[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Solubility of Soaps and of Some Salts in Mixtures of Solvents, One of Which Is of Glycolic Type

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Soaps, though strikingly insoluble in the common organic solvents, have been found[2] in the case of sodium stearate to dissolve in G–H mixtures, where G stands for any glycol or any dihydroxylic compound and H stands for any hydrocarbon-dissolving compound such as a hydrocarbon itself, a chlorinated hydrocarbon, an alcohol, a ketone, an ester or the like. We shall call such general behavior co-solvency, or mixsolvency; the individual solvents, co-solvents; any mixture of solvents showing co-solvency, mixsolvents; and this particular type of co-solvency, G–H effect. The terms "co-dissolve" and "cosolubility" then require no further definition.

The aim of the present paper is to extend the previous studies[2,3] of co-solvency to a wide variety of G–H mixtures using pure samples of soap, to offer a consistent interpretation of the facts, and to explore the theoretical consequences of this interpretation with regard to the wider question of solubility in organic solvents. Some data for inorganic salts are included and it is also shown that methyl alcohol, phenol, and a few other hydroxylic compounds resemble glycols in their solvent properties.

Experimental

Materials.—All solvents used were the best commercially available. They were properly dried and fractionated before use. The inorganic chemicals and organic salts were also best grade, mostly C. P. materials. The sodium nitronates were prepared by Miss Irene Behrendt by neutralizing 1-nitropropane and 2-nitropropane in alcoholic solution with alcoholic sodium hydroxide. The alcohol was evaporated off on the water-bath and the finely powdered salt was dried at about 100° for one hour before use.

Sodium oleate, the chief soap used in the present work, was a special Kahlbaum preparation which was tested and found to be neutral. Stearate and palmitate were prepared from stearic acid (Eastman Kodak Company) and palmitic acid (Kahlbaum) by neutralization in hot alcoholic solution followed by evaporation to dryness. Sodium laurate and myristate were samples prepared by Lever Brothers Company, and were slightly brown. All soaps were dried at 105° for three hours prior to use.

Methods.—Solubility determinations were made by an analytical method. Different proportions of solvents to a total of 15 g., in 1-ounce screw cap bottles, were measured from 10 cc. burets calibrated with regard to the weights of each of the solvents. The soap was added in half-gram portions followed by vigorous shaking until a small portion remained undissolved. The solubility bottles were then shaken in a mechanical shaker in an air thermostat at 27–28° for about six hours and then transferred to a thermostat at 25 ± 0.05° and allowed to stand for at least eight hours. The solutions were next filtered through a coarse fritted glass filter under a pressure of 10 pounds of nitrogen for thick solutions or through a rapid filter paper by gravity for the thin solutions in an air thermostat at 25–25.5° until about 8–12 g. of the solutions were collected. The whole filtration usually took about one to three minutes. Care was taken to reduce to a minimum any loss of the volatile solvent by evaporation during this process. The filtrate was weighed and analyzed.

For analysis, three methods were followed. To the solution a slight excess of 1 *N* alcoholic hydrochloric acid was added, followed by about 5 cc. of chloroform. The solutions were then diluted with water to between 100 and 200 cc., whereupon the chloroform containing the fatty acid separated out. The whole was then filtered through a moist filter paper which retained the chloroform, layer. After first washing it with jets of water, this layer was transferred by puncturing the apex of the filter paper, and by washing with a jet of alcohol into a glass basin. It was then treated in one of the following three ways: (1) dissolving in neutral alcohol and titrating with standard caustic soda solution using phenolphthalein as indicator; (2) evaporating on a water-bath, adding a little alcohol if necessary to drive off any water present, and heating the fatty acid to constant weight at 90 ± 2°. (3) The third method[4] is a very rapid one. It consists in directly titrating the soap solution in the presence of sufficient ethylene or propylene glycol with a standard (0.2 *N*) perchloric acid in glycol–isopropyl alcohol mixture (1:1 by volume) using methyl red or thymol blue as indicator. Both the indicators yield equally accurate results but the color change of thymol blue is a little easier to follow with the unaided eye. However, most of the work was done with methyl red as the suitability of thymol blue for this purpose was discovered only toward the concluding stages of the present work. All three methods were tested with known weights of sodium oleate and were found to agree within 1 part in 500. Solubility in the pure volatile solvents was determined by evaporating off a known weight of the saturated solution to a constant weight at about 105°.

The solubility values recorded herein for various salts other than soap were obtained by different analytical methods. For nitrite, arsenite, hyposulfite, alkyl nitronates and borate, direct titration[4] in glycolic solvent was used. For aluminates and hypophosphites standard methods[5] of analyzing aluminum and phosphorus acids were used after evaporating off the solvent by prolonged heating on a water-bath with occasional addition of water. Bifluoride was estimated by direct titration with standard alkali after dilution with water.

All solubility values in this paper, unless otherwise stated, are given in grams per 100 g. solvent. Solvent composition is given in weight per cent. of the total solvent.

I. Soaps

1. Sodium Oleate.

—The solubilities of sodium oleate in various G–H mixtures at 25° are presented in Tables I–III and in Figs. 1 to 7. All the co-solvency curves have maxima showing a strong increase of solubility of soap in the mixture as compared with the respective solvents.

These soap solutions are clear fluids of comparatively low viscosity, even a solution contain-

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[2] Palit, *J. Indian Chem. Soc.*, **19**, 271 (1942).

[3] Palit and McBain, *Ind. Eng. Chem.*, **38**, 741 (1946).

[4] Palit, *Ind. Eng. Chem., Anal. Ed.*, **18**, 246 (1946); *Oil & Soap*, **23**, 58 (1946).

[5] Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, New York, N. Y.

TABLE I

CO-SOLUBILITY OF SODIUM OLEATE IN VARIOUS G–H MIXTURES AT 25°; SOLUBILITIES ARE GIVEN IN GRAMS OF SOAP PER 100 G. OF SOLVENT

