sents the average of at least three determinations, and each value of the polymer viscosity is the average of two determinations. The data conform to the equation

$$\log_{10} \eta_{170} = 5.120 + 4.725 \log_{10} [\eta] \qquad (3)$$

The relationship yielded by the data of Fox and Flory[10] is

$$\log_{10} \eta_{217} = 4.69 + 5.31 \log_{10} [\eta] \qquad (4)$$

Considering the differences in temperature and method of measurement together with the fact that the polymers used in the present experiments were of variable heterogeneity in molecular weight, the agreement is good.

Although only two points are shown, it is likely that copolymers of isobutylene and diolefins, the latter being present in relatively small proportions, will follow the same or similar relationship. Hence the apparent discrepancy between these data and previous data of Zapp and Baldwin[6] lies in the fact that the molecular weight range previously covered was narrow (140,000 to 550,000). The present data can also be approximated by equation (1) over limited molecular weight ranges.

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[10] Private communication.

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Conductance of Long Chain Quaternary Salts in Bromophenolate Blue Solutions

BY EUGENE L. COLICHMAN[1]

The affinity of bromophenolate blue anions for long chain quaternary cations is the basis for several analytical methods[2,3,4] of determining both cationic and anionic active compounds. Such an electrostatic interaction in dilute aqueous solutions results in a color change from purple to blue without precipitation. The optical clarity

TABLE I

CONDUCTIVITY FUNCTIONS OF QUATERNARY SALTS IN 1.5×10^{-5} *M* AQUEOUS BROMOPHENOLATE BLUE SOLUTIONS AT 25°

$C \times 10^5$	$\bar{L}_s \times 10^6$	$(\bar{L}_{R_2D})_{exp.} \times 10^6$	$\Delta\bar{L}_s/\Delta C \times 10$
n-Myristyltrimethylammonium Bromide			
3.0	3.9	0.0	1.00
4.5	5.4	.1	1.00
6.0	6.9	.0	1.00
8.9	9.8	.0	1.00
11.9	12.8	.0	0.90
17.9	18.2		.983
23.8	24.0		.950
29.8	29.7		
n-Cetyltrimethylammonium Bromide			
3.0	3.9	0.0	1.00
3.9	4.8	.1	0.943
5.6	6.4	.0	1.00
8.4	9.2	.2	1.07
11.2	12.2		1.07
14.0	15.2		1.07
16.8	18.2		1.11
28.0	29.5		
n-Cetyltrimethylammonium Chloride			
3.0	3.8	0.1	1.00
3.5	4.3	.1	0.90
4.5	5.2	.0	.948
6.4	7.0	.0	942
7.1	7.6	.0	1.00
8.4	8.9	.0	0.50
9.6	9.5		.907
12.8	12.4		.842
19.1	17.7		.852
31.9	28.6		.844
63.8	55.5		
n-Cetyltrimethylammonium Nitrate			
3.0	3.7	0.0	0.908
4.1	4.7	.0	.890
5.9	6.3	.0	.920
8.4	8.6	.0	.765
11.8	11.2		.863
14.7	13.7		.867
17.7	16.3		.864
23.6	21.4		
n-Octadecyltrimethylammonium Bromide			
3.0	3.9	0.2	1.00
4.1	5.0	.2	1.50
5.1	6.5	.0	1.40
6.1	7.9	.0	1.40
7.1	9.3		1.45
8.2	10.9		1.30
10.2	13.5		1.20
15.3	19.6		
n-Laurylpyridinium Chloride			
18.6	22.0		1.17
23.2	27.4		1.20
27.8	32.9		1.12
37.1	43.3		1.08
46.4	53.3		1.12
55.7	63.7		1.11
65.0	74.0		1.09
92.8	104.3		
Hyamine 1622			
9.4	10.8		0.892
14.0	13.9		.894
18.7	18.1		.915
25.7	24.5		.943
32.7	30.8		.950
46.8	44.5		.877
93.6	85.5		.847
140.4	125		.832
187.2	164		

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[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**, No. 934, 424 (1938); (b) Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

of these solutions was confirmed with the aid of a spectrophotometer. Conductance measurements on these mixtures were made in order to study the nature of this important reaction.

In Table I are tabulated the conductance results for the various quaternary salts employed in the effective conductometric titrations of a given aliquot of disodium bromophenolate blue solution. The concentration of the disodium salt of brom phenol blue was held constant at 1.5 × 10^{-5} M in all measurements. C refers to the total normality of the quaternary salt added. $\bar{L}_s$ is the measured specific conductivity of the solution minus the conductivity of the water. R_2D refers to the "ion-pair" compound formed between quaternary cations and divalent dye anions.

