

THE CONDUCTIVITY OF ROSANILINE HYDROCHLORIDE IN WATER
AND CERTAIN ORGANIC SOLVENTS.—By HAROLD S. DAVIS,
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Within the last fifteen years, the knowledge of the conductivity of electrolytes in solvents, other than water, has been greatly increased. An historical summary of the work done in this field up to 1903 is given by Walden.¹

When a solute dissolves in a solvent to form a conducting solution, the magnitude of the conductivity under given conditions of temperature and concentration depends upon (1) the solute, and (2) the solvent. But while investigation has hitherto extended to a wide range of solvents, only a very limited number of solutes have been studied. Walden, for example, who has been the principal worker on this subject, confines his attention to tetra methyl ammonium iodide and one or two of its homologues. As regards these salts, he has shown² that the dissociation decreases as we advance in homologous series, that is, is greater for tetra methyl ammonium iodide than for the corresponding ethyl compound.

He has further shown empirical relations

- (1) Between the dissociating power of a solvent and its dielectric constant.
- (2) Between the temperature coefficient of conductivity of a solvent and the conductivity at infinite dilution.
- (3) Between the dielectric constant of the solvents and the molecular dilution at which they show equal dissociation of the same salt.

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1. Walden, P. : *Zeitschr. f. phys. Chem.*, **46**, 103, (1903).

2. Walden, P. : *Zeitschr. f. phys. Chem.*, **54**, 129, (1906).

These laws having been derived from measurements of the conductivity of certain salts of the aliphatic series, the present work was undertaken in order to extend investigation to solutes containing the benzene nucleus.

The solute chosen was fuchsine. The solvents used were water, methyl alcohol, ethyl alcohol, and acetic acid.

Some Properties of Fuchsine. Fuchsine $C_{20}H_{20}N_3Cl$ is the hydrochloric acid salt of rosaniline (triamido di-phenyl tolyl carbinol). It crystallizes in very small rhombic plates which are sparingly soluble in water and dissolve readily in ethyl alcohol.¹

Like all the salts of rosaniline it is very hygroscopic, a fact which must be remembered in quantitative work.²

It is a powerful dye and colours the hands and dishes strongly red. From these, however, it is easily removed by dipping in a weak solution of sodium nitrite which has been slightly acidified. The dye is thus diazotized and may be removed by washing.

No data can be found about the melting point in Beilstein, in Thorpe's or Carnelley's tables or in any standard work of reference. The melting point was, therefore, determined as described in this paper and found to be 216.8°C.

The dye was also found to be readily soluble in methyl alcohol and acetic acid and fairly soluble in acetyl chloride and acetone. It is insoluble in acetic ester.

Purification of Fuchsine. Merck's C. P. fuchsine was recrystallized three times from water. A sample from each was dried at 120 and a solution made, (in order to obtain complete solution of the salt, in this and all subsequent measurements, it was found necessary to warm the solution). It was found that the conductivity decreased about ten per cent. for the first recrystallization, three for the second, and that the change for the third was inappreciable.

1. Allen, A. H. : "Commercial Organic Analysis," Vol. 3, Part I, p. 276.

2. Hoffman : Proc. Roy. Soc. 12 2, (1862).

The final recrystallization was made from the so-called conductivity water and the sample was dried at 120°C to constant weight and preserved in a weighing tube in a desiccator.

Determination of the Melting Point of Fuchsine. The final sample was tested for its melting point. An ordinary melting point flask with sulphuric acid was used, but it was found difficult to observe the exact temperature of fusion with a capillary tube made as ordinarily described in the text books. The trouble disappeared, however, when the capillary tube, containing the fuchsine, was drawn so as to terminate in a point. Into this tube a little column of fuchsine, about 2 mm. in height was tightly packed. It was then easy to observe when the substance in the very point of the tube began to fuse. The fuchsine melted fairly sharply at 216.8°C.

