values of k_s and k_i are the same for the two forms. Using S_0^r, S^r, S_0^a and S^a for the solubilities of the racemic and active forms in water and salt solutions, Eq. (3) can be applied to the results for each. Then, for solubility experiments in solutions of a given salt, k_sC_s can be eliminated giving

$$k_i = \frac{\log S_0^r/S^r - \log S_0^a/S^a}{(S^a - S_0^a) - (S^r - S_0^r)} \qquad (4)$$

In practice when the data obey the Setschenow equation it is more convenient to use

$$k_i = \frac{K^r - K^a}{\dfrac{S^a - S_0^a}{C_s} - \dfrac{S^r - S_0^r}{C_s}} \qquad (5)$$

Once k_i is obtained, the value of k_s can be calculated from Eq. (3), written for either form. Table I gives the results of such calculations for several salts. In making the calculations the recorded molal concentrations have been converted to molar using an apparent molar volume of 125 ml./mole for mandelic acid. Actually the results are very similar if molal concentrations and activity coefficients are used throughout. Where necessary, notably for experiments with the mandelate salts, corrections for the dissociation of mandelic acid have been made.

TABLE I

SALTING OUT AND SELF-INTERACTION PARAMETERS FOR MANDELIC ACID AT 25°

Salt	K^r	K^a	k_i	k_s
LiCl	+0.40	+0.20	−0.30	0.125
NaCl	+ .30	.185	− .25	.12
KCl	+ .155	+ .10	− .22	.07
RbCl	+ .135	+ .072	− .28	.04
CsCl	− .002	− .001	...	− .002
NH_4Cl	+ .21	+ .11	− .26	.07
$LiNO_3$	+ .21	+ .115	− .27	.07
$NaNO_3$	.095	+ .07	...	.04
KNO_3	− .04	− .00	...	− .02
$CsNO_3$	− .165	− .097	− .22	− .06
Na Mandelate	− .35	− .205	− .23	− .12
Cs Mandelate	− .89	− .31	− .27	− .18
		Av.	− .255	

The most significant point from Table I is that the values of k_i calculated from the data for the various salts are constant to within the variation of the experimental data. Furthermore the resulting values of k_s are similar to those for the comparable non-electrolytes, benzoic acid[5] and phthalic acid.[6] Finally the negative value of k_i shows, as expected, that mandelic acid is "salted in" by itself. The average value of k_i, −0.25, is quite large but it seems reasonable when compared with the value for phenol for which, from the freezing point data of Jones and Bury,[7] the k_i value is about −0.16.

These results for mandelic acid suggest that a comparison of salt effects from solubility measurements for two non-electrolytes of different solubility can be quite misleading unless the self-interaction is corrected for. Similarly for a non-electrolyte of high solubility, salt effects obtained from solubility studies can be quite different from those obtained by other procedures, for example vapor pressure or distribution.

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Coördination of Silver Ion with Methyl Esters of Oleic and Elaidic Acids

BY PETER L. NICHOLS, JR.[1]

The coördination of silver ion with unsaturated compounds has been studied extensively by Lucas and co-workers.[2,3] Their information was obtained largely by partition studies using carbon tetrachloride and 1 *N* aqueous silver nitrate as the immiscible solvent pair. An attempt to determine the argentation constants of methyl oleate and methyl elaidate with the above solvent pair was quickly found to be impractical since the amount of material transferred to the aqueous silver nitrate phase was negligible. Preliminary experiments showed that satisfactory results could be obtained with isoöctane as one phase and aqueous methanol as the other phase. The *cis*-isomer was found to have a greater argentation constant than the *trans*-isomer, but the magnitudes of the constants for the most part were considerably greater than those found for *cis*- and *trans*-olefins distributed between carbon tetrachloride and 1 *N* aqueous silver nitrate. Accordingly, it is recognized that a distribution of this type might be used as a basis for the separation of *cis*- and *trans*-isomers as well as for the separation of saturated and unsaturated fatty acid esters or olefinic compounds in general.

Experimental

Preparation of Materials.—We are indebted to H. B. Knight for generous samples of methyl oleate and methyl elaidate. The iodine values of these preparations were about one unit lower than theoretical. However, the only possible contamination (as indicated by spectrophotometric analysis) was that of saturated esters and these would have a negligible effect on the distribution experiments.

Reagent grade chemicals were used throughout. Isoöctane (A.S.T.M. grade) had an iodine value of 0.07, a satisfactorily low value. Solutions of isoöctane and methanol containing various amounts of water were prepared as follows: upper layer, a large amount of isoöctane was shaken successively with several small portions of methanol containing a given amount of water; lower layer, methanol containing a given amount of water was shaken successively with several small portions of isoöctane.

The solutions of isoöctane saturated with a particular methanol solution were added to weighed amounts of the methyl esters in a volumetric flask and made to the mark at 25 ± 0.01°. All solutions were stored at this temperature until used in the distribution experiments.

Solutions of aqueous methanol containing silver nitrate were prepared by dissolving silver nitrate in the appropriate amount of water and then diluting to the mark and saturating the solution as described above. Flasks containing the silver nitrate solutions were wrapped at all times with a

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[2] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

[3] H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943).

black cloth. Solutions of potassium nitrate were made up in a similar manner.

