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Viscosity of Binary Mixtures of Alkyl Acetates with Hexane, Tetrachloromethane, and Trichloromethane

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The viscosity η for binary mixtures of methyl acetate (MA), ethyl acetate (EA), *n*-amyl acetate (nAA), isoamyl acetate (iAA), decyl acetate (DeA), and dodecyl acetate (DoA) with hexane and of MA, EA, nAA, and iAA with tetrachloromethane and trichloromethane has been measured at 303.15 K over the entire range of composition. The viscosity data have been correlated with the equations of Grunberg and Nissan; Hind, McLaughlin, and Ubbelohde; Tamura and Kurata; Katti and Chaudhri; McAllister; Heric and Brewer; and Auslaender. The viscosity deviations $\Delta\eta$ and excess Gibbs energy of activation ΔG^{*E} of viscous flow based on Eyring's theory have been calculated. The results have been analyzed in terms of disruption of dipolar association of alkyl acetate and molecular interaction between alkyl acetate and chloromethane.

KEY WORDS: alkyl acetate; chloromethane; Gibbs energy of activation; hexane; liquid mixtures; molecular interactions; tetrachloromethane; trichloromethane; viscosity.

1. INTRODUCTION

In a previous paper [1] measurements of excess molar volumes for binary mixtures of methyl acetate (MA), ethyl acetate (EA), *n*-amyl acetate (nAA), and isoamyl acetate (iAA) with C_6H_{14}, CCl_4, and $CHCl_3$ have been reported. The results indicated specific interactions between alkyl acetate and chloroalkane. To confirm the earlier conclusion, it has been judged necessary to employ viscosity measurements, as such studies provide significant information for the elucidation of the fundamental behavior of liquid mixtures and for the prediction of molecular interactions

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operating between like and unlike pairs. This study will also be useful to examine various empirical equations used to correlate viscosity data of binary mixtures.

2. EXPERIMENTAL

The source and purification process of pure liquids MA, EA, nAA, iAA, hexane, tetrachloromethane, and trichloromethane have been described in our earlier paper [1]. Decyl acetate and dodecyl acetate were prepared by dissolving decan-1-ol (Merck, Schuchardt; 97%) and dodecan-1-ol (Koch-Light), respectively, in excess acetic anhydride (AnalaR) in the presence of dry pyridine [2]. 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 by measuring their physical properties. They were better than 99.8 mol% for all samples except decyl and dodecyl acetates, where it was better than 99 mol%.

The viscosity η was measured with a modified Ubbelohde suspended-level viscometer [3]. The viscometer was designed so as to reduce surface tension effects to negligible values [4]. The details of the experimental procedure have been described earlier [6]. The apparatus was submerged in a thermostatic bath maintained constant at 303.15 ± 0.05 K. The viscometer has been calibrated so as to determine the two constants C and B in the equation $\eta/\rho = Ct - B/t$, obtained by measuring the flow time t with pure water, benzene, and cyclohexane [5]. Flow time for doubly distilled water was more than 210 s. The flow time of a definite volume of liquid through the capillary was measured with an accurate stopwatch with a precision of ± 0.1 s. Four or five sets of readings for the flow times were taken for each pure liquid or liquid mixture and the arithmetic mean was taken for the calculations. The densities ρ required to convert kinematic viscosities into dynamic viscosities η were taken from our previous papers [1, 2] and were obtained with an Anton Paar vibrating-tube densimeter (DMA 60/602) with a thermostated bath controlled to ± 0.01 K.

The mixtures were prepared by mixing known masses of pure liquids in airtight narrow-mouth stoppered bottles. All the mass measurements were performed on an electronic balance (Mettler AE 163; Switzerland) with a precision of ± 0.1 mg, and the possible error in the mole fractions is estimated to be $< 10^4$. The error in viscosity η is estimated to be less than 0.002 mPa · s.

3. RESULTS

The experimental viscosity data of binary mixtures at 303.15 K are presented in Table I. For a compact and smooth representation, the values of η were fitted to a polynomial equation of the form

$$\eta = \sum_{i=0}^{m} A_i x_1^i \tag{1}$$

The coefficients A_i obtained from a least-squares fit with equal weights assigned to each point are listed in Table II together with the standard deviations σ.

The viscosity deviations from a linear dependence on mole fraction are calculated from

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i \eta_i \tag{2}$$

where η and η_i represent the viscosities of the mixture and of the pure component i. On the basis of the theory of absolute reaction rates [7], the excess Gibbs energy of activation $\Delta G^{*\mathrm{E}}$ of viscous flow may be calculated from

$$\Delta G^{*\mathrm{E}}/RT = \{\ln(\eta V/\eta_2 V_2) - x_1 \ln(\eta_1 V_1/\eta_2 V_2)\} \tag{3}$$

where V is the molar volume of the mixture and V_i is the molar volume of the pure component i. $\Delta G^{*\mathrm{E}}$ data are included in Table I. The estimated uncertainty of $\Delta G^{*\mathrm{E}}$ is about 15 J · mol^{-1}. The values of $\Delta\eta$ and $\Delta G^{*\mathrm{E}}/RT$ for each mixture have been fitted to the Redlich–Kister polynomial equation

$$Y^{\mathrm{E}} = x_1(1 - x_1) \sum_{i=0}^{m} A_i (1 - 2x_1)^i \tag{4}$$

The coefficients A_i of Eq. (4), and the standard deviations σ are given in Table III.