The thermometer used was an ordinary one, graduated only to degrees. It was standardized by placing it in a distilling flask, containing boiling naphthalene, according to the method outlined by Gattermann in his "Laboratory Manual of Organic Chemistry," page 66.

The B. P. of naphthalene is about 217°C, the M. P. of fuchsine is about 216.8°C.

An attempt was also made to find the melting point by having the substance in a capillary tube complete an electric circuit according to the method outlined by Beilstein.¹ No change in the resistance could be detected, however, even when the substance became fused. It seems, therefore, even when fused to be a nonconductor.

Conductivity Measurements. All resistances were measured by means of the Wheatstone bridge. The bridge used was manufactured by Queen & Co. and the coils were originally (1895) guaranteed to $\frac{1}{100}$ of one per cent. and the bridge wire to $\frac{1}{100}$ of one per cent.

1. Beilstein : "Organische Chemie," vol. I, page 37.

Conductivity measurements were made at three temperatures, 25°C, 18°C, and 0°C. The first two were obtained in a bath, stirred by an electric motor, and with gas supply regulated by a thermostat. The temperature of this bath remained steady to a tenth of a degree.

The 0° bath consisted of two dishes. The outside one was filled with cracked ice, moistened with distilled water and the inner one was filled with about equal volumes of ice and water. The temperature of the cell immersed in the ice in the inner vessel remained steady at 0°C.

The cell used was about three inches in height and two in diameter. The electrodes were platinized. The constant of this cell was checked every two or three days by a standard potassium chloride solution. This solution was made from a sample prepared from Merck's C. P. chloride "for analytical purposes" by recrystallization four times from water. It was then dried in a desiccator for four or five weeks. For this sample I am indebted to Mr. C. B. Nickerson of the Chemical Department at Dalhousie College.

Preparation of Solutions. A weighed amount of fuchsine was placed in a calibrated (400 cc. or 100 cc.) flask and dissolved, and liquid added to the 400 cc. mark. It was then diluted, by the addition of pure water, to make a $\frac{1}{100}$ N. solution. In most cases the dilution required was from 2-4 cc. per 400. Some trouble and inaccuracy is caused by froth on the surface of the liquid.

20 cc. of this solution was placed by a pipette in the cell and further dilution carried out in the cell itself by two 10 cc. pipettes, one for withdrawal and one for delivery. All these pipettes were standardized.

Notation.

V = No. of liters which contain 1 mol. of dissolved solute
($C_{20}H_{20}N_3Cl = 337.4$ gr.)

τ = Temperature in Centigrade degrees.

κ° & κ^{25} = Specific conductivity of solvent (in reciprocal Siemen's units) at $\tau = 0^{\circ} - 25^{\circ}\text{C}$.

κ_1° & κ^{25} = Specific conductivity of solution (in reciprocal Siemen's units) at $\tau = 0^{\circ} - 25^{\circ}\text{C}$.

λ_p^t = Molecular conductivity of the solution at dilution V with correction for κ the conductivity of the pure solvent.

$\lambda_1, \lambda_2,$ etc. = corrected values of the conductivity of independent experiments.

C = temperature coefficient of the electrical conductivity for the interval $25^{\circ} - 0^{\circ}\text{C}$.

ϵ = dielectric constant at 20°C .

Conductivity of Fuch sine in Water. All the water used in these experiments was prepared in the usual way, either by the method of Jones and Mackay¹ or the modification of that method used by Jones and Lindsay².

Quite a little difficulty was experienced with either method even when the distillation was fairly slow. This difficulty was overcome by a drop catcher, so simple that it seems worth description. A four litre flask contained the original distilled water with a little sulphuric acid and potassium permanganate. From this a tube passed into a retort, containing distilled water, a little sodium hydroxide, and some permanganate. So far it is identical with the apparatus of Jones and Mackay. Into the neck of this retort was thrust that of a smaller one and the steam had finally to pass out the top of this through a tube with an expanded bulb into a block tin condenser. All the joints in the two retorts were made fairly tight with asbestos paper. Without any trouble this apparatus gave water of conductivity $1.4 - 1.6 \times 10^{-6}$ (reciprocal Siemen's units).

