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Influence of the Molecular Structure on the Volumetric Properties and Viscosities of Dialkyl Adipates (Dimethyl, Diethyl, and Diisobutyl Adipates)

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This paper reports new measurements of the density of dimethyl adipate (DMA) and diisobutyl adipate (DiBA) over 12 isotherms from (293.15 to 403.15) K and 15 isobars from (0.1 to 140) MPa. The density of diethyl adipate (DEA) in the same conditions has already been published in a previous work. Viscosity data for the three fluids are also presented from (283.15 to 373.15) K at 0.1 MPa. The influence of the size of the adipate chains on the thermophysical properties has been analyzed. The correlation of the densities against pressure and temperature with the Tammann–Tait equation were used to obtain the isothermal compressibility and the isobaric thermal expansivity. The linear dependence between the tangent bulk modulus at atmospheric pressure and the secant bulk modulus at 100 MPa recently proposed by Kiselev et al. is also used in this work to calculate the isothermal compressibility at atmospheric pressure.

Introduction

In the scope of investigating more benign lubricants we have concentrated our interest on diesters which have excellent properties for industrial applications.¹ They are environmentally friendly and have low cost, low toxicity, and great stability. Diesters are often blended with polyalphaolefins to help additive solubility and to act as seal swelling agents.² Applications include gear oils, engine oils, compressors oils, grease, metal-working, and biodegradable hydraulic fluids.² The small size of their molecules combined with the high polarities makes them effective and novel solvents.^{1,3} Diesters are also used as additives to diesel fuel in direct injection engines.⁴ For the applications of diesters the knowledge of the thermophysical properties is essential. Unfortunately, reliable thermophysical property data are scarce at present for these fluids. In this work we have focused our attention on thermophysical properties of some adipates which are a subgroup of diesters.

In recent years, several authors have initiated the study of the thermophysical properties of adipates. Hence, Ince¹ has measured the density of dimethyl adipate at 293.2 K and 0.1 MPa with an Anton Paar DMA 5400 densimeter with an uncertainty of 0.05 kg·m⁻³. Korösl and Kováts⁵ have determined density values of dimethyl adipate at 0.1 MPa and (293.15 and 353.15) K by using an ASTM pycnometer with uncertainties of (0.3 and 0.6) kg·m⁻³, respectively. Comuñas et al.⁶ have reported density data of diethyl adipate (DEA) from (0.1 to 140) MPa and from (293.15 to 403.15) K using an Anton Paar DMA HPM with a density uncertainty of 0.05 %. Later, Meng et al.⁷ have also published density and viscosity data of diethyl adipate from (303.15 to 363.15) K and from (0.1 to 20) MPa. These

authors have used a vibrating wire viscometer with a density uncertainty of 0.2 % and a viscosity uncertainty of 2 %. De Lorenzi et al.⁸ have reported the density of di(2-ethylhexyl)adipate ($M_w = 370.57 \text{ g}\cdot\text{mol}^{-1}$) at 0.1 MPa and from (288.17 to 367.65) K and the viscosity at the same pressure and from (291.29 to 368.49) K. These authors have used a vibrating tube densimeter, model DMA 602HD-DMA60 (Anton Paar) with an estimated precision around 0.03 kg·m⁻³.

With the aim to complete the database of thermophysical properties of dialkyl adipates in the present work, dimethyl adipate (DMA) and diisobutyl adipate (DiBA) are studied. Thus, density, isothermal expansivities, and thermal isobaric expansivities have been reported from (293.15 to 403.15) K and up to 140 MPa, together with viscosity at 0.1 MPa from (278.15 to 373.15) K for DMA, DiBA, and diethyl adipate (DEA). The data reported in this paper have been compared with those previously published^{6,7} for DEA to analyze the influence of the molecular structure in density and viscosity.

Experimental Section

Materials. Dimethyl adipate (CAS number 627-93-0, C₁₄H₂₆O₄, molar mass: 174.19 g·mol⁻¹), diisobutyl adipate (CAS number 141-04-8, C₈H₁₄O₄, molar mass: 258.35 g·mol⁻¹), and diethyl adipate (CAS number 141-28-6, C₁₀H₁₈O₄, molar mass: 202.25 g·mol⁻¹) were obtained from Aldrich with 99 % purity. Water was purified using a Milli-Q Plus system. The molecular structures of dialkyl adipates studied in this work are presented in Figure 1.