4. CORRELATING EQUATIONS

Apart from expressing η as a polynomial fit, several semiempirical relations have been proposed to estimate the dynamic viscosity η of liquid mixtures in terms of pure-component data [8, 9]. We have examined equations proposed by Grunberg and Nissan [10], Tamura and Kurata [11],

Table I. Viscosities and Gibbs Energies of Activation of Viscous Flow of Binary Mixtures at 303.15 K

x_1	η (mPa · s)	ΔG^{*E} (J · mol^{-1})
(1) MA + C_6H_{14}		
0.0000	0.2776	
0.1069	0.2760	−31
0.2040	0.2755	−60
0.3060	0.2772	−77
0.4060	0.2809	−84
0.4998	0.2857	−86
0.6020	0.2937	−74
0.6984	0.3048	−43
0.8014	0.3165	−26
0.8998	0.3298	−9
1.0000	0.3448	
(2) EA + C_6H_{14}		
0.0000	0.2776	
0.1060	0.2774	−81
0.1995	0.2799	−132
0.3097	0.2869	−162
0.4073	0.2945	−181
0.5055	0.3045	−186
0.6094	0.3179	−177
0.7062	0.3331	−155
0.8061	0.3523	−115
0.9036	0.3748	−62
1.0000	0.4005	
(3) nAA + C_6H_{14}		
0.0000	0.2776	
0.1004	0.3030	−27
0.2054	0.3329	−51
0.2980	0.3626	−67
0.4030	0.4007	−78
0.5009	0.4430	−71
0.6017	0.4937	−52
0.6958	0.5456	−37
0.8016	0.6101	−23
0.8978	0.6752	−12
1.0000	0.7522	
(4) DeA + C_6H_{14}		
0.0000	0.2776	
0.2001	0.4713	364
0.4057	0.7528	513
0.5086	0.9289	513
0.5995	1.1162	502
0.7551	1.4731	376
1.0000	2.1455	
(5) DoA + C_6H_{14}		
0.0000	0.2776	
0.1919	0.5038	434
0.3182	0.7197	587
0.4783	1.0787	657
0.5220	1.2000	657
0.7480	1.9580	477
1.0000	3.0894	
(6) MA + CCl_4		
0.0000	0.8427	
0.1004	0.7630	−17
0.1926	0.7035	−9
0.2864	0.6472	−4
0.4018	0.5870	11
0.5025	0.5405	32
0.6004	0.5006	58
0.7001	0.4608	72
0.8964	0.3807	24
1.0000	0.3448	
(7) EA + CCl_4		
0.0000	0.8427	
0.1014	0.7580	−76
0.1972	0.6991	−100
0.2976	0.6483	−101
0.3940	0.6016	−109
0.4966	0.5603	−96
0.5986	0.5236	−76

Table I. *(Continued)*

x_1	η (mPa·s)	ΔG^{*E} (J·mol^{-1})
0.6989	0.4883	−64
0.8020	0.4572	−37
0.8980	0.4289	−18
1.0000	0.4005	
(8) nAA + CCl_4		
0.0000	0.8427	
0.0945	0.8029	−74
0.1925	0.7788	−107
0.3042	0.7586	−129
0.4017	0.7482	−131
0.5021	0.7413	−124
0.6003	0.7378	−111
0.7016	0.7385	−88
0.8080	0.7427	−55
0.9075	0.7460	−30
1.0000	0.7522	
(9) iAA + CCl_4		
0.0000	0.8427	
0.1037	0.8143	−15
0.1985	0.8011	3
0.3020	0.7904	29
0.4018	0.7782	42
0.5027	0.7656	49
0.6030	0.7549	56
0.7015	0.7451	62
0.7985	0.7325	54
0.9013	0.7155	27
1.0000	0.6997	
(10) MA + $CHCl_3$		
0.0000	0.5129	
0.1026	0.5228	154
0.2027	0.5250	269
0.3012	0.5197	346
0.4009	0.5018	360
0.5028	0.4782	342
0.6033	0.4508	294
0.7158	0.4176	211
0.8130	0.3893	127
0.8983	0.3686	71
1.0000	0.3448	
(11) EA + $CHCl_3$		
0.0000	0.5129	
0.1062	0.5361	181
0.2031	0.5455	288
0.3050	0.5471	362
0.4094	0.5381	387
0.5069	0.5255	389
0.6112	0.5028	342
0.8080	0.4504	184
0.9027	0.4254	95
1.0000	0.4005	
(12) nAA + $CHCl_3$		
0.0000	0.5129	
0.0995	0.5918	312
0.2017	0.6667	549
0.2998	0.7250	686
0.3984	0.7678	745
0.5049	0.7991	743
0.5912	0.8048	670
0.7005	0.8002	532
0.8153	0.7844	344
0.8911	0.7722	209
1.0000	0.7522	
(13) iAA + $CHCl_3$		
0.0000	0.5129	
0.1037	0.5821	288
0.2076	0.6427	492
0.3010	0.6846	597
0.3983	0.7145	639
0.5044	0.7309	613
0.6009	0.7377	551
0.6966	0.7338	447
0.8058	0.7252	306
0.8911	0.7143	176
1.0000	0.6997	

