

Density, Kinematic Viscosity, and Refractive Index for Bis(2-ethylhexyl) Adipate, Tris(2-ethylhexyl) Trimellitate, and Diisononyl Phthalate

Lorenzo De Lorenzi, Maurizio Fermeglia,* and Giovanni Torriano

DICAMP, Department of Chemical, Environmental and Raw Material Engineering, Piazzale Europa 1, 34127 Trieste, Italy

Density and kinematic viscosity at temperatures from 288.15 K and 358.15 K and refractive indexes from 288.15 K and 323.15 K were measured for three esters: bis(2-ethylhexyl) adipate, tris(2-ethylhexyl) trimellitate, and diisononyl phthalate. Parameters for models fitting the experimental pure component data are reported.

Introduction

The aim of the present investigation is the characterization of the behavior of the kinematic and dynamic viscosity and density versus temperature for three ester plasticizers from 288.15 and 358.15 K. In addition, the refractive index was measured from 288.15 and 323.15 K.

The high molecular weight esters measured in the present investigation have been considered as model components representative of the behavior of a class of esters in view of a possible application as additives to lubricant bases for the automotive industry (Mortier and Orszulik, 1992). The components considered are bis(2-ethylhexyl) adipate [bis(2-ethylhexyl) hexanedioic acid ester], tris(2-ethylhexyl) trimellitate [tris(2-ethylhexyl) 1,2,4-benzene-tricarboxylic acid ester], and diisononyl phthalate.

The esters investigated in this work are suitable for many applications, particularly when a high value of the viscosity is required. Moreover, on account of their compatibility, they are suitable for blending with a mineral lubricating oil, to improve the viscosity index (VI) of the oil. The viscosity index is defined and calculated according to ASTM-D-2270 93 only for compounds with a kinematic viscosity higher than $2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 373.15 K. The esters studied in this work meet this requirement.

Only few and relatively old experimental data are available in the open literature for high molecular weight esters (Bried et al., 1947), and no data are available for their mixtures with natural lubricant bases.

Experimental Section

A new automatic computer-based method for data acquisition and instrument control has been designed and implemented (Ranut, 1997) for the measurements reported in this paper. The digital output of the quantities from the measuring device is recorded on a computer. The data acquisition system collects both density and viscosity data as a function of composition and/or temperature, performs a statistical treatment of the data, and stores the results in a relational database (MS SQL server 6.5). The database is directly connected to the Web via an Internet Data

* To whom correspondence should be addressed: mauf@dicamp.univ.trieste.it; www.dicamp.univ.trieste.it/~mau.

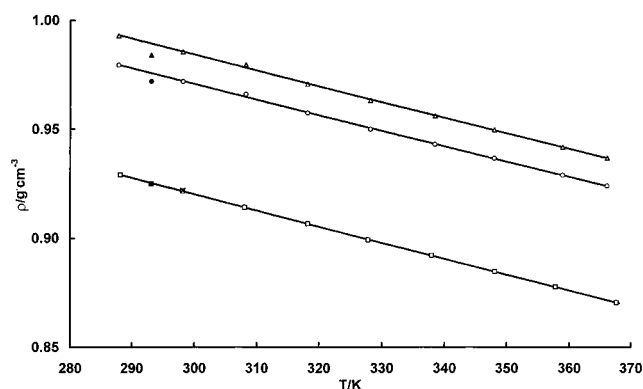


Figure 1. Density vs temperature for (□) bis(2-ethylhexyl) adipate, (○) diisononylphthalate, and (△) tris(2-ethylhexyl) trimellitate. Black symbols refer to literature data (see Table 1). Lines refer to the DIPPR model with parameters from Table 3.

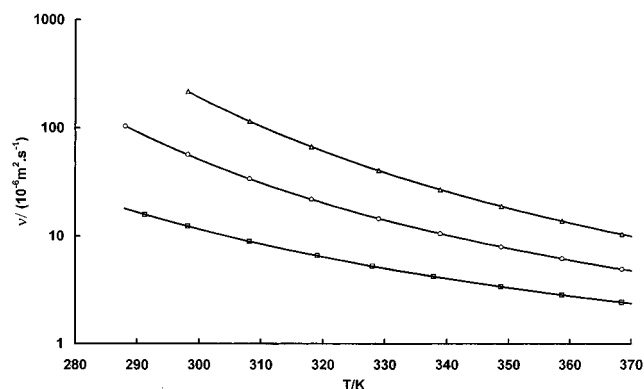


Figure 2. Kinematic viscosity vs temperature for (□) bis(2-ethylhexyl) adipate, (○) diisononyl phthalate, and (△) tris(2-ethylhexyl) trimellitate. Black symbols refer to literature data (Bried et al., 1947). Lines refer to eq 5 with parameters from Table 7.

