nary ammonium chloride. Although this linear relationship between concentration of trimethyl quaternary and absorbance was observed, there appeared to be some changes in the level of absorbance for a given range at different times. To overcome these variations and for best results during quantitative analysis, two standard mixtures, one containing less and the other more trimethyl quaternary than the sample, were run on either side of the sample on each paper. The absorbances of these two standards were then used as a calibration for calculating the amount of trimethyl quaternary in the sample.

Figure 3 is a photograph of several typical chromatograms of mixtures of purified compounds and of commercial materials.

Table IV lists results obtained on some synthetic mixtures and commercial samples.

REFERENCES

1. Bregoff, H., Roberts, E., and Delwiche, C., J. Biol. Chem., *205*, 565 (1953).
2. Franks, F., Nature, *176*, 693 (1955).
3. Fumasoni, S., Mariani, E., and Torraca, G., Chem. Ind., *69* (1956).
4. Garcia, I., and Couerbe, J., Chim. Anal., *38*, 432 (1956).

[Received April 1, 1960]

Fractionation of Castor Oil Methyl Esters by Liquid-Liquid Extraction

C. M. LAKSHMANAN and G. S. LADDHA, Alagappa Chettiar College of Technology, University of Madras, Guindy, Madras, India

LIQUID-LIQUID extraction technique has recently been applied to the fractionation of castor oil methyl esters obtained by the methylation of castor oil. A recent analysis of castor oil by Sreenivasan *et al.* (4) gives the following composition: ricinoleic acid 86.0%, dihydroxy stearic acid 1.9%, oleic acid 5.1%, linoleic acid 3.5%, and saturated acids 3.5%. McCormack and Bolley (3) indicate that while methyl esters other than methyl ricinoleate do not interfere with the ricinoleic acid reactions, it is nevertheless desirable to have the purest possible starting-material. They studied the separation of castor oil methyl esters by means of liquid-liquid extraction, using methyl alcohol and heptane at 8.4°C. and 24°C. It was observed that the hydroxyl value of esters in the methanol phase was greater than that of esters in the hydrocarbon phase. Kasturirangan and Laddha (2) studied the fractionation of castor oil methyl esters with furfural and cyclohexane at 30°C. The two-phase region for the system, castor oil methyl esters-furfural-cyclohexane, was much larger than for the system, castor oil methyl esters-methanol-heptane, at 24°C. and 8.4°C. indicating that furfural-cyclohexane gives a better performance. This fractionation of methyl esters of castor oil into fractions of preferably hydroxy and nonhydroxy esters is based on the observation that polar solvents will have more affinity for hydroxy esters. Further investigations indicated the possibility of the use of furfural-hexane and nitromethane-hexane as suitable solvents. In the present paper equilibrium and distribution data for the systems, castor oil-methyl esters-furfural-hexane and castor oil methyl esters-nitromethane-hexane, are presented. The effect of the change of concentration of the esters and solvents on fractionation of esters has also been studied.

Experimental

Materials used are given below.

Castor oil methyl esters were obtained by the methylation of castor oil, using HCl as catalyst. The mixed methyl esters thus obtained had the following physical and chemical constants: density $d^{30/4}$ 0.9250, refractive index 1.4602, specific rotation $[\alpha]^{30°/D}$ 5.48, saponification value 183.1, iodine value (Wij's, 30 min., 31°C.) 82.8, and hydroxyl value 165.8.

Furfural supplied by Allied Chemical and Dye Corporation, New York, was purified by vacuum distillation each time just before use. The specifications were density $d^{30/4}$ 1.124 and refractive index at 30° C. 1.5184.

Nitromethane from Fluka AG Chemische Fabrik Buschs SG. (Switzerland) was fractionally distilled, and the fraction between 100.5°–101.5°C. was collected and used. The specifications were density $d^{30/4}$ 1.1237 and refractive index at 30°C. 1.3770.

n-Hexane, as laboratory reagent-grade petroleum fraction supplied by B.D.H. Ltd., was rectified and the fraction collected between 67°–70°C. was used. The physical constants were density $d^{30/4}$ 0.6782 and refractive index at 30°C., 1.3761.

