one another. It is obvious that our ignorance of the details of the molecular shapes renders impossible the accurate prediction of properties which must be strongly influenced by them, but it appears to be possible to explain, in qualitative fashion, the complex dielectric behavior of the alcohols on the basis of simple and not unreasonable assumptions.

Summary

The dielectric constants of twenty-two isomeric octyl alcohols have been measured over a wide range of temperature and an indication of their tendency toward anomalous dispersion and absorption for a wave length of 600 meters has been obtained.

Solutions of 2-methylheptanol-3 in benzene have been measured in order to obtain the electric moment of the molecule, which is close to that of *n*-octyl alcohol and the lower alcohols.

The great differences among the dielectric constants of the isomers are attributed to the effects of molecular orientation, which causes the dielectric constants of the tertiary methylheptanols and two of the secondary to increase with rising temperature instead of decreasing in the normal manner.

The explanation of the values of the dielectric constants in terms of molecular orientation is consistent with the observed tendencies toward anomalous dispersion and absorption and with the results of the x-ray diffraction measurements of Stewart.

PRINCETON, NEW JERSEY

[CONTRIBUTION NO. 610 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

CHEMICAL KINETICS IN HIGHLY DILUTE SOLUTION. BROMO-ACETATE AND THIOSULFATE IONS IN THE PRESENCE OF SODIUM ION AT 25°

BY VICTOR K. LA MER[1]

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It has been shown by Slator[2], as well as others,[3] that reactions of the type

$$BrCH_2COO^- + S_2O_3^{--} \longrightarrow S_2O_3CH_2COO^{--} + Br^- \qquad (1)$$

in which a halogen is replaced by thiosulfate are bimolecular and singularly free from side reactions. Since thiosulfate can be determined with great precision and comparative ease, reactions of this type are particularly well adapted for testing quantitatively, theories of salts catalysis, since the reaction rate can be followed very accurately in the region of high

[1] Paper presented at the Minneapolis Meeting of the American Chemical Society, September, 1929.

[2] Slator, *J. Chem. Soc.*, **87**, 485 (1905), and earlier papers.

[3] Krapivin, *Z. physik. Chem.*, **82**, 439 (1913); see also *J. Chim. Phys.*, **10**, No. 2, 289 (1912), for data on the chloro-acetate reaction.

dilution. In addition no change in ionic strength occurs during the progress of the reaction. In this paper we shall present preliminary data for the reaction rate in the presence of sodium ion by extending the data of Krapivin[3] at 25° from a concentration of 0.01 N (0.025μ) to concentration as low as 0.0005 N (0.00125μ).

According to Brönsted,[4] a bimolecular reaction follows the scheme

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X} \longrightarrow \text{Resultants} \qquad (2)$$

where X is a critical collision complex of great instability whose charge Z_{X} should equal the algebraic sum of the charges on the reactants; namely, $Z_{\mathrm{X}} = Z_{\mathrm{A}} + Z_{\mathrm{B}}$. The general velocity equation for Scheme I becomes

$$\frac{-\mathrm{d}x}{\mathrm{d}t} = k_0 \times C_{\mathrm{A}} \times C_{\mathrm{B}} \times \frac{f_{\mathrm{A}} \times f_{\mathrm{B}}}{f_{\mathrm{X}}} \qquad (3)$$

where k_0 is the true velocity constant independent of salt effects for a given reference medium and the factor $F_{\mathrm{A}} = f_{\mathrm{A}} \times f_{\mathrm{B}}/f_{\mathrm{X}}$ takes account of the change in velocity with changing environment.

Inasmuch as *individual ion* activities like f_{A} and f_{B} are not accessible to direct measurement owing to uncertainties in liquid junction potentials, and particularly since the very fugitive nature of X itself precludes any attempt to determine the individual behavior of f_{X} by any of the customary thermodynamic methods, it is evident that the quantitative verification of this theory must be obtained in the region of such highly dilute solutions that the activity coefficients of the individual ions may reasonably be expected to follow the Debye-Hückel[5] limiting law, *i. e.*, they are determined solely by the valence type and the concentration.

