Viscosities of Dilute Solutions of the Triglycerides Triolein, Trilinolein, Tristearin, Tripalmitin, and Trimyristin in Benzene and *p*-Xylene

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Dynamic viscosities and densities were determined for the systems triolein + benzene and trilinolein + benzene at 25, 30, and 35 °C and trilinolein + *p*-xylene at 25, 30, 35, 40, and 45 °C, and kinematic viscosities, for the systems trimyristin + benzene, tristearin + benzene, and tripalmitin + benzene at 25, 30, and 35 °C and trimyristin + *p*-xylene at 25, 30, 35, 40, and 45 °C and at atmospheric pressure. These properties were correlated with the composition and temperature of the solutions through empirical relations. The calculated values were in agreement with the experimental data in the temperature range of the measurements.

Introduction

Properties of fatty oils such as density and viscosity are useful in the design of methods and equipments for the processing of the fatty oils to value-added products (*1*). Triglycerides are the most abundant single class of lipids. Additionally, dilute-solution viscosimetry in lipids (*2–6*) is useful in understanding the effect of changes in size and structure of the solute via the measurement of intrinsic viscosity.

This work is part of a systematic study on viscosities of triglycerides in various solvents. These studies will be used to contribute to modeling of the mobile phase's rheological properties of high-performance liquid chromatography and reverse-phase liquid chromatography of triglycerides. High-performance liquid chromatography's detection system based on light scattering is one of the most promising techniques for separating and quantifying the extremely complex mixtures of triglycerides that constitute natural oils (*7–8*). Light scattering is proportional to the radius of gyration of the solute, a physical property that is related to the viscosity of dilute solutions. Furthermore the use of viscosity for detection has been applied in the characterization of complex natural mixtures by high-performance size-exclusion chromatography (*9*). A common factor in high-performance liquid chromatography, reverse-phase liquid chromatography, and high-performance size-exclusion chromatography is that a significant part of the driving force for solute transfer arises from the nature of the pair interactions among neighboring solute and solvent molecules. Hence the binary solute–solvent viscosimetric studies for a series of triglycerides will be of use for quantifying triglyceride–solvent interactions.

The viscosities of mixtures have been represented by single equations to describe the effects of temperature and composition.

Materials

Purities (wt %) of the components (given by the manufacturer) were as follows: benzene (Ferak), purity better than 99.7; *p*-xylene (Fluka), purity better than 99.5; tristearin (Sigma), purity better than 99.0; tripalmitin (Sigma), purity better than 99.0; trimyristin (Roth), purity better than 99.0; triolein (Fluka), purity better than 99.0; trilinolein (Fluka), purity better than 98.0.

The physical properties of the solvents used are in accordance with data reported in the literature (*10–20*) and given in Table I.

Table I. Comparison of Experimental and Literature Values of Densities and Viscosities for Benzene and *p*-Xylene

		ρ/g cm^{-3}		$10^{-3}\eta$/(Pa s)	
solvent	T/°C	this work	lit.	this work	lit.
benzene	25	0.8734	0.87354 (*10*)	0.6060	0.6028 (*11*)
	25		0.87368 (*11*)		0.606 (*19*)
	25		0.87373 (*12*)		
	30	0.8682	0.8679 (*13*)	0.5651	0.565 (*17*)
	30		0.8682 (*15*)		0.564 (*19*)
	35	0.8628	0.8632 (*14*)	0.5284	0.5292 (*14*)
	35		0.8629 (*15*)		
p-xylene	25	0.8566	0.8568 (*16*)	0.6050	
	25		0.85674 (*18*)		
	30	0.8523	0.8525 (*16*)	0.5702	0.566 (*17*)
	30				0.566 (*20*)
	35	0.8479	0.8482 (*16*)	0.5381	

Experimental Section

Solutions were prepared by weight in a ground-glass-joint conical flask by using a Mettler balance with an accuracy of ±0.0001 g. The viscosities of the pure components and mixtures in various temperatures were measured in a glass Ubbelohde microcuvette with a capillary diameter of 0.4 mm, manufactured by Shott Gerate. An automated Shott viscosimeter (Model Series AVS 300) was used with fiber-optic detectors replacing visual reading. Efflux time was determined to within 0.01. The manufacturer provided the calibration constant (k = 0.009 533) that relates the efflux time to the kinematic viscosity. In all determinations, the kinetic energy correction was made (*21*). The temperature bath was a Shott Gerate Model CT1150 connected to a Shott Gerate CK100 cooling device. The temperature was maintained constant to +0.01 °C. The standard deviation of the viscosity measurements was 0.1%.

