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Viscosities and Densities of Dilute Solutions of Glycerol Trioleate + Octane, + *p*-Xylene, + Toluene, and + Chloroform

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Dynamic viscosities (η) and densities (ϱ) of dilute solutions of glycerol trioleate + chloroform, at 10, 15, 20, 25, and 30 °C, and of glycerol trioleate + octane, + *p*-xylene, + toluene, at 20, 25, 30, 35, and 40 °C, were measured. The dynamic viscosities and the excess volumes were correlated with the composition and temperature through empirical relations. The standard deviations from the derived viscosity equation were of the same order of magnitude as the experimental uncertainties. The excess volumes (V^E) have been derived from the density measurements. V^E values were positive for the glycerol trioleate + chloroform system and negative for the other mixtures over the entire range of mole fractions covered in this study. The departure from the ideal behavior is explained on the basis of specific interactions between the components in these mixtures.

Introduction

A survey of the literature shows that very few measurements have been made on the viscosities of binary mixtures containing the most abundant single class of lipids, namely the triacylglycerol esters (*1, 2*). The dynamic viscosity (η) of dilute solutions of various triglycerides in benzene has been expressed in terms of the molecular structural characteristics of the solute, employing an empirical relationship (*3*) which is similar to the equation expressing the retention time of reversed phase liquid chromatography (RPLC). Solution viscometry and densitometry in triglycerides have been used to describe the effect of changes in size and structure of the solute; hence, this study for a series of solvents will be useful for quantifying triglyceride−solvent interactions, which will be used to contribute to modeling of the mobile phase's rheological properties of high-performance liquid chromatography (*3*).

Thermodynamic and transport properties of fatty oils are useful in the design of methods and equipments for the processing of the fatty oils to value-added products (*4, 5*). Hence, it was thought to be worthwhile to extend the study to dilute triglyceride solutions in various solvents.

The viscosities and excess volumes of mixtures have been represented by single equations to describe the effects of temperature and composition. An attempt was also made to explain, in terms of specific interactions between the components in these mixtures, the departure of the ideal behavior of the calculated excess volume (V^E).

Experimental Section

Reagents. Purities of the components (given by the manufacturer) were as follows: glycerol trioleate (Fluka), purity better than 99.0 mass %; *p*-xylene (Fluka), purity better than 99.5 mass %; toluene (Ferak), purity better than 99.5 mass %; octane (Sigma), purity better than 99.0 mass %; carbon tetrachloride (Merck), purity better than 99.7 mass %. Chloroform (Merck), purity between 99.1 and 99.4 mass %, was further purified as follows: The chloroform was shaken five times with about half its volume of water, then dried over anhydrous sodium sulfate for at least 24 h, and distilled, according to the method in the literature (*6*).

Measurements. Solutions were prepared by mass in a ground-glass-joint conical flask 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 Schott Geräte. An automated Schott viscometer (Models Series AVS 300 and AVS 310) was used with fiber-optic detectors replacing visual reading. Efflux time was determined to within 0.01 s. The viscometer was calibrated by using distilled water, toluene, cyclohexane, and benzene (Ferak > 99.5 mass %). A survey of the literature (*7, 8*) showed that there are considerable differences of viscosity values given by different workers (discrepancies between 0.010 and 0.020 mPa·s). Also, it was observed that water was not a good solvent for calibration, since it is difficult to have consis-

Table 1. Comparison of Experimental and Literature Values of Densities (ϱ) and Viscosities (η) for Pure Compounds