Experimental procedure. The equilibrium solubility data were determined by the synthetic method described by Treybal (5) at 30°C. For determining the phase distribution data, known mixtures of ternary constituents comprising castor oil methyl esters, polar and nonpolar solvents well within the heterogeneous region were placed in the constant temperature bath at 30 ± 0.1°C. after vigorous agitation and allowed to separate into two phases after attaining equilibrium. The individual phases were then separated and weighed. A weighed quantity of each phase was taken in a distilling flask, and the solvents were distilled in a water bath. Traces of solvents remaining were removed under vacuum by drying the esters on a water bath to constant weight under a stream of carbon dioxide. The total weight of the esters thus obtained from the two phases was checked against the weight of esters taken originally in the ternary mixture. The fractions of methyl esters thus obtained from the polar and nonpolar solvent phases were evaluated in terms of their hydroxyl values by following the pyridine-acetic anhydride method of Burton and Robert Shaw (1).

TABLE I

Equilibrium Tie-Line Data for the System, Castor Oil Methyl Esters-Furfural-Hexane at 30°C.

Mixture taken			Esters in		Hydroxyl values	
Esters	Furfural	Hexane	Furfural phase	Hexane phase	Furfural phase	Hexane phase
%	%	%	%	%		
4.40	25.00	70.60	7.33	3.51	186.3	147.9
5.10	45.35	49.55	6.39	3.75	185.4	133.5
5.20	59.30	35.00	6.28	4.09	181.8	120.3
8.85	25.08	66.07	12.70	7.72	185.1	148.2
9.96	39.43	50.61	12.61	7.67	179.8	142.9
11.10	53.95	34.95	12.22	8.33	174.2	129.7
13.67	25.00	61.33	18.30	11.97	185.9	152.2
15.36	39.45	45.19	18.35	11.95	177.2	141.9
16.40	48.59	35.01	18.15	11.78	175.0	135.5
18.60	25.07	56.33	24.08	16.13	179.9	154.5
20.26	35.18	44.56	23.35	16.78	175.0	147.6
21.27	43.77	34.97	23.14	16.62	170.8	140.3
22.92	25.00	52.08	26.31	22.40	169.3	161.3
24.87	35.72	39.41	26.36	21.62	170.9	148.3
25.29	39.69	35.02	26.31	20.65	166.5	148.0
25.38	29.58	45.04	28.00	24.25	166.9	160.5

TABLE II

Equilibrium Tie-Line Data for the System, Castor Oil Methyl Esters-Nitromethane-Hexane at 30°C.

Mixture taken			Esters in		Hydroxyl values	
Esters	Nitromethane	Hexane	Nitromethane phase	Hexane phase	Nitromethane phase	Hexane phase
%	%	%	%	%		
5.02	60.00	34.98	3.68	7.53	192.1	142.8
7.25	77.16	15.59	5.72	15.88	184.0	134.2
10.11	54.59	35.30	6.05	15.65	190.0	149.7
12.30	35.00	52.70	6.79	15.20	195.9	157.4
11.74	73.24	15.02	7.86	28.18	182.7	141.5
15.43	59.17	25.40	8.31	27.95	187.9	154.6
20.80	40.00	39.20	8.21	27.66	191.3	159.7
16.70	68.30	15.00	9.75	36.84	180.4	149.9
20.17	59.93	19.90	10.64	36.56	182.4	157.2
28.50	40.00	31.50	10.77	36.16	184.8	162.5
20.50	64.50	15.00	12.27	39.05	175.3	156.4
24.89	55.92	19.19	13.14	38.41	174.3	159.3
32.60	40.00	27.40	14.11	37.94	180.5	164.1
26.75	59.26	13.99	19.01	36.35	173.3	160.4

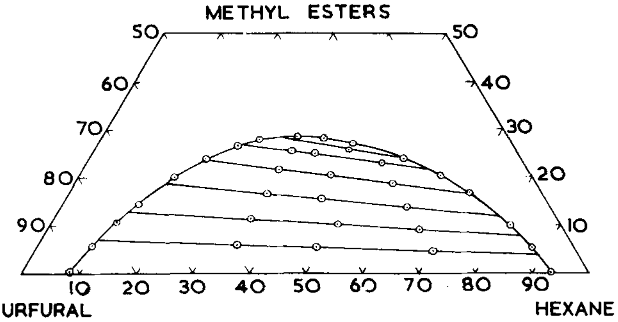

FIG. 1. Castor oil methyl esters, furfural-hexane system at 30°C.

