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Viscometric Study of (an Aliphatic Methyl Ester + Heptane or Nonane) at the Temperature 298.15 K

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Kinematic viscosities of binary mixtures composed of an aliphatic methyl ester (acetate, butanoate, hexanoate, octanoate, or decanoate) and an *n*-alkane (heptane or nonane) have been determined at 298.15 K and atmospheric pressure for the whole range of compositions. With density data it has been possible to determine other properties of the mixtures, such as the dynamic viscosity and the viscosity deviation. The experimental results have been used to test several empirical and semiempirical equations adopted previously to correlate viscosity−composition data. Additionaly, experimental results are compared with those obtained by applying the group-contribution models UNIVAC and UNIFAC−VISCO.

Introduction

Experimental viscosity results exhibit information on the structure of liquids and are required in the design of processes which involve mass transfer, fluid flow, etc. This has motivated the development of an extensive and varied range of empirical and semiempirical equations to represent the viscosity−composition data of liquid mixtures. A large portion of these equations has been recently revised and classified by Monnery et al. (1995). Of particular importance, however, are the predictive methods based on the concept of functional group, which allow the determination of viscosities for systems which have not been investigated. Wu (1986) and Chevalier et al. (1988) proposed the group-contribution methods UNIVAC and UNIFAC−VISCO, respectively. Both models derive from the reaction rate theory (Glasstone et al., 1941) and the basic ideas of the UNIFAC model, as proposed by Fredenslund et al. (1975) to predict activity coefficients. Both UNIVAC and UNIFAC−VISCO are able to predict the mixture viscosities, but they require the viscosities of the pure components.

This work is part of a research project dealing with the experimental study of several thermodynamic and transport properties, aimed at improving our understanding of the molecular interactions which characterize the physico−chemical behavior of an aliphatic methyl ester + an *n*-alkane + (an *n*-alkane or an *n*-alkanol or an 1-chloroalkane) ternary systems. In this paper experimental kinematic viscosity data, measured at 298.15 K and atmospheric pressure, for $\{CH_3(CH_2)_mCOOCH_3$ (m = 0, 2, 4, 6, 8) + $CH_3(CH_2)_nCH_3$ (n = 5,7)$\}$ binary mixtures are reported. Densities of these mixtures, reported by us as excess volumes (Matos et al., 1994), have been used in this work to calculate the dynamic viscosities and the viscosity deviations from a mole fraction average. Kinematic or dynamic viscosity−composition results have been used to test the applicability of the equations proposed by Grunberg and Nissan (1949), McAllister (1960) (assuming three-body and four-body interactions), Hind et al. (1960), Heric (1966), and Lobe (1973) to these kinds of mixtures. Kinematic viscosities were also compared with those predicted by the UNIVAC and UNIFAC−VISCO models when the structural and energetic sets of parameters proposed by the authors of both models were used.

Kinematic viscosity data for three of the mixtures considered in this study, $\{CH_3(CH_2)_mCOOCH_3$ (m = 0,2,4) + $CH_3(CH_2)_5CH_3\}$, exist in the literature (Dusart et al., 1978). We present a comparison with these results. To our knowledge, there is no futher kinematic viscosity data reported in the literature for the remaining mixtures.

Experimental Section

Materials. Heptane (better than 99.5 mol % pure) and the remaining liquids (better than 99.0 mol % pure) used in this work were obtained from Fluka. All liquids were used without further purification. However, they were stored over molecular sieves (Union Carbide 0.4 nm, Fluka) for several days and degassed just before use. The purity of liquids was checked by comparing the measured physical properties values with those reported in the literature. Densities ρ at 298.15 K were reported previously (Matos et al., 1994) and showed to be in good agreement with the corresponding literature data. Other properties such as kinematic viscosity ν, dynamic viscosity η (=$\nu\rho$), and refraction index at the sodium D line n_D are compared in Table 1.

Apparatus and Procedure. Binary mixtures were prepared by mass using a Mettler balance with a precision of ±0.02 mg. The uncertainty of the mole fraction in the methyl ester was estimated to better than $\pm 5 \times 10^{-5}$.