		ϱ/(g·cm^{-3})		η/(mPa·s)	
solvent	t/°C	this work	lit.	this work	lit.
toluene	20	0.8669	0.8666 (*10*)	0.5887	0.589 (*11*)
	25	0.8623		0.5541	0.554 (*11*)
	30	0.8576	0.8573 (*10*)	0.5226	0.522 (*11*)
	35	0.8531		0.4920	0.493 (*11*)
	40	0.8482	0.8480 (*10*)	0.4659	0.466 (*11*)
benzene	20	0.8786	0.8784 (*10*)	0.6508	0.652 (*7a*)
	25	0.8734	0.8734 (*12a*)	0.6044	0.606 (*7a*)
	30	0.8681	0.8680 (*10*)	0.5627	0.564 (*7a*)
	35	0.8628	0.8629 (*12a*)	0.5218	
c-hexane	25	0.7739	0.7737 (*13, 14*)	0.8987	0.896 (*7b*)
	30	0.7692	0.76914 (*15*)	0.8263	0.825 (*7b*)
	35	0.7645	0.7645 (*16*)	0.7020	0.702 (*7b*)
p-xylene	25	0.8565	0.8568 (*12b*)	0.6045	0.604 (*17*)
	30	0.8522	0.8525 (*12b*)	0.5694	0.569 (*18*)
	35	0.8479	0.8482 (*12b*)	0.5355	
chloroform	20	1.4883	1.4878 (*19*)	0.5674	0.563 (*7c*)
	25	1.4788	1.4785 (*19*)	0.5394	0.537 (*7c*)
	30	1.4696	1.4691 (*19*)	0.5119	0.510 (*7c*)
n-octane	20	0.7026	0.7022 (*9b*)	0.5424	0.539 (*7d*)
	40	0.6863	0.6860 (*9b*)	0.4295	0.429 (*7d*)
glycerol trioleate	37			39.884	
	40	0.8989	0.8988 (*20*)		
	45		0.8952 (*2*)		29.322 (*2*)
	70				13.8 (*21*)

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Table 2. Experimental Density (ϱ) and the Derived Excess Volume V^E for Glycerol Trioleate + Chloroform, + Octane, + p-Xylene, + Toluene, at Different Temperatures

	10 °C		15 °C		20 °C		25 °C		30 °C	
10^2x_1	ϱ/ ($g \cdot cm^{-3}$)	V^E/ ($cm^3 \cdot mol^{-1}$)	ϱ/ ($g \cdot cm^{-3}$)	V^E/ ($cm^3 \cdot mol^{-1}$)	ϱ/ ($g \cdot cm^{-3}$)	V^E/ ($cm^3 \cdot mol^{-1}$)	ϱ/ ($g \cdot cm^{-3}$)	V^E/ ($cm^3 \cdot mol^{-1}$)	ϱ/ ($g \cdot cm^{-3}$)	V^E/ ($cm^3 \cdot mol^{-1}$)
					Glycerol Trioleate + Chloroform					
0.0000	1.5075	0.0000	1.4980	0.0000	1.4883	0.0000	1.4788	0.0000	0.4696	0.0000
0.0728	1.5031	−0.0379	1.4937	−0.0417	1.4841	−0.0454	1.4748	−0.0493	1.4654	−0.0400
0.0907	1.4996	0.0808	1.4902	0.0792	1.4806	0.0776	1.4713	0.0759	1.4622	0.0740
0.2440	1.4879	0.1419	1.4788	0.1343	1.4695	0.1265	1.4605	0.1119	1.4515	0.1169
0.4913	1.4743	−0.0037	1.4652	−0.0028	1.4560	−0.0085	1.4471	0.0143	1.4382	−0.0143
0.7824	1.4544	0.0994	1.4456	0.0973	1.4368	0.0853	1.4282	0.0706	1.4196	0.0709
1.3218	1.4207	0.2854	1.4123	0.2829	1.4040	0.2620	1.3960	0.2365	1.3878	0.2342
1.6719	1.3999	0.4578	1.3918	0.4545	1.3839	0.4271	1.3762	0.3938	1.3683	0.3893
3.0775	1.3245	1.5437	1.3173	1.5347	1.3106	1.4744	1.3042	1.4031	1.2972	1.3861
100.00	0.9194	0.0000	0.91601	0.0000	0.9126	0.0000	0.9092	0.0000	0.9057	0.0000

