Evaluation of the diffusion coefficient of the zincate ion using a rotating disk electrode

ELISABETE JORGE PESSINE,[1] SILVIA M. L. AGOSTINHO, AND HÉLIO C. CHAGAS
Department of Fundamental Chemistry, University of São Paulo, CP 20780, Brazil

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Using a rotating Hg-film disc electrode, the diffusion coefficient of the zincate ion in a 1–4 M aqueous solution of NaOH was measured. Experiments covered a temperature range from 25 to 40°C. The experimental results are in agreement with the predictions of the Stokes–Einstein theory for diffusivity. The obtained Stokes radii decrease with increasing alkali concentration, but the ratio $D\eta/T$ is reasonably constant within the whole range of temperature investigated.

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Utilisant une électrode à disque tournant de mercure sous forme de film et opérant à des températures allant de 25 à 40°C, on a mesuré le coefficient de diffusion de l'ion zincate dans des solutions aqueuses de NaOH de 1 à 4 M. Les résultats expérimentaux sont en accord avec les prévisions qui peuvent être faites à l'aide de la théorie de diffusivité de Stokes et Einstein. Les rayons de Stokes qui sont obtenus diminuent avec une augmentation de la concentration en base; toutefois, le rapport $D\eta/T$ est raisonnablement constant sur tout l'intervalle des températures étudiées.

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Introduction

The electrochemical behaviour of zinc in alkaline aqueous media has been the subject of a relatively large number of investigations (1–6) due to the importance of this system for both industrial electrodeposition processes and high density electrical batteries. With regard to the latter, corrosion is one of the principal factors that restricts the application of the zinc–zincate system as an efficient energy source over very long periods of time. In the range of 1—10 M alkali, the predominant corrosion product is the complex ion tetrahydroxyzincate (7–9).

Many authors have observed that transport of the zincate ion from the electrode surface to the bulk of the solution is the rate limiting step in the process of zinc dissolution. Any kinetic study of the zinc–zincate system thus requires a knowledge of the diffusion coefficient (D) of the zincate ion. However, since the available literature data for the diffusion coefficient of zincate ion is both very scarce and discordant (10), many authors have employed only an order of magnitude estimate of the diffusion coefficient in the analysis of their kinetic studies (4, 11–13). Several factors account for the existence of discrepancies in the available diffusion coefficient data: (*a*) most of the published results are based on the polarographic method (10) in alkaline media, conditions under which the zincate ion presents maxima of the second kind created by kinetic factors owing to the movement of solution past the drop surface, and these maxima overestimate the limiting current; (*b*) the zincate ion is reduced at a very negative potential, restricting the utilization of certain types of solid electrodes. In this case the hydrogen evolution occurs at potentials near those of zincate reduction (due to the low hydrogen overvoltage) making the evaluation of the cathodic limiting current of the reduced ion difficult.

In the present work we report a determination of the diffusion coefficient of the zincate ion in alkaline medium using an amalgamated gold rotating disk electrode. The rotating disk electrode provides one of the most accurate electrochemical methods for evaluation of diffusion coefficients (14, 15) due in part to the fact that the method is based on an exact mathematical solution for the diffusive–convective problem, and that the electrode has a uniformly accesible surface. As pointed out by Opekar and Beran (16), this method offers additional advantages in relation to conventional polarography and other such methods. From the dependence of the limiting current on the angular velocity of the disk, it is possible to separate currents from two different processes when only one is diffusion controlled; this is the case for simultaneous reduction of the zincate ion and hydrogen evolution, the former being controlled by diffusion while the latter is chemically controlled at the same potential (13, 17). The use of an amalgamated gold rotating disk electrode further facilitates the determination of the limiting current for zincate ion reduction due to the high hydrogen overvoltage of mercury.

