[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

The Viscosities of Perchloric Acid Solutions

BY L. H. CLARK AND G. L. PUTNAM

Introduction

There is reason to believe that the efficiency of electrolytic cells for the production of ozone[1] may be improved by the study of the anode film temperature in relation to current density and viscosity of the electrolyte. In order to correlate the effect of the viscosity of the electrolyte (aqueous perchloric acid) on anode film temperature, it is necessary to have available the viscosities of the electrolyte at various concentrations for temperatures well below 0°. Since this data could not be found in the literature, experiments were conducted for the purpose of measuring the viscosity of aqueous perchloric acid solutions as a function of temperature and concentration.

In electrolytic cells, such as the one using perchloric acid for the production of ozone, it is believed that the electrode temperature—not the temperature of the electrolyte—is the temperature which controls the primary formation of electrode products. Since the efficiency of the electrolytic cell can be markedly affected by controlling the temperature difference between the anode and electrolyte, it is of great importance to study the variables affecting this temperature.

To correlate the effect of viscosity on the anode film temperature, we have measured the viscosity of 20, 40 and 60% perchloric acid solutions. The temperature range, being limited by the freezing point of the solutions, varies from +50 to −58°. This paper presents the results of these viscosity measurements. A later paper will correlate viscosity to anode film temperature and current efficiency.

Not much work has been done on the viscosity of perchloric acid solutions. Van Wyk[2] and Reyher[3] give values for various concentrations of perchloric acid at 20, 25 and 50° only. As far as could be ascertained from the literature, no authors have previously measured the viscosity of aqueous perchloric acid solutions below 0°.

Experimental

Apparatus.—The viscosity measurements were made using an Ostwald viscometer suspended in a Dewar flask containing the temperature controlled bath. The Dewar flask had a strip of unsilvered glass on the side to permit visual observations of the indices on the viscometer. Uniformity in the temperature of the bath was obtained by an electric stirrer placed in the flask.

The volume of efflux of the viscometer was approximately 1.45 ml. The working volume was 10 ml., this quantity of the desired solution always being pipetted into the viscometer in order to maintain a constant head of solution. The time of efflux was observed by visual observation of the meniscus and was measured to 0.1 of a second using a Waltham type A-8 stopwatch, which on checking against an electric timer showed a negligible difference in one hour. The time of efflux varied from 26 to 1788 seconds for the calibrating liquids and from 24.2 to 710 seconds for the perchloric acid solutions. No kinetic energy corrections were applied as they were less than the experimental error of the work.

In order to measure as accurately as possible the temperature of the solution in the viscometer, a calibrated glass-enclosed copper–constantan thermocouple was inserted directly in the solution in the reservoir of the Ostwald viscometer. Temperatures were read to the nearest 0.1°. The temperature of each run represents an average of several temperatures recorded during the run. The bulb of the viscometer was always kept below the level of the cooling liquid to aid in equalizing temperatures before the liquid passed through the capillary tube.

The viscometer was calibrated by measuring the time of efflux of liquids of known viscosity and density; and subsequently, plotting the computed ratios of kinematic viscosity to time of discharge *versus* the reciprocal of the discharge time squared. This method of calibrating the viscometer is the one described by the Bureau of Standards.[4] The calibrating liquids included distilled water,[5,6] pure ethyl alcohol[5,6] and a 38.6 weight per cent. sulfuric acid solution.[4] The time of efflux for the liquids was measured at temperatures ranging from +45 to −50°, four determinations being made at each temperature.

Since a straight line was obtained for the calibration curve over the range of kinematic viscosities and temperatures measured, the following equation will hold for any unknown over the same range of kinematic viscosities

$$\left(\frac{\eta}{\rho}\right)_T = At - \frac{B}{t}$$

where η/ρ = kinematic viscosity; t = time of flow in seconds; A, B = constants of the instrument, T = temperature of the liquid.

Materials.—Twenty per cent., 40 and 60% weight solutions of C. P. perchloric acid in water were measured at temperatures between −58 and +50°.

