A NOTE ON THE PREVENTION OF CORROSION OF BRASS CONDENSER TUBES

N. SUBRAMANYAN, K. BALAKRISHNAN, PL. ANNAMALAI AND B. SATHIANANDHAM

Central Electrochemical Research Institute, Karaikudi

INTRODUCTION

IN equipment meant for the transfer of heat from one medium to another as in heat-exchangers or condensers, the condenser tubes are mostly made of copper-base alloys, like Admiralty metal and cupro-nickel, because of their high thermal conductivity and good mechanical strength. However, even such alloys are not exempt from corrosion, which can take different forms. Homogeneity of the tube-material is very important and among the brasses the 70% copper/30% zinc alloy is a single (alpha) phase solid solution[1] and is generally preferred to Muntz metal (60% copper/40% zinc alloy) which consists of two phases (alpha brass and beta brass) and is, therefore, more vulnerable to corrosion, though mechanically stronger than the single phase alloy.[2] However, even Admiralty brass containing 70% copper/29% zinc/1% tin is reported[3] to have occasionally undergone longitudinal splitting due to internal stresses. Aluminium-brass containing 2% aluminium in brass containing 76% copper is said to be used extensively in marine condensers and in steam condensers of tide-water power stations, where the high velocities of the circulating water and air-bubble impingement may have a severe wearing-out action on Admiralty metal and other brasses.[4] But the failure of aluminium-brass tubes also in condensers in a thermal power station has been reported[5] and some of the condenser tubes had developed longitudinal, transcrystalline cracks as shown in Figs. 1 and 2.

Among the methods for making condenser tubes resistant to corrosion, metallic coatings like tin, lead and chromium have also been mentioned.[6] Nevertheless, the most common practice is to employ corrosion-inhibitors in the water itself or in the condensate in steam-raising equipment, with the object of neutralizing the effects of carbon dioxide and removing oxygen in the system. Hydrazine is commonly used for the removal of oxygen, while morpholine and cyclohexylamine are generally used[7] for neutralizing, though of late, some film-forming amines like octadecylamine are reported[8] to be successfully used.

In view of the possibility that the amines, generally considered as inhibitors may themselves promote corrosion by release of ammonia under the conditions of high temperature and pressure prevailing in thermal power installations, a study of the effects of amines as corrosion inhibitors for copper and copper base alloys has been taken up. Some interesting preliminary observations made on the action of cyclohexylamine and morpholine on aluminium-brass in the course of this study are reported.

FIGS. 1–2. Fig. 1. Longitudinal cracks observed in the aluminium-brass heat exchanger-tubes of the Thermal Power Station at Dhuvaran. Fig. 2. Transcrystalline cracks of the aluminium-brass heat-exchanger tubes, × 1300.

EXPERIMENTAL

(a) *Steam-test.*—Aluminium-brass (Copper 76·11, Zinc 21·31 and Aluminium 2·38%) coupons of size 5 cm. × 1 cm. of 18 BWG cut from the heat-exchanger tubes obtained from the thermal power station of the Gujarat Electricty Board at Dhuvaran, pickled in dilute sulphuric acid for two minutes and polished with cloth buff were used. LR grade amines

and double distilled water were employed to prepare the corresponding solutions, which were then saturated with air. A copper boiler was used to heat the water-inhibitor mixture and the steam was taken through a glass-condenser tube cooled by circulating water with provision to hang the metal coupon in duplicate. Another specimen was suspended above the condensing column so as to expose it to steam before condensation. The condensate was manually transferred to the boiler at frequent intervals. At the end of the tests, the specimens were dried and photographed and later, the weight-loss

observed, that in the absence of the inhibitors, the surface of the specimen is only very slightly tarnished, whereas with increasing amine contents the surface is tarnised at increased rates, resulting finally in a black film over the entire surface. The difference between a specimen exposed to condensate alone and that to condensate containing 0·1% cyclohexylamine is brought out in Fig. 3.

The corrosion rates of aluminium-brass in steam condensates corresponding to different amine contents in the boiler-water are given in Table I.

