claudetite, or other common ABX_3 structures which were examined for analogies. The symmetry of ϵ-Ga_2O_3 is apparently lower than hexagonal or tetragonal. That ϵ-Ga_2O_3 is not merely a chance intermediate structure obtained under very specific conditions, but is a definite structure is borne out by the fact that when $GaAlO_3$, or its solid solutions with Ga_2O_3 and Al_2O_3, is heated in air 100° above the equilibrium transformation temperature, a series of ϵ-phase solid solutions form,[1] showing a regular displacement of lines in the X-ray pattern with increasing aluminum content.

Using a furnace adapted for use with the X-ray spectrometer, the pattern of δ-Ga_2O_3 was found to disappear and that of ϵ-Ga_2O_3 appear at 525° within 30 minutes. This inversion was effected at 500° but not at 475° when held at temperature for one week. The inversion of ϵ-Ga_2O_3 to β-Ga_2O_3 occurs readily at 870 ± 15° with a marked heat effect.

Equilibrium Relations in the System Ga_2O_3–H_2O.—Laubengayer and Engle[14] investigated phase relations in the system Ga_2O_3–H_2O using closed bombs and under limited pressure conditions. They reported the occurrence of a metastable trihydrate obtained at 170°, and a monohydrate stable from room temperature to 300°, above which β-Ga_2O_3 is the stable phase. We were unable to prepare or prove the existence of $Ga_2O_3{\cdot}3H_2O$, but in other respects our data agree with those of Laubengayer and Engle. Only one monohydrate, GaO_2H completely analogous to AlO_2H, diaspore, was obtained; under no conditions could we obtain a boehmite structure. Data obtained from some 200 runs have extended the work to pressures from 50 to 25,000 p.s.i. up to 800°. Starting from α-Ga_2O_3, δ-Ga_2O_3, GaO_2H and gels, with time of reaction varying from half an hour to over two weeks, GaO_2H was obtained below and β-Ga_2O_3 above 300 ± 5°. Pressure had very little effect on the decomposition temperature of GaO_2H. The possible existence of a low-pressure stability field for α-Ga_2O_3 was investigated. At pressures as low as 50 p.s.i. the conversion of α-Ga_2O_3 and GaO_2H to β-Ga_2O_3 was realized. Failure to obtain the conversion at 15 p.s.i. pressure is ascribed to sluggishness of the reaction. The equilibrium diagram has only two fields, those for β-Ga_2O_3 and GaO_2H, separated by a univariant line at 300 ± 5°.

Acknowledgment.—This investigation is part of a research program on the stability relations of minerals at high pressure and temperature, sponsored by the Geophysics Branch of the Office of Naval Research.

STATE COLLEGE, PENNSYLVANIA RECEIVED JULY 26, 1951

---

[14] A. W. Laubengayer and H. R. Engle, THIS JOURNAL, **61**, 1210 (1939).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF PORTLAND]

Polarographic Maxima Suppression in Alcohol–Water Mixtures

BY EUGENE L. COLICHMAN

The various factors involved and their influences on polarographic maxima are studied here. The concentrations of colloidal agents necessary to suppress maxima, the M.S.P. values, are seen to increase with increasing alcohol content of the solvent. A linear relationship is noted. An empirical maxima suppression equation is deduced and discussed. The results are interpreted in terms of previously reported micelle phenomena.

The relationship between maxima suppression and micelle formation (for colloidal type suppressors) was examined and reported[1] earlier. The suppressor concentration, precisely sufficient to eliminate the maximum under consideration, has been termed the maximum suppression point (M.S.P.). It has been shown that in order to avoid possible misinterpretation of polarographic results, particular attention should be given to the quantity of suppressor used. For each given suppressor, the role played by: (a) the reducible species, (b) the supporting electrolyte, and (c) the solvent, in relation to the maximum suppression point (M.S.P.), bears investigation. The present report deals with this problem in alcohol–water mixtures.