Connector, thus providing access by the Internet community. These data acquisition system does not improve the global accuracy of the data since the temperature probes and sensors and the characteristics of the thermostatic baths are not changed. It only speeds up the

Table 1. Physical Properties and Purity of the Esters

	purity source	chemical composition	boiling point	n at $T = 293.15$ K	$\rho/\text{g}\cdot\text{cm}^{-3}$ at $T = 293.15$ K	$\rho/\text{g}\cdot\text{cm}^{-3}$ at $T = 298.15$ K
adipate						
bis(2-ethylhexyl)	99% ^b Fluka	bis(2-ethylhexyl) hexanedioic acid ester	487.15 K at 5 mm ^c	1.4474 ^b 1.44735 ^f	0.925 ^b 0.92539 ^f	0.922 ^d 0.92165 ^f
trimellitate						
tris(2-ethylhexyl)	99% ^a Aldrich	tris(2-ethylhexyl) benzene-1,2,4-tricarboxylic acid ester	687.15 K ^a	1.485 ^a 1.48645 ^f	0.984 ^a 0.98933 ^f	
phthalate						
diisononyl	ester content 99+%, mixture of C9 isomers ^{a,e} Aldrich	diisononyl 1,2-benzenedicarboxylic acid ester		1.485 ^a 1.48610 ^f	0.972 ^a 0.97578 ^f	

^a Data supplied by Aldrich. ^b Data supplied by Fluka. ^c Data from *CRC Handbook of Chemistry and Physics*, 73rd ed., 1992–93. ^d Data from Bried et al. 1947. ^e Contains 0.15% dioctyl phthalate. ^f Interpolated data of this work.

Table 2. Experimental Density Data

T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$
bis(2-ethylhexyl) adipate	tris(2-ethylhexyl) trimellitate	diisononyl phthalate			
288.17	0.929 21	287.90	0.992 93	287.90	0.979 43
298.15	0.921 65	298.15	0.985 44	298.15	0.971 87
308.04	0.914 16	308.22	0.979 52	308.22	0.966 07
318.17	0.906 52	318.10	0.970 71	318.10	0.957 39
327.82	0.899 18	328.17	0.963 19	328.17	0.950 03
337.95	0.892 02	338.44	0.956 17	338.44	0.943 08
348.10	0.884 57	348.01	0.949 75	348.01	0.936 74
357.79	0.877 53	358.91	0.941 80	358.91	0.928 89
367.65	0.870 40	366.12	0.936 83	366.12	0.923 96

Table 3. Parameters and Standard Deviations of the DIPPR Model

	bis(2-ethylhexyl) adipate	tris(2-ethylhexyl) trimellitate	diisononyl phthalate
a	0.5962	0.6999	0.6862
b	0.7427	0.7754	0.7468
c	413.80	377.69	381.59
d	1.1443	1.1121	0.9786
$\sigma/\text{g}\cdot\text{cm}^{-3}$	1.2×10^{-4}	6.9×10^{-4}	6.7×10^{-4}

measurements and contributes in reducing systematic errors.

Materials. All esters were supplied by Aldrich or Fluka and were employed as received, without any further purification. The stated purity of the chemicals and their main properties are reported in Table 1 along with a comparison with the literature values. The diisononyl phthalate is really a mixtures of C9 isomers with a maximum content of 0.15% of the main impurity (dioctyl phthalate); this purity is considered satisfactory for the purpose of the present investigation of characterizing the behavior of these esters as an additive to lubricant bases.