	20 °C		25 °C		30 °C		35 °C		40 °C	
10^2x_1	ϱ/ $g \cdot cm^{-3}$	V^E/ $cm^3 \cdot mol^{-1}$	ϱ/ $g \cdot cm^{-3}$	V^E/ $cm^3 \cdot mol^{-1}$	ϱ/ $g \cdot cm^{-3}$	V^E/ $cm^3 \cdot mol^{-1}$	ϱ/ $g \cdot cm^{-3}$	V^E/ $cm^3 \cdot mol^{-1}$	ϱ/ $g \cdot cm^{-3}$	V^E/ $cm^3 \cdot mol^{-1}$
					Glycerol Trioleate + Octane					
0.0000	0.7026	0.0000	0.6986	0.0000	0.6946	0.0000	0.6905	0.0000	0.6863	0.0000
0.0908	0.7037	0.0025	0.6998	−0.0209	0.6958	−0.0207	0.6917	−0.0205	0.6876	−0.0201
0.1916	0.7052	−0.0402	0.7011	−0.0397	0.6972	−0.0635	0.6932	−0.0631	0.6889	−0.0379
0.4907	0.7093	−0.1487	0.7053	−0.1722	0.7014	−0.1962	0.6974	−0.2202	0.6932	−0.1947
1.0096	0.7155	−0.1975	0.7115	−0.2193	0.7076	−0.2416	0.7037	−0.2633	0.6995	−0.2600
2.6085	0.7331	−0.3947	0.7293	−0.4273	0.7254	−0.4805	0.7216	−0.5220	0.7175	−0.5376
3.5551	0.7437	−0.8362	0.7399	−0.8790	0.7360	−0.9225	0.7322	−0.9633	0.7281	−0.9776
5.9967	0.7630	−0.6992	0.7593	−0.7582	0.7555	−0.8182	0.7517	−0.8731	0.7474	−0.8995
8.2971	0.7788	−0.7558	0.7751	−0.8365	0.7714	−0.8875	0.7677	−0.9620	0.7638	−1.0065
100.00	0.9126	0.0000	0.9092	0.0000	0.9057	0.0000	0.9024	0.0000	0.8989	0.0000
					Glycerol Trioleate + p-Xylene					
0.0000	0.8607	0.0000	0.8565	0.0000	0.8522	0.0000	0.8479	0.0000	0.8434	0.0000
0.0755	0.8614	−0.0473	0.8571	−0.0471	0.8538	−0.0313	0.8485	−0.0464	0.8440	−0.0460
0.1496	0.8616	−0.0351	0.8574	−0.0496	0.8531	−0.0331	0.8488	−0.0474	0.8442	−0.0302
0.4118	0.8628	−0.0711	0.8586	−0.0681	0.8543	−0.0649	0.8500	−0.0608	0.8455	−0.0567
0.7318	0.8642	−0.0978	0.8600	−0.0921	0.8557	−0.0863	0.8515	−0.0950	0.8471	−0.1040
1.1392	0.8658	−0.1190	0.8616	−0.1097	0.8573	−0.1004	0.8531	−0.1050	0.8486	−0.1097
1.5262	0.8675	−0.1799	0.8632	−0.1677	0.8591	−0.1723	0.8550	−0.1906	0.8505	−0.1920
2.4689	0.8706	−0.2063	0.8665	−0.2212	0.8624	−0.2186	0.8583	−0.2463	0.8539	−0.2383
2.9082	0.8721	−0.2466	0.8680	−0.2588	0.8639	−0.2529	0.8598	−0.2772	0.8555	−0.2834
3.5134	0.8737	−0.2431	0.8696	−0.2510	0.8656	−0.2590	0.8615	−0.2782	0.8573	−0.2979
4.6780	0.8767	−0.2920	0.8727	−0.2920	0.8687	−0.2920	0.8647	−0.3217	0.8604	−0.3113
6.0745	0.8797	−0.2988	0.8758	−0.3102	0.8718	−0.3217	0.8679	−0.3412	0.8637	−0.3374
100.00	0.9126	0.0000	0.9092	0.0000	0.9057	0.0000	0.9024	0.0000	0.8989	0.0000
					Glycerol Trioleate + Toluene					
0.0000	0.8669	0.0000	0.8623	0.0000	0.8576	0.0000	0.8531	0.0000	0.8482	0.0000
0.0651	0.8671	0.0717	0.8625	0.0806	0.8578	0.0903	0.8533	0.1003	0.8484	0.0111
0.1141	0.8673	0.0059	0.8628	0.0074	0.8582	−0.0044	0.8536	−0.0028	0.8487	−0.0011
0.3237	0.8682	−0.0078	0.8637	−0.0038	0.8591	−0.0130	0.8545	−0.0087	0.8498	−0.0117
0.6694	0.8696	−0.0139	0.8652	−0.0194	0.8606	−0.0244	0.8560	−0.0153	0.8513	−0.0196
0.9965	0.8710	−0.0382	0.8665	−0.0402	0.8620	−0.0412	0.8575	−0.0422	0.8528	−0.0421
1.5005	0.8731	−0.0926	0.8687	−0.0894	0.8642	−0.0992	0.8597	−0.0943	0.8551	−0.1027
1.7363	0.8738	−0.0759	0.8694	−0.0846	0.8650	−0.1066	0.8607	−0.1139	0.8560	−0.1194
2.1735	0.8750	−0.0661	0.8707	−0.0701	0.8662	−0.0718	0.8618	−0.0736	0.8572	−0.0730
3.0324	0.8776	−0.0858	0.8733	−0.0971	0.8690	−0.1053	0.8646	−0.0973	0.8601	−0.1023
4.0607	0.8802	−0.1024	0.8761	−0.1213	0.8718	−0.1360	0.8676	−0.1336	0.8631	−0.1443
100.00	0.9126	0.0000	0.9092	0.0000	0.9057	0.0000	0.9024	0.0000	0.8989	0.0000

