

Viscosity of Triglycerides + Alcohols from 278 to 313 K

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The viscosities of triacetin + butanol, tributyrin + butanol, tricaprylin + butanol, tributyrin + ethanol, and tributyrin + hexanol have been measured over the composition range from 278 to 313 K. The results are compared with Hildebrand's model.

Introduction

Knowledge of the viscosities of liquids and liquid mixtures is important, not only for chemical engineering calculations involving fluid flow, matter transfer, and heat transmission, but also in order to develop theories on the liquid state.

In this study we present experimental results for the viscosity of triacetin + butanol, tributyrin + butanol, tricaprylin + butanol, tributyrin + ethanol, and tributyrin + hexanol over the temperature range from 278 to 313 K.

Expressions were found relating characteristic parameters from Hildebrand's equation to composition. Furthermore, deviations were observed when the triglyceride concentration predominated in the solution, which was ascribed to a decrease in the free volume and to the validity of the equation over the measured temperature range.

Experimental Section

Three alcohols and three triglycerides were used, whose purities determined by gas chromatography were as follows: ethanol, 99.8 mass %; 1-butanol, 99.5 mass %; 1-hexanol, 98.0 mass %; triacetin, 99.0 mass %; tributyrin, 98.0 mass %; tricaprylin, 97.0 mass %.

The solutions were prepared by mass, using a Mettler P1210 single-pan balance with a precision of ± 0.01 g. Mole fractions x were accurate to ± 0.001 . Measurements were made in a thermostated Hetofrig bath, controlled to ± 0.1 K.

The Newtonian rheological behavior of the solutions was measured with a rotation viscometer with an accuracy of 99%. The dynamic viscosity was measured with a Haake Model B/BH Höppler falling-ball viscometer accurate to ± 0.001 mPa·s. Molar volumes were found from the density measured with a DMA 46 digital densimeter with an incorporated thermostat. Measurements were accurate to $\pm 1 \times 10^{-4}$ g·cm⁻³.

Results and Discussion

The viscosity and density results are given in Tables 1-5.

Hildebrand (1), on the basis of work by Batschinski (2), proposed the following equation, based on the free volume model:

$$\phi = B \frac{V - V_0}{V_0} \quad (1)$$

where ϕ is the fluidity (inverse of viscosity), B is a constant, V is the molar volume, and the parameter V_0 , called the limit

Table 1. Density ρ and Viscosity η for Triacetin + Butanol

x	ρ /(g·cm ⁻³)	η /(mPa·s)	x	ρ /(g·cm ⁻³)	η /(mPa·s)	x	ρ /(g·cm ⁻³)	η /(mPa·s)	x	ρ /(g·cm ⁻³)	η /(mPa·s)
$T = 278$ K						$T = 298$ K					
0.0	0.8218	4.38	0.6	1.0872	13.68	0.0	0.8061	2.52	0.6	1.0666	5.57
0.1	0.8867	4.38	0.7	1.1128	18.70	0.1	0.8697	2.40	0.7	1.0918	6.99
0.2	0.9404	5.35	0.8	1.1360	26.51	0.2	0.9222	2.70	0.8	1.1146	9.02
0.3	0.9856	6.55	0.9	1.1565	40.02	0.3	0.9664	3.12	0.9	1.1353	11.93
0.4	1.0246	8.25	1.0	1.1755	65.37	0.4	1.0049	3.71	1.0	1.1529	16.31
0.5	1.0580	10.48				0.5	1.0378	4.50			
$T = 283$ K						$T = 303$ K					
0.0	0.8178	3.79	0.6	1.0820	10.55	0.0	0.8021	2.23	0.6	1.0616	4.65
0.1	0.8825	3.70	0.7	1.1075	14.03	0.1	0.8654	2.11	0.7	1.0866	5.79
0.2	0.9358	4.49	0.8	1.1306	19.39	0.2	0.9176	2.34	0.8	1.1091	7.34
0.3	0.9808	5.45	0.9	1.1512	28.02	0.3	0.9616	2.69	0.9	1.1299	9.49
0.4	1.0196	6.59	1.0	1.1698	43.17	0.4	1.0002	3.17	1.0	1.1472	12.62
0.5	1.0530	8.18				0.5	1.0331	3.82			
$T = 288$ K						$T = 308$ K					
0.0	0.8138	3.28	0.6	1.0768	8.33	0.0	0.7983	1.97	0.6	1.0561	3.96
0.1	0.8782	3.18	0.7	1.1023	10.82	0.1	0.8611	1.87	0.7	1.0813	4.86
0.2	0.9312	3.71	0.8	1.1252	14.62	0.2	0.9130	2.06	0.8	1.1036	6.07
0.3	0.9761	4.41	0.9	1.1455	20.34	0.3	0.9568	2.36	0.9	1.1244	7.72
0.4	1.0147	5.32	1.0	1.1642	29.65	0.4	0.9948	2.75	1.0	1.1415	10.03
0.5	1.0479	6.56				0.5	1.0276	3.27			
$T = 293$ K						$T = 313$ K					
0.0	0.8100	2.86	0.6	1.0713	6.73	0.0	0.7943	1.76	0.6	1.0509	3.41
0.1	0.8737	2.76	0.7	1.0968	8.63	0.1	0.8569	1.67	0.7	1.0760	4.15
0.2	0.9265	3.14	0.8	1.1196	11.34	0.2	0.9085	1.83	0.8	1.0982	5.10
0.3	0.9709	3.69	0.9	1.1404	15.38	0.3	0.9521	2.07	0.9	1.1191	6.39
0.4	1.0098	4.40	1.0	1.1586	21.67	0.4	0.9901	2.40	1.0	1.1358	8.12
0.5	1.0425	5.37				0.5	1.0227	2.84			

