CXXIII.—*The Relative Concentrations of Various Electrolytes required to salt out Soap Solutions.*

By JAMES WILLIAM McBAIN and ALBERT VINCENT PITTER.

IN a series of papers from this laboratory on the soap-boiling processes, it has been shown that there is a remarkable family likeness between the various soaps, whether pure, mixed or commercial, and that they differ in degree rather than in kind (McBain and Burnett, J., 1922, **121**, 1320; McBain and Langdon, J., 1925, **127**, 852; McBain and Elford, this vol., p. 421; McBain and Walls, *Fourth Report on Colloid Chemistry of the Brit. Assocn. for the Advancement of Science*, 1922, 244; McBain, Chap. in Vol. I of J. Alexander's forthcoming treatise on Colloids).

It has been shown that the phase-rule equilibria for each soap or mixture of soaps are affected in the same way by various salts; so that numerical ratios exist between the concentrations of individual salts required to produce the same effect upon any soap. Further, the effects in a mixture of electrolytes are additive. Likewise, the behaviour of a mixture of soaps seems to be approximately that expected from their respective constituents, apart from formation of curd or crystals.

Hence in order to be able to predict the concentration of any salt, or mixture of salts, required to obtain a specified equilibrium in any soap or mixture of soaps, two things are necessary. First, sufficient points must be established for the phase-rule diagram of each pure soap, using any one salt. Second, the numerical ratios between the concentrations of various salts required to produce a given salting out must be established with one concentration of any one soap. It is the object of the present communication to obtain the numerical ratios between various salts, using in every case $0{\cdot}25N_w$(weight normal)-sodium palmitate and making the definite comparison at 90°.

EXPERIMENTAL.

The method used has been sufficiently described in the papers previously mentioned. It depends on the separation of two isotropic liquid layers from one homogeneous liquid on gradual cooling from high temperatures.

$0{\cdot}25N_w$-Sodium palmitate solutions were sealed up in strong glass tubes with various weights of specimens of the purest salts obtainable, and heated (in many cases far above the boiling point) until the contents of the tube were seen to be clear and perfectly homogeneous. They were then cooled slowly in a bath of glycerol until separation occurred. The experiments were carried out at different times during the past 5 years by C. S. Adams, L. S. Staddon, and the authors, with different samples of sodium palmitate, but the whole work was repeated this year by one of us (A. V. P.), using three different specimens of soap.

The results are in the following tables, all the qualitative observations of appearance, etc., being suppressed for lack of space.

Concentrations are given in every case in weight normality (N_w) defined here as g.-mols. (not equivalents) per 1000 g. of water. The data are also given in g. per 100 g. of total system.

Table I gives results obtained with a sample (*a*) of ordinary sodium palmitate obtained from Messrs. Kahlbaum in March, 1925. It was shown to be the sodium salt of a mixture of fatty acids of mean molecular weight about half-way between palmitic and stearic.

Table II gives results obtained with a sample (*b*) of pure sodium palmitate specially prepared by Messrs. Kahlbaum in September, 1925. Analysis showed it to contain 0·0081 equivalent excess alkali per mol.

Table III gives results (*c*) obtained by making up the systems with palmitic acid " Kahlbaum " and sodium hydroxide solutions, by the method of Bunbury and Martin (J., 1914, **105**, 417).

Table IV compares the concentrations of the various salts in mols. and in % by weight required to salt out at 90°, sodium chloride being taken as standard=1·00.

TABLE I.

Minimum concentrations of various salts required to salt out solutions of $0{\cdot}25N_w$*-sodium palmitate. March sample* (*a*)*—impure.*

Sodium hydroxide.

N ...	0·933	1·10	1·10	1·11	1·17	1·30
Temp.	—	87	87·1	90	105·5	131·2°

Sodium nitrate.

N_w ...	0·951	1·02	1·199	1·336
Temp.	80·7	108	151·8	173·6°

Sodium chloride.

N_w ...	0·873	0·913	0·915	0·942	0·985	1·004	1·098	1·099	1·253
Temp.	80·3	97·5	111	119·7	128·5	134·2	156·9	157·5	178·1°

Sodium acetate.

N_w ...	0·796	0·839	0·872	0·895	0·992[1]	1·047	1·12	1·23
Temp.	83	93	96·8	101	124·5	135·2	146	158°

TABLE II.

Minimum concentrations of various salts required to salt out solutions of 0·25N_W-*sodium palmitate. September sample* (*b*)—*pure.*

Sodium hydroxide.

N_w ...	0·994	1·130	1·214	1·303	1·337
Temp.	—	91·7	108	129·3	138°

Sodium nitrate.