Kinematic viscosity measurements of the pure substances and their mixtures were made with a Schott Geräte apparatus, which consists of a thermostatic bath (CT-1450) and a stand which contains two TC (thermal conductance) sensors settled transversally to the capillary viscometer, with the purpose of automatically measuring the running time of the meniscus between two fixed positions. A Schott KPG Ubbelohde capillary viscometer previously calibrated

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Table 1. Experimental Kinematic Viscosities (ν), Dynamic Viscosities (η), and Refractive Indices (n_D) of Pure Liquids at 298.15 K and Their Comparison with Literature Values

	ν/mm^2·s^{-1}		η/mPa·s		n_D	
liquid	this work	lit.	this work	lit.	this work	lit.
methyl acetate	0.394	0.3881[a] 0.392[b]	0.365	0.364[b]	1.3591	1.35925[f]
methyl butanoate	0.609		0.543	0.541[d]	1.3851	1.3849[g]
methyl hexanoate	0.947		0.833		1.4032	1.4029[g]
methyl octanoate	1.463		1.276		1.4150	1.4148[g]
methyl decanoate	2.235		1.941		1.4238	1.4232[g]
heptane	0.572	0.5702[c]	0.389	0.3967[b] 0.3870[e]	1.3853	1.3852[h] 1.3855[i]
nonane	0.927	0.9206[c]	0.662	0.6696[b]	1.4033	1.4035[i] 1.40311[b]

[a] Wei and Rowley (1984). [b] Riddick et al. (1986). [c] Chevalier et al. (1990). [d] *TRC Thermodynamic Tables* (1976). [e] Kouris and Panayiotou (1989). [f] De Soria et al. (1988). [g] Ortega et al. (1990). [h] Treszcanowicz (1990). [i] Ortega and Matos (1986).

Table 2. Kinematic Viscosities (ν), Dynamic Viscosities (η), and Viscosity Deviations ($\Delta\eta$) at 298.15 K for the Methyl Alkanoates (1) + *n*-Alkanes (2) Mixtures

