These considerations convey, at least qualitatively, an understanding about the stability of the radicals as depending on the constitution of the particular dye and on pH. We may emphasize once more, at this occasion, that practically none of the organic radicals that had been known prior to the discovery of the semiquinones, exhibit that particular type of strongly symmetrical resonance structure which has just been described as characteristic of the semiquinones. Correspondingly, those older radicals are usually not stable enough to be capable of any appreciable existence in the presence of water, in contrast to the semiquinone radicals.

Summary

Potentiometric oxidative and reductive titrations of Bindschedler's green and phenol blue at various pH's have been carried out. The slope of the titration curves indicates that an intermediate semiquinone radical is formed. The ionization constants for the reduced, half-oxidized, and oxidized forms of these dyes as well as the semiquinone formation constant have been determined. The latter depends on pH.

The ionization constants have been checked by spectrophotometric measurements. The absorption bands of all the three forms of each of these two dyestuffs are shown.

The discussion correlates the stability of the three forms, and especially that of the free radical, with general ideas about molecular stability derived from the electronic theory of the chemical bond and the principle of resonance. The type of resonance stabilizing the free radical is very different from the type of resonance stabilizing the oxidized form of the dye itself. The relative stability of the three forms of a dyestuff (oxidized, half-reduced radical, and reduced) is accounted for, qualitatively at least. The results are summarized in Figs. 4, 5, 6.

NEW YORK, N. Y. RECEIVED APRIL 22, 1938

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH AND THE PHYSICS DEPARTMENT OF COLUMBIA UNIVERSITY]

Potentiometric and Magnetometric Study of the Duroquinone System

BY L. MICHAELIS, M. P. SCHUBERT, R. K. REBER,[1] J. A. KUCK[1] AND S. GRANICK

Among the numerous reversible bivalent two-step oxidation–reduction systems studied so far only a few cases of simple quinones have been subjected to an experimental study. They are concerned with orthoquinones. This paper adds an example of a paraquinone. A suitable representative avoiding the difficulties due to the instability of most quinones in alkaline solution, is duroquinone (tetramethylbenzoquinone). Although there is a limit to the stability of duroquinone also, no observable irreversible alteration by alkali occurs at all, during the period of time necessary for the experiments, at the temperature, 30°, even at the highest pH that reasonably may be used for experiments of this type. Because of its slight solubility, the experiments were performed with buffer solution containing 20 volume per cent. of pyridine, which, though reacting chemically with other quinones, serves only as a solvent for duroquinone. The process of reduction was studied both by the potentiometric and the magnetometric methods. Both methods agree in the final result. In sufficiently alkaline solution a free semiquinone radical of brown color is formed as intermediate step of the reversible reduction. This radical is strongly paramagnetic. In contrast to the semiquinone of phenanthrenequinonesulfonate, which is a representative of the orthoquinones, the semiquinone of duroquinone has no measurable tendency to form a valence-saturated, dimeric form in the dissolved state.

1. Potentiometric Experiments

Reductive titration with leuco-rosinduline G G was used. In sufficiently alkaline solutions, pH >9, the potentials are instantaneously and reproducibly established at concentrations down to 6×10^{-5} molarity. At lower pH values, the establishment of the potentials in low concentrations, about 10^{-4} m, is relatively sluggish, though eventually leading to definite and reproducible values. For this reason titration curves for duroquinone at pH < 9 are somewhat less accurate than those at pH > 9. This uncertainty has no

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[1] Members of the staff of the College of the City of New York.