tently reproducible results within ±0.2% over a period of time. It was decided that toluene, cyclohexane, and benzene were the best solvents for calibration (Table 1).

The temperature bath was a Schott Geräte Model CT 1150 connected to a Schott Geräte CK 100 cooling device. The temperature was maintained constant to ±0.01 °C. The estimated error in the viscosity measurements was ±0.002 mPa·s. For each measurement, sufficient time was allowed for thermal equilibrium to be attained. Extra precautions were taken to avoid evaporation of the volatile solvents by using two traps filled with solvent vapor (one trap at the experiment temperature and the other at the environment temperature).

Density measurements were made with a vibrating densitometer (Antor Paar Model DMA 40) with an estimated precision of ±0.0001 $g \cdot cm^{-3}$. A temperature-controlled bath (constant to ±0.01 °C) was used. Calibration was carried out with doubly distilled water, air, and carbon tetrachloride. The densities of air and water were given by the manufacturer, and that of carbon tetrachloride was taken from ref 9a.

Results and Discussion

The performance of the viscometer and the densitometer was assessed by measuring and comparing the viscosities and densities of the pure components with those reported in the literature (*2, 7–21*) (Table 1).

The experimental densities and the derived excess molar volumes V^E for the systems glycerol trioleate + chloroform, + octane, + p-xylene, and + toluene, at various temperatures, are given in Table 2. The experimental viscosities

Table 3. Experimental Viscosities (η) for Glycerol Trioleate + Chloroform, + Octane, + *p*-Xylene, + Toluene, at Different Temperatures

	η/mPa·s				
10^2x_1	10 °C	15 °C	20 °C	25 °C	30 °C
		Glycerol Trioleate + Chloroform			
0.0000	0.6293	0.5962	0.5659	0.5378	0.5119
0.0728	0.6499	0.6156	0.5839	0.5545	0.5275
0.0907	0.6541	0.6195	0.5875	0.5581	0.5306
0.2440	0.7086	0.6703	0.6352	0.6030	0.5725
0.4913	0.7776	0.7347	0.6950	0.6576	0.6237
0.7824	0.9175	0.8628	0.8133	0.7684	0.7270
1.3218	1.1754	1.0999	1.0317	0.9701	0.9137
1.6719	1.2680	1.1865	1.1088	1.0417	0.9804
3.0775	2.0212	1.8640	1.7329	1.5845	1.4740