Table 2. Density ρ and Viscosity η for Tributyrin + Butanol

x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$
$T = 278 \text{ K}$						$T = 298 \text{ K}$					
0.0	0.8218	4.38	0.6	1.0077	10.59	0.0	0.8061	2.52	0.6	0.9893	5.23
0.1	0.8807	4.59	0.7	1.0200	12.27	0.1	0.8640	2.61	0.7	1.0014	5.96
0.2	0.9215	5.48	0.8	1.0300	14.26	0.2	0.9042	3.00	0.8	1.0115	6.73
0.3	0.9518	6.51	0.9	1.0391	16.67	0.3	0.9339	3.46	0.9	1.0205	7.66
0.4	0.9748	7.68	1.0	1.0468	19.63	0.4	0.9566	3.99	1.0	1.0280	8.68
0.5	0.9928	9.05				0.5	0.9744	4.58			
$T = 283 \text{ K}$						$T = 303 \text{ K}$					
0.0	0.8178	3.79	0.6	1.0031	8.75	0.0	0.8021	2.23	0.6	0.9847	4.54
0.1	0.8765	3.95	0.7	1.0153	10.05	0.1	0.8599	2.31	0.7	0.9967	5.14
0.2	0.9172	4.66	0.8	1.0254	11.55	0.2	0.8998	2.64	0.8	1.0068	5.77
0.3	0.9474	5.46	0.9	1.0344	13.33	0.3	0.9294	3.03	0.9	1.0157	6.54
0.4	0.9703	6.41	1.0	1.0421	15.62	0.4	0.9521	3.48	1.0	1.0233	7.38
0.5	0.9882	7.50				0.5	0.9699	3.97			
$T = 288 \text{ K}$						$T = 308 \text{ K}$					
0.0	0.8138	3.28	0.6	0.9985	7.27	0.0	0.7983	1.97	0.6	0.9801	3.95
0.1	0.8723	3.41	0.7	1.0106	8.30	0.1	0.8557	2.04	0.7	0.9922	4.45
0.2	0.9127	3.97	0.8	1.0207	9.50	0.2	0.8957	2.33	0.8	1.0022	5.01
0.3	0.9429	4.64	0.9	1.0297	10.96	0.3	0.9251	2.68	0.9	1.0112	5.64
0.4	0.9657	5.41	1.0	1.0374	12.61	0.4	0.9478	3.06	1.0	1.0187	6.32
0.5	0.9836	6.27				0.5	0.9654	3.45			
$T = 293 \text{ K}$						$T = 313 \text{ K}$					
0.0	0.8100	2.86	0.6	0.9938	6.15	0.0	0.7943	1.76	0.6	0.9754	3.48
0.1	0.8680	2.98	0.7	1.0060	6.99	0.1	0.8515	1.83	0.7	0.9874	3.90
0.2	0.9084	3.44	0.8	1.0160	7.96	0.2	0.8911	2.08	0.8	0.9975	4.37
0.3	0.9382	3.99	0.9	1.0251	9.11	0.3	0.9205	2.38	0.9	1.0064	4.89
0.4	0.9611	4.63	1.0	1.0327	10.35	0.4	0.9431	2.70	1.0	1.0139	5.49
0.5	0.9790	5.33				0.5	0.9607	3.06			

