

The apparent transference number of barium ion in these solutions is 0.012; by using the non-electrolyte trichloroacetic acid as reference solute, the true transference number has been shown to be about one-half of this.

It has been demonstrated that the process of conduction in these solutions cannot depend upon

a simple ionic migration. This conclusion strongly supports the theory of conduction by intermolecular proton jumps which has been much discussed as an explanation of the anomalous mobilities of hydrogen and hydroxyl ions in aqueous solutions.

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[CONTRIBUTION FROM THE GAYLEY CHEMICAL LABORATORY OF LAFAYETTE COLLEGE]

The Fluidity of Anisole

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I. Introduction

In a recent investigation of the temperature coefficient of conductance of salts in anisole,¹ it was necessary to obtain the fluidity of the solvent as a function of temperature. This was calculated by one of the authors according to Bingham's method,² using the atomic temperature constants of Bingham and Spooner, and an association factor of 1.25, derived from considerations based on the theory of protection. It is the purpose of this paper to present the experimental determinations of the fluidity and association of anisole, and to compare the association with the previously predicted values.

II. Experimental

Measurements were made in a Bingham viscometer number 1-34, the apparatus being essentially that previously described by the authors.³

Anisole was purified by the method of Bien, Kraus and Fuoss,¹ and was distilled into the viscometer directly before use.

Densities for use in the kinetic energy correction term were calculated from Bien's empirical formula.

TABLE I

THE VISCOSITY AND FLUIDITY OF ANISOLE AT DIFFERENT TEMPERATURES

<i>t</i> , °C.	η , centipoises		ϕ , rhes
2.00	1.5082	1.5083	66.30
10.00	1.2931	1.2923	77.36
20.00	1.0863	1.0858	92.08
30.00	0.9280	0.9280	107.76
40.00	.8047	.8048	124.26
60.00	.6274	.6278	159.34
80.00	.5064	.5066	197.43
100.00	.4190	.4192	238.63

(1) Bien, Kraus and Fuoss, *THIS JOURNAL*, **56**, 1860 (1934).

(2) Bingham and Spooner, *J. Rheology*, **3**, 221 (1932); *Physics*, **4**, 387 (1933).

(3) Bingham and Geddes, *Physics*, **4**, 203 (1933); **5**, 42 (1934).

The experimental results are given in Table I, in which left and right limb determinations of η are given. It is observed that the maximum deviation is only 0.07%.

III. Discussion

The relationship between the fluidity of anisole and the temperature in degrees absolute is expressed over the range covered by the equation $0.7093 \phi = (T^2 - 562.95 T + 104,632)^{1/2} + T - 387.5$ (1)

From this, the absolute temperatures actually required for fluidities of 50, 100, and 200 rhes can be obtained. These are listed in Table II, together with the values calculated from the atomic temperature constants, and the association "n." (n = observed absolute temperature/calculated absolute temperature.) Extrapolated values are given in parentheses.

Fluidity in rhes	Absolute temperature		Association "n"
	Obs.	Calcd.	
50	(262.4)	209.9	(1.250)
100	298.2	239.8	1.244
200	354.2	282.3	1.255

It is seen that the observed associations agree remarkably well with the predicted value of 1.25. No definite value for the association effect upon introducing an OCH₃ group into a compound had been determined, which may account for the very slight discrepancy noted. It is found to be a mildly protective group, being just below H in the scale.³

Summary

The fluidity of anisole has been measured over the temperature range 2-100°, and represented by a formula of the usual type.