Although the colorimetric and conductimetric experiments of Brönsted and Livingston[6] furnish the most striking and most convincing evidence that Equation 3 is correct in principle, yet owing to irregularities in the data one cannot state definitely whether the discrepancies which they observed from the behavior predicted by the Debye limiting law arise primarily from unavoidable experimental errors or whether the deviations really represent specific individual properties which do not vanish completely in the concentration range $\mu = 0.00135$ to 0.01. In fact, the authors are careful to point out that "the character of these deviations is of great interest in the study of chemical kinetics, and ought to be the object of a more careful investigation." When we recognize that the critical complex in their Reaction II is of the tetravalent type, and that the activity coefficients of trivalent ions do not follow the limiting law even qualitatively at dilutions as low as 0.001μ in the presence of divalent ions

[4] (a)Brönsted, *Z. physik. Chem.*, **102,** 169 (1922); (b) **115,** 337 (1925); (c) Columbia University Lectures, "Contemporary Developments in Chemistry," March, **1927.**

[5] (a) Debye and Hückel, *Physik. Z.*, **24,** 185 (1923); (b) Brönsted and La Mer, THIS JOURNAL, **46,** 555 (1924); (c) La Mer, *Trans. Am. Electrochem. Soc.*, **61,** 631 (1927).

[6] Brönsted and Livingston, THIS JOURNAL, **49,** 435 (1927).

of opposite sign, as has been shown in numerous recent publications from this Laboratory,[7] it would not have been surprising if still more conspicuous deviations had intruded. That they do not appears to be due to the fact that the authors' choice of solvents was such that the ions of opposite sign were always of the univalent type.

Before extending our kinetic studies to include the complications of high valence ions of opposite sign, it seemed advisable to prove that Reaction I actually obeys the Debye limiting law when the ion of opposite sign is univalent. While these experiments were in progress, a paper by Kappana,[8] working under the direction of J. C. Ghosh, has appeared in which the same reaction is followed at 30, 40 and 50° for the primary purpose of proving that the temperature coefficient is practically independent of the salt concentration, as predicted by the theories of Debye and of Ghosh and which make it desirable to record our results without further delay.

Experimental

The reaction was followed by mixing equivalent quantities of dilute solutions of sodium thiosulfate and sodium bromo-acetate in a thermostat kept at 25 ± 0.005° and removing appropriate aliquots (10–25 cc.) at definite time intervals. The reaction was stopped by adding excess iodine solution followed by back titration with thiosulfate. In the more dilute solutions (See Tables I and II), where the half time of the reaction is slow (about 55 hours at 0.001 N) and the volume of an appropriate aliquot should be between 100 to 200 cc., it was found more convenient and accurate to measure out the reactants separately in each flask and titrate the entire contents directly with the standard iodine. The normality of the iodine and thiosulfate solutions was changed from 0.01 to 0.001 N to meet the requirements of each experiment. They were carefully restandardized against each other just before starting a run. In Runs 25, 26 and 27 it was found that the titer of the very dilute thiosulfate solutions changed slightly during the two and one-half day period of observation, and the initial value for a was taken as the mean value, since it is reasonable to suppose that the same change was occurring in the reaction flask as in the absence of bromo-acetate.

The sodium bromo-acetate solutions for each run were made by weighing into a volumetric flask an appropriate amount of Kahlbaum's bromoacetic acid, kept over phosphorus pentoxide. Boiled water was added and the contents neutralized with 0.2 N sodium hydroxide to a faint pink color with phenolphthalein. This procedure gives a double check upon

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[7] (a) La Mer and Mason, THIS JOURNAL, **49**, 410 (1927), also p. 363; (b) La Mer and Cook, *ibid.*, **51**, 2622 (1929); La Mer and Goldman, **51**, 2632 (1929); (c) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928); and reference 5 (c) for a general account.