Table II. Coefficients A_i and Standard Deviations $\sigma(\eta)$ of Eq. (1) for the Viscosity η (mPa·s) of Binary Mixtures

Mixture	A_0	A_1	A_2	A_3	A_4	$\sigma(\eta)$
MA + C_6H_{14}	0.2781	−0.0361	0.1085	−0.0053		0.0006
EA + C_6H_{14}	0.2770	−0.0007	0.0906	0.0333		0.0006
AA + C_6H_{14}	0.2783	0.2194	0.1909	0.0639		0.0009
DeA + C_6H_{14}	0.2776	0.8342	0.4689	1.0939	−0.5292	0.0028
DoA + C_6H_{14}	0.2775	0.9506	0.9686	1.4026	−0.5098	0.0020
MA + CCl_4	0.8416	−0.8166	0.5498	−0.2319		0.0020
EA + CCl_4	0.8416	−0.8928	1.0252	−0.8956	0.3220	0.0018
nAA + CCl_4	0.8404	−0.4079	0.5110	−0.1925		0.0019
iAA + CCl_4	0.8402	−0.2344	0.2524	−0.1596		0.0023
MA + $CHCl_3$	0.5113	0.2041	−0.7083	0.3375		0.0016
EA + $CHCl_3$	0.5124	0.2918	−0.6620	0.2575		0.0011
nAA + $CHCl_3$	0.5126	0.8220	−0.0690	−1.2554	0.7427	0.0016
iAA + $CHCl_3$	0.5121	0.7530	−0.5397	−0.3285	0.3034	0.0014

Table III. Coefficients A_i and Standard Deviations σ of Eq. (4)

Mixture	Property	A_0	A_1	A_2	σ
MA + C_6H_{14}	$\Delta\eta$ (mPa·s)	−0.0968	−0.0015		0.0008
	$\Delta G^{*E}/RT$	−0.1318	−0.0618	0.0722	0.0015
EA + C_6H_{14}	$\Delta\eta$ (mPa·s)	−0.1446	0.0143		0.0008
	$\Delta G^{*E}/RT$	−0.3046	−0.0283		0.0020
AA + C_6H_{14}	$\Delta\eta$ (mPa·s)	−0.2824	0.0370		0.0011
	$\Delta G^{*E}/RT$	−0.1082	−0.0517	0.0379	0.0021
DeA + C_6H_{14}	$\Delta\eta$ (mPa·s)	−1.1832	0.0198	0.1274	0.0028
	$\Delta G^{*E}/RT$	0.8276	0.0737	0.0847	0.0030
DoA + C_6H_{14}	$\Delta\eta$ (mPa·s)	−2.1797	0.1894	0.1204	0.0020
	$\Delta G^{*E}/RT$	1.0474	0.0914		0.0015
MA + CCl_4	$\Delta\eta$ (mPa·s)	−0.2008	−0.1013	−0.0686	0.0019
	$\Delta G^{*E}/RT$	0.0655	−0.1250	−0.0690	0.0044
EA + CCl_4	$\Delta\eta$ (mPa·s)	−0.2456	−0.1438	−0.0956	0.0023
	$\Delta G^{*E}/RT$	−0.1463	−0.1398	−0.0862	0.0028
nAA + CCl_4	$\Delta\eta$ (mPa·s)	−0.2213	−0.1084	−0.0649	0.0016
	$\Delta G^{*E}/RT$	−0.1949	−0.1135	−0.0669	0.0019
nAA + CCl_4	$\Delta\eta$ (mPa·s)	−0.0111	−0.0937	−0.0731	0.0024
	$\Delta G^{*E}/RT$	0.0906	−0.1071	−0.0837	0.0029
MA + $CHCl_3$	$\Delta\eta$ (mPa·s)	0.2021	0.1530	−0.0302	0.0017
	$\Delta G^{*E}/RT$	0.5477	0.2480	−0.0991	0.0028
EA + $CHCl_3$	$\Delta\eta$ (mPa·s)	0.2697	0.1319		0.0014
	$\Delta G^{*E}/RT$	0.6099	0.1979	−0.0293	0.0021
nAA + $CHCl_3$	$\Delta\eta$ (mPa·s)	0.6519	0.1037	−0.1767	0.0018
	$\Delta G^{*E}/RT$	1.1709	0.3466	−0.0898	0.0018
iAA + $CHCl_3$	$\Delta\eta$ (mPa·s)	0.5024	0.1244	−0.0856	0.0018
	$\Delta G^{*E}/RT$	0.9819	0.3368		0.0017

Hind et al. [12], Katti and Chaudhri [13], McAllister [14], Heric and Brewer [15], and Auslaender [16].

The Grunberg–Nissan phenomenological equation [10] reads

$$\eta = \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}) \tag{5}$$

where G_{12} is a parameter proportional to the interchange energy and has been regarded as an indicator for the nonideal behavior of binary mixtures. A semiempirical equation due to Tamura and Kurata [11] is

$$\eta = x_1 V_1 \eta_1 + x_2 V_2 \eta_2 + 2(x_1 x_2 V_1 V_2)^{1/2} C \tag{6}$$

where C is an adjustable parameter.