TABLE I

Molar concn., of duroquinone $\times 10^4$	pH	100 cc. of the buffer contains 20 cc. of pyridine, and	Mean normal potential, E_m, v.	Index potential E_i Left:right of the titration curve, mv.		Average	$\sqrt{k}$ (k = semiquinone formation constant)	$E_2 - E_1$, mv.
2.4	7.40	47 cc. 0.067 M KH_2PO_4 + 23 cc. 0.067 M Na_2HPO_4	−0.226	13	14	..	~ 0	$\sim -\infty$
2.4	7.56	40 cc. 0.067 M KH_2PO_4 + 40 cc. 0.067 M Na_2HPO_4	− .2285	13	15	..	~ 0	$\sim -\infty$
2.4	8.71	2.00 g. sodium veronal + 2.5 cc. 1 M HCl	− .299	15	14	..	~ 0	$\sim -\infty$
2.4	11.50	70 cc. 0.067 M Na_2HPO_4 + 2.2 cc. of 1.086 N NaOH	− .4645	15.7	15.8	15.75	0.19	−87
2.4	11.76	70 cc. 0.067 M Na_2HPO_4 + 3.2 cc. of 1.086 N NaOH	− .4805	17.5	18.0	17.75	0.45	−42
2.4	12.26	1.6 cc. 1.086 N NaOH 0.74 g. KCl	− .504	20	21	20.5	0.84	− 9.1
2.4	12.74	5 cc. 1.086 N NaOH 0.74 g. KCl	− .524	26	26	26.0	1.62	+25.1
2.4	12.92	7.5 cc. 1.086 N NaOH 0.74 g. KCl	− .530	29.5	29.5	29.5	2.15	+39.9
4.9	13.01	10 cc. 1.086 N NaOH 0.74 g. KCl	− .533	31	32	31.5	2.46	+46.9
1.2	13.00	Same	− .532	29.5	30.5	30.0	2.21	+41.3
0.6	12.96	Same	− .532	32	32	32	2.54	+48.6
2.4	13.01	Same	− .532	33	32	32.5	2.62	+50.2
2.4	13.28	20 cc. 1.086 N NaOH 0.74 g. KCl	− .538	36	36	36	3.23	+60.0
2.4	13.51	40 cc. 1.086 N NaOH 0.74 g. KCl	− .548	39	39	39	3.79	+69.4

noticeable bearing on the values of E_m, the mean normal potential, but it affects somewhat the values for E_1 and E_2, the normal potentials of the lower and the higher steps of oxidation, since at $p\text{H} < 9$ the index potential E_i is very close to its minimum value 14.3 mv., and under these circumstances a small error in E_i involves a distinct error in E_1 and E_2. It will be seen, however, that no uncertainty in the construction of the curve (Fig. 1) ensues herefrom, except for the fact that the ionization constant of the radical cannot be determined with accuracy. All that we can say is that it is greater than 10^{-11}. Probably it is very much greater than 10^{-11}, by analogy with the semiquinone of phenanthrenequinonesulfonate.[2] The titration experiments are summarized in Table I, and the normal potentials, plotted against pH according to calculations from these experiments, are shown in Fig. 1. The bend correlated to the acid dissociation of the radical has been located tentatively at pH 11; it may be in reality at a much smaller pH value. In any case, it can be seen that the radical is practically incapable of existence in neutral or acid solution.

The initial concentration of duroquinone has been varied in these experiments in the ratio 1:16 without producing any variation in the shape of the titration curve at any given pH, in contrast to the case of phenanthrenequinonesulfonate.[3] This clearly indicates that there is no measurable tendency to dimerization of the radical. This result is confirmed by the magnetic method up to much higher concentrations.

One striking difference of this paraquinone from the two orthoquinones previously investigated is this. An *o*-quinone shows an acidic ionization, at pH around 9, due to the addition of an OH^- *ion* in alkaline solution. A *p*-quinone does not show this type of ionization, obviously because the acidifying influence of one CO group upon another is distinct only if the two CO groups are in close proximity. In any case, within the pH range experimentally available no ionization is noticeable. A consequence of this fact is that the E_1 and the E_2 curves do not run parallel in strongly alkaline solution, and hence the maximum ratio of semiquinone to total dye $(s/a)_{\text{max.}}$ continuously increases with increasing pH, whereas in the two orthoquinones investigated[2,4] it reaches a maximum value constant for any $p\text{H} > 11.5$.