As in previous work, highly surface-active (non-reducible) colloidal agents are used so that both "positive" and "negative" maxima will be reduced by all the suppressors; and, therefore, Heyrovsky's sign rule[2] need not be considered. Neutral supporting electrolytes are employed throughout to eliminate the effect of acidity. The three colloidal agents investigated here are: gelatin, lauryltrimethylammonium bromide and methyl cellulose (not previously studied). These represent[3] typical cationic and non-ionic colloidal agents. Where possible, a study of the systems dealt with earlier has been extended into the alcohol region. Additional systems have also received attention so that the effect of valence, both in the ions of the reducible species and in the supporting electrolyte, might be observed.

Experimental

A Sargent–Heyrovský Polarograph, Model XII, equipped with a Sargent Circulator and Thermostat, S-181835 and S-84805, was used at 25.00 ± 0.05°. The capillary passed 2.867 mg./sec. (open circuit), for an average drop time of 2.50 sec. in 0.50 *M* aqueous sodium nitrate, when under a pressure of 78.5 cm. of mercury. A drop time of 3.0 sec. was employed in all the maxima suppression experiments. The nitrogen gas was freed of oxygen by means of several vanadium–zinc amalgam wash bottles placed in series.[4] The oxygen free nitrogen was then passed through a sodium hydroxide solution and finally water and/or the concentration of alcohol under investigation before introducing the

---

[1] E. L. Colichman, THIS JOURNAL, **72**, 4036 (1950).

[2] (a) J. Heyrovsky, "Actualites scientifiques et industrielles," No. 90, Paris 1934; (b) J. Heyrovsky and M. Dillinger, *Collection Czechoslov. Chem. Communs.*, **2**, 626 (1930).

[3] The gelatin used here will act as cationic material, see exptl. section of ref. 1 for justification.

[4] L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

purified nitrogen into the cell. A mercury pool type electrolysis cell, Sargent S-29305, was used in all determinations. Baker C.P. and reagent grade chemicals were used without further purification. The commercial 95% ethanol was distilled once before use.

Results and Discussion

The mercury pool cell used here can be and was thoroughly cleaned between each determination. This type cell is superior to the H-cell used previously[1] for these investigations. Since it is not practical to change the agar plug between each determination, adsorption errors can influence the M.S.P. results when an H-cell is used even though the cell is thoroughly rinsed with alcohol and water between runs. Furthermore, the relative $E_{1/2}$ values obtained with the mercury pool cell offer no disadvantage since these voltages are not pertinent to the maxima suppression investigation, and thus are not cited.

As discussed previously,[1] the maximum suppression point (M.S.P.) of a given suppressor is obtained by plotting values of i_m/i_d (ratio of diffusion current at maximum and when suppressed) *vs.* log C. An extrapolation from the straight line relationship obtained, to where i_m/i_d is unity, corresponds to complete suppression. The M.S.P.'s so obtained for the various neutral electrolyte systems in alcohol–water solutions are given in Table I. The variation of maximum suppression point with solvent composition is apparent. For a given dilute concentration of reducible ion, each solvent composition yields a definite M.S.P. seemingly irrespective of the nature of the ion being reduced or the supporting electrolyte. In this regard, it should be mentioned that all supporting electrolytes were maintained at 0.1 M to eliminate the influence[5] of large ionic strength differences in comparing the results. Maxima due to organic species do not seem to show the orderly behavior noted here with inorganic ions. Instead, for each given colloidal type maximum suppressor, the quantity necessary to suppress the maximum varies considerably with each organic compound investigated, even at a fixed concentration of reducible species.

Fig. 1a

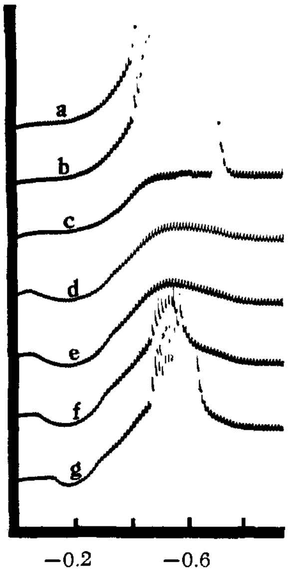
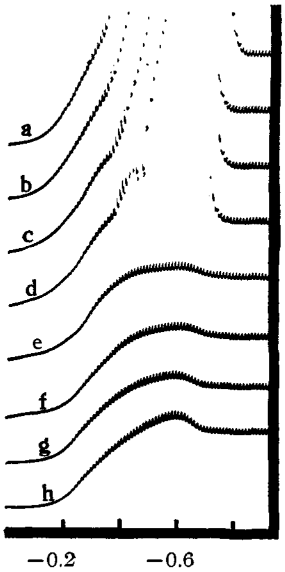


Fig. 1b



$E_{d.e.}$ *vs.* S.C.E., volt.