		Per cent. glycol in the solvent mixture[a]					
		0	20	40	60	80	100
	(a) Propylene glycol–alcohols						
1	Ethyl alcohol[b]	1.61	5.18	8.77	12.41	12.87	11.72
2	*n*-Propyl alcohol[c]	1.13	6.04	11.39	16.15	16.89	11.72
3	Isopropyl alcohol[c]	0.25	3.60	7.45	11.18	13.92	11.72
4	*n*-Butyl alcohol[c]	.98	7.97	14.51	18.35	18.86	11.72
5	Isobutyl alcohol[c]	.68	6.41	11.78	17.64	18.25	11.72
6	*s*-Butyl alcohol[c]	.42	3.92	9.42	14.33	15.88	11.72
7	*t*-Butyl alcohol[c]	.24	1.95	5.63	10.71	14.14	11.72
8	Allyl alcohol[c]	1.05	5.55	10.07	13.25	14.34	11.72
9	*n*-Amyl alcohol[c]	0.85	8.82	16.54	21.15	21.02	11.72
10	Isoamyl alcohol[c]	.69	7.72	15.30	19.83	20.17	11.72
11	*s*-Amyl alcohol[c]	.18	3.09	10.90	16.48	18.39	11.72
12	*n*-Hexyl alcohol[c]	.62	9.70	17.97	22.41	21.56	11.72
13	*n*-Octyl alcohol[c]	.58	12.53	20.75	25.12	23.65	11.72
14	Isoöctyl (2-ethylhexanol)	.45	11.04	18.01	22.50	21.90	11.72
15	Lauryl alcohol	.4 *ca.*	13.72	21.43	24.96	23.81	11.72
16	Cetyl alcohol	Solid		Solid paste		24.29	11.72
17	Phenol	Solid	21.54	28.21	28.77	24.05	11.72
18	Cyclohexanol	0.36	5.28	12.37	16.78	17.25	11.72
19	Benzyl alcohol	.59	5.61	11.55	15.69	16.53	11.72
	(b) Ethylene glycol–alcohols						
20	Ethyl alcohol	1.61	8.49	15.65	21.61	23.68	16.43
21	*n*-Propyl alcohol	1.13	10.46	21.24	28.50	28.85	16.43
22	*n*-Butyl alcohol	0.98	12.88	25.35	32.28	32.90	16.43
23	*n*-Amyl alcohol	.85	14.74	27.48	34.48	33.64	16.43
	(c) Diethylene glycol–alcohols						
24	Ethyl alcohol	1.61	8.13	12.41	15.46	14.91	8.05
25	*n*-Propyl alcohol	1.13		16.03	19.92	18.74	8.05
26	*n*-Butyl alcohol	0.98	10.46	19.26	23.23	21.26	8.05
27	*n*-Amyl alcohol	.85		20.28	24.77	22.27	8.05
	(d) Propylene glycol–chlorinated hydrocarbons						
28	Methylene chloride[c]	0.02	12.11	22.89	26.28	23.99	11.72
29	Chloroform[c,d]	.02	16.14	26.45	28.20	26.17	11.72
30	Carbon tetrachloride[c]	.02	16.40	24.04	27.11	23.71	11.72
31	Ethylene chloride	.02	10.61	18.73	22.03	21.45	11.72
32	*t*-Butyl chloride[e]	.12	14.09	23.57	28.44	26.01	11.72
	(e) Diethylene glycol–chlorinated hydrocarbons						
33	Methylene chloride	0.02	14.67	22.33	23.66	19.39	8.05
34	Chloroform	.02	18.04	25.05	26.51	20.14	8.05
35	Carbon tetrachloride	.02	16.63	24.73	25.75	21.47	8.05
36	Ethylene chloride	.02	10.38	17.22	19.68	15.00	8.05
	(f) Propylene glycol–other oxygenated solvents						
37	Acetone[c]	0.02	1.46	6.93	14.04	14.98	11.72
38	Methyl ethyl ketone	.07	3.99	9.28	14.25	16.20	11.72
39	Dioxane	.06	1.45	4.56	7.93	10.91	11.72
40	Ethyl acetate[c]	.06	4.36	10.90	15.35	16.68	11.72
41	Ethylene chlorohydrin[c]	1.80	6.02	9.86	12.72	14.09	11.72
42	Trimethylene chlorohydrin	1.44	5.36	9.79	12.96	13.19	11.72
43	Trichloro-*t*-butyl alcohol	Undiss. solid		17.48	18.59	16.71	11.72

[a] In the case of some of the co-solvents, the data refer to different values for the percentage of the glycol as noted by the corresponding footnote. [b] Per cent. glycols are 0, 24.5, 46.3, 66.0, 83.8 and 100. [c] Per cent. glycols are 0, 20.2, 40.5, 60.4, 80.2 and 100. [d] At 17.5 per cent. propylene glycol, the solubility is 14.09. [e] Per cent. glycols are 0, 23, 44.4, 64.2, 82.7 and 100.

ing 20–30% soap being quite a free-flowing liquid. They are practically devoid of foaming power. They have less tendency than aqueous solutions to form gel or curd on cooling; and they pass practically unchanged in composition through an ultrafilter. However, they have good detergent power.

Behavior of Various H Solvents—(a) Alcohols.—Figures 1–3 show that by using a series of normal straight-chain alcohols with the same glycol, the co-solvency increases steadily with increase of the number of carbon atoms. For the same glycol the maximum in the co-solvency curve tends to be nearer to the glycol end for the higher homologs. Both of these points indicate that as the hydrocarbon portion in the alcohol increases it becomes more powerful as an H-solvent. Allyl alcohol, however, is much less powerful than the corresponding saturated alcohol as an H co-solvent, perhaps because it is a more polar compound and so a less powerful hydrocarbon solvent.

For cetyl alcohol (see Fig. 1, curve L), which is a waxy solid not completely miscible with propylene glycol, adding sodium oleate produces a clear liquid.

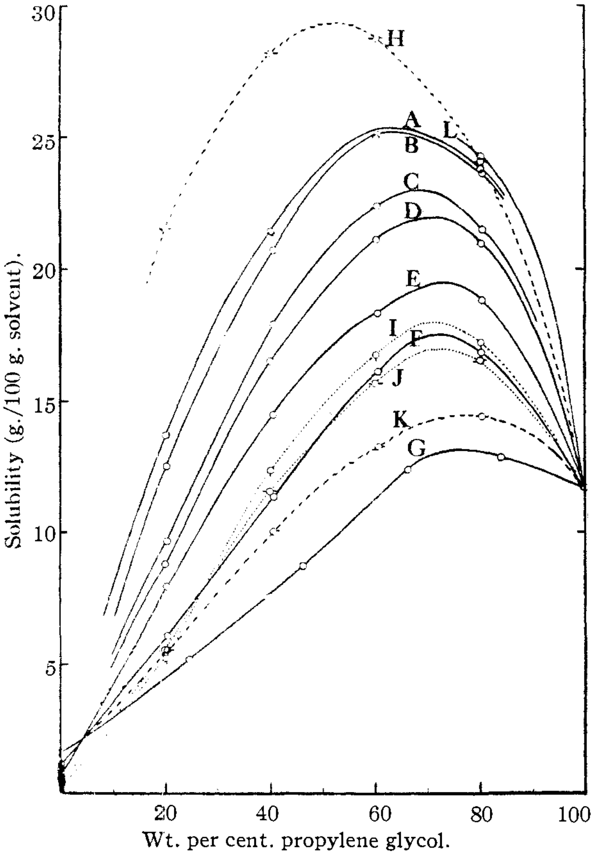

Fig. 1.—Solubility of sodium oleate in propylene glycol-*n*-alcohols and some cyclic alcohols, at 25°: A, lauryl alcohol; B, octyl alcohol; C, hexyl alcohol; D, amyl alcohol; E, butyl alcohol; F, propyl alcohol; G, ethyl alcohol; H, phenol; I, cyclohexanol; J, benzyl alcohol; K, allyl alcohol; L, cetyl alcohol.

