Thermochimica Acta, 129 (1988) 249–262
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

VOLUMES OF MIXING AND VISCOSITIES OF METHYLACETATE + n-ALKANES AND n-BUTYLACETATE + n-ALKANES AT 298.15 K: AN INTERPRETATION IN TERMS OF THE VAN–PATTERSON, THE ABSOLUTE RATE AND FREE VOLUME THEORIES

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(Received 21 September 1987)

ABSTRACT

The excess molar volumes V^E, viscosities η, excess viscosities $\Delta \ln \eta$ and excess activation energies of viscous flow $\Delta G^{\star E}$ of the binary mixtures of methylacetate+ and n-butylacetate + n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, n-tetradecane and n-hexadecane have been determined at 298.15 K as a function of the mole fraction. All the mixtures studied exhibit positive excess molar volumes which increase with the length of the n-alkane chain. The excess viscosities and excess activation energies of viscous flow are negative for lower n-alkane systems and turn positive for longer n-alkane systems. The Van–Patterson, the absolute rate and free volume theories predict the experimental data only poorly.

INTRODUCTION

Extensive experimental and theoretical studies have been undertaken on binary mixtures of alkyl acetates with n-alkanes with the aim of investigation of the interactions in ester + hydrocarbon systems [1–6]. Analysis of heats of mixing data for this class of mixtures in terms of the Flory–Patterson theory explained the variation of the contact interaction parameter X_{12} with the chain length of n-alkane, the ester, or both in terms of the energetic effects associated with dipolar interactions and with a correlation of molecular orientational order in pure component liquid and mixtures. The purpose of the present work is to report the excess molar volumes V^E, viscosities η, excess molar viscosities $\Delta \ln \eta$, and excess molar activation energies of viscous flow $\Delta G^{\star E}$ of methylacetate + and n-butylacetate + n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, n-tetradecane, and n-hexadecane at 298.15 K. Results for V^E and $\Delta \ln \eta$ corresponded to those

0040-6031/88/$03.50

for the Van–Patterson, absolute rate and free volume theories [7–9]. The procedure followed is similar to that applied previously to an aromatic hydrocarbon [10,11] and cyclohexane + n-alkane [12].

EXPERIMENTAL

Materials

All hydrocarbons, methylacetate and n-butylacetate used were obtained from Fluka AG (pure grade). Methylacetate (purum, > 99.0%, CH_3COOCH_3), n-butylacetate (puriss, > 99.0%, $CH_3COO(CH_2)_3CH_3$), n-hexane (puriss, > 99.5%, C_6H_{14}), n-heptane (puriss, > 99.5%, C_7H_{16}), n-octane (puriss, > 99.5%, C_8H_{18}), n-nonane (puriss, > 99.5%, C_9H_{20}), n-decane (puriss, > 99.5%, $C_{10}H_{22}$), n-dodecane (puriss, > 99.5%, $C_{12}H_{26}$), n-tetradecane (puriss, > 99.5%, $C_{14}H_{30}$), and n-hexadecane (puriss, > 99.5%, $C_{16}H_{34}$) were used without further purifications. All liquids were stored over a freshly activated molecular sieve of type 4A (Union Carbide) and filtered before use. The estimated purities as determined by gas–liquid chromatographic analysis were in all cases better than 99.5 mol%. Densities (ρ) and viscosities (η) of the pure liquids were found to be in good agreement with values published in the literature [7,8,13–17].

Density measurements

The densities of the pure liquids and the binary mixtures were measured at 298.15 K with an Anton Paar digital densimeter (DMA 601) with a thermostatted bath controlled to ± 0.01 K. The overall precision of the densities measured was estimated to be better than 4×10^{-6} g cm^{-3}. Binary mixtures were prepared on a weight basis and the mole fraction error is estimated to be $< 1 \times 10^{-4}$. From the measured densities, the molar excess volumes were obtained from the relation

$$V_m^E = x_1 M_1 \left(\rho_m^{-1} - \rho_1^{-1}\right) + x_2 M_2 \left(\rho_m^{-1} - \rho_2^{-1}\right) \quad (1)$$

where M_i, ρ_i and x_i designate, respectively, the molar mass, density and the mole fraction of the methylacetate or n-butylacetate ($i = 1$) and n-alkane ($i = 2$). Quantities with subscript m refer to the solution mixture. The possible error in the mole fraction is estimated to be less than 3×10^{-4}. The imprecision in the determination of V^E is estimated to be $< 1.5 \times 10^{-3}$ cm^3 mol^{-1}.

Viscosity measurements

The viscosities were determined using a suspended Ubbelhode viscometer in a bath controlled to ± 0.01 K at 298.15 K. The flow time was determined electronically using an electronic timer (Schott-Gerate Model AVS 400) with a precision of ±0.01 s.

RESULTS AND DISCUSSION

The following equation was fitted to the experimental molar volumes of mixing (Table 1) at different concentrations

$$V^{\mathrm{E}} = x(1-x)\sum_{i=0}^{k} A_i(1-2x)^i \tag{2}$$

Values of A_i and standard deviation s were determined by the least-squares method with all points weighted equally, and are given in Table 2.