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(2) L. Michaelis and M. P. Schubert, *J. Biol. Chem.*, **119**, 133 (1937).

(3) L. Michaelis and E. S. Fetcher, THIS JOURNAL, **59**, 2460 (1937).

(4) L. Michaelis, *ibid.*, **58**, 873 (1936).

Magnetometric Measurements

The method used was what may be called the slow-reduction method as described in a previous paper[5] with the magnetic balance of Wills and Boeker, modified by Woodbridge.[6] The change of magnetic susceptibility of the solution was measured during the period of reduction. The duration of this reductive period depends on *p*H and on the concentrations. The concentration of glucose was usually adjusted so as to stretch the time of reaction approximately over one hour.

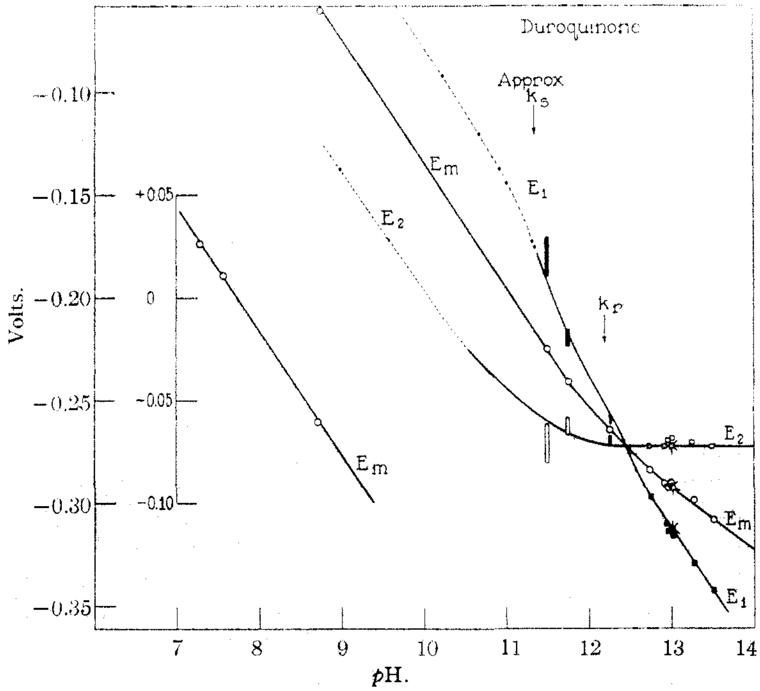

Fig. 1.—The mean normal potential, E_m; the normal potential of the lower step of oxidation, E_1, and the normal potential of the higher step of oxidation, E_2, of duroquinone plotted against *p*H. The left-hand curve is an extension of the main curve. The point designated ϙ- corresponds to three separate experiments with coinciding results.

In order to compare these measurements with those obtained potentiometrically one has to know the *p*H of the solution. In general, the *p*H will not be constant during the reduction. First, from the non-acid duroquinone the acidic semiquinone and the acidic hydroquinone are formed gradually. Since in these experiments the concentration of the quinone has to be taken much higher than in the potentiometric experiments, this fact has to be taken into consideration. Second, as the sugar acts as a reductant it is oxidized to various acids. So a sufficient excess of sodium hydroxide has to be added in order to minimize the effect of these acidic molecular species on the *p*H during the reduction. The following experiments will show that the experimental conditions chosen were such as to render any change of *p*H during the reduction negligible. All of these experiments were carried out by measuring the potential of the platinum electrode after adding some drops of 1% colloidal palladium, and while bubbling with hydrogen until the reduction was complete and the hydrogen potential was constant. (1) A solution just as used for the magnetic experiments no. 12 to 15, containing sodium hydroxide and pyridine, but without duroquinone and without glucose, showed *p*H 13.05. (2) The same solution, containing glucose, showed *p*H 13.01. (3) After adding in addition the duroquinone and rapidly reducing it by PdH_2 in the electrode vessel to the hydroquinone, *p*H was 12.99. (4) The same solution, containing glucose and the duroquinone as in (3) was allowed to stand at 30° in a closed bottle until the reduction by glucose was complete. Then the solution was poured into the electrode vessel, and after addition of colloidal palladium the potential in hydrogen was measured. This showed *p*H 13.00.