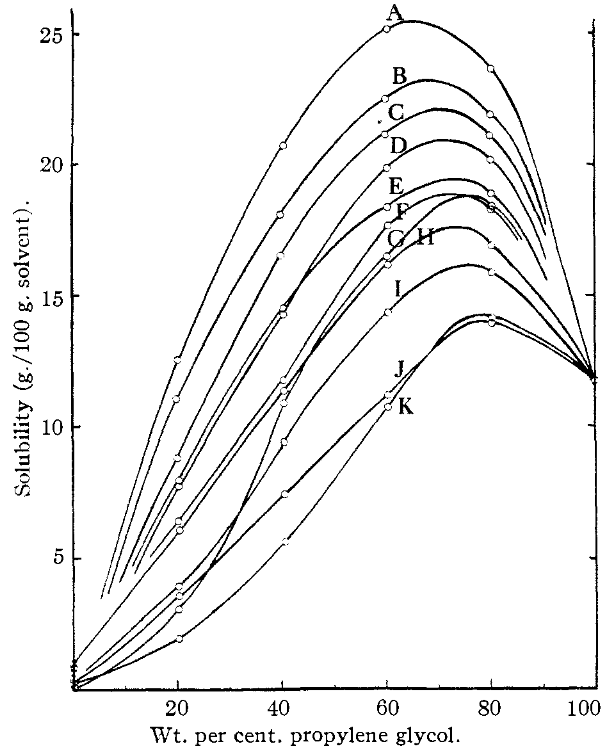

Fig. 2.—Solubility of sodium oleate in propylene glycol-isomers of propyl, butyl, amyl and octyl alcohols, at 25°: A, *n*-octyl; B, isoöctyl (2-ethyl-hexanol); C, *n*-amyl; D, isoamyl; E, *n*-butyl; F, isobutyl; G, secondary isoamyl; H, *n*-propyl; I, secondary isobutyl; J, isopropyl; K, *t*-butyl.

With propylene glycol and different isomeric alcohols (Fig. 2) the power of co-solvency is always in the order normal > iso > secondary > tertiary, and the difference between the iso and secondary is much greater than that between normal and iso. That is, the more the chains are branched, or the more the hydroxyl group is moved inwards from the extreme end position, the less is the hydrocarbon-dissolving activity of the alcohol.

The aromatic and cyclic hydroxylic compounds like benzyl alcohol and cyclohexanol are rather weak H-solvents in comparison with the aliphatic alcohol of the same number of carbon atoms. Phenol, however, produces a strong co-solvency.

(b) **Chlorinated Hydrocarbons.**—All chlorinated hydrocarbons (Fig. 4) have been found to be very powerful co-solvents with glycols and are stronger than the corresponding alcohols, standing second only to pure hydrocarbons such as benzene. Of the four chlorinated hydrocarbons the order is found to be the same in the case of both propylene glycol and diethylene glycol and is chloroform > carbon tetrachloride > methylene chloride > ethylene chloride. A slightly higher maximum was obtained with tertiary butyl chloride and propylene glycol. Some of these liquids are miscible in all proportions but many pairs have

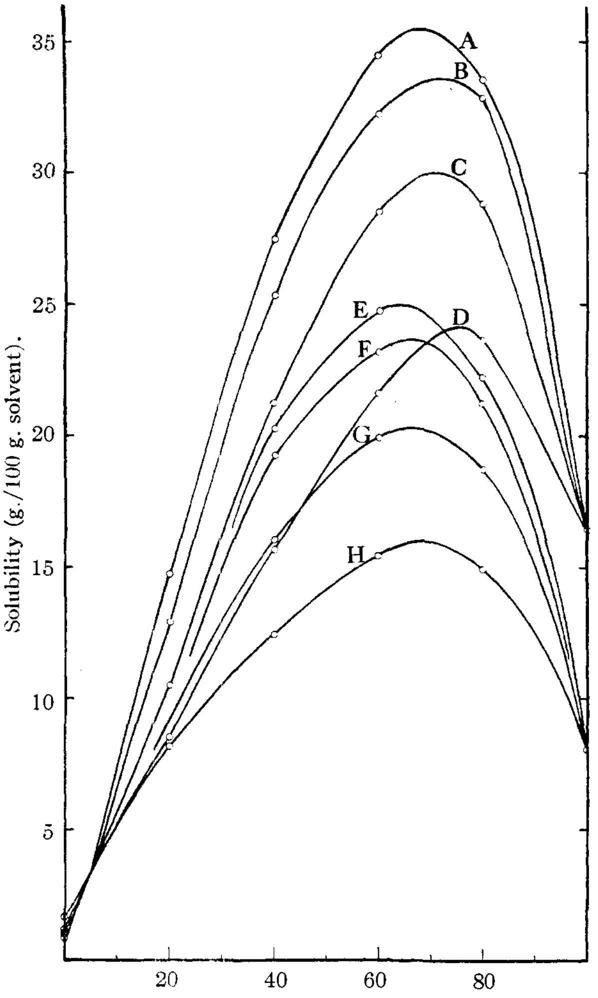

Fig. 3.—Solubility of sodium oleate in mixtures of ethylene glycol and *n*-alcohols, and diethylene glycol and *n*-alcohols, at 25°: ethylene glycol with A, *n*-amyl; B, *n*-butyl; C, *n*-propyl; D, *n*-ethyl; diethylene glycol with E, *n*-amyl; F, *n*-butyl; G, *n*-propyl; H, *n*-ethyl.

but limited solubility in each other until sufficient soap is added.

It might be pointed out that the maxima in the co-solvency curves occur nearly in the same region if expressed as weight fractions but they are well separated from each other when expressed in mole fractions. This applies also to the preceding case of the alcohols. Further, the maximum solubility produced by these chlorinated hydrocarbons is nearly the same if expressed in weight per cent. or volume per cent. though not if expressed in mole per cent. For the comparatively high molecular weight solutes like soaps the amount dissolved per unit volume or unit weight is more comparable than the mole fraction.

(c) **Other H-Solvents.**—A few other H-solvents, such as ethers, ketones, esters, etc., have been studied (see Table I and Fig. 5). Although fairly good solvents for ordinary hydrocarbons, they are far less effective as H co-solvents for soap than the corresponding alcohols or hydrocarbons. Of the compounds studied the co-dissolving power with propylene glycol is in the order ethyl acetate > methyl ethyl ketone > acetone > dioxane. Dioxane has little if any co-solvent power.