The composition of these solutions, expressed as per cent. perchloric acid, was determined by titrating two weighed portions of each solution. The percentages obtained were 20.0, 40.0 and 60.0. As a check on these determinations the specific gravity at 23°/23° of each solution was determined on a Westphal balance. The densities at 23° were then calculated and converted to percentages.[7] The average difference between the measurements by titration and specific gravity was less than 0.1 weight per cent.

In order to calculate the viscosity of these solutions from the kinematic viscosity, it is necessary

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[1] Putnam, Moulton, Fillmore and Clark, *J. Electrochem. Soc.*, **93**, 211-221 (1948).

[2] Van Wyk, *Z. anorg. Chem.*, **48**, 1 (1906).

[3] Reyher, *Z. physik. Chem.*, **2**, 744 (1888).

[4] Vinal and Craig, *J. Research Natl. Bur. Standards*, **10**, 781-793 (1933).

[5] "International Critical Tables," Vol. V, pp. 10-11 (1929).

[6] *Ibid.*, Vol. III, pp. 25, 27 (1928).

[7] Perry, "Chemical Engineers' Handbook," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 421.

TABLE I

GRAMS PER ML. DENSITIES OF PERCHLORIC ACID SOLUTIONS

Temp., °C.	Weight per cent. perchloric acid 10	20	30	40	50	60
50	1.041	1.107	1.181	1.267	1.375	1.494
40	1.046	1.113	1.188	1.276	1.385	1.507
30	1.051	1.119	1.195	1.285	1.395	1.520
20	1.056	1.125	1.203	1.294	1.405	1.534
10	1.061	1.131	1.210	1.303	1.415	1.547
0	1.066	1.137	1.217	1.312	1.425	1.560
−10		1.144	1.225	1.321	1.435	1.573
−20			1.232	1.330	1.445	1.586
−30				1.339	1.455	1.599
−40				1.348	1.465	
−50				1.357		
−58				1.364		

to know the density of each solution at each temperature. Data from Perry,[7] from Markham,[8] and our own experimental results at temperatures below 0° have been used as a basis for computing densities needed at the various concentrations and temperatures. By experimentally determining the densities of perchloric acid solutions at several temperatures below 0°, it was found that a linear interpolation of the densities is valid, straight lines being obtained when temperature was plotted *vs.* the combined data of Perry,[7] Markham[8] and our own. Table I gives the densities of perchloric acid interpolated from the combined data of Perry, Markham and the authors.

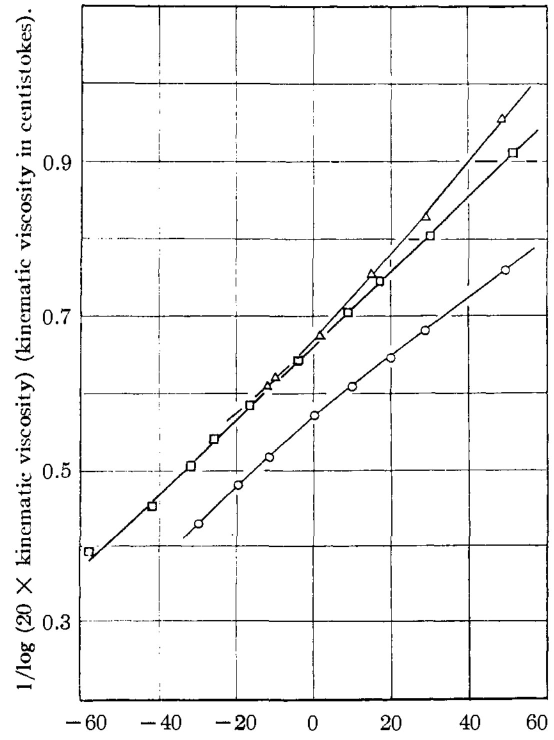

Fig. 1.—Perchloric acid viscosities: ○, 60 wt. % $HClO_4$; □, 40 wt. % $HClO_4$; △, 20 wt. % $HClO_4$.