Hind et al., [12] have proposed the following equation:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 \eta_{12} \tag{7}$$

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. This equation has been theoretically derived by Bearman and Jones [17] from statistical mechanical theory.

Katti and Chaudhri [13] derived the following equation:

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 W_{\text{vis}}/RT \tag{8}$$

where W_{vis} is an interaction term.

All four of the above equations contain one adjustable parameter. The two-parameter McAllister equation [14] based on the Eyring's theory of absolute reaction rates [7] and three-body interaction model is

$$\begin{aligned} \ln \nu = {} & x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} + x_2^3 \ln \nu_2 \\ & - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln(\tfrac{2}{3} + M_2/3M_1) \\ & + 3x_1^2 x_2 \ln(\tfrac{1}{3} + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1) \end{aligned} \tag{9}$$

where Z_{12} and Z_{21} are interaction parameters and M_i and ν_i are the molecular mass and kinematic viscosity of pure component i. The two-parameter Heric and Brewer equation [15] is of the form

$$\begin{aligned} \ln \nu = {} & x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 + \ln(x_1 M_1 + x_2 M_2) \\ & + x_1 x_2 [\alpha_{12} + \alpha_{21}(x_1 - x_2)] \end{aligned} \tag{10}$$

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

Table IV. Values of the Parameters in Eqs. (5)–(8) and Standard Percentage Deviations $\sigma(\%)$ in Correlating Viscosities of Binary Mixtures at 303.15 K

	Eq. (5)		Eq. (6)		Eq. (7)		Eq. (8)	
Mixture	G_{12}	$\sigma(\%)$	C	$\sigma(\%)$	η_{12}	$\sigma(\%)$	W_{vis}/RT	$\sigma(\%)$
MA + C_6H_{14}	−0.30	0.43	0.28	0.74	0.26	0.26	−0.11	0.62
EA + C_6H_{14}	−0.38	0.26	0.28	0.25	0.27	0.46	−0.30	0.24
AA + C_6H_{14}	−0.11	0.55	0.36	1.04	0.37	0.70	−0.10	0.53
DeA + C_6H_{14}	0.83	0.48	0.18	10.65	0.61	2.21	1.06	0.70
DoA + C_6H_{14}	0.70	0.58	0.39	4.80	0.63	0.80	0.84	0.67
MA + CCl_4	0.01	1.17	0.46	2.11	0.48	1.74	0.04	1.19
EA + CCl_4	−0.17	1.05	0.49	1.92	0.49	1.95	−0.17	1.04
nAA + CCl_4	−0.30	0.91	0.71	0.55	0.68	1.06	−0.21	0.84
iAA + CCl_4	−0.02	0.90	0.79	0.85	0.76	0.93	0.07	0.82
MA + $CHCl_3$	0.50	2.14	0.52	2.89	0.53	2.87	0.52	2.12
EA + $CHCl_3$	0.59	1.48	0.60	1.63	0.59	2.03	0.61	1.46
nAA + $CHCl_3$	0.97	2.50	0.94	1.53	0.93	1.54	1.15	2.77
iAA + $CHCl_3$	0.80	2.40	0.85	0.77	0.85	1.59	0.98	2.69
average		1.14		2.29		1.40		1.21

Table V. Values of the Parameters in Eqs. (9)–(11) and Standard Percentage Deviations $\sigma(\%)$ in Correlating Viscosities of Binary Mixtures at 303.15 K

	Eq. (9)			Eq. (10)			Eq. (11)			
Mixtures	Z_{12}	Z_{21}	$\sigma(\%)$	α_{12}	α_{21}	$\sigma(\%)$	B_{12}	A_{21}	B_{21}	$\sigma(\%)$
MA + C_6H_{14}	0.38	0.38	0.37	−0.11	0.06	0.37	−0.47	1.53	1.37	0.20
EA + C_6H_{14}	0.40	0.39	0.19	−0.30	0.03	0.19	−0.13	0.87	2.64	0.23
AA + C_6H_{14}	0.66	0.50	0.27	−0.10	0.05	0.27	1.59	3.18	0.52	0.32
DeA + C_6H_{14}	2.22	1.13	0.15	1.05	−0.09	0.15	0.55	1.71	1.05	0.21
DoA + C_6H_{14}	1.66	0.96	0.41	0.84	−0.08	0.41	0.98	2.28	0.68	0.30
MA + CCl_4	0.42	0.44	0.45	0.05	0.13	0.45	0.27	0.14	4.81	0.52
EA + CCl_4	0.46	0.44	0.43	−0.17	0.14	0.43	0.25	0.10	5.78	0.19
nAA + CCl_4	0.71	0.56	0.30	−0.21	0.11	0.30	2.63	0.45	−1.80	0.15
iAA + CCl_4	0.75	0.60	0.38	0.07	0.11	0.38	0.47	0.13	9.15	0.18
MA + $CHCl_3$	0.39	0.45	0.53	0.52	−0.25	0.53	−0.53	0.72	1.59	0.41
EA + $CHCl_3$	0.47	0.49	0.27	0.60	−0.20	0.27	−1.30	0.56	4.14	0.30
nAA + $CHCl_3$	0.84	0.78	0.46	1.15	−0.35	0.46	1.45	0.44	−1.84	0.29
iAA + $CHCl_3$	0.76	0.72	0.17	0.98	−0.34	0.17	1.46	0.40	−1.90	0.09
average			0.34			0.34				0.26