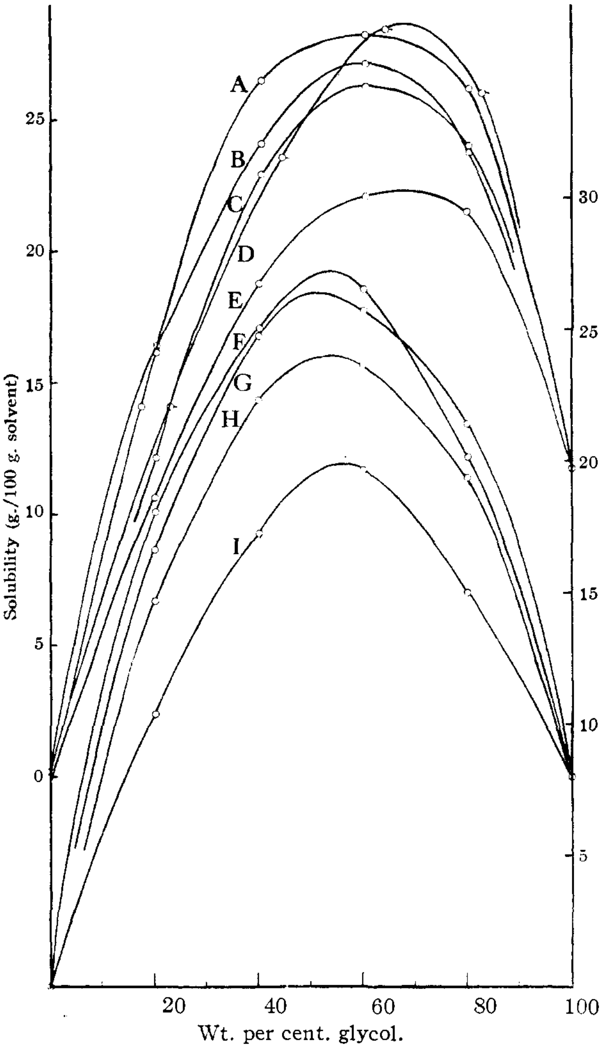

Fig. 4.—Solubility of sodium oleate in propylene glycol and diethylene glycol-chlorinated hydrocarbons, at 25° (ordinates shown on the left-hand scale). Propylene glycol: A, chloroform; B, carbon tetrachloride; C, methylene chloride; D, *t*-butyl chloride; E, ethylene chloride. Diethylene glycol: (ordinates shown on the right-hand scale) F, chloroform; G, carbon tetrachloride; H. methylene chloride; I, ethylene chloride.

Though the co-solvent power of H-solvents varies in a regular manner from member to member within the same group, the effects of two groups are not additive. For example, chlorinated solvents have very strong co-solvency as evidenced by the effect of tertiary butyl chloride, chloroform, etc., and alcohols are fairly strong in this respect. But if a hydrogen atom in an alco-

TABLE II

SOLUBILITY OF SODIUM OLEATE IN G–H MIXTURES USING DIFFERENT GLYCOLS, WITH *n*-AMYL ALCOHOL AS CO-SOLVENT (25°)

Solubilities are given in grams of soap per 100 grams of solvent

		Per cent. glycol in the solvent mixture					
		0	20	40	60	80	100
1	Ethylene glycol	Data in Table I					
2	Propylene glycol						
3	Diethylene glycol						
4	α-Monochlorohydrin, $CH_2ClCHOHCH_2OH$	0.85	...	12.56	16.98	16.88	1.16
5	Monoacetin	.85	...	10.50	12.70	10.48	2.51
6	Glycerol	.85	...	34.62	42.68	34.36	8.53
7	Dibutyl tartrate	.85	...	25.94	36.55	42.15	41.27
8	Phenol	.85	1.53	2.94	6.16	4.67	...
9	Catechol[a]	6.63 (10:90)	17.69 (30:80)	24.97 (40:60)			

[a] Ethyl alcohol was used as co-solvent for solubility reasons; figures in parentheses following the solubility values give the corresponding values of catechol: alcohol.

hol is replaced by a chlorine atom, the H activity of the resulting compound is markedly lower than that either of a chlorinated compound or of an alcohol, as is illustrated by ethylene chlorohydrin and propylene chlorhydrin (see Fig. 5).

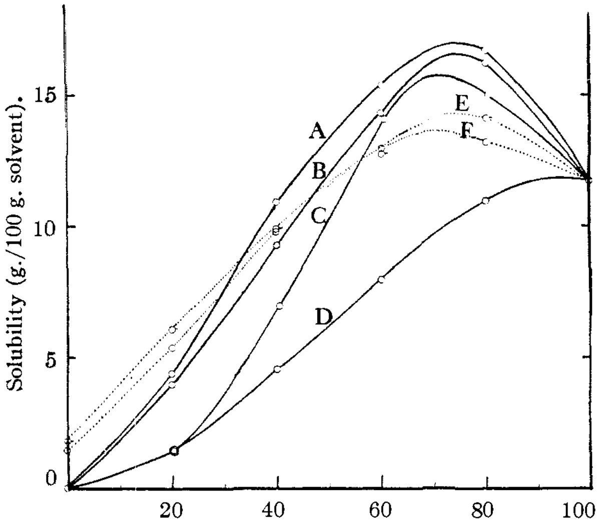

Fig. 5.—Solubility of sodium oleate in propylene glycol–various solvents, at 25°: A, ethyl acetate; B, methyl ethyl ketone; C, acetone; D, dioxane; E, ethylene chlorohydrin; F, propylene chlorohydrin.

Behavior of Various Glycols.—Table II and Fig. 6 represent the results with various glycols for sodium oleate using *n*-amyl alcohol as co-solvent. All dihydroxylic compounds show co-solvent power for soap. Also, polyhydroxy compounds show this behavior, and for the simple compound glycerol the co-dissolving power is higher than any glycol containing 2 or 3 carbon atoms.

The co-dissolving power is in the order ethylene glycol > diethylene glycol > propylene glycol > α-monochlorohydrin > monoacetin. Further, the maximum is produced when the solvent mixture contains 60–80 weight per cent. Phenol has a small but definite co-dissolving power for soap in combination with an H-solvent. The mutual solubilizing power of phenol and soap in water is the basis of many commercial disinfectants. This co-dissolving power is a special property of phenol but is almost non-existent in aliphatic hydroxyl compounds, such as alcohol–benzene and butyl alcohol–benzene. Cyclohexanol, and even methyl alcohol, show slight co-solvency with benzene (see Table III and Fig. 7).

The physical state of the glycol is not of any importance as will be evidenced by the behavior of catechol (curve I, Fig. 6), which acts as a powerful G co-solvent for soap. Many other solid di-

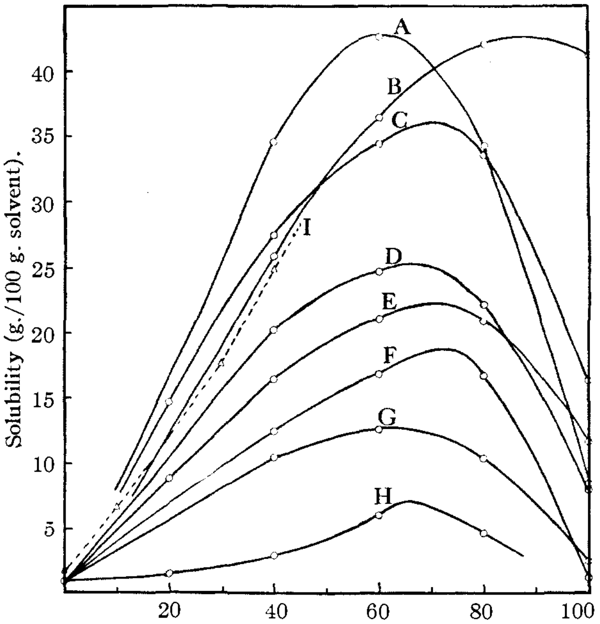

Fig. 6.—Solubility of sodium oleate in *n*-amyl alcohol–glycols, at 25°: A, glycerol; B, dibutyl tartrate; C, ethylene glycol; D, diethylene glycol; E, propylene glycol; F, α-monochlorohydrin; G, monoacetin: H, phenol; I, catechol (ethyl alcohol as co-solvent).