Table 3. Density ρ and Viscosity η for Tricaprylin + Butanol

x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$
$T = 278 \text{ K}$						$T = 298 \text{ K}$					
0.0	0.8218	4.38	0.6	0.9501	28.64	0.0	0.8061	2.52	0.6	0.9342	12.28
0.1	0.8760	7.22	0.7	0.9553	33.65	0.1	0.8604	3.87	0.7	0.9395	14.02
0.2	0.9046	10.96	0.8	0.9597	39.12	0.2	0.8887	5.49	0.8	0.9439	16.05
0.3	0.9225	15.06	0.9	0.9633	45.25	0.3	0.9067	7.15	0.9	0.9476	18.00
0.4	0.9347	19.38	1.0	0.9662	51.74	0.4	0.9188	8.84	1.0	0.9504	19.98
0.5	0.9434	23.94				0.5	0.9275	10.54			
$T = 283 \text{ K}$						$T = 303 \text{ K}$					
0.0	0.8178	3.79	0.6	0.9461	22.70	0.0	0.8021	2.23	0.6	0.9302	10.29
0.1	0.8721	6.11	0.7	0.9513	26.43	0.1	0.8561	3.37	0.7	0.9354	11.73
0.2	0.9006	9.10	0.8	0.9557	30.63	0.2	0.8846	4.73	0.8	0.9398	13.34
0.3	0.9185	12.29	0.9	0.9593	35.12	0.3	0.9024	6.13	0.9	0.9434	14.82
0.4	0.9307	15.63	1.0	0.9623	39.43	0.4	0.9146	7.53	1.0	0.9464	16.58
0.5	0.9394	19.13				0.5	0.9235	8.91			
$T = 288 \text{ K}$						$T = 308 \text{ K}$					
0.0	0.8138	3.28	0.6	0.9421	18.11	0.0	0.7983	1.97	0.6	0.9264	8.74
0.1	0.8680	5.20	0.7	0.9474	21.00	0.1	0.8523	2.97	0.7	0.9317	9.89
0.2	0.8966	7.60	0.8	0.9518	24.22	0.2	0.8809	4.12	0.8	0.9361	11.20
0.3	0.9145	10.11	0.9	0.9554	27.40	0.3	0.8987	5.28	0.9	0.9397	12.39
0.4	0.9267	12.67	1.0	0.9583	30.83	0.4	0.9108	6.46	1.0	0.9427	13.79
0.5	0.9355	15.36				0.5	0.9197	7.57			
$T = 293 \text{ K}$						$T = 313 \text{ K}$					
0.0	0.8100	2.86	0.6	0.9381	14.85	0.0	0.7943	1.76	0.6	0.9223	7.48
0.1	0.8639	4.47	0.7	0.9433	17.09	0.1	0.8482	2.62	0.7	0.9276	8.44
0.2	0.8925	6.41	0.8	0.9478	19.51	0.2	0.8767	3.61	0.8	0.9320	9.52
0.3	0.9103	8.45	0.9	0.9514	22.09	0.3	0.8945	4.59	0.9	0.9356	10.52
0.4	0.9225	10.56	1.0	0.9544	24.75	0.4	0.9067	5.56	1.0	0.9386	11.57
0.5	0.9313	12.65				0.5	0.9156	6.51			

molar volume, is defined as the volume at which 1 mol of molecules are so tightly packed that they show no diffusion or viscous flow.

The parameter B represents the molecules capacity to absorb momentum due to mass, flexibility, or molecular rotation.

Hildebrand's model for the liquid state is successful as a model of liquid transport properties, giving predictions of moderate accuracy for compressed gases and liquids (3), polymer solutions (4), binary mixtures (5, 6), the diffusion of

free radicals in solution (7), the thermal conductivity of liquids (8), the fluidity of fused salts (9), and the diffusion of liquid metals (10).