x_1	ν/mm^2·s^{-1}	η/mPa·s	$\Delta\eta$/mPa·s	x_1	ν/mm^2·s^{-1}	η/mPa·s	$\Delta\eta$/mPa·s
Methyl Acetate (1) + Heptane (2)							
0.0714	0.550	0.378	−0.0093	0.5933	0.438	0.341	−0.0338
0.1439	0.530	0.369	−0.0165	0.7023	0.422	0.341	−0.0311
0.1953	0.516	0.363	−0.0213	0.7964	0.410	0.344	−0.0259
0.2923	0.494	0.355	−0.0270	0.8801	0.402	0.350	−0.0179
0.3938	0.473	0.348	−0.0315	0.9385	0.397	0.356	−0.0105
0.5006	0.453	0.343	−0.0340				
Methyl Butanoate (1) + Heptane (2)							
0.1060	0.557	0.388	−0.0173	0.5989	0.553	0.437	−0.0442
0.2020	0.550	0.391	−0.0291	0.6875	0.560	0.454	−0.0409
0.3062	0.546	0.399	−0.0372	0.7944	0.572	0.478	−0.0333
0.3814	0.545	0.406	−0.0417	0.8971	0.588	0.508	−0.0192
0.4930	0.548	0.420	−0.0449				
Methyl Hexanoate (1) + Heptane (2)							
0.1126	0.587	0.412	−0.0270	0.5921	0.729	0.581	−0.0709
0.2066	0.605	0.435	−0.0457	0.6856	0.770	0.628	−0.0654
0.2908	0.625	0.460	−0.0581	0.7836	0.818	0.683	−0.0539
0.3885	0.655	0.495	−0.0665	0.8832	0.873	0.747	−0.0341
0.4907	0.690	0.536	−0.0709				
Methyl Octanoate (1) + Heptane (2)							
0.0765	0.606	0.422	−0.0349	0.5093	0.898	0.707	−0.1337
0.0994	0.617	0.433	−0.0442	0.5863	0.968	0.776	−0.1330
0.1151	0.625	0.441	−0.0501	0.5945	0.976	0.784	−0.1323
0.1883	0.665	0.480	−0.0760	0.6832	1.066	0.874	−0.1210
0.2045	0.675	0.490	−0.0804	0.6928	1.076	0.884	−0.1195
0.2856	0.726	0.539	−0.1033	0.7854	1.181	0.989	−0.0966
0.2977	0.734	0.547	−0.1061	0.8030	1.202	1.010	−0.0913
0.3848	0.797	0.608	−0.1223	0.8760	1.293	1.102	−0.0640
0.4153	0.820	0.631	−0.1264	0.8870	1.308	1.117	−0.0588
0.4927	0.883	0.693	−0.1330	0.9238	1.357	1.167	−0.0414
Methyl Decanoate (1) + Heptane (2)							
0.1008	0.660	0.466	−0.0794	0.5944	1.320	1.068	−0.2435
0.1999	0.758	0.554	−0.1452	0.6834	1.486	1.224	−0.2256
0.2890	0.861	0.646	−0.1915	0.7811	1.690	1.417	−0.1843
0.3841	0.985	0.759	−0.2261	0.8895	1.943	1.659	−0.1105
0.4927	1.147	0.907	−0.2467				
Methyl Acetate (1) + Nonane (2)							
0.0979	0.853	0.615	−0.0179	0.6125	0.562	0.445	−0.0351
0.1777	0.798	0.581	−0.0282	0.7188	0.513	0.419	−0.0295
0.2126	0.775	0.567	−0.0319	0.7996	0.477	0.401	−0.0235
0.3144	0.714	0.531	−0.0376	0.8874	0.439	0.383	−0.0154
0.3968	0.668	0.504	−0.0402	0.9436	0.417	0.374	−0.0078
0.4910	0.620	0.477	−0.0392				
Methyl Butanoate (1) + Nonane (2)							
0.1130	0.870	0.631	−0.0176	0.6002	0.689	0.548	−0.0426
0.2015	0.827	0.609	−0.0290	0.6936	0.666	0.542	−0.0375
0.2891	0.790	0.590	−0.0376	0.7934	0.643	0.538	−0.0296
0.3977	0.750	0.572	−0.0427	0.8890	0.625	0.538	−0.0182
0.4856	0.722	0.560	−0.0442				
Methyl Hexanoate (1) + Nonane (2)							
0.0982	0.906	0.658	−0.0208	0.5902	0.886	0.710	−0.0529
0.1959	0.892	0.660	−0.0355	0.6983	0.894	0.733	−0.0484
0.2981	0.884	0.667	−0.0460	0.7953	0.907	0.760	−0.0380
0.3744	0.881	0.675	−0.0510	0.8924	0.923	0.791	−0.0236
0.4883	0.881	0.691	−0.0545				
Methyl Octanoate (1) + Nonane (2)							
0.0990	0.947	0.690	−0.0328	0.5937	1.157	0.934	−0.0925
0.1968	0.974	0.725	−0.0578	0.6887	1.219	1.002	−0.0829
0.2897	1.008	0.765	−0.0749	0.7862	1.286	1.078	−0.0667
0.3810	1.048	0.810	−0.0859	0.8882	1.366	1.167	−0.0404
0.4918	1.102	0.871	−0.0930				
Methyl Decanoate (1) + Nonane (2)							
0.1149	1.010	0.742	−0.0670	0.5871	1.521	1.233	−0.1799
0.1917	1.075	0.803	−0.1042	0.6966	1.682	1.391	−0.1620
0.2932	1.171	0.895	−0.1420	0.7889	1.833	1.539	−0.1320
0.3874	1.271	0.991	−0.1665	0.8923	2.019	1.724	−0.0793
0.4898	1.392	1.108	−0.1805				

by Schott Geräte was used. The viscometer constant was periodically checked using deionized doubly distilled water and benzene (Riddick et al., 1986) as standard reference fluids. The control of the capillary temperature was carried out to an accuracy of ±0.01 K by means of a digital thermometer Anton Paar DT 100-20. The kinematic viscosities were calculated from the equation

$$\nu = C(t - \theta) \tag{1}$$

where C is the viscometer constant and θ the Hagenbach correction. The times, t, measured using an automatic stopwatch AVS-350 with a precision of ±0.01 s, employed in eq 1 were averaged over five consecutive measurements. θ values were provided by Schott Geräte. The accuracy was estimated to be better than ±0.2%.

The refraction indices of the pure substances were determined to a precision of $\pm 1 \times 10^{-4}$ units of n_D, by means of an Atago Abbe refractometer model 3T thermostated at (298.15 ± 0.01) K with a Polyscience digital temperature controller.