TABLE III

SOLUBILITY OF SODIUM OLEATE IN PROPYLENE GLYCOL–BENZENE, METHYL ALCOHOL–BENZENE, AND CYCLOHEXANOL–BENZENE

Solubility in grams of soap per 100 g. solvent

	Per cent. G-solvent in the solvent mixture 0	20	40	60	80	100
Propylene glycol–benzene (at 20°)	0.04	14.32	26.35	29.82	31.47	10.82
Methyl alcohol–benzene (at 25°)	.04	3.94	6.89	10.31	12.25	12.38
Cyclohexanol–benzene (at 25°)	.04	0.31	1.04	2.13	0.70	0.36

hydroxylic compounds, *e. g.*, *p-t*-butylcatechol, 2,3-dihydroxydiphenyl and glycerol monostearate solubilize soap in H-solvents. Gallic acid or its sodium salts, pyrogallol, etc., have been patented[6] to solubilize insoluble medicinal compounds in water.

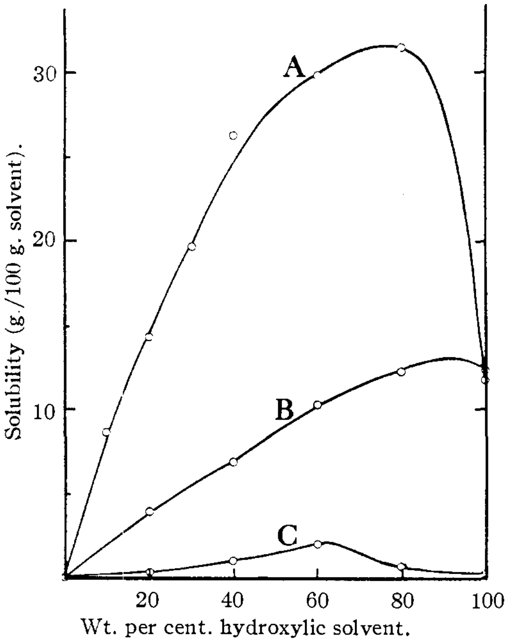

Fig. 7.—Solubility of sodium oleate in (A) propylene glycol-benzene, at 20°; (B) methyl alcohol-benzene, at 25° and (C) cyclohexanol-benzene, at 25°.

2. Soaps Other Than Sodium Oleate.—Results for four different soaps in the same G–H mixture are given in Table IV and Fig. 8. As the hydrocarbon portion of the soap increases, the proportion of H-solvent, *n*-butyl alcohol, necessary to produce the maximum effect also increases. Also, the percentage increase of solubility at the optimum composition over the value which it would have had if the solubility had been merely the average of the two solvents, increases rapidly with increase in the number of carbon atoms. In other words, with decreased number of carbon atoms the maximum becomes less prominent (expressed as percentage increase) and it also drifts steadily toward the glycol.

TABLE IV

SOLUBILITY OF SOAPS IN ETHYLENE GLYCOL–*n*-BUTYL ALCOHOL (25°)

Solubilities are given in grams of soap per 100 g. of solvent

	Per cent. glycol in the solvent mixture 0	20	40	60	80	100
Sodium laurate	0.52	7.84	15.09	20.14	20.05	11.92
Sodium myristate	.28	4.58	10.12	12.88	11.23	4.00
Sodium palmitate	.08	2.49	5.85	7.14	5.16	1.19
Sodium stearate	.05	1.47	3.37	3.79	2.16	0.48

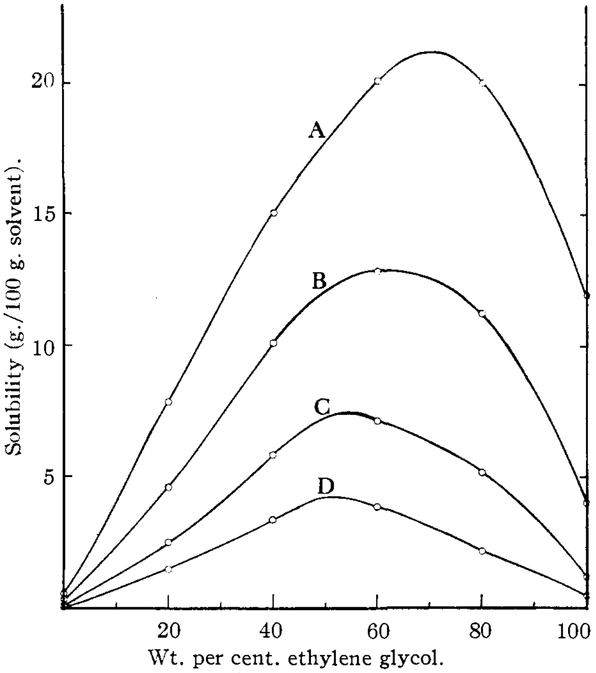

Fig. 8.—Solubility of four saturated soaps in *n*-butyl alcohol–ethylene glycol mixtures, at 25°: A, sodium laurate; B, sodium myristate; C, sodium palmitate; D, sodium stearate.

The solubility of the sodium salts of fatty acids in pure glycols, when plotted against the number of carbon atoms in the soap and expressed as the log of molal concentration, falls on a straight line from C_{10} to C_{18} but sharply changes its course below C_{10} (Fig. 9). This behavior resembles other properties of the salts of fatty acids, which show sharp transition in behavior from C_{10} onward. The linear relation seems to be in line with a thermodynamic prediction[7] made in the field of high polymers that the solubility of homologs of high polymers should decrease exponentially as the chain length increases. The solubility data for sodium salts of C_2 to C_{18} acids in ethylene and propylene glycols are given in Table V. It should be noted from the last column of Table V that as the hydrocarbon portion of the fatty acid salt increases, the ratio of solubility in ethylene glycol to solubility in propylene glycol steadily decreases,

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(6) Bird and Kuna, U. S. Patent 2,407,624 (1946).

(7) Ott, "High Polymers," Vol. V, Interscience Publishers, New York, N. Y., 1943.

TABLE V

SOLUBILITY OF SODIUM SALTS OF FATTY ACIDS IN GLYCOLS (25°)

Salt	No. C atoms	Ethylene glycol molality	Propylene glycol molality	Ratio E.G./P.G.
Acetate	2	3.540		
Propionate	3	3.221	2.072	1.55
Valerate	5	2.511	1.742	1.44
Caproate	6	2.641	1.988	1.33
Caprylate	8	1.746	1.343	1.30
Caprate	10	0.823	0.642	1.28
Laurate	12	.536	.549	0.98
Myristate	14	.160	.197	.81
Palmitate	16	.0426	.0679	.63
Stearate	18	.0156	.0299	.52

which shows the importance of a proper G–H balance in the solvent for such solutes.