If the following metathesis occurs: 1.5×10^{-5} M $\overset{+}{\mathrm{Na}}_2\overset{-}{\mathrm{D}}$ + C molar $\overset{+}{\mathrm{R}}\overset{-}{\mathrm{X}}$ yields 1.5×10^{-5} M R_2D + 3.0×10^{-5} M $\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{X}}$, then, $\bar{L}_s = \bar{L}_{R_2D} + \bar{L}_{NaX} + \bar{L}_{\text{excess RX}}$ assuming Kohlrausch's law of independent ion migration is applicable here. The experimental values of $\bar{L}_{R_2D}$, labelled $(\bar{L}_{R_2D})_{exp.}$, calculated on the above basis, are seen to be zero or negligible in all the cases reported. This fact substantiates the validity of the above assumption and is taken as proof of the complete formation of non-conducting ion-pairs, R_2D, in the most dilute aqueous solutions. The $\Delta\bar{L}_s/\Delta C$ *vs.* C data indicates that some of the quaternary salts show deviations from linear conductance relationships, but no critical micelle phenomenon is warranted on the basis of these results alone. The conductance results do not differentiate between unassociated R_2D and possible non-conducting associated micelle forms of the ion-pair compound.

$\bar{L}_{NaX}$ values from recognized sources[5] and Tartar's conductance values,[6] were used in calculating the experimental values of $\bar{L}_{R_2D}$ from the measured $\bar{L}_s$ values. By interpolation and extrapolation from Tartar's results on the lauryl and cetyl quaternaries, $\Lambda_{C_{14}}$, $\Lambda_{C_{16}}$ and $\Lambda_{C_{18}}$ were approximated as 20, 19 and 18. The small uncertainty in the absolute values used for Λ_{R^+} is not very significant in establishing the phenomena of ion-pair formation in these dilute aqueous solutions.

Experimental

All quaternary salts used in the conductance measurements were recrystallized three times from ethanol–benzene mixtures. The *n*-cetyltrimethylammonium bromide was obtained initially as J. T. Baker's C. P. compound. The corresponding chloride and nitrate were prepared by metathesis of the appropriate silver salt with *n*-cetyltrimethylammonium bromide in absolute methanol.

n-Myristyl- and *n*-octadecyltrimethylammonium bromides were prepared from Eastman Kodak Co. White Label *n*-myristyl and *n*-octadecyl bromides by refluxing with a slight excess of alcoholic trimethylamine solution until a test portion showed complete solubility in water. The *n*-laurylpyridinium chloride was prepared similarly with Eastman Kodak Co. White Label *n*-lauryl chloride and alcoholic pyridine. This reaction was catalyzed by adding a few crystals of potassium iodide.

Hyamine 1622 (Röhm and Haas Co.) is 100% active *p*-tertiary octylphenoxyethoxyethyldimethylbenzylammonium chloride.

The stock solution of disodium salt of brom phenol blue was prepared from National Aniline Co. Reagent Grade brom phenol blue and C. P. sodium hydroxide.

Conductivities were measured at 1000 cycles with a Dyke–Jones bridge (Leeds and Northrup Co.) and an oscilloscope detector. A pyrex Erlenmeyer type conductance cell,[7] with a cell constant equal to 0.0552, was maintained at 25.00 ± 0.01° in an oil thermostat. The specific conductivity of the water, obtained by distillation through a Barnstead block tin still, varied only between 0.9 and 1.0 × 10^{-6} ohm^{-1} cm.$^{-1}$.

Each concentration measured was prepared in a seasoned pyrex volumetric flask by adding volume aliquots of standard dye and quaternary solutions which were stored in Jena glass bottles. Then, to minimize adsorption errors, the cell was rinsed with several portions of each dye–quaternary concentration before recording the equilbrium conductance value.

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[5] (a) Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1943; (b) MacDougall, "Physical Chemistry," Macmillan Co., New York, N. Y., 1936, pp. 475–479.

[6] Tartar, THIS JOURNAL, **65**, 692 (1943).

[7] Fuoss and Kraus, THIS JOURNAL, **55**, 21 (1933).

The Decomposition of Diphosphopyridinenucleotide (DPN) and Adenosinetriphosphate (ATP) by Ultraviolet Light

BY C. E. CARTER[1]

The inactivation of cozymase (DPN) of horse red blood cells by ultraviolet light was first reported by Runnstrom, Lennerstrand and Borei.[1a] A study of the products of this photochemical reaction has not been made, although Runnstrom, *et al.*, reported that, while cozymase activity of red cells irradiated with ultraviolet light was lost, cophosphorylase activity remained, indicating that the adenylic acid moiety of the molecule was unaltered. Resolution of the products of the reactions of DPN and ATP with ultraviolet light by techniques of partition paper chromatography is reported in this paper.

Materials and Methods

Adenosinetriphosphate (ATP) as the free acid and diphosphopyridinenucleotide (DPN) were purchased from the Schwarz Laboratories, New York. ATP when chromatographed showed one principal component and a small amount of a second component, having the distribution value (*RF* value) and spectrum of adenosine-5-phosphoric acid, which accounted for 12% of the total 260 mμ absorption of the mixture. DPN was homogenous when chromatographed but assayed only 38% pure by the hydrosulfite reduction procedure of Lepage.[2]

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[1] Biology Division, Oak Ridge National Laboratory, operated by Carbide and Carbon Chemicals Corporation under Contract No. W-7405-eng-26 for the Atomic Energy Commission, Oak Ridge, Tennessee.

[1a] J. Runnstrom, A. Lennerstrand and H. Borei, *Biochem. Z.*, **271**, 15 (1934).

[2] G. A. Lepage, *J. Biol. Chem.*, **168**, 623 (1947).