	η/mPa·s				
10^2x_1	20 °C	25 °C	30 °C	35 °C	40 °C
		Glycerol Trioleate + Octane			
0.0000	0.5425	0.5103	0.4810	0.4541	0.4295
0.0908	0.5531	0.5204	0.4903	0.4628	0.4377
0.1916	0.5668	0.5329	0.5020	0.4737	0.4478
0.4907	0.6068	0.5699	0.5360	0.5055	0.4774
1.0096	0.6753	0.6331	0.5947	0.5596	0.5277
2.6085	0.9348	0.8701	0.8126	0.7605	0.7134
3.5551	1.1102	1.0300	0.9579	0.8936	0.8357
5.9967	1.6382	1.5046	1.3875	1.2842	1.1909
8.2971	2.2676	2.0641	1.8939	1.7408	1.6059
		Glycerol Trioleate + *p*-Xylene			
0.0000	0.6433	0.6045	0.5694	0.5355	0.5064
0.0755	0.6573	0.6175	0.5813	0.5465	0.5168
0.1496	0.6699	0.6292	0.5923	0.5567	0.5261
0.4118	0.7209	0.6762	0.6359	0.5968	0.5636
0.7318	0.7825	0.7329	0.6883	0.6454	0.6090
1.1392	0.8597	0.8042	0.7541	0.7060	0.6650
1.5262	0.9594	0.8955	0.8379	0.7833	0.7368
2.4689	1.1847	1.1012	1.0266	0.9558	0.8959
2.9082	1.2908	1.1972	1.1150	1.0367	0.9704
3.5134	1.4214	1.3156	1.2224	1.1344	1.0601
4.6780	1.7773	1.6368	1.5131	1.3987	1.3021
6.0745	2.2411	2.0614	1.8854	1.7326	1.6046
		Glycerol Trioleate + Toluene			
0.000	0.5887	0.5541	0.5226	0.4920	0.4659
0.0651	0.06007	0.5652	0.5329	0.5016	0.4748
0.1141	0.6111	0.5749	0.5419	0.5101	0.4827
0.3237	0.6517	0.6124	0.5768	0.5425	0.5130
0.6694	0.7201	0.6756	0.6355	0.5965	0.5635
0.9965	0.7951	0.7447	0.6992	0.6557	0.6185
1.5005	0.9362	0.8679	0.8126	0.7602	0.7155
1.7363	0.9710	0.9064	0.5482	0.7930	0.7459
2.1735	1.0729	0.9993	0.9337	0.8710	0.8182
3.0324	1.3057	1.2119	1.1289	1.0508	0.9851
4.0607	1.6163	1.4928	1.3855	1.2839	1.1983

Table 4. Parameters and Standard Deviation σ(var) for Viscosity (Eq 1) and for the Excess Volume (Eq 8)

	glycerol trioleate			
parameter	+ chloroform	+ octane	+ *p*-xylene	+ toluene
		Equation 1		
$10^{-3}a_0$	0.812467	1.0686	1.1144	1.0816
$10^{-4}a_1$	5.2019	0.65766	−0.16306	1.0485
$10^{-6}a_2$	−3.0704	0.0027814	0.55095	−0.19115
$10^{-7}a_3$	4.4967	0.0037247	−0.6648	−0.57821
$10^{-8}a_4$	6.0275	−0.015731	0.10391	2.3737
$10^{2}b_0$	3.5493	1.4169	1.4372	1.4733
$10b_1$	−43.079	0.028622	5.2191	−0.77302
$10^{-1}b_2$	45.503	−0.11196	−3.3143	1.1407
$10^{-3}b_3$	−16.316	−0.0014081	0.46712	0.058922
$10^{-4}b_4$	17.702	0.0093479	−0.079836	−0.83795
$10^{3}\sigma(\eta)$	4.2	1.5	5.4	6.1
		Equation 8		
$10^{-2}a_0$	−0.34659	3.4664	−0.86978	2.1342
a_1	0.92253	−2.2489	0.44039	−1.3958
$10^{4}a_2$	−18.875	32.1890	−8.3955	22.169
$10^{-3}a_3$	−25.843	0.49745	3.8584	2.9742
$10a_4$	−37.088	16.7159	4.7875	2.5053
$10^{-5}a_5$	37.652	1.0495	−2.9895	−6.0439
$10^{-7}a_6$	−22.157	−0.75219	1.0425	4.14669
$10^{-8}a_7$	59.0009	1.4376	−1.6638	−11.6246
$10^{-9}a_8$	−57.807	−0.83794	0.98370	11.4074
$10^{3}\sigma(V^{E})$	43.4	17.3	13.6	7.2

are given in Table 3.

Viscosities. The following Arrhenius-type relationship between dynamic viscosity (η), temperature (t), and molar fractions of solute x_1 was assumed (*1*):

$$\eta/(\text{mPa·s}) = F_2(x_1)\, e^{F_1(x_1)/(T/\text{K})} \qquad (1)$$

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

$$F_1(x_1) = \sum_{i=0}^{4}(a_i x_1^i) \qquad (2)$$

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

The parameters, of the preceding relationships 2 and 3, were calculated from the experimental results using a nonlinear optimization technique developed previously (*22*), which permits simultaneous variation of the parameters a_i and b_i. The values of the adjustable coefficients (a_i, b_i) are listed in Table 4 along with the standard deviation. Standard deviation values σ(var) of var were defined by

$$\sigma(\text{var}) = [\sum_{i=0}^{N}(\text{var}_i^{\text{calcd}} - \text{var}_i^{\text{exptl}})^2/(N - Q)]^{0.5} \qquad (4)$$

where N is the number of data points, Q is the number of adjustable parameters in the equation, and var is the variable denoting viscosity. The average deviation of the viscosity data calculated from eq 4 was better than 5.0×10^{-3} mPa·s.