Fig. 1a.—Effect of lauryltrimethylammonium bromide on 0.004 M $CuCl_2$ in 0.1 M KCl in 25% alcohol, $M \times 10^4$: (a) 0; (b) 0.3; (c) 1.2; (d) 3.0;. (e) 6.0; (f) 10; (g) 20; f $^1/_{100}$.

Fig. 1b.—Effect of lauryltrimethylammonium bromide on 0.004 M $CuCl_2$ in 0.1 M $MgSO_4$ in 25% alcohol, $M \times 10^4$: (a) 0; (b) 0.3; (c) 0.6; (d) 1.2; (e) 2.0; (f) 4.0; (g) 10; (h) 15; f $^1/_{100}$.

The M.S.P. of a given colloidal suppressor has been found to vary directly in accordance with the concentration of the species being reduced. This direct concentration dependency (usually at around 0.005 M and lower) has been noted for all the reducible species investigated here, with all the colloidal maxima suppressors, and in all the solvent compositions. For example, the results in Fig. 2 show that the M.S.P. of gelatin changes from $0.66 \times 10^{-2}\%$ when cupric ion is 1.33×10^{-3} M to $2.00 \times 10^{-2}\%$ when copper is changed to 4.00×10^{-3} M.

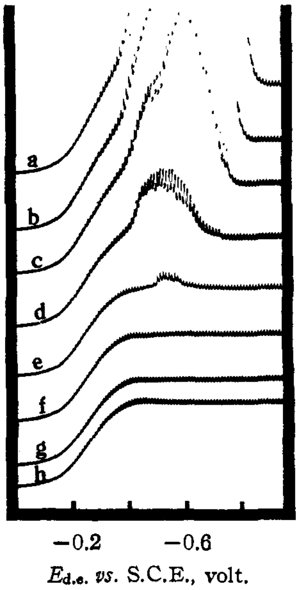


Fig. 2a.—Effect of gelatin on 0.004 M $CuCl_2$ in 0.1 M $MgSO_4$ in 25% alcohol, $\% \times 10^2$: (a) 0; (b) 0.3; (c) 0.6; (d) 1.0; (e) 1.5; (f) 2.0; (g) 3.0; (h) 4.0. f $^1/_{100}$.

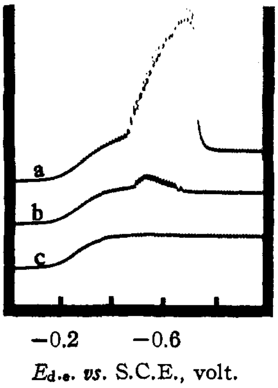


Fig. 2b.—Effect of gelatin on 0.00133 M $CuCl_2$ in 0.1 M $MgSO_4$ in 25% alcohol, $\% \times 10^2$: (a) 0; (b) 0.30; (c) 0.66. f $^1/_{100}$.

It should not be inferred that all colloidal type suppressors will infallibly suppress all inorganic maxima according to the regularity noted in the results cited here. The surface process involved in suppressing maxima is undoubtedly much too complex to allow such an all-inclusive generalization to apply. Specific influences such as substantivity[6] might well make a particular result anomalous. For example, the results given in Fig. 1 show that a

---

[5] The effect of ionic strength on polarographic properties has been studied recently by D. D. DeFord and D. L. Andersen, THIS JOURNAL, **72**, 3918 (1950), and shown to be an important consideration.

