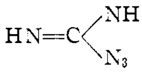
$HN{=}C(NHNO_2)(N_3)$

X

rapidity on addition of a base to form salts of 5-nitroaminotetrazole. Hence it is of considerable interest that nitroguanyl azide can be titrated potentiometrically with a base and that the form of the curve shows only one break which is equivalent to the complete neutralization of 5-nitroaminotetrazole to the di-acid salt. Using the half-neutralization point as corresponding to the second proton of 5-nitroaminotetrazole a value of k_{c_2} of 5×10^{-7} is obtained which is in very good agreement with the value obtained by titration of the acid itself. It is interesting to note that the initial *p*H of a water solution of nitroguanyl azide is acidic to the extent expected for an acid with a K_c of about 10^{-6}. This can only be due to the dissociation of the proton from the nitramide group.

Acknowledgment.—We wish to thank Professors Martin Kilpatrick and Mary L. Kilpatrick for the helpful discussions held during the course of this work. The interest and many helpful comments of Professor L. F. Audrieth are very much appreciated. The support of the U. S. Naval Ordnance Test Station, China Lake, California, under Research Contract N-123S-61517 is gratefully acknowledged.

CHICAGO 16, ILLINOIS RECEIVED AUGUST 21, 1950

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

Surface and Interfacial Tension Titrations of Long Chain Quaternary Salts in Brom Phenol and Brom Thymol Blue Solutions

BY EUGENE L. COLICHMAN

Surface tension and drop time (effective interfacial tension) results of a series of long chain quaternary salts in titrations *vs* brom phenol and brom thymol blue are reported herein. These properties, ordinarily intrinsic, are applied here to the quantitative analysis of surface-active materials. These results show the micellar nature of the quaternary-dye "ion-pair" compound as formed in aqueous solutions. The relation of the presently observed phenomenon to polarography and to determinations of critical micelle concentrations is noted.

The effective conductometric titrations previously reported[1] showed that the known[2,3,4] affinity of brom phenolate blue anions for long chain cations is due to "ion-pair" formation in dilute aqueous solutions probably followed by aggregation into micelles. These results suggested the possibility of quantitative determinations of long chain quaternary salts, by employing the specific reactants, brom phenol and brom thymol blue, in surface and "effective" interfacial tension titrations. Furthermore, the present results establish the nature of the state of aggregation of the "ion-pair" compound in solution.

Surface and interfacial tension measurements on all types of surface-active materials as a means of detecting critical micelle concentrations have been reported[5,6,7] frequently. The minima in these surface tension–concentration curves, earlier attributed to time effects, is now known[8,9,10] to be due to the presence of impurities. However, the analytical possibilities of such measurements have not been explored previously. That metathesis reactions (*viz.* long chain quaternary cations and brom phenolate or brom thymolate blue anions) can be characterized by surface and "effective" interfacial tension titrations is shown here.

Experimental

Octab (Rhodes Chemical Co.) is 100% octadecylbenzyldimethylammonium chloride. Cepacol (Wm. S. Merrell Co.) is a proprietary antiseptic solution, 250 p.p.m. cetyl pyridinium chloride. The other quaternary salts used here were described previously[1] as were the purification and standardization procedures. The 0.100% brom phenol (B.P.B.) and brom thymol (B.T.B.) blue standard solutions were prepared from C.P. chemicals by recognized procedure.[11]

The buffer solutions[12] were prepared from C.P. materials as follows: *p*H 2.00–4.00, potassium acid phthalate and hydrochloric acid; *p*H 4.00–5.50, potassium acid phthalate and sodium hydroxide; *p*H 6.00–8.05, potassium dihydrogen phosphate and sodium hydroxide. A Beckman *p*H Meter, Model G, was used in checking the *p*H values.

Surface tension measurements (uncor.), by the ring method, were made using a Cenco–DuNuoy Interfacial Tensiometer, No. 70540.