Results

The experimental results of viscosity measurements are shown in Fig. 1. In plotting these curves, the reciprocal of the log (20 × kinematic viscosity in centistokes) was plotted against temperature as recommended by Vinal.[4] This was done in order to obtain an approximately linear relationship which permits a more accurate interpolation of the curves. The values of the function 1/[log (20 × kinematic viscosity)] were read from Fig. 1 at each 10° of temperature and these values replotted as isothermal lines having per cent. composition of solution as the abscissas. These new working curves facilitated the reading of the kinematic viscosities of perchloric acid at the desired temperatures and compositions.

Table II gives a summary of the numerical values for the absolute viscosity of aqueous perchloric acid solutions at various temperatures. The values for the 10% perchloric acid solution have been obtained by interpolation of the working curves from 20% perchloric to pure water.[9]

TABLE II

ABSOLUTE VISCOSITIES OF PERCHLORIC ACID SOLUTIONS IN CENTIPOISES

Temp., °C.	Weight per cent. perchloric acid 10	20	30	40	50	60
50	0.560	0.610	0.700	0.820	1.051	1.552
40	0.666	0.721	0.815	0.960	1.260	1.855
30	0.812	0.867	0.959	1.142	1.492	2.190
20	1.006	1.040	1.144	1.338	1.782	2.73
10	1.318	1.357	1.451	1.681	2.265	3.38
0	1.66	1.779	1.921	2.165	2.77	4.29
−10		2.355	2.555	2.88	3.86	6.50
−20			3.48	4.01	5.50	9.75
−30				5.90	8.56	17.1
−40				9.10	14.0	
−50				16.3		
−58				23.3		

Discussion

Accuracy.—Considering sources of error as discussed by Vinal,[4] it is believed that the viscosity values determined in this paper are in error by not more than 1 to 3%. These statements, however, are based on the assumption that the viscosities and densities of the liquids used in calibrating the viscometer, as given in the literature, are sufficiently accurate for the purpose.

Comparison with Accepted Values.—The only values for the viscosity of perchloric acid solutions were taken from the early literature.[2,3,10] Data are available only for 20, 25 and 50° and a comparison of these with our data at 20 and 50° has been made in Table III. Since the 25° values were for very dilute solutions only, they are not shown in the comparison. It is seen that excellent agreement has been obtained for nearly all the

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(8) Markham, THIS JOURNAL, **63**, 874–875 (1941).

(9) "International Critical Tables," **5**, 10 (1929).

(10) *Ibid.*, Vol. V, p. 12 (1929).

TABLE III

VISCOSITIES[a] OF PERCHLORC ACID SOLUTIONS—COMPARISON OF EXPERIMENTAL RESULTS WITH LITERATURE[2,3,9]

$HClO_4$, % by wt.	η, 20°C. (Lit.)	η, 20°C. (Exp.)	η, 50°C. (Lit.)	η, 50°C. (Exp.)
10	1.01	1.006	0.572	0.562
20	1.035	1.040	0.610	0.610
30	1.135	1.144	0.682	0.700
40	1.338	1.338	0.808	0.820
50	1.783	1.782	1.068	1.051
60	2.73	2.73	1.60	1.552

[a] η = Absolute viscosity in centipoises.

given values. The value at 50° for 60% concentration shows the greatest deviation (about 3%).

Summary

Measurements of the viscosity of perchloric acid solutions containing 20 to 60% acid have been made over a temperature range from +50 to −58°, except as the measurements were limited by the freezing points. The viscosity of these solutions at 0° is about three times as great as at +50°, but at −50° the viscosity is about thirty times as great.