The parameters for pure component liquids required in the calculations of volume of mixing V^{E} in the Van–Patterson theory are listed in tables 1 and 4 in refs. 2 and 3. The interactional parameter X_{12} was calculated from eqn. (6) in ref. 18 and the excess molar enthalpies ΔH_{M} data of binary mixtures of methylacetate + n-alkanes and n-butylacetate + n-alkanes at 298.15 K available in the literature [1,6]. Values of ΔH_{M} and X_{12} at $x = 0.5$ are listed in Table 3. Using the parameters of the pure component liquids and the interactional parameter X_{12}, we have calculated the total excess molar volumes V^{E}, the interactional contribution $\Delta V_{\mathrm{inter}}$, the free volume contribution ΔV_{F} and the internal pressure contribution $\Delta V_{\mathrm{P}}^{\star}$ to V^{E} from the Van–Patterson equation [9]

$$\begin{aligned} V^{\mathrm{E}}/x_1V_1^{\star} - x_2V_2^{\star} = {} & \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}}{(4/3\tilde{V}^{-1/3}-1)}\psi_1\theta_2\frac{X_{12}}{P_1^{\star}}(\Delta V_{\mathrm{inter}}) \\ & - \frac{(\tilde{V}_1-\tilde{V}_2)^2(14/9\tilde{V}^{-1/3}-1)}{(4/3\tilde{V}^{-1/3}-1)\tilde{V}}\psi_1\psi_2(\Delta V_{\mathrm{F}}) \\ & + \frac{(\tilde{V}_1-\tilde{V}_2)(P_1^{\star}-P_2^{\star})}{P_2^{\star}\psi_1+P_1^{\star}\psi_2}\psi_1\psi_2(\Delta V_P^{\star}) \end{aligned} \tag{3}$$

The results obtained are listed in Table 3 with experimental data.

The excess molar viscosities ($\Delta\ln\eta$) and excess activation energies ($\Delta G^{\star\mathrm{E}}$) were calculated from [7,8]

$$\Delta\ln\eta = \ln\eta - [x\ln\eta_1 + (1-x)\ln\eta_2] \tag{4}$$

$$\Delta G^{\star\mathrm{E}} = RT[\ln\eta V - (x\ln\eta_1V_1 + (1-x)\ln\eta_2V_2)] \tag{5}$$

The results obtained are listed in Table 1 and presented in Figs. 5–8, respectively. Using the parameters of the pure component liquids and excess molar enthalpies of the mixtures, we have calculated the total excess viscosity $\Delta\ln\eta$, enthalpy contribution $\ln\eta_H$, the residual or noncombina-

TABLE 1

Experimental excess molar volumes, viscosities, excess molar viscosities and excess molar activation energies of viscous flow for (x)alkylacetate+($1-x$)n-alkanes at 298.15 K

x	ρ (g cm^{-3})	V^{E} (cm^{3} mol^{-1})	η (cP)	$\Delta \ln \eta$ (cP)	ΔG^{*E} (J mol^{-1})
(x)methylacetate+($1-x$)n-hexadecane					
0.0393	0.77109	0.2310	2.9239	0.0298	131
0.1180	0.77365	0.6392	2.6191	0.0848	374
0.3657	0.78569	1.5197	1.8194	0.2400	1026
0.4814	0.79456	1.6845	1.4909	0.2835	1209
0.5357	0.79969	1.7289	1.3499	0.2980	1267
0.6520	0.81390	1.7095	1.0859	0.3243	1340
0.7625	0.83397	1.4816	0.8431	0.3064	1267
0.8682	0.86059	1.2438	0.6349	0.2411	950
0.9609	0.90126	0.4843	0.4379	0.0640	293
(x)methylacetate+($1-x$)n-dodecane					
0.0900	0.74971	0.5198	1.2434	0.0182	139
0.2130	0.75612	1.0112	1.0803	0.0359	293
0.3361	0.76641	1.4457	0.9577	0.0739	469
0.4514	0.77787	1.5947	0.8306	0.0800	540
0.5533	0.79144	1.7463	0.7377	0.0926	593
0.6236	0.80266	1.6735	0.6777	0.0982	608
0.6972	0.81653	1.5776	0.6144	0.0949	584
0.7671	0.83234	1.4588	0.5570	0.0868	531
0.8924	0.87187	0.9511	0.4527	0.0407	297
0.9377	0.89197	0.5982	0.4171	0.0172	168
(x)methylacetate+($1-x$)n-decane					
0.0803	0.73129	0.4407	0.7987	−0.0057	49
0.1876	0.73952	0.9109	0.7291	−0.0091	115
0.3354	0.75387	1.3530	0.6485	−0.0052	202
0.4452	0.76742	1.5362	0.5969	−0.0035	261
0.4760	0.77180	1.5599	0.5809	−0.0002	264
0.5538	0.78408	1.5898	0.5456	0.0009	278
0.6180	0.79602	1.5378	0.5186	0.0026	281
0.7363	0.82269	1.3768	0.4714	0.0039	257
0.8315	0.85100	1.1550	0.4356	0.0024	227
(x)methylacetate+($1-x$)n-octane					
0.1268	0.71056	0.7316	0.4797	−0.0340	−14
0.2408	0.72368	1.1430	0.4518	−0.0585	−24
0.3370	0.73678	1.3660	0.4361	−0.0640	−5
0.4310	0.75177	1.4710	0.4213	−0.0693	4
0.5066	0.76555	1.4992	0.4108	−0.0710	10
0.5788	0.78041	1.4793	0.4021	−0.0701	15
0.6440	0.79552	1.4193	0.3953	−0.0669	19
0.7570	0.82692	1.1517	0.3849	−0.0584	13
0.8528	0.85862	0.9298	0.3786	−0.0451	6