Experimentally determined values of the as-

sociation agree with those predicted on the basis of the theory of protection. This illustrates the utility of the theory in obtaining approximate

values of the fluidity of compounds for which experimental data are not available.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Photo-decomposition of Gaseous Ethyl Iodide and a Comparison of the Photo-change in the Gaseous and Condensed States

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Certain properties of the iodides of the simpler organic radicals suggest the utility of investigating this group of compounds in the study of the photo-behavior of substances. The lower members of the alkyl iodides have a general similarity in absorption spectra, indicating a common type of excitation as the initial process in photo-changes; nevertheless, it is experimentally observed that the efficiency of the light in causing chemical changes varies markedly from member to member of the series, and with the state of aggregation for a given compound, facts which afford opportunity for the accumulation of data from which some understanding of the relation between the net photochemical action and such factors as the constitution of the molecule and its possible degradation products in various environments may ultimately be obtained. Moreover, the possession by the alkyl iodides of at least two different types of absorption in the region of the spectrum readily accessible to not unduly complicated experiment may allow us to correlate photochemical action with the type of excitation supposed to occur in these different regions.

The ultraviolet absorption spectra of the gaseous alkyl iodides have a characteristic continuum with a maximum at about 2500 Å., and methyl and ethyl iodides have a well developed band spectrum of greater intensity than the continuum, beginning near 2000 Å. and extending into the Schumann region.¹ We have found that gaseous vinyl iodide has a similar well-defined band spectrum in the same region, although in this case the region between the end of the first continuum, at 2300 Å., and the band spectrum is occupied by an intense continuous absorption.

The new results reported here are chiefly concerned with the photo-behavior of ethyl iodide

in the band region. In the continuum, the quantum yield in the decomposition of liquid ethyl iodide has been found to be about one, at 3100 Å., and to diminish with increasing wave length, although there are indications that the actual values are probably high.² Ethyl iodide vapor at 50 mm. is reported by Emschwiller to decompose on exposure to the full light of the mercury arc with a very low yield, not more than one hundredth of that for the decomposition of hydrogen iodide gas.³ In hexane and in benzene solution the yield is 0.58 at 2610 Å., at 25° in ethyl iodide concentrations from 0.007 to 1.38 moles per liter and 0.3 at 3130 Å.⁴ Methyl iodide has a very low yield in the continuum, both in the gaseous state (0.02 at 0° and 141 mm.)⁵ and in hexane solution (0.05 at 25° and 1.78 molar).⁴

Experimental

In the region of continuous absorption, the light from a 6-inch Hanovia quartz mercury arc, operating at about 150 volts, was filtered by 5 cm. of bromine vapor at its saturation pressure at 15°, 3 cm. of chlorine at one atmosphere, and 3 cm. of 1 *N* acetic acid so as to yield the lines between 2800 and 2500 Å. with an energy center at about 2600 Å.

Illumination in the band region was effected by the light of a condensed spark with zinc or aluminum electrodes. The spark gap, an adaptation of that of Wiig and Kistiakowsky,⁶ was driven by a 10,000-volt transformer consuming 3.3 kilowatts in the primary, with a 0.04 microfarad oil immersed parallel plate condenser which could be run continuously for four hours as capacity.⁷

Monochromatization of the light was effected by focal isolation by means of quartz lenses, as used by Wiig and Kistiakowsky in their study of the ammonia decomposition.⁶ Spectral photographs showed that the zinc spec-

(2) T. Iredale, *J. Phys. Chem.*, **33**, 290 (1929).

(3) G. Emschwiller, *Ann. chim.*, **17**, 413 (1932).

(4) W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

(5) J. R. Bates and R. Spence, *This Journal*, **53**, 1689 (1931).

(6) E. C. Wiig and G. B. Kistiakowsky, *ibid.*, **50**, 1806 (1932).

(7) It may be worth while to remark that in constructing these condensers we found it best not to shellac the thin copper sheeting used as plates to the glass but simply to tie up the bundle of copper and glass plates with string and immerse them in oil. With shellac, air bubbles tend to form between the copper and glass which may eventually lead to breakdown.

(1) G. Hertzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930); A. Henrici, *Z. Physik*, **77**, 35 (1932); G. Scheibe, F. Povenz and C. F. Linström, *Z. physik. Chem.*, **B20**, 283 (1933).