cancel each other to a first approximation. In contrast, the solubility of AgCl in the presence of either common ion clearly shows complexing. Interestingly enough the complexing of Ag^+ by Cl^- and of Cl^- by Ag^+ appear to be remarkably similar. The large extent of this complexing at room temperature combined with the known increasing solubility of AgCl in water with temperature suggest the necessity of obtaining AgCl solubilities in media containing a common ion before making definitive interpretations concerning thermodynamic data involving the Ag, AgCl (sat.) electrode in such media.

Acknowledgment.—We wish to express our appreciation to P. F. Thomason and co-workers of the Ionic Research and Development Group of the Analytical Chemical Division of the Oak Ridge National Laboratory for all analytical work in connection with our solubility program.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE JOHNSON FOUNDATION FOR MEDICAL PHYSICS, UNIVERSITY OF PENNSYLVANIA]

Some Phase Relationships in the Three-component Liquid System CO_2–H_2O–C_2H_5OH at High Pressures

BY LOUIS C. W. BAKER[1] AND THOMAS F. ANDERSON

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Phase diagrams for the liquid system CO_2–H_2O–C_2H_5OH are reported covering the temperature range 10 to 50° at pressures from 3000 lb./in.^{2} down to the vapor pressures of the respective mixtures. Liquid–vapor critical data are included. In most respects the diagrams are typical of systems wherein one component (C_2H_5OH) is completely miscible with each of the other two components while the latter are only sparingly soluble in one another. However, for ternary mixtures containing a given $C_2H_5OH:H_2O$ molar ratio, isobaric temperature rise causes first an increase and later a decrease in the extent of the region wherein only one liquid phase exists. The temperature of maximum extent of the region of one liquid phase increases with increasing pressure and decreases with increasing $C_2H_5OH:H_2O$ molar ratio. These effects are attributable to temperature-dependent variation in the extent of molecular association.

The properties of liquid carbon dioxide solutions have received relatively little study[2] although the liquid has potentialities for considerable interest as a solvent. The linear CO_2 molecule has no over-all dipole moment and the liquid has a very low dielectric constant.[3] However, the ends of the molecule are undoubtedly considerably more negative than its center, offering opportunities for hydrogen bonding and other forms of molecular association. It is challenging to consider the following facts, for example: (1) water is practically insoluble in liquid CO_2, although the solid $CO_2 \cdot 8H_2O$ is stable, at elevated pressures, at temperatures up to 8° and perhaps higher[4-6]; (2) this paper shows ethyl alcohol to be miscible with liquid CO_2, marked diminution in total molal volume taking place upon mixing[4,7]; (3) measurements with the propyl and butyl alcohols indicate rapidly decreasing solubility with increasing carbon chain length[7]; but (4) glycerol is practically insoluble in liquid CO_2.[8] Several examples of minimum critical solution temperatures have been reported for liquid CO_2 solutions of organic substances.[7]

This paper reports phase diagrams, determined with moderate accuracy, for the liquid system CO_2–H_2O–C_2H_5OH, at temperatures from 10 to 50° and at pressures from 3000 lb./in.^{2} down to the vapor pressures of the mixtures. Liquid–vapor critical data, within that range of conditions, are included. The results are potentially useful in the "critical point drying method" for electron microscope specimens.[9] The experimental approach has novel features.

Pure water and pure liquid CO_2 exhibit very limited mutual solubility. However, the latter was found to be completely miscible with absolute ethyl alcohol, as anticipated on the basis of frag-

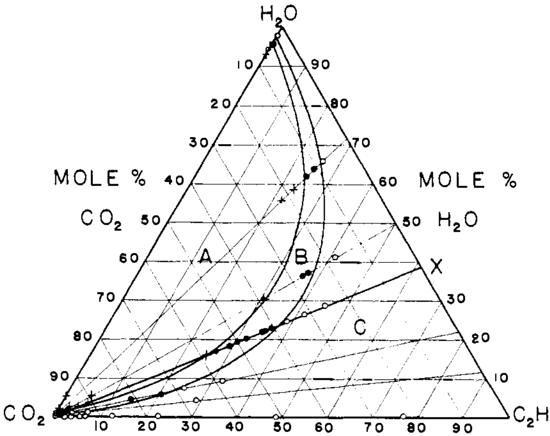

Fig. 1.—Within the ranges of conditions cited: A, area of two liquid phases; C, area of one liquid phase; B, area of one or two liquid phases depending upon temperature and pressure. Experimental points are indicated.