Measurement Technique. The density ρ as a function of pressure and temperature was measured with a high pressure vibrating tube densimeter Anton Paar DMA HPM which is adequate to perform measurements up to 140 MPa. The calibration of this equipment has been performed with vacuum, water,⁹ and decane⁶ from (293.15 to 403.15) K up to 140 MPa. The temperature of the vibrating tube cell is controlled through

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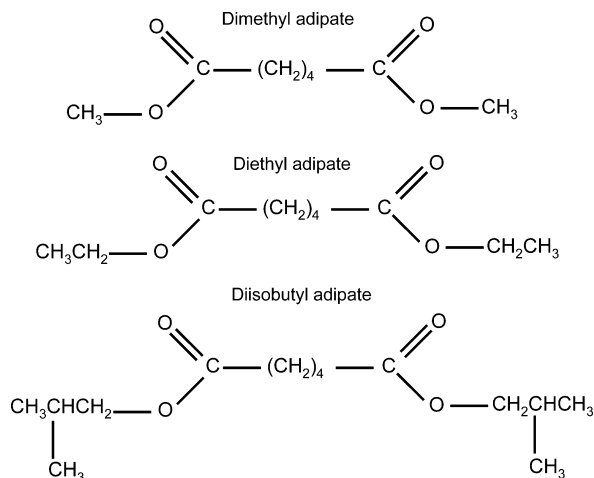


Figure 1. Molecular structures of dialkyl adipates.

a thermostatic bath Julabo Polystat 36 and measured inside the cell block with an AOIP PN 5207 thermometer with an uncertainty of ± 0.05 K. The temperature was kept constant within ± 0.01 K. The pressure of the system was applied with a piston pressure intensifier (Top Industries) and measured with an absolute manometer HBM PE 200/2000 with an uncertainty of ± 0.1 % of full scale 0.2 MPa. The estimated density uncertainty is less than 0.1 %. The calibration procedure has been previously verified by using 1-butanol and toluene.⁶ Viscosity at atmospheric pressure was measured with a rotational automated viscometer Anton Paar Stabinger SVM3000 with cylinder geometry. This apparatus has a density measuring cell that also employs the oscillating U-tube principle. This equipment uses Peltier elements for fast and efficient thermostability. The temperature uncertainty is ± 0.02 K from (288.15 to 378.15) K. The reproducibility of the dynamic viscosity measurements is 0.35 % from (288.15 to 378.15) K. In the present work the viscosity uncertainty has been checked with two reference fluids from Cannon Instrument (S60 and N100) finding that the deviations are lower than 1 %.

Results and Discussion

Density measurements have been performed from (293.15 to 403.15) K and up to 140 MPa. Densities for dimethyl adipate and diisobutyl adipate as a function of pressure and temperature are displayed in Tables 1 and 2. No density data are reported at the lowest temperature (293.15 K) and at pressures higher than 100 MPa. At these conditions large fluctuations were observed in the periods of the vibrating tube. This fact is probably due to the appearance of solid–liquid equilibria. At atmospheric pressure the melting temperature of DMA is around 283.15 K.

The values reported in our previous work⁶ for diethyl adipate are added in Figure 2 with those reported here. At fixed temperature and pressure the following trend is found for densities: $\rho_{\text{DMA}} > \rho_{\text{DEA}} > \rho_{\text{DiBA}}$. In addition, the density values of these adipates are lower than those of di(2-ethylhexyl)adipate.⁸ So, density decreases with the molecular size (molar mass or number of carbon atoms). This is the usual behavior of liquids with polar molecules, for which the increase of the nonpolar groups induces a decrease of density. We assume that the increase of the size of the adipate chains causes both a dilution of the intermolecular forces among the ester groups and a loosening of the closely packed arrangement of the molecules by disrupting the local configurational order, and hence a less efficient packing (bigger molar volume). In addition, although

the molar mass increases simultaneously with the length of the adipate chains, the ratio of heavy atoms to the number of carbons in the molecule diminishes, which also contributes to lower density values.^{10,11}

The experimental density values have been correlated successfully using the following Tammann–Tait type equation:

$$\rho = \frac{\rho_0}{1 - C \ln\left(\frac{B + p/\text{MPa}}{B + 0.1}\right)} \quad (1)$$

where ρ_0 and B are given by:

$$\rho_0/\text{kg}\cdot\text{m}^{-3} = A_0 + A_1(T/\text{K}) + A_2(T^2/\text{K}^2) \quad (2)$$

$$B/\text{MPa} = B_0 + B_1(T/\text{K}) + B_2(T^2/\text{K}^2) \quad (3)$$

Coefficients A_i ($i = 0, 1, 2$) have been determined in a preliminary fit of the density at 0.1 MPa as a function of the temperature. Coefficients B_j ($j = 0, 1, 2$) and C have been further fitted to the density measurements, at pressures different than 0.1 MPa, using the Levenberg–Marquardt algorithm. Table 3 reports the values of A_i and B_i coefficients. The standard deviations of these correlations are (0.3 and 0.2) $\text{kg}\cdot\text{m}^{-3}$ for DMA and DiBA, respectively. It was 0.3 $\text{kg}\cdot\text{m}^{-3}$ for DEA.⁶

The density values have also been determined with the Anton Paar Stabinger SVM3000 apparatus. The average relative deviation between the data measured with the DMA HPM and those from SVM3000 equipment is 0.13 % for the three dialkyl adipates. The density values reported in the present work for dimethyl adipate at 0.1 MPa has been compared with those reported previously by Ince¹ and by Korösl and Kováts⁵ finding relative deviations of 0.02 % and 0.1 %, respectively.

