Density-Composition Data for Cottonseed Oil-Solvent Mixtures[1]

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THE increasing use of solvents in the processing of vegetable oil-bearing materials and of vegetable oils has created a definite need for complete density data for oil-solvent mixtures over a wide range of temperatures. Such data have been reported (1, 2) for binary mixtures of cottonseed, peanut, and soybean oils, each with one or more of the following solvents: commercial hexane, acetone, 2-butanone, ethylene dichloride, and trichloroethylene. This report extends the data to mixtures of cottonseed oil with methyl pentane, diethyl ether, trichloroethylene, and tetrachloroethylene. An equation has been derived which makes it possible to adjust these data so that they apply with reasonable accuracy to other refined and crude cottonseed oils, and even to soybean and peanut systems with corresponding solvents.

Density determinations were made for 11 different concentrations of oil in each solvent varying from 0 to 100% by weight at a number of temperatures from the point of incipient phase separation to within 10° to 15°C. of the boiling point of the solvent. The technique and procedure used were the same as previously described (1).

The cottonseed oil was a commercial unwinterized, refined, bleached, and deodorized oil, which had a Wijs iodine value of 108, a free fatty acid content of 0.2% as oleic acid, and a peroxide number of 16 millimoles per kilogram. The diethyl ether was an anhydrous analytical reagent grade meeting A.C.S. specifications. The methyl pentane, trichloroethylene, and tetrachloroethylene were current technical grades.[4]

Density-Composition Data

The experimental data for the various binary systems are given in Tables I, II, II, and IV. For each system the density values were plotted against the temperature for each composition investigated. This results in a series of almost straight lines, as exemplified by Figure 1, which represents the data for the system cottonseed oil-methyl pentane. From these smoothed curves, when plotted on a large scale, it is possible to read the values of the densities for the various compositions at constant temperature at intervals of 10°C. and to plot a family of density-composition isotherms for each system, as shown for the system cottonseed oil-methyl pentane in Figure 2.

An empirical equation of the form

$$D = a + bP + cP^2 + dP^3 \qquad \text{(Equation 1)}$$

was fitted to each of the density-composition isotherms at intervals of 10°C. In this equation D equals the density at any composition, P, expressed in weight percentage of oil, and a, b, c, and d are arbitrary constants. The constants for each isotherm are listed in Table V. The average deviation of the experimental data from the curves represented by the equations is ± 0.0007.

The curves of Figure 1 can be constructed directly by solving Equation 1 for selected percentage compositions at each temperature, using the proper constants as indicated in Table V. For example, the curve for 11.08% cottonseed oil with methyl pentane can be obtained by substituting 11.08 for P in each of the isotherm equations for this system, solving for D, and thus finding the value of the density at each temperature. These equations can be used to con-

TABLE I

Density Data for Cottonseed Oil-Methyl Pentane Mixtures

Composition wt. % oil	Temperature				
	−10°C.	0°C.	+10°C.	+25°C.	+40°C.
	g./ml.	g./ml.	g./ml.	g./ml.	g./ml.
0.00	0.6862	0.6771	0.6687	0.6650	0.6423
11.08	0.7080[a]	0.7006	0.6914	0.6778	0.6649
19.78	0.7271[a]	0.7197	0.7117	0.6984	0.6855
30.53	0.7504[a]	0.7426	0.7343	0.7224	0.7095
39.29	0.7706[a]	0.7633	0.7560	0.7438	0.7317
50.33	0.7977[a]	0.7903	0.7825	0.7721	0.7587
60.07	0.8238[a]	0.8161	0.8085	0.7967	0.7851
69.08	0.8485[a]	0.8412	0.8336	0.8224	0.8105
80.69	....	0.8739	0.8667	0.8560	0.8445
90.37	....	0.9026	0.8954	0.8847	0.8742
100.00	....	0.9319	0.9247	0.9145	0.9044

[a] Cloudy.