[8] Kappana, *J. Indian Chem. Soc.*, **6**, 45 (1929); also **5**, 293 (1928) for chloro-acetate.

TABLE I

REACTION VELOCITY DATA ON THE BIMOLECULAR REACTION $BrCH_2COONa + Na_2S_2O_3$ AT HIGH DILUTION

Temp., 25°; initial concentrations of reactants of equal normality in all cases.

Run 25. $a = b = 0.001\ N$

50.03 cc. of 0.002 N sodium thiosulfate + 50.03 cc. of 0.002 N sodium bromo-acetate in each flask. Reaction stopped in each flask by addition of excess of dilute I_2 solution (No. 8), and back titrated with thiosulfate of approximately 0.002 N concentration. Initial titer in terms of I_2 solution No. 8 = 99.21 cc., the average of six determinations carried out over the period of two and one-half days for which the reaction was followed.

Flask no.	Elapsed time, minutes	I_2 No. 8 used, cc.	$\frac{x}{a-x}$	$\frac{1}{at} \times \frac{x}{a-x} = k$	
1	2036	59.89	0.6565	0.3224	Av. k = 0.317 ± 0.003
2	2065	60.00	.6535	.3164	Log $k-1$ = 0.501
3	2133	59.03	.6807	.3191	μ = 0.0500
4	2271	57.97	.7114	.3132	
5	3318	48.56	1.0430	.3143	

Run 26. $a = b = 0.0006666\ N$

Same as Run 25 except for addition of 50.03 cc. of boiled water to each flask.

1	2062	69.89	0.4195	0.3051	Av. k = 0.3040 ± 0.0008
2	2066	70.03	.4167	.3027	Log $k-1$ = 0.483
3	2320	67.50	.4698	.3038	μ = 0.04082
4	3350	59.00	.6815	.3051	
5	3511	57.96	.7117	.3031	

Run 27. $a = b = 0.00050\ N$

Same as Run 25 except for addition of 100.06 cc. of boiled water to each flask.

1	2112	75.58	0.3127	0.2962	Av. k = 0.2981
2	3356	66.02	.5027	.2996	Log $k-1$ = 0.474
3	3559	64.80	.5310	.2984	μ = 0.03536

TABLE II

SUMMARY OF DATA FOR THE BIMOLECULAR REACTION $BrCH_2COO^- + S_2O_3^{--}$ AT HIGH DILUTION IN THE PRESENCE OF SODIUM ION. INITIAL CONCENTRATIONS OF BOTH REACTANTS OF IDENTICAL NORMALITY

No.	Normality	No. of titrns. in each run	$\sqrt{\mu}$	$k = \frac{1}{at}\left(\frac{x}{a-x}\right)$	Average log $k-1$	Observer
27	0.000500	3 (S)[a]	0.0354	0.298 ± 0.001	0.474	V. K. L.
26	.000666	5 (S)	.0408	.3040 ± .0008	.483	V. K. L.
25	.001000	5 (S)	.0500	.317 ± .003	.501	V. K. L.
22	.001666	5 (S)	.0645	.325 ± .004	.512 (?)	R. W. F.
21	.002500	4 (S)	.0791	.355 ± .004	.549	R. W. F.
20	.002500	5 (S)	.0791	.353 ± .002		R. W. F.
23	.005	6 (al)[a]	.1118	.385 ± .008	.586	R. W. F.
19	.005	6 (al)	.1118	.383 ± .007		
6	.005	5 (al)	.1118	.387 ± .003		R. W. F.
4	.005	3 (al)	.1118	.384 ± .002		and V. K. L.
2	.01	5 (al)	.1581	.4461 ± .0005	.649	R. W. F. and
5	.01	3 (al)	.1581	.445 ± .003		V. K. L.