The temperature and pressure dependence of the isothermal compressibility, κ_T , was calculated according to its definition:

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \quad (4)$$

from the analytical differentiation of eq 1 with respect to pressure. This method is certainly the most direct way to obtain reliable isothermal compressibility values¹² from density measurements. From eq 1 the following expression is obtained:

$$\kappa_T/\text{MPa}^{-1} = \frac{C}{(B + p) \left[1 - C \ln \frac{B + p}{B + 0.1} \right]} \quad (5)$$

The values of parameter C and of B_i coefficients for the temperature function $B(T)$ are taken from Table 3. We have estimated an uncertainty of 1 % in the isothermal compressibility. This value has also been checked in our previous work on DEA⁶ by comparing the values of κ_T for toluene reported by the National Institute of Standards and Technology (NIST) and those obtained from eq 5. The isothermal compressibility for dimethyl and diisobutyl adipate is summarized in Table 4. The values for DEA are from our previous work.⁶ The behavior of the isothermal compressibility as a function of pressure for the three dialkyl adipates can be seen in Figure 3 at two different temperatures. This property decreases with pressure and increases with temperature for the three dialkyl adipates. Probably

Table 1. Experimental Densities, $\rho/\text{kg}\cdot\text{m}^{-3}$, for Dimethyl Adipate at Different Pressures, p , and Temperatures, T

p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$											
	T/K											
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15
0.1	1061.5	1051.8	1042.1	1031.6	1022.6	1012.3	1002.2	992.2	981.9	972.2	961.7	951.5
10	1067.7	1058.0	1048.9	1038.9	1029.6	1020.4	1010.8	1000.6	991.0	981.1	971.7	961.4
20	1073.6	1064.4	1055.6	1045.7	1036.8	1028.1	1018.4	1008.9	999.5	990.4	981.5	971.6
30	1079.2	1070.5	1061.8	1052.1	1043.6	1034.8	1025.6	1016.6	1007.7	998.7	990.1	980.8
40	1084.5	1076.0	1067.5	1058.3	1049.9	1041.3	1032.8	1023.7	1014.8	1006.3	998.2	989.3
50	1089.6	1081.5	1073.2	1063.9	1056.0	1047.6	1039.0	1030.4	1021.8	1013.9	1005.9	997.3
60	1094.7	1086.7	1078.6	1069.1	1061.5	1053.5	1045.4	1036.8	1029.0	1020.5	1013.0	1004.5
70	1099.5	1091.5	1083.7	1074.4	1066.9	1058.6	1051.2	1042.9	1035.0	1027.0	1019.7	1011.5
80	1104.2	1096.1	1088.7	1079.3	1072.0	1064.2	1056.7	1048.5	1040.9	1033.2	1026.0	1018.2
90	1108.5	1100.6	1093.2	1084.2	1076.9	1069.3	1061.9	1053.9	1046.4	1039.0	1032.1	1024.5
100	1112.8	1104.7	1097.2	1088.9	1082.0	1074.1	1067.3	1059.2	1051.0	1044.7	1037.7	1030.2
110		1108.9	1101.5	1093.3	1086.8	1079.0	1072.2	1064.3	1056.3	1050.1	1043.1	1035.9
120		1113.1	1105.6	1097.9	1091.1	1083.9	1076.6	1069.1	1061.6	1055.2	1048.7	1041.3
130		1117.0	1109.8	1102.2	1095.5	1088.3	1081.3	1074.1	1066.0	1059.9	1053.8	1046.6
140		1120.9	1113.8	1106.2	1099.8	1092.4	1085.6	1078.5	1071.2	1065.1	1058.5	1051.6