TABLE I

S. No.	Composion*	pH	Condition	Weight loss in mgm./ 10 cm.$^{-2}$ per 150 hr.
1	Steam	6·8	Dry	4·3
2	Steam	6·8	Condensate	2·6
3	Steam + 0·001% CHA	8·0	Condensate	2·9
4	Steam + 0·005% CHA	9·6	Condensate	2·4
5	Steam + 0·1% CHA	10·6	Condensate	11·0
6	Steam + 0·1% morpholine	8·9	Condensate	2·5
7	Steam + 0·1% morpholine	··	Dry	1·8
8	Steam + 1·33% morpholine	10·45	Dry	3·2
9	Steam + 1·33% morpholine	10·45	Condensate	9·0

* The amine dosages are with reference to the boiler-water.

was determined after cleaning them in 5% sulphuric acid.

(b) *Polarization Studies.*—Aluminium-brass coupons of the size 12 mm. × 12 mm. with a stem of 20 mm. were cut from the heat-exchanger tubes and mounted in a glass-tube. The unwanted area of the specimens was marked off with bee's wax-resin mixture or with Araldite resin. These electrode-specimens were prepared in the same manner as under (a) above. AR grade sodium chloride and LR grade (BDH) amines were used in preparing the solutions. The solution was saturated with oxygen before starting the experiment and the polarization was carried out in a Pyrex glass cell with suitable ground glass joints for introducing the platinum auxiliary electrode, the working electrode and the Luggin capillary tube to connect the reference electrode. The current needed was drawn from a 90 V battery through suitable high resistances in series and the experiments were carried out at room temperature (≈ 35° C.).

RESULTS AND DISCUSSION

(a) Steam-test

At the end of 150 hours of exposure of the specimens to condensing steam, it is

Consistent with the surface-tarnishing, it can be seen that the addition of excess of the amines does not help in bringing down corrosion, but on the other hand, accelerates it at increased concentrations, though the pH of the condensate has been raised to values in the range 8·0–10·6. This would indicate that though the amines are able to take care of any acidic constituent like carbon dioxide in the steam or in the condensate, they may have a deleterious effect on brass, perhaps, by aiding the anodic dissolution in the presence of air or oxygen.

The nature of the film on the specimens was examined to see whether it was hydrophobic or hydrophilic. It was found that at all the concentrations of cyclohexylamine employed the film was hydrophilic. But it was interesting to observe that in the case of morpholine, a hydrophobic film was obtained at a concentration of 0·10%.

However, even with morpholine at higher concentrations, the film formed was not hydrophobic (Fig. 4).

(b) Polarization Studies

Galvanostatic measurements.—The polarization behaviour of aluminium brass in 0·01 N