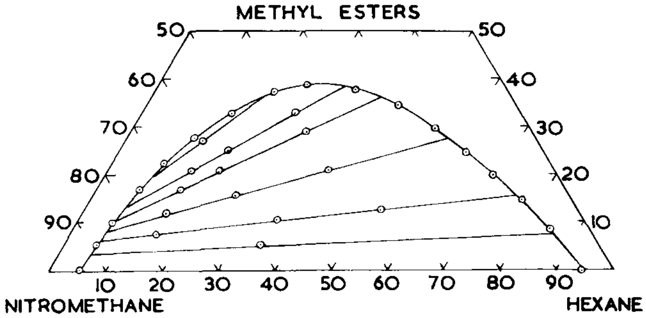

FIG. 2. Castor oil methyl esters, nitromethane-hexane system at 30°C.

Results

The equilibrium data for the systems, castor oil methyl esters-furfural-hexane and castor oil methyl esters-nitromethane-hexane, are given in Tables I and II with the hydroxyl values of the methyl esters obtained from the polar and nonpolar solvent phases. Although it is realized that castor oil methyl esters are not a single component, the results of these investigations are best represented by plotting the ternary-phase distribution data on the conventional triangular diagrams. This has been done in Figures 1 and 2. The two-phase region in the case of the ternary system, methyl esters-nitromethane-hexane, is greater than that for the system, methyl esters-furfural-hexane, but tie lines in the case of nitromethane as solvent slope towards the solvent end of the diagram, indicating much lesser concentration of the methyl esters in the nitromethane phase as compared to furfural as the solvent. The estimated plait point for the system, methyl esters-nitromethane-hexane, corresponds to 24.2% methyl esters, 64.9% nitromethane, and 10.9% hexane while for the system, methyl esters-furfural-hexane, it corresponds to 27.2% methyl esters, 29.4% furfural, and 43.4% hexane. The plait point represents the maximum concentration of esters that can possibly be handled in the extraction columns.

The esters obtained from the polar and nonpolar solvent phases were analyzed for hydroxyl values to determine the extent of fractionation. It is observed that hydroxy acid esters are preferentially distributed in the polar solvent phase and the values are comparable with that of the hydroxyl value of pure methyl ricinoleate at lower concentrations of methyl esters in the original mixture. The hydroxyl values of pure methyl recinoleate is 179.5. The higher hydroxyl values of ester samples obtained from polar solvent phases may be attributed to the presence of methyl dihydroxy stearate, which is present up to 2% in the mixed esters of castor oil. The hydroxyl value of pure methyl dihydroxy stearate is 339.4. The presence of a little quantity of methyl dihydroxy stearate therefore will show a higher hydroxyl value.

It may be observed that nitromethane has a greater affinity to hydroxy esters as compared with furfural since the esters obtained from the nitromethane phase show higher hydroxyl values even at high concentrations of esters in the original mixtures.

The effect of the change in concentration of the solvents along the same tie-lines was also studied. It is observed that, with the increase in concentration of the polar solvent, the hydroxyl values of ester samples obtained from the polar solvent phase decrease. Effect of varying the composition of methyl

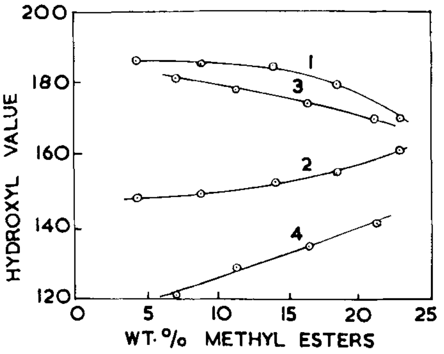

FIG. 3. Change of hydroxyl value for castor oil methyl esters, furfural-hexane system.

1. Esters from furfural phase at 25% furfural
2. Esters from hexane phase at 25% furfural
3. Esters from furfural phase at 35% hexane
4. Esters from hexane phase at 35% hexane

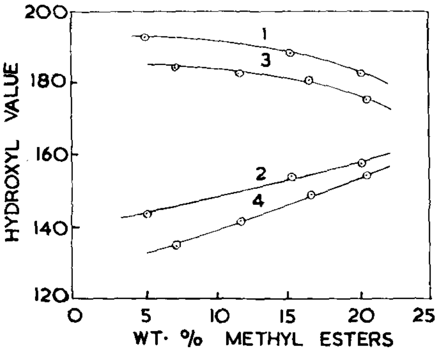

FIG. 4. Change of hydroxyl value for castor oil methyl esters, nitromethane-hexane system.