TABLE 1 (continued)

x	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (cP)	$\Delta \ln \eta$ (cP)	ΔG^{*E} (J mol^{-1})
(x)methylacetate + (1 − x)n-hexane					
0.1056	0.66995	0.6295	0.2969	−0.0607	−114
0.2943	0.70294	1.1729	0.2941	−0.1085	−185
0.4514	0.73689	1.3313	0.2996	−0.1219	−198
0.5616	0.76471	1.2455	0.3071	−0.1196	−191
0.6895	0.80158	1.1411	0.3189	−0.1080	−169
0.7175	0.81130	1.0052	0.3223	−0.1030	−163
0.8224	0.84882	0.7016	0.3420	−0.0621	−85
0.9171	0.88681	0.4500	0.3650	−0.0192	−7
(x)n-butylacetate + (1 − x)n-hexadecane					
0.0797	0.77314	0.3051	2.7781	0.0162	89
0.1270	0.77527	0.4423	2.6062	0.0235	134
0.2518	0.78161	0.7681	2.2274	0.0543	271
0.3552	0.78803	0.9270	1.9437	0.0737	350
0.4446	0.79455	1.0065	1.7165	0.0839	404
0.5252	0.80119	1.0791	1.5393	0.0963	445
0.5544	0.80388	1.0858	1.4842	0.1038	465
0.5940	0.80794	1.0439	1.3896	0.0975	449
0.7165	0.82230	0.9167	1.1487	0.0914	415
0.8169	0.83716	0.7273	0.9655	0.0690	301
0.8982	0.85201	0.4957	0.8340	0.0449	208
0.9520	0.86380	0.2759	0.2759	0.7539	113
(x)n-butylacetate + (1 − x)n-tetradecane					
0.1284	0.76644	0.4139	1.8246	0.0048	70
0.2404	0.77352	0.6662	1.6216	0.0123	129
0.3362	0.78046	0.8377	1.4673	0.0196	175
0.4227	0.78767	0.9276	1.3393	0.0252	206
0.5018	0.79512	0.9720	1.2303	0.0270	224
0.5367	0.79868	0.9855	1.1833	0.0291	226
0.5715	0.80244	0.9892	1.1416	0.0321	234
0.6959	0.81780	0.9335	0.9335	0.9929	222
0.8024	0.83439	0.7001	0.8736	0.0232	171
0.8903	0.85081	0.4450	0.7842	0.0137	108
0.9480	0.86335	0.2318	0.7283	0.0044	50
(x)n-butylacetate + (1 − x)n-dodecane					
0.1330	0.75547	0.4207	1.2308	−0.0154	4
0.2982	0.76910	0.7575	1.0896	−0.0224	24
0.4364	0.78292	0.8765	0.9867	−0.0255	35
0.4791	0.78763	0.9037	0.9597	−0.0236	43
0.5426	0.79520	0.9056	0.9188	−0.0230	47
0.6830	0.8147	0.7630	0.8358	−0.0201	45
0.7904	0.83195	0.6650	0.7782	−0.0167	36
0.8705	0.84703	0.4525	0.7393	−0.0124	24
0.9238	0.85825	0.2855	0.7176	−0.0052	22
0.9757	0.87012	0.1074	0.6938	−0.0029	5

(continued)

TABLE 1 (continued)