Table 2. Experimental Densities, $\rho/\text{kg}\cdot\text{m}^{-3}$, for Diisobutyl Adipate at Different Pressures, p , and Temperatures, T

p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$											
	T/K											
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15
0.1	951.7	942.8	934.2	925.6	916.7	908.1	899.3	890.2	882.3	873.2	864.7	856.8
10	958.4	949.9	941.6	933.4	924.9	916.3	908.0	899.9	891.5	883.6	875.3	867.3
20	964.7	956.4	948.5	940.5	932.4	924.3	916.2	908.7	900.5	893.1	885.1	877.3
30	970.6	962.6	954.9	947.3	939.3	931.5	923.7	916.4	908.6	901.7	893.9	886.5
40	976.1	968.3	960.9	953.7	945.8	938.3	930.9	923.7	916.5	909.6	902.1	894.8
50	981.4	974.0	966.6	959.7	952.0	944.7	937.7	930.4	923.3	916.6	909.5	902.7
60	986.4	979.1	972.1	965.2	957.8	950.8	943.9	936.9	930.1	923.5	916.6	909.9
70	991.2	984.2	977.2	970.6	963.3	956.3	950.0	943.2	936.4	929.4	923.2	916.6
80	995.9	989.0	982.0	975.6	968.5	961.8	955.5	948.9	942.2	935.7	929.5	923.3
90	1000.3	993.4	986.7	980.5	973.4	967.0	960.8	954.1	947.8	941.2	935.3	929.4
100	1004.7	997.8	991.2	985.3	978.2	971.8	965.7	959.4	953.2	946.7	941.1	935.0
110	1008.7	1002.1	995.6	989.8	982.8	976.5	970.5	964.4	958.2	951.8	946.2	940.3
120	1012.7	1006.3	999.9	994.2	987.3	981.1	974.9	969.0	963.2	957.0	951.4	945.5
130	1016.6	1010.3	1003.9	998.3	991.6	985.5	979.5	973.7	967.8	961.5	956.3	950.6
140	1020.3	1014.0	1007.9	1003.0	995.7	989.7	983.7	978.1	972.5	966.1	960.9	955.4

this is due to the fact that the capacity of a liquid to contract reduces when the pressure increases or when the temperature decreases, since free intermolecular space decreases. Furthermore, an increase on κ_T occurs when the molar mass of the adipate increases. Similar behavior has been previously found for other polar fluids such as dialkyl carbonates¹³ and polyglycol ethers.¹⁴

Recently Kiselev et al.¹⁵ have proposed a simple method to predict the isothermal compressibility of liquids at atmospheric

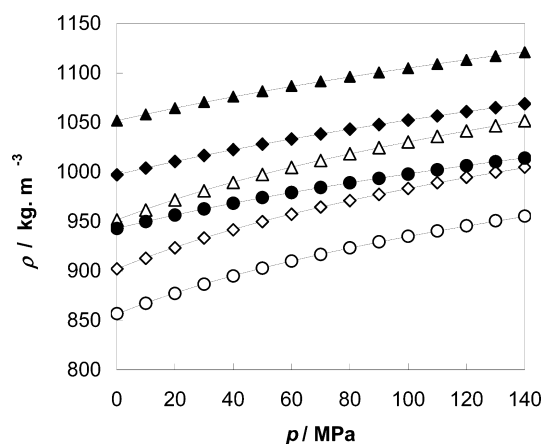


Figure 2. Density for dialkyl adipates as a function of pressure. Δ , DMA (this work); \diamond , DEA (Comuñas et al.⁶); and \circ , DiBA (this work), at 303.15 K (solid symbols) and at 403.15 K (open symbols). —, Tamman–Tait equation.

Table 3. Coefficients and Results Obtained for the Tammann–Tait Equation Correlation

parameters	dimethyl adipate	diethyl adipate ^a	diisobutyl adipate
$A_0/\text{kg}\cdot\text{m}^{-3}$	1326.620	1268.554	1227.159
$A_1/\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$	-0.8342	-0.8531	-0.99239
$10^3 A_2/\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-2}$	-0.23883	-0.13911	0.18087
B_0/MPa	527.077	551.817	483.993
$B_1/\text{MPa}\cdot\text{K}^{-1}$	-1.72910	-2.02917	-1.74112
$10^3 B_2/\text{MPa}\cdot\text{K}^{-2}$	1.50360	2.03826	1.73065
C	0.08991	0.08884	0.08850
AAD %	0.02	0.02	0.02
DM %	0.09	0.09	0.11
bias %	0.0002	-0.001	-0.0005
$\sigma/\text{kg}\cdot\text{m}^{-3}$	0.3	0.3	0.2

^a From Comuñas et al.⁶

pressure from experimental compression at high pressure. This method can also be used to determine the density at high pressures from the isothermal compressibility at atmospheric pressure. These authors have proposed an empirical correlation between the tangent bulk modulus (inverse of the isothermal compressibility) at atmospheric pressure, κ_{T0} , given by:

$$\frac{1}{\kappa_{T0}} = V_{0.1\text{MPa}} \left(\frac{\partial P}{\partial V} \right)_T \quad (6)$$

and the secant bulk modulus at 100 MPa, $\bar{\kappa}_{100}$, given by

$$\bar{\kappa}_{100}/\text{MPa} = -100 \left(\frac{V_{0.1\text{MPa}}}{V_{0.1\text{MPa}} - V_{100\text{MPa}}} \right) \quad (7)$$