Results and Discussion

The densities of the mixtures were used jointly with the experimental ν results to calculate the dynamic viscosities , and the viscosity deviation function $\Delta\eta$ defined as

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \tag{2}$$

where x_i is the mole fraction. The subscripts 1 and 2 make reference to the methyl ester and the *n*-alkane, respectively.

Table 2 lists the experimental results, and those computed from them, for each mixture. The data were correlated with the composition, according to a polynomial equation of variable degree

$$Y = a\sum_{k=0}^{N} A_k Z^k \tag{3}$$

using ($a = 1$; $Z = x_1$) when $Y \equiv \nu$ or η, and ($a = x_1x_2$; $Z = x_1 - x_2$) when $Y \equiv \Delta\eta$. The A_k parameters, obtained using an unweighted least-squares method, and the standard deviations, are listed in Table 3.

The average absolute deviation (AAD) between the kinematic viscosity data in this study and those reported by Dusart et al. (1978) for the mixtures {$CH_3(CH_2)_m$-$COOCH_3$ ($m = 0, 2, 4$) + $CH_3(CH_2)_5CH_3$} decreases as m increases (2.4% for $m = 0$, 1.9% for $m = 2$, 0.33% for $m = 4$). Our experimental results are systematically lower, at any composition, for $m = 0$ and 2. Similar disagreements

Table 3. Parameters A_k and Standard Deviations σ Obtained with Eq 3 for Different Properties at 298.15 K of the $\{CH_3(CH_2)_mCOOCH_3$ (1) + C_nH_{2n+2} (2)} Binary Systems

m	n	property	A_0	A_1	A_2	A_3	A_4	σ
0	7	$\nu/mm^2 \cdot s^{-1}$	0.5721	−0.3292	0.2653	−0.2140	0.0997	0.0003
		η/mPa·s	0.3890	−0.1691	0.2281	−0.2095	0.1264	0.0002
		$\Delta\eta$/mPa·s	−0.1352	−0.0220	−0.0319			0.0002
2	7	$\nu/mm^2 \cdot s^{-1}$	0.5719	−0.1704	0.3519	−0.2825	0.1382	0.0003
		η/mPa·s	0.3890	−0.0361	0.2714	−0.2012	0.1201	0.0004
		$\Delta\eta$/mPa·s	−0.1795	−0.0189	−0.0297			0.0003
4	7	$\nu/mm^2 \cdot s^{-1}$	0.5722	0.0844	0.4060	−0.2495	0.1339	0.0005
		η/mPa·s	0.3893	0.1565	0.3553	−0.2028	0.1347	0.0006
		$\Delta\eta$/mPa·s	−0.2864	−0.0342	−0.0320			0.0006
6	7	$\nu/mm^2 \cdot s^{-1}$	0.5712	0.4285	0.3686	0.0950		0.0005
		η/mPa·s	0.3882	0.4228	0.3307	0.1338		0.0005
		$\Delta\eta$/mPa·s	−0.5335	−0.0741	−0.0098	0.0224		0.0003
8	7	$\nu/mm^2 \cdot s^{-1}$	0.5718	0.8051	0.6124	0.2445		0.0012
		η/mPa·s	0.3894	0.6815	0.6895	0.0729	0.1074	0.0008
		$\Delta\eta$/mPa·s	−0.9867	−0.1335	−0.0264	−0.0401		0.0005
0	9	$\nu/mm^2 \cdot s^{-1}$	0.9273	−0.8134	0.5350	−0.3660	0.1111	0.0006
		η/mPa·s	0.6622	−0.5263	0.4431	−0.3527	0.1386	0.0004
		$\Delta\eta$/mPa·s	−0.1564	0.0369	−0.0337			0.0004
2	9	$\nu/mm^2 \cdot s^{-1}$	0.9273	−0.5508	0.2886	−0.0568		0.0009
		η/mPa·s	0.6619	−0.2969	0.1779			0.0005
		$\Delta\eta$/mPa·s	−0.1787	0.0009				0.0005
4	9	$\nu/mm^2 \cdot s^{-1}$	0.9270	−0.2540	0.4458	−0.3068	0.1351	0.0004
		η/mPa·s	0.6620	−0.0729	0.3666	−0.2633	0.1407	0.0003
		$\Delta\eta$/mPa·s	−0.2178	0.0087	−0.0354			0.0003
6	9	$\nu/mm^2 \cdot s^{-1}$	0.9264	0.1782	0.3573			0.0012
		η/mPa·s	0.6612	0.2716	0.2821	0.0607		0.0009
		$\Delta\eta$/mPa·s	−0.3730	−0.0295	−0.0231			0.0006
8	9	$\nu/mm^2 \cdot s^{-1}$	0.9269	0.6599	0.5899	−0.0429	0.1012	0.0003
		η/mPa·s	0.6621	0.6291	0.5602	−0.0255	0.1150	0.0003
		$\Delta\eta$/mPa·s	−0.7233	−0.1029	−0.0292			0.0003