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(1) Department of Chemistry, Boston University, Boston 15, Massachusetts.

(2) E. L. Quinn and C. L. Jones, "Carbon Dioxide," Am. Chem. Soc. Monograph No. 72, Reinhold Publ. Co., New York, N. Y., 1936, p. 94–112.

(3) F. Linde, *Wied. Ann.*, **56**, 546 (1895); H. Riegger, *Ann. Phys.*, **59**, 753 (1919); W. Herz, *Z. physik. Chem.*, **103**, 269 (1922); F. G. Keyes and J. G. Kirkwood, *Phys. Rev.*, **36**, 754 (1930).

(4) W. Hempel and J. Seidel, *Ber.*, **31**, 2997 (1898).

(5) S. Wroblewsky, *Wied. Ann.*, **17**, 103 (1892); *Compt. rend.*, **94**, 212 (1882).

(6) P. Villard, *ibid.*, **119**, 368 (1894); *Ann. chim. phys.*, **11**, 355 (1897).

(7) E. H. Büchner, *Z. physik. Chem.*, **54**, 665 (1906).

(8) E. L. Quinn, *Ind. Eng. Chem.*, **20**, 735 (1928).

(9) T. F. Anderson, *J. Appl. Phys.*, **21**, 724 (1950); *Trans. N. Y. Acad. Sci.*, [II] **13**, 130 (1951).

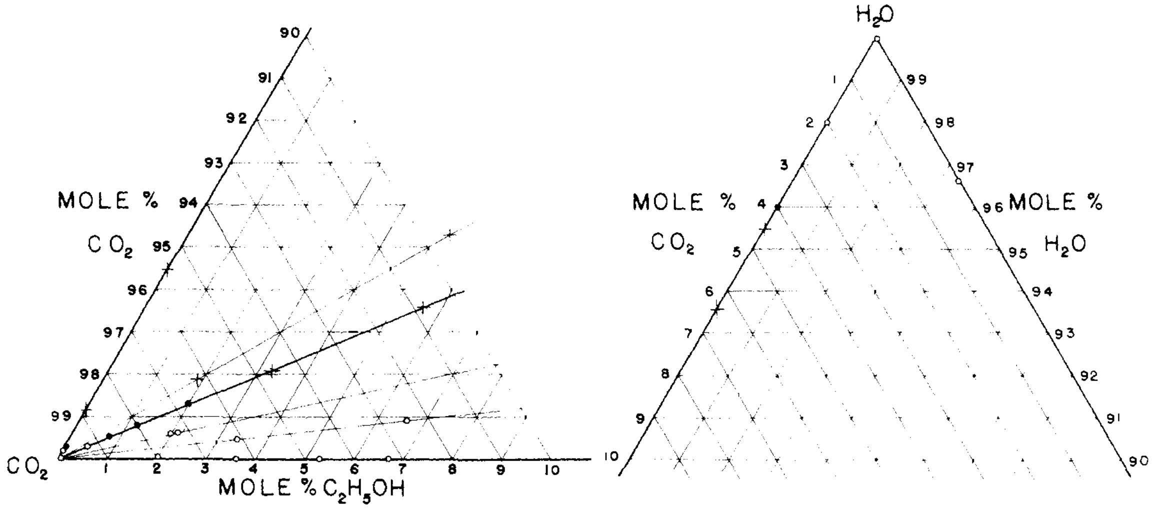

Fig. 2.—Details of corners of Fig. 1: ×, points in area A; ●, points in area B; ○, points in area C. Critical conditions were determined for most of the latter in the CO$_2$-rich corner.