Table 4. Isobaric Thermal Expansivity and Isothermal Compressibility of DMA and DiBA at Different Pressures and Temperatures

<i>T</i> /K	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15
Dimethyl Adipate										
<i>p</i> /MPa	$10^4 \alpha_p / (K^{-1})$									
0.1	9.31	9.44	9.58	9.72	9.86	10.01	10.16	10.31	10.47	10.63
10	8.96	9.07	9.18	9.29	9.39	9.50	9.61	9.72	9.83	9.94
30	8.38	8.45	8.51	8.57	8.63	8.69	8.74	8.80	8.85	8.90
50	7.91	7.95	7.99	8.02	8.05	8.07	8.09	8.11	8.13	8.15
70	7.52	7.54	7.55	7.57	7.57	7.58	7.58	7.58	7.58	7.58
90	7.19	7.19	7.20	7.19	7.19	7.18	7.16	7.15	7.14	7.12
110	6.90	6.90	6.89	6.88	6.86	6.84	6.82	6.80	6.77	6.76
130	6.66	6.65	6.63	6.61	6.58	6.56	6.53	6.50	6.47	6.45
$10^4 \kappa_T / (MPa^{-1})$										
0.1	6.37 ^a	6.75 ^a	7.17 ^a	7.62 ^a	8.11 ^a	8.64 ^a	9.22 ^a	9.85 ^a	10.52 ^a	11.27 ^a
10	5.99	6.33	6.69	7.08	7.50	7.95	8.44	8.96	9.53	10.13
30	5.35	5.62	5.90	6.20	6.53	6.87	7.23	7.61	8.01	8.44
50	4.84	5.06	5.29	5.53	5.78	6.05	6.33	6.63	6.93	7.25
70	4.42	4.60	4.79	4.99	5.20	5.42	5.64	5.88	6.12	6.37
90	4.07	4.23	4.39	4.56	4.73	4.91	5.10	5.29	5.48	5.68
110	3.78	3.91	4.05	4.19	4.34	4.49	4.65	4.81	4.97	5.14
130	3.52	3.64	3.76	3.89	4.01	4.14	4.28	4.42	4.55	4.70
Diisobutyl Adipate										
$10^4 \alpha_p / (K^{-1})$										
0.1	9.36	9.41	9.46	9.51	9.56	9.62	9.67	9.72	9.77	9.83
10	8.94	8.96	8.98	9.00	9.02	9.05	9.07	9.10	9.14	9.18
30	8.25	8.23	8.21	8.20	8.18	8.17	8.17	8.18	8.19	8.23
50	7.71	7.67	7.63	7.59	7.56	7.53	7.52	7.52	7.54	7.58
70	7.27	7.22	7.16	7.12	7.08	7.04	7.03	7.02	7.05	7.10
90	6.91	6.85	6.79	6.73	6.69	6.65	6.63	6.64	6.66	6.72
110	6.61	6.54	6.47	6.42	6.37	6.33	6.31	6.32	6.35	6.42
130	6.35	6.27	6.21	6.15	6.10	6.06	6.05	6.06	6.10	6.17
$10^4 \kappa_T / (MPa^{-1})$										
0.1	7.67 ^a	8.15 ^a	8.66 ^a	9.21 ^a	9.79 ^a	10.40 ^a	11.06 ^a	11.74 ^a	12.46 ^a	13.19 ^a
10	7.12	7.53	7.96	8.42	8.90	9.41	9.94	10.49	11.06	11.64
30	6.22	6.53	6.86	7.19	7.55	7.91	8.28	8.66	9.05	9.43
50	5.53	5.78	6.03	6.29	6.56	6.84	7.12	7.40	7.68	7.96
70	4.99	5.19	5.39	5.60	5.81	6.03	6.25	6.47	6.68	6.90
90	4.54	4.71	4.88	5.05	5.23	5.40	5.58	5.75	5.93	6.10
110	4.18	4.32	4.46	4.61	4.75	4.90	5.05	5.19	5.33	5.47
130	3.87	3.99	4.11	4.24	4.36	4.49	4.61	4.73	4.85	4.97

^a Determined with eq 8.