sodium chloride solution containing different amounts of cyclohexylamine (CHA) and
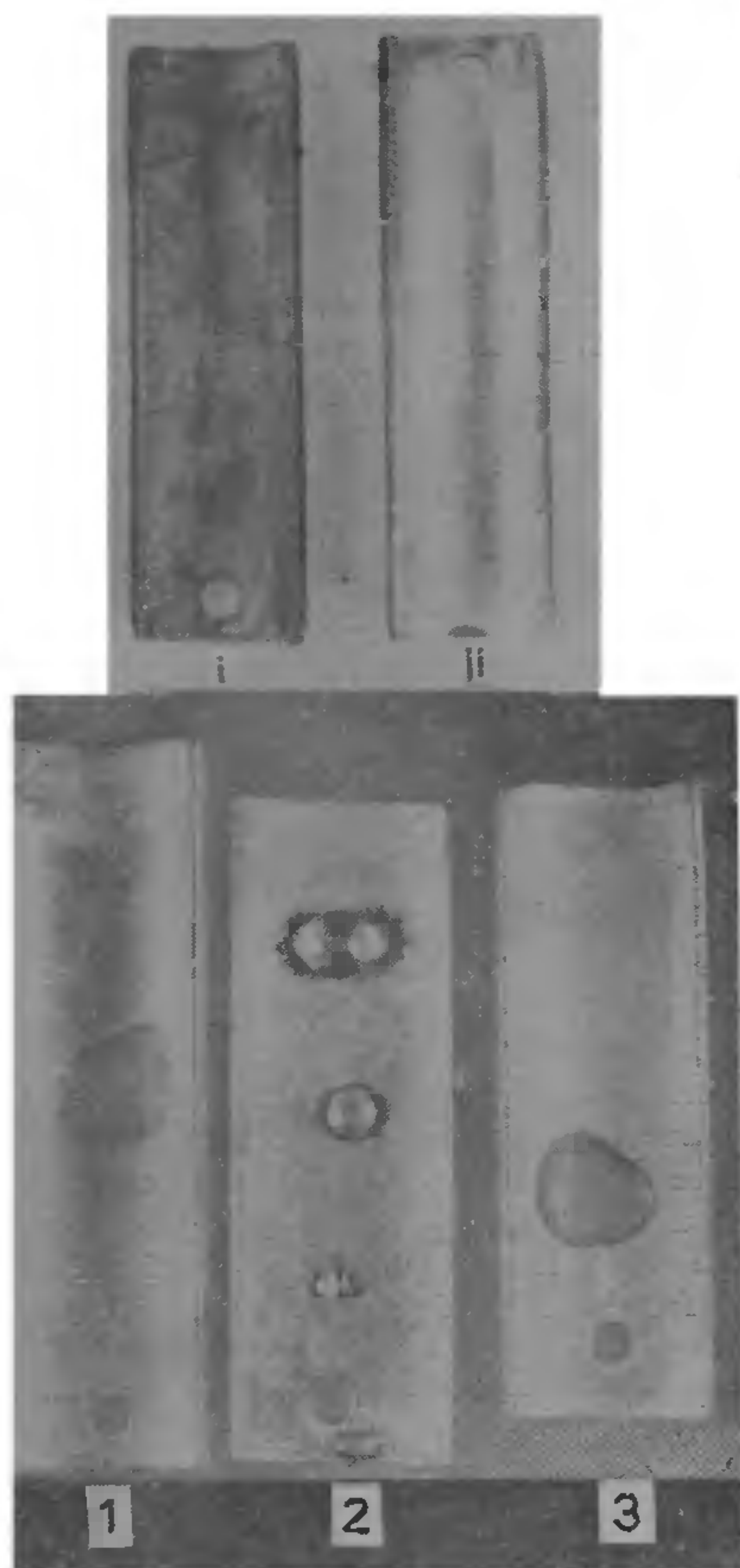

FIG. 3-4. Fig. 3. Aluminium-brass coupons, exposed to condensate. (i) Steam *plus* 0·1 % cyclohexylamine. (ii) Steam containing no amine. Fig. 4. Nature of the corrosion product on aluminium-brass after exposure to condensates containing amines. (1) 0·1 % CHA; (2) 0·1 % morpholine and (3) 1·33 % morpholine.

morpholine at room temperature are shown in Figs. 5 and 6. In the case of 0·005% CHA, the anodic polarization behaviour is almost identical with that in sodium chloride whereas the cathodic polarization is slightly more than that in sodium chloride. When 0·1% CHA is employed, only the anodic polarization is increased appreciably. In the case of morpholine the anodic polarization is enhanced to a much greater extent than in the case of CHA. The slight increase in cathodic polarization

observed (*see* Fig. 6) in the case of 0·1% morpholine disappears when the concentration