The "effective" interfacial tension measurements were obtained by using a functional dropping mercury electrode[13]; however, polarographic measurements were not involved. As in polarographic work, the drop times, recorded with a stop watch, were obtained as average values by counting ten drops. Capillaries, 0.03–0.05 mm. internal diameters, employed at 3 to 6 second drop times, as recommended[13] in polarography, were found satisfactory and necessary here. Drop times greater than 6 seconds were erratic and not reproducible.

Twenty-five to one hundred ml. of the various buffer solutions and aliquot portions of the 0.100% dye solutions were added to cylindrical dishes in establishing the desired initial concentrations of ionic dye species. Portions of standard quaternary solutions were added dropwise from microburets. Mechanical stirring in between increment additions was found to be desirable. About two minutes was required for turbulence to subside after each addition

---

[1] Colichman, THIS JOURNAL, **72**, 1834 (1950).

[2] (a) Auerbach, *Anal. Chem.*, **15**, 492 (1943); (b) **16**, 739 (1944).

[3] Colichman, *ibid.*, **19**, 430 (1947).

[4] (a) Hartley and Runnicles, *Proc. Roy. Soc.* (*London*), **168A**, 420 (1938); (b) Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

[5] Adam and Shute, *ibid.*, **34**, 758 (1938).

[6] Nutting, Long and Harkins, THIS JOURNAL, **62**, 1496 (1940).

[7] Tartar, Sivertz and Reitmeier, *ibid.*, **62**, 2375 (1940).

[8] Miles and Shedlovsky, *J. Phys. Chem.*, **48**, 57 (1944).

[9] Miles, *ibid.*, **49**, 71 (1945).

[10] Brady, *ibid.*, **53**, 56 (1949).

[11] Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 4th ed., p. 942.

[12] Britton, "Hydrogen Ions," D. Van Nostrand Co., Inc., New York, N. Y., Vol. I, Chap. 16.

[13] Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., Revised Reprint, 1946, pp. 240–243.

and preceding each surface tension or drop time determination. An empirical constant rate of approaching the surface film break point was necessary in order to obtain reproducible results in the surface tension titrations. Drop time data were obtained as in polarography. The least clear solutions required strong illumination in order that drop times could be observed accurately.

Results and Discussion

The surface tension and drop time titration results on the various quaternary salts are presented in Table I. The ionization values of brom phenol and brom thymol blue in the various buffer solutions were calculated from the respective pK values,[14] 4.05 and 7.10, and correspond, in both cases, to the extent of the following type reaction: $HD^- \leftrightarrow H^+ + D^=$. In each determination the buffer solutions were used to obtain the desired ratio of equivalents of HD^- to $D^=$. In observing the effect of the concentration of these two species on the results, it was necessary to vary the ratio of HD^- to $D^=$ from low to very high values. Ionic equivalents (calcd.) refer to the total equivalents of HD^- and $D^=$ present in each titration. Agreement between the dye equivalents (calcd.) and equivalents of quaternary salt (used) is seen in Table I. An average deviation of ±1.4% is noted. It is seen (Table I) that both the surface tension and drop time methods yield comparable results.

TABLE I

SURFACE TENSION AND DROP TIME TITRATION RESULTS

A. 0.002700 *M* cetyltrimethylammonium bromide *vs.* B.P.B.

Expt.	Ioniz., %	Total dye concn. (at end-pt.), formality × 10^5	Ionic equiv. dye (calcd.) × 10^6	Quat. salt equiv. (used) × 10^6
1	$0.9^{s,e}$	10.62	6.02	6.18
2	$0.9^{d,e}$	10.65	6.02	5.78
3	$12.2^{s,f}$	10.57	6.69	6.76
4	$12.2^{d,f}$	10.59	6.69	6.59
5	$44.2^{s,g}$	5.58	4.30	4.12
6	$44.2^{s,g}$	10.86	8.60	8.52
7	$44.2^{d,g}$	10.82^a	8.59	8.65
8	$44.2^{d,g}$	10.85	8.59	8.52
9	$73.8^{s,h}$	10.36	20.70	20.00
10	$73.8^{d,h}$	5.54^b	10.36	Poorly defined end-pt.
11	$73.8^{d,h}$	14.56	10.36	10.46
12	$73.8^{d,h}$	24.42	15.55	15.40
13	$73.8^{d,h}$	24.35	15.55	15.68
14	$90.0^{s,i}$	2.88^b		No end-point
15	$90.0^{s,i}$	14.46	33.88	32.97
16	$90.0^{d,i}$	8.00^b		No end-point
17	$90.0^{d,i}$	14.40	33.84	33.50
18	$90.0^{d,i}$	18.00^b		No end-point