Apparatus and Procedure.—All distributions were carried out in a water-bath at 25 ± 0.01°. Iodine flasks of 250-ml. capacity, equipped with mercury seal type stirrers but using glycerol as a seal, were used. A piece of glass tubing sealed to the end of a glass rod effectively stirred the layers, which appeared in the form of a fine emulsion during the stirring. Several runs in which the flasks were flushed with nitrogen before starting the experiment showed no difference from those carried out in air. Twenty ml. of saturated isoöctane solution containing approximately 0.3 g. of ester was added to 20 ml. of the aqueous methanol solution saturated with isoöctane. Stirring was continued for 30 minutes. Stirring for longer periods gave the same results. Usually the layers separated completely in less than 30 minutes. A 10-ml. sample of upper layer was withdrawn for analysis with the aid of a Luer syringe attached to a pipet by means of rubber tubing.

Analytical Procedure.—The customary procedure using Wijs solution[4] proved satisfactory for the analysis of the upper layer provided that the sample was allowed to stand one hour in contact with reagent. In each analysis 10 ml. of Wijs solution was added to 10 ml. of the upper layer from a distribution experiment. A blank was run on 10 ml. of isoöctane saturated with the appropriate methanol solution.

Results and Discussion

The notation and assumptions regarding activities of previous workers[2,3] were used with the substitution of isoöctane for carbon tetrachloride and aqueous methanol for water. The argentation constant, K_0, has been expressed previously[2] by equation (1).

$$K_0 = \frac{(\mathrm{Bt})_{x\mathrm{N\ AgNO_3}} - (\mathrm{B})_{\mathrm{iso}/K_\mathrm{D}}}{(\mathrm{B})_{\mathrm{iso}}[\mathrm{Agt})_{x\mathrm{N\ AgNO_3}} - ((\mathrm{Bt})_{x\mathrm{N\ AgNO_3}} - (\mathrm{B})_{\mathrm{iso}/K_\mathrm{D}})]} \qquad (1)$$

If K_D is very large the term $(\mathrm{B})_{\mathrm{iso}/K_\mathrm{D}}$ may be neglected in Eq. (1). However, in most of our work this approximation could not be used.

If one can alter K_D without materially altering K_E, the effect will be reflected by a corresponding change in K_0. One way to alter K_D is to change the ratio of water to methanol in the aqueous phase. Another way is to change the ionic strength of the phase containing silver nitrate.

From the above discussion it is apparent that K_E is to be preferred to K_0 as a measure of the relative coördination tendencies of double bonds in different types of olefins, but when the substances being compared have essentially the same distribution constants, as for example *cis*- and *trans*-isomers, K_0 would serve as an adequate measure of these tendencies under the same conditions.

The constants obtained for the isomeric methyl oleate and methyl elaidate in several solvent combinations are shown in Table I. The striking differences in argentation constants for the two isomers are in close agreement, even to order of magnitude, with previous observations.[3] It appears from the limited data in Table I that K_E is relatively unaffected by changes in methanol concentration and that K_0 is inversely proportional to K_D but this is not certain. Experimental error in the measurements, together with possible large changes in activity coefficient due to large changes in silver ion concentrations, obscure any accurate interpretation of the differences in equilibrium constants.

By use of increasing concentrations of methanol it has been shown that relatively large amounts of methyl oleate and methyl elaidate can be removed from isoöctane in a single extraction. The fraction of olefin removed in a single extraction is shown in equation (2) which was checked experimentally.

TABLE I

ARGENTATION CONSTANTS AND DISTRIBUTION RATIO FOR THE DISTRIBUTION OF METHYL OLEATE AND METHYL ELAIDATE BETWEEN ISOÖCTANE AND AQUEOUS METHANOL[a]

Concn. of methanol, %	Concn. of $AgNO_3$, N	Methyl oleate[d] K_D	Methyl oleate[d] K_0	Methyl oleate[d] K_E	Methyl elaidate[d] K_D	Methyl elaidate[d] K_0	Methyl elaidate[d] K_E
60	1.0	[b]	0.02	...	..	0.02	...
90	0.2	[b]	.46[c]	...	..	.17	...
95	.16	10.5	.79	8.2	10.1	.29	2.9
100	.05	4.2	2.02	8.4	3.9	.81	3.1

[a] Except where noted the average value for two runs is recorded. [b] Too high for a reasonable estimate by the analytical method used. [c] Average value for three runs. [d] Initial concentration in isoöctane layer is approx. 0.05 molar.

$$F = \frac{(\mathrm{Bt})_{x\mathrm{N\ AgNO_3}}}{(\mathrm{B})_\mathrm{T}} = \frac{K_0K_\mathrm{D}(\mathrm{Agt}) + K_0(\mathrm{B})_\mathrm{T} + 1}{K_0K_\mathrm{D}(\mathrm{Agt}) + K_0K_\mathrm{D}(\mathrm{B})_\mathrm{T} + 2K_0(\mathrm{B})_\mathrm{T} + K_\mathrm{D} + 1} \qquad (2)$$

In order to attain anything like complete separation a number of successive extractions would be required. The technique of countercurrent distribution, as employed by Craig,[5,6] or paper chromatography could be easily adapted to the solvent combinations used in the present work. In a Craig apparatus the number of transfers, *n*, required to obtain a desired separation can be calculated by approximate relations derived by Nichols.[7] Using the argentation constants for methyl oleate and methyl elaidate for 90% methanol and 0.2 *M* silver nitrate, calculations show that approximately 300 transfers would be required for reasonably complete separation.

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(8) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

Benzyl Esters of Amino Acids[1]

BY HERBERT K. MILLER[2] AND HEINRICH WAELSCH

The synthesis of carboxyl-substituted peptides is greatly facilitated by the use of benzyl esters of amino acids instead of the commonly employed ethyl esters since the benzyl group can be removed by hydrogenation with palladium catalyst under the same conditions as used for the removal of the carbobenzoxy group thus avoiding the need for saponification.[3]

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(1) This report is in part from a dissertation submitted by Herbert K. Miller in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

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