For the very dilute regime glycerol trioleate concentration < $0.002x_1$, the following general relationship has been applied:

$$\ln \eta = k_0 + k_1 \ln \eta_0 + k_2(\text{CN}) + k_3(\text{DB}) + k_4 c \qquad (5)$$

The parameters k_i (i = 0, ..., 4) have the following values: $k_0 = -0.0443$, $k_1 = 1.0004$, $k_2 \times 10^3 = 0.9416$, $k_3 \times 10^3 = -1.6352$, and $k_4 \times 10^3 = 3.4742$. η_0 is the dynamic viscosity of solvent at the corresponding temperature, CN is the total number of carbon atoms participating in the three fatty chains, DB is the total number of double bonds, and c is the concentration of a triglyceride, ranging from 4 to 10 g/L. The parameters k_i have been determined in the literature (*3*) from benzene solutions of various triglycerides. The above equation fits well the viscosities of *p*-xylene and toluene solutions, while it is not so successful for the viscosities of chloroform and octane solutions (Table 5).

Excess Volumes. The excess volumes were calculated using the equations

$$V_m = (x_1M_1 + x_2M_2)/\varrho \qquad (6)$$

$$V^E = V_m - (x_1V_1 + x_2V_2) = [(x_1M_1 + x_2M_2)/\varrho] - (x_1V_1 + x_2V_2) \qquad (7)$$

where V_m, V_1, and V_2 are the molar volumes of the solution and the pure components, M_1 and M_2 are the molar weights of the components, and ϱ is the density of the solution. The values of the excess volumes V^E are listed in Table 2 and plotted in Figure 1 as a function of molar fraction x_1, for temperature 25 °C. The values were fitted into a poly-

Table 5. Comparison between Calculated and Experimentally Measured Dynamic Viscosities of Glycerol Trioleate + Chloroform, + Octane, + *p*-Xylene, + Toluene

solvent	t/°C	c/g·L^{-1}	η_{calcd}/mPa·s	η_{exptl}/mPa·s	$\delta\eta$/mPa·s	c/g·L^{-1}	η_{calcd}/mPa·s	η_{exptl}/mPa·s	$\delta\eta$/mPa·s
chloroform	25	6.80	0.5514	0.5545	−0.0031	12.00	0.5615	0.5581	0.0034
octane	25	4.90	0.5198	0.5204	−0.0006	10.28	0.5296	0.5329	−0.0033
p-xylene	25	5.37	0.6168	0.6175	−0.0007	10.58	0.6281	0.6292	−0.0012
toluene	25	5.37	0.5653	0.5652	0.0001	9.37	0.5732	0.5749	−0.0017

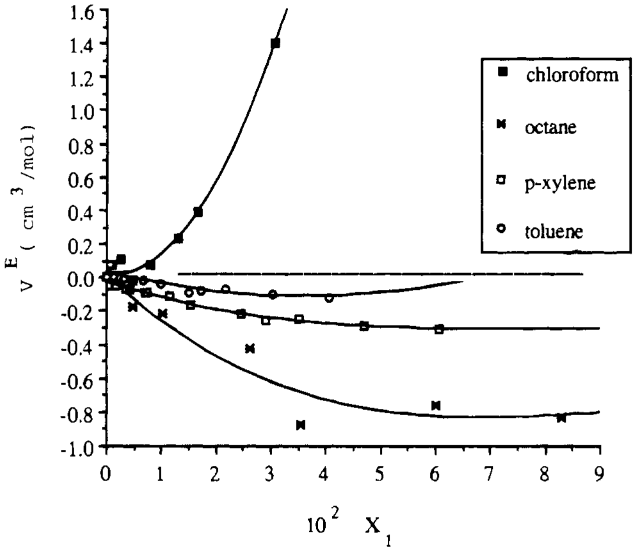

Figure 1. Molar excess V^E for glycerol trioleate + solvents at 25 °C, as a function of the mole fraction x_1 of glycerol trioleate.