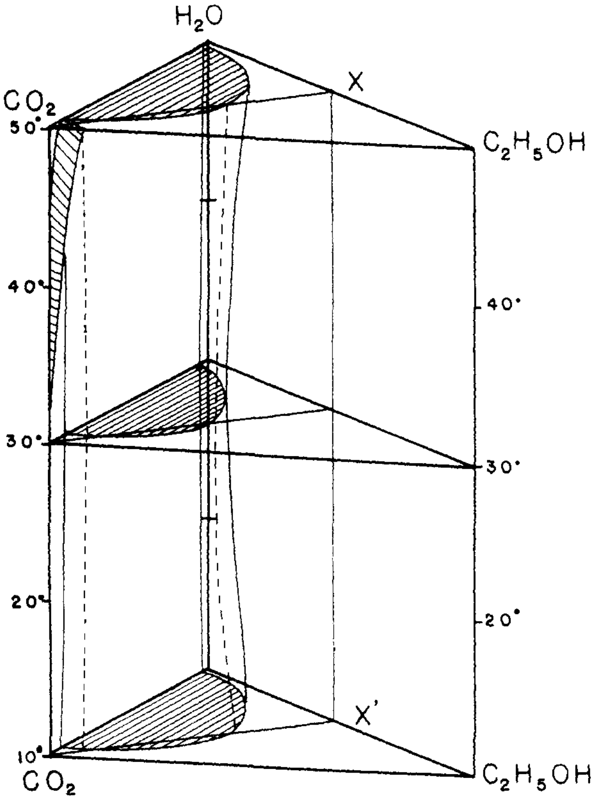

Fig. 3.—General form of diagram, see text below. The plane XX'CO$_2$(10°)CO$_2$(50°) intersects the isobaric surface of the region of two liquids at the dotted lines. A portion of the heterobaric liquid-vapor critical envelope is shown in the CO$_2$ corner.

mentary older results.[7] Within the range of conditions cited, a 95 weight % solution of ethyl alcohol in water is also completely miscible with liquid CO$_2$.

The general findings are summarized by Figs. 1 and 2.

Figure 3 represents the general form of the phase diagrams of which Fig. 1 is a projection. The lower end of the liquid–vapor critical envelope is seen in the CO$_2$ corner. That envelope, of course, is not isobaric. It is composed of the "second critical points" of the mixtures[10] (*i.e.*, the points at which the distinction between the gaseous phase and the liquid phase vanishes). The vertical columnar volume represents the region of two liquids. One of the isobaric surfaces of that region is represented. A slight indentation in that surface, locating temperatures of maximum extent of the region of one liquid phase, runs as a broad shallow valley in a counterclockwise helical path up that surface. The valley's depth appears to be negligible near its ends. As the pressure is raised the region of two liquids is slightly decreased in size and the location of the helical valley is displaced upward, sometimes to temperature ranges higher than those illustrated.

Experimental

An extremely sturdy glass-and-steel liquid level gage,[11] manufactured for service on very high-pressure steam boilers, was adapted for use as a glass-walled bomb. The interior volume (about 35 cc.) was all visible between the two 1.0 inch-thick pre-strained Pyrex glass plates which formed opposite sides of the bomb. Each plate covered a 1.3 cm.-wide side of the interior chamber. The bomb, containing a large ball bearing, was mounted on a motor-driven rocking mechanism which was submerged in a well-stirred water-bath. As the bomb rocked slowly, the steel ball rolled from one end of the interior chamber to the other, providing efficient stirring. A powerful light was shone, by means of a submerged mirror, through the glass walls of the bomb chamber and toward the observer. The contents of the bomb could be watched through a window in the side of the water-bath. One end of the bomb was fitted with an aneroid high pressure gage, of negligible volume, which was calibrated in place and periodically checked against an hydraulic dead-weight balance. The other end of the bomb was fitted with a fine-bore high pressure valve of negligible volume.

Solutions were prepared, in relatively large amounts, from known weights of absolute ethyl alcohol and recently boiled distilled water.

A typical run was made as follows. The water-bath was emptied and the dried bomb-chamber was swept out with

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(10) J. P. Kennen, *Phil. Mag.*, **40**, 173 (1895); H. C. Weber, "Thermodynamics for Chemical Engineers," John Wiley and Sons, Inc., New York, N. Y., 1939, p. 33–43.

(11) Jerguson Gage & Valve Co., Somerville, Massachusetts, Catalogue Unit No. 264, p. 3, Gauge No. 11-T-30.