x	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (cP)	$\Delta \ln \eta$ (cP)	$\Delta G^{\star E}$ (J mol^{-1})
(x)n-butylacetate + (1 − x)n-decane					
0.3547	0.76348	0.7508	0.7515	-0.0521	-77
0.4366	0.77405	0.7973	0.7352	-0.0544	-80
0.5375	0.78820	0.8013	0.7168	-0.0579	-84
0.6473	0.80533	0.7493	0.7018	-0.0543	-78
0.7119	0.81631	0.6821	0.6958	-0.0483	-68
0.8212	0.83686	0.4751	0.6854	-0.0386	-57
0.9331	0.86026	0.2412	0.6851	-0.0137	-16
(x)n-butylacetate + (1 − x)n-nonane					
0.0459	0.71894	0.1501	0.6602	-0.0170	-36
0.1339	0.72896	0.3880	0.6474	-0.0383	-77
0.2324	0.74104	0.5831	0.6291	-0.0689	-143
0.3814	0.76120	0.7431	0.6318	-0.0675	-130
0.4218	0.76712	0.7535	0.6304	-0.0705	-135
0.4836	0.77641	0.7778	0.6314	-0.0702	-133
0.5989	0.79506	0.7507	0.6320	-0.0714	-137
0.6580	0.80543	0.6865	0.6382	-0.0628	-117
0.7574	0.82364	0.5997	0.6466	-0.0516	-95
0.8386	0.84017	0.4067	0.6563	-0.0384	-71
0.9486	0.86405	0.1575	0.6723	-0.0164	-32
(x)n-butylacetate + (1 − x)n-octane					
0.0442	0.70432	0.2175	0.5144	-0.0159	-34
0.1275	0.71579	0.4121	0.5154	-0.0375	-81
0.2822	0.73863	0.6472	0.5241	-0.0643	-138
0.3556	0.75022	0.7016	0.5333	-0.0676	-144
0.4596	0.76753	0.7195	0.5465	-0.0724	-154
0.5629	0.78573	0.6884	0.5633	-0.0712	-151
0.6356	0.79916	0.6421	0.5776	-0.0666	-141
0.7305	0.7305	0.5428	0.5991	-0.0568	-120
0.8441	0.84119	0.3391	0.6298	-0.0388	-82
0.9724	0.86978	0.0577	0.6725	-0.0094	-20
(x)n-butylacetate + (1 − x)n-heptane					
0.0364	0.68565	0.1023	0.4006	-0.0085	-53
0.1529	0.70538	0.3548	0.4135	-0.0406	-93
0.2504	0.72262	0.4857	0.4295	-0.0558	-127
0.3266	0.73650	0.5476	0.4449	-0.0636	-145
0.4281	0.75569	0.5648	0.4667	-0.0698	-160
0.5399	0.77757	0.5351	0.4974	-0.0674	-154
0.6531	0.80046	0.4699	0.5328	-0.0604	-138
0.7531	0.82181	0.3727	0.5696	-0.0493	-113
0.8609	0.84439	0.2914	0.6155	-0.0298	-67
0.9693	0.86908	0.0576	0.6674	-0.0079	-18

TABLE 1 (continued)

x	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (cP)	$\Delta \ln \eta$ (cP)	$\Delta G^{\star E}$ (J mol^{-1})
(x)n-butylacetate + (1 − x)n-hexane					
0.1335	0.68350	0.2458	0.3275	−0.0323	−75
0.2322	0.70492	0.3336	0.3509	−0.0436	−102
0.3294	0.72629	0.3589	0.3762	−0.0530	−124
0.4644	0.75606	0.3668	0.4191	−0.0546	−128
0.5644	0.77835	0.3249	0.4558	−0.0521	−123
0.6697	0.80180	0.2807	0.4996	−0.0459	−108
0.8002	0.83078	0.2341	0.5626	−0.0331	−78
0.8967	0.85254	0.1444	0.6164	−0.0202	−47
0.9324	0.86092	0.0603	0.6456	−0.0029	−6

torial entropy contribution $\ln \eta_S$ and the free volume contribution $\ln \eta_V$ from [8,19]

$$\begin{aligned}\Delta \ln \eta_{\text{th}} &= -\Delta H_{\text{M}}/RT + \Delta S^R/R \\ &\quad + \left[1/(\tilde{V}-1) - x_1/\left(\tilde{V}_1 - 1\right) - x_2/\left(\tilde{V}_2 - 1\right)\right] \end{aligned} \tag{6}$$

where $\ln \eta_H = -\Delta H_{\text{M}}/RT$

$\ln \eta_V = \left[1/(\tilde{V}-1) - x_1/\left(\tilde{V}_1 - 1\right) - x_2/\left(\tilde{V}_2 - 1\right)\right]$

TABLE 2

Coefficients A_i of eqn. (2) and standard deviation s

System	A_0	A_1	A_2	A_3	A_4	s
$C_3H_6O_2$						
n-$C_{16}H_{34}$	6.7799	1.2974	2.2129	2.9064	1.2349	0.0034
n-$C_{12}H_{26}$	6.6970	1.5949	1.3668	0.9143	1.1031	0.0011
n-$C_{10}H_{22}$	6.2930	0.6004	0.7090	2.5805	2.4524	0.0045
n-C_8H_{18}	5.9465	0.1408	1.9082	−1.3524	–	0.0033
n-C_6H_{14}	5.1638	1.1047	1.4938	−0.7224	–	0.0041
$C_6H_{12}O_2$						
n-$C_{16}H_{34}$	4.2554	−0.4803	−0.2530	−0.5855	1.6553	0.0022
n-$C_{14}H_{30}$	3.9268	−0.8357	0.3842	0.4437	–	0.0033
n-$C_{12}H_{26}$	3.5989	−0.0348	0.2728	−0.3899	0.2900	0.0050
n-$C_{10}H_{22}$	3.2404	−0.4384	0.1479	5.0869	6.0943	0.0036
n-C_9H_{20}	3.1085	0.1143	0.2651	0.0189	−0.0132	0.0005
n-C_8H_{18}	2.9063	0.2189	−0.2318	1.8276	1.3205	0.0033
n-C_7H_{16}	2.1569	0.4235	1.2131	0.0398	−1.0043	0.0044
n-C_6H_{14}	1.3414	0.2377	1.6113	0.5530	−1.4947	0.0006