The correlation is a linear dependence between both properties given by:

$$\frac{1}{\kappa_{T0}} = -455.9 + 0.9865 \bar{\kappa}_{100} \quad (8)$$

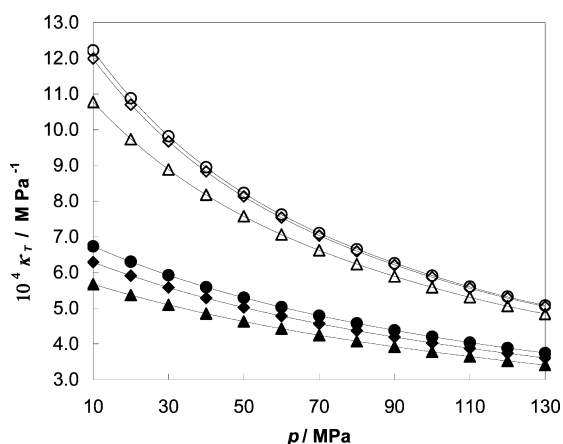


Figure 3. Isothermal compressibility for dialkyl adipates as a function of pressure. Δ , DMA (this work); \diamond , DEA (Comuñas et al.⁶); and \circ , DiBA (this work), at 293.15 K (solid symbols) and at 403.15 K (open symbols).

Kiselev et al.¹⁵ have obtained this correlation using density data from different compound such as alkanes, alcohols, ketones, esters, glycols, and mercury. These authors also found that, when mercury is excluded, due to its compressibility is significantly different to that of the other fluids, parameters of eq 8 change very slightly, the new correlation being:

$$\frac{1}{\kappa_{T0}} = -438.9 + 0.9756 \bar{\kappa}_{100} \quad (9)$$

We have also used eqs 8 and 9 to calculate the isothermal compressibility at atmospheric pressure of dialkyl adipates. To perform this calculation, experimental data of density at atmospheric pressure and at 100 MPa reported in Table 1 have been used to calculate the ratio $V_{0.1MPa} / (V_{0.1MPa} - V_{100MPa})$.

The isothermal compressibilities at atmospheric pressure calculated from eqs 8 and 9 have been compared with those obtained, in the present work, with eq 5 for DMA and DiBA and with those previously reported for DEA.⁶ Comparisons between κ_T values obtained from eqs 5 and 8 give average absolute deviations of 1.5 %, 1.7 %, and 1.8 % for dimethyl, diethyl, and diisobutyl adipate, respectively. The maximum deviations are 2.7 %, 2.5 %, and 2.5 %, respectively. When eq 9 is used instead of eq 8, the deviations are the same. We must point out that it is likely best to use eqs 8 and 9 than eqs 1 and

5 to determine isothermal compressibility at atmospheric pressure because of the fact that derivatives of eq 1 at this pressure could be distorted because 0.1 MPa is a boundary point (minimum pressure).

Some authors¹² determine the isobaric thermal expansivity by calorimetry, but this property is very often indirectly obtained from $\rho(T)$ data.^{16,17} Thus, the isobaric thermal expansivity, α_p , can be obtained according to its definition:

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (10)$$

by analytical differentiation of eq 1 taking into account the temperature dependence of $\rho_0(T)$ and $B(T)$ given by eqs 2 and 3. This derived property can be expressed as follows:

$$\alpha_p / \text{K}^{-1} = -\frac{A_1 + 2A_2(T/\text{K})}{\rho_0 / \text{kg} \cdot \text{m}^{-3}} - \frac{C(0.1 - p/\text{MPa})}{(B + p/\text{MPa})(B + 0.1)} - \frac{B_1 + 2B_2(T/\text{K})}{\left[1 - C \ln \left(\frac{B + p/\text{MPa}}{B + 0.1} \right) \right]} \quad (11)$$

The values of C , A_1 , A_2 , B_1 , and B_2 parameters are taken from Table 3. The uncertainty in the isobaric thermal expansivity, 4 %, has been estimated in our previous work.⁶ Notice that in ref 6 comparisons have been performed between the values reported by the NIST for toluene and those obtained when eq 11 is used. Some authors mention that the estimated isobaric thermal expansivity depends on the form of functions $B(T)$ and $\rho_0(T)$, and they recommend deriving the isobaric thermal expansivity from the isobaric densities. So, in the present work another possibility to calculate the isobaric thermal expansivity has been considered. Over each isobar the density was correlated with the temperature using a simple polynomial function (similar to eq 2). The polynomial correlation $\rho(T)$ is performed at fixed pressure, and then the derivative respect to temperature, $(\partial \rho / \partial T)_p$, is determined.

Thus, at each pressure we suppose that:

$$\rho_p / \text{kg} \cdot \text{m}^{-3} = D_0 + D_1(T/\text{K}) \quad (12)$$

and consequently,

$$\alpha_p / \text{K}^{-1} = -\frac{D_1}{D_0 + D_1(T/\text{K})} \quad (13)$$

For each pressure we get a different set of D_0 and D_1 . In this case a total of 30 parameters are needed over the full temperature and pressure experimental range for each adipate. The standard deviations, σ , of the $\rho_p(T)$ correlations at fixed pressure are lower than $0.4 \text{ kg} \cdot \text{m}^{-3}$ for DMA, DEA,⁶ and DiBA. The comparison among the α_p values for dimethyl and diisobutyl adipate calculated from the global correlation, eq 11, with those obtained with the individual correlations at each fixed pressure gives an average absolute deviation lower than 1 %, which is lower than the estimated uncertainty.