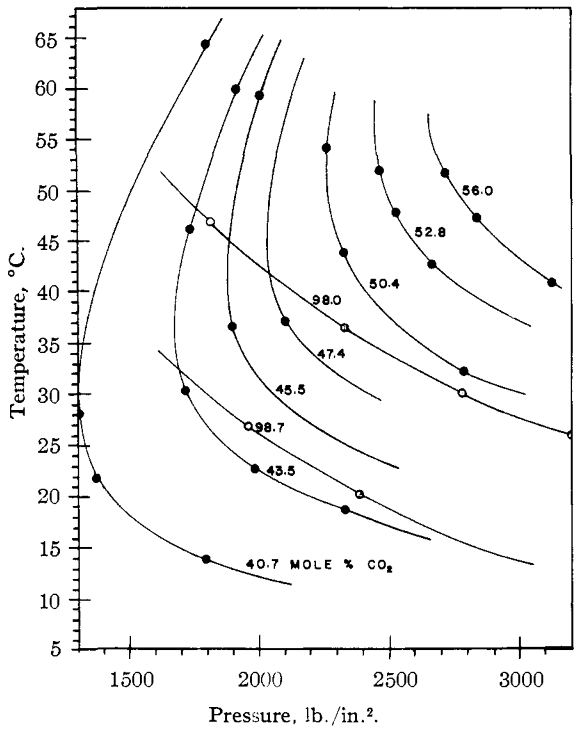

Fig. 4.—Temperatures and pressures of phase separations for various mixtures *made with* 61.0 mole % solution of alcohol in water. These mixtures all lie on line CO_2-X, Fig. 1. The mole % CO_2 is indicated for each. The two types of curves shown lie on opposite sides of the intersection of the line CO_2-X with area A, Fig. 1. (For mixtures containing about 50 mole % CO_2, the CO_2-rich liquid phase is the more dense of the two liquid phases below 10°; and it is the less dense liquid phase above that temperature.)

CO_2. Then a known weight of a given alcohol–water solution was injected with a calibrated syringe, the nozzle of which was temporarily inserted through the open valve into the bomb chamber. A high pressure stainless steel tube, running from an inverted cylinder of C.P. liquid CO_2, was swept out and connected to the valve on the bomb. The water-bath was then filled with ice-water. Liquid CO_2 (under its room temperature vapor pressure) was thereupon run into the bomb chamber, filling it at 0°. This procedure ensured that only liquid phases would be present after the temperature was raised as described below. The valve on the bomb was closed and the mixture was rocked to stir it at 0°. The pressure fell during this stirring, it being obvious that a marked decrease in total molal volume accompanied the dissolution.[4] More CO_2 was then admitted and the contents were stirred as before. The line to the CO_2 tank was then disconnected and, in its place, a rubber tube was fitted to the valve on the bomb. This tube led to a precision "wet test meter"[12] containing several liters of water through which CO_2 had just been bubbled for 20 minutes. While the bomb rocked, the temperature of the bath was rapidly raised until only one liquid phase was present, provided the temperature required was not over 60°. The temperature was then lowered fairly rapidly to determine roughly the temperature of separation of two liquid phases. The point of separation of the two phases was then determined accurately by covering again the appropriate portion of the temperature range very slowly. Reproducibility was consistently within 0.1°. The thermometer used was calibrated against one recently checked by the U. S. Bureau of Standards. The temperature and pressure at which the two phases separated were noted. The bath was then raised to 60°, and the valve on the bomb was cracked, allowing a little of the homogeneous mixture within the bomb to blow off very slowly through the wet test meter. The valve was closed again, and the temperature and pressure of separation of two liquid phases were again determined for that portion of the mixture remaining in the bomb. This partial blowing off procedure was repeated several times; and for each ternary mixture within area B, Fig. 1, several points were thus obtained. Observations were discontinued when the pressure was so low that a vapor phase appeared. The remaining CO_2 in the bomb was then blown off slowly through the wet test meter. The total reading on that instrument then showed the amount of CO_2 which had been in the bomb originally, measured as volume of water-saturated gas at the current atmospheric pressure and at the temperature of the water within the meter. Thus the over-all mole fraction could be calculated. Most of the alcohol and water generally remained in the bomb (not much being swept out during the final blow off); but the small amounts of these compounds which entered the wet test meter dissolved, when the gas was bubbled through it, in the large volume of water the meter contained. Excellent reproducibility was obtained on duplicate runs.

