lower the surface tension of Nujol or hydrogenated tetraisobutylene. The measurements are hampered, however, by low solubility and a tendency to separate on cooling. In water, Woo's unpublished measurements show that they lower the surface tension from 72 to 31 dynes in extreme dilution, namely, 0.02 and 0.2% solutions, respectively, thereafter remaining constant up to 1% solution.

The sulfated sodium naphthenic or petroleum soaps supplied by the Sherwood Petroleum Company are oil-soluble, not water-soluble. They actually raise the surface tension of *n*-hexane from the value 20.2 to 20.4 or 20.5 for 10% solution and to 22.3 for 50% solution, thus giving a type II curve.

A number of especially interesting solutes of different types could not be tested on account of their insolubility, but a non-electrolytic detergent showed no appreciable lowering in Nujol although 14 and 24% solutions gave the small lowerings of 0.5 and 2.0 dynes. Butyric acid likewise is ineffective, the lowering being 0.5, 0.9 and 2.0 dynes for 1, 9 and 20% solutions, respectively. Lauric acid in 3% solution gave the distinctly greater lowering of 2 dynes. Triethanolamine oleate in 0.5 and 9% gave a lowering of 1 dyne and 2 dynes; thymotic acid in 1% solution 0.8 dynes; and stearic acid gave 1 dyne lowering for 0.7%. Calcium and zinc stearates have practically no effect.

It is evident that appreciable lowering and the production of a type III curve in these hydrocarbons require such a degree of polarity that the solute forms a strong electrolyte or colloidal electrolyte in water.

The only explanation to account for the minimum found in a type III curve is that put forward by McBain[3] based upon the electrical double layer. Now in the present non-ionizing solvents this would have to be a condensed Helmholtz double layer of the classical type instead of the partly diffuse type existing in water. However, the Helmholtz double layer is adequate for explaining lowering of surface or interfacial tension.

These novel observations evidently should suggest many other approaches and experiments to investigators in this field and are significant as a guide to other phenomena in hydrocarbon systems.

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(3) McBain, Ford and Wilson, *Kolloid. Z.*, **78**, 1 (1937).

Alkanolamines. VIII. Reaction of Ethanolamines on *p*-Nitrobenzoic Acid

BY M. MELTSNER, DANIEL GREENFIELD AND HARRY ROSENZWEIG

In some of the previous papers of this series[1,2,3,4] it was shown that alkanolamines, but not their salts, may reduce an aromatic nitro group and that the unreduced and reduced compounds may form addition compounds with the alkanolamines. This is now confirmed by the following experiment on the action of ethanolamines on *p*-nitrobenzoic acid.

Experiment I.—One mole of ethanolamine and one mole of *p*-nitrobenzoic acid were heated at 100° for four hours. The brown solid residue, after extraction with ether and chloroform, was crystallized from alcohol. A white compound of m. p. 168° was obtained. An ether extraction of this substance from dilute hydrochloric acid yielded *p*-nitrobenzoic acid while the hydrochloric acid layer on evaporation gave a white solid, m. p. 82°, corresponding to ethanolamine hydrochloride. The white compound was therefore an addition product, $NO_2C_6H_4COOH\cdot NH_2CH_2CH_2OH$.

Similarly diethanolamine yielded $NO_2C_6H_4COOH\cdot NH(CH_2CH_2OH)_2$, m. p. 138°, and triethanolamine yielded $NO_2C_6H_4COOH\cdot N(CH_2CH_2OH)_3$, m. p. 116°.

Experiment II.—One mole of ethanolamine was refluxed with one mole of *p*-nitrobenzoic acid in an oil-bath for two hours. The reaction mixture was treated several times with cold water and filtered. The filtrate was evaporated to dryness on the water-bath and the residue extracted with alcohol. Evaporation of the alcohol gave a solid identified as *p*-aminobenzoic acid by its positive test for the amino group, its melting point (186°) and the melting point of the dinitrobenzoate (195°). The dry residue, insoluble in alcohol, was recrystallized from hot water and gave $NO_2C_6H_4COOH\cdot NH_2CH_2CH_2OH$.

The residue, insoluble in cold water, was extracted with chloroform to isolate some more *p*-aminobenzoic acid and then recrystallized from hot water. There was obtained in large amounts a pale yellow compound, m. p. 130°, which was identified as the addition product of two moles of ethanolamine and one mole of azoxybenzoic acid: N calcd., 13.72; found, 13.64. The compound can be reduced to yield *p*-aminobenzoic acid. Hydrolysis of the compound with alkali gave *p,p'*-azoxybenzoic acid which was identified by means of its ethyl ester. Hydrolysis of the compound with hydrochloric acid yielded monoethanolamine hydrochloride.

Experiment III.—Four moles of diethanolamine and one mole of *p*-nitrobenzoic acid were heated for two hours at 180°. The reaction mixture was washed with chloroform, extracted with hot water and filtered. On cooling, yellow crystals are obtained and identified as *p*-aminobenzoic acid.

