

TEMPERATURE EFFECTS IN ALTERNATING CURRENT POLAROGRAPHY*

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Little published data are available on the temperature coefficients of the heights of a.c. polarographic waves. With reversibly and nearly reversibly reduced, unadsorbed, depolarizers, it is expected on theoretical grounds (Breyer and Bauer 1960) that the temperature coefficient of the a.c. wave-height will be about 0.3% per degC less than that of the corresponding d.c. step-height; this expectation is qualitatively confirmed by Breyer, Gutmann, and Hacobian's (1950) data on zinc(II) and cadmium(II) (a.c. temperature coefficient=0.4% per degC between 20 and 40 °C), by that of Yasumori and Eguchi (1960) on chloride in 10M sulphuric acid (a.c. temperature coefficient=0.6% per degC at 30 °C), and by that of Itsuki and Suzuki (1959) on copper(II) and zinc(II) in ammoniacal solutions; for lead(II) (Yasumori and Nishimura 1960) the a.c. wave-height changed with time at temperatures above 20 °C.

With only partly reversible (i.e. slow) electrochemical processes, the temperature coefficient of the a.c. wave depends on the temperature-dependence of the electrochemical rate constant (Breyer and Bauer 1960), and would be expected to be larger than for a reversible process. In addition, the change in rate constant with temperature will result in different temperature coefficients of the a.c. wave-height when different frequencies of the superposed alternating voltage are used. Randles and Somerton (1952) have measured the activation energies of several reactions from determination by a.c. measurements, at different temperatures, of the rate constant; however, a modified a.c. bridge technique was used which did not provide data on the temperature coefficients of the a.c. wave-heights.

In the case of adsorbed depolarizers, Breyer and Bauer (1955) found that the temperature coefficient of the a.c. wave-height varied with concentration of the depolarizer, in accordance with the expected lowering of the extent of adsorption with increasing temperature.

It is apparent that investigation of the effect of temperature on a.c. waves can provide a useful tool in the study of the nature and mechanism of electrode processes. In this communication, we report results obtained with a number of inorganic depolarizers.

The results presented in Table 1 were obtained with alternating voltages of 60 c/s and 10 mV r.m.s., and were corrected for series resistance effects; measure-

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ments were carried out at 20, 40, 60, and 80 °C. The temperature coefficients were calculated from the formula

$$i_2 = i_1(1 + x/100)^{(T_2 - T_1)},$$

where i_2 , i_1 are the currents at temperatures T_2 and T_1 , and x the temperature coefficient in % per degC. Coefficients calculated in this way are more constant with temperature than those calculated by means of the formula

$$\frac{(i_2/i_1) - 1}{T_2 - T_1} \times 100.$$

The temperature coefficients of the d.c. steps are, with the exception of that for the reduction of tin, all of the expected order of magnitude for diffusion-controlled processes, and therefore do not provide any other indication of the mechanisms of the reductions. The a.c. temperature coefficients are about 0.5%

TABLE 1
TEMPERATURE COEFFICIENTS OF INORGANIC DEPOLARIZERS

System Studied	Temperature a.c. Wave- Height (% per degC)	Coefficient of d.c. Step- Height (% per degC)
10 ⁻³ M Cd(II) in 1M KCl+0.1M HCl ..	0.6	1.1
10 ⁻³ M Tl(I) in 0.5M H ₂ SO ₄ ..	0.4	1.0
2×10 ⁻⁴ M Sb(III) in 0.5M HCl ..	0.4-0.9*	1.1
10 ⁻³ M Cu(II) in 0.5M H ₂ SO ₄ ..	1.5-0.7†	1.3
10 ⁻³ M In(III) in 1M KCl+0.1M HCl ..	1.6-0.6†	1.5-0.8†
10 ⁻³ M Pb(II) in 1M KCl+0.1M HCl ..	—‡	1.0
2×10 ⁻⁴ M Sn(II) in 0.5M HCl ..	1.7	3.2
10 ⁻³ M Zn(II) in 0.1M KCl+10 ⁻³ M HCl ..	2.5-1.0†	1.4-0.9†

* Increases with temperature.

† Decreases with temperature.

‡ a.c. wave-height decreases between 20 and 60 °C and then increases to 80 °C.

per degC less than the d.c. values for cadmium(II), thallium(I), and antimony(III), in qualitative accordance with the expected behaviour (above) of reversible processes; with copper(II) and indium(III), the a.c. and d.c. values are virtually the same, perhaps indicating that the a.c. process is partly kinetically controlled; in the case of tin(II), even the d.c. values alone indicate some unusual type of reaction.

From the present point of view, lead(II) and zinc(II) are interesting because the a.c., but not the d.c., temperature coefficients indicate that the processes are not simple, reversible ones; thus is it immediately evident that the further study of these systems is likely to be rewarded by insight into the nature of other than the simplest type of electrochemical reaction.

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