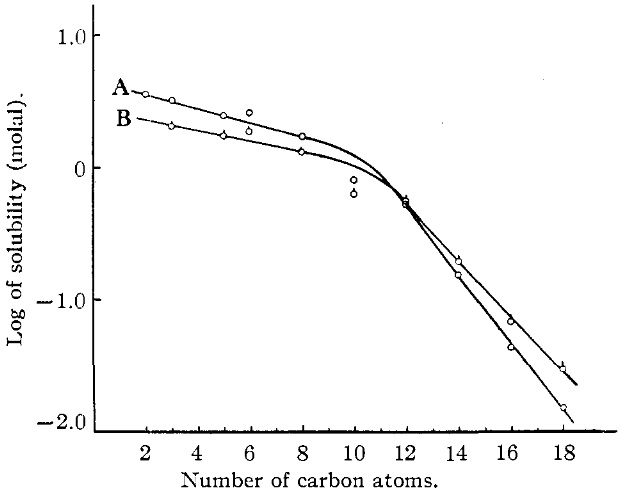

Fig. 9.—Solubility of sodium salts of fatty acids in ethylene glycol (curve A) and propylene glycol (curve B).

The co-solvency of soaps in G–H mixtures is also exhibited by metallic soaps. They show strong co-solvency depending on the metallic radical, even sometimes stronger than the sodium soaps, but they differ radically from the behavior of alkali metal soaps in that the maximum co-solvency is produced near the H-solvent end and never near the glycolic end. They are less polar than the sodium soaps.[8]

Discussion

Glycolic hydroxyl groups have a special power not possessed by the aliphatic alcohols, which have practically no co-dissolving power. The postulated hydrogen bonding power of glycols has received a striking confirmation from some results in the analytical field. It follows directly from Brönsted's concept of acids that any acidic solvent will increase the apparent basic power of a base dissolved in it. It has been shown by the author[4] that weak bases such as ammonia or alkyl amines show a strong base titration curve in glycol, and bases such as sodium acetate which are too weak to be satisfactorily titrated by strong acids in water can be titrated directly with sharp end-point by strong acids in glycolic solvents.

Comparison of the Various Glycols.—Glycols may be considered from three aspects: (a) their power of dissolving a soap unaided, (b) their maximum co-dissolving power for a soap in mixture with an H-solvent, and (c) the position of the co-solvency maximum, *i. e.*, the optimum composition of co-solvent.

(a) The solubility of soaps in individual glycols depends on the G–H balance within the glycol molecule itself and the effective strength of each group. Glycerol, though it shows very strong co-solvency, shows poor solubility for soap because of its almost complete lack of H activity. In comparing ethylene glycol with propylene glycol, the former, due to its symmetry and the mutual inductive effect of the OH groups, will have a stronger G activity, and the latter, due to the methyl group, will have less G activity but more H activity. The net effect will depend on the soap used as solute. The higher the molecular weight of the soap, the greater is its content of hydrocarbon; hence, the solubility of soap in propylene glycol compared with that in ethylene glycol should steadily increase with the number of carbon atoms. Thus, sodium laurate is found to be almost equally soluble in both; higher soaps are even less soluble in ethylene than in propylene glycol, whereas lower soaps are more soluble in ethylene glycol as is shown in Fig. 9.

(b) The co-solvent power of a mixture of a glycol with an H solvent is the net effect of the hydrogen bonding power of the glycol (G activity) and the hydrocarbon-dissolving power (H activity) of the alkyl groups present in the co-solvents. The G activity of a glycol depends on the electropositivity or electrophilic nature of its hydroxylic hydrogens. From analogy with the change of strength of acids occasioned by the introduction of different groups we can make qualitative deductions about the efficiency of different glycols in this respect. Introduction of alkyl groups reduces the strength of acids; for the same reason the maximum co-solvency with ethylene glycol is always higher than with propylene glycol (see the data and curves for alcohols and previous data[2] for sodium stearate). Introduction of hydroxyl groups increases the strength of an acid. Hence glycerol has stronger co-solvent power than the lower glycols. Interposition of methylene groups reduces the strength of dibasic acids; hence trimethylene glycol shows very weak G activity.[2] However, in diethylene glycol the glycolic property is maintained through the simultaneous presence of the electron-attracting ethereal oxygen atom.

Dibutyl tartrate aptly illustrates our basic con-

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[8] Palit and McBain, *J. Am. Oil Chem. Soc.*, **24**, 190 (1947).

cept. The hydroxylic hydrogens of dibutyl tartrate are strongly electropositive owing to the electron-drainage effect of the two —$COOC_4H_9$ groups. Also, the two butyl groups have sufficient hydrocarbon-dissolving power. Thus, it combines in one molecule both strong G activity and H activity. It is the strongest solvent for soap of any investigated to date. Also, owing to its balance in G and H activity, its solvent power for soap increases only slightly by the addition of an H-solvent and the maximum co-solvency is very near the glycolic end (see Fig. 6).

(c) The composition of the optimum mixture is fixed by the amount of hydrocarbon-dissolving groups present in the glycol itself. If the glycol is poor in its content of hydrocarbon-dissolving groups it will require more H-solvent to produce the maximum solubility, and, conversely, if the glycol is rich in hydrocarbon portion it will require less H co-solvent to develop its maximum co-dissolving power. Hence with the same co-solvent and solute ethylene glycol requires more H solvent than propylene glycol. Diethylene glycol is like ethylene glycol. Glycerol, having the weakest, and dibutyl tartrate, having the strongest H activity, require, respectively, the most and the least proportion of H solvent to produce an optimum mixture. However, as is seen from Fig. 6, monochlorohydrin requires a larger proportion of H solvent than ethylene glycol, just as chlorine derivatives of ethyl alcohol or propyl alcohol are very poor H solvents.

In such industries as lacquer, rubber or lubricating greases, one of the co-solvents is often given a special name such as "polar helper," whereas both co-solvents are essential and a non-polar co-solvent may be as effective as a "polar helper." Hence the term "polar helper" is not justified and the term "co-solvent" is more appropriate and sufficient.

Interaction between Glycol and H-Solvent.—So far we have been considering the glycol and H-solvent as acting concurrently but independently. There is, however, no reason why the glycol should not hydrogen bond with oxygen or similar electron-rich centers present in such H-solvents as ketones, ethers, nitriles, esters, etc. Thus, though it is well known that acetone or dioxane or ethyl acetate is a fairly good solvent for hydrocarbons, they are unexpectedly ineffective as H co-solvents for soaps (Fig. 5). Their weak co-solvency is not owing to some peculiar inability on their part to dissolve the hydrocarbon portion of the soap but is owing to their deactivating the glycol to some extent by forming hydrogen bonds between their donor oxygens and the electrophilic hydrogens of the glycols.

The idea helps in understanding differences between similar compounds. For example, the G activity of a glycol should be diminished on addition of an alcohol, and the oxygen atom of the alcohol will hydrogen bond with some of the acidic hydrogens of the glycol. This is increasingly effective in the order tertiary > secondary > primary alcohols, and accounts for the observed co-solubility of soap which is in the reverse order (Fig. 2). In fact, the oxygen atoms of the tertiary alcohols are so effective in hydrogen bonding that they leave very little co-solvency. Such an interaction will also cause the co-solvency maximum to move toward the glycol end. Thus, oxygenated H-solvents are usually found to have the maxima nearer to the glycol end than those of the non-oxygenated solvents, as can be seen by comparing the chlorinated hydrocarbons with alcohols, esters, ethers, etc.