In the case of water I have given the actual measurements and corrections in some detail.

The same methods are of course used throughout in all the measurements.

1. Jones, H. C. and E. Mackay : Amer. Chem., 19, 283, (1897).

2. Jones, H. C. and C. Lindsay : Amer. Chem., 28, 329, (1902).

Experiment 1.

$$\kappa^{25} \text{ for water} = 1.161 \times 10^{-6}$$

$$\kappa^0 \text{ for water} = 1.07 \times 10^{-6}$$

ν	100	200	400	800	1600	3200
$\tau = 25^\circ$						
κ_1^{25}	8.340×10^{-4}	4.316	2.191	1.109	.5627	.2899
$\kappa_{1 \text{ corr.}}^{25}$	8.324×10^{-4}	4.320	2.175	1.093	0.5466	0.2738
λ^{25}	83.24	86.00	87.00	87.44	87.46	87.62
$\tau = 0^\circ \text{C.}$						
κ_1^0						0.107×10^4
$\kappa_{1 \text{ corr.}}^0$						0.159×10^4
λ^0						50:90

Experiment 2.

$$\kappa_{25} = 1.161 \times 10^{-6}$$

$$\kappa_0 = 1.07 \times 10^{-6}$$

ν	100	200	400	800	1600	3200
$\tau = 25^\circ$						
κ_1^{25}	8.267×10^{-4}	4.324	2.191	1.098	0.548	0.281
$\kappa_{1 \text{ corr.}}^{25}$	8.251×10^{-4}	4.308	2.175	1.082	0.532	0.265
$\lambda_{\text{corr.}}^{25}$	82.51	86.16	87.00	86.56	85.10	84.70
$\tau = 0^\circ \text{C.}$						
κ_1^0			1.202×10^{-4}	0.607	0.308	0.157
$\kappa_{1 \text{ corr.}}^0$			1.181×10^{-4}	0.596	0.287	0.146
λ^0			47.24	47.68	45.90	46.07

Experiment 3.

$\kappa^{25} = 2.00 \times 10^{-6}$

$\kappa^{18} = 1.17 \times 15^{-6}$

v	100	200	400	800	1600	3200	
$\tau = 25^\circ$ κ^{25}	8.267×10^{-4}	4.292	2.182	1.102	0.556	0.290	
$\kappa_{1\text{corr}}^{25}$	8.247×10^{-4}	4.272	2.162	1.082	0.536	0.270	
$\kappa_{1\text{corr}}^{25}$	82.47	85.44	85.48	86.56	85.79	86.40	
κ_1^0				0.592	0.300	0.152	
$\kappa_{1\text{corr}}^0$				0.580	0.288	0.140	
λ_{corr}^0				46.40	46.10	44.80	
Collection of results for $\text{C}_{20}\text{H}_{20}\text{N}_3 \text{Cl}$, and Water at 25°c. and 0°c.							
v	100	200	400	800	1600	3200	α
$\tau = 25$ λ_1^{25}	83.2	86.0	87.0	87.4	87.5	87.6	
λ_2^{25}	82.5	86.1	87.0	86.5	85.1	84.7	
λ_3^{25}	82.4	85.4	85.4	86.5	85.8	86.4	
Mean λ^{25}	82.7	85.8	86.5	86.8	86.1	86.2	87.0
$\tau = 0$ λ_1^0						[50.9]	
λ_2^0				47.6	45.9	46.7	
λ_3^0			47.2	46.4	49.1	44.8	
Mean λ^0			47.2	47.0	46.0	48.1	
C_{0-25}			.0375	0.539	.0348	.0318	

Mean $\text{C}_{0-25} = .0345$.

