fect the electronic configuration of the nitrogen atoms or at least stand in different relation to them.

The high moment of azodibenzoyl indicates that this compound cannot have a simple *trans* form as is found in azobenzene. This is in line with the observation that benzalazin[4] likewise possesses a moment, intermediate between that of azobenzene and azodibenzoyl.

Summary

The dipole moments of a series of seven hydrazides and related derivatives have been determined and discussed.

CORVALLIS, OREGON RECEIVED MARCH 29, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

The Binary Systems of Some Fatty Acids[1]

BY M. KULKA AND R. B. SANDIN

A number of investigators working on binary systems formed by even-numbered fatty acids have come to the conclusion that there is definite compound formation, usually of the type 1 mole A:1 mole B. Probably the best example of this is the case of palmitic and stearic acids. This system has been investigated by de Visser[2] and by Shriner, Fulton and Burks.[3] De Visser concluded that mixed crystals were formed in the vicinity of the 50% mixture, whereas Shriner and his co-workers have concluded that their curve indicates compound formation. In this connection it should be pointed out that Slagle and Ott,[4] doing work on X-ray studies of mixtures of fatty acids, have come to the conclusion that the existence of a transition point for mixtures of palmitic and stearic acids may indicate a change in modification only.[5] Whatever conclusions we come to, as a result of all the work recorded up to the present time, this fact stands out, *viz.*, that the already determined melting point curves of binary systems of even-numbered fatty acids and differing by two carbon atoms, are all very similar. There are always two inflections in each curve. One inflection is very close to the equimolecular mixture of the two acids and indicates compound formation to many workers. The second inflection occurs very close to the mixture which contains 0.725 mole per cent. of the lower melting acid. This point corresponds to the eutectic temperature.

Very recently Smith[6] working with "odd-even" acid systems has shown two definite changes in the direction of the curve for the binary system, margaric acid–stearic acid. Again these two points correspond very closely to the two points of inflection recorded for binary systems of even-numbered fatty acids. According to Smith "it seemed unlikely that the covalency forces would differ sufficiently to prevent compound formation between 'odd' and 'even' acids."

The purpose of the present investigation was to extend the information on the binary systems of fatty acids. Three systems which do not seem to be recorded in the literature were investigated, *viz.*, palmitic–myristic, lauric–capric and lauric–undecylic. The first two systems will complete the series of recorded ones (systems of even-numbered fatty acids and differing by two carbon atoms) from *n*-eicosanic acid to capric acid. The third system studied adds another example to the type investigated by Smith,[6] *viz.*, margaric acid–stearic acid.

Experimental

Fatty Acids.—Eastman fatty acids were recrystallized repeatedly from acetone until constant capillary tube melting points were obtained, *viz.*: palmitic acid, m. p. 62.6–62.9°; myristic acid, m. p. 54.5–54.8°; lauric acid, m. p. 43.9–44.1°; capric acid, m. p. 31.3–31.8°; undecylic acid, m. p. 28.8–29.2°.

Determination of Freezing Points.—The freezing points of the mixtures were determined in the apparatus similar to that used for determination of molecular weights by the freezing point method. The temperature of the outside bath was maintained 3° below the freezing point of the particular mixture used. The degree of supercooling allowed

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(1) Abstracted in part from a thesis submitted by M. Kulka to the Graduate School of the University of Alberta for the degree of Master of Science.

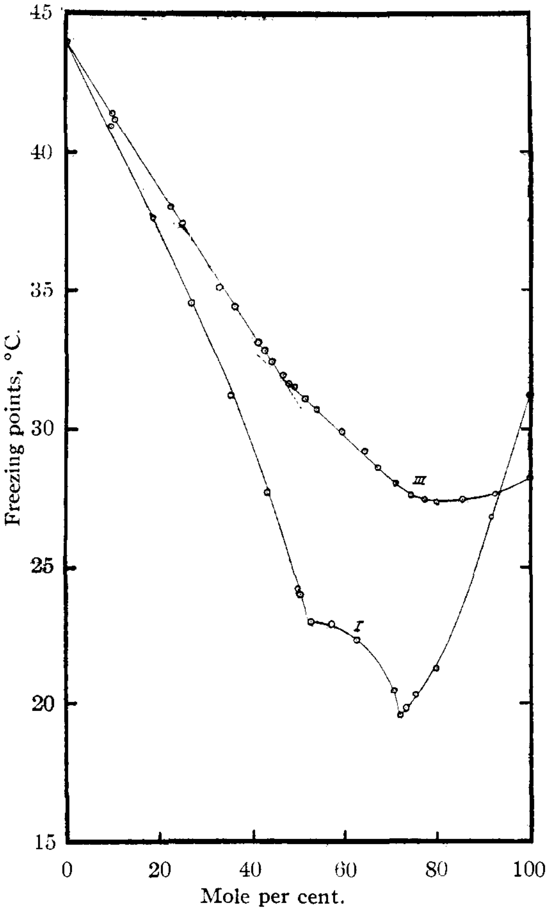
(2) De Visser, *Rec. trav. chim.*, **17**, 182 (1898).

