over a considerable range of concentration below and above the stoichiometric requirements for the possible constituents, FeCNS<sup>++</sup>, Fe(CNS)<sub>2</sub><sup>+</sup>, Fe(CNS)<sub>3</sub>, Fe(CNS)<sub>6</sub><sup>m</sup>, the pairs of curves (fixed thiocyanate-variable ferric ion; fixed ferric ionvariable thiocyanate) overlap. For solutions of identical color intensity, x in equation (1) must be the same, if we ascribe the color to the one complex Fe(CNS)<sub>n</sub><sup>3-n</sup>. For any point on any pair of overlapping curves then  $(a - x)(b - nx)^n =$  $(b - x)(a - nx)^n$ . This equation is satisfied for all values of x only if n = 1, that is, if the complex is Fe(CNS)<sup>++</sup>.

Another interesting confirmation may be noted by considering identical values of x (*i. e.*, per cent. transmission) for any two points lying on two different series of curves. For these points we would have the relation  $(a - x)(b - nx)^n =$  $(c - x)(d - nx)^n$ , where a and c are the two concentrations of ferric ion and b and d the corresponding thiocyanate concentrations producing the identical color. As a first approximation this may be written as  $ab^n = cd^n$ , since x is relatively small. The experimental points all satisfy this equation only for n = 1; that is, ab = cd for any two points on different curves where the color is the same.

DEPARTMENT OF CHEMISTRY THE CITY COLLEGE, COLLEGE OF THE CITY OF NEW YORK NEW YORK CITY, N. Y. RECEIVED FEBRUARY 11, 1941

# The Fungistatic Properties of Binary Fatty Acid Mixtures

By Charles Hoffman, T. R. Schweitzer and Gaston Dalby

The fungistatic properties of the fatty acids containing 1 to 14 carbon atoms have been reported.<sup>1</sup> This earlier study was made with each individual acid in as pure state as possible. In testing the fungistatic properties of a binary mixture it was found that the inhibiting power of the fatty acids was not additive, and that on the contrary there was a definite subtractive effect especially marked if the mixture consisted of a weak and strong fungistatic acid.

The method used was exactly as previously reported.<sup>1</sup> In the tables the inhibiting concentrations of the mixture are compared with the respective inhibiting concentrations of the pure acids at each pH value. Since a definite subtractive effect exists at pH 8 it is difficult to attribute

(1) Hoffman. Schweitzer and Dalby, Food Research, 4, 539 (1939).

ute this effect to any variation in the respective concentrations of non-ionized and ionized acid molecules. At pH 8 the acids are essentially in the form of the salts.

Acetic and caprylic acids form an interesting mixture in that acetic is a weak fungistat and caprylic a strong one.

#### TABLE I

### THE FUNGISTATIC PROPERTIES OF MIXTURES OF ACETIC AND CAPRYLIC ACIDS

Case 1, 50% acetic and 50% caprylic (all percentages are molar). Case 2, 25% acetic and 75% caprylic. Case 3, 75% acetic and 25% caprylic.

٥H	Molar concn. <sup>a</sup> of mix- ture for inhibition	Calcd. conen. <sup>a</sup> acid p in inhi mix Acetic	molar of each resent ibiting ture Caprylic	Molar o of pur for inh Acetic	% Effective- ness of caprylic							
Case 1												
<b>2</b>	0.0049	0.0025	0.0025	0.035	0.0012	48						
<b>5</b>	. 006 <b>9</b>	.0035	.0035	.0875	.0018	51						
6	.0294	.0147	. 0147	ineff.	.0080	54						
7	.0784	.0392	.0392	ineff.	.0196	50						
Case 2												
<b>2</b>	.0020	.0005	.0015	.0350	.0012	80						
5	.0032	.0008	.0024	.0875	.0018	75						
7	.0320	. 0080	.0240	ineff.	. 0190	79						
8	.090	.022	.067	ineff.	.048	72						
Case 3												
<b>2</b>	.0049	.0037	.0012	.0350	.0012	100						
5	.0111	.0083	.0028	.0875	.0018	64						
7	.135	. 10 <b>1</b>	.034	ineff.	.0190	56						

<sup>a</sup> The molar concentration is the total concentration and includes both the dissociated and undissociated fatty acid molecules.