TABLE 3

Experimental and predicted excess molar volumes of (x)methylacetate + $(1-x)$n-alkanes at 298.15 K

System		$\Delta H_M^{b,c}$	X_{12}	V_{expt}^E	V_{th}^E	ΔV_F	$\Delta V_P^\star$	ΔV_{inter}
$C_3H_6O_2$	(1)							
n-$C_{16}H_{34}$	(2)	2445 [a]	100	1.6950	2.7188	0.6810	1.6293	1.7705
n-$C_{12}H_{26}$	(2)	2146 [b]	98	1.6743	2.5731	0.4246	1.2979	1.6998
n-$C_{10}H_{22}$	(2)	1995 [a]	95	1.5733	2.4695	0.2901	1.0843	1.6743
n-C_8H_{18}	(2)	1835 [b]	92	1.4867	2.2736	0.1429	0.7693	1.6467
n-C_6H_{14}	(2)	1690 [b]	91	1.2910	1.9139	0.0150	0.2562	1.6727
$C_6H_{12}O_2$	(1)							
n-$C_{16}H_{34}$	(2)	1560 [a]	57	1.0638	1.7045	−0.1586	0.4831	1.3801
n-$C_{14}H_{30}$	(2)	1428 [c]	55	0.9817	1.6161	−0.1080	0.4015	1.3324
n-$C_{12}H_{26}$	(2)	1303 [c]	53	0.8997	1.5143	−0.0523	0.2849	1.2817
n-$C_{10}H_{22}$	(2)	1171 [c]	50	0.8101	1.3285	−0.0144	0.1536	1.1893
n-C_9H_{20}	(2)	1107 [c]	51	0.7773	1.2650	−0.0065	0.1119	1.1447
n-C_8H_{18}	(2)	1043 [c]	49	0.7266	1.0956	−0.0025	−0.0466	1.1447
n-C_7H_{16}	(2)	980 [c]	48	0.5392	0.9054	−0.0196	−0.1897	1.1147
n-C_6H_{14}	(2)	920 [c]	48	0.3353	0.5869	−0.0818	−0.4323	1.1010

[a] Extrapolated. [b] Ref. 1. [c] Ref. 6.

and

$$\ln \eta_S = \Delta S^R/R = 3x_1 \frac{P_1^\star V_1^\star}{RT_1^\star} \ln\left(\frac{\tilde{V}_1^{1/3}-1}{\tilde{V}^{1/3}-1}\right) - 3x_2 \frac{P_2^\star V_2^\star}{RT_2^\star} \ln\left(\frac{\tilde{V}_2^{1/3}-1}{\tilde{V}^{1/3}-1}\right)$$

The calculated values are listed in Table 4.

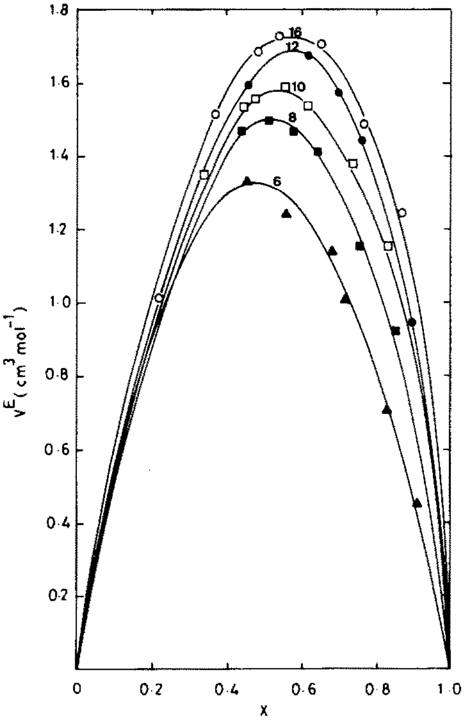
TABLE 4

Experimental and calculated parameters related to the viscosities of n-alkanes(1) + methylacetate(2) and n-butylacetate(2) at 298.15 K

System		$\ln \eta_H$	$\ln \eta_S$	$\ln \eta_V$	$\Delta \ln \eta_{th}$	$\Delta \ln \eta_{expt}$	$\Delta \ln \eta_{expt} - \Delta \ln \eta_{th}$
$C_3H_6O_2$	(2)						
n-$C_{16}H_{34}$	(1)	−0.9864	−0.9927	0.1827	−1.7964	0.2880	2.0844
n-$C_{12}H_{26}$	(1)	−0.8657	−0.7306	0.0828	−1.5135	0.0860	1.5995
n-$C_{10}H_{22}$	(1)	−0.8657	−0.5758	0.0371	−1.3434	0.0010	1.3444
n-C_8H_{18}	(1)	−0.7403	−0.3791	0.0026	−1.1168	−0.0700	1.0468
n-C_6H_{14}	(1)	−0.6818	−0.1116	−0.0066	−0.7800	−0.1220	0.6580
$C_6H_{12}O_2$	(2)						
n-$C_{16}H_{34}$	(1)	−0.6293	−0.5378	0.0807	−1.0865	0.0910	1.1775
n-$C_{14}H_{30}$	(1)	−0.5761	−0.4293	0.0488	−0.9567	0.0300	0.9867
n-$C_{12}H_{26}$	(1)	−0.5257	−0.2860	0.0216	−0.7900	−0.0275	0.7625
n-$C_{10}H_{22}$	(1)	−0.4724	−0.1425	0.0038	−0.6111	−0.0570	0.5541
n-C_9H_{20}	(1)	−0.4466	−0.0921	−0.0011	−0.5398	−0.0720	0.4678
n-C_8H_{18}	(1)	−0.4206	0.0392	0.0010	−0.3804	−0.0730	0.3074
n-C_7H_{16}	(1)	−0.3954	0.1481	0.0094	−0.2379	−0.0700	0.1679
n-C_6H_{14}	(1)	−0.3711	0.2857	0.0293	−0.0561	−0.0550	0.0011