These experiments show that addition of glucose slightly shifted the *p*H of the sodium hydroxide solution, as may be expected, but that the effect on *p*H of any chemical reaction during the reduction is within the limits of error in the measurement of *p*H in such strongly alkaline solutions.

So we may put for experiments 12, 13, 14, and 15, *p*H = 13.00. For this *p*H we derive from the curve Fig. 1, $E_2 - E_1$ = 40 mv. Hence the semiquinone formation constant k = 4.64; and $(s/a)_{\text{max.}}$ = 0.517 ± 0.01. The limits of error are based on the assumption that the limit of error in the index potential, E_i, from which $E_2 - E_1$ has to be calculated, is ± 0.5 mv. The magnetic measurement yields $(s/a)_{\text{max.}}$ = 0.519 as average for the four parallel experiments, 12

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(5) L. Michaelis, G. F. Boeker and R. K. Reber, This Journal, **60**, 202 (1938); L. Michaelis, R. K. Reber and J. A. Kuck, *ibid.*, **60**, 214 (1938).

(6) A. P. Wills and G. F. Boeker, *Phys. Rev.*, **42**, 687 (1932); D. B. Woodbridge, *ibid.*, **48**, 672 (1935).

to 15. The agreement is satisfactory. The calculation of $(s/a)_{\text{max.}}$ is based on the difference in the value of susceptibility of its maximum point in the half reduced state, and the final, time-independent value after the completion of the reduction, and on the principle set forth in the previous paper[5] by assuming that the contribution of one mole of the free radical to the total susceptibility, in the direction of paramagnetism, amounts to $2.94/T$ units, where T is the absolute temperature. According to Van Vleck, "all odd polyatomic molecules should presumably conform to this formula."[7] Certainly this radical does.

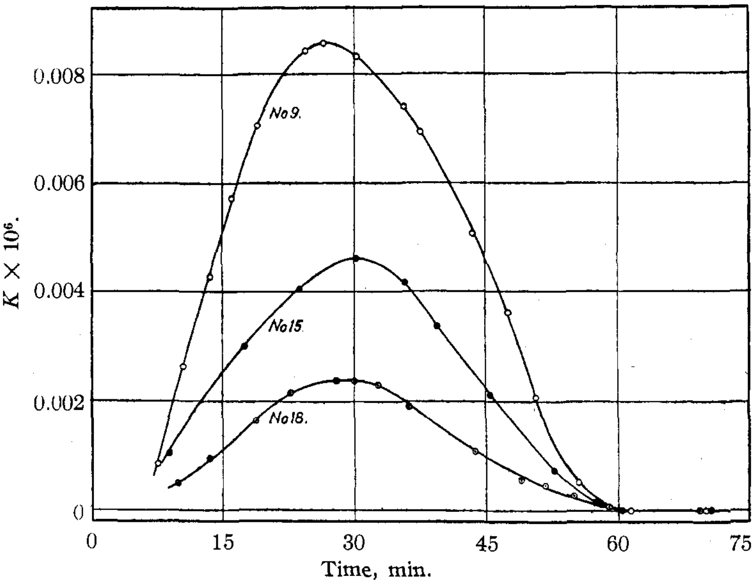

Fig. 2.—Magnetic susceptibility of duroquinone plotted against time, for three of the experiments tabulated in Table II. The time-independent diamagnetic susceptibility after the completion of the reduction is taken as zero point.