Bertrand (11) applied this model with satisfactory results to binary and ternary mixtures of short-chain organic solvents, and satisfactorily predicted the viscosity of mixtures from their composition and the values of V , V_0 , and B for the components.

Flores et al. (12, 13) studied mixtures of oleic and lauric acid with hexane, cyclohexane, trichloroethylene, and tetra-

Table 4. Density ρ and Viscosity η for Tributyrin + Ethanol

x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$
$T = 278 \text{ K}$						$T = 298 \text{ K}$					
0.0	0.8031	1.57	0.6	1.0183	10.27	0.0	0.7854	1.11	0.6	0.9999	5.15
0.1	0.8921	2.47	0.7	1.0277	12.27	0.1	0.8742	1.59	0.7	1.0091	5.97
0.2	0.9400	3.73	0.8	1.0349	14.30	0.2	0.9220	2.22	0.8	1.0162	6.78
0.3	0.9708	5.20	0.9	1.0413	16.67	0.3	0.9525	2.92	0.9	1.0226	7.71
0.4	0.9913	6.77	1.0	1.0468	19.63	0.4	0.9731	3.63	1.0	1.0280	8.68
0.5	1.0066	8.46				0.5	0.9884	4.38			
$T = 283 \text{ K}$						$T = 303 \text{ K}$					
0.0	0.7986	1.43	0.6	1.0138	8.50	0.0	0.7808	1.03	0.6	0.9952	4.48
0.1	0.8877	2.19	0.7	1.0231	10.05	0.1	0.8698	1.44	0.7	1.0045	5.14
0.2	0.9356	3.24	0.8	1.0302	11.65	0.2	0.9178	1.98	0.8	1.0115	5.82
0.3	0.9663	4.44	0.9	1.0366	13.45	0.3	0.9482	2.58	0.9	1.0178	6.58
0.4	0.9868	5.71	1.0	1.0421	15.62	0.4	0.9684	3.19	1.0	1.0233	7.38
0.5	1.0021	7.07				0.5	0.9839	3.81			
$T = 288 \text{ K}$						$T = 308 \text{ K}$					
0.0	0.7943	1.31	0.6	1.0095	7.09	0.0	0.7766	0.95	0.6	0.9910	3.91
0.1	0.8835	1.95	0.7	1.0187	8.31	0.1	0.8657	1.31	0.7	1.0002	4.48
0.2	0.9315	2.83	0.8	1.0257	9.57	0.2	0.9137	1.78	0.8	1.0071	5.04
0.3	0.9620	3.82	0.9	1.0320	10.95	0.3	0.9440	2.29	0.9	1.0134	5.67
0.4	0.9825	4.86	1.0	1.0374	12.61	0.4	0.9644	2.81	1.0	1.0187	6.32
0.5	0.9978	5.95				0.5	0.9797	3.35			
$T = 293 \text{ K}$						$T = 313 \text{ K}$					
0.0	0.7898	1.20	0.6	1.0047	6.01	0.0	0.7721	0.89	0.6	0.9864	3.43
0.1	0.8789	1.75	0.7	1.0139	7.02	0.1	0.8612	1.21	0.7	0.9955	3.92
0.2	0.9268	2.49	0.8	1.0209	8.03	0.2	0.9091	1.61	0.8	1.0024	4.40
0.3	0.9575	3.32	0.9	1.0273	9.15	0.3	0.9394	2.06	0.9	1.0086	4.92
0.4	0.9778	4.18	1.0	1.0327	10.35	0.4	0.9597	2.51	1.0	1.0139	5.49
0.5	0.9932	5.09				0.5	0.9751	2.97			