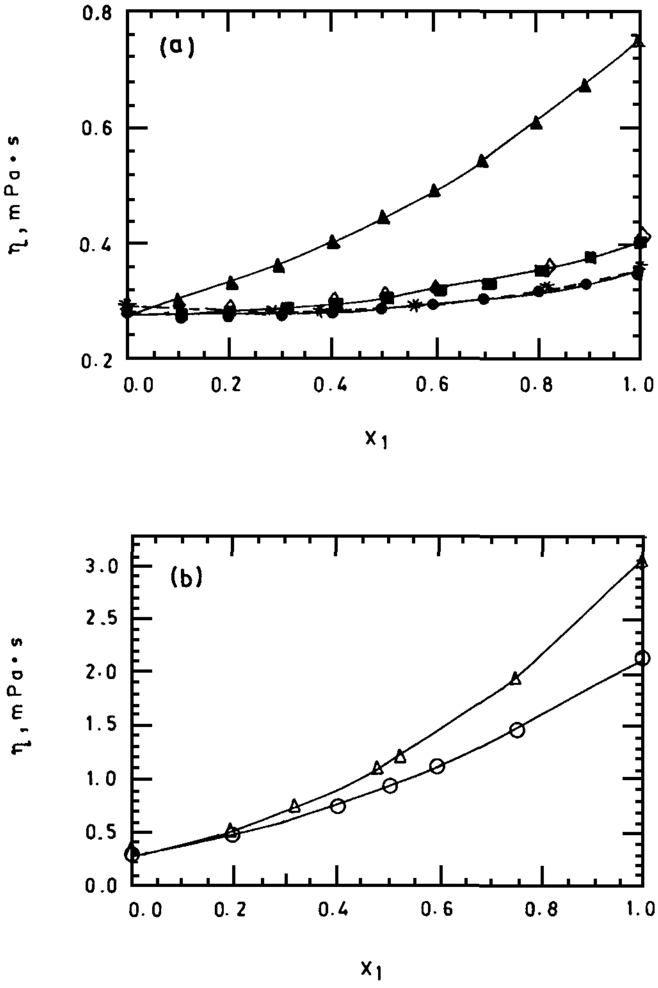

Fig. 1. Viscosity η for alkyl acetate + hexane at 303.15 K. Alkyl acetate: (a) MA, (●) this work and (∗) Wei and Rowley [18] at 298.15 K; EA, (■) this work and (◇) Oswal and Dave [20]; nAA (▲), (b) DeA (○); DoA (△). (——) Calculated with Eq. (1).

The less complicated three-parameter Auslaender equation [16] has the form

$$x_1(x_1 + B_{12}x_2)(\eta - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta - \eta_2) = 0 \cdots \tag{11}$$

where B_{12}, A_{21}, and B_{21} are the parameters representing binary (1, 2) interactions. The correlating ability of each of Eqs. (5)–(11) was tested by calculating the standard percentage deviations $\sigma(\%)$ between the experimental and the calculated viscosity as

$$\sigma\% = \left[\frac{1}{n-k}\sum\left\{\frac{100(\eta_{\text{exp}} - \eta_{\text{cal}})}{\eta_{\text{exp}}}\right\}^2\right]^{1/2} \tag{12}$$

where n represents the number of data points and k the number of numerical coefficients in the respective equation.

The results of the correlating equations, Eqs. (5)–(11), are compiled in Tables IV and V. The values of the different parameters and the percentage

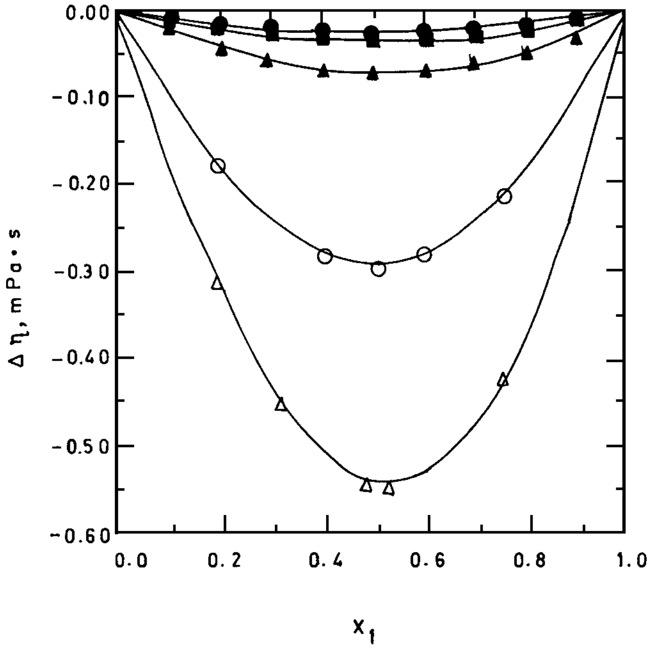

Fig. 2. Deviations of viscosity $\Delta\eta$ from linear additivity on mole fraction of alkyl acetate for alkyl acetate + hexane mixtures at 303.15 K. (——) Calculated with Eq. (4). Symbols as in the legend to Fig. 1.

standard deviations $\sigma(\%)$ listed in Tables IV and V were obtained from the experimental viscosity data using the method of least squares.