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$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1(1 - x_1)[a_0 + a_1t + a_2t^2 + (a_3 + a_4t)x_1 + a_5{x_1}^2 + a_6{x_1}^3 + a_7{x_1}^4 + a_8{x_1}^5] \quad (8)$$

where a_i (i = 0, 8) denotes adjustable parameters and t (K) the temperature of the solution.

The parameters a_i of the preceding relationship 8 were calculated from the experimental results using the fitting technique described under Viscosities. These are listed in Table 4 along with the standard deviation estimate according to eq 4, where var is the variable denoting excess volume. Equation 8 fits reasonably well for the glycerol trioleate + toluene solution (standard deviation 7.2 × 10^{-3} cm^3·mol^{-1}).

The departure of the excess volumes (V^E) from ideal behavior is explained on the basis of specific interactions between the components in these mixtures.

(i) Glycerol Trioleate + Chloroform. The disruption of the hydrogen-bonded chloroform network and the simultaneous hydrophobic harpoon-like packing (*4*) of the acyl chains of glycerol trioleate contribute to the increase of V^E, as is depicted in Figure 1. Also, the differences (geometrical effects) in size and shape of the two molecules yield positive V^E values as a consequence of the steric hindrance.

These results are in agreement with those reported for the system pentyl acetate + 1-chlorobutane (*23*), where V^E is slightly positive (0.01 cm^3·mol^{-1}). The same effect is exhibited by the dichloromethane + pentane system, where the positive V^E is explained as breaking of liquid order of the nonpolar molecule of pentane by the polar molecule of dichloromethane (*24*).

On the other hand, the carbon tetrachloride in binary mixtures with the esters propyl acetate, butyl acetate, and ethyl butyrate takes negative V^E values (*25*).

(ii) Glycerol Trioleate + Octane. The system glycerol trioleate + octane exhibits negative values for V^E (Figure 1). The magnitude of V^E observed may be explained in terms of interstitial accommodation. The negative excess volume reflects the similarity between glycerol trioleate, which contains three −R chains, and nonpolar octane.

As has been reported in many papers (*26−29*), components containing −C=O carbonyl group ketones or esters show the interesting effect of decrease for the V^E values with increase in the number of carbon atoms. This can be explained by taking into account that as the basic nature of the carbonyl group increases with the length of the chain of the methyl ester, the interactions between the molecules of the ester are weakening, to allow a greater contact between the alkane and the *n*-chain of the ester. This effect causes the positive contribution to the V^E values of the mixture to decrease progressively, while for the binary system methyl octanoate + heptane the V^E is close to zero but still positive (*27*).

(iii) Glycerol Trioleate and p-Xylene and Toluene. These mixtures produce V^E values less negative than the glycerol trioleate + octane system (Figure 1). This reflects (a) the dissimilarity between glycerol trioleate and *p*-xylene and toluene, which has a positive effect on V^E, and (b) the specific interaction between glycerol trioleate and π electrons of the atomic ring which has a negative effect that outweighs the previous effect (a) (*25*).

It is interesting to compare results of mixtures of alkyl alkanoates in benzene. The values of V^E decrease with the increase in chain length of esters. Thus, the V^E is positive for propyl acetate + benzene but negative for ethyl butyrate + benzene (*25*). The system ethyl acetate + *p*-xylene shows V^E values slightly negative at dilute solution and gradually turns to small positive V^E values at more concentrated solutions (*18*).

In conclusion, V^E positive values were recorded for the glycerol trioleate + chloroform system, while V^E negative values were exhibited by the glycerol trioleate + octane, + *p*-xylene, and + toluene binary systems. The departure from ideal behavior is most noted for the binary glycerol trioleate + octane and + chloroform mixtures. The Arrhenius-type exponential fit is successful in describing the viscometric behavior of all binary systems presented in this study.

Glossary

η, η_1, η_2	dynamic viscosity of the solution and pure components in mPa·s
ϱ	density of the solution in g·cm^{-3}
a_i, b_i	adjustable coefficients in eqs 2, 3, 8
σ	standard deviation (eq 4)
x_1	molar fraction of the glycerol trioleate
x_2	molar fraction of the solvent
t	temperature in K
V	molar volumes of the solution, glycerol trioleate and solvent
M	molar weights of the components
N	number of data points
Q	total number of the adjustable parameters
V^E	excess molar volume

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Literature Cited

(1) Tasioula-Margari, M.; Demetropoulos, I. N. *J. Chem. Eng. Data* **1992**, *37*, 77.