(3) Shriner, Fulton and Burks, THIS JOURNAL, **55**, 1494 (1933).

(4) Slagle and Ott, *ibid.*, **55**, 4404 (1933).

(5) The authors call attention to the work done on binary systems of even-numbered fatty acids by Morgan and Bowen [*J. Soc. Chem. Ind.*, **43**, 346 (1924)]; Bhatt, Watson and Patel [*J. Indian Inst. Sci.*, **13A**, Pt. 11, 141 (1930)]; and Piper, Chibnall and Williams [*Biochem. J.*, **28**, 2182 (1934)].

(6) Smith, *J. Chem. Soc.*, 625 (1936).



Capric → Curve I ← Lauric
Undecylic → Curve III ← Lauric

Fig. 1.

was in the neighborhood of 0.3°. For measuring the temperature of the mixtures of fatty acids and of the outside bath, thermometers which were calibrated to 0.1° and which had been compared with one calibrated at the Physikalisch-Technische Reichsanstalt, were used. Corrections were made for the exposed mercury column. In each determination a plot of time *vs.* temperature was made and from this curve the true freezing point was obtained, corrected for the degree of supercooling by extrapolation. Mixtures of the fatty acids were made by weighing out definite amounts of each acid. The data obtained are summarized in Tables I–III.

Discussion

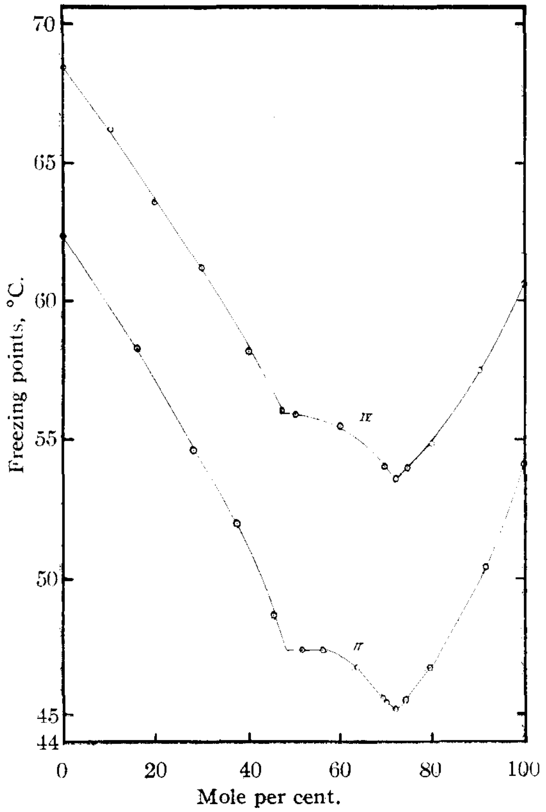
Curves I and II, which, respectively, represent the binary systems of capric and lauric acids, and myristic and palmitic acids, show clearly the two transition points already mentioned. To bring out the similarity between these two curves and that of the palmitic–stearic acid systems, the data of Shriner, Fulton and Burks[3] are shown in Curve IV. The eutectic temperature for myristic and palmitic acids is 45.2°, at a composition of 0.725 mole of myristic and 0.275 mole of palmitic acid. The eutectic temperature for capric

Table I

Freezing Points of Binary Mixtures

Data plotted in Curve I

Capric, mole %	Lauric, mole %	F. p., °C.
100.0	0.0	31.2
91.7	8.3	26.8
79.9	20.1	21.3
75.6	24.4	20.3
73.4	26.6	19.8
72.5	27.5	19.6
71.1	28.9	20.4
62.5	37.5	22.3
57.3	42.7	22.9
52.6	47.4	23.0
50.0	50.0	24.0
49.7	50.3	24.2
43.0	57.0	27.7
35.2	64.8	31.2
27.1	72.9	34.5
18.9	81.1	37.6
9.6	90.4	40.9
0.0	100.0	43.9



Myristic → Curve II ← Palmitic
Palmitic → Curve IV ← Stearic

Fig. 2.