Densities were determined with a Robertson specific gravity bottle with an accuracy of ±0.0001, calibrated with distilled water at each temperature. Density measurements for the solvents also were made by use of a vibrating densimeter (Anton Paar Model DMA 40).

Experiments were generally performed in five replicates for each composition, and the results were averaged.

Results and Discussion

Experimental density (g cm^{-3}) and dynamic viscosity (10^{-3} Pa s) data at 25, 30, and 35 °C for the unsaturated triglyceride (triolein + benzene, trilinolein + benzene, trilinolein + *p*-xylene) systems are shown in Table II. Experimental kinematic viscosity (m^2 s^{-1}) data at 25, 30, and 35 °C for the saturated triglyceride (tristearin + benzene, tripalmitin + benzene, trimyristin + benzene, trimyristin + *p*-xylene) systems are shown in Table III. In the cases of trimyristin + *p*-xylene and trilinolein + *p*-xylene the temperature range covered included 40 and 45 °C. The maximum concentrations for the saturated lipids tristearin, tripalmitin, and trimyristin were determined by the solubility to benzene and *p*-xylene, which was approximately 0.016 mol kg^{-1}. The unsaturated triglycerides trilinolein and triolein were studied in the range 0–0.12 mol kg^{-1}.

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Table II. Densities and Viscosities for Unsaturated Triglycerides Triolein + Benzene, Trilinolein + Benzene, and Trilinolein + *p*-Xylene

	at 25 °C		at 30 °C		at 35 °C	
$10^{-2}x$	ρ/(g cm^{-3})	$10^{-3}\eta$/(Pa s)	ρ/(g cm^{-3})	$10^{-3}\eta$/(Pa s)	ρ/(g cm^{-3})	$10^{-3}\eta$/(Pa s)
			Triolein + Benzene			
1.0089	0.8763	0.8347	0.8713	0.7753	0.8663	0.7219
0.8697	0.8760	0.8092	0.8709	0.7525	0.8659	0.7013
0.6457	0.8753	0.7579	0.8703	0.7052	0.8651	0.6577
0.4187	0.8747	0.7009	0.8696	0.6529	0.8643	0.6095
0.2049	0.8740	0.6494	0.8689	0.6052	0.8636	0.5658
0.1078	0.8737	0.6281	0.8686	0.5855	0.8632	0.5476
0.0535	0.8736	0.6159	0.8684	0.5754	0.8630	0.5384
0.0368	0.8735	0.6130	0.8683	0.5720	0.8629	0.5349
0.0000	0.8734	0.6060	0.8682	0.5651	0.8628	0.5284
			Trilinolein + Benzene			
0.9645	0.8771	0.8054	0.8726	0.7492	0.8676	0.6986
0.7049	0.8762	0.7485	0.8715	0.6975	0.8665	0.6515
0.4505	0.8753	0.6974	0.8704	0.6502	0.8652	0.6077
0.1751	0.8742	0.6401	0.8691	0.5970	0.8638	0.5580
0.1044	0.8739	0.6257	0.8688	0.5836	0.8634	0.5455
0.0838	0.8738	0.6216	0.8687	0.5797	0.8633	0.5419
0.0515	0.8736	0.6153	0.8685	0.5739	0.8631	0.5365
0.0427	0.8736	0.6136	0.8685	0.5723	0.8630	0.5350
0.0000	0.8734	0.6060	0.8682	0.5651	0.8628	0.5284
			Trilinolein + *p*-Xylene			
0.6113	0.8597	0.6966	0.8553	0.6549	0.8512	0.6170
0.5322	0.8593	0.6861	0.8549	0.6455	0.8508	0.6085
0.4524	0.8589	0.6742	0.8545	0.6346	0.8504	0.5985
0.3771	0.8585	0.6627	0.8542	0.6238	0.8500	0.5885
0.2914	0.8581	0.6494	0.8537	0.6115	0.8495	0.5769
0.2170	0.8577	0.6380	0.8534	0.6008	0.8491	0.5668
0.1435	0.8573	0.6268	0.8530	0.5903	0.8487	0.5570
0.0712	0.8570	0.6159	0.8526	0.5801	0.8483	0.5474
0.0000	0.8566	0.6050	0.8523	0.5702	0.8479	0.5381

	at 40 °C		at 45 °C	
$10^{-2}x$	ρ/(g cm^{-3})	$10^{-3}\eta$/(Pa s)	ρ/(g cm^{-3})	$10^{-3}\eta$/(Pa s)
		Trilinolein + *p*-Xylene		
0.6113	0.8470	0.5824	0.8428	0.5507
0.5322	0.8466	0.5747	0.8424	0.5437
0.4524	0.8462	0.5654	0.8420	0.5352
0.3771	0.8458	0.5561	0.8416	0.5265
0.2914	0.8453	0.5453	0.8411	0.5163
0.2170	0.8449	0.5358	0.8407	0.5074
0.1435	0.8445	0.5265	0.8403	0.4986
0.0712	0.8441	0.5174	0.8398	0.4900
0.0000	0.8437	0.5086	0.8394	0.4817

