

On the Properties of Dipicrylamines

BY JACOB KIELLAND

Very little has been published about the chemical and physical properties of dipicrylamines, though dipicrylamine (2,4,6-hexanitrodiphenylamine) has been known as an explosive for many years, and its sodium or ammonium salt ("Aurantia") has been used on account of its dyeing properties, and as a light filter in photography.

Recently, dipicrylamine has been shown to be of importance for the quantitative determination of potassium¹; consequently, these compounds and their properties are of some interest. Further, it has been shown by the author that specific attraction forces, of interest for the theory of strong electrolytes, occur even in very dilute solutions of dipicrylamines. Hence, he feels

intermediate and high concentrations. The solvent effect is of minor importance, as was found from preliminary absorption measurements, carried out with a Zeiss Stufenphotometer.

The molecular extinction coefficient at 463 $m\mu$ was in all cases about 2.2×10^4 , but the curves in acetone, etc., appeared a little steeper than in water. For dilute solutions in water, Bouguer-Beer's law was found approximately valid, but since the Stufenphotometer does not work with monochromatic light, one does not feel justified in presenting more extensive data.

In order to give an idea of the color of the aqueous solutions, in the "fundamental, universal color language,"³ a chromatic analysis was carried out, on the basis of measured extinction curves at different concentrations. Hardy's method of ten selected ordinates³ was applied, and the computation based upon ICI normal observer, ICI illuminant C and ICI primary stimuli. From Table I,

TABLE I
CHROMATIC ANALYSIS OF AQUEOUS SOLUTIONS OF DIPICRYLAMINATES

| | 0 | 5 | 10 | (Concentration $10^4 \times$ moles per liter) | | | | 200 | 500 | 1000 | |
|------------------------------|--------------------------|-------|-------|---|-------|-------|-------|-------|-------|-------|-------|
| | | | | 20 | 40 | 60 | 100 | | | | |
| Dominant wave length, $m\mu$ | ... | 573.8 | 574.1 | 574.8 | 576.3 | 577.7 | 580.3 | 585 | 593 | 600 | |
| Relative brightness, % | 100.0 | 96.3 | 93.5 | 88.7 | 81.0 | 75.5 | 67.5 | 54.0 | 38.4 | 28.3 | |
| Excitation purity, % | 0 | 14 | 26 | 47 | 76 | 90 | 98 | 99.6 | 99.8 | 99.9 | |
| Trichromatic coefficients | { red green violet | 0.310 | 0.332 | 0.352 | 0.389 | 0.446 | 0.478 | 0.511 | 0.549 | 0.595 | 0.628 |
| | | .316 | .343 | .368 | .415 | .468 | .484 | .482 | .448 | .403 | .371 |
| | | .374 | .325 | .280 | .196 | .086 | .038 | .007 | .003 | .002 | .001 |

justified in presenting some measurements recently made.

Purification of Material.—The hexanitrodiphenylamine (made by Skaanska Bomullskrutsaktiebolaget) was dissolved by the equivalent amount of alkali to give an aqueous solution (at about 50°) containing 15 to 20% dipicrylamine. After filtration, a crude mass of sodium dipicrylamine was salted out by the addition of an equal volume with concentrated (50°) aqueous sodium nitrate. In order to remove any impurities still present, the red crystalline mass was then treated three times with an excess of 65–70% nitric acid, leaving a yellow crystalline mass of dipicrylamine.² The washed crystals (solubility product about 10^{-10} , according to Kielland¹) were dissolved in alkali and salted out as described above, filtered and washed rapidly with a little chilled water. After recrystallizing twice from conductivity water, the brilliant red crystal mass finally was dried to constant weight in a desiccator at room temperature.

Color

Solutions.—Dipicrylamine solutions are strongly colored, yellow at high dilutions, and orange to red at

(1) (a) Winkel and Maas, *Angew. Chem.*, **49**, 827 (1936); (b) Kielland, *Ber.*, **71**, 220 (1938); (c) Kolthoff and Dendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94 (1939).

(2) Microscopic examination showed that the exchange of sodium by hydrogen proceeded fairly rapidly inward, the crystal shape apparently not being distorted.

the pronounced change in hue at about $10^{-4} N$ is easily seen; the color is typical orange between 10^{-4} and $10^{-3} N$, red at higher, and yellow at lower concentrations. The very high excitation purity of all solutions above $10^{-4} N$, together with the relatively high corresponding brightness figures, is of importance for the use of dipicrylamines as light filters.

Solids.—The color of solid dipicrylamine is yellow to orange (according to purity and particle size), that of the solid dipicrylamines red. Using the Zeiss Stufenphotometer with Kugel-reflector, some spectral reflection curves were measured, and the resulting chromatic analysis (Table II) may serve as an illustration (based on ICI illuminant C).