1. Esters from nitromethane phase at 59.6% nitromethane
2. Esters from hexane phase at 59.6% nitromethane
3. Esters from nitromethane phase at 15% hexane
4. Esters from hexane phase at 15% hexane

esters at a constant concentration of polar or nonpolar solvent was also determined. Figure 3 shows the effect on hydroxyl values of esters fractionated at 25% furfural and 35% hexane for the system, methyl esters-furfural-hexane. Figure 4 shows a similar effect for the system, nitromethane-methyl esters-hexane, at 59–60% nitromethane and 15% of hexane. It is observed that the hydroxyl values of esters from the polar solvent phase decrease with a higher concentration of esters. It may also be seen that the increase of hydroxyl values of esters in the polar solvent is accompanied by a decrease in the hydroxyl values of the esters obtained from the nonpolar solvent phase.

Conclusion

The phase equilibrium data are presented for methyl esters-furfural-hexane and methyl esters-nitromethane-hexane at 30°C.

The hydroxyl values of ester samples obtained from the furfural and nitromethane phases indicate that furfural and nitromethane can be used as solvents for fractionating hydroxy esters from the mixed esters obtained by the methanolysis of castor oil.

Acknowledgment

The authors are grateful to the University of Madras for the award of a research fellowship for this investigation.

REFERENCES

1. Burton, D., and Robertshaw, C. F., "Sulphated Oils and Allied Products," p. 129, A. Harvey, publishers (1939).
2. Kasturirangan, K., and Laddha, G. S., J. Madras Univ., B. 25, No. 3, 213 (1955).
3. McCormack, R. H., and Bolley, D. S., J. Am. Oil Chemists' Soc., *31*, 408 (1954).
4. Sreenivasan, B., Kamath, N. R., and Kane, J. G., J. Am. Oil Chemists' Soc., *33*, 61 (1956).
5. Treybal, R. E., "Liquid Extraction," p. 20, McGraw Hill Book Company, New York (1951).

[Received June 24, 1959]

Synthesis of Polyoxyethylene Derivatives of Diesters of Sucrose with Long-Chain Fatty Acids

SABURO KOMORI, MITSUO OKAHARA, and KENZO OKAMOTO,
Department of Chemical Technology, Faculty of Engineering, Osaka University, Osaka, Japan

A NUMBER of publications concerning the long-chain fatty acid monoesters of sucrose have appeared since the synthesis of the sucrose monoesters was first reported in 1956 by Osipow and co-workers (1). The method of preparation (2,3,4), properties (5,6,7), and uses (8,9) have been investigated in detail.

Sucrose monoesters are said to be inexpensive as compared with other nonionic surfactants and have many desirable properties as solubilizing (8) or emulsifying agents for food or cosmetics. However, in the manufacture of sucrose monoesters, sucrose diesters are inevitable by-products responsible for a lowered surface-activity because of the poor solubility of the diesters in water. For certain purposes the sucrose monoesters can be separated and purified by recrystallizing the mixture from acetone or ethanol (1,6,10), but this method is difficult and costly, and from an industrial standpoint it is more desirable to use the mixture of mono- and diesters without further refining.

Although sucrose diesters can be simply prepared by alcoholysis by using a 2:1 molar ratio of the methyl ester to sucrose (11), sucrose diesters of acids of chain length greater than myristic acid are practically insoluble in water, and their use as emulsifying agents is limited to the formation of water in oil emulsions.

Accordingly since it is important to find new uses for sucrose esters, we have attempted to increase the solubility in water of palmitic and stearic acid esters by reaction with ethylene oxide in order to make use of them as solubilizing or emulsifying agents. Sucrose esters resemble sorbitan monoesters in properties, and it can be expected that solubilizing properties similar to those of the "Tweens" (12,13) could be obtained by the introduction of polyoxyethylene radicals.

The reaction of sucrose with ethylene oxide has been reported by DeGroote (14,15,16), by the use of xylene as the solvent, and by sodium methylate as the catalyst in an autoclave at 150–170°.

In the present research sucrose diesters were chosen as the starting materials. Pure sucrose dimyristate, dipalmitate, distearate, dioleate, and dierucate were prepared by interesterification between sucrose and the methyl esters, using formylmorpholine as the solvent, and the properties of the diesters were studied. The diesters were then caused to react with ethylene oxide in an autoclave, with an alkaline catalyst such as sodium hydroxide, potassium hydroxide, or tertiary amines (17).

The polyoxyethylene derivatives of diesters of sucrose with long-chain fatty acids were found to be oily or waxy products soluble in water; the surface