are detected when comparing the ν results at 298.15 K reported by Dusart et al. (1978) for the mixtures methyl benzoate + heptane and ethyl benzoate + heptane with those reported by Blanco et al. (1993) (3 and 2.2%, respectively) and for the mixtures heptane + octane with those reported by Chevalier et al. (1990) (1.5%). In all mentioned cases the ν results by Dusart et al. (1978) are larger at any composition. Besides, the kinematic viscosity values reported herein for the mixtures methyl acetate + heptane or nonane are coherent with those reported by Wei and Rowley (1984) for the mixture methyl acetate + hexane as well as with those reported by De Soria et al. (1988) for the mixture methyl acetate + pentane.

Parts a and b of Figure 1 show the variation with composition of viscosity deviation for mixtures containing heptane and nonane, respectively. The differences between $\Delta\eta$ values obtained herein and those calculated from results by Dusart et al. (1976, 1978) ranged between 3.1 and 6.3%. However, in comparison with our data, the asymmetries of the curves $\Delta\eta(x_1)$ are similar for all cases.

Figure 2 shows that values of $\Delta\eta$ calculated at equimolar fraction decrease as the number of CH_2 groups in the radical R in methyl ester $RCOOCH_3$ increases. This sequence, tightly related to the weakening of the dipole−dipole interactions with the increase of the R volume, is also observed for the excess molar volumes V^E (Matos et al., 1994) and for the excess molar enthalpies H^E (Ortega et al., 1990, 1991) of these mixtures. However, the molecular size differences as well as the dispersion forces (Fort and Moore, 1966) also play a relevant role in the justification of the observed behavior. In fact, the application of the molecular group contribution model by Nitta et al. (1977) to the studied mixtures indicates that the dispersive contribution to $V^E$and H^E is significantly higher than any of the other contributions considered in the model.

In order to evaluate their utility to describe the viscometric behavior of this kind of mixture, the following equations relating viscosities of binary mixtures as a function of those of the pure components were selected:

—McAllister (for three-body interactions) (1960):

$$\ln(\nu M) = x_1^3 \ln(\nu_1 M_1) + x_2^3 \ln(\nu_2 M_2) + 3x_1^2 x_2 \ln(\nu_{12} M_{12}) + 3x_1 x_2^2 \ln(\nu_{21} M_{21}) \quad (4)$$

$$M_{ij} = (2M_i + M_j)/3$$

—McAllister (for four−body interactions) (1960):

$$\ln(\nu M) = x_1^4 \ln(\nu_1 M_1) + x_2^4 \ln(\nu_2 M_2) + 4x_1^3 x_2 \ln(\nu_{1112} M_{1112}) + 6x_1^2 x_2^2 \ln(\nu_{1122} M_{1122}) + 4x_1 x_2^3 \ln(\nu_{2221} M_{2221}) \quad (5)$$

$$M_{1112} = (3M_1 + M_2)/4 \qquad M_{1122} = (M_1 + M_2)/2 \qquad M_{2221} = (M_1 + 3M_2)/4$$

—Grunberg and Nissan (1949):

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \quad (6)$$

—Hind et al. (1960):

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

—Heric (1966):

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln M + \beta_{12} + \beta_{21}(x_1 - x_2) \quad (8)$$

—Lobe (1973):

$$\nu = \phi_1 \nu_1 \exp[\phi_2 \alpha_{12} \ln(\nu_2/\nu_1)] + \phi_2 \nu_2 \exp[\phi_1 \alpha_{21} \ln(\nu_2/\nu_1)] \quad (9)$$