5. DISCUSSION

Viscosity measurements for the MA + C_6H_{14}, EA + C_6H_{14}, MA + $CHCl_3$, EA + CCl_4, and EA + $CHCl_3$ have been reported earlier [18–20]. The present values of viscosity are in close agreement with our previously reported values for EA + C_6H_{14}, EA + CCl_4, and EA + $CHCl_3$. Direct comparison for MA + C_6H_{14} and MA + $CHCl_3$ is not possible, as the literature data [18] are at 298.15 K while the present η values are at 303.15 K. However, the pattern of variation of η with composition is the same (Figs. 1 and 5) and shows similar deviations in viscosity $\Delta\eta$.

The experimental results for η, $\Delta\eta$, G_{12}, and ΔG^{*E} of alkyl acetate + hexane are plotted in Figs. 1–4. It can be seen that negative deviations from the linearity for alkyl acetate + hexane mixtures are observed and their magnitude increases with the increase in the number of carbon atoms in

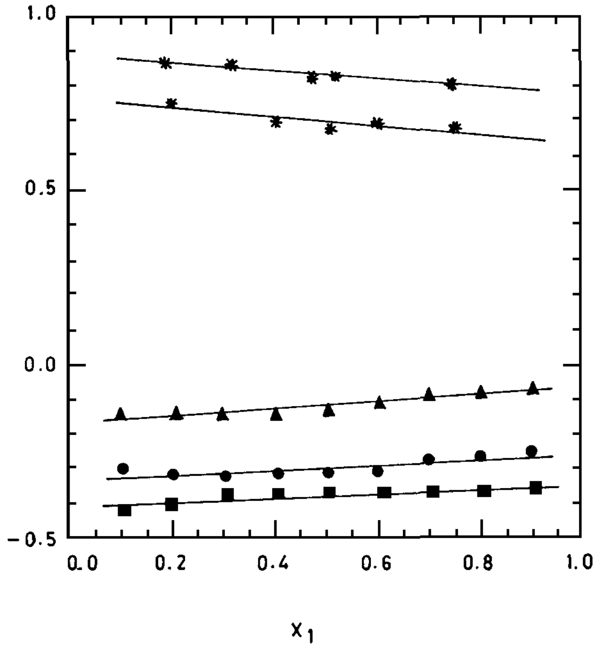

Fig. 3. Variation of Grunberg–Nissan parameter G_{12} of Eq. (5) with mole fraction x_1 of alkyl acetate in alkyl acetate + hexane mixtures. Symbols as in the legend to Fig. 1.

the alkyl acetate molecule. Similar results were also observed for alkyl alkanoate + heptane series [21].

The excess molar volumes V^E and excess enthalpies H^E [1, 2, 22] indicated that dipolar association in pure alkyl acetate diminishes by the addition of hexane molecules. In turn, the cohesive forces between the pairs of unlike molecules are far less than the forces between the pairs of like molecules. As a result, negative deviations in the viscosity $\Delta\eta$ are observed. Furthermore, the dependence of the Grunberg–Nissan parameter G_{12} (Fig. 3) reveals that the present mixtures are not regular solutions [23]. The excess Gibbs energies of activation ΔG^{*E} of flow (Fig. 4) for the binary mixtures of methyl acetate, ethyl acetate, and amyl acetate are negative, while they are positive for those involving decyl acetate and dodecyl acetate. The expected small negative values of ΔG^{*E} for the latter two mixtures due to the disruption of dipolar order in decyl and dodecyl acetates have been masked by the positive contribution because of the difference in the molar volume and viscosity of the two components in the mixtures. The ΔG^{*E} is an increasing function of the size difference [21].

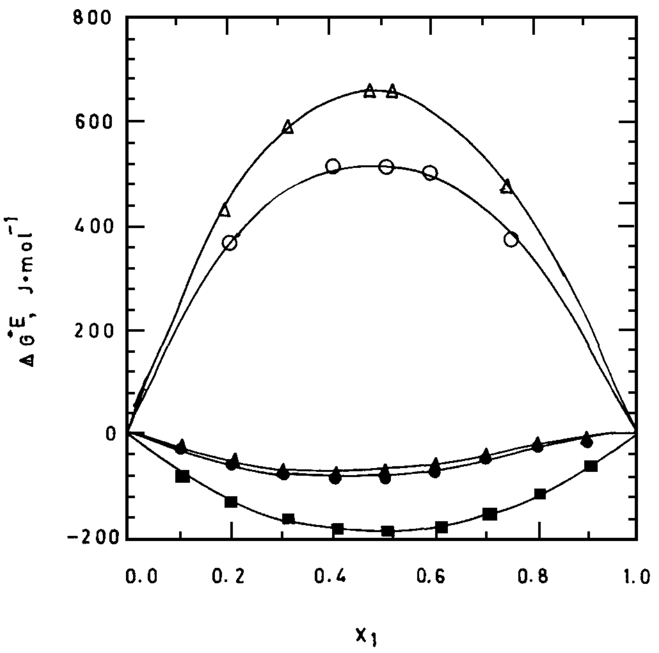

Fig. 4. Excess Gibbs energy of activation ΔG^{*E} of viscous flow for alkyl acetate + hexane mixtures at 303.15 K. Symbols as in the legend to Fig. 1. (——) Calculated with Eq. (4).