Monohydroxylic Compounds with Glycolic Solvent Power.—Phenols and cresols have been known for a long time to have strong solvency for soap. Phenol has one strongly polar hydroxyl group. The cause of this strong polarity is the highly electronegative phenyl group. Furthermore, this hydroxyl group affects the whole benzene ring, particularly the hydrogens in the ortho and para position, which therefore further contributes to their hydrogen bonding power. Phenol has also a strong hydrocarbon dissolving power and hence it is a combination of G–H in one molecule. This explains its high soap solvency and also that of many other hydroxylic compounds such as cresols, terpineol, cholesterol, cyclohexanol, etc,

The soap solvency of phenol, however, is much less than the typical glycols (Table II and Fig. 6). The effectiveness of cyclohexanol is probably less than that of phenol, as is shown by its weak, though definite, G activity with a powerful co-solvent, *e. g.*, benzene (data in Table III and co-solvency curve in Fig. 7).

Compounds such as glycol chlorohydrin (CH_2ClCH_2OH), lactates ($CH_3CHOHCOOR$), nitro alcohols ($CH_2OHCH_2NO_2$) and Cellosolve, have been observed to have weak but perceptible G activity in mixtures with benzene, co-dissolving sodium oleate, owing to the hydroxylic hydrogen being made more positive by the other negative groups in the molecule.

Methyl alcohol has much more solvent power for soaps than any of the common organic solvents. This is shown by the data in Table III and the co-solvency curve for methyl alcohol–benzene (curve B of Fig. 7).

II. Solutes other than Soaps

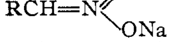
Salts of Monobasic Acids.—If the COO^- group forms a hydrogen bond with glycol, any XOO^- group where X is any other negative element should also behave similarly. Further, if R in RXOONa is small enough, this salt should show high solubility in glycols but little or no co-solvency in G–H mixtures. Nitronates have the structure  $RCH{=}N\begin{smallmatrix}\nearrow O\\ \searrow ONa\end{smallmatrix}$ and are found to be very highly soluble in glycol, the values for

TABLE VI

SOLUBILITY OF SOME SODIUM SALTS, 25°

Salt	Solvent	Glycol:Co-solvent	Solubility g./100 g. solvent
Sodium acetate	Ethylene glycol–n-amyl alcohol	100:0	29.05
		80:20	22.57
		0:100	0.31
Sodium benzoate	Ethylene glycol–n-amyl alcohol	100:0	24.87
		80:20	21.95
		60:40	17.09
		40:60	12.08
		0:100	1.25
Sodium benzoate	Propylene glycol–chloroform	100:0	15.44
		80:20	13.13
		60:40	10.24
		40:60	7.25
		20:80	3.58
		0:100	0.07
Sodium propyl nitronate	Ethylene glycol–n-amyl alcohol	100:0	39.51
		80:20	34.89
Sodium isopropyl nitronate	Propylene glycol–n-amyl alcohol	100:0	21.84
		80:20	18.82
		0:100	0.24

propyl and isopropyl derivatives being shown in Table VI. They, however, show very little G–H effect (*cf.* Fig. 10); likewise sodium benzoate and sodium acetate (Table VI, Fig. 10). This shows the importance of the size of R. Sulfinates have high glycolic solubility. The sulfonates, however, have poor solubility in glycols, like any organic salt in the usual organic solvents. Sodium carbonate, however, is soluble in less than its own weight of glycerol.

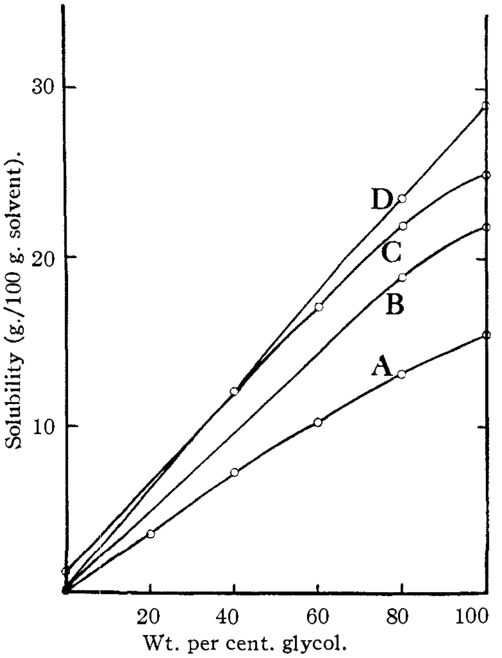


Fig. 10.—Solubility of some sodium salts in solvent mixtures at 25°: A, sodium benzoate in propylene glycol–chloroform; B, sodium isopropyl nitronate in propylene glycol–n-amyl alcohol; C, sodium benzoate in ethylene glycol–n-amyl alcohol; D, sodium acetate in ethylene glycol–n-amyl alcohol.

Sodium metaborate, BO_2Na, aluminate, AlO_2Na, nitrite, NO_2Na, hypophosphite, H_2PO_2Na, metaarsenite, AsO_2Na, chlorite, ClO_2Na, etc., have the requisite structure, XOO^- for glycolic interaction, the occurrence of which is shown by their high solubility in glycols, some of the values being shown in Table VII. Solubilities in glycols which range from 3 to 40% should be regarded as exceptionally high compared to the values in the usual organic solvents, which are generally of the order of a fraction of a per cent.

TABLE VI

SOLUBILITY OF SOME INORGANIC SALTS IN GLYCOLS, 25°

Solubility in grams per 100 g. of solvent

Sodium salt	Formula	Ethylene glycol	Propylene glycol
Propylnitronate	C_3H_7COONa	39.51	...
Isopropylnitronate	i-C_3H_7COONa	...	21.84
Nitrite	NOONa	16.78	8.47
Metaborate	BOONa	6.98	3.36
Aluminate	AlOONa	3.57	0.36
Hypophosphite	H_2POONa	33.01	9.70
Metaarsenite	AsOONa	28.06	20.84
Chlorite	ClOONa	Highly soluble, but reacts	
Bifluoride	HFFNa	2.78	...
Hyposulfite	$(SOONa)_2$	1.34	0.37
Oxalate	$(COONa)_2$	0.064	0.028

The xanthates $\mathrm{ROC}^{\mathrm{S}}_{\mathrm{SNa}}$, though not strictly comparable to the fatty acid salts due to the intervention of the oxygen atom, might be expected to show glycolic interaction, and if R is large enough, to show G–H effect. Experimentally, potassium ethyl xanthate is found to be highly soluble in glycol, the solution tending to form a jelly before the saturation limit is reached. Cellulose xanthates used in the viscose rayon industry should show glycolic interaction and several patents[9] suggest addition of glycols and polyhydroxy compounds to the viscose bath.