Experimental

All solutions were prepared using analytical grade reagents and triply distilled water. The zincate solutions (1–10 mM) were prepared by adding appropriate aliquots of an aqueous zinc sulfate stock solution ($ZnSO_4 \cdot 7H_2O$ in water) to NaOH solution (1–4 M). The solutions were deoxygenated with purified nitrogen prior to all measurements. Prior to amalgamation, the gold disk electrode (ϕ = 0.465 cm) was mechanically polished with emery paper and with chromic oxide (1–5 μ) and rinsed with water and ethyl alcohol. Simply placing mercury on the electrode surface and removing the excess by rotating the disk at 10 000 rpm (18) failed to give reproducible results. This problem was overcome by leaving the electrode immersed in mercury for several days. Prior to each experiment a new layer of mercury was added and the excess removed as before.

All experiments were performed at 25, 30, 35, and 40°C. Viscosities of the sodium hydroxide solutions were determined at the same temperatures. The electronic equipment and cell has been described previously (19). A saturated calomel – potassium chloride electrode was used as reference electrode and a platinum foil as the counter electrode.

Results

Voltammograms were determined for solutions containing 1, 2, 4, 6, 8, and 10 mM zincate ion in aqueous NaOH (1, 2, 3, and 4 M) at several temperatures (25, 30, 35, and 40°C) and at different angular velocities of the disk electrode ($f^{1/2}$ = 2, 3, 4, 5, 6, 7 Hz$^{1/2}$).

Figure 1 shows a typical I–V curve for the reduction of the zincate ion (A) and the hydrogen evolution (B) on the rotating

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[1] Comissão nacional de energia nuclear, Departamento de Metalurgia, Caixa Postal 11049. Pinheiros, São Paulo, Brazil.

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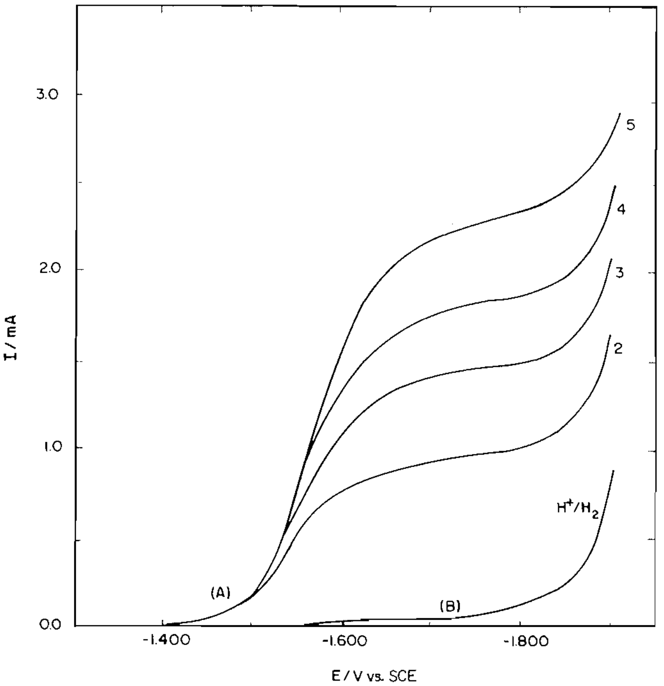

FIG. 1. Current–voltage relationships on Au-amalgamated disk electrode. (A) 2 mM $Zn(OH)_4^{2-}$ reduction. (B) Hydrogen evolution in free zincate ion solution. Both curves at 25°C, in 4 M aqueous NaOH with frequency of the rotating disk electrode varying from 2 to 5 $Hz^{1/2}$.