[6] Recent results, E. L. Colichman, *ibid.*, **73**, 1795 (1951); *ibid.*, **73**, 3385 (1951), show the pronounced influence of substantivity on surface tension, interfacial tension and spectra.

change in supporting electrolyte from magnesium sulfate to potassium chloride results in a system that is still suppressible at the same M.S.P., but susceptible to reappearance of the maximum at concentrations somewhat above the M.S.P. The fact that copper exists in the form of a negative "chloro cupric ion" might well make its behavior in the presence of the strongly cationic-active suppressor unique.

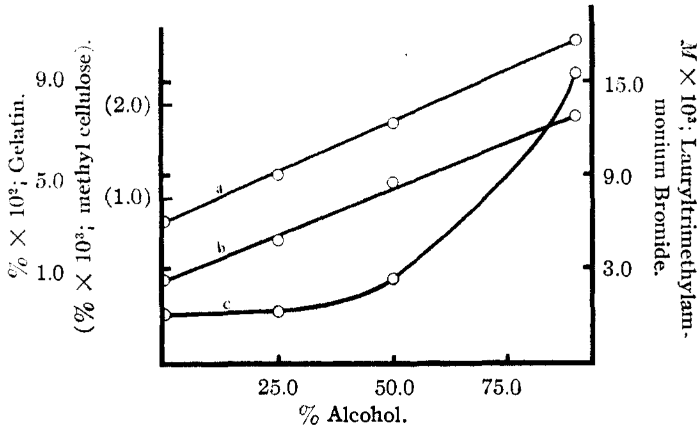


Fig. 3.—Effect of alcohol concentration on maxima suppression points (M.S.P.): (a) methyl cellulose; (b) gelatin; (c) lauryltrimethylammonium bromide.

The states of aggregation of the proteins in gelatin are undoubtedly altered by alcohol additions. These alterations are due to protein ionization differences as well as denaturation effects. The combining power of the protein fractions is thereby changed, and it is reasonable to expect that the ability of gelatin to suppress polarographic maxima should be greatly influenced by the concentration of alcohol present.

On the basis of previous evidence cited,[1] it was shown that the M.S.P. values for a given colloidal type maximum suppressor are comparable to their "classical" critical micelle concentrations. It is, however, erroneous to assume that all maxima suppression involves micelle formation. For example, phenols which behave according to Heyrovsky's sign rule[2] suppress maxima and are non-colloidal. Even for strictly colloidal type suppressors, specific interaction abilities (*e.g.*, the known[7,8,9] binding ability of proteins for both inorganic and organic ions) can complicate the micelle phenomenon. Thus for materials such as gelatin, maxima suppression may in part be due to reaction with the reducible species at the mercury drop surface or other adsorption phenomena.[10,11] The very small quantities of gelatin at the M.S.P. values preclude any possibility of interaction in the "bulk" of the solutions as an explanation for the results.

It is significant to note (Fig. 3) that the maxima suppression points (M.S.P.) of methyl cellulose and gelatin increase linearly with increasing concentration of alcohol over the entire range investigated, 0 to 90%. On the other hand, lauryltrimethylammonium bromide's M.S.P. values increase linearly up to about 30% alcohol and then suddenly increase markedly. This behavior is qualitatively analogous to the variation found by Ralston and Hoerr.[12] With increasing alcohol content of solvent, the critical micelle concentration of a related cationic-active salt, laurylammonium chloride, was seen to undergo an abrupt change. In general, the increased solvent power of alcohol for the hydrocarbon portion of any of the surface-active suppressor molecules is antagonistic toward micelle formation. In the case of the quaternary ammonium salt, this antagonism results in a break in the linear M.S.P. relationship above about 30% alcohol presumably due to a marked repression of ionic micelle formation.[13-16] Ionic micelle formation in the case of gelatin is undoubtedly small and not possible at all in the case of methyl cellulose. Possibly this is the reason why discontinuities in the M.S.P. values are not found in these cases.