TABLE II

Density Data for Cottonseed Oil-Diethyl Ether Mixtures

Composition wt. % oil	Temperature			
	−10°C.	0°C.	+10°C.	+25°C.
	g./ml.	g./ml.	g./ml.	g./ml.
0.00	0.7474	0.7363	0.7251	0.7087
9.86	0.7640	0.7537	0.7427	0.7270
20.39	0.7819	0.7727	0.7625	0.7472
30.30	0.8004	0.7914	0.7815	0.7673
40.65	0.8198	0.8112	0.8016	0.7886
50.11	....	0.8315	0.8229	0.8096
58.94	....	0.8469	0.8386	0.8266
71.17	....	0.8704	0.8630	0.8518
79.36	....	0.8882	0.8815	0.8700
89.76	....	0.9108	0.9036	0.8931
100.00	....	0.9319	0.9247	0.9145

TABLE III

Density Data for Cottonseed Oil-Trichloroethylene Mixtures

Composition wt. % oil	Temperature					
	0°C.	10°C.	25°C.	40°C.	59.8°C.	80.4°C.
	g./ml.	g./ml.	g./ml.	g./ml.	g./ml.	g./ml.
0.00	1.4971	1.4800	1.4557	1.4307	1.3960	1.3606
10.67	1.4069	1.3923	1.3704	1.3484	1.3189	1.2880
19.75	1.3400	1.3267	1.3070	1.2871	1.2613	1.2346
30.15	1.2671	1.2552	1.2372	1.2195	1.1960	1.1710
40.36	1.2038	1.1928	1.1766	1.1606	1.1393	1.1181
47.85	1.1616	1.1512	1.1363	1.1212	1.1013	1.0815
60.19	1.1007	1.0913	1.0778	1.0642	1.0463	1.0281
70.82	1.0483	1.0398	1.0273	1.0146	0.9984	0.9822
80.31	1.0078	0.9996	0.9883	0.9765	0.9610	0.9454
90.70	0.9667	0.9592	0.9483	0.9376	0.9234	0.9090
100.00	0.9319	0.9247	0.9145	0.9044	0.8912	0.8778

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[4] The methyl pentane obtained from Phillips Petroleum Company under the trade name, "methylpentanes," was reported to contain approximately 85% 2- and 3-methylpentanes with the balance composed principally of 2,3-dimethylbutane, normal hexane, and cyclopentane. The trichloroethylene and tetrachloroethylene were of E. I. du Pont de Nemours manufacture.

The mention of firm names and trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

TABLE IV

Density Data for Cottonseed Oil-Tetrachloroethylene Mixtures

Composition wt. % of oil	Temperature								
	0°C.	10°C.	25°C.	40°C.	59.85°C.	79.8°C.	81.4°C.	100.6°C.	101.1°C.
	g./ml.	g./ml.	g./ml.	g./ml.	g./ml.	g./ml.	g./ml.	g./ml.	g./ml.
0.00	1.6544	1.6348	1.6111	1.5885	1.5547	1.5214	....	....	1.4841
9.72	1.5394	1.5246	1.5029	1.4809	1.4512	1.4216	....	....	1.3877
20.10	1.4320	1.4191	1.3995	1.3798	1.3537	....	1.3254	1.2992	....
30.14	1.3416	1.3296	1.3124	1.2951	1.2714	....	1.2454	1.2221	....
39.86	1.2659	1.2555	1.2392	1.2234	1.2021	....	1.1797	1.1584	....
50.19	1.1909	1.1817	1.1667	1.1522	1.1328	....	1.1127	1.0940	....
60.23	1.1279	1.1188	1.1052	1.0920	1.0742	....	1.0554	1.0380	....
69.94	1.0728	1.0645	1.0515	1.0393	1.0229	....	1.0055	0.9896	....
80.02	1.0195	1.0116	0.9999	0.9884	0.9732	....	0.9570	0.9422	....
90.07	0.9742	0.9669	0.9559	0.9451	0.9309	0.9168	....	....	0.9019
100.00	0.9319	0.9247	0.9145	0.9044	0.8912	0.8780	....	....	0.8641

struct the density-temperature curve for any desired mixture of oil and solvent; and from this curve it is possible to read accurately the density of this mixture at any desired temperature.

Conversely, it is possible to find the composition of a mixture of cottonseed oil and methyl pentane from its density at a given temperature. To accomplish this the density-composition isotherm for that temperature is plotted from the points where this temperature ordinate intersects the curves of Figure 1.