B. 0.002700 *M* cetyltrimethylammonium bromide *vs.* B.T.B.

24	$0.1^{s,g}$	16.20	9.56	9.40
25	$0.1^{d,g}$	16.20	9.56	9.34
26	$20.3^{d,k}$	15.95	11.50	11.53
27	$50.0^{s,l}$	11.14	9.56	9.65
28	$50.0^{d,l}$	11.14	9.56	9.62
29	$70.0^{d,m}$	3.08	5.42	5.42
30	$70.0^{s,m}$	5.94	10.84	10.86
31	$70.0^{d,m}$	5.94	10.84	10.72
32	$70.0^{d,m}$	15.53	16.25	16.22
33	$90.0^{d,n}$	10.96^b		No end-point
34	$90.0^{d,n}$	19.14	24.25	24.34

C. 0.002500 *M* hyamine 1622 *vs.* B.T.B.

35	$20.3^{s,k}$	3.09	3.87	3.82
36	$20.3^{d,k}$	3.09	3.87	3.80
37	$20.3^{d,k}$	8.68^b		No end-point
38	$50.0^{s,l}$	3.08	4.82	4.89
39	$50.0^{d,l}$	3.08	4.82	4.87
40	$70.0^{d,m}$	3.08^b		No end-point

D. 0.002500 *M* hyamine 1622 *vs.* B.P.B.

41	$12.2^{s,f}$	2.89	3.38	3.45
42	$12.2^{d,f}$	2.89	3.38	3.42
43	$12.2^{s,f}$	4.26	5.07	5.15
44	$12.2^{d,f}$	4.26	5.07	5.12
45	$12.2^{d,f}$	5.60^b		No end-point
46	$44.2^{s,g}$	2.87	4.35	4.39
47	$44.2^{d,g}$	2.87	4.35	4.37

E. 0.001360 *M* octab *vs.* B.P.B.

48	$12.2^{s,f}$	5.48	6.74	6.76
49	$12.2^{d,f}$	5.48	6.74	6.72
50	$44.2^{s,g}$	2.85	3.87	3.80
51	$44.2^{d,g}$	2.85	3.87	3.82

F. 0.001360 *M* octab *vs.* B.T.B.

52	$20.3^{s,k}$	5.84	7.72	7.80
53	$20.3^{d,k}$	5.84	7.72	7.78

G. 1/4000 cetylpyridinium chloride (cepacol) *vs.* B.P.B.

54	$96.7^{s,j}$	1.04	2.31	2.38

[a] This determination at around 3 sec. drop time, all others at 5.5–6.0 sec. [b] Concn. at calcd. end-pt. [s] Surface tension method. [d] Drop time method. Buffer solns.. pH: [e] 2.00; [f] 3.00; [g] 3.95; [h] 4.50; [i] 5.00; [j] 5.50; [k] 6.50; [l] 7.10; [m] 7.47; [n] 8.05.

Figures 1, 2 and 3 show some of the types of curves found in observing the above results. All of the curves exhibit the "leveling off" phenomenon at the equivalence point corresponding to charge neutralization of the dye anions present by quaternary cations added. It has been shown in previous investigations[5,6,7] that attainment of a substantially constant surface tension is indicative of micelle formation. In investigations employing pure quaternary salt solutions, the "leveling off" point corresponds to a stable micelle, solely concentration dependent, and termed the critical micelle concentration. The situation is somewhat different when anionic dye species are present in solution along with the cationic quaternary salts. Under these conditions, the number of equivalents of both the anionic and cationic species present must be considered. It is seen that completely formed dye-quaternary micelles (as exemplified by attainment of a plateau in all curves) require that at least equivalent quantities of quaternary cations be present. The present results thus indicate mixed micelle formation between the substantive cationic and anionic species, and show how substantivity might well influence critical micelle concentrations of surface-active materials. Corrin and Harkins[15] found that in the dye-spectra method the charge and nature of the dye molecules, employed in determining critical micelle concentrations of surface-active materials, can influence the results. In order to

---

(14) Brode, THIS JOURNAL, 46, 593 (1924).