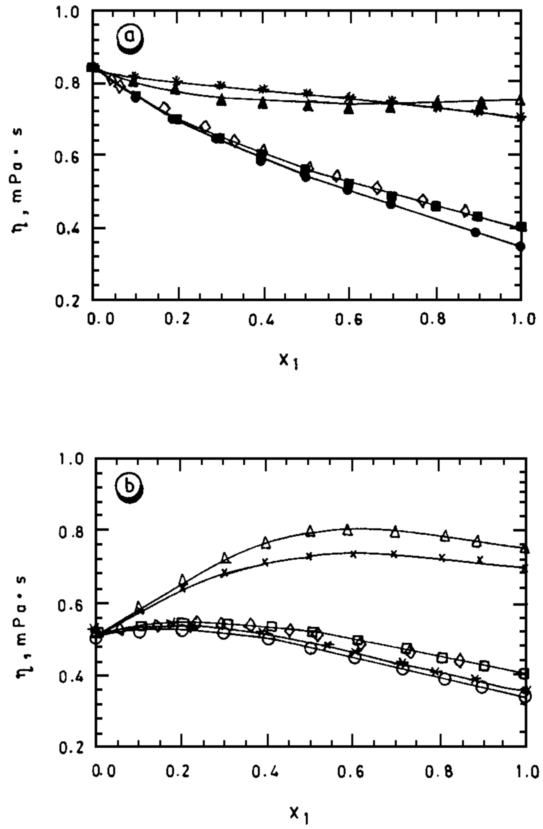

Fig. 5. Viscosity η for alkyl acetate + tetrachloromethane and + trichloromethane at 303.15 K. Alkyl acetate: (a) MA (●); EA, (■) this work and (◇) Oswal and Rathnam [19]; nAA (▲); iAA (*). (b) MA, (□) this work and (*) Wei and Rowley [18] at 298.15 K; EA, (□) this work and (◇) Oswal and Rathnam [19]; nAA (△); iAA (+). (——) Calculated with Eq. (1).

The experimental results for η, $\Delta\eta$, G_{12}, and ΔG^{*E} of alkyl acetate + tetrachloromethane and alkyl acetate + trichloromethane are plotted in Figs. 5–8. The values of $\Delta\eta$, ΔG^{*E}, and G_{12} are negative for all four mixtures of alkyl acetate + tetrachloromethane, except ΔG^{*E} and G_{12} for MA + CCl_4, which are positive. The values of ΔG^{*E} and G_{12} decrease with the increase in alkyl chain length in the ester. The values of ΔG^{*E} and G_{12} are less negative or more positive for mixtures involving isoamyl acetate compared to the amyl acetate mixtures.

It appears from comparing the results for alkyl acetate + tetrachloromethane with the corresponding mixture of alkyl acetate + hexane that the dipolar dissociation is partly counterbalanced by the appearance of specific Cl ··· O interactions in alkyl acetate and tetrachloromethane. In the present case the O of ester group of alkyl acetate acts as an electron donor, while the Cl of CCl_4 acts as a sacrificial σ acceptor. This graded behavior is consistent with the excess enthalpy, volume, and compressibility results [24, 25].

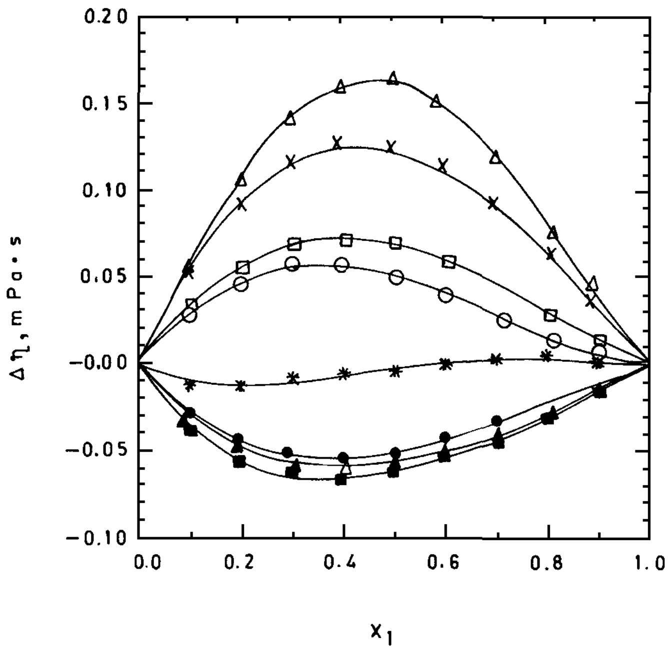

Fig. 6. Deviations of viscosity $\Delta\eta$ from linear additivity on mole fraction of alkyl acetate for alkyl acetate + tetrachloromethane and + trichloromethane mixtures at 303.15 K. Symbols as in the legend to Fig. 5. (——) Calculated with Eq. (4).