Similar families of curves can be drawn for the density of the other oil-solvent systems. In each case the data of Table V are sufficient to determine the density of any composition at a given temperature or the composition corresponding to any density at a given temperature.

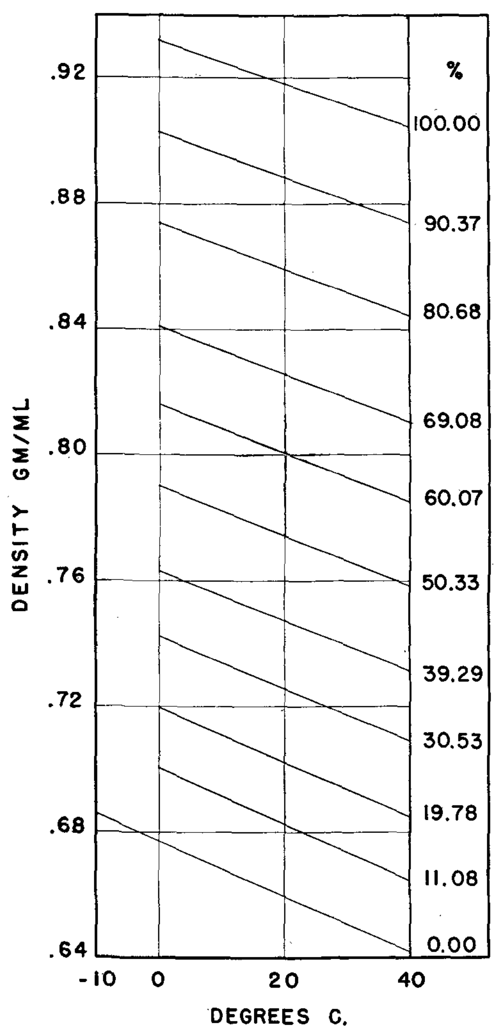

FIG. 1. Density-temperature curves at constant composition for the cottonseed oil-methyl pentane system.

If two liquids form ideal solutions, there is by definition no change in total volume on mixing. Therefore, when specific volume is plotted against weight percentage a straight line is obtained. The deviation from linearity calculated from the 20°C. equations for the four solvent-cottonseed oil systems above is greatest in the case of diethyl ether (a maximum of 0.0144), a little less for the methyl pentane (0.0109), and is comparatively small for the tri- and the tetrachloroethylene. The corresponding data for the hexane systems with cottonseed, peanut, and soybean oils (1) gave maximum deviations of 0.0073, 0.0059, and 0.0064, respectively, at 10°C. For the cottonseed oil systems with acetone and 2-butanone the deviations were within the experimental accuracy. In none of these nine systems are the deviations negative. This indicates that there is either no change in volume or a shrinkage of volume upon mixing the components.

Applicability of Data

It is apparent that the density-composition isotherms for cottonseed oil will vary with the density of the oil used. Since the data here reported were obtained with a refined cottonseed oil, there was some question as to their applicability to estimation of the concentration of crude cottonseed oil miscellas from density measurements.

The following method suggests itself for adjusting the density-composition-isotherm data for a given solvent (Table V) so that it will apply to a random cottonseed oil having, for example, a slightly higher density, the difference in density at the temperature in question being ΔD. The adjusted isotherm would be expected to be above the known isotherm and to coincide with it at 0% oil. Let us assume that the difference in density is distributed linearly along the curve so that, for example, it is $0.25\Delta D$ at 25% oil composition. The adjusted density, D(adjusted), can then be found by adding $0.25\ \Delta D$ to the known density or, in general, for a $P\%$ oil concentration

$$D\ (\text{adjusted}) = D + P/100\ \Delta D \qquad (\text{Equation 2})$$

where D is the density calculated from the corresponding data in Table V and ΔD equals the density at the temperature in question of the random oil minus the density of the oil sample used for obtaining the data in Table V. From Equation 1 it then follows that

$$D\ (\text{adjusted}) = a + (b + \Delta D/100)\ P + cP^2 + dP^3 \qquad (\text{Equation 2})$$

