

SUMMARY OF RESULTS

Two types of magnetic memory phenomena in low fields have been observed in rocks. The first one consists of a transition from a constricted loop to a thick loop on subjecting the rock to a high field and back to a constricted loop after a certain recovery time. This may be called the 'Constriction memory effect'. The second type involves line to elliptic loop and back to line transition with a fixed recovery period and this may be called the 'Line memory effect'. For both these transitions the physical processes occurring in the rocks are probably the same and similar to those discussed by Brissonneau⁸ to account for the behaviour of the dilute solid solution of carbon in iron. He explains the variation of magnetization of iron with time due to reorientation of displaced Bloch walls from their initial equilibrium positions, through a process of diffusion. Considering the similarity of both the phenomena Neel¹⁰ suggests that the same process of displacement and diffusion of Bloch walls may be the cause for the memory effects observed in rocks. However, it seems that these phenomena could also be caused by interacting single domain grains of varying sizes. A wide range of grain sizes is possible in volcanic rocks either due to rapid cooling or by slight alteration which may break down some of the original multidomain

grains into smaller single domain grains, whose relaxation time is highly dependent on the size.¹¹ Thus, the presence of single domain grains of different relaxation times, in principle, can cause a variation of the magnetization of a rock containing them.

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INDIRECT POLAROGRAPHIC DETERMINATION OF STABILITY CONSTANTS

III. CDTA Complexes

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THE usefulness of the indirect polarographic method for the determination of stability constants of metal ion complexes even when they are not reducible or irreversibly reduced at the dropping mercury electrode is being investigated.^{1,2} This paper reports the determination of stability constants of 1-2 diamino cyclohexane tetra acetic acid (CDTA) complexes of sodium and lithium using thallium as indicator ion.

EXPERIMENTAL

Current-potential curves were taken on a manual polarograph. All experiments were

carried out in 0.1M potassium nitrate at $30 \pm 0.5^\circ \text{C}$. A Cambridge Bench Type pH meter was used for pH measurements.

A standard solution of CDTA (M/s. Suhrid Gelgy Ltd.) was prepared by the method of Pribil *et al.*³ B. D. H. AnalaR samples of thallous sulphate, lithium nitrate and sodium nitrate were used for the preparation of standard solutions.

RESULTS AND DISCUSSION

A one-electron reversible wave with the half-wave potential at -0.4562 V vs. S.C.E., was

obtained for thallium in 0.1 M potassium nitrate. Polarograms of 0.6 mM thallium solutions were taken in 0.1 M CDTA medium, pH being varied by the addition of potassium hydroxide. The half-wave potentials, determined from log-plots, at different pH are given in Table I.

TABLE I

Half-wave potentials of thallium in CDTA at different pH

Tl=0.6 mM; CDTA=0.1M; KNO₃=0.1M; Capillary—1

pH	E _{1/2} - V vs. S.C.E.	i _d μA
7.72	0.5111	1.54
8.45	0.5306	1.41
8.77	0.5562	1.35
9.66	0.6122	1.26
10.94	0.6721	1.25
11.46	0.7036	1.25
13.50	0.7426	1.32

-(E_{1/2})_s=0.4562 V vs. S.C.E.; (i_d)_s=2.86 μA.

CDTA is present in solution as a mixture of H₄Y (Undiss), H₃Y⁻, H₂Y⁻², HY⁻³, and Y⁻⁴. The concentration of Y⁻⁴ can be calculated from the pH of the solution and the pK values of CDTA from the equation,

$$C_y = (Y^{-4}) \theta \quad (1)$$

where C_y is the total concentration of CDTA and

$$\theta = \frac{(H)^4}{K_1 K_2 K_3 K_4} + \frac{(H)^3}{K_2 K_3 K_4} + \frac{(H)^2}{K_3 K_4} + \frac{(H)}{K_4} + 1 \quad (2)$$

The co-ordination number was calculated as one and the stability constant of thallium-CDTA complex as 10^{5.84} using the equation

$$\Delta E_{1/2} = 0.06 \log K_c \frac{(id)_s}{(id)_c} - 0.06 \cdot p \log (Y^{-4}) \quad (3)$$

Sodium and Lithium-CDTA Complexes.—The half-wave potentials of thallium were measured in the presence of different concentrations of sodium (or lithium) nitrate and CDTA at pH above 13. CDTA exists as Y⁻⁴ at pH above 13, the pK₄ value being 11.70. The free ligand

concentration was calculated from a plot of the half-wave potentials of thallium vs. log (C_y/θ). The concentrations of free sodium ion and the complex could be calculated and the stability constant of the complex determined from

$$K_{NaY} = \frac{[NaY]}{[Na][Y]} \quad (4)$$

The stability constants of sodium and lithium complexes are given in Tables II and III. The log of the stability constants of the sodium-CDTA complex is 2.70 and that of lithium complex is 4.13.

TABLE II

Stability constants of sodium-CDTA complex

Tl=0.6 mM; pH≈13; Capillary—1;
Log K_{TlY}=5.84; (i_d)_s=2.86 μA;
NaNO₃+KNO₃=0.1 M

NaNO ₃ M	CDTA M	E _{1/2} - V vs. S.C.E.	i _d μA	Log K _{NaY}
0.10	0.02	0.5887	1.30	2.68
0.10	0.03	0.6010	1.35	2.71
0.10	0.04	0.6113	1.29	2.73
0.04	0.02	0.6222	1.26	2.66
0.08	0.02	0.5973	1.34	2.66

TABLE III

Stability constants of Lithium-CDTA complex

Tl=0.6 mM; pH≈13; Capillary—2; Log K_{TlY}=5.84;
(i_d)_s=2.80 μA

LiNO ₃ M	KNO ₃ M	CDTA M	E _{1/2} - V vs. S.C.E.	i _d μA	Log K _{LiY}
0.10	0.1	0.02	0.509	1.60	4.04
0.10	0.1	0.04	0.529	1.50	4.13
0.04	0.1	0.02	0.539	1.43	4.14
0.10	..	0.02	0.510	1.60	4.03

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