It should be ascertained also that the oxidation of glucose itself does not entail any measurable change in magnetic susceptibility. This was proved in the following experiment.

TABLE II

Expt.	T, °C.	P	G	S	a	$K \times 10^6$	s	$s/a_{\text{max.}}$
1	20	3	61.1	0.52	0.0142	0.00945	0.00750	0.528
2	20	3	419	.52	.0143	.00417	.00331	.226[a]
3	20	3	243	1.00	.0147	.01020	.00810	.550
4	30	3	53.4	1.00	.01337	.00915	.00745	.557
5	30	3	52.4	2.00	.0139	.01045	.00850	.612
6	30	3	300	2.00	.01427	.01095	.00893	.625
7	30	3	302.2	2.00	.01427	.01108	.00902	.632
8	30	3	90.2	0.60	.01445	.00788	.00642	.444
9	30	2	80.4	.61	.01431	.00850	.00692	.482
10	30	2	78.6	.60	.01440	.00810	.00659	.457
11	30	2	72.8	.60	.01430	.00831	.00677	.473
12	30	2	39.2	.60	.00712	.00430	.00351	.493
13	30	2	39.2	.60	.00754	.00491	.00400	.531
14	30	2	39.2	.60	.00717	.00461	.00375	.523
15	30	2	39.2	.60	.00703	.00457	.00373	.530
16	30	2	20.0	.60	.00355	.00217	.00177	.506
17	30	2	20.1	.60	.00353	.00228	.00186	.527
18	30	2	24.0	.60	.00356	.00238	.00194	.540

P = ml. of pyridine in 10 ml. of solution.
G = mg. of glucose in 10 ml. of solution.
S = ml. of 2.00 N NaOH in 10 ml. of solution.
s = calculated molar concentration of the semiquinone radical.
a = molar concentration of duroquinone added.
K = difference between the susceptibility at the maximum point and the time independent value at the end of the reaction.

[a] The exceptionally low value of $(s/a)_{\text{max.}}$ in experiment no. 2 is due to the fact that the amount of glucose in comparison with that of sodium hydroxide is so high that pH is considerably lower than in experiment no. 1.

A fresh solution just as in the magnetic experiment, but without duroquinone, was measured in the magnetic balance. Another portion of this solution was bubbled for five hours with air under conditions such as to avoid any evaporation and to keep the volume unchanged, and was then put in the magnetic balance. The oxidation of the sugar had not been allowed to proceed too far in order to ensure the absence of dissolved oxygen during the magnetic observation. The result was that the diamagnetic susceptibility was the same as without previous oxidation, within the limits of error ($\pm$ 0.0002 $\times$ 10^{-6} unit).

Discussion of the Problem of Dimerization

With regard to the formation of either a paramagnetic free semiquinone radical or a dimeric, valence-saturated, non-paramagnetic molecular species on the oxidation level of a quinhydrone, the following statements may serve as actual material for the discussion.

(1) For the benzoquinone system, no statement can be made for alkaline solution because of the instability of benzoquinone in alkali. In acid solution, on mixing benzoquinone and hydroquinone, the solid crystals of quinhydrone are precipitated, and the remaining mother liquor contains practically nothing but a mixture of quinone and hydroquinone. The crystals of

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(7) J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford University Press, 1932, p. 274.

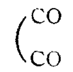
quinhydrone are diamagnetic[8] and so are representatives of a dimeric form, which may be considered as a compound of quinone and hydroquinone with the same justification as a dimerized radical.