Other analogous compounds are bifluoride, $\left[\mathrm{H}{<}^{\mathrm{F}}_{\mathrm{F}}\right]^{-}\mathrm{Na}^{+}$; triiodide, $\left[\mathrm{I}{<}^{\mathrm{I}}_{\mathrm{I}}\right]^{-}\mathrm{Na}^{+}$; thioacetate, $\left[\mathrm{RC}{<}^{\mathrm{S}}_{\mathrm{O}}\right]^{-}\mathrm{Na}^{+}$; cyanate, $\left[\mathrm{C}{<}^{\mathrm{N}}_{\mathrm{O}}\right]^{-}\mathrm{Na}^{+}$; and amide salt, $\left[\mathrm{RC}{<}^{\mathrm{O}}_{\mathrm{NH}}\right]^{-}\mathrm{Na_3}^{+}$ and should have high solubility in glycols.

Salts of Dibasic Acids.—The $\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}}$ surface is more electropositive in dibasic than in monobasic acids as is shown by their higher dissociation constants. Hence, the former have less glycolic interaction, since the hydrogen bond formation is conditioned by the electronegativity

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(9) Cairncross and Goddell, U. S. Patent 1,814,543 (1931).

of the oxygen atom. Therefore, sodium oxalate shows much less solubility in glycols than sodium acetate or benzoate (Tables VI and VII). Sodium hyposulfite, $(SO_2Na)_2$, being a salt of a dibasic acid, shows fair solubility but less than other similar compounds.

Acknowledgment.—The author gratefully acknowledges his indebtedness to Prof. James W. McBain for his interest and advice.

Summary

Any mixture consisting of two solvents, one of the glycolic type (called G-solvent) and the other any organic solvent which can dissolve hydrocarbons, *e. g.*, higher alcohols, chlorinated hydrocarbons, etc. (called H-solvent), has been found to have better solvent power for soaps than any of the pure solvents alone. Extensive study of the solvent property of various G–H mixtures has been made.

The glycol forms hydrogen bonds with the $—COO^-$ end of the soap, and the alkyl group of the soap is dissolved by the H-solvent, and thus the mixture is more effective than the individual solvents. The cause of the hydrogen-bonding power of glycol in comparison with alcohols is ascribed to the effect of the interaction of one electronegative group on another, making the hydroxylic hydrogen atom of glycols more positive than it would otherwise be. The long known soap-dissolving power of phenols, cresols, methyl alcohol, etc., is also explained from this viewpoint.

It has also been shown that inorganic salts having the group XOO^-, where X is any non-metallic element, *e. g.*, nitrites, hypophosphites, etc., have very high solubility in glycols owing to this glycolic interaction.

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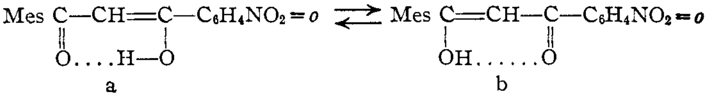
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

A Study of the Direction of Enolization of Mesitoyl-*o*-nitrobenzoylmethane and Mesitoyl-*p*-nitrobenzoylmethane

BY R. PERCY BARNES, GLADYS ESTELLE PINKNEY[1] AND WILLIAM A. DACOSTA[1]

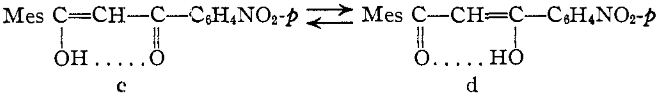
In continuation of the study of the direction of enolization of β-diketones,[2] we have made mesitoyl-*o*-nitrobenzoylmethane and mesitoyl-*p*-nitrobenzoylmethane and after carrying out certain reactions on related compounds conclude that their enolic modifications are (VII) and (VII′), respectively. These substances are 100% enolic in methanol solution.

First *o*-nitrobenzaldehyde and *p*-nitrobenzaldehyde were condensed separately with acetomesitylene to give the chalcones (I) and (I′), which were brominated to the dibromides (III) and (III′).


$$\text{Mes }\underset{\underset{\text{O}\ldots\text{H}}{\|}}{\text{C}}—\text{CH}=\underset{\underset{\text{O}}{|}}{\text{C}}—C_6H_4NO_2=o \rightleftarrows \text{Mes }\underset{\underset{\text{OH}\ldots\ldots}{|}}{\text{C}}=\text{CH}—\underset{\underset{\text{O}}{\|}}{\text{C}}—C_6H_4NO_2=o$$

a b

VII


$$\text{Mes }\underset{\underset{\text{OH}\ldots\ldots}{|}}{\text{C}}=\text{CH}—\underset{\underset{\text{O}}{\|}}{\text{C}}—C_6H_4NO_2\text{-}p \rightleftarrows \text{Mes }\underset{\underset{\text{O}\ldots\ldots}{\|}}{\text{C}}—\text{CH}=\underset{\underset{\text{HO}}{|}}{\text{C}}—C_6H_4NO_2\text{-}p$$

c d

VII′

The dibromide (III) was converted by treatment with alcoholic potassium hydroxide to the methyl ether (V), which upon hydrolysis gave rise to the enol (VII). Dibromide (III′) upon treatment with alcoholic potassium hydroxide went directly to the enol (VII′).

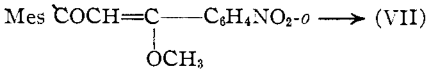
$MesCOCH_3 + o\text{-}NO_2C_6H_4CHO \longrightarrow$

$Mes\ COCH{=}CHC_6H_4NO_2\text{-}o \longrightarrow$

I

$Mes\ COCHBrCHBrC_6H_4NO_2 = o \longrightarrow$

III


$$\text{Mes COCH}=\underset{\underset{\text{OCH}_3}{|}}{\text{C}}—C_6H_4NO_2\text{-}o \longrightarrow (\text{VII})$$

V

$MesCOCH_3 + p\text{-}NO_2C_6H_4CHO \longrightarrow$

$MesCOCH{=}CHC_6H_4NO_2\text{-}p \longrightarrow$

I′

$MesCOCHBrCHBrC_6H_4NO_2\text{-}p \longrightarrow (\text{VII}')$

III′

Secondly, *o*-nitroacetophenone and *p*-nitroacetophenone were condensed separately with 2,4,6-trimethylbenzaldehyde to give the chalcones (II) and (II′), which in turn were brominated to (IV) and (IV′). Dibromide (IV) was treated as was its isomer (III), producing the methyl ether (VI), which was also hydrolyzed to the enol (VII). Dibromide (IV′) upon treatment with alcoholic potassium hydroxide went directly to enol (VII′).

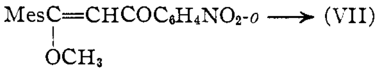
$Mes\ CHO + CH_3COC_6H_4NO_2\text{-}o \longrightarrow$

$MesCH{=}CHCOC_6H_4NO_2\text{-}o \longrightarrow$

II

$MesCHBrCHBrCOC_6H_4NO_2\text{-}o \longrightarrow$

IV


$$\text{Mes}\underset{\underset{\text{OCH}_3}{|}}{\text{C}}=\text{CHCOC}_6H_4NO_2\text{-}o \longrightarrow (\text{VII})$$

VI

$MesCHO + CH_3COC_6H_4NO_2\text{-}p \longrightarrow$

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[1] In partial fulfillment of the requirements for the Master's Degree.

[2] R. Percy Barnes and Jonathan L. Snead, THIS JOURNAL, **67**, 138 (1945).