(2) Eduljee, G. H.; Boyes, A. P. *J. Chem. Eng. Data* **1980**, *25*, 249.

(3) Tasioula-Margari, M.; Demetropoulos, I. N. *J. Am. Oil Chem. Soc.* **1992**, *69*, 1112.

(4) Ibemesi, J. A.; Igwe, I. O. *J. Am. Oil Chem. Soc.* **1991**, *68*, 147.

(5) Kapseu, C.; Kayem, G. J.; Balesdent, D.; Schuffenecker, L. *J. Am. Oil Chem. Soc.* **1991**, *68*, 128.

(6) *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Furniss, B. S., Hannaford, A. J., Rogers, Y., Smith, P. W. C., Tatchell, A. R., Eds.; Longman: London, 1979.

(7) *Landolt-Börnstein, Transport Phänomene I*; Springer-Verlag: Berlin, 1969; Band II, Teil 5, Bandteil a: (a) p 158, (b) p 157, (c) p 195, (d) p 161.

(8) Riddick, J. A.; Bunger, W. B. In *Organic Solvents. Techniques of Chemistry*; Wiley-Interscience: New York, 1970; Vol. II.

(9) *Landolt-Börnstein, Dampf-Kondensat*; Springer-Verlag: Berlin, 1960; Band 2, Teil 2, Bandteil a: (a) p 199, (b) p 197.

(10) Sumer, B. K. M.; Thompson, U. A. R. *J. Chem. Eng. Data* **1968**, *13*, 30.

(11) Byers, C. H.; Williams, D. F. *J. Chem. Eng. Data* **1987**, *32*, 344.

(12) *Landolt-Börnstein, Mechanisch-Thermische Zustandsgrössen*; Springer-Verlag: Berlin, 1971; Band 2, Teil 1, (a) p 911, (b) 643.

(13) Wel, I. C.; Rowley, R. L. *J. Chem. Eng. Data* **1984**, *29*, 332.

(14) Papanastasiou, G. E.; Ziogas, I. I. *J. Chem. Eng. Data* **1991**, *36*, 46.

(15) Scatchard, G.; Wood, S. E.; Mochel, J. M. *J. Am. Chem. Soc.* **1946**, *68*, 1960.

(16) Bamelis, P.; Huyskens, P.; Meeussen, E. *J. Chim. Phys.* **1965**, *62*, 158.

(17) Fermeglia, M.; Lapasin, R. *J. Chem. Eng. Data* **1988**, *33*, 415.

(18) Rathnam, M. V. *J. Chem. Eng. Data* **1988**, *33*, 14.

(19) Inés, A.; Katz, M. *Thermochim. Acta* **1989**, *156*, 199.

(20) *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; 1989–1990, CRC Press: p c-291.

(21) Callaghan, P. T.; Jolley, K. W. *Chem. Phys. Lipids* **1980**, *27*, 49.

(22) Evagelakis, G. A.; Rizos, J. P.; Lagaris, I. E.; Demetropoulos, I. N. *Comput. Phys. Commun.* **1987**, *46*, 401.

(23) Prolongo, M. G.; Masegosa, R. M.; Hernandez-Fuentes, I. *J. Phys. Chem.* **1984**, *88*, 2163.

(24) Postigo, M. A.; Zurita, J. L.; De Soria, M. L. G.; Katz, M. *Can. J. Chem.* **1986**, *64*, 1966.

(25) Oswal, S. *Can. J. Chem.* **1988**, *66*, 111.

(26) Anwel, Q.; Hoffman, E. D.; Munk, P. *J. Chem. Eng. Data* **1992**, *37*, 55.

(27) Pintos, M.; Bravo, R.; Baluja, M. C.; Andrade, M. I. P.; Roux-Desgranges, G.; Grolier, J. P. E. *Can. J. Chem.* **1988**, *66*, 1179.

(28) Dernini, S.; Polcaro, A. M.; Ricci, P. F. *J. Chem. Eng. Data* **1987**, *32*, 194.

(29) De Soria, M. L. G.; Zurita, J. L.; Postigo, M. A.; Katz, M. *Thermochim. Acta* **1988**, *130*, 249.

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