Construction of Diagrams

For a given run, the temperatures and pressures of liquid phase separations were plotted against one another and a smooth curve was drawn through the points (Fig. 4). Different runs involving varying proportions of CO_2 but the same $C_2H_5OH:H_2O$ ratio (*e.g.*, 61.0 mole % alcohol) thus gave a family of curves (Fig. 4) from which temperatures of separation at a given pressure can be read. Alternatively one may ascertain pressures of separation at a given temperature.

The point X, Fig. 1, represents a specific (*i.e.*, 61.0 mole %) alcohol-water solution. All mixtures made by injecting varying quantities of that solution into the bomb, as described in the above procedure, have compositions falling on the line joining X and the CO_2 corner. In Fig. 3 these compositions coincide with the plane XX'CO_2(10°)CO_2(50°). The dotted lines, Fig. 3, representing the intersections of this plane with an isobaric surface of the region of two liquids, may be plotted by reading temperatures from Fig. 4 at the pressure in question. Figure 5 represents the plane XX'CO_2(10°)CO_2(50°), with such intersections plotted for three different pressures. The locations of temperatures of maximum extent of the region of one phase are obvious in Fig. 5.

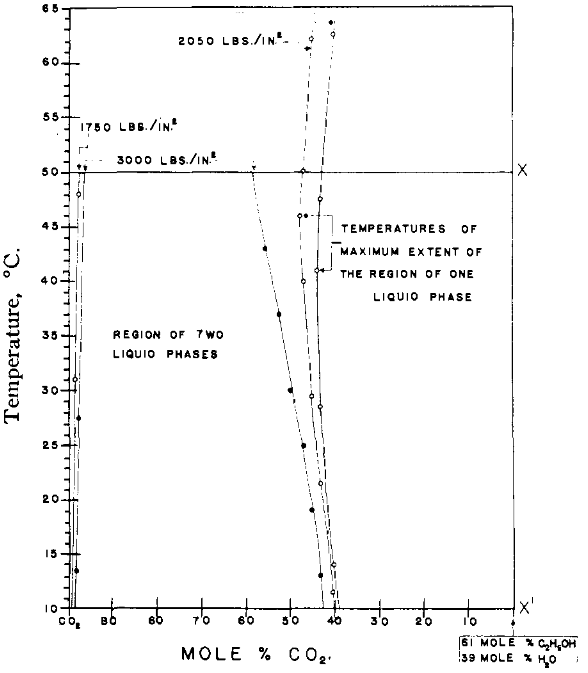

Fig. 5.—The plane XX'CO_2(10°)CO_2(50°), Fig. 3, showing three of the isobaric intersections of the plane with the region of two liquids. Plotted with readings from Fig. 4.

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[12] "Fisher's Modern Laboratory Appliances," Fisher Scientific Co. Catalogue, New York, N. Y., 1952, p. 497, No. 11-165.

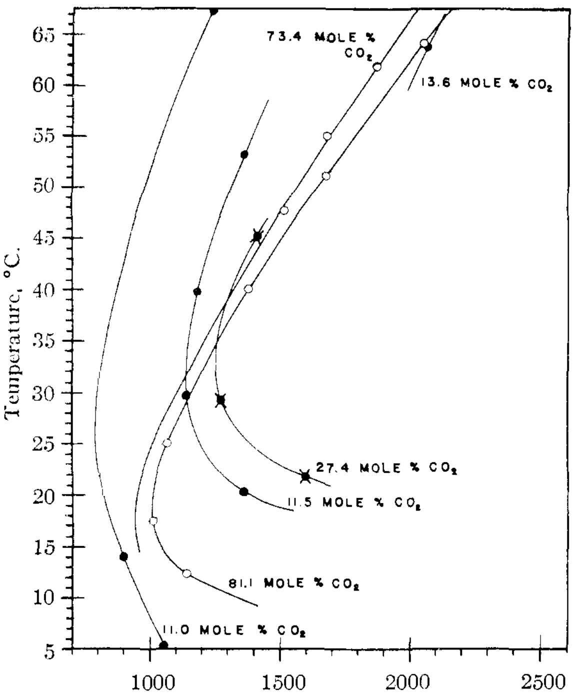

Fig. 6.—○, points on *PT* curves for mixtures *made with* 77.9 mole % alcohol-water solution; ●, points determined for mixtures *made with* 28.1 mole % alcohol-water solution; ✖, points determined for mixture *made with* 50.0 mole % alcohol-water solution.