Methyl Alcohol and Fuchsine.

The methyl alcohol used was Kahlbaum's purest.

$$\kappa^{25} = 5.5 \times 10^{-6}$$

$$\kappa^0 = 3.9 \times 10^{-6}$$

ν	100	200	400	800	1600	∞
$\tau = 25^\circ$						
(1) κ_1^{25}	5.417×10^{-4}	2.938	1.573	0.825	0.435	
(2) κ_1^{25}	5.417×10^{-4}	2.953	1.561	0.835	0.445	
Mean κ_1^{25}	5.417×10^{-4}	2.945	1.667	0.830	0.440	
$\kappa_{1\text{corr.}}^{25}$	5.362×10^{-4}	2.890	1.512	0.775	0.385	
λ^{25}	53.6	57.8	60.5	62.0	61.6	63.5
$\tau = 0^\circ$						
(1) κ_1^0	3.861×10^{-4}	2.073	1.150	0.579	0.306	
(2) κ_1^0	3.861×10^{-4}	2.100	1.114	0.590	0.309	
Mean κ_1^0	3.861×10^{-4}	2.086	1.132	0.584	0.308	
$\kappa_{1\text{corr.}}^0$	3.822×10^{-4}	2.047	1.093	0.545	0.269	
λ^0	38.22	40.9	43.7	43.6	43.0	
C_{0-25}	0.0161	0.0164	0.0154	0.0168	0.0172	

 Mean $C_{0-25} = 0.0164$.

Ethyl Alcohol and Fuchsine.

The alcohol used was ordinary market product. It was allowed to stand with digestion over burnt lime and distilled from the same. It was then allowed to stand over dehydrated copper sulphate and distilled from this.

$$\kappa^{25} \text{ for alcohol} = 0.25 \times 10^{-6}$$

$$\kappa^{\circ} \text{ (calculated)} = 0.20 \times 10^{-6}$$

ν	100	200	400	800	1600
$\tau = 25^{\circ}$					
(1) κ_1^{25}	2.141×10^{-4}	1.175	0.6261	0.3260	0.1662
(2) κ_2^{25}	2.118×10^{-4}	1.156	0.6266	0.3222	0.1641
Mean κ_1^{25}	2.129×10^{-4}	1.165	0.6263	0.3241	0.1651
Mean κ_1^{25} _{corr}	2.127×10^{-4}	1.163	0.6138	0.3216	0.1626
λ^{25}	2.127	23.26	24.54	25.72	26.03
$\tau = 0$					$\lambda_{\infty} = 26.0$
(1) κ_1°	1.324×10^{-4}	0.734	0.380	0.2016	0.1032
(2) κ_1°	1.323×10^{-4}	0.720	0.382	0.2010	0.1016
Mean κ_1°	1.323×10^{-4}	0.727	0.381	0.2013	0.1023
Mean κ_1° _{corr}	1.321×10^{-4}	0.725	0.379	0.1993	0.1003
λ°	13.21	14.50	15.15	15.94	16.04
C_{0-25}	0.0244	0.0241	0.0241	0.0244	0.0255
Mean C_{0-25}	$C_{0-25} =$	0.0245			

Acetic Acid and Fuchsine.

The acetic acid used was Baker's C. P. It was purified by freezing and washing the crystals obtained thoroughly with pure acid. $\kappa^{25} = 0.53 \times 10^{-6}$.

In part of one experiment No. 2 at 25, the original acid used was $\kappa^{25} = 1.05 \times 10^{-6}$.