The following functional relationship between dynamic viscosity η, the temperature T, and the molar fraction of solute x_1 was assumed:

$$\eta/(10^{-3}\ \text{Pa s}) = F_2(x_1)\, e^{F_1(x_1)/(T/\text{K})} \quad (1)$$

$F_1(x)$ and $F_2(x)$ are defined as follows:

$$F_1(x_1) = 10^6 \sum_{i=0}^{4} (a_i\, x_1{}^i) \quad (2)$$

$$F_2(x_1) = \sum_{i=0}^{4} (b_i\, x_1{}^i) \quad (3)$$

The above Arrhenious type relation, eq 1, in this particular form has been proposed by Papanastasiou and co-workers (*22*).

Relation 1 with a slightly modified polynomial form for relation 3 was used to describe the relationship between kinematic viscosity ν, temperature T, and the molar fraction x_1 in order to balance the effect of the very low concentrations used due to low solubilities of the saturated triglycerides

$$F'_2(x_1) = \sum_{i=0}^{4} (b_i\, x_1{}^i (10^i)) \quad (4)$$

Table III. Experimental Kinematic Viscosity Data of the Saturated Triglycerides + Benzene and *p*-Xylene

	$10^{-6}\nu$/(m^2 s^{-1})				
$10^{-2}x$	25 °C	30 °C	35 °C	40 °C	45 °C
			Trimyristin + *p*-Xylene		
0.1757	0.7296	0.6908	0.6551	0.6223	0.5922
0.1618	0.7259	0.6874	0.6522	0.6197	0.5898
0.1412	0.7227	0.6845	0.6495	0.6173	0.5877
0.1284	0.7214	0.6833	0.6484	0.6162	0.5867
0.0864	0.7165	0.6787	0.6440	0.6120	0.5826
0.0693	0.7135	0.6759	0.6414	0.6095	0.5803
0.0320	0.7068	0.6697	0.6356	0.6043	0.5754
0.0000	0.7064	0.6690	0.6346	0.6040	0.5754
			Trimyristin + Benzene		
0.2063	0.7269	0.6819	0.6410		
0.1509	0.7179	0.6740	0.6341		
0.1289	0.7147	0.6709	0.6311		
0.1251	0.7142	0.6704	0.6305		
0.1016	0.7102	0.6665	0.6268		
0.0528	0.7011	0.6578	0.6185		
0.0256	0.6965	0.6537	0.6148		
0.0000	0.6938	0.6509	0.6124		
			Tripalmitin + Benzene		
0.1696	0.7296	0.6850	0.6445		
0.1513	0.7273	0.6830	0.6426		
0.1258	0.7231	0.6789	0.6386		
0.1164	0.7212	0.6770	0.6368		
0.0902	0.7150	0.6709	0.6308		
0.0673	0.7089	0.6651	0.6253		
0.0582	0.7066	0.6629	0.6232		
0.0332	0.7006	0.6574	0.6181		
0.0180	0.6974	0.6545	0.6155		
0.0000	0.6938	0.6509	0.6124		
			Tristearin + Benzene		
0.0992	0.7233	0.6786	0.6379		
0.0821	0.7180	0.6735	0.6332		
0.0715	0.7163	0.6721	0.6321		
0.0612	0.7145	0.6706	0.6308		
0.0515	0.7118	0.6684	0.6289		
0.0395	0.7075	0.6645	0.6254		
0.0276	0.7027	0.6600	0.6212		
0.0000	0.6938	0.6509	0.6124		

Table IV. Parameters for Equations 6 and 7 for the Density ρ of Triglycerides + Benzene and Triglycerides + *p*-Xylene

parameter	*p*-xylene + trilinolein	benzene + trilinolein	benzene + triolein
$10^{-2}a_0$	−0.101 02	−0.123 38	−0.123 247
$10^{-1}a_1$	0.063 4749	0.158 181	0.060 3114
a_2	−0.358 501	−0.266 607	−0.095 3669
$10b_0$	0.115 757	0.126 185	0.126 133
$10b_1$	−0.149 300	−0.529 778	−0.181 319
10^3b_2	0.118 933	0.097 0597	0.029 2399
$10^{-3}\sigma(\rho)$	0.0953	0.207	0.0932

