ESTIMATION OF β-NAPHTHOL IN ALUMINIUM SOAP

by

S. C. Ganguli, B. K. Datta Gupta and C. P. Ramaswami

Explosives Research & Development Laboratory, Kirkee

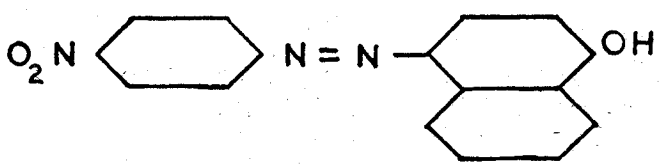
ABSTRACT

A method is described for the determination of β-naphthol in aluminium soaps based on the formation of dye para red by coupling the former with diazotised p-nitraniline under controlled temperature and pH and estimation of the colour developed after extraction with alcoholic NaOH. The method has been found to be reasonably accurate under the experimental conditions.

Introduction

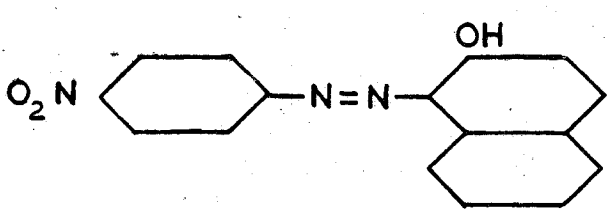
β-naphthol is often added as an anti-oxidant to prevent deterioration of the unsaturated acid molecule during the preparation of aluminium soap of pure or mixed fatty acids. Its amount in the final soap is critical both for stability and gelling properties.

Liebmann[1] developed a method for the estimation of α-naphthol in β-naphthol by coupling the former with diazotised p-nitraniline in acid medium with the formation of a red compound.



I

He took advantage of the fact that whereas α-naphthol couples with diazotised p-nitraniline in acid medium, β-naphthol couples with p-nitranine at a higher pH with the formation of the dye para red.



II

In the method for the determintation of β-naphthol in aluminium soaps described here, advantage has been taken of the above observation by Liebmann regarding the pH of coupling, and the fact that whereas (II) is insoluble

in aqueous NaOH and soluble in alcoholic NaOH, most of the colouring matters formed by the interaction of other ingredients present in aluminium soap are soluble in aqueous NaOH.

Experimental

Preparation of diazotised p-nitraniline—1·38 gms of p-nitraniline were stirred with 12 ml of water and 9 ml 1:1 H_2SO_4 (1·84) —crushing lump and warming to help solution if required. The solution is then cooled to below 5°C and 10 ml of 1 N $NaNO_2$ solution (Temp. below 5°C) is added slowly with stirring regardless of the free amine that separates out. The amine re-dissolves as the diazonium salt. The solution is tested with starch iodide paper for excess $NaNO_2$. If there is no excess, further quantity of $NaNO_2$ solution is added drop by drop till an excess is indicated. It is essential to have some excess of $NaNO_2$ for preventing the precipitation of unreacted p-nitraniline during dilution in the later operations. Too much excess is also to be avoided as otherwise nitrosonaphthols may be formed. The solution is now diluted to 50 ml, filtered, diluted to 100 ml and preserved at low temperatures. (Below 5°C).

Preparation of control aluminium soap without β-naphthol by metathetic process

A 10 per cent solution of a neutral sodium soap of the fatty acids of which an aluminium soap is required is slowly added to a 5 per cent alum solution at room temperature in the ratio Na : Al=2 : 1. The pH value of the mixture is adjusted to 5·0 to 5·8 by neutralising with 10 per cent Na_2CO_3 solution, heated at 60°C for maturing, filtered, washed free from sulphates and dried in a current of hot air at 80°—90°C.

Standardisation

All operations except photometric comparison are to be carried out with solution cooled to 15°—20°C.

0·5 gms of aluminium soap prepared in the laboratory without β- naphthol are dissolved in toluene with a few ml alcohol to obtain a thin uniform solution and diluted to 100 ml with toluene in a 500 ml separating funnel. 5 ml of a 0·008% W/V solution of β-naphthol in toluene is added and thoroughly mixed by shaking. This is followed by a mixture of 1 ml diazotised p-nitraniline and 10 ml buffer solution (20% W/V sodium acetate trihydrate —pH 5·9). The funnel is shaken vigorously with occasional immersion in ice water to avoid rise in temperature and concomitant secondary reactions.

The soap is then decomposed with 1 ml Conc. HCl and the lower aqueous layer drained off. Operation to be repeated once or twice but too much acid is to be avoided as it may affect the azo colour.

10 ml aq. NaOH (5% W/V) is now added to the solution in the separating funnel and shaken well. 20 ml water is now added, gently shaken and the lower aqueous layer drawn off without losing any of the soap.