Volumetric behaviour

The experimental excess molar volumes V^E are positive over the whole mole fraction range for all systems studied at 298.15 K and becomes more positive as the length of n-alkane chain increases (Figs. 1 and 2). Values of V^E obtained here are found to be in reasonable agreement with values published in the literature for some systems studied previously [1]. Comparing the two sets of results for methylacetate + n-alkanes and the n-butylacetate + n-alkanes, the magnitude of V^E increases as the n-alkane chain-length increases. For mixtures containing a common n-alkane, V^E decreases with increasing alkylacetates chain-length. Table 3 gives the calculated equimolar values of the three contributions ΔV_{inter}, ΔV_P^* and ΔV_F) to V^E, according to eqn. (3), together with ΔH_M and X_{12}. An analysis of each of the three theoretical contributions to V^E shows that the interactional contribution is positive and increases as the chain-length of the n-alkane increases for any alkylacetates. This behaviour indicates that ΔH_M should also change in the



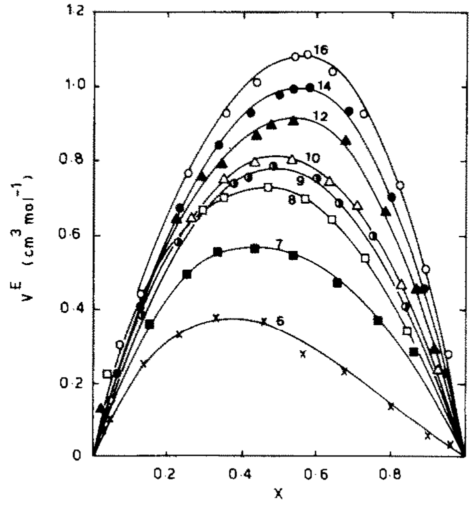
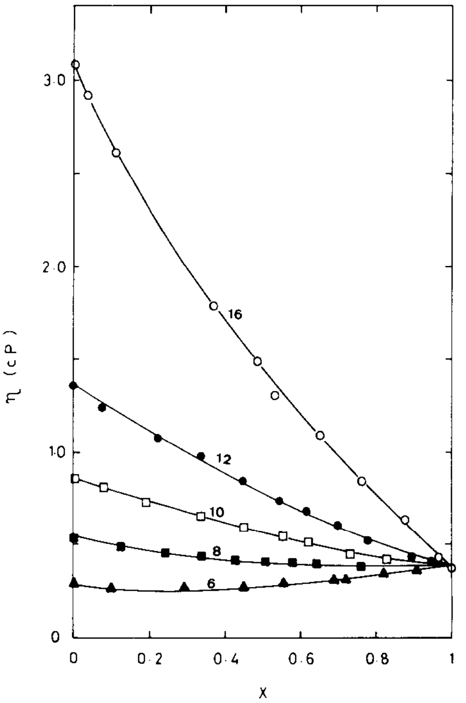


Fig. 1. Excess molar volumes of (x)methylacetate + (1 − x)n-alkanes at 298.15 K. Labels indicate the number of carbon atoms in n-alkanes.

Fig. 2. Excess molar volumes of (x)n-butylacetate + (1 − x)n-alkanes at 298.15 K. Labels indicate the number of carbon atoms in n-alkanes.

same fashion. The free volume contribution is negative due to the positive curvature of $\tilde{V}(T)$. The third contribution $\Delta V_P^{\star}$, due to the differences in internal energy and in reduced volume of the components, is negative for systems where $P_1^{\star}$(alkylacetate) is higher than $P_2^{\star}$(n-alkane) and $\tilde{V}_1 < \tilde{V}_2$. The $\Delta V_P^{\star}$ contribution is larger than the free volume contribution ΔV_F. This is due to the larger difference that exists between the $P^{\star}$ parameters for alkylacetates and n-alkanes than between $\tilde{V}$.

In the 0.2516–1.0238 cm^3 mol^{-1} range, the calculated values of V^E were much larger than those found experimentally. To obtain a better fit to the experimental V^E, the X_{12} values were changed to 45.0 and 32.0 J cm^{-3} for methylacetate and n-butylacetate, respectively. The need to change the values of X_{12} calculated from the experimental values of ΔH_M to predict V^E values contrasts with dioxane + n-alkane systems [9] where V^E agreed reasonably with ΔH_M values of X_{12}. The behaviour of this class of mixtures is similar to that of nitromethane + n-alkane systems [9]. It has been suggested that this difference is probably due to the polarity of alkylacetate.