The isobaric intersections of the region of two liquids with other planes, radiating from the CO_2 corner of Fig. 3, may be similarly plotted from the data obtained using other alcohol-water proportions (Fig. 6). An assemblage of such planes determines the surfaces of the region of two liquids. The data for other planes are necessarily more fragmentary than are those for the mixtures involving 61.0 mole % alcohol-water solutions, because of the angles at which the planes intersect the region of two liquids. However, the data are quite adequate to establish the generalizations given in the introductory discussion and to indicate the magnitudes of the effects.

Liquid-vapor critical data for CO_2, for CO_2-absolute alcohol solutions, for liquid CO_2 saturated with water, and for one ternary mixture are listed in Table I, which may be used to plot that portion of the heterobaric critical envelope illustrated in Fig. 3. These data were obtained by a technique, similar to that described, wherein the bomb was partially filled with an appropriate volume of liquid CO_2 or liquid CO_2 solution. The temperature and pressure of the separation of a gaseous phase and a liquid phase were observed upon slow cooling of the mixture from above the critical point. For each of the solutions, the point so determined is the "second critical point,"[10] *i.e.*, the temperature and pressure at which the distinction between the gaseous and the liquid phase vanishes. In this region of composition, each of these points is extremely close to the "first critical point",[10] *i.e.*, the temperature (and corresponding pressure) above which liquefication within the gaseous phase cannot be brought about by isothermal increase of pressure.

TABLE I

LIQUID-VAPOR CRITICAL DATA

Composition, mole %			Critical temp., °C.	Critical pressure, lb./in.²
CO_2	C_2H_5OH	H_2O		
100	0	0	31.0	1070
98.0	2.0	0	37.9	1150
96.4	3.6	0	40.7	1200
94.7	5.3	0	45.6	1300
93.3	6.7	0	47.8	1345
99.8	0	0.2 (satd.)	31.7	..
97.5	2.0	0.6	38.1	1195

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PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Silver-Silver Chloride Reference Electrode in Acetonitrile Polarography[1]

BY ALEXANDER I. POPOV AND DAVID H. GESKE[2]

RECEIVED OCTOBER 24, 1956

An external reference electrode has been prepared for polarographic studies in acetonitrile. A silver-silver chloride electrode in acetonitrile solution saturated with silver chloride and trimethylethylammonium chloride was found to be reproducible and non-polarizable. Potentiometric measurements were made to relate the reference electrode to Pleskov's scale. The polarographic behavior of a number of metallic perchlorates in 0.1 *M* tetra-*n*-butylammonium perchlorate was studied. Approximate calculation of a number of half-wave potentials was done and comparison made with observed values. New data are presented for reduction of thallous and stannous ions.

Introduction

The use of acetonitrile as a solvent for polarographic measurements was first reported by Wawzonek and Runner.[3] These authors employed a mercury pool reference anode and either 0.1 *M* tetra-*n*-butylammonium iodide or 0.1 *M* tetra-*n*-butylammonium perchlorate as the supporting electrolyte. In later publications Wawzonek, *et al.*,[4] reported polarographic measurements on some organic compounds in the same solvent. The study of hydrogen ion reduction in acetonitrile has been described recently by Vlcek.[5]

After the work reported in this paper was completed, a dissertation by Coetzee[6,7] reported a comprehensive polarographic study of a number of

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[1] Abstracted in part from the Ph.D. Thesis of David H. Geske, State University of Iowa, 1957.

[2] National Science Foundation Predoctoral Fellow.

[3] S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 457 (1952).

[4] S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *ibid.*, **102**, 235 (1955); **103**, 456 (1956).

[5] A. A. Vlcek, *Chem. Listy*, **48**, 1741 (1954); *Coll. Czech. Chem. Comm.*, **20**, 636 (1955).

[6] J. F. Coetzee, *Diss. Abs.* (Minnesota), **16**, 1071 (1956).

[7] J. F. Coetzee, Ph.D. thesis, University of Minnesota; I. M. Kolthoff and J. F. Coetzee, THIS JOURNAL, **79**, 870 (1957).