SEATTLE, WASHINGTON RECEIVED FEBRUARY 21, 1949

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA]

The Density and Transition Points of Solid Hexamethylethane

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Numerous studies have been made of the various solid phases of *n*-paraffin hydrocarbons. As a result a considerable amount of knowledge has accumulated concerning their crystal structure, transition points and latent heats. In contrast a corresponding knowledge of the branched hydrocarbons is exceedingly small. The reason for this is undoubtedly the great difficulty encountered in preparing these compounds in the pure state. Calingaert, Soroos, Hnizda and Shapiro prepared recently hexamethylethane in a high state of purity.[1] In a series of measurements dealing with the physical chemical properties of this hydrocarbon, they detected the existence of an unstable solid phase just below the melting point. To establish the nature of these solid phases, the above investigators sent two samples of this material to our laboratory, requesting us to measure its densities and coefficient of expansion by the dilatometer method used previously for some of the *n*-paraffin hydrocarbons.[2]

We were informed that the m. p. of both of the samples was 100.63° and that they had a purity of 99.96 ± 0.04%. One of the characteristics of this hydrocarbon is its small liquid range (5.61°) at normal pressures and another is its high sublimation pressure. It was therefore necessary to develop a special technique for transferring this compound from the glass stoppered ampoule in which it was received to the dilatometer.

Experimental Procedure

Preliminary measurements soon verified the observations of the workers from the chemical research laboratories of the Ethyl Corporation. After several unsuccessful methods were tried for filling the bulb, the following was adopted. The bulb, a funnel with a long drawn out stem and the ampoule containing the hydrocarbon were sealed in a glass tube as shown in Fig. 1. To avoid sublimation during the sealing operation, Dry Ice was placed about the lower end of the containing vessel. The sealing process having been completed, the vessel was then exhausted and refilled with hydrogen several times to remove the air. At the last filling, the hydrogen pressure was brought up to about 2.5 atmospheres. The tube was now inverted and heat applied at the upper end while dry ice was placed about the lower end which contained the bulb. In this manner any amount of hydrocarbon could be melted and run into the bulb. The glass tube was then broken in the center, the bulb removed, stoppered and weighed. The procedure from here on was then the same as with the other hydrocarbons.

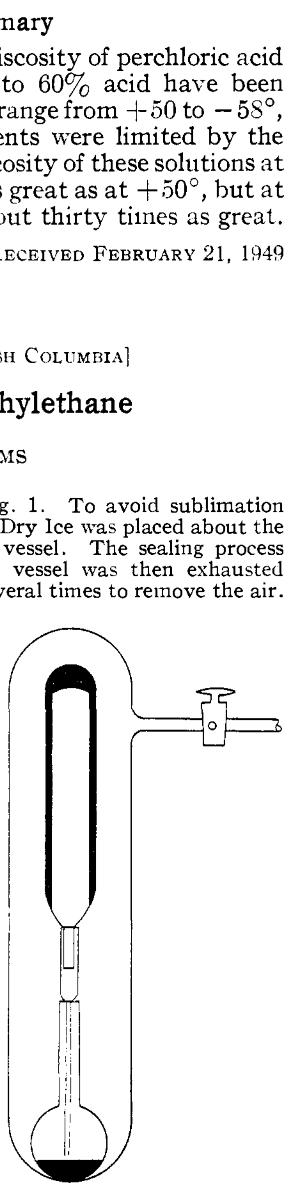

Fig. 1.—Filling the bulb.

A series of density measurements was then made over a temperature range of from 20.69 to 103.50° on the two different lots of materials. Both samples within the limits of accuracy of the measurements gave the same density values. Measurements were first made over intervals of about 2° with both ascending and descending temperatures. In regions near the transition points and rapid density changes the temperature intervals were in the neighborhood of 0.10 to 0.20°, which required an extraordinary amount of bath temperature control. This was found possible with the use of a sensitive thermoregulator and a calibrated Leeds and Northrup platinum resistance thermometer. The absolute density values are considered to be correct to only the third place of decimals while the differential values are within three units of the fourth place. Two phases were found to exist between 20° and the m. p., 100.63°. The density values are given in Table I. The values up to 90° were taken from a large scale plot constructed from the density values obtained in numerous runs. Above 90° to the m. p. actual values of a typical run for phase (1) are given in order to illustrate the manner of approaching a suspected transition or melting point. A similar set of values is given for phase 2.

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(1) Calingaert, Soroos, Hnizda and Shapiro, THIS JOURNAL, **66**, 1389 (1944).

(2) Seyer, Keays and Patterson, *ibid.*, **66**, 179 (1944).