TABLE II
COLOR OF SOLIDS

| | Commercial dipicrylamine, amorphous powder | Potassium dipicrylamine crystals | |
|------------------------------|--|----------------------------------|-------|
| Dominant wave length, $m\mu$ | 587 | 650 | |
| Relative brightness, % | 19 | 10 | |
| Excitation purity, % | 47 | 22 | |
| Trichromatic coefficients | { red green violet | 0.425 | 0.305 |
| | | .375 | .415 |
| | | .200 | .280 |

(3) Hardy, "Handbook of Colorimetry," Technology Press, Boston, 1936.

Particle Size

Ultrafiltration.—Ultrafiltration analysis according to Ferry⁴ was carried out with 10^{-3} *N* potassium dipicrylamine in water at 20°. As filters were used Membran- and Ultrafeinfiler from Membranfiltergesellschaft in Göttingen, membranes of the Elford type made according to the directions given by Bauer and Hughes,⁵ as well as cellophane, swollen in concentrated zinc chloride as suggested by McBain and Stuewer.⁶ Normal filtration was effected in all experiments, with no blocking effects detectable. The maximum relative concentration⁷ was 100% even at mean pore diameters of only 10 $m\mu$, and very near to 100% at about 4 $m\mu$. The end-point consequently was so low as to justify the conclusion that the dipicrylamine did not appear in colloidal dispersion.

Dialysis.—The dialysis coefficient of the dipicrylamine anion in 10^{-3} *N* aqueous solution was measured by a Cuprophane membrane at 18°, by the method of Brintzinger.⁸ The solvent was in all cases 0.5 *N* sodium nitrate; concentrations were measured photometrically, and ferricyanide and thiosulfate were employed as reference substances.

The resulting ionic weight was found equal to the formula weight (438) = 10%. Hence, in very dilute solutions, the dipicrylamine anion probably carries no complex bound water in the sense described by Brintzinger,⁹ nor is it associated or polymerized in such a manner as to affect the process of dialysis. In this connection perhaps it may be mentioned that Brintzinger and Schall¹⁰ also found the theoretical molecular weight for most of the ionic dyes studied by them.

The precision of measurement, however, does not exclude the possibility that a small fraction of the anions may have been present as double ions.

Density and Molal Volume.—The densities d^{18}_4 of sodium dipicrylamine solutions were measured at molalities from 0.01 to 0.13, using a pycnometer (volume about 30 ml.) of the Sprengel type, as modified by Riiber.¹¹ All solutions were made up by weight, and all weighings corrected to vacuum. Temperature was maintained with a precision of $\pm 0.01^\circ$. The results are given in Table III.

TABLE III
MEASURED DENSITIES OF SODIUM DIPICRYLAMINATE SOLUTIONS

| G. per 1000 g. of water | Molality | d^{18}_4 |
|-------------------------|----------|------------|
| 5.68 | 0.01232 | 1.00140 |
| 6.885 | .01493 | 1.00198 |
| 13.66 | .02963 | 1.00526 |
| 35.90 | .0779 | 1.01582 |
| 60.45 | .1311 | 1.02710 |

Since the work of Masson¹² it has been known that for most electrolytes the apparent molal

volume of a solute is a linear function of $c^{1/2}$, and a convenient method of computation has been suggested by Gucker.¹³ In the present case there results the equation

$$\Phi(V_2) = 235 + 3.0c^{1/2} \text{ ml. per mole} \quad (1)$$

The densities of solutions obeying Masson's rule are found from

$$d = d_1 + c(M_2 - d_1 \Phi^0)/1000 - c^{3/2} (d_1/1000)(\partial\Phi/\partial c^{1/2}) \quad (2)$$

Hence, for sodium dipicrylamine at 18°

$$d^{18}_4 = 0.99862 + 0.2263c - 0.0030c^{3/2} \quad (3)$$

The densities at other temperatures may be calculated similarly, taking¹⁴ the molal volume at 0 and 10° approximately 4 and 2.5 ml. lower than the figure at 18°.

Freezing Point Depression.—The freezing points of aqueous solutions of sodium dipicrylamine at concentrations from 5×10^{-3} to 5×10^{-2} *N* were measured, using a platinum resistance thermometer¹⁵ for calorimetric purposes, of the type described by Dickinson and Mueller,¹⁶ and made by the Leeds and Northrup Company.

A differential method of measurement was used. The arrangement made it possible to detect temperature variations of about 1 to 2 $\times 10^{-4}^\circ$. Samples for analysis were taken with a chilled pipet immediately after the final readings, and the concentrations determined¹⁷ by measuring the conductivity at 0°. The results are reported in Table IV.