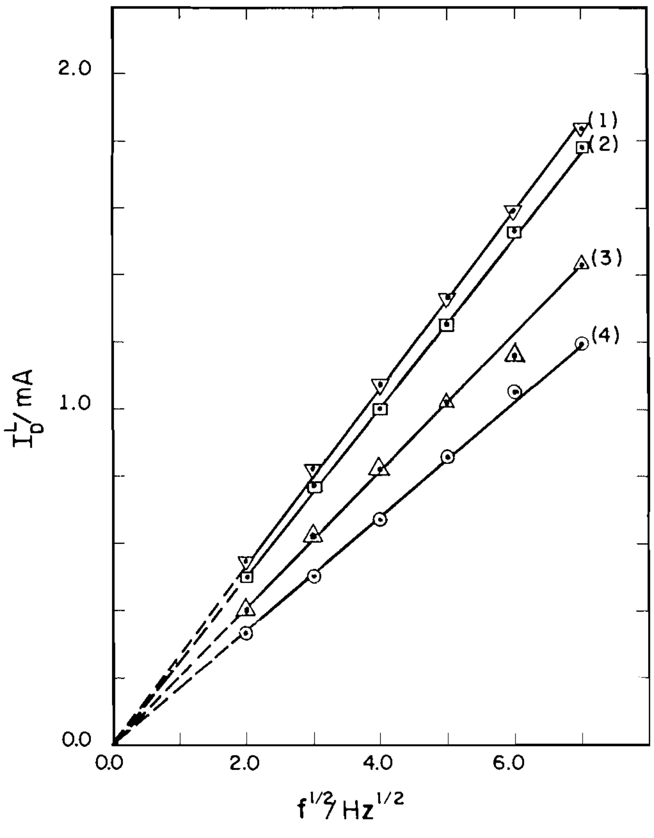

FIG. 2. Limiting diffusion current for $Zn(OH)_4^{2-}$: 8 mM deposition vs. $f^{1/2}$, varying NaOH concentrations. (1) 1 M, (2) 2 M, (3) 3 M, (4) 4 M. Area = 0.17 cm^2.

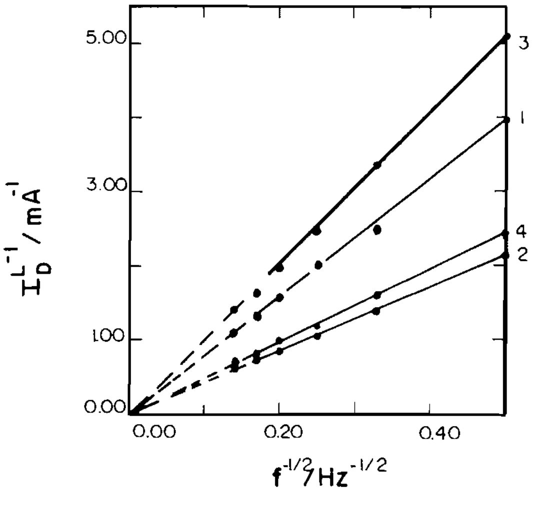

FIG. 3. Variation of $1/I_D^L$ with $f^{-1/2}$ at potential $E = -1.625$ vs. SCE and T = 25°C for: (1) 1 M NaOH, 4 mM $Zn(OH)_4^{2-}$; (2) 2 M NaOH, 8 mM $Zn(OH)_4^{2-}$; (3) 3 M NaOH, 4 mM $Zn(OH)_4^{2-}$; and (4) 4 M NaOH, 10 mM $Zn(OH)_4^{2-}$.

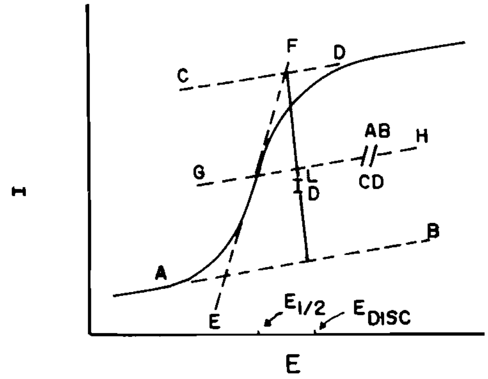

FIG. 4. Graphic evaluation of the limiting diffusion current without influence of H^+ ion discharge reaction and some residual current (22).

Hg-film disc electrode. Almost similar curves have been obtained in other situations studied here. This means that the wave of the zincate ion reduction begins at potentials less negative than the H^+ ion discharge waves. Thus, the influence of this last reaction on the measurements of the limiting diffusion current for the $Zn(OH)_4^{2-}$ reduction at the potential considered here is less pronounced.