(2) For duroquinone in alkaline solution the free paramagnetic semiquinone radical is the only form in which the quinhydrone arises. In acid solution, no quinhydrone can be detected at all on mixing duroquinone and durohydroquinone in solution. It is extremely difficult also to obtain a solid quinhydrone. When a mixture of duroquinone and durohydroquinone, say in methanol, is evaporated even to dryness, no quinhydrone is formed. On heating the dry residue to about 200°, a dark brown mass is formed which on cooling again becomes yellow. If it is cooled very rapidly, dark brown crystalline specks may survive, which disappear either spontaneously or on gently warming. If the hot brown mass is cooled down sufficiently slowly, all the brown color may disappear. It is formed over again on heating strongly. Obviously the formation of duroquinhydrone is a strongly endothermic reaction. The substance is not capable of existence at room temperature except in a metastable or transient state.

(3) Phenanthrenequinone-3-sulfonate, an orthoquinone, forms a paramagnetic radical in alkaline solution, which, when present in not too low a concentration, is in equilibrium with its non-paramagnetic dimeric compound. In acid solution, the free radical cannot be detected in any safely measurable concentration at all, whereas the dimeric compound is easily formed to a great extent in solutions of sufficiently high concentration of the parent substances.

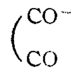
These facts may be interpreted as follows:

Let (I) be the symbol for any quinone. Then (II) is the semiquinone radical in a sufficiently alkaline solution, and (III) the same in a sufficiently acid solution. In (II) there is a strong symmetrical resonance, one electron oscillating from the one O atom to the other. This is not the case in (III) where the fixed proton fixes the electron, too. So (II) should be more stable than (III). This greater stability may find its expression in two ways: (a) the tendency of dismutation is smaller in (II) than in (III). This accounts for the fact that the semiquinone radical is more stable in alkaline than in acid solution, indicated by the fact that the semiquinone formation constant increases with increasing pH for all quinones that have been amenable to measurement yet. (b) The tendency toward dimerization is smaller in (II) than in (III). This explains why the dimerization constant should be greater in acid than in alkaline solution.[2]



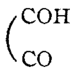
$\left(\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\right.$

(I)



$\left(\begin{matrix}\mathrm{CO^-}\\ \mathrm{CO}\end{matrix}\right.$

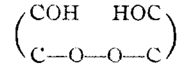
(II)



$\left(\begin{matrix}\mathrm{COH}\\ \mathrm{CO}\end{matrix}\right.$

(III)

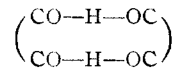
As regards the structure of the dimeric compound, one suggestion is the peroxide structure (IV).



$\left(\begin{matrix}\mathrm{COH} & & \mathrm{HOC}\\ \mathrm{C{-}O{-}O{-}C} & & \end{matrix}\right)$

(IV)

The peroxide of Goldschmidt and Steigerwald[9] derived from chlorophenanthrol is colorless; the color appears only when the radical is formed by dissociation of the peroxide. So, one has to resort to the meriquinone structure proposed long ago by Willstätter and Piccard.[10] Expressing their idea in modern terms, one may assume two hydrogen bonds as in (V) for the dimeric form in the solid state. This hydrogen bond involves a resonance between two fictitious structures, in which alternately the one and the other half of the molecule is in the quinoid or in the benzenoid state, in the same way as is the case for any quinoid dyestuff, say of the indophenol type. This accounts for the deep color much more plausibly than does a peroxide structure.



$\left(\begin{matrix}\mathrm{CO{-}H{-}OC}\\ \mathrm{CO{-}H{-}OC}\end{matrix}\right)$

(V)

The same structure will hold for the soluble dimeric quinhydrone of phenanthrenequinonesulfonate, which represents the quinhydrone practically as it exists in acid solution, and as it exists in equilibrium with the free radical in alkaline solution. This dimeric molecule (V) is such a weak acid that it can exist, to a certain extent, even in rather strongly alkaline solution, provided it can exist in an acid solution.

So we have to discuss on what the existence of this dimeric form depends. The answer is that there must be no steric hindrance for a sufficiently close approach of each pair of atoms which are to be bridged by the hydrogen bond. If the quinone

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[8] Some time ago Dr. C. D. Coryell in Professor L. Pauling's laboratory, at our request, measured the susceptibility of crystalline benzoquinhydrone and found it to be diamagnetic, in confirmation of unpublished experiments of several physicists about which we had personal information.