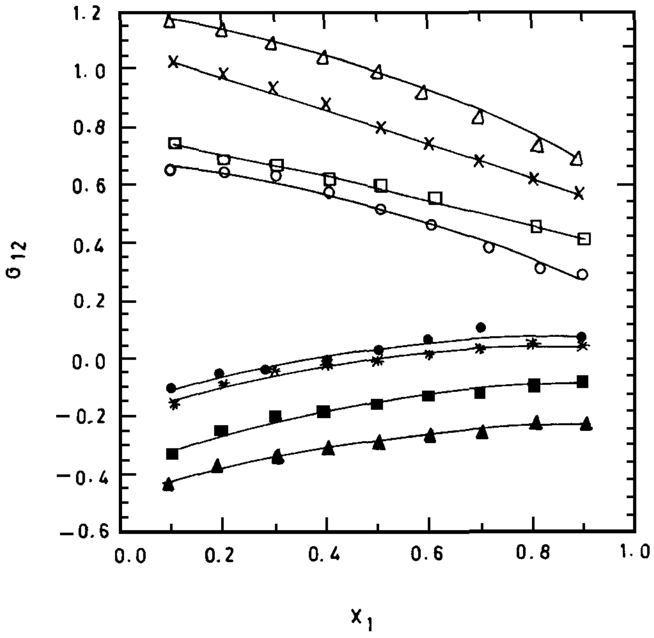

Fig. 7. Variation of Grunberg–Nissan parameter G_{12} of Eq. (5) with mole fraction x_1 of alkyl acetate in alkyl acetate + tetrachloromethane and + trichloromethane mixtures. Symbols as in the legend to Fig. 5.

As shown in Fig. 5b, maxima in each of the viscosity curves are observed for the mixtures of alkyl acetate with trichloromethane. Contrary to this, there are no maxima in any of the four alkyl acetate + tetrachloromethane systems. The positive values of $\Delta\eta$ and ΔG^{*E} (Figs. 6 and 8) increase with an increase in chain length of the acetate. According to Fort and Moore [26] and Nigam and Mahl [27], such results are indicative of complex formation through H-bonding between alkyl acetate and trichloromethane. These conclusions are well supported by very large and negative excess enthalpies of mixing over the complete composition range for methyl acetate and ethyl acetate mixtures with trichloromethane systems [28].

The values of $\sigma(\%)$ are in the range from 0.24 to 10.65% for the single-parameter Eqs. (5)–(8), from 0.15 to 0.53% for the two-parameter Eqs. (9) and (10), and from 0.09 to 0.52% for the three-parameter Eq. (11). The average percentage standard deviations $\langle\sigma(\%)\rangle$ for Eqs. (5)–(8), with a single parameter, are 1.15, 2.29, 1.40, and 1.21, respectively; for Eqs. (9) and (10), with two parameters, $\langle\sigma(\%)\rangle$ is 0.34; and for the three-parameter Eq. (11), $\langle\sigma(\%)\rangle$ is 0.26. From an analysis of the results it was observed that the use of the two-parameter equations [(9) and (10)]

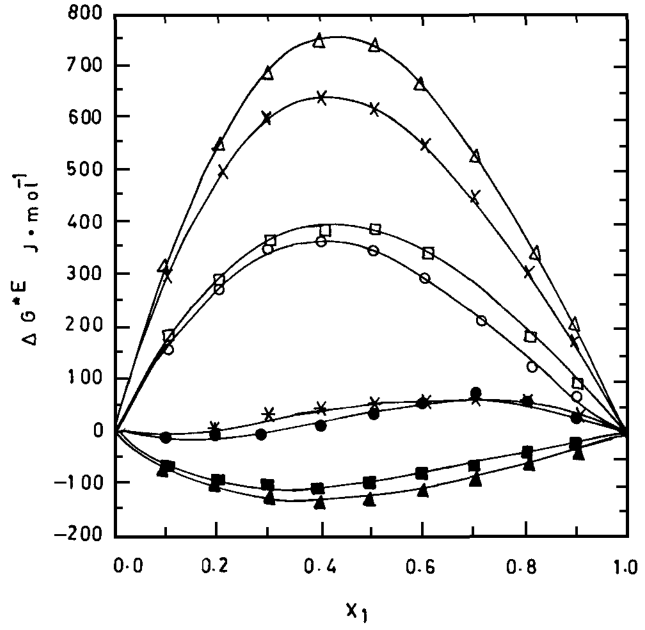

Fig. 8. Excess Gibbs energy of activation ΔG^{*E} of viscous flow for alkyl acetate + tetrachloromethane and + trichloromethane mixtures at 303.15 K. Symbols as in the legend to Fig. 5. (——) Calculated with Eq. (4).

reduces the values of $\sigma(\%)$ significantly below those of single-parameter equations. In most systems the three-parameter Eq. (11) proposed by Auslaender [16] gives very good results. The correlating ability improves in the sequence Tamura and Kurata < Hind et al. < Katti and Chaudhri < Grunberg and Nissan < McAllister ≈ Heric and Brewer < Auslaender equations.

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