Figure 2 demonstrates the linear dependence of the limiting diffusion current on the angular velocity at different concentrations of zincate ion in 1 M NaOH (25 ± 1°C). The same behaviour was observed for zincate solutions over the entire range of sodium hydroxide concentration and temperature studied. The diffusion coefficient of the zincate ion was calculated from these straight lines by linear regression using the Levich equation under diffusion control (20).

To compare the results obtained using both the Levich's diffusion and mixed controlled equations (20, 21), Fig. 3 has been constructed. Here are shown the variation of I^{-1} with $f^{-1/2}$ at E = 1.625 V vs. SCE (standard calomel electrode). This potential was taken after the determination of the limiting diffusion current of the $Zn(OH)_4^{2-}$ reduction using the scheme displayed in Fig. 4 (22). The calculated D values are listed in Tables 1 and 2.

TABLE 1. Average values of the zincate ion diffusion coefficient ($D \times 10^6$ cm^{2}s^{-1}) as a function of NaOH concentration and temperature*

NaOH concentration (M)	Temperature (°C) 25	30	35	40
1	4.90±0.20	5.40±0.30	7.10±0.10	6.70±0.10
2	4.60±0.20	4.70±0.20	4.90±0.20	6.30±0.10
3	3.80±0.10	4.00±0.10	4.80±0.20	6.40±0.10
4	3.10±0.10	3.40±0.10	4.10±0.20	5.50±0.20

*Each result of the table corresponds to an average of sixty measurements over a wide range of angular velocities of the disk electrode ($f^{1/2} = 2, 3, 4, 5, 6$ Hz$^{1/2}$) and zincate ion concentration (1, 2, 4, 6, 8, 10 mM); at least two independent voltamograms were constructed for each condition.

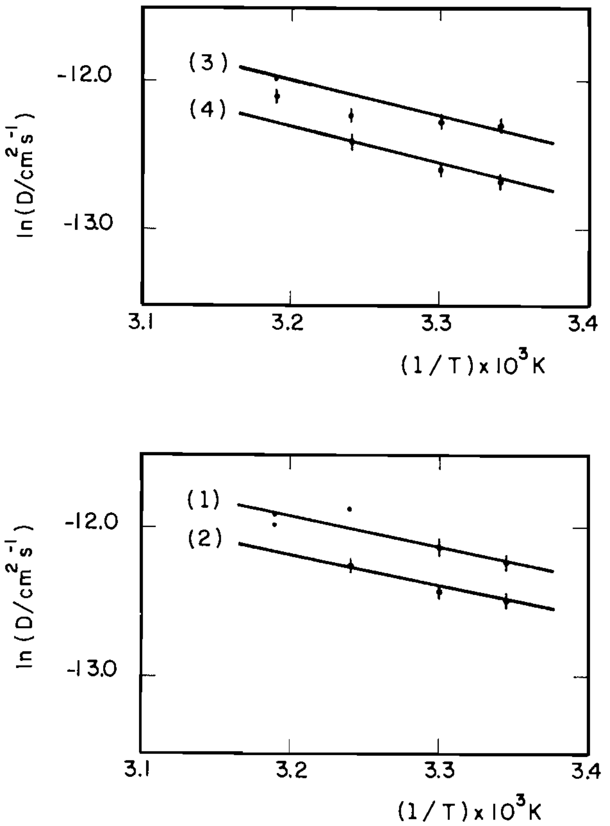

FIG. 5. Zincate ion diffusion coefficient vs. $1/T$ varying NaOH concentrations (1) 1 M, (2) 3 M, (3) 2 M, and (4) 4 M.

Figure 5 shows the temperature dependence of the diffusion coefficient at each sodium hydroxide concentration. From these data, we obtain the value of (10.00 ± 0.40) kcal/mol for the diffusion activation energy for zincate ion. The values of the solvodynamic radii (Table 3) were determined from the Stokes–Einstein equation (23).