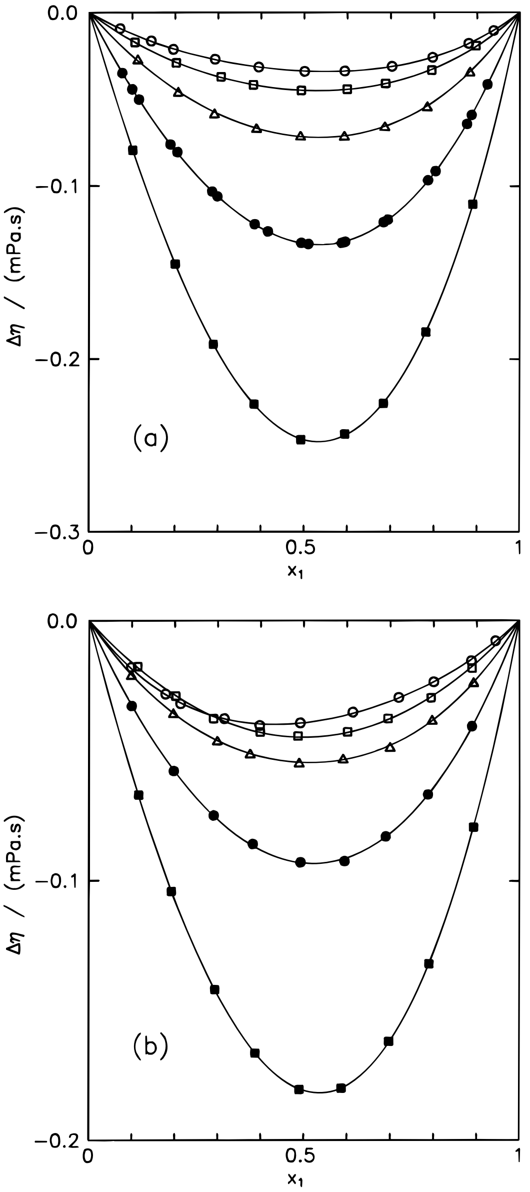

Figure 1. Viscosity deviations $\Delta\eta$ at 298.15 K for $\{x_1CH_3(CH_2)_m$-$COOCH_3 + x_2CH_3(CH_2)_5CH_3$ (a) or $+ x_2CH_3(CH_2)_7CH_3$ (b)$\}$ binary systems plotted *vs* the mole fraction of methyl ester: (0) $m = 0$; $m = 2$; (△) $m = 4$; (●) $m = 6$; (■) $m = 8$.

In the above equations M_i and ϕ_i are the molecular mass and the volume fraction of the ith component, respectively. is the mean molecular mass of the mixture computed $M = x_1M_1 + x_2M_2$. All the undefined symbols are adjustable parameters.

Since for equations containing a single parameter it is customary to compute its value for each composition (Fort and Moore, 1966), a single value of this parameter was used in this work to characterize the system. All the fittings were carried out in combination with Marquardt's algorithm (1963). Table 4 shows the parameter values obtained from McAllister's formulas. In Table 5 the parameters obtained from the remaining formulas are listed. Parts a and b of Figure 3 show the variation of these parameters *vs* the number of CH_2 groups in the methyl esters. In the graph we have omitted the parameters α_{12} and α_{21} because they do not present a regular distribution. Similarly, we have omitted ν_{12} and ν_{21}, although they show a regular distribution, in favor of the representation of the quartic equation parameters; the latter parameters fit to the experimental data with a global average error (considering all the studied systems) smaller than that produced by the former parameters. We remark that the ν_{1122} parameter in McAllister's formula presents values practically intermediate to the values of ν_{1112} and ν_{2221} parameters. When this is taken into account in the fitting, the standard deviations obtained do not show significant changes, although they are slightly larger.