F G. 5. Anodic and cathodic polarization of aluminium brass in 0·01 N NaCl containing CHA. ⊙ → 0·01 N NaCl alone ; △ → 0·01 N NaCl + 0·005 % CHA ; ● → 0·1 % CHA.
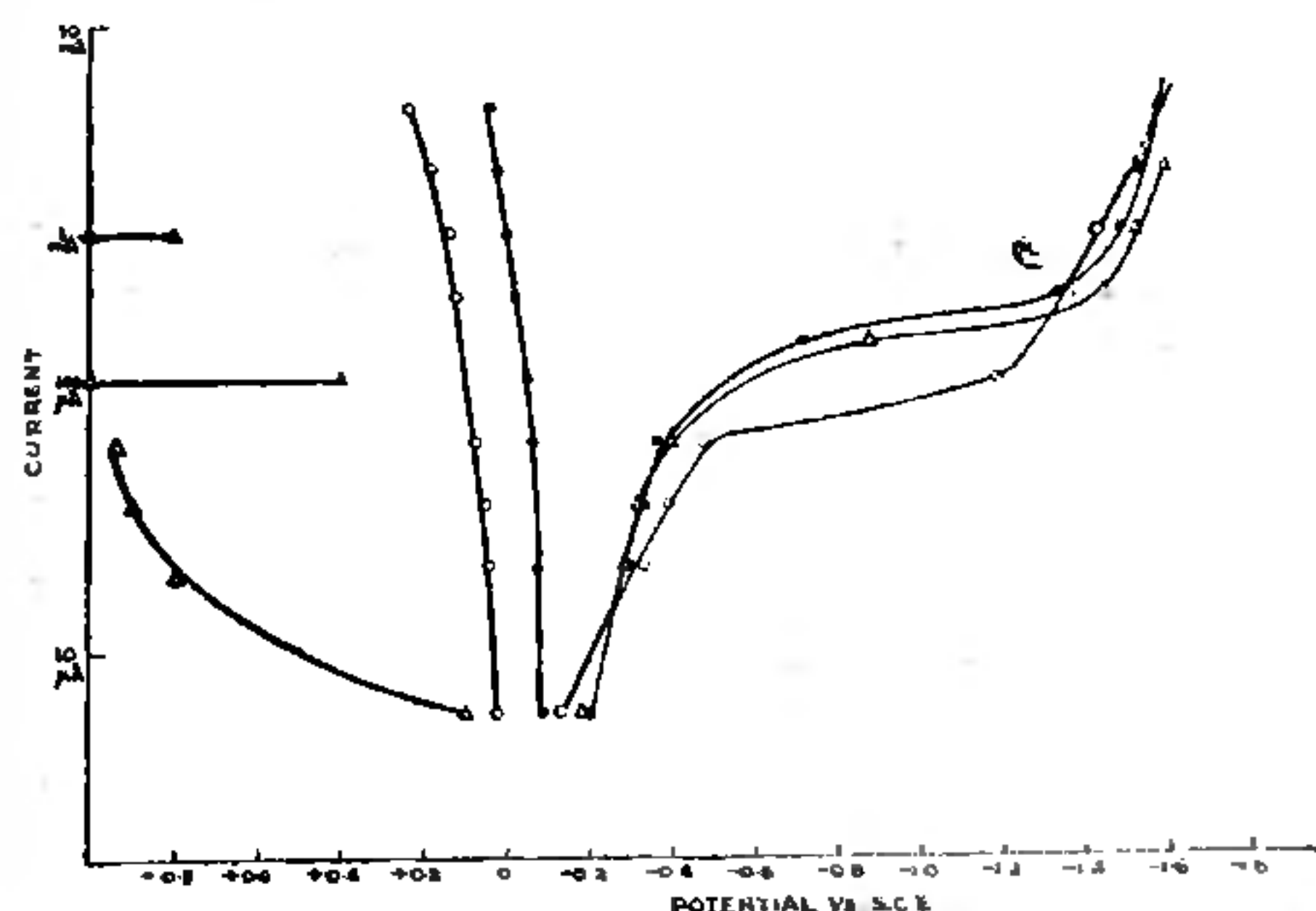

FIG. 6. Anodic and cathodic polarization of aluminium brass in 0·01 N NaCl containing morpholine. ● → 0·01 N NaCl alone ; ⊙ → 0·01 N NaCl + 0·1 % morpholine , △ → 0·01 N NaCl + 1·0 % morpholine.

is increased to 1%. It may be noted that these polarization experiments carried out at room temperature do not correspond to the increased corrosion rate of aluminium-brass observed at higher concentrations of the amines in steam tests (as shown in Table I). This may, perhaps, be attributed to either the action of ammonia liberated by degradation of the amine or to the accelerated attack of the specimen by the amines at the higher concentrations. This aspect of the problem is being investigated.

Conclusion

The preliminary experiments reported in this note bring out the following points : (1) Even morpholine can form a hydrophobic film on condenser tubes at a concentration of 0·10%. (2) At concentrations of 0·1% CHA or of 1·33% morpholine, the corrosion of aluminium-brass

in the presence of air in the steam is more than at lower concentrations.