TABLE IV
FREEZING POINT DEPRESSIONS OF SODIUM DIPICRYLAMINATE IN WATER

| Concn., moles per liter c | Density d^{18}_4 | Depression δ , °C. | Per mole δ/m | Function f |
|-----------------------------|--------------------|---------------------------|---------------------|--------------|
| 0.00572 | 1.0012 | 0.0196 | 3.43 | 0.078 |
| .00986 | 1.0022 | .0325 | 3.30 | .114 |
| .01021 | 1.0022 | .0333 | 3.27 | .123 |
| .01087 | 1.0023 | .0347 | 3.18 | .144 |
| .01337 | 1.0029 | .0415 | 3.09 | .169 |
| .01696 | 1.0037 | .0510 | 3.00 | .193 |
| .02149 | 1.0048 | .0620 | 2.88 | .225 |
| .02840 | 1.0063 | .0780 | 2.74 | .264 |
| .02982 | 1.0067 | .0783 | 2.62 | .295 |
| .03450 | 1.0077 | .0900 | 2.60 | .301 |
| .03625 | 1.0082 | .0919 | 2.52 | .319 |
| .03765 | 1.0084 | .0948 | 2.50 | .325 |
| .05005 | 1.0113 | .1138 | 2.25 | .393 |

(13) Gucker, *J. Phys. Chem.*, **38**, 306 (1934).

(14) Compare the variation with temperature of \bar{V}^0_2 for other sodium salts, see La Mer and Gronwall, *J. Phys. Chem.*, **31**, 393 (1927).

(15) The writer is indebted to the Institute of Organic Chemistry, Trondheim, for the loan of thermometer with accessories.

(16) Dickinson and Mueller, *Bull. Bur. Standards*, **9**, 483 (1913).

(17) Compare Lange, *Z. physik. Chem.*, **168**, 169 (1934).

(4) Ferry, *Chem. Rev.*, **18**, 373 (1936).
 (5) Bauer and Hughes, *J. Gen. Physiol.*, **18**, 143 (1935).
 (6) McBain and Stuewer, *J. Phys. Chem.*, **40**, 1157 (1936).
 (7) Optical analysis with Zeiss Stufenphotometer.
 (8) Brintzinger, *Z. anorg. allgem. Chem.*, **232**, 415 (1937).
 (9) Brintzinger and Osswald, *ibid.*, **225**, 312 (1935).
 (10) Brintzinger and Schall, *ibid.*, **225**, 213 (1935).
 (11) Riiber, *Z. Elektrochem.*, **29**, 334 (1923).
 (12) Masson, *Phil. Mag.*, [7] **8**, 218 (1929); see also Gucker, *Chem. Rev.*, **13**, 111 (1933).

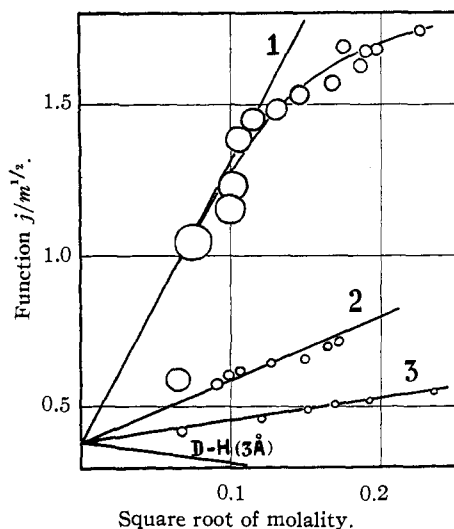


Fig. 1.—Freezing point measurements of sodium dipicrylamine (1); picric acid (2); and sodium dinitrophenolate (3).

Activity Coefficients.—The activity coefficients of the solute at 0° were computed from plottings (Fig. 1) of $j/m^{1/2}$ against $m^{1/2}$, according to the method of Abel, Redlich and Lengyel¹⁸

$$-\log_{10}\gamma = (j + 2 \int_0^{m^{1/2}} (j/m^{1/2}) dm^{1/2})/2,303 \quad (4)$$

where j is the Lewis-Randall function $[1 - \vartheta/(3.718 m)]$. The values at even molalities are given in Table V, and may be represented by the equation

$$-\log_{10}\gamma = 0.486\mu^{1/2}/(1 + \mu^{1/2}) + (9.0 - 50m)m \quad (5)$$

where μ denotes the ionic strength $\mu = \frac{1}{2}\sum m_i z_i^2$.