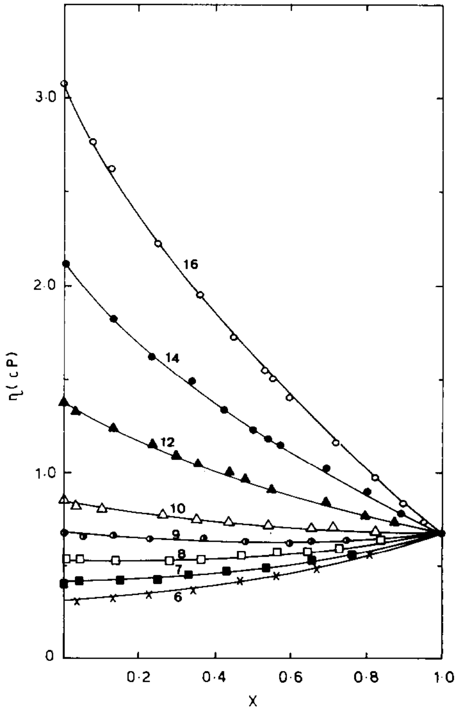


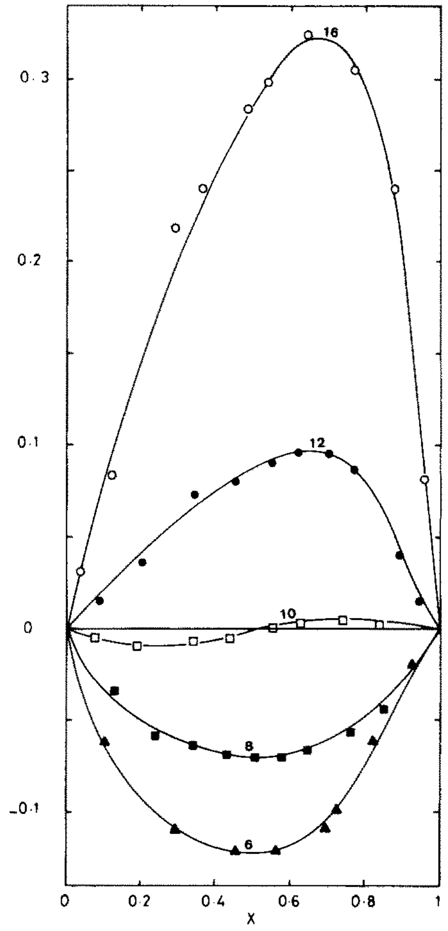
Fig. 3. Viscosity of (x)methylacetate + $(1-x)$n-alkanes at 298.15 K. Labels indicate the number of carbon atoms in n-alkanes.

Fig. 4. Viscosity of (x)n-butylacetate + $(1-x)$n-alkanes at 298.15 K. Labels indicate the number of carbon atoms in n-alkanes.

This indicates that the Van–Patterson theory [9] does not take into the account the polar contribution effect. The less polar n-butylacetate gives less difference between the experimental and predicted V^E than that of the higher polarity methylacetate. We believe that the original Prigogine–Flory–Patterson theory should be amended to have another polar contribution effect.

Viscosimetric behaviour

Experimental data of viscosity, η are given in Table 1 and plotted in Figs. 3 and 4 as a function of the mole fraction x of methylacetate or n-butylace-



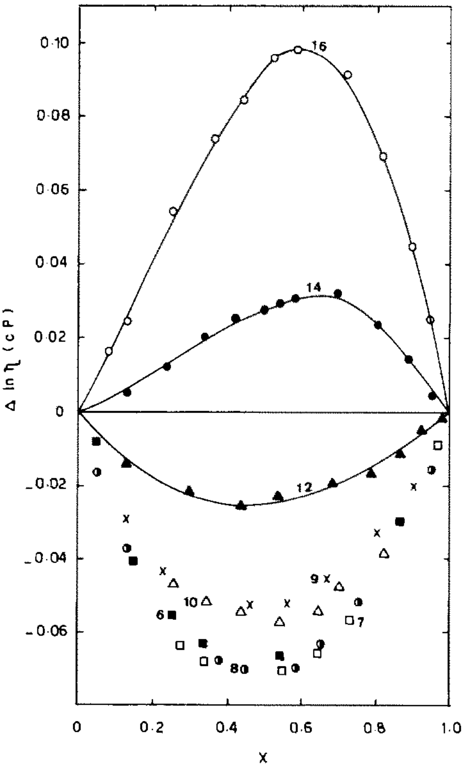
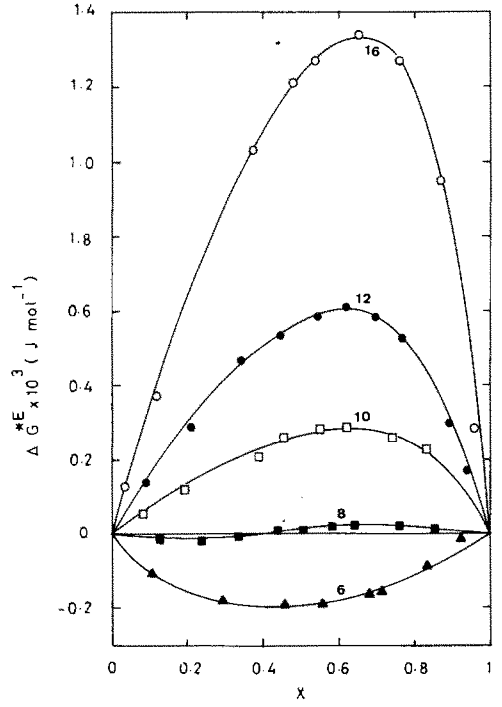