Table 5. Density ρ and Viscosity η for Tributyrin + Hexanol

x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	x	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$
$T = 278 \text{ K}$						$T = 298 \text{ K}$					
0.0	0.8298	8.64	0.6	0.9975	11.45	0.0	0.8150	4.44	0.6	0.9794	5.56
0.1	0.8737	7.72	0.7	1.0121	12.84	0.1	0.8579	4.00	0.7	0.9938	6.15
0.2	0.9085	8.05	0.8	1.0251	14.53	0.2	0.8921	4.09	0.8	1.0065	6.84
0.3	0.9369	8.57	0.9	1.0363	16.61	0.3	0.9199	4.30	0.9	1.0176	7.68
0.4	0.9606	9.35	1.0	1.0468	19.63	0.4	0.9430	4.65	1.0	1.0280	8.68
0.5	0.9805	10.26				0.5	0.9626	5.05			
$T = 283 \text{ K}$						$T = 303 \text{ K}$					
0.0	0.8262	7.25	0.6	0.9930	9.38	0.0	0.8115	3.82	0.6	0.9749	4.80
0.1	0.8698	6.46	0.7	1.0076	10.43	0.1	0.8541	3.47	0.7	0.9893	5.27
0.2	0.9044	6.70	0.8	1.0205	11.78	0.2	0.8881	3.54	0.8	1.0019	5.86
0.3	0.9327	7.11	0.9	1.0316	13.43	0.3	0.9157	3.72	0.9	1.0130	6.54
0.4	0.9562	7.70	1.0	1.0421	15.62	0.4	0.9387	4.00	1.0	1.0233	7.38
0.5	0.9760	8.44				0.5	0.9582	4.36			
$T = 288 \text{ K}$						$T = 308 \text{ K}$					
0.0	0.8226	6.10	0.6	0.9886	7.74	0.0	0.8079	3.30	0.6	0.9705	4.15
0.1	0.8660	5.45	0.7	1.0031	8.59	0.1	0.8502	3.02	0.7	0.9848	4.57
0.2	0.9005	5.60	0.8	1.0159	9.67	0.2	0.8840	3.08	0.8	0.9973	5.07
0.3	0.9286	5.94	0.9	1.0271	10.93	0.3	0.9115	3.26	0.9	1.0084	5.63
0.4	0.9520	6.41	1.0	1.0374	12.61	0.4	0.9344	3.49	1.0	1.0187	6.32
0.5	0.9717	6.99				0.5	0.9539	3.79			
$T = 293 \text{ K}$						$T = 313 \text{ K}$					
0.0	0.8190	5.18	0.6	0.9840	6.53	0.0	0.8042	2.87	0.6	0.9660	3.64
0.1	0.8619	4.65	0.7	0.9986	7.24	0.1	0.8463	2.65	0.7	0.9803	4.00
0.2	0.8962	4.76	0.8	1.0113	8.10	0.2	0.8800	2.71	0.8	0.9928	4.42
0.3	0.9242	5.03	0.9	1.0225	9.11	0.3	0.9073	2.85	0.9	1.0038	4.90
0.4	0.9475	5.44	1.0	1.0327	10.35	0.4	0.9301	3.07	1.0	1.0139	5.49
0.5	0.9672	5.92				0.5	0.9494	3.33			

chloroethylene, showed that these mixtures obey Hildebrand's equation, and established that the parameters B and V_0 follow a parabolic and linear law, respectively, with the molar fraction of acid in the mixture. Muñoz et al. (14) reached the same conclusion from a study on mixtures of methyl myristate in the same solvents.

For the solutions studied this equation also fitted the results satisfactorily, and a linear relationship was observed between the fluidity and the molar volume.

The parameters B and V_0 along with uncertainties at 95% probability are given in Table 6. Analysis of the parameters

B and V_0 showed that both are affected by significant relative errors, and that these errors increase at higher mole fractions of triglyceride, which leads to the belief that the model is no good at higher glyceride concentrations.

The relationship $(V - V_0)/V_0$ for each solution and temperature decreases as the concentration of triglyceride in the solution increases, which indicates that the larger triglyceride molecules group together more compactly than the smaller alcohol molecules. In the case of solutions of tributyrin with ethanol, butanol, or hexanol, it was observed that for molar triglyceride fractions of over 0.5, the quotient