(15) Corrin and Harkins, *ibid.*, 69, 679 (1947).

prevent these added complications, the concentration of dye used must be considerably lower than the surface-active compound under investigation. The present results show the difficulties that can arise if such is not the case. In employing a dye to determine the critical micelle concentration of other surface-active species, any dependency of the results on the quantity of dye used should be noted and reported.

Both brom phenol and brom thymol blue in the absence of quaternary salts have no effect on the surface tension of the aqueous solutions over the entire range of concentration at which the dyes are employed. Neverthless, when surface-active quaternary salts are added to the dye solutions, satisfactory inflection points are observed in the surface tension curves. The quaternary salts by themselves lower the drop time in the aqueous buffer solutions while the pure dye solutions raise the drop time. The much sharper inflections at the end-points in the drop time curves are thus accounted for on this basis. The nature of the drop time curves, in the region before the end-point, is not amenable to simple explanation. The plateau, once the end-point is attained, indicates a stable mixed micelle.

Neither method will show an inflection point at those *p*H's where the percentage ionization is near completion and thus the concentration of HD^- is too low. At 99.2% ionization end-points are not detected even at dye concentrations which ordinarily yield sharp inflections at lower ionization values. A comparison of experiments 14 and 15, 16 and 17, and 33 and 34 shows that increasing the concentration of HD^- can result in normal end-points. The concentration of dye can be increased only within certain limits which depend upon the extent of compatibility in the various buffer solutions. For example, at 99.2% ionization, precipitation occurs before the concentration of HD^- can be increased sufficiently to allow its determination by either method. Titrations are limited to those concentrations of dye which will yield a stable dispersion of the dye-quaternary metathesis compound. Results show that brom thymol blue requires a higher minimum concentration of HD^- than brom phenol blue in order to yield a satisfactory end-point. In the case of B.T.B. probably the critical micelle concentration is higher for the metathesis compound. Those experiments which fail to show end-points perhaps are at concentrations of HD^- below the critical concentration necessary for micellar formation with the cationic species present.

Surface tension as a possible analytical tool for investigating the extent and nature of reactions has received little attention. The apparent scarcity of such data on mixtures possibly is due to difficulties in interpretation of such results. Prideaux and Coleman,[16] in a series of investigations involving the combination of fatty acids with nitrogen bases, show the potentialities of surface tension measurements in deducing the state of existence of ionic and molecular species in solution. Surface tension measurements[17] on dilute potassium chloride and mercuric chloride solutions have been used to show the formation of double salts in aqueous solution, such as $KCl \cdot 2HgCl_2$ and $2KCl \cdot HgCl_2$. The present results suggest further applications of the sur-

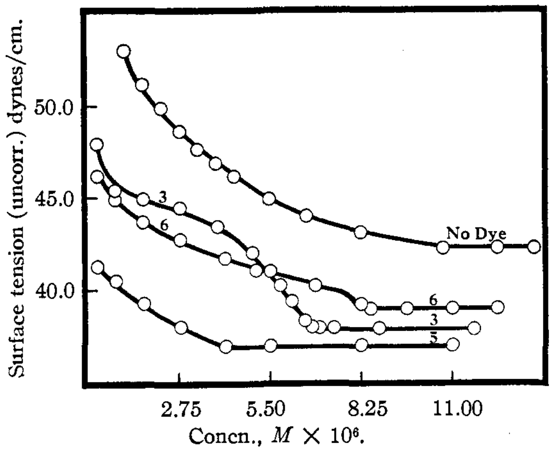

Fig. 1.—Typical surface tension curves of 0.00270 *M* cetyltrimethylammonium bromide *vs.* B.P.B. Numbers refer to experiments in Table I.