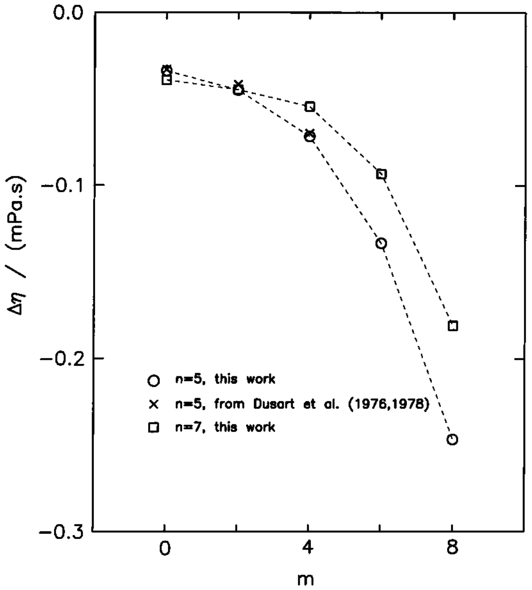

Figure 2. Plots of $\Delta\eta$ calculated at the equimolar fraction and at 298.15 K of $\{CH_3(CH_2)_mCOOCH_3$ ($m = 0, 2, 4, 6, 8$) $+ CH_3(CH_2)_n$-CH_3 ($n = 5, 7$)$\}$ binary systems *vs* m. Data of $\Delta\eta$ ($x_1 = 0.5$) calculated from Dusart *et al.* (1976, 1978) for mixtures containing heptane are also included.

The best fit of the data was obtained using McAllister's equation, assuming four-body interactions, with a global average error less than 0.05%. The global average errors corresponding to the remaining equations show the following increasing sequence: 0.10% (three-body interaction McAllister and Heric formulas), 0.19% (Lobe formula),

Table 4. Values of Parameters and Standard Deviations σ Obtained for the $\{CH_3(CH_2)_mCOOCH_3$ (1) $+ C_nH_{2n+2}$ (2)$\}$ Binary Systems Using Eqs 4 and 5

system		McAllister (eq 4) (for three-body interactions)			McAllister (eq 5) (for four-body interactions)			
m	n	ν_{12}	ν_{21}	σ/mm^2·s^{-1}	ν_{1112}	ν_{1122}	ν_{2221}	σ/mm^2·s^{-1}
0	7	0.4176	0.4793	0.001	0.4064	0.4555	0.4960	0.0003
2	7	0.5419	0.5248	0.001	0.5520	0.5436	0.5304	0.0003
4	7	0.7541	0.6138	0.001	0.7908	0.6916	0.5962	0.001
6	7	1.0632	0.7463	0.001	1.1467	0.8934	0.6936	0.001
8	7	1.4980	0.9480	0.001	1.6432	1.1987	0.8241	0.001
0	9	0.5666	0.6994	0.001	0.5156	0.6261	0.7492	0.001
2	9	0.6581	0.7620	0.001	0.6450	0.7077	0.7999	0.001
4	9	0.8723	0.8527	0.001	0.8848	0.8724	0.8652	0.0003
6	9	1.1941	0.9914	0.001	1.2492	1.0986	0.9684	0.001
8	9	1.6456	1.1969	0.001	1.7684	1.4111	1.1154	0.0004

Table 5. Values of Parameters and Standard Deviations σ Obtained for the $\{CH_3(CH_2)_mCOOCH_3$ (1) + C_nH_{2n+2} (2)$\}$ Binary Systems Using Eqs 6−9

system		Grunberg−Nissan (eq 6)		Hind et al. (eq 7)		Heric (eq 8)			Lobe (eq 9)		
m	n	d	σ/mPa·s	η_{12}	σ/mPa·s	β_{12}	β_{21}	σ/mPa·s	α_{12}	α_{21}	σ/mm^2·s^{-1}
0	7	−0.3846	0.002	0.3069	0.002	−0.1476	−0.0195	0.001	2.0298	−3.8008	0.002
2	7	−0.3564	0.001	0.3742	0.002	−0.3043	0.0167	0.001	−1.2183	6.5358	0.003
4	7	−0.2173	0.003	0.4656	0.003	−0.2130	0.0561	0.001	0.4683	0.2174	0.001
6	7	−0.0233	0.003	0.5649	0.005	−0.0107	0.0578	0.001	0.9660	−0.6108	0.001
8	7	0.2184	0.001	0.6701	0.011	0.1641	0.0241	0.002	1.2613	−0.9450	0.002
0	9	−0.1533	0.001	0.4319	0.003	0.2234	0.1184	0.001	1.5654	−2.8188	0.004
2	9	−0.2860	0.001	0.5132	0.001	−0.1605	−0.0094	0.001	0.7660	−3.0564	0.001
4	9	−0.2818	0.001	0.6360	0.001	−0.2484	0.0233	0.001	−14.4932	32.0088	0.001
6	9	−0.1921	0.004	0.7808	0.002	−0.1892	0.0505	0.001	0.3954	0.2764	0.001
8	9	−0.0437	0.004	0.9382	0.008	−0.0296	0.0356	0.001	1.0293	−0.7301	0.001