Table 6. Values of Parameters B and V_0 of Hildebrand's Equation

x	triacetin + butanol		tributyryn + butanol		tricaprylin + butanol		tributyryn + ethanol		tributyryn + hexanol	
	$B/$ ($\text{mPa}^{-1}\cdot\text{s}^{-1}$)	$V_0/$ ($\text{cm}^3\cdot\text{mol}^{-1}$)	$B/$ ($\text{mPa}^{-1}\cdot\text{s}^{-1}$)	$V_0/$ ($\text{cm}^3\cdot\text{mol}^{-1}$)	$B/$ ($\text{mPa}^{-1}\cdot\text{s}^{-1}$)	$V_0/$ ($\text{cm}^3\cdot\text{mol}^{-1}$)	$B/$ ($\text{mPa}^{-1}\cdot\text{s}^{-1}$)	$V_0/$ ($\text{cm}^3\cdot\text{mol}^{-1}$)	$B/$ ($\text{mPa}^{-1}\cdot\text{s}^{-1}$)	$V_0/$ ($\text{cm}^3\cdot\text{mol}^{-1}$)
0.0	9.6 ± 0.8	88 ± 14	9.6 ± 0.8	88 ± 14	9.6 ± 0.8	88 ± 14	11.5 ± 0.4	54 ± 3	7.1 ± 0.7	121 ± 25
0.1	10.4 ± 0.7	98 ± 14	9.4 ± 0.7	108 ± 16	7.3 ± 0.6	128 ± 21	11.4 ± 0.5	78 ± 7	7.5 ± 0.7	138 ± 25
0.2	10.2 ± 0.7	108 ± 14	8.6 ± 0.6	127 ± 18	5.8 ± 0.5	167 ± 29	10.1 ± 0.6	101 ± 12	7.4 ± 0.6	154 ± 26
0.3	9.3 ± 0.7	117 ± 17	7.7 ± 0.5	147 ± 20	4.8 ± 0.4	207 ± 38	8.6 ± 0.6	124 ± 16	7.0 ± 0.6	170 ± 24
0.4	8.4 ± 0.6	127 ± 17	7.0 ± 0.5	167 ± 25	4.1 ± 0.4	246 ± 49	7.5 ± 0.5	147 ± 20	6.5 ± 0.5	187 ± 30
0.5	7.4 ± 0.6	137 ± 22	6.4 ± 0.5	187 ± 28	3.6 ± 0.4	286 ± 60	6.6 ± 0.5	170 ± 24	6.1 ± 0.5	203 ± 32
0.6	6.3 ± 0.6	146 ± 26	5.8 ± 0.4	206 ± 31	3.3 ± 0.4	325 ± 72	5.9 ± 0.5	193 ± 30	5.6 ± 0.5	220 ± 36
0.7	5.5 ± 0.6	156 ± 31	5.2 ± 0.4	226 ± 37	2.9 ± 0.3	365 ± 82	5.3 ± 0.4	216 ± 35	5.2 ± 0.4	236 ± 38
0.8	4.6 ± 0.5	166 ± 38	4.8 ± 0.4	246 ± 39	2.6 ± 0.3	405 ± 94	4.8 ± 0.4	239 ± 41	4.7 ± 0.4	252 ± 43
0.9	3.9 ± 0.5	175 ± 46	4.4 ± 0.4	266 ± 46	2.4 ± 0.3	444 ± 105	4.4 ± 0.4	262 ± 46	4.4 ± 0.4	269 ± 47
1.0	3.1 ± 0.5	185 ± 56	4.0 ± 0.3	286 ± 48	2.2 ± 0.3	484 ± 122	4.0 ± 0.3	286 ± 48	4.0 ± 0.3	286 ± 48

Table 7. Values of Parameters V_{01} and V_{02} of Equation 2

solution	$V_{01}/(\text{cm}^3\cdot\text{mol}^{-1})$	$V_{02}/(\text{cm}^3\cdot\text{mol}^{-1})$
triacetin + butanol	88.2 ± 0.1	185.1 ± 0.3
tributyryn + butanol	87.9 ± 0.1	285.4 ± 0.4
tricaprylin + butanol	88.0 ± 0.1	483.8 ± 0.2
tributyryn + ethanol	54.7 ± 0.1	285.7 ± 0.3
tributyryn + hexanol	121.3 ± 0.1	285.5 ± 0.3

Table 8. Values of Parameters a , b , and c of Equation 3

solution	a	b	c
triacetin + butanol	0.099	-0.049	0.246
tributyryn + butanol	0.096	0.091	0.061
tricaprylin + butanol	0.104	0.349	-0.013
tributyryn + ethanol	0.072	0.135	0.045
tributyryn + hexanol	0.129	0.014	0.107

Table 9. Values of Parameter B Obtained from Equation 3

solution	$B(x=1)$	$B(x=0)$
triacetin + butanol	3.4	10.1
tributyryn + butanol	4.0	10.4
tricaprylin + butanol	2.3	9.6
tributyryn + ethanol	3.9	13.9
tributyryn + hexanol	4.0	7.1

$(V - V_0)/V_0$ remains practically constant, which proves that, from that concentration up, tributyrin molecules form similar structures in solutions with all three alcohols.