TABLE V

Constants for Density-Composition Isotherm Equations for Cottonseed Oil Systems

Temperature (°C.)	Constants	Solvent			
		Methyl pentane	Diethyl ether	Trichloro-ethylene	Tetrachloro-ethylene
−10°	a	0.6860	0.7475	....	....
	b	1.8811×10^{-3}	1.6240×10^{-3}	....	....
	c	7.112×10^{-6}	4.344×10^{-6}	....	....
	d	-4.96×10^{-9}	-1.111×10^{-8}	....	....
0°	a	0.6772	0.7362	1.4970	1.6540
	b	1.9591×10^{-3}	1.6600×10^{-3}	-8.9646×10^{-3}	-1.2418×10^{-2}
	c	6.244×10^{-6}	5.611×10^{-6}	4.7516×10^{-5}	7.4594×10^{-5}
	d	-4.17×10^{-9}	-2.777×10^{-8}	-1.4511×10^{-7}	-2.2660×10^{-7}
+10°	a	0.6684	0.7248	1.4808	1.6370
	b	1.9838×10^{-3}	1.7850×10^{-3}	-8.7267×10^{-3}	-1.2135×10^{-2}
	c	5.833×10^{-6}	2.936×10^{-6}	4.4439×10^{-5}	7.1213×10^{-5}
	d	-4.87×10^{-10}	-8.27×10^{-9}	-1.2841×10^{-7}	-2.1155×10^{-7}
+20°	a	0.6597	0.7134	1.4635	1.6200
	b	1.9687×10^{-3}	1.8690×10^{-3}	-8.4292×10^{-3}	-1.1871×10^{-2}
	c	6.612×10^{-6}	2.610×10^{-6}	4.0532×10^{-5}	6.8282×10^{-5}
	d	-4.64×10^{-9}	-8.69×10^{-9}	-1.0796×10^{-7}	-1.9811×10^{-7}
+30°	a	0.6508	0.7077[a]	1.4468	1.6041
	b	2.0434×10^{-3}	1.8880×10^{-3}	-8.2580×10^{-3}	-1.1720×10^{-2}
	c	4.619×10^{-6}	2.406×10^{-6}	3.9981×10^{-5}	6.7046×10^{-5}
	d	7.42×10^{-9}	-6.26×10^{-9}	-1.0935×10^{-7}	-1.9070×10^{-7}
+40°	a	0.6422	....	1.4299	1.5877
	b	2.0116×10^{-3}	....	-8.0565×10^{-3}	-1.1395×10^{-2}
	c	6.337×10^{-6}	....	3.8878×10^{-5}	6.2093×10^{-5}
	d	-2.32×10^{-9}	....	-1.0796×10^{-7}	-1.6390×10^{-7}
+50°	a	....	....	1.4129	1.5700
	b	....	....	-7.9121×10^{-3}	-1.1225×10^{-2}
	c	....	....	3.9161×10^{-5}	6.2396×10^{-5}
	d	....	....	-1.1541×10^{-7}	-1.7350×10^{-7}
+60°	a	....	....	1.3962	1.5535
	b	....	....	-7.6424×10^{-3}	-1.1022×10^{-2}
	c	....	....	3.5571×10^{-5}	6.0796×10^{-5}
	d	....	....	-9.593×10^{-8}	-1.6660×10^{-7}
+70°	a	....	....	1.3792	1.5368
	b	....	....	-7.4661×10^{-3}	-1.0803×10^{-2}
	c	....	....	3.5521×10^{-5}	5.9125×10^{-5}
	d	....	....	-1.0330×10^{-7}	-1.6410×10^{-7}
+80°	a	....	....	1.3620	1.5189
	b	....	....	-7.1752×10^{-3}	-1.0494×10^{-2}
	c	....	....	3.2043×10^{-5}	5.5830×10^{-5}
	d	....	....	-8.667×10^{-8}	-1.5020×10^{-7}
+90°	a	....	....	....	1.5025
	b	....	....	....	-1.0273×10^{-2}
	c	....	....	....	5.3422×10^{-5}
	d	....	....	....	-1.3850×10^{-7}
+100°	a	....	....	....	1.4866
	b	....	....	....	-1.0150×10^{-2}
	c	....	....	....	5.3489×10^{-5}
	d	....	....	....	-1.4190×10^{-7}

[a] For 25°C.