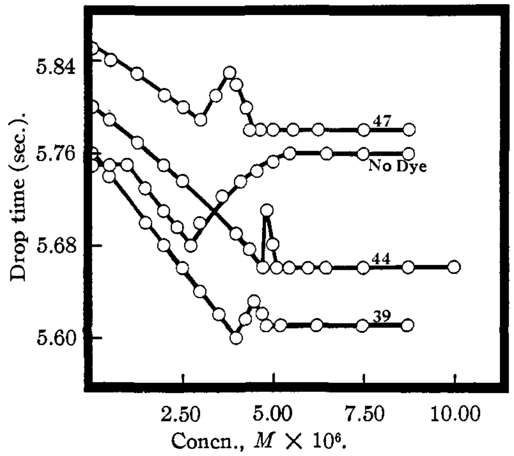

Fig. 2.—Typical drop time curves of 0.00250 *M* hyamine 1622 *vs.* B.P.B. and B.T.B. Numbers refer to experiments in Table I.

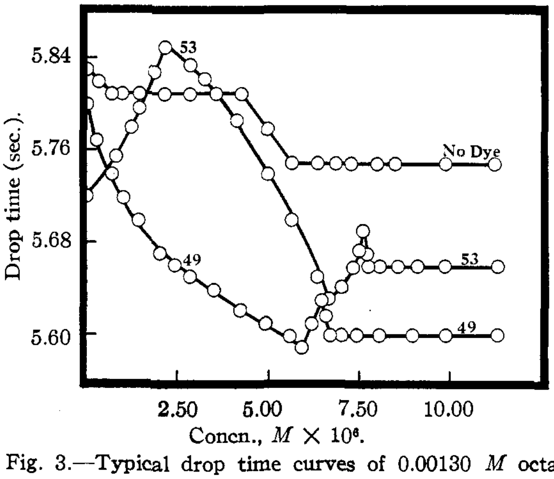

Fig. 3.—Typical drop time curves of 0.00130 *M* octab *vs.* B.P.B. and B.T.B. Numbers refer to experiments in Table I.

---

(16) Prideaux and Coleman, *J. Chem. Soc.*, 1346 (1936); 462 and 1022 (1937).

(17) Arcay and Marcot, *Compt. rend.*, **209**, 881 (1939).

face and interfacial tension methods in studying the nature of reactions in solution.

Kolthoff and Lingane[18] point out that the rate of flow of a given amount of mercury from a set capillary under a constant pressure head on the dropping mercury and at constant temperature is practically independent of the medium in which the drop forms. The drop time, however, is directly proportional to the interfacial tension at the mercury–medium interface. In the present results both quaternary salts and the dyes employed influence the mercury–medium interfacial tension. This is the basis for calling the drop time results here "effective" interfacial tension measurements.

Pronounced changes in the "effective" mercury–medium interfacial tension have been observed in polarographic work when surface-active substances are present. Damping and shifting of polarographic waves seem to accompany these changes. This phenomenon has been made[19,20] the basis for quantitative determinations of surface-active substances by polarographic adsorption analyses. Recent results[21] explain the nature of the adsorption phenomenon.

[18] Kolthoff and Lingane, *Chem. Revs.*, **24**, 1 (1939).

[19] Schwartz, Shroder and Stackelberg, *Z. Elektrochem.*, **48**, 6 (1942).

[20] Stackelberg and Schutz, *Kolloid-Z.*, **105**, 20 (1943).

[21] Colichman, THIS JOURNAL, **72**, 4036 (1950).