TABLE V

MEAN STOICHIOMETRIC ACTIVITY COEFFICIENTS OF SODIUM DIPICRYLAMINATE IN WATER AT 0°

| Concn., moles per 1000 g. of water | Activity coefficient $\gamma =$ |
|------------------------------------|---------------------------------|
| 0.001 | 0.947 |
| .002 | .916 |
| .005 | .840 |
| .01 | .739 |
| .02 | .602 |
| .03 | .509 |
| .04 | .440 |
| .05 | .387 |

In Fig. 2 are also plotted the activity coefficients at 0° for the related compounds sodium dinitrophenolate, sodium picrate and picric acid, calculated from the freezing points measured by Lange and Herre.¹⁹ The dipicrylamines obviously have such low activities that some strong

(18) Abel, Redlich and Lengyel, *Z. physik. Chem.*, **132**, 189 (1928).

(19) Lange and Herre, *ibid.*, **181**, 329 (1938).

association effects must be present. From pH measurements it is evident, however, that dipicrylamine is not a typical weak electrolyte. Thus, it is most probable that strong forces appear between the anions, a view which is confirmed by the measurements below.

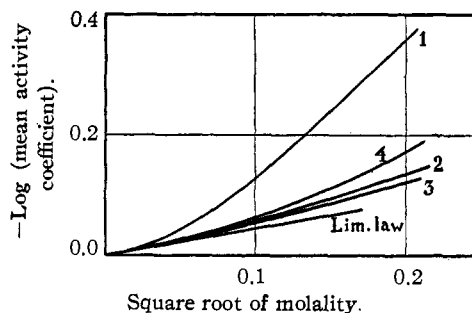


Fig. 2.—Activity coefficients at 0° for sodium dipicrylamine (1); sodium picrate (2); sodium dinitrophenolate (3); and picric acid (4).

Equivalent Conductivity

Experimental.—Conductivity measurements were carried out in a 20-ml. cell of the pipet type designed by Washburn.²⁰ The cell constants were determined with the 0.1 and 0.01 D solutions of potassium chloride described by Parker and Parker.²¹ The measurements were made with an improved Wheatstone bridge described by Jones and Josephs.²² Measurements at 700 and 2000 cycles gave identical results within $\pm 0.05\%$.

All solutions were made up by weight from purified (see above), dried sodium dipicrylamine and doubly distilled "equilibrium" water.²³ Since the carbonic acid present may produce some colloidal dipicrylamine which may disturb the electrode functions and sound minima, a little sodium carbonate was usually added to the distilled water; the conductivity of the latter thus was increased from about 0.5 to 1.0×10^{-6} mhos, the proper correction of which was allowed for.

Results.—The conductance measurements were carried out at 0° with solutions of concentrations ranging from 10^{-3} to 10^{-1} N , and the results are presented in Table VI and in Fig. 3.

Up to concentrations about 0.03 N , the measurements may be given by the equation

$$1 - f_{\mu} = (0.219 + 29.5/\Delta_0)c^{1/2} - Bc \quad (6)$$

(20) Washburn, *THIS JOURNAL*, **38**, 2431 (1916).

(21) Parker and Parker, *ibid.*, **46**, 312 (1924).

(22) Jones and Josephs, *ibid.*, **50**, 1049 (1928). The writer wishes to thank Dr. L. Tronstad and K. Stokland at the Institute of Applied Inorganic Chemistry, Trondheim, for the loan of the generator as well as the cells.

(23) Kendall, *ibid.*, **38**, 2460 (1916).

TABLE VI
CONDUCTIVITY OF SODIUM DIPICRYLAMINATE IN WATER
AT 0°

| Concn. moles per liter | Density d_4^0 | Conductivity $10^3 \times K$ | Equiv. cond. Λ_c |
|------------------------|-----------------|------------------------------|--------------------------|
| 0.00138 | 1.0002 | 0.0515 | 37.3 |
| .00582 | 1.0012 | .2120 | 36.45 |
| .00667 | 1.0014 | .2427 | 36.35 |
| .00936 | 1.0020 | .3370 | 36.0 |
| .01480 | 1.0032 | .527 | 35.6 |
| .0211 | 1.0047 | .744 | 35.3 |
| .0294 | 1.0066 | 1.022 | 34.75 |
| .0426 | 1.0096 | 1.450 | 34.0 |
| .0475 | 1.0107 | 1.600 | 33.65 |
| .0764 | 1.0173 | 2.458 | 32.15 |
| .1177 | 1.0268 | 3.521 | 29.9 |

The coefficient $B = 2.5$ is probably larger than for any other uni-univalent electrolyte, the highest value reported being given by Lange and Herre¹⁹ as $B = 1.7$ for sodium picrate.