N_w ...	1·05	1·110	1·22	1·302
Temp.	87	114	148·9	164·3°

Sodium chloride.

N_w ...	0·955	0·971	0·999	1·110	1·199
Temp.	89·6	98·5	105·5	135·3	157°

*Sodium iodide.**

N_w ...	0·802	0·844	0·872	0·887	0·905	0·987
Temp.	67·4	70·4	74·2	75·5	89·5	106·5°

Sodium bromide.

N_w ...	0·865	0·895	0·920	0·955	0·966	0·986	0·982	1·109	1·20
Temp.	77	92	93	109·3	111·5	118	120·4	154·5	172°

Sodium acetate.

N_w ...	0·821	0·900	0·966	1·00	1·063	1·128	1·305
Temp.	75	91·7	102·5	108	123	133	154°

Sodium carbonate.

N_w ...	0·887	0·897	0·933	0·953	0·983	0·995	1·064	1·064	1·107	1·157	1·211
Temp.	90	91	106·7	110·8	118	120·3	136	137·6	143	153	159·6°

Sodium sulphate.

N_w ...	0·826	0·904	0·963	0·997	1·074	1·11	1·18
Temp.	90	103·5	119·7	134	147·5	151·6	164·5°

Sodium tungstate.

N_w ...	0·651	0·700	0·738	0·801
Temp.	93·8	114·4	132	153°

Sodium tartrate.

N_w ...	0·634	0·676	0·699	0·757	0·778	0·790	0·903
Temp.	85	104·5	115	137·2	141	151·5	176°

* A different sample of sodium palmitate was used in this case.

TABLE III.

Minimum concentrations of various salts required to salt out solutions of 0·25N_W-*sodium palmitate. Pure samples* (*c*) *prepared from palmitic acid " Kahlbaum " and sodium hydroxide solution.*

Sodium hydroxide.

N_w ...	1·097	1·127	1·253	1·341
Temp.	86·3	97·3	121	138·4°

Sodium chloride.

N_w ...	0·965	1·00	1·017	1·044	1·116	1·199
Temp.	92·6	105·5	114	120	140·7	161°

Sodium thiocyanate.

N_w ...	0·757	0·814	0·950	1·027
Temp.	86	110·5	146	173·3°

TABLE IV.

Minimum concentrations of various electrolytes (hydroxide and salts of sodium) required to salt out 0·25$\mathrm{N_w}$*-solutions of sodium palmitate at* 90° *(sodium chloride*=1·00).

		Concn. reqd.		Ratio.	
Electrolyte.*	Mol. wt.	N_w.	% by wt.	$N_w : N_w$.	% : %.
Hydroxide	40·01	(1·110) (a)	3·99	1·24	0·86
		1·127 (b)	4·05	1·18	0·82
		1·106 (c)	3·97	1·16	0·80
				Mean 1·19	Mean 0·83
Nitrate	85·01	(0·970) (a)	7·16	1·08	1·54
		1·056 (b)	7·74	1·11	1·56
				Mean 1·10	Mean 1·55
Chloride	58·45	(0·895) (a)	4·66	1·00	1·00
		0·953 (b)	4·95	1·00	1·00
		0·955 (c)	4·96	1·00	1·00
				Mean 1·00	Mean 1·00
Iodide	149·9	0·905 (d)	11·27	0·95	2·19
Bromide	102·9	0·898 (b)	7·95	0·94	1·61
Acetate	82·02	(0·838) (a)	6·03	0·94	1·30
		0·895 (b)	6·42	0·94	1·30
				Mean 0·94	Mean 1·30
Carbonate	106·0	0·887 (b)	8·08	0·93	1·63
Sulphate	142·1	0·826 (b)	9·89	0·87	2·00
Thiocyanate	81·07	0·763 (c)	5·46	0·80	1·10
Tungstate	294	0·645 (b)	15·1	0·68	3·04
Tartrate	194·3	0·645 (b)	10·46	0·68	3·12

(a) = March sample of sodium palmitate (impure).

(b) = September sample of sodium palmitate (pure).

(c) = Sodium palmitate prepared from palmitic acid "Kahlbaum" and sodium hydroxide.

* Sodium fluoride also was tested, but it was not sufficiently soluble to salt out the palmitate at 90°.

The electrolytes used, with the exception of sodium thiocyanate, were dried by heating at 120—130°. The sodium thiocyanate was dried to constant weight in a vacuum over calcium chloride at room temperature.

All our numerical results are summarised in Table IV, showing the absolute and relative amounts of the various electrolytes required to salt out sodium palmitate at 90°.

