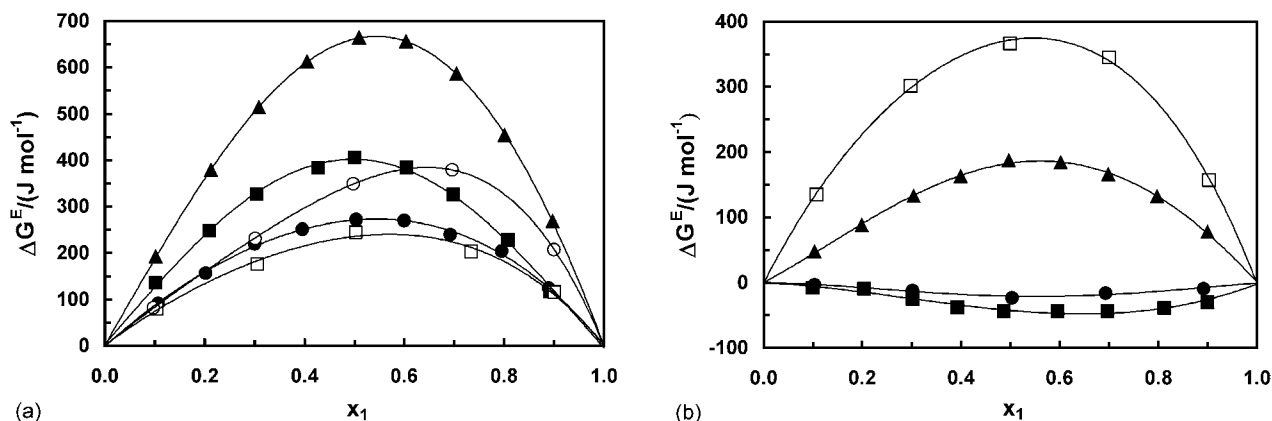


Fig. 4. (a) Excess Gibbs energy of activation of viscous flow for tetrahydrofuran + haloalkane at 303.15 K. Experimental points: CCl_4 (●), CHCl_3 (■), $\text{CHCl}_2\text{CHCl}_2$ (▲), $1\text{-C}_6\text{H}_{13}\text{Cl}$ (□), $1\text{-C}_6\text{H}_{13}\text{Br}$ (○). (b) Excess Gibbs energy of activation of viscous flow for tetrahydrofuran + alkyl ethanoate at 303.15 K. Experimental points: $\text{CH}_3\text{CO}_2\text{CH}_3$ (●), $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ (■), $\text{CH}_3\text{CO}_2\text{C}_4\text{H}_9$ (▲), $\text{CH}_3\text{CO}_2\text{C}_5\text{H}_{11}$ (□).

$\text{C}_4\text{H}_8\text{O} + \text{CH}_3\text{CO}_2\text{C}_4\text{H}_9$, $\text{C}_4\text{H}_8\text{O} + \text{CH}_3\text{CO}_2\text{C}_5\text{H}_{11}$ while negative values for $\text{C}_4\text{H}_8\text{O} + \text{CH}_3\text{CO}_2\text{CH}_3$ and $\text{C}_4\text{H}_8\text{O} + \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$.