ν	100	200	400	800	1600	∞
$\tau = 25^\circ$						
$\lambda_{1\text{corr}}^{25}$	6.75	7.36	8.25	9.36	10.99	
$\lambda_{2\text{corr}}$	6.80	9.38	10.88			
Mean λ	6.77	8.37	9.60	9.30	10.99	12.5
$\tau = 18^\circ$						
$\lambda_{1\text{corr}}^{18}$	5.94	6.16	6.88	[9.28]	8.64	
$\lambda_{2\text{corr}}^{18}$	5.73	6.14	7.04	8.00		
Mean λ^{18}	5.83	6.15	6.96	8.64	8.64	

Conclusions.

The main conclusion drawn from the preceding work, is that the presence of the benzene nucleus in the solute does not make any marked difference in its behaviour as an electrolyte from that of a solute which does not contain the nucleus.

With reference to the first of the three laws enumerated by Walden, that is the well known Nernst-Thompson hypothesis, the following table shows that the amount of dissociation of fuchsine, an aromatic solute, in a solvent stands in some marked relation to the dielectric constant of the solvent. This is exactly what Walden found in the case of tetra methyl

ammonium iodide an aliphatic solute, as the following comparative table shows:

Solvent	Dielectric Constant Dissociation at $\nu = 100$ Fuchsine N (C_6H_3) ₄ I		
	Water	81.7	95%
Methyl Alcohol	32.5 — 34.8	84%	73%
Ethyl Alcohol	21.7 — 27.4	81%	54%
Acetic Acid	6.46	53%	...

The other empirical relations which Walden himself has worked out are those:

- (2) Between the temperature coefficient of conductivity and the conductivity of infinite dilution.¹
- (3) Between the dielectric constants of the solvents and the molecular dilutions at which they show equal dissociation of the same solute.

I have been unable to find these relations for the conductivity of rosaniline hydrochloride in the four solvents used, and indeed it would not be permissible to draw any conclusion with such a limited number of solvents.

The following table shows the general similarity in the conductivity of solutions of the aliphatic and aromatic solutes.

Solvent	Fuchsine N (C_6H_3) ₄ I		Fuchsine N (C_6H_3) ₄ I	
	λ_{ν}^{25}	λ_{ν}^{15}	λ_{ν}^{25}	λ_{ν}^{15}
Water	87	...	0.036
Methyl Alcohol	63.5	124	0.016	0.015
Ethyl Alcohol	26.2	60	0.024	0.023
Acetic Acid	12.5	5.6

1. It is worthy of note that in calculating the temperature coefficient between 15° and 25° Walden does not use the temperature coefficient c as he has previously defined it.

$$c = \frac{\lambda_{\nu}^{\tau} - \lambda_{\nu}^{\circ}}{\lambda_{\nu}^{\circ} \tau} \text{ but as } c = \frac{\lambda_{\nu}^{25} - \lambda_{\nu}^{15}}{\lambda_{\nu}^{15} \nu 10}$$

This, of course, does not amount to the same thing. If the temperature coefficient of his acetic-acid solutions is calculated as first defined, it is found to be above .26 instead of .056 and this value when multiplied by the conductivity at infinite dilution 5.6 gives a constant 2.0 which is near the value of 1.3 required according to his empirical law.

Ostwald's dilution law holds fairly well for the more concentrated solutions of fuchsine in methyl and ethyl alcohols, and acetic acid.

The following table gives the value of a for these three solvents where a is defined as—

$$a = \frac{\frac{\lambda\nu}{\lambda\infty}}{\left(1 - \frac{\lambda\nu}{\lambda\infty}\right)^\nu}$$

ν	Methyl Alcohol a	Ethyl Alcohol a	Acetic Acid a
100	4.60	3.48	0.615
200	4.79	3.56	0.680
400	4.83	3.42	0.635
800	4.75	(6.00)	(0.270)

It does not hold for the solutions in water, nor should we expect it to since at even the greatest concentration used, the salt was about 95% dissociated.

This investigation was suggested and carried out under the direction of Prof. E. Mackay, and I wish to take this opportunity of gratefully acknowledging his advice and kindly criticism.

DALHOUSIE UNIVERSITY,
March 8th, 1911.