ACKNOWLEDGEMENT

1. Bassett, H. N., *The Chemical Technology of Steam-raising Plant*, Edward Arnold & Co., London, 1931, p. 116.

2. Evans, U. R., *The Corrosion and Oxidation of Metals*, Edward Arnold & Co., London, 1960, p. 471.

3. —, *Ibid.*, p. 471.

4. Uhlig, H. H., *Corrosion Handbook*, John Wiley & Sons Inc., London, 1948, p. 558.

5. Private Communication from the Thermal Power Station, Dhuvaran of the Gujerat Electricity Board.

6. Bassett, H. N., *The Chemical Technology of Steam-raising Plant*, London, Edward Arnold & Co., 1931, p. 138.

7. Bregman, J. L., *Corrosion Inhibitors*, The Macmillan Co., New York, 1963, p. 55.

8. —, *Ibid.*, p. 57.

ROTATIONAL ANALYSIS OF SOME VISIBLE BANDS OF BiF MOLECULE

B. S. MOHANTY AND K. N. UPADHYA

Department of Spectroscopy, Banaras Hindu University, Varanasi-5, India

THE visible (A-X) band system of BiF has been investigated in emission in high frequency discharge by Howell[1] and in absorption by Morgan.[2] Rao and Rao[3,4] have made rotational analysis of 9 bands, (0,0), (0,1), (1,0), (0,2), (0,3), (2,0), (1,4), (2,5) and (3,3) of this system by photographing them in the second order of a 21 ft. concave grating spectrograph with a dispersion of $1 \cdot 25$ Å/mm. The present study of these bands was undertaken to determine more accurately the molecular constants of BiF by recording them under higher dispersion and resolution.

The bands were excited in a hollow cathode discharge. Exposures of six to eight hours on band is shown in Fig. 1. An inspection of the rotational structure of the bands reveals the presence of only two branches, P and R, well resolved even for low J values.

Rotational analysis of fifteen bands (0,0), (0,1), (1,0), (0,2), (0,3), (1,2), (2,1), (2,2), (3,3), (1,4), (2,5), (3,6), (3,7), (2,6) and (4,7) have been made by fixing the absolute J numbering by the criterion suggested by Youngner and Winnans.[5] The combination differences for common level are correct to $\pm \cdot 03$ cm.$^{-3}$ The $\Delta_2 F(J)/J + \frac{1}{2}$ plot is quite smooth upto low J values. Rotational constants for these bands are given in Table I.

TABLE I

Band assignment	$B_v{'}$ (cm.$^{-1}$)	$B_r{''}$ (cm.$^{-1}$)	$D_e{'}$ (cm.$^{-1}$) $\times 10^{-6}$	$D_s{''}$ (cm.$^{-1}$)	ν_0 (cm.$^{-1}$)
0, 0	0·2090	0·2295	0·25	0·27	22892·13
0, 1	0·2090	0·2279	0·25	0·22	22384·10
1, 0	0·2082	0·2295	0·25	0·27	23260·35
0, 2	0·2090	0·2264	0·25	0·17	21881·00
0, 3	0·2090	0·2247	0·25	0·18	21382·25
1, 2	0·2082	0·2264	0·25	0·17	22257·65
2, 1	0·2075	0·2279	0·26	0·22	23130·55
2, 2	0·2075	0·2264	0·26	0·17	22627·75
3, 3	0·2070	0·2247	0·26	0·17	22492·10
1, 4	0·2082	0·2233	0·25	0·17	21264·99
2, 5	0·2075	0·2217	0·26	0·18	21145·10
3, 6	0·2070	0·2206	0·26	0·18	21023·50
3, 7	0·2070	0·2191	0·26	0·18	20543·25
2, 6	0·2075	0·2203	0·26	0·18	20660·41
4, 7	0·2065	0·2191	0·26	0·18	20901·75

$r_e{'} = 2 \cdot 150$ Å; $r_e{''} = 2 \cdot 050$ Å.

concave grating spectrograph with a dispersion of $0 \cdot 33$ Å/mm. An enlargement of the (0, 0) Blue Rapid Plates were sufficient to record these bands in the second order of a 35 ft.