The following equation was used to relate the density ρ to the temperature T and the molar fraction of solute x_1 (*23*):

$$\rho/(\text{g cm}^{-3}) = G_2(x_1)\, e^{G_1(x_1)(T/\text{K})} \quad (5)$$

$G_1(x_1)$ and $G_2(x_1)$ are defined as follows

$$G_1(x_1) = \sum_{i=0}^{2} (a_i\, x_1{}^i) \quad (6)$$

$$G_2(x_1) = \sum_{i=0}^{2} (b_i\, x_1{}^i) \quad (7)$$

The parameters of the preceding relationships were calculated from the experimental results using a nonlinear optimization technique developed previously (*24*) which permits simultaneous variation of the parameters a_i and b_i. The parameters are listed

Table V. Parameters for Equations 2 and 3 for the Dynamic Viscosity η of Triglycerides + Benzene and Triglycerides + *p*-Xylene

parameter	*p*-xylene + trilinolein	benzene + trilinolein	benzene + triolein
$10^{-2}a_0$	0.108 289	0.125 919	0.124 973
$10^{-2}a_1$	0.250 602	0.096 9200	0.745 446
a_2	−0.641 439	0.148 226	0.087 9608
$10^{2}a_3$	0.831 193	−0.538 715	−0.146 927
$10^{5}a_4$	0.153 505	0.084 6303	0.006 08353
$10^{-1}b_0$	0.160 156	0.088 7254	0.091 5852
b_1	0.263 2839	0.237 8740	0.067 4530
$10^{2}b_2$	0.296 7012	0.110 7112	0.031 9703
$10^{4}b_3$	−0.193 405	−0.106 490	−0.045 5948
$10^{7}b_4$	−0.123 3649	−0.013 8450	−0.001 01398
$10^{-3}\sigma(\eta)$	0.489	0.899	0.718

Table VI. Parameters for Equations 2 and 4 for the Kinematic Viscosity ν of Triglycerides + Benzene and Triglycerides + *p*-Xylene

parameter	*p*-xylene + trimyristin	benzene + trimyristin	benzene + tripalmitin	benzene + tristearin
$10^{-2}a_0$	0.096 8983	0.113 680	0.113 636	0.114 986
$10^{-1}a_1$	0.193 832	0.490 689	0.596 262	−1.346 91
$10^{2}a_2$	0.136 826	−0.372 575	−0.540 805	2.881 25
$10^{4}a_3$	−3.514 26	−0.771 668	−0.262 757	−12.239
$10^{7}a_4$	1.418 316	0.794 645	0.884 3518	−2.7205
$10^{-1}b_0$	0.273 691	0.153 085	0.153 33	0.146 672
b_1	−0.226 902	−0.225 955	−0.240 8379	0.700 322
$10^{2}b_2$	0.134 7660	0.217 806	0.239 533	−1.131 37
$10^{3}b_3$	0.977 757	0.193 013	0.507 498	0.510 558
$10^{5}b_4$	−0.678 714	−0.361 07	−0.579 4698	4.232 69
$10^{-2}\sigma(\nu)$	0.0583	0.0741	0.0909	0.1046

in Tables IV–VI. Standard deviation values σ(var) of var defined by

$$\sigma = \left(\frac{\sum_{i=0}^{N} (\mathrm{var}_i^{\mathrm{calc}} - \mathrm{var}_i^{\mathrm{expt}})^2}{N - Q} \right)^{0.5} \quad (8)$$

where N is the number of data points and Q is the number of adjustable parameters in the equation and var is the variable denoting density, dynamic viscosity, or kinematic viscosity. The standard deviation played the role of the objective function for the selected optimization scheme. The program was set to terminate the search for an improved set of adjustable parameters once a σ(var) reached a preset value. For the densities fit, the σ(density)/(g cm^{-3}) target value was set better than 2×10^{-4}; for the unsaturated triglycerides, the σ(dynamic viscosity)/(10^{-3} Pa s) target value was better than 5×10^{-4}; and for the saturated triglycerides, the σ(kinematic viscosity)/(m^2 s^{-1}) target value was better than 1×10^{-3}. These σ values obtained by the nonlinear optimization are overall indicating a significantly closer fit to the experimental values than the forced linearization that is frequently used (*22*).

Glossary

a_i, b_i	coefficients in eqs 2–4, 6, and 7
m	molarity of the solution
x_1	molar fraction of the solute
T	temperature
η	dynamic viscosity of the solution
ν	kinematic viscosity of the solution
ρ	density of the solution
σ	standard deviation, eq 8

Registry No. Benzene, 71-43-2; triolein, 122-32-7; trilinolein, 537-40-6; *p*-xylene, 106-42-3; trimyristin, 555-45-3; tristearin, 555-43-1; palmitin, 11140-06-0.

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