Discussion and conclusion

Figure 6 compares the literature data for the zincate ion diffusion coefficient at 25°C in different alkaline media. The largest discrepancies in D values occur at alkali concentrations between 1 and 5 M. The polarographic values obtained by Dirkse (7) in KOH media are about five times larger than those of Meites (24) in NaOH media, a difference much too large to be ascribable to the change from potassium to sodium hydroxide.

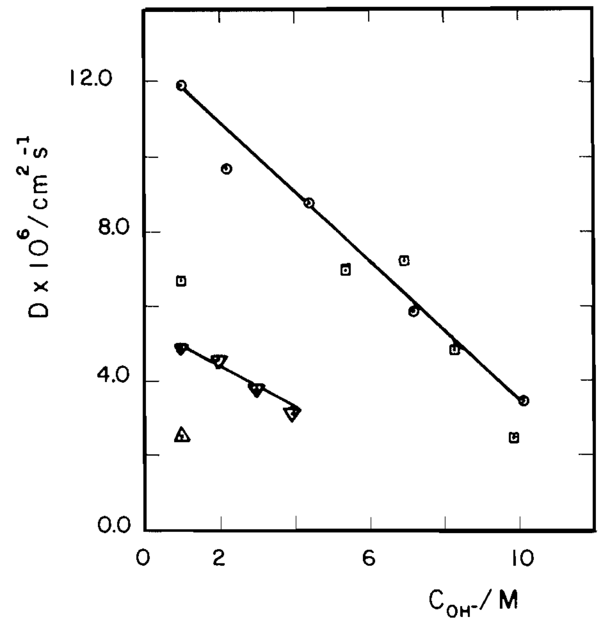

FIG. 6. Zincate ion diffusion coefficient at 25 C vs. OH$^-$ concentrations. (○, ⊡) McBrien and Cairns (10); (△) Meites (24); and (▽) authors' data.

Indeed, McBreen's and Cairns' values (10) for the same alkali concentrations, are intermediate between these former values.

The value of 9×10^{-6} cm^2/s was used by Popova *et al.* (12) without reference to its origin and is listed in the Bard Encyclopedia (25). The results of Nanis (cf. 10) using the capillary method, indicate that the diffusion coefficient is independent of the zincate ion concentration over the range of 0.02–0.4 M. Finally, mention must be made of the values determined by Payne and Bard (26) using chronocoulometry (6.11×10^{-6} cm^2/s) and polarography (6.40×10^{-6} cm^2/s). These values were not included in Fig. 6 because it is not clear which alkali concentration was employed.

The results presented in this work (Tables 1 and 2), obtained through a great number of experiments and employing one of the most accurate electrochemical methods, show an accuracy of about 4% for the value of the diffusion coefficient of the zincate ion.

Quickenden and Jiang (27) have reported that the use of the diffusion control, instead of the mixed control, Levich equation in the evaluation of the diffusion coefficient introduces dispersion in the results obtained using the rotating disc method. The

TABLE 2. $Zn(OH)_4^{2-}$ diffusion coefficient ($D \times 10^6$ cm^2 s^{-1}) as a function of aqueous NaOH concentration and temperature using mixed control Levich equation

NaOH concentration (M)	Temperature (°C)			
	25	30	35	40
1	4.80±0.30	5.50±0.20	6.90±0.10	6.70±0.20
2	4.60±0.20	4.70±0.10	5.10±0.20	6.10±0.10
3	3.80±0.20	4.10±0.10	4.80±0.10	6.00±0.20
4	2.90±0.10	3.50±0.10	4.20±0.20	5.10±0.20