In order to test the validity of this equation the 30°C. density-composition isotherm was experimentally determined for mixtures of trichloroethylene with a crude solvent-extracted cottonseed oil whose density at that temperature was 0.9155 as compared to 0.9114 for the refined oil used in Table V. The data are given in the first two columns of Table VI. The third column shows the corresponding density values calculated by substituting the various values of P in Equation 3 (ΔD being $+$ 0.0041). As shown in the next column, the errors in the calculated densities are all less than 0.0011 with the exception of the 30.72% point, and for this mixture the experimental value was evidently too high, as shown by its falling above the smooth curve drawn through all the points.

A more common use of the adjusted density-isotherm would be to estimate the composition of crude oil miscellas from their densities. This can best be done graphically, by plotting Equation 3 and then reading from the curve the percentages corresponding to each experimental density. The compositions so obtained for the density values in the second column of Table VI are given in the fifth column. The errors involved, given in the last column, are all less than 0.40%.

Refined cottonseed oils have densities which may vary over a range corresponding to a maximum ΔD of about 0.0020 g./ml. (3). Since this is only half as great as the ΔD values involved in the crude cot-

TABLE VI

Density-Composition Data at 30°C. for the System Crude Cottonseed Oil-Trichloroethylene as Determined Experimentally and by Calculation from Equation 3.

($\Delta D = 0.9155 - 0.9114 = 0.0041$)

Composition wt. % oil	Experimental density	Calculated density	Density error	Calculated wt. % of oil	Composition error
	g./ml.	g./ml.	g./ml. × 1000		%
0.00	1.4468	1.4468	0.0	0.00	0.00
9.60	1.3715	1.3715	0.0	9.60	0.00
19.86	1.2990	1.2985	−0.5	19.78	−0.08
30.72	1.2316	1.2289	−2.7	30.35	−0.37
39.85	1.1770	1.1760	−1.0	39.66	−0.19
50.21	1.1219	1.1212	−0.7	50.06	−0.15
61.05	1.0696	1.0693	−0.3	60.99	−0.06
71.29	1.0245	1.0246	−0.1	71.27	−0.02
81.28	0.9835	0.9843	+0.8	81.48	+0.20
90.60	0.9482	0.9493	+1.1	90.91	+0.31
100.00	0.9155	0.9155	0.0	0.00	0.00

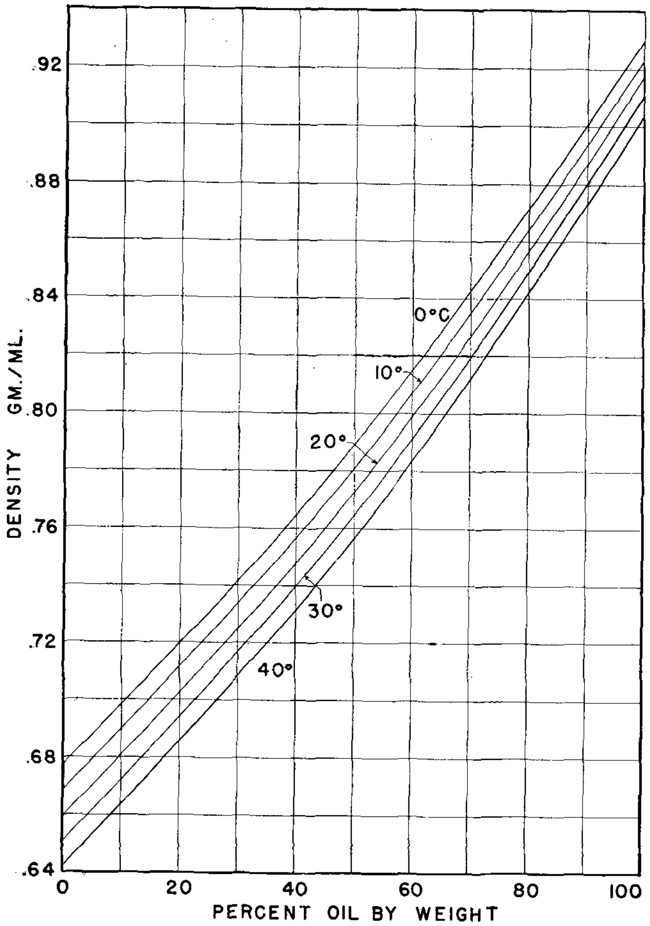

FIG. 2. Density-composition isotherms for the cottonseed oil-methyl pentane system.

tonseed oil system just considered, it can perhaps be assumed that the oil-solvent isotherms of Table V can be used satisfactorily in conjunction with Equation 3 to construct adjusted isotherms for any refined cottonseed oil with these solvents.