(1) Meltsner, *et al.*, THIS JOURNAL, **57**, 2554 (1935).
(2) Kremer, *ibid.*, **59**, 1681 (1937).
(3) Kremer and Kress, *ibid.*, **60**, 1031 (1938).
(4) Meltsner, *et al.*, *ibid.*, **60**, 1236 (1938).

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The Oxidation–Reduction Potential of Vitamin K_1

BY BYRON RIEGEL, PERRIN G. SMITH[1] AND CARL E. SCHWEITZER

Because of the increasing physiological importance of oxidation–reduction systems, the oxidation–reduction potential of pure synthetic vitamin K_1 has been determined. Such potentials are also important for elucidating the structures of quinones and for this reason, at the suggestion of Professor L. F. Fieser, we first measured the potential of the vitamin in potent alfalfa concentrates. This value, 358 mv., in conjunction with the C-H analysis and the absorption spectrum first published by Dam, Karrer, *et al.*,[2] provided strong evidence that vitamin K_1 was a 2,3-dialkyl-1,4-naphthoquinone. This was evident from the values of Table I.

TABLE I

	E_0 in mv.
1,4-Naphthoquinone	484[a]
2-Methyl-1,4-naphthoquinone	408[a] 422[b]
2,3-Dimethyl-1,4-naphthoquinone	340[a]

[a] L. F. Fieser and M. Fieser, THIS JOURNAL, **57**, 491 (1935).

[b] J. W. H. Lugg, A. K. Macbeth and F. L. Winzor, *J. Chem. Soc.*, 1457 (1936).

This information together with other known facts led to the prediction of the first specific structure[3] for vitamin K_1 which later proved to be correct.

Karrer and colleagues[4] have reported the oxidation–reduction potential $E_m = +5$ mv. for vitamin K_1. It is not absolutely clear, from their experimental data, how their value compares with other quinone potentials because they did not use the customary method. However, from a consideration of the *p*H of the solvent used it seems that their value of the oxidation–reduction potential E_0 is about 400 mv. This estimation does not take into account a possible junction potential.

In the fractionation of alfalfa extracts it was found that a stock solution of 3% vitamin K_1 concentration had the best keeping qualities and gave the most reliable potentials over a period of time. More highly refined concentrates showed considerable variation in both bioassay and potential upon storage. Because of these variations and the occasional presence of other substances which affected the oxidation–reduction curve it seemed advisable to delay publication until the determination could be made on the pure vitamin.

The length of time required to establish equilibrium (in some instances twenty-four hours for the complete titration) in the case of the refined concentrates made it necessary to employ a stable reference electrode. The Ag–AgCl electrode was found to be very suitable for this purpose since it is stable for at least several weeks.

The oxidation–reduction potential of pure vitamin K_1 was found to be 363 mv. at 20°.

Experimental

The preparation of the vitamin K active concentrates[5] from alfalfa has been described. The synthetic vitamin K_1 used in this work was prepared according to the method of Fieser.[6]

In the solvent used, 95% ethanol 0.2 *N* in hydrochloric acid and 0.2 *N* in lithium chloride, the positive potential of the Ag–AgCl electrode against the hydrogen electrode in the same solvent was approximately 200 mv. This value varies somewhat in different lots of the same solvent depending on the exact chloride ion concentration. However, it is necessary to determine the potential against the hydrogen electrode only once for any one lot of solvent. In the solvent used for the determination of the potential of the pure vitamin the Ag–AgCl electrode gave a value of +203 mv. against the hydrogen electrode. The solubility of the vitamin at room temperature was found to be about 5 mg. per ml. in the above solvent. This same solvent was used to prepare the very dilute solution of titanium trichloride used in the potentiometric titrations. Both platinized and bright platinum electrodes were used and gave the same results although the platinized electrodes seemed to reach equilibrium more rapidly.

Two independent determinations, checking within 1 mv., gave a potential of +160 mv. for the vitamin against the Ag–AgCl electrode. Thus the vitamin potential, E_0, against the hydrogen electrode is 363 mv. All measurements were made at 20°.

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(1) Abbott Research Fellow.

(2) H. Dam, A. Geiger, J. Glavind, P. Karrer, W. Karrer, E. Rothschild and H. Salomon, *Helv. Chim. Acta*, **22**, 310 (1939).

(3) L. F. Fieser, D. M. Bowen, W. P. Campbell, M. Fieser, E. M. Fry, R. N. Jones, B. Riegel, C. E. Schweitzer and P. G. Smith, THIS JOURNAL, **61**, 1925 (1939).

(4) P. Karrer and A. Geiger, *Helv. Chim. Acta*, **22**, 945 (1939).

(5) B. Riegel, C. E. Schweitzer and P. G. Smith, *J. Biol. Chem.*, **129**, 495 (1939).

(6) L. F. Fieser, THIS JOURNAL, **61**, 3467 (1939).