[9] St. Goldschmidt and Ch. Steigerwald, *Ann.*, **438**, 202 (1924).

[10] R. Willstätter and J. Piccard, *Ber.*, **41**, 1458 (1908).

is an orthoquinone, there is no steric restriction on forming these bonds. In a paraquinone, however, the two bonds can be formed only by putting the planes of the two six-carbon rings flatly one upon the other. This will be easily possible in benzoquinone, but in duroquinone the voluminous side chains prevent a sufficiently close approach. It may be briefly and preliminarily mentioned that the ease with which a solid quinhydrone is formed by mixing a quinone with the corresponding hydroquinone, decreases with the number of CH_3 groups which substitute the H atoms. In the tetramethyl compound, duroquinone, no quinhydrone is formed at all at room temperature.

The authors are deeply indebted to Columbia University for the use of their facilities.

Summary

Duroquinone in a strongly alkaline solution forms a free paramagnetic semiquinone radical of brown color as intermediate step of the reduction. There is no dimeric form of this radical; in other words, no compound corresponding to the ordinary crystalline benzoquinhydrone, which is a dimeric diamagnetic molecule, is formed from duroquinone and durohydroquinone either from alkaline or acid solutions. Solid benzoquinhydrone is a compound formed from quinone and hydroquinone by two hydrogen bonds. These bonds cannot be formed in duroquinone due to steric hindrance.

The maximum percentage of the duro-semiquinone radical in equilibrium with its parent substances continuously increases with increasing *p*H. At *p*H 13 this maximum is about 50%, a result which is the same whether derived from potentiometric or magnetic observations.

NEW YORK, N. Y. RECEIVED MAY 2, 1938

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Influence of Surface Tension on the Measurement of Viscosity
The Viscosity of Methanol

BY GRINNELL JONES AND HOLMES J. FORNWALT

Introduction

In recent years many measurements of viscosity of solutions of salts in water and in methanol have been carried out in this Laboratory by an improved technique.[1] The various sources of experimental error in determining the measurement of the viscosity of dilute solutions have been studied and discussed in an earlier paper. When measurements were extended to concentrated solutions and especially when the viscosity of methanol was compared with that of water it became apparent that the possibility of two additional sources of error which are negligible for relative measurements of dilute solutions should be considered, namely, errors due to unequal drainage and errors due to surface tension. The drainage error has recently been studied by Jones and Stauffer[2] with results which show that this source of error may be disregarded safely in measurements on methanol.

Surface tension can influence the measurement of viscosity by the Ostwald viscometer because the effective hydrostatic head which drives the liquid through the capillary is not solely determined by the dimensions and mounting of the instrument and the volume of liquid contained therein but is influenced by the capillary rise of the liquid in the two arms of the viscometer. Since this capillary rise is a function of the surface tension divided by the density, it will be different for the solutions and for the pure solvent.[3]

In this paper is given a mathematical analysis of the problem that has led to the development of a method of estimating the magnitude of the correction which should be applied to the results obtained with the Ostwald viscometer. This analysis guided the design of another instrument in which the error due to surface tension was minimized as much as other considerations of design permitted. The viscosity of methanol was then measured with reference to water in both the old and new instruments. The results are compared

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[1] Grinnell Jones and co-workers, THIS JOURNAL, **51**, 2950 (1929); **55**, 624, 4124 (1933); **57**, 2041 (1935); **58**, 619, 2558 (1936); **59**, 484 (1937); *Physics*, **4**, 215 (1933).

[2] Grinnell Jones and R. E. Stauffer, THIS JOURNAL, **59**, 1630 (1937).

[3] M. P. Applebey [*J. Chem. Soc.*, **97**, 2013 (1910)] has applied a correction for the effect of surface tension by a method which is a rough approximation.