Density Measurements. A vibrating tube digital densimeter, model DMA 602H-DMA 60 (Anton Paar), connected with a Heterofrig (Heto Birkerød) constant temperature bath circulator, with a stability of ± 0.01 K, was employed to measure density. It was equipped with calibrated thermometers, suitable to work between 288.15 and 318.15 K with a precision of ± 0.01 K. For the densimeter calibration, nitrogen and double-distilled water were employed. Working procedures between 288.15 and 318.15 K are described in more details in Fermeglia and Lapasin (1988), Fermeglia et al. (1990), and De Lorenzi et al. (1996). The estimated precision in the density, in this temperature range, is better than 3×10^{-5} g·cm⁻³. To

Table 4. Experimental Refractive Index and Eykman Constant (Eq 3)

T/K	n	C	T/K	n	C	T/K	n	C
bis(2-ethylhexyl) adipate	tris(2-ethylhexyl) trimellitate	diisononyl phthalate						
288.35	1.4491	0.640	288.15	1.4879	0.647	288.15	1.4883	0.657
292.95	1.4474	0.640	294.35	1.4856	0.648	294.35	1.4860	0.657
298.15	1.4454	0.640	298.15	1.4842	0.648	298.15	1.4846	0.657
302.95	1.4435	0.640	302.75	1.4825	0.648	302.75	1.4828	0.657
307.75	1.4418	0.641	307.95	1.4806	0.648	307.95	1.4809	0.657
312.25	1.4399	0.640	313.35	1.4785	0.648	313.35	1.4788	0.657
317.55	1.4379	0.640	318.15	1.4767	0.648	318.15	1.4769	0.657
322.85	1.4359	0.640	322.25	1.4751	0.648	322.25	1.4753	0.657

Table 5. Parameters and Standard Deviations for Eq 4

	bis(2-ethylhexyl) adipate	tris(2-ethylhexyl) trimellitate	diisononyl phthalate
c	1.5607	1.5649	1.5980
q	-0.00039	-0.00038	-0.00038
σ	3.8×10^{-5}	3.5×10^{-5}	3.3×10^{-5}

extend the temperature range of the measuring device, limited by the restricted set of Paar calibrated thermometers, the procedure reported in detail in De Lorenzi et al. (1997) was adopted. The precision of the temperature measurements obtained in the extended temperature range is estimated to be ± 0.04 K. Consequently, density precision in the same temperature range is estimated to be 4×10^{-5} g·cm⁻³.

Viscosity Measurements. An Ubbelohde suspended-level capillary viscometer coupled with a Schott electronic timer (AVS 300) was employed to measure viscosity. The estimated precision in the directly measured quantity is ± 0.01 s. The thermostat was a Haake F3 instrument, with a stability of ± 0.02 K, and the temperature was measured with an accuracy of ± 0.01 K. Working procedures are described by Fermeglia and Lapasin (1988), Fermeglia et al. (1990), and De Lorenzi et al. (1996, 1997). A calibration of the capillary viscometer has been performed with a standard oil at 293.15 K and was extended to higher temperatures by using a 99+ purity dodecane (De Lorenzi et al., 1997). The estimated precision in kinematic viscosity measurements in the whole temperature range is 1×10^{-4} mm² s⁻¹.

Refractive Index Measurements. An Abbe ATAGO type 3 refractometer was employed to determine the refractive index for the sodium-D line from 288.15 and 323.15 K. It was connected with the above-mentioned Heterofrig constant-temperature bath circulator (stability ± 0.01 K), and the temperature was measured with an

Table 6. Experimental Kinematic Viscosity and Calculated Dynamic Viscosity between 293.15 and 358.15 K

<i>T</i> /K	$\nu/10^{-6} \text{ m}^2\cdot\text{s}^{-1}$	$\eta/\text{mPa}\cdot\text{s}$	<i>T</i> /K	$\nu/10^{-6} \text{ m}^2\cdot\text{s}^{-1}$	$\eta/\text{mPa}\cdot\text{s}$	<i>T</i> /K	$\nu/10^{-6} \text{ m}^2\cdot\text{s}^{-1}$	$\eta/\text{mPa}\cdot\text{s}$
bis(2-ethylhexyl) adipate			tris(2-ethylhexyl) trimellitate			diisononyl phthalate		
291.29	15.883	14.720				288.10	104.09	101.95
298.15	12.326	11.359	298.15	216.50	213.39	298.15	56.920	55.334
308.17	8.8741	8.1113	308.16	115.06	112.56	308.16	34.006	32.812
319.06	6.5208	5.9071	318.08	67.438	65.485	318.09	21.964	21.035
327.98	5.2271	4.7005	328.96	40.695	39.196	328.98	14.539	13.812
337.87	4.2036	3.7496	338.87	27.102	25.911	338.88	10.506	9.9061
348.72	3.3880	2.9952	348.72	18.950	17.984	348.74	7.9028	7.3961
358.64	2.8366	2.4874	358.63	13.764	12.966	358.65	6.1446	5.7089
368.49	2.4248	2.1091	368.46	10.356	9.6844	368.49	4.9024	4.5214