TABLE I

MAXIMA SUPPRESSION POINTS (M.S.P.)[a] OF COLLOIDAL AGENTS IN ALCOHOL–WATER SOLUTIONS[b]

Reducible salt	Alc., % 0	25	50	90
Methyl cellulose (% × 10^3) in				
$MnCl_2$	0.76	1.1	1.7	2.5
$CuCl_2$	.70	1.2	1.8	2.6
$Cr_2(SO_4)_3$	.80	1.3	1.8	2.8
$Cr(NO_3)_3$		1.3	1.9	2.9
Gelatin (% × 10^2) in				
$MnCl_2$	0.50	1.9	4.3	7.2
$CuCl_2$	0.53	2.0	4.5	7.0
$Cr_2(SO_4)_3$		2.3	5.1	7.8
$Cr(NO_3)_3$			4.8	8.0
Lauryltrimethylammonium bromide (M × 10^3) in				
$MnCl_2$		0.21	2.0	15
$CuCl_2$	0.09	.20	n.s.[c]	15
$Cr_2(SO_4)_3$	.09	.25	2.4	16
$Cr(NO_3)_3$		.20	2.5	16

[a] The M.S.P. value reported for each colloidal agent in each alcohol–water mixture is an average value obtained by investigating the following supporting electrolytes in each case. The 0.1 M supporting electrolytes were: KCl, LiCl, K_2SO_4 and $MgSO_4$. Due to solubility limitations KCl and K_2SO_4 were used only at 0 and 25% alcohol, and $MgSO_4$ at 0, 25 and 50%. [b] The reducible ions responsible for the maxima are present at 0.004 M. [c] Not suppressible by even extremely large concentrations.

The linear relationships found between the maxima suppression points (M.S.P.) and increasing

---

(7) G. Scatchard and E. S. Black, *J. Phys. Colloid Chem.*, **53**, 88 (1949).

(8) I. M. Klotz, *et al.*, THIS JOURNAL, **68**, 1486, 2299 (1946).

(9) L. G. Longsworth and C. F. Jacobsen, *J. Phys. Colloid Chem.*, **53**, 126 (1949).

(10) K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 594 (1947).

(11) B. Keilin, THIS JOURNAL, **70**, 1984 (1948).

(12) A. W. Ralston and C. W. Hoerr, *ibid.*, **68**, 2460 (1946).

(13) J. W. McBain and W. J. Jenkins, *J. Chem. Soc.*, **121**, 2325 (1922).

(14) J. W. McBain and M. E. McBain, *Proc. Roy. Soc.* (*London*), **139A**, 26 (1933).

(15) K. Hess and J. Gundermann, *Ber.*, **70B**, 1800 (1937).

(16) K. Hess, W. Philippoff and H. Kiessig, *Kolloid Z.*, **88**, 40 (1939).

alcohol concentration follow a general empirical equation, $S = K_1C + K_2AC$, where

S = concentration of suppressor needed (M.S.P. value)
A = concentration of ethanol in volume percentage
C = concentration of reducible ionic species in molarity (must be dilute solutions, below about 5×10^{-3} M)
K_1 and K_2 = constants characteristic of particular suppressor

A small value of K_1 indicates that the suppressor functions at low concentrations. The magnitude of K_2 is indicative of the susceptibility to change of the M.S.P. values by increasing alcohol concentration. These values are given in Table II for the colloidal suppressors investigated here. Similar determinations for other useful colloidal agents should prove helpful in choosing proper maxima suppressor concentrations, understanding their function, and ensuring their proper use in polarography.

TABLE II

MAXIMA SUPPRESSION CONSTANTS OF COLLOIDAL AGENTS IN ALCOHOL–WATER SOLUTIONS

Colloidal agent	K_1	K_2
Methyl cellulose[a]	0.19	0.0054
Gelatin[a]	1.3	.19
Lauryltrimethylammonium bromide[b]	0.023[c]	.0013[c]

[a] Based on concn. in percentage in empirical equation. [b] Based on concn. in molarity in empirical equation. [c] Value satisfactory up to about 30% alcohol.