20 ml of hot water (80°—90°C) and 1—2 ml aq. NaOH are now added shaken well and the lower aqueous layer drained off as soon as separation occurs. The operation may have to be repeated once for removing nearly all the soap.

50 ml cold petroleum ether (40°—60°C) is added to mixture in the separating funnel which is then washed with 20 ml portion of cold aqueous NaOH till the washings are clear.

The azo dye II formed by the reaction between β-naphthol and diazotised p-nitraniline is now extracted from the toluene petroleum ether in the separating funnel by alcoholic NaOH (IN in 60% alcohol) till further colour is not extracted—This requires about 100 ml. The combined extract is diluted to 200 ml with alcoholic NaOH. This constitutes a standard solution representing 0·002 mg β-naphthol/ml. Aliquote portions of this standard solution are diluted with alcoholic NaOH so as to obtain 50 ml solutions containing 0·0015, 0·001, 0·0005 and 0·00025 mg β-naphthol/ml. The absorption is now read in an Adam Hilger Spekker Absorptiometer with Ilford Filter No. 604 transmitting 500—550 mμ. in a 1 cm cell. The initial point is taken with water as 1·00 drum reading. A standard absorption curve is now obtained (Fig. 1).

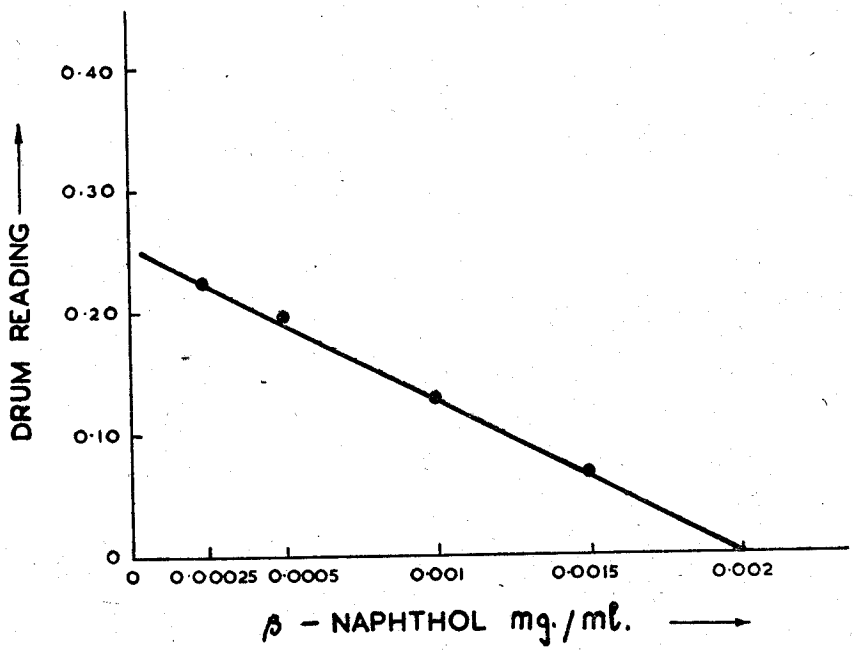


FIG. 1

Estimation

0·5 gms of aluminium soap whose β-naphthol content is to be estimated is treated exactly as under standardisation upto the stage of alcoholic NaOH extract except that the known quantity of β-naphthol is not added. If the β-naphthol content of 0·5 gms of aluminium soap exceeds 0·4 mg, the alcoholic NaOH extract should be suitably diluted so that not more than 0·4 mg β-naphthol is present in 200 ml of the final solution as Beer's Law is not obeyed beyond this region (Fig. 2). Similarly if the β-naphthol content of 0·5 gms of aluminium soap is less than 0·05 mg correspondingly larger quantities of sample will have to be taken (Fig. 3). The light absorption of the solution is read as in standardisation and the β-naphthol content read from the graph.