[a] (al) means that aliquots were removed at definite time intervals and titrated; (S) means that each titration was made using the entire contents of flask set up as a separate experiment.

the concentration of bromo-acetate. Unless the weight of bromo-acetic acid and the alkali necessary to neutralize agreed to 0.1%, the mixture was made up again. Carefully performed experiments showed that the titration value of the acid was exactly that given by the formula. The purity was further tested by mixing 25 cc. of approximately 0.1 *N* bromo-acetic acid, neutralizing and then adding 25 cc. of 0.3020 *N* thiosulfate. Under these conditions the reaction is complete in twenty-four hours. The ratios of the equivalents of thiosulfate consumed to equivalents of sodium hydroxide to titrate the acid in five experiments were 0.997, 1.014, 1.000, 1.007 and 0.957, or an average of 1.005 (calcd., 1.000).

We emphasize the matter of purity since our first preparation of bromo-acetic acid, furnished by a well-known manufacturer, contained only 90% of the theoretical amount of replaceable bromine although the sodium hydroxide titration was almost 100%.

Moisture was in some way present when the batch was bottled and slow hydrolysis to glycolic acid occurred on storage. Although this hydrolytic reaction is very slow in neutral solution and does not affect our results, it is sufficiently rapid in acid solutions that one cannot make up stock solutions of bromo-acetic acid as is customary in kinetic technique and expect to use them over any considerable period of time without obtaining erroneous results.

The chief source of error seems to reside in the determination of the starch–iodide end-point. Titrations were made rapidly to avoid oxygen error, which should be slight in neutral solution. The effect of access of air during the course of the reaction deserves further study.

Detailed data are given only for the extremely dilute experiments. The probable errors are the arithmetic mean of the individual *k* values. All volumetric glassware was calibrated and the two stop watches when used over a period of twenty-four hours were checked against jeweler's time.

Discussion

The data of Table II are plotted as crosses in Fig. 1, the upper curve being plotted to a scale to take in Krapivin's data (circles), while the lower curve emphasizes the data in dilute solution.

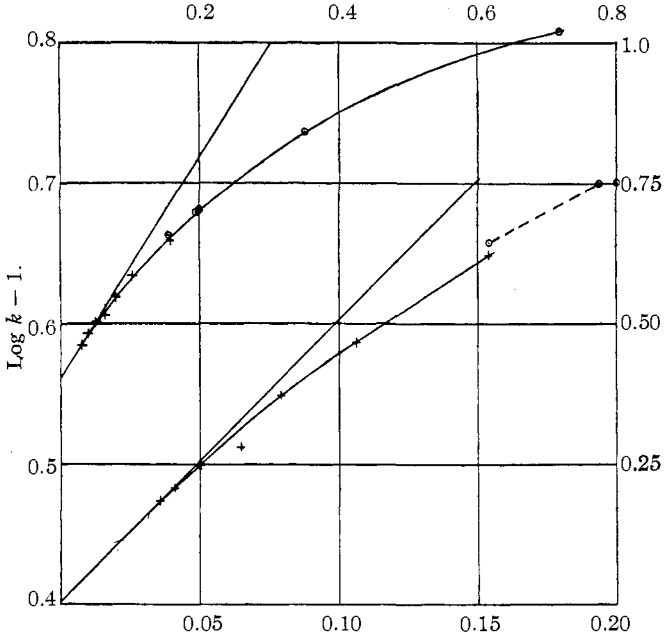
Introducing the Debye–Hückel limiting law, $\log_{10} f_i = -0.50Z_i^2\sqrt{\mu}$ in Equation 2, one gets

$$\log k_{\text{obs.}} = \log k_0 + Z_A Z_B \sqrt{\mu} \qquad (4)$$

so that on plotting $\log k_{\text{obs.}}$ against the square root of the ionic strength, the data approach a straight line having a slope $Z_A Z_B = (-2)(-1) = +2$, with an intercept leading to a value of $\log k_0 = 0.42$ or $k_0 = 0.263$.