References

- [1] D.D. Deshpande, S.L. Oswal, *J. Chem. Thermodyn.* 7 (1975) 155–159.
- [2] S.L. Oswal, R.P. Phalak, *Int. J. Thermophys.* 13 (1992) 251–267.
- [3] S.L. Oswal, R.P. Phalak, *J. Solution Chem.* 22 (1993) 43–58.
- [4] S.L. Oswal, P. Oswal, R.P. Phalak, *Int. J. Thermophys.* 17 (1996) 1255–1267.
- [5] S.L. Oswal, P. Oswal, R.P. Phalak, *J. Solution Chem.* 27 (1998) 507–520.
- [6] S.L. Oswal, R.L. Gardas, R.P. Phalak, *J. Mol. Liquid* (in press).
- [7] L. Grunberg, A.H. Nissan, *Nature* 164 (1949) 799–800.
- [8] M. Tamura, M. Kurata, *Bull. Chem. Soc. Jpn.* 25 (1952) 32–37.
- [9] R.K. Hind, E. McLaughlin, A.R. Ubbelohde, *Trans. Faraday Soc.* 56 (1960) 328–334.
- [10] P.K. Katti, M.M. Chaudhri, *J. Chem. Eng. Data* 9 (1964) 442–443.
- [11] R.A. McAllister, *AIChE J.* 6 (1960) 427–431.
- [12] E.L. Heric, *J. Chem. Eng. Data* 11 (1966) 66–68.
- [13] G. Auslaender, *Brit. Chem. Eng.* 9 (1964) 610–618.
- [14] W. Heller, *J. Phys. Chem.* 69 (1965) 1123–1129.
- [15] A.Z. Tasic, B.D. Djordjevic, D.K. Grozdanic, *J. Chem. Eng. Data* 37 (1992) 310–313.
- [16] A. Pineiro, P. Brocos, A. Amigo, M. Pintos, R. Bravo, *J. Chem. Thermodyn.* 31 (1999) 931–942.
- [17] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic Solvents Physical Properties and Methods of Purification*, Wiley, New York, 1986.
- [18] S.L. Oswal, P.P. Palsanawala, *Acoust. Lett.* 13 (4) (1989) 66–73.
- [19] S.G. Patel, S.L. Oswal, *J. Chem. Soc. Faraday Trans.* 88 (1992) 2497–2502.
- [20] S.S. Joshi, T.M. Aminabhavi, R.H. Balundgi, *Ind. J. Tech.* 29 (1991) 541–544.
- [21] S. Rodriguez, C. Lafuente, H. Artigas, F.M. Royo, J.S. Urieta, *J. Chem. Thermodyn.* 31 (1999) 139–149.
- [22] R.T. Legmann, D.R. Mcmillan, W.E. Woolf, *J. Chem. Phys.* 17 (1949) 369–373.
- [23] E.B. Freyer, J.C. Hubbard, D.H. Andrews, *J. Am. Chem. Soc.* 51 (1929) 759–770.
- [24] M. Aoi, K. Arakawa, *Bull. Chem. Soc. Jpn.* 53 (1980) 845–849.
- [25] S.L. Oswal, B.M. Patel, A.M. Patel, N.Y. Ghael, *Fluid Phase Equilib.* 206 (2003) 313–329.

- [26] J. Ortega, J.S. Matos, *J. Chem. Eng. Data* 32 (1987) 464–466.
- [27] R.C. Weast, *Hand Book of Chemistry and Physics*, 59th ed., Chemical Rubber Co, Cleveland, OH, 1979.
- [28] F.A. Missenard, in: R.C. Reid, J.M. Prausnitz, B.E. Poling (Eds.), *The Properties of Gases and Liquids*, fourth ed., McGraw-Hill, 1987.
- [29] J. Timmermans, *Physico Chemical Constant of Pure Organic Compounds*, 1965.
- [30] R.T. Lagemann, E.G. McLeroy, O. Milner, *J. Am. Chem. Soc.* 73 (1951) 5891.
- [31] S.L. Oswal, P. Oswal, P.S. Modi, J.P. Dave, R.L. Gardas, *Thermochim. Acta* 410 (2004) 1–14.
- [32] G.C. Benson, O. Kiyohara, *J. Chem. Thermodyn.* 11 (1979) 161–164.
- [33] S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw-Hill, New York, 1941.
- [34] K. Nakanishi, H. Shairai, *Bull. Chem. Soc. Jpn.* 43 (1970) 1634–1642.
- [35] M.D. Guillen, C. Gutierrez Losa, *J. Chem. Thermodyn.* 10 (1978) 567–576.
- [36] D.V.S. Jain, S.B. Saini, V. Chaudhry, *Ind. J. Chem.* 18A (1979) 198–200.
- [37] S.K. Suri, B.J. Chawla, *J. Chem. Eng. Data* 26 (1981) 268–270.
- [38] S.C. Sharma, L.M. Joshi, J. Singh, *J. Chem. Thermodyn.* 21 (1989) 331.