PORTLAND, OREGON

RECEIVED JUNE 29, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Reaction of Dilute Iodine and Ammonia Solutions

BY R. K. MCALPINE

The decolorization of an iodine solution by ammonia at relatively low *p*H cannot be accounted for in terms of hydrolysis to form HIO or the production of $N_2H_3I_3$. The reaction involved is readily reversible as shown by the ease with which the color decreases with increasing amounts of NH_3 and increases on the addition of KI or NH_4Cl. Assuming that NH_2I is formed the net reaction would be $2NH_3 + I_2 \rightleftarrows NH_2I + NH_4^+ + I^-$. A series of 24 decolorization experiments involving varying amounts of 3 different NH_4Cl–NH_4OH solutions and five 0.01N KI_3 solutions with differing amounts of KI were carried out. The data gave values for the equilibrium constant of this reaction ranging from 1.2 to 2.6, the average being 1.8. The precipitation of $N_2H_3I_3$ and the dissolving of this compound in excess of ammonia solution may be represented by the equations $NH_2I + 2I_2 + 3NH_3 = N_2H_3I_3 + 2NH_4^+ + 2I^-$ and $N_2H_3I_3 + NH_3 = 3NH_2I$.

At present, chemists generally regard this reaction as involving, first, the hydrolysis of the iodine in the somewhat alkaline solution to form HIO, and, second, the reaction of NH_3 with the HIO to form nitrogen iodide, $N_2H_3I_3$; followed later by slow conversion in part to iodate and iodide, and in part by decomposition. This idea of the primary reaction was expressed clearly by Seliwanov[1] confirmed by Chattaway,[2] and retained by Partington.[3]

There have been occasional suggestions that NH_2I and NHI_2 might be intermediates in the formation of nitrogen iodide. Thus Cremer and Duncan[4] wrote equations for the action of HIO on NH_3, giving NH_2I and NI_3 as successive products, and Roederer,[5] having obtained some evidence for the formation of NH_2I in the reaction of dry NH_3 on I_2 dissolved in CCl_4, noted the possibility that even in aqueous solutions NH_2I may be formed and then rearranged to give the nitrogen iodide. However, these suggestions appear to be simple speculations without experimental support.

It is now possible to report direct experimental studies which make it appear very probable that the initial reaction between iodine and ammonia does involve the formation of iodamine, NH_2I. These experiments are concerned mainly with the loss in color which occurs when standard amounts of iodine solutions are added to buffered solutions containing varying amounts of NH_4Cl and of NH_4OH. This loss of color cannot be accounted for in terms of simple hydrolysis of the iodine in the somewhat alkaline solution to form HIO, nor can it be due to the formation of nitrogen iodide in solution. Two simple experiments are sufficient to justify this statement. First: when 50 ml. of 0.01 N KI_3 solution is added to 200 ml. of 0.2 M Na_2HPO_4 no recognizable decolorization takes place, yet with 25 ml. of 5 N NH_4OH present and sufficient NH_4Cl to give the same *p*H as before, over 90% of the color is lost. Second: when 50 ml. of the 0.01 N KI_3 solution is added to 200 ml. of water containing only 1 ml. of 5 N NH_4OH a moderate black precipitate forms within a few minutes, proving that nitrogen iodide is sufficiently insoluble to precipitate if it were being formed as a main product in this reaction.

From the consideration of such experiments it was concluded that the soluble, colorless form of iodine is probably iodamine, NH_2I. The only alternative explanation would be to assume that ammonium hypoiodite is being formed as a very slightly ionized compound such that the hydrolysis of the iodine and the dissociation of the HIO, which normally take place very slightly under the conditions given, are actually being carried nearly to completion by the removal of the hypoiodite ion as the ammonium salt. Such an assumption is too highly improbable to warrant serious consideration.

As additional support for the belief that NH_2I is formed as the primary product in the reaction of dilute iodine and ammonia solutions the attempt was made to use the decolorization experiments as a basis for calculating an equilibrium constant for

---

[1] Th. Seliwanov, *Ber.*, **27**, 1012 (1894).

[2] F. D. Chattaway and K. J. P. Orton, *Am. Chem. J.*, **24**, 342 (1900).

[3] J. R. Partington, "Textbook of Inorganic Chemistry," 6th ed., The Macmillan Co., New York, N. Y., p. 527.

[4] H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 2750 (1930).

[5] E. Roederer, *Z. anorg. allgem. Chem.*, **226**, 144 (1936).