accuracy of ± 0.02 K. Instrument calibration was carried out with double distilled water, and measurement precision is estimated to be better than 1×10^{-4} .

The temperature probes used in all the measurements were calibrated against a platinum resistance thermometer (Rosemount Model 162 CE) and checked at the water triple point. The accuracy reported in this paper was obtained on the basis of repeated experiments on all pure components at selected temperatures for all the properties measured.

Results and Correlations

Density. The density results at the various temperatures are reported in Table 2. Figure 1 compares the experimental, literature, and calculated values.

The Daubert and Danner (DIPPR) equation (Daubert and Danner, 1989) was fit to the experimental data

$$\rho/\text{g}\cdot\text{cm}^{-3} = a/\{b^{1+(1-(TK)/\sigma)^d}\} \quad (1)$$

where ρ is the density in $\text{g}\cdot\text{cm}^{-3}$ and a , b , c , d are adjustable parameters. The parameters obtained in the data regression are reported in Table 3 along with the residual data standard deviation σ

Refractive Index. Refractive index was measured in the temperature interval from 288.15 to 323.15 K. The experimental results are reported in Table 4 along with the Eykman empirical constant C (Riddick et al., 1986), evaluated according to

$$C = (n^2 - 1)/[(n + 0.4)\rho/(\text{g}\cdot\text{cm}^{-3})] \quad (2)$$

where n is the refractive index and ρ is the density, interpolated at the correct temperature by means of eq 1.

Table 4 shows that the refractive indexes of the phthalate and of the trimellitate esters have similar values. Constant values of the Eykman constant give support that both density and refractive index values are accurate. It offers, moreover, an accurate means for calculating density from refractive index and vice versa (Riddick et al., 1986). The refractive index results were fitted with a linear equation

$$n = c + q(TK) \quad (3)$$

where c and q are adjustable parameters. These parameters and fit standard deviation σ are reported in Table 5.

Kinematic Viscosity. The experimental kinematic viscosity data from 293.15 K and 358.15 K are reported in Table 6 and in Figure 2 along with the literature values for the adipate (Bried et al., 1947). Table 6 reports the dynamic viscosity calculated from the experimental kinematic viscosity using the interpolated density obtained by eq 1.

Table 7. Goletz and Tassios Model Parameters, Viscosity Index, and Standard Deviations

	bis(2-ethylhexyl) adipate	tris(2-ethylhexyl) trimellitate	diisononyl phthalate
$A \times 10^{-6}$	0.1048	0.0504	0.0803
B	648.23	1030.46	774.10
C	-162.17	-174.94	-180.14
$\sigma/10^{-6} \text{ m}^2\cdot\text{s}^{-1}$	1.3×10^{-3}	1.9×10^{-3}	2.8×10^{-3}
VI	103	73	50

Kinematic viscosity (ν) was fitted to the Goletz and Tassios equation (Reid et al., 1989)

$$\nu/\text{m}^2\cdot\text{s}^{-1} = Ae^{\{B/[(TK)+C]\}} \quad (4)$$

where A , B , and C are adjustable parameters. Parameters of the Goletz and Tassios equation and the viscosity index (VI), calculated according to ASTM D 2270-93, are reported in Table 7.

Conclusions

For all esters tested, the density values can be fitted to the Daubert and Danner model with σ values around 1×10^{-4} . The experimental density values compare well with the few data available in the open literature.

A linear relation was used to fit the refractive index vs temperature. The Eykman correlation holds for the three esters tested and supports the claimed accuracy of both the density and refractive index results. Marked differences were found among the esters on the effect of temperature on the kinematic viscosity. The data measured are in excellent agreement with the literature data available. The Goletz and Tassios equation was employed to fit the experimental data with σ values around 1×10^{-3} .

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