Fig. 5. Excess viscosity of (x)methylacetate + $(1-x)$n-alkanes at 298.15 K. Labels indicate the number of carbon atoms in n-alkanes.

Fig. 6. Excess viscosity of (x)n-butylacetate + $(1-x)$n-alkanes at 298.15 K. Labels indicate the number of carbon atoms in n-alkanes.

tate at 298.15 K. All binary mixtures deviate from ideality and show a negative deviation. The values of excess viscosity $\Delta \ln \eta$ obtained from eqn. (4) are listed in Table 1. The value of $\Delta \ln \eta$ is negative for lower n-alkane systems and becomes more positive for longer n-alkane systems (Figs. 5 and 6). The excess activation energy of viscous flow, $\Delta G^{\star E}$ obtained from eqn. (5) are given in Table 1. Also $\Delta G^{\star E}$ is negative for lower n-alkane systems and becomes more and more positive for longer n-alkane systems over the whole mole fraction range. The large and positive $\Delta \ln \eta$ and $\Delta G^{\star E}$ may be attributed to the short-range orientational order in pure n-alkanes. This has been observed for other systems studied previously [10,11]. The predicted excess viscosity from the pure component parameters and excess enthalpies of binary mixtures and the three contributions, $\ln \eta_H$, $\ln \eta_V$ and $\ln \eta_S$ to the viscosity mixtures are found to be in poor agreement with experimental values as shown in Table 4. The difference between the experimental and predicted values $\Delta \ln \eta_{\text{expt}} - \Delta \ln \eta_{\text{th}}$ becomes larger and more positive as the number of carbon atoms increases in the n-alkanes and decreases in al-



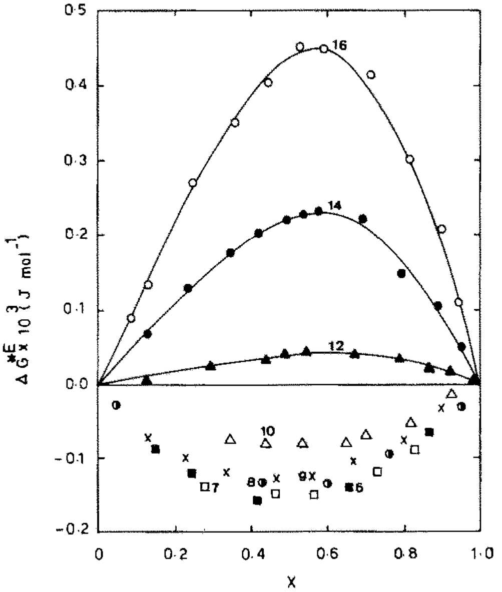


Fig. 7. Excess activation energy of viscous flow of (x)methylacetate + (1 − x)n-alkanes at 298.15 K. Labels indicate the number of carbon atoms in n-alkanes.

Fig. 8. Excess activation energy of viscous flow of (x)n-butylacetate + (1 − x)n-alkanes at 298.15 K. Labels indicate the number of carbon atoms in n-alkanes.

kylacetates. This difference is probably due to: (i) the overestimation of the entropy contribution determined from free volume difference , (ii) neglecting the effect of orientational order and taking the experimental ΔH_{M} rather than X_{12}, (iii) the polarity of alkylacetates, and (iv) the conformational effects in n-alkanes and alkylacetates.

LIST OF SYMBOLS

$A_0, A_1, \ldots, A_i$	coefficients in representation of excess molar volume by eqn. (2)
k	number of coefficients in eqn. (2)
P	pressure
$P^\star$	characteristic pressure
T	thermodynamic temperature
$T^\star$	characteristic temperature
V^{E}	excess molar volume
$V^\star$	characteristic volume
$\tilde{V}$	reduced volume
X_{12}	interchange interaction parameter in Flory theory
x	mole fraction of alkylacetates
ΔH_{M}	excess molar enthalpy
ΔV_{F}	free volume contribution to V^{E}
$\Delta V_P^\star$	pressure effect contribution to V^{E}
$\Delta V_{\mathrm{inter}}$	interactional contribution to V^{E}
$\Delta G^{\star\mathrm{E}}$	excess activation energy of viscous flow
ΔS^{R}	residual entropy
$\Delta \ln \eta$	the excess viscosity
η_i	viscosity of pure component
η	viscosity of mixture
ρ_i	density of pure component
ρ_{m}	density of mixture
θ_2	contact surface fraction
ψ	energy fraction
s	standard deviation

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