Our results when combined with those of Krapivin show clearly that although the slope in the region 0.35μ is only one-fourth that predicted by (4), the slope of the experimental curve continuously approaches and finally reaches the limiting value at $\mu \leqq 0.0025$ or $\sqrt{\mu} \leqq 0.05$. The manner of approach is also what would be expected from the equation containing the factor of ion size in the first approximation of the Poisson–Boltzmann equation (ref. 7).

The data lend no support whatsoever to the theory of Soper,[9] that the theoretical slope should be two-thirds the value Z_AZ_B. Soper's theory[9] is not only unsound from both a thermodynamic and kinetic point of view, but in developing it the author is obliged to ignore all of the accurate solubility data supporting the Debye theory that have accumulated. The apparent agreement with the two-thirds slope which he obtains in many cases is fortuitous and results from a misunderstanding of the range of applicability of the limiting law. Kappana has also obtained data at concentrations as low as 0.0025μ. His data are sensibly parallel to ours; however, he draws a Debye limiting slope through his data at 30° up to 0.015μ, followed at this point by an *abrupt* change in slope to a value approximately two-thirds of the theoretical. On plotting his data at 60° we find that the transition is not abrupt but as smooth as the accuracy



$\sqrt{\mu}$ ($BrCH_2COO^- + S_2O_3^{--}$).

⊙, Krapivin; +, La Mer.

Fig. 1.

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[9] Soper, *J. Phys. Chem.*, **31,** 1790 (1927); **32,** 67 (1928).

of the data warrant. We feel confident that some of the data at 30° must be in error.

It is of interest to note that in Krapivin's data at 0.01 N the addition of 0.01 N sodium bromide, iodide or nitrate produced identical effects, as did the further addition of 0.01 N bromo-acetate, *i. e.*, k increased from 0.455 to 0.502–0.505. This is in agreement with the principle of specific interaction, (see ref. 7b). On the other hand, addition of 0.01 N sodium thiosulfate gave a value of $k = 0.504$, while 0.01 N sodium sulfate increased k to 0.516, even though the ionic strength is the same as in the presence of sodium thiosulfate.

Our experiments are being continued from the standpoint of specific salt effects and the effect of the relative position of the charge and the bromine atom upon the velocity.

The assistance given by Mr. R. W. Fessenden is gratefully acknowledged.

Summary and Conclusions

The velocity data of the reaction $BrCH_2COO^- + S_2O_3{}^{--} \longrightarrow S_2O_3\text{-}CH_2COO^{--} + Br^-$ studied by Krapivin for the sodium salts at moderate dilutions have been extended from 0.01 N to 0.0005 N. The data strongly support Brönsted's theory of reaction velocity. In the presence of sodium ions the limiting slope predicted from the Debye theory holds from 0.001 N (0.0025μ) down to the lowest concentration studied. At higher concentrations the slope falls off, reaching a value of one-fourth the theoretical value at 0.35μ. The experiments are being continued.

New York, N. Y.

NOTES

A Simple Laboratory Vacuum Regulator.—Among various methods of maintaining a constant temperature in the range from room temperature to nearly red heat, the vapor-bath with boiling liquid under constant, automatically controlled, reduced pressure is perhaps the most convenient and satisfactory. The device described in this note for controlling the degree of vacuum and thus the temperature is not new in principle, but its simplicity and utility make it available to any chemical laboratory. A device based upon similar principles has recently been described.[1] The chief difference between the two devices consists in the use of a glass stopcock in the present instance instead of the combination of a rubber stopper and capillary tube to control the ingress of air.

The essential features of the apparatus are shown in Fig. 1. The mercury in the manometer AA′ is adjusted by means of the leveling bottle F to such a position that when contact is broken with the platinum wire sealed into the closed arm A, the height h corresponds to the degree of

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[1] S. P. Miller and P. V. McKinney, *Ind. Eng. Chem.*, **20**, 552 (1928).