When acetic and caprylic acids are present in equimolecular proportions approximately 50% of the stronger fungistat, caprylic, is inactivated. Where caprylic is present in 75% molar concentration, approximately 25% is inactivated. In case 3, where acetic acid is present in greater concentration than caprylic, the per cent. of caprylic inactivated is not so regular over the various pH values.

The subtractive effect of a weak fungistat on a

### TABLE II

THE FUNGISTATIC PROPERTIES OF AN EQUIMOLECULAR MIXTURE OF ACETIC AND PROPIONIC ACIDS

¢H	Molar concn. <sup>4</sup> of mix- ture for in- hibition	Calcd. molar concn. <sup>a</sup> of each acid present in inhibiting mixture Acetic Propionic		Molar concn. <sup>4</sup> of pure acid for inhibition Acetic Propionic		% Ef- fective- ness of pro- pionic
<b>2</b>	0.0164	0.0082	0.0082	0.0350	0.0054	65
5.5	0.1190	0.0595	0.0595	ineff.	0.0405	6 <b>8</b>

<sup>a</sup> The molar concentration is the total concentration and includes both the dissociated and undissociated fatty acid molecules stronger one is also shown by the adjacent homologs, acetic and propionic acids.

The definite subtractive effect exerted by a weak fungistatic fatty acid on a strongly fungistatic fatty acid suggests (1) the presence of a molecular aggregate at the cellular interface similar to that of a dimer in non-polar solvents or (2) the adsorption of one acid molecule on the cellular surface blocks the adsorption of another molecule which is statistically equivalent to the acids acting in pairs.

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## Note on the System Sodium Dichromate-Water

# BY WINSLOW H. HARTFORD

While the solubility of this salt has been investigated,<sup>1</sup> the equilibrium conditions at temperatures below  $0^{\circ}$  have received no attention. The accompanying data and graph represent several types of measurements on sodium dichromate.

**Experimental.**—The sodium dichromate used was C. P. granular dihydrate, containing a small amount of the anhydrous salt. It analyzed: Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O, 100.3%; Cl, <0.005%; SO<sub>4</sub>, 0.003%; Ca, <0.003%; Al, <0.002%; insoluble, 0.005%. The methods recommended by the *American Chemical Society* for potassium dichromate<sup>2</sup> were used in determining impurities, while the dichromate content was determined by electrometric titration.<sup>8</sup> All solutions were checked for dichromate content by electrometric titration.

Data for solutions saturated with either of the solid phases below 0° were determined by study of the freezing point in a 500-ml. container provided with agitator, using a 4-liter insulated jug containing alcohol to which solid carbon dioxide was added as needed for cooling. A calibrated low-temperature thermometer was used, and readings were taken on both rising and falling temperatures. Good thermal breaks were obtained and an accuracy of about



Fig. 1.—O, Hartford; ●, Mylius and Funk; ▽, Schreinemakers; +, Gerassimov; □, Rakovskii and Nikitina; △, Robertson; ◇, Yuskevich and Karzhavin.

 (a) Mylius and Funk, Wiss. Abhandl. physik-tech. Reichanstalt, **3**, 443 (1900).
(b) Schreinemakers, Z. physik. Chem., **55**, 71 (1906).
(c) Robertson, J. Soc. Chem. Ind., **43**, 334 (T) (1924).
(d) Yuskevich and Karzhavin, J. Chem. Ind. (U. S. S. R.), **3**, [14] 1119 (1926).
(e) Gerassimov, Z. anorg. aligem. Chem., **181**, 321 (1930); Trans. Inst. Pure Chem. Reagents (Moscow), **11**, 114 (1931).
(f) Rakovskii and Nikitina, *ibid.*, **11**, 5 (1931). References published prior to 1800 have not been used in this work.  $0.3^\circ$  in temperature and 0.2% in dichromate content was obtained.

Solubility above 0° was determined by rotating samples

(2) Committee on Analytical Reagents, American Chemical Society, Ind. Eng. Chem., 17, 756 (1925); Ind. Eng. Chem., Anal. Ed., 1, 171 (1929); 3, 221 (1931); 12, 639 (1940).

(3) Kelley and co-workers, Ind. Eng. Chem., 9, 780 (1917).