The α_p values obtained for DMA and DiBA with the global correlation (eq 11) are reported in Table 4. We have not indicated in this table the α_p values at (293.15 and 403.15) K because the $(\partial \rho / \partial T)_p$ values in the boundary points T_{\min} and T_{\max}

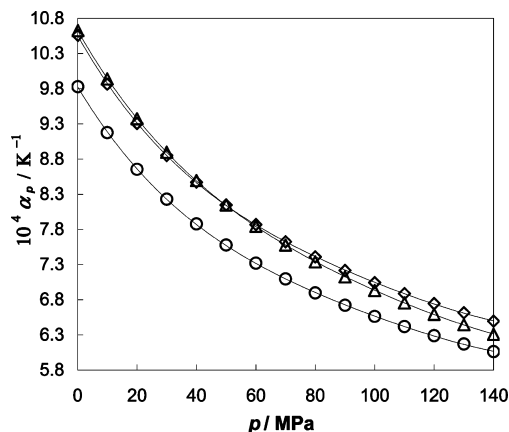


Figure 4. Isobaric thermal expansivities versus pressure at 393.15 K. Δ , DMA (this work); \diamond , DEA (Comuñas et al.⁶) and \circ , DiBA (this work).

Table 5. Experimental Viscosity, η (mPa·s), of Dialkyl Adipates Measured with the SVM3000 Rotational Viscometer at Atmospheric Pressure

T/K	dimethyl adipate	diethyl adipate	diisobutyl adipate
283.15	4.39	4.57	8.56
288.15	3.82	3.99	7.22
293.15	3.36	3.51	6.17
298.15	2.98	3.12	5.33
303.15	2.67	2.79	4.65
308.15	2.40	2.51	4.09
313.15	2.18	2.28	3.63
318.15	1.99	2.07	3.24
323.15	1.82	1.90	2.92
328.15	1.68	1.75	2.64
333.15	1.55	1.61	2.40
338.15	1.44	1.49	2.19
343.15	1.34	1.39	2.01
348.15	1.25	1.29	1.85
353.15	1.17	1.21	1.71
358.15	1.10	1.13	1.59
363.15	1.03	1.06	1.48
368.15	0.97	1.00	1.38
373.15	0.92	0.94	1.29

can be strongly distorted. It has been observed that the effect of changing the temperature or the pressure has more impact on the values of the isothermal compressibility than on the isobaric thermal expansivity. In Figure 4 α_p values obtained in the present work for DMA and DiBA have been plotted as a function of pressure together with those values previously calculated for diethyl adipate.⁶ The isobaric thermal expansivity is similar for the three dialkyl adipates in the most of the experimental pT range. The differences between the values are lower than the estimated uncertainty. The isobaric thermal expansivity decreases with increasing pressure for all of the isotherms as can be seen in Figure 4 and Table 4. This is likely due to the fact that the capacity of a liquid to expand reduces when the pressure increases, since free intermolecular space decreases.

Dynamic viscosities of DMA, DEA, and DiBA have been measured from (278.15 to 373.15) K, at atmospheric pressure. The data are displayed in Table 5. The behavior of the viscosity at 0.1 MPa as a function of temperature, $\eta(T)$, was described using the following modification of Andrade's equation also known as three-coefficient Vogel–Fulcher–Tammann (VFT) equation:

$$\eta(T) = A \exp \left(\frac{B}{T - C} \right) \quad (14)$$

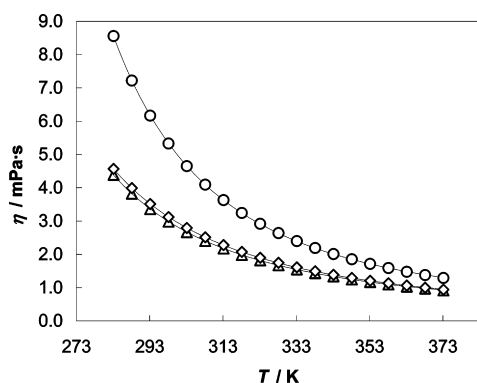
Table 6. Parameters of Vogel–Fulcher–Tammann (VFT), Equation 14

	DMA	DEA	DiBA
$A/\text{mPa}\cdot\text{s}$	0.08136	0.06693	0.07869
B/K	562.829	642.341	628.453
C/K	141.958	131.021	149.107
$\sigma/\text{mPa}\cdot\text{s}$	0.006	0.006	0.006