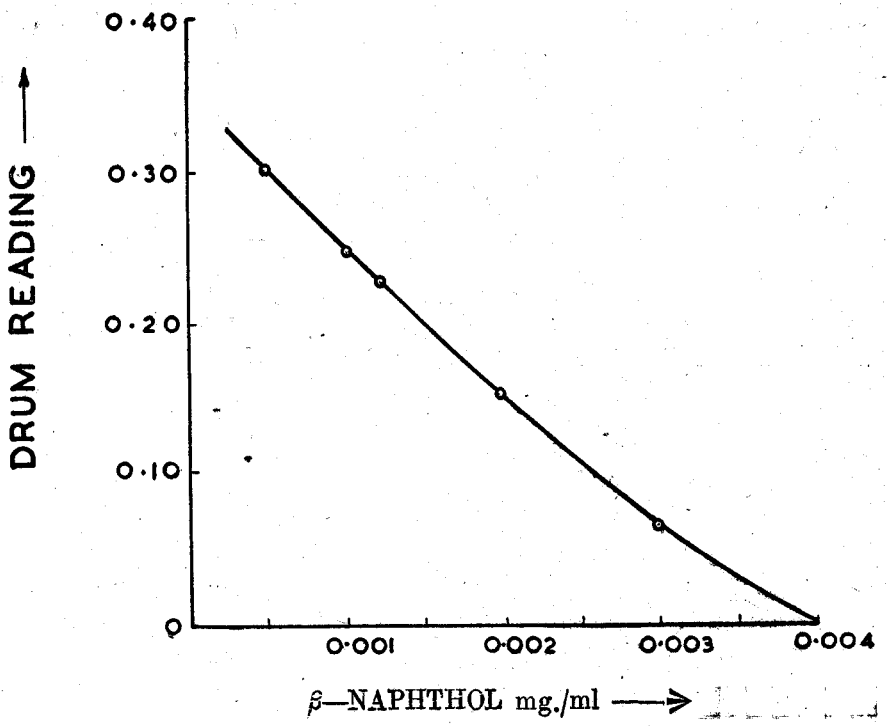


FIG. 2

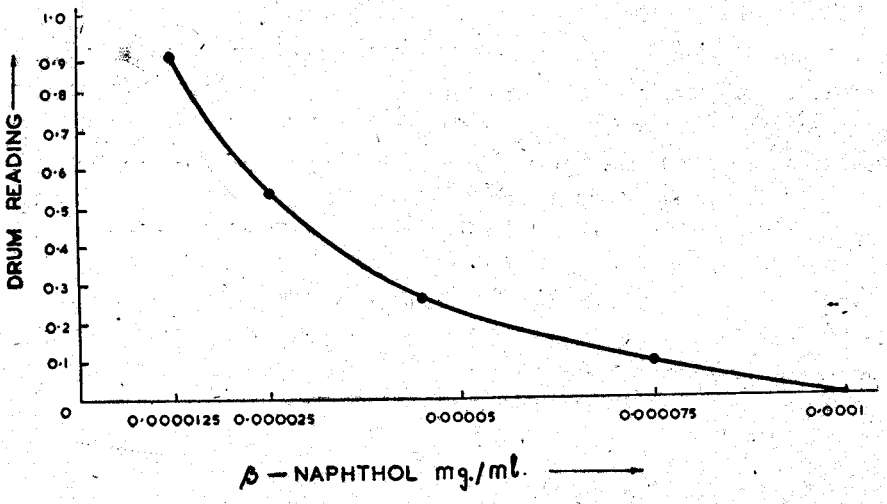


FIG. 3

Results

TABLE 1

Aluminium soap prepared in the laboratory without β-naphthol by the metathetic process and the β-naphthol content estimated after adding known quantities of β-naphthol to the soap.

Quantity of sample taken (gm)	Quantity β—naphthol added (mg)	Quantity β—naphthol estimated	Diff. (%)
0·25	0·000125	0·000123	—1·6
	0·000250	0·000250	..
	0·00050	0·000502	+0·4
	0·00100	0·000996	—0·4
0·50	0·000250	0·000248	—0·8
	0·000500	0·000500	..
	0·001000	0·000998	—0·2
1·00	0·00050	0·000498	—0·4
	0·00100	0·000998	—0·2

TABLE 2

Aluminium soap of normal supply

The original β-naphthol content estimated, known quantity of β-naphthol added and the recovery of added β-naphthol determined.

Sample No.	Original β—naphthol %(a) (estimated)	Added β—naphthol % (b) (Actual)	Total a+b	Found a+b
1	0·18	0·20	0·38	0·38
2	0·195	0·10	0·295	0·29
3	0·23	0·07	0·30	0·29

TABLE 3

Results of repeat determination of β-naphthol in some samples of aluminium soap of normal supply

Sample No.	% β-naphthol
1	0·18, 0·18, 0·175
2	0·20, 0·19, 0·195
3	0·09, 0·08, 0·09
4	0·20, 0·22, 0·21
5	0·16, 0·16, 0·155
6	0·23, 0·21, 0·22

Discussion

The standardisation has been carried out after the requisite quantity of β-naphthol has been added to a solution of aluminium soap and not to a solution of β-naphthol only. It has been found that the dyestuff is not completely extracted by alc. NaOH from the toluene-petroleum ether layer unless some soap is present. Any soap could have been added, but the process described has the additional advantage of serving as a blank.

It will be seen from Fig. 1 that Beer's Law is strictly obeyed by the alcoholic NaOH extract of dye II wi hin the concentration region 0·002 mg/ml to 0·00025 mg/ml.

Acknowledgement

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Reference

1. Liebmann., *J. Soc. Chem. Industry*, **16**, 294, 1897.