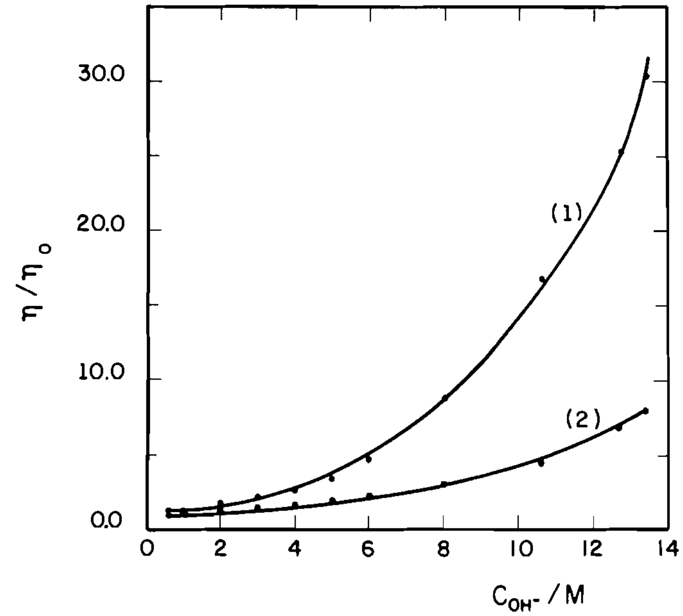

FIG. 7. Viscosity of (1) NaOH and (2) KOH vs. their concentrations.

TABLE 3. Solvodynamic radius of the zincate ion and the Stokes–Einstein coefficient

NaOH (M)	T(°C)	$(D\eta/T) \times 10^{10}$ (cm^{2}PK^{-1}s^{-1})	$r \times 10^8$ (cm)
1	25	1.97	3.71
	30	1.68	4.35
	35	1.94	3.75
	40	1.66	4.40
			$\bar{r}$ = 4.10±0.40
2	25	1.98	3.69
	30	1.73	4.22
	35	1.56	4.68
	40	1.89	3.85
			$\bar{r}$ = 4.10±0.40
3	25	2.04	3.58
	30	1.90	3.83
	35	2.02	3.62
	40	2.36	3.09
			$\bar{r}$ = 3.50±0.30
4	25	2.14	3.41
	30	2.06	3.54
	35	2.16	3.38
	40	2.51	2.91
			$\bar{r}$ = 3.30±0.30

zincate ion D values listed in Tables 1 and 2, evaluated with both Levich's equations varying over a narrow range, demonstrate that the nature of the surface reaction has more of an influence on the results than the way experimental data are treated.

The data in Table 3 indicate that the ratio $D\eta/T$ is temperature independent, within the experimental error, but increases with increasing sodium hydroxide concentration. The solvodynamic radius decreases about 20% in going from 1 to 4 M NaOH. Since both potentiometric and spectroscopic studies of the zincate ion system have shown that, in this hydroxide concentration range, the predominant species being tetrahydroxyzincate $Zn(OH)_4^{2-}$, the observed decrease in the solvodynamic radius can not be ascribed to a change in the complexation equilibria. We, therefore, attribute the decrease in the solvodynamic radius with increasing alkali concentration, to competition between solvation of $Zn(OH)_4^{2-}$, Na^+, and OH^-. This competition was especially important at sodium hydroxide concentrations above 2 M (Fig. 7). Indeed, at 4 M alkali there are only seven water molecules available for supporting electrolysis, or roughly the number of water molecules necessary to complete the first solvation shell of Na^+ and OH^-. In a study of the formate anion diffusion coefficient in different electrolytes (NaOH and KOH), Heitbaum and Gonzalez-Velasco (28) found that the solvodynamic radius of the formate anion is smaller in 5 M NaOH than in 5 M KOH. This can be explained in terms of the smaller ionic radius of the sodium ion (r = 0.95 Å) relative to the potassium ion (r = 1.33 Å) which results in a greater degree of solvation of the former. Consequently, in NaOH solution there will be less water available for hydration of the formate anion explaining the smaller solvodynamic radius as compared to the KOH medium.

The data (29) in Fig. 7 show that the viscosity is strongly dependent on the nature of the cation in the alkali concentration range above 2 M, being smaller for KOH solutions than for NaOH solutions. The source of this difference is probably the same as that outlined above. The data for the activation energy as a function of alkali concentration are not sufficiently precise to reveal a trend of the type expected on the basis of the significant change (20%) in the solvodynamic radius.

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