PORTLAND, OREGON RECEIVED JUNE 14, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AND RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

Oxidation Potentials of the Pu(III)-Pu(IV) and Fe(II)-Fe(III) Couples in Perchloric Acid Solution—Heat Content and Entropy Changes[1]

BY ROBERT E. CONNICK AND WILLIAM H. MCVEY

The formal potential of the cell: Pt:H_2:1 *M* $HClO_4$; 1 *M* $HClO_4$, $Pu(ClO_4)_3$, $Pu(ClO_4)_4$: Au was found to be −0.982 volt at 25°. This value differs significantly from that previously reported and is consistent with the idea that Pu^{+4} is partially complexed by chloride ion in 1 *M* HCl. A formal potential scheme involving the +3, +4 and +6 oxidation states of plutonium in 1 *M* perchloric acid was derived. The e.m.f. was measured as a function of temperature and the change in heat content for the reaction $Pu^{+3} + H^+ = Pu^{+4} + {}^1/_2H_2$ was found to be +13.52 kcal./mole, compared with 11.3 kcal./mole obtained by Evans from calorimetric measurements. Approximate entropies for the ions Pu^{+4} and PuO_2^{++} were found to be −77 and −18 e.u., respectively. These are very nearly equal to those for the corresponding ions of uranium. The heat and free energy of the reaction $Fe^{++} + H^+ = Fe^{+++} + {}^1/_2H_2$ were measured and compared with previously determined values.

Introduction

The oxidation potential of the couple $Pu^{+3} = Pu^{+4} + e^-$ has been reported by Hindman, *et al.*,[2,3,4] to be −0.945 volt in 1 *M*[5] perchloric acid and −0.966 volt in 1 *M* hydrochloric acid at 25°. These potentials can differ appreciably[6] only because of a change in the activity coefficients of Pu(III) and Pu(IV) in going from perchloric acid to hydrochloric acid; significant changes might occur through complex ion formation. There is no evidence that perchlorate ion complexes any +3 or +4 ions in aqueous solution and some evidence that it does not form complexes with Pu^{+3} and Pu^{+4}.[7] On the other hand it is well known that chloride ion complexes Pu^{+4} although there is no evidence of its complexing Pu^{+3} in 1 *M* hydrochloric acid.[7] If it is assumed that the potentials in perchloric acid and hydrochloric acid solution differ primarily because of chloride complexing of Pu(IV), the potential for perchloric acid should be more negative. Just the opposite has been reported in the above cited work.

It was believed that the error, if it existed, lay in the perchloric acid data as the hydrochloric acid measurements were very carefully performed.

Further evidence that the perchloric acid measurement might be in error came from combining the value of −1.067 volts given by Hindman[2] for the Pu(IV)–Pu(VI) couple in 1 *M* perchloric acid with the Pu(III)–Pu(IV) potential to give −0.122 volt for the reaction

$$3Pu(IV) = Pu(VI) + 2Pu(III) \qquad (1)$$

in 1 *M* perchloric acid at 25°. From this datum one calculates a value of 8×10^{-5} for the equilibrium quotient expressed in terms of gross concentrations

$$K = (Pu(VI))(Pu(III))^2/(Pu(IV))^3$$

where parentheses are used to indicate concentrations in moles per liter of solution at 25°. This value, however, is in disagreement with the directly measured value which Kasha[8] found to be $K = 0.041$.

In repeating the e.m.f. measurements in perchloric acid it seemed desirable to extend the determinations to other temperatures in order to obtain the heat and entropy of the reaction. Evans[9] had previously measured the heat of oxidation of Pu^{+3} to Pu^{+4} calorimetrically.

[1] Research performed under the auspices of the United States Atomic Energy Commission.

[2] J. C. Hindman, Manhattan District Project Report CN-2289, p. 1, November 1, 1944.

[3] J. J. Howland, Jr., K. A. Kraus and J. C. Hindman, Manhattan District Project Report CN-1371, p. 8, March 1, 1944.

[4] J. J. Howland, Jr., J. C. Hindman and K. A. Kraus, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Plutonium Project Record, McGraw-Hill Book Co., Inc., 1949, p. 133.

[5] The symbol *M* is used throughout this paper to indicate concentrations expressed in moles per liter of solution at 25°.

[6] The liquid junction potentials present in the cell measurements could not possibly account for the reported difference in the potential in 1 *M* $HClO_4$ and 1 *M* HCl.

[7] J. C. Hindman, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Plutonium Project Record, McGraw-Hill Book Co., Inc., 1949, p. 370.

[8] M. Kasha, *ibid.*, p. 295.

[9] M. W. Evans, *ibid.*, p. 282.