For all the solutions studied, a linear relationship was found between the values of V_0 and the molar fraction of the triglyceride in the solution, as follows:

$$V_0 = V_{01} + (V_{02} - V_{01})x \quad (2)$$

where V_{01} and V_{02} are the limit volumes of the alcohol and the triglyceride, respectively, and x is the molar fraction of the triglyceride in the solution.

The parameters V_{01} and V_{02} , along with uncertainties at 95% probability, are given in Table 7. These parameters match the values of V_0 obtained for the triglycerides and alcohols when applying Hildebrand's equation.

Furthermore, the values of $1/B$ are related with the molar fraction of the triglyceride through an expression such that

$$1/B = a + bx + cx^2 \quad (3)$$

where a , b , and c are parameters of correlation.

The parameters obtained from the adjustment are given in Table 8. The values of B obtained from eq 3 for $x = 1$ and $x = 0$ are given in Table 9. It has been observed that the value of B estimated for ethanol using eq 3 is the only value not lying between the error limits for the value of B obtained for this alcohol by applying Hildebrand's equation, although the relative difference is not significant.

Ertl and Dullien (15) have proven that Hildebrand's equation shows deviations at reduced temperatures below 0.46. The reduced temperature values of the triglycerides constituting the studied solutions have been calculated, using the value of the critical temperatures estimated by means of the method of Lydersen (16), while the critical temperatures of the alcohols have been taken directly from the literature (17). Their values make it clear that Hildebrand's equation displays deviations, and these deviations become more marked when the triglyceride concentration predominates in the mixture.

Conclusions

The equation proposed by Hildebrand is not suitable as an equation for predicting the viscosity of the solutions studied herein, since the value of the parameter B for the solutions may not be easily estimated using the values of the pure components. Their degree of validity decreases as the concentration of triglyceride in the solution increases and when it is applied at reduced temperatures below 0.46, in concordance with the literature.

Literature Cited

- Hildebrand, J. H. *Science* 1971, 174, 490.
- Batschinski, A. J. *Z. Phys. Chem.* 1913, 84, 643.
- Hildebrand, J. H. *Viscosity and Diffusivity*, John Wiley: New York, 1977.
- Sridhar, T.; Chhabra, R. P.; Uhlherr, P. H. T.; Potter, O. E. *Rheol. Acta* 1978, 17, 519.
- Cullinan, H. T.; Kosanovich, G. *AIChE J.* 1975, 21, 195.
- Kosanovich, G.; Cullinan, H. T. *Ind. Eng. Chem. Fundam.* 1976, 15, 41.
- Sridhar, T.; Potter, O. E. *J. Phys. Chem.* 1977, 81, 2679.
- Chhabra, R. P.; Sridhar, T.; Uhlherr, P. H. T.; Potter, O. E. *AIChE J.* 1980, 26, 522.
- Chhabra, R. P.; Hunter, R. J. *Rheol. Acta* 1981, 20, 203.
- Chhabra, R. P.; Sridhar, T. *J. Phys. Chem. Liq.* 1983, 13, 37.
- Bertrand, G. L. *Ind. Eng. Chem. Fundam.* 1977, 16, 492.
- Flores Luque, V.; Gómez Herrera, J.; Cabrera Martín, J. *Grasas Aceites (Seville)* 1979, 30, 1.
- Flores Luque, V.; Galan Vallejo, M.; Cantero Moreno, D.; Quiroga Alonso, J. M. *Grasas Aceites (Seville)* 1979, 30, 75.
- Muñoz Cueto, Ma. J.; Galan Vallejo, M.; Flores Luque, V. *Grasas Aceites (Seville)* 1990, 41, 59.
- Ertl, H.; Dullien, F. A. L. *AIChE J.* 1973, 19, 1215.
- Lydersen, A. L. *Estimation of Critical Properties of Organic Compounds*. University of Wisconsin College of Engineering, Engineering Experimental Station Report 3; Madison, WI, 1955.
- Reid, C. R.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill Book Co.: New York, 1977.

Received for review April 1, 1993. Revised September 13, 1993. Accepted October 11, 1993.*

* Abstract published in *Advance ACS Abstracts*, December 1, 1993.