An examination of all the available data has shown further that Equation 3 can be used to calculate with reasonable accuracy the density isotherms of solvent mixtures of soybean oil or peanut oil from the corresponding cottonseed oil isotherms. Thus, calculations similar to those of Table VI were made to show the agreement between the experimental curves for the soybean oil-hexane (1), peanut oil-hexane (1), and soybean oil-trichloroethylene (2) systems and the curves calculated from the corresponding adjusted cottonseed oil isotherms (1). The cottonseed oil-trichloroethylene data used were obtained from Table V. The errors in density and composition are given in Table VII for the 25°C. isotherms for soybean oil and peanut oil in hexane ($\Delta D = +0.0024$ and -0.0029, respectively), and for the 50°C. isotherm for soybean oil in trichloroethylene ($\Delta D = +0.0041$). The agreement in the case of the peanut oil-hexane system is well within the experimental accuracy. For the soybean oil systems the maximum error in the calculated density, with the the exception of one point which falls off the smooth curve, is less than 0.0012 g./ml. The absolute error in composition is 0.50% or less. The corresponding errors for the 0° and 40°C. isotherms for the hexane systems are almost the same as at 25°C. When the 25°C. isotherm for the soybean oil-hexane system is calculated from the corresponding peanut oil data (1) ($\Delta D = +0.0053$), the errors involved are less than when the cottonseed oil system is used as a basis—a maximum absolute error of 0.43% in composition.

TABLE VII

Errors in Calculated Values of Density and Percentage Composition for Peanut and Soybean Oil Systems f om Adjusted Cottonseed Oil Data

Composition wt. % oil	Soybean oil-hexane[a] 25°C.		Peanut oil-hexane[a] 25°C.		Soybean oil-trichloroethylene[b] 50°C.	
	Density error[c]	Composition error[c]	Density error	Composition error	Density error	Composition error
	g./ml. × 1000	%	g./ml. × 1000	%	g./ml. × 1000	%
0	0.0	0.00	0.0	0.00	0.0	0.00
10	+0.1	−0.04	+0.1	−0.04	+1.8	+0.25
20	+0.3	−0.14	+0.2	−0.09	+0.3	+0.05
30	+0.7	−0.32	+0.2	−0.08	−0.4	−0.07
40	+0.9	−0.39	+0.2	−0.07	−0.8	−0.15
50	+1.2	−0.50	+0.2	−0.06	−0.9	−0.19
60	+1.2	−0.48	+0.2	−0.05	+0.3	+0.06
70	+1.2	−0.46	+0.3	−0.08	+1.1	+0.26
80	+1.1	−0.41	+0.2	−0.06	+0.9	+0.23
90	+0.7	−0.25	+0.1	−0.03	+0.6	+0.16
100	0.0	0.00	0.0	0.00	0.0	0.00

[a] From cottonseed oil, peanut oil, and soybean oil data reported by Magne and Skau (1).
[b] From cottonseed oil data in Table V and smoothed experimental values of Johnstone, Spoor, and Goss (2).
[c] Calculated value minus experimental value.

Summary

Complete density-composition-temperature data have been reported for binary systems of a refined cottonseed oil with methyl pentane, diethyl ether, trichloroethylene, and tetrachloroethylene from the point of incipient phase separation to within 10° to 15°C. of the boiling point of the solvent. These data can be used to calculate the density knowing the composition and temperature or, conversely, the composition knowing the density and temperature.

An equation has been derived which makes it possible to adjust these data so that they apply with reasonable accuracy to other refined and crude cottonseed oils and even to soybean or peanut oil systems with the same solvents.

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