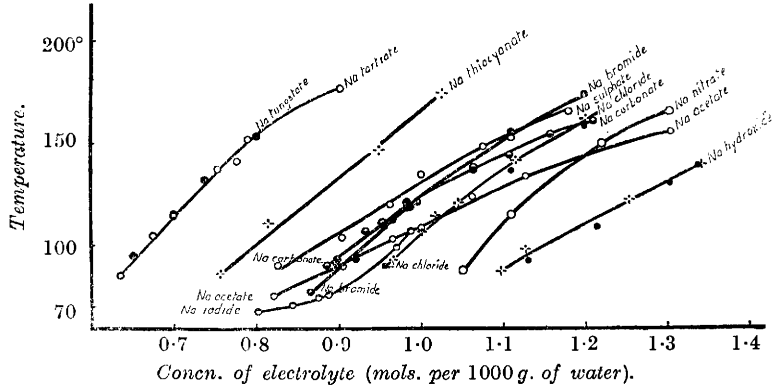
The only published data of sufficient accuracy by which to check our results are those from the Karlsruhe laboratory, which are based upon ratios obtained by Richert (*Dissert.*, Karlsruhe, 1911) for carbonate and hydroxide. He found, for various soaps, that 1·01 mols. of carbonate and 1·27 equivalents of hydroxide had the same effect as 1 equivalent of sodium chloride, whereas we have found 0·93 and 1·19, respectively. The divergence from our results amounts to about 6%.

To show the effect of temperature upon the various electrolytes the results have been plotted in Fig. 1. The figure shows that the ratios are not quite constant and independent of temperature, although the deviation does not exceed about 6%. This gives a second measure of the extent to which these data are generally valid, and they are borne out by an analysis of our unpublished data on commercial oils and fats as well as other results from the Karlsruhe laboratory and also the well-known data of Merklen.

An immense amount of information can be derived from these approximate numerical ratios which enables prediction to be made, well within 10%, of the maximum concentration of salts which may be added to any soap solution without salting it out. They enable all the complicated mixtures used in commercial soap boiling to be reduced to a common basis for comparison and control. Taken in conjunction with the equilibrium diagrams now becoming available for pure and commercial soaps, whether derived from sodium or potassium, they facilitate the approximate prediction of the concentration of any mixture of electrolytes required to produce a given effect.

FIG. 1.

Concentrations of electrolytes required to salt out 0·25N$_W$-*sodium palmitate.*



(*The crosses indicate results obtained with solutions made up from palmitic acid "Kahlbaum."*)

Perhaps the most unexpected feature of Table IV is that, as a first approximation, the salts do not replace each other equivalent for equivalent, but rather mol. for mol. irrespective of their valency. For example, sodium thiocyanate comes, in this respect, between sodium sulphate and sodium tungstate; and one mol. of sodium carbonate exactly replaces one equivalent of acetate or iodide.

The results here discussed bear no relation whatsoever to the

Hoffmeister series, as may be seen from the order of the electrolytes in Table IV. Equally, the results are at variance with what might have been expected from the equation of the Donnan equilibrium, since here the order of the electrolytes is irrespective of their valency.

The most comparable factor common to all the salts seems to be the concentration of the sodium ion. Although no data are available for the actual mixtures in the soap solutions, yet this point may be brought out from an examination of such conductivity data for aqueous solutions of pure electrolytes as are given in Landolt-Börnstein-Roth's "Tabellen." The concentration of the sodium ion for all the electrolytes except the acetate, thiocyanate, carbonate, tartrate, and hydroxide is almost exactly two-thirds normal, whereas for these five cases it is $0{\cdot}5N_w$, $0{\cdot}54N_w$, $0{\cdot}58N_w$, $0{\cdot}76N_w$, and $0{\cdot}8N_w$, respectively. It is clear, therefore, that the equilibria are not exclusively determined by the degree of dissociation into sodium ion, although this is predominant. Matters are not improved by an attempt to substitute for concentration of sodium ion, its activity. The data are available for the chloride and hydroxide and the activities are proportional to the total concentrations required to produce the same effect, whereas they should have been inversely proportional, thus revealing a discrepancy of about 40%.

Summary.

1. Measurements have been made of the relative salting-out action of eleven different electrolytes on soap solutions.

2. With the aid of numerical ratios derived therefrom it is possible to compare, predict, and control all the various equilibria obtained with pure and commercial soaps with any mixture of electrolytes to within an accuracy of about 5 to 10%.

UNIVERSITY OF BRISTOL.

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