The values obtained from A , B , and C are gathered in Table 6. The standard deviations of these correlations are 0.006 for DMA, DEA, and DiBA. The viscosity for the three adipates has been plotted in Figure 5 as a function of temperature at 0.1 MPa. Our viscosity data for diethyl adipate from (303.15 to 373.15) K are in agreement with those previously reported by Meng et al.⁷ An average absolute deviation of 2 % has been found between both data series. Viscosities of DMA and DEA are very close over the entire temperature interval, being around 2 mPa·s at 313.15 K. Furthermore, the adipate with the branched chains (DiBA) has the higher viscosities. The following sequence is accomplished: $\eta_{\text{DiBA}} > \eta_{\text{DMA}} \approx \eta_{\text{DEA}}$. The increase of the viscosity with the increase of the branching degree is quite general also for other types of compounds. Thus, for pentaerythritol and other esters, it was also found that for viscosity the effect of the increase of the branching degree of molecules is stronger than that of the increase of the number of methylene groups in the chains of the esters.¹⁸ Besides, the viscosities of the branched compound di(2-ethylhexyl) adipate are also bigger than those of the three adipates studied.⁸ This sequence is the opposite of that already commented above for density.

The Angell strength parameter $D = B/C$, B and C being the parameters obtained from eq 14, is large for “strong” liquids where the viscosity approaches an Arrhenius or Andrade ($C = 0$) temperature dependence and is small for “fragile” liquids.^{19,20} The D values obtained for DMA, DEA, and DiBA are respectively 3.96, 4.90, and 4.21. In the present work we have also determined the Angell strength parameter of di(2-ethylhexyl)adipate by fitting the viscosity values reported in the literature,⁸ finding a value of 4.41. Recently, Harris et al.^{21,22} have found for 2-ethylhexyl benzoate, bis(2-ethylhexyl) phthalate, and squalane a D value of 2.75, 4.76, and 5.28 respectively and for ionic liquid values ranging from 4.6 to 8.9. For glycerol, 1,10-di(4-methoxy-5-methyl-phenyl)cyclohexane, and SiO_2 at atmospheric pressure the Angell parameter reaches values of 18, 27, and 161, respectively.^{23,24} From these results it can be concluded that the three studied adipates are quite “fragile”; that is, they do not follow Arrhenius behavior.

By general agreement it is considered that a liquid on being cooled practically becomes a glass when the viscosity equals

**Figure 5.** Dynamic viscosity as a function of temperature for \diamond , DMA; \triangle , DEA; and \circ , DiBA. —, modified Andrade equation.

10^{15} mPa·s. The T_g values obtained from this hypothesis and those determined by calorimetry depend, among other reasons, on the ability of the viscosity correlation equation used to perform the extrapolation. Pensado et al.,²⁵ using Vogel–Fulcher–Tammann (VFT) correlations, have estimated glass transition temperatures T_g at atmospheric pressure for three pentaerythritol esters finding a very good agreement with T_g data measured by differential scanning calorimetry (DSC). In the present work we have used the same procedure by fitting the viscosity values of di(2-ethylhexyl)adipate⁸ with the VFT equation obtaining a T_g value of 177 K. A value of 173 K has been obtained by Fried et al.²⁶ for this compound. Both values are in good agreement. In addition we have obtained T_g values from the VFT correlation for dimethyl, diethyl, and diisobutyl adipates obtaining (57, 154, and 171) K, respectively. Unfortunately, we have not found any other experimental or predicted T_g value for these compounds.

Conclusions

Densities of dimethyl adipate (DMA) and diisobutyl adipate (DiBA) in the temperature range from (293.15 to 403.15) K and at pressures up to 140 MPa have been reported. Using our previous data for diethyl adipate (DEA) obtained in the same conditions,⁶ we checked that the pressure and temperature dependencies of dialkyl adipates densities were accurately represented by eq 1, which was then used to calculate isothermal compressibilities and isobaric thermal expansivities. It is a useful tool for the industry applications of dialkyl adipates, where thermophysical properties are indispensable, to have the parameters of the Tammann–Tait equation because it permits the interpolation of the density values. Furthermore, the correlation recently proposed by Kiselev et al.¹⁵ has been used to calculate isothermal compressibility at atmospheric pressure. The values obtained with this correlation have been compared with those calculated by using eq 1. Both data are in good agreement with average absolute deviation lower than 2 %. Finally the influence of the temperature and branching effect on experimental viscosities of DMA, DiBA, and DEA has also been put into evidence.

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Received for review March 13, 2010. Accepted July 13, 2010. The authors are grateful to the Ministerio de Ciencia e Innovación (Spain) for the financial support to the project (CTQ2005-09176-C02-01/PPQ) and to the Xunta de Galicia (PGIDIT06PXIC20640PN). L.L. would like to acknowledge the financial support of the Ramon y Cajal Program from the Ministerio de Ciencia y Educación (Spain).

JE100237H