TABLE II

Data plotted in Curve II

Myristic, mole %	Palmitic, mole %	F. p., °C.
100.0	0.0	54.1
91.3	8.7	50.4
79.7	20.3	46.7
74.6	25.4	45.5
72.5	27.5	45.2
70.6	29.4	45.4
69.4	30.6	45.6
63.9	36.1	46.7
56.3	43.7	47.3
51.5	48.5	47.3
45.3	54.7	48.7
37.4	62.6	51.9
28.3	71.7	54.7
16.0	84.0	58.3
0.0	100.0	62.3

TABLE III

Data Plotted in Curve III

Undecylic, mole %	Lauric, mole %	F. p., °C.
100.0	0.0	28.2
92.4	7.6	27.6
85.4	14.6	27.4
80.0	20.0	27.3
77.6	22.4	27.4
74.6	25.4	27.6
71.3	28.7	28.0
67.6	32.4	28.6
64.6	36.4	29.2
59.3	40.7	29.9
53.8	46.2	30.7
50.9	49.1	31.1
48.7	51.3	31.5
47.5	52.5	31.6
46.3	53.7	31.9
44.0	56.0	32.4
42.6	57.4	32.8
41.2	58.8	33.1
36.1	63.9	34.4
33.0	67.0	35.1
25.0	75.0	37.4
22.6	77.4	38.0
10.3	89.7	41.2
9.8	90.2	41.4
0.0	100.0	43.9

and lauric acids is 19.6°, at a composition of 0.725 mole of capric acid and 0.275 mole of lauric acid. Curve III shows the freezing points of mixtures of undecylic and lauric acids. An examination of this curve will indicate a small but definite change in direction near the middle of the system. This is somewhat similar to what Smith[6] obtained for the stearic–margaric system, and according to him is just what would occur if a compound was formed.

Summary

The following binary systems of fatty acids have been investigated, *viz.*: myristic–palmitic, capric–lauric, and undecylic–lauric.

EDMONTON, ALBERTA, CANADA RECEIVED APRIL 30, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA]

The Effect of Anions on the Titration of Aluminum Chloride

BY T. H. WHITEHEAD, J. P. CLAY AND C. R. HAWTHORNE

Introduction

The potentiometric titration of aluminum salt solutions by sodium hydroxide has been studied by a number of investigators.[1] All of these have noted the important role played by the anion of the aluminum salt. If the amount of aluminum in the salt is calculated on the basis of equivalents of sodium hydroxide required to produce an inflection of the titration curve in the region of *p*H 7, the values obtained are invariably too low. The most recent explanation offered for this discrepancy by Jander[1] is that the hydrolytic products of aluminum salts are complex compounds to which may be assigned Werner structures.

One of the authors has reported[2] previously on the effect of anions in changing the *p*H values of basic aluminum salt solutions and aluminum oxychloride hydrosols.

The present paper is a study of the effect of several anions on the potentiometric titration of aluminum chloride solution in order to compare these effects with previous studies. The role of some cations also is noted.

Experimental

All reagents were of C. P. quality and tested for purity. Solutions were made up in Pyrex glassware and standardized in the usual manner.

All potentiometric titrations were carried out at 25° using a saturated quinhydrone electrode with bright platinum electrodes and saturated calomel half-cell.

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(1) Blum, THIS JOURNAL, **35**, 1499 (1913); Hildebrand, *ibid.*, **35**, 863 (1913); Davis and Farnham, *J. Phys. Chem.*, **36**, 1057 (1932); Treadwell and Zurcher, *Helv. Chim. Acta*, **15**, 980 (1932); Jander and Jahr, *Kolloid Beihefte*, **43**, 295 (1936).

(2) Whitehead and Clay, THIS JOURNAL, **56**, 1844 (1934).