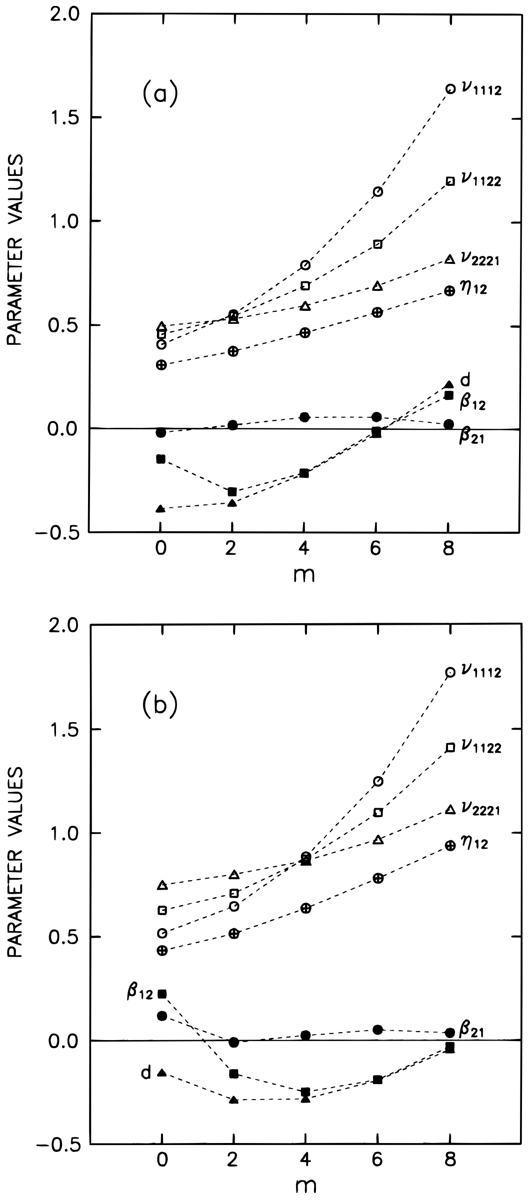

Figure 3. Plot of parameter values involved in eqs 5−8 *vs m* for $\{x_1CH_3(CH_2)_mCOOCH_3$ (m = 0, 2, 4, 6, 8) + $x_2CH_3(CH_2)_5CH_3$ (a) or + $x_2CH_3(CH_2)_7CH_3$ (b)$\}$ binary mixtures.

0.32% (Grunberg−Nissan formula), and 0.46% (Hind et al. formula).

The (x_1, ν) experimental results were also used to test the predictive capability of the UNIVAC and UNIFAC−VISCO group-contribution models. The structural parameters of the groups used in UNIVAC (CH_3COO for acetates, CH_2COO, CH_2, and CH_3) and those relative to the interactions among them were extracted from Wu (1986). The AAD between our experimental and theoretical results oscillates between 0.3% (methyl decanoate + heptane) and 3.4% (methyl butanoate + nonane). For the UNIFAC−VISCO model the groups used are CH_3, CH_2 and COO, and the parameters employed for the application of the model were those reported by Chevalier et al. (1988). In this case the AAD oscillates between 0.2% (methyl acetate or methyl butanoate or methyl hexanoate + nonane) and 1.1% (methyl acetate + heptane).

Conclusions

Kinematic viscosities of the binary mixtures $\{CH_3(CH_2)_m$-$COOCH_3$ (m = 0, 2, 4, 6, 8) + C_nH_{2n+2} (n = 7, 9)$\}$ were measured at 298.15 K and atmospheric pressure over the whole range of compositions. The dynamic viscosities, obtained from density and kinematic viscosity results, show negative deviations from a linear dependence on mole fraction.

All of the selected correlative models are capable of representing with a higher or lesser degree of accuracy the viscometric behavior of the studied mixtures. And the values of the parameters for most of the models vary regularly with the increase in the number of carbon atoms in the methyl ester. The overall average absolute deviations are in all cases lower than 0.5%. It should be noted the excellent results obtained with the equation by Grunberg and Nissan despite the fact that it contains a single parameter.

The tested group contribution models forecast viscosities which are in good agreement with our experimental results, the overall average absolute deviations being lower than 0.6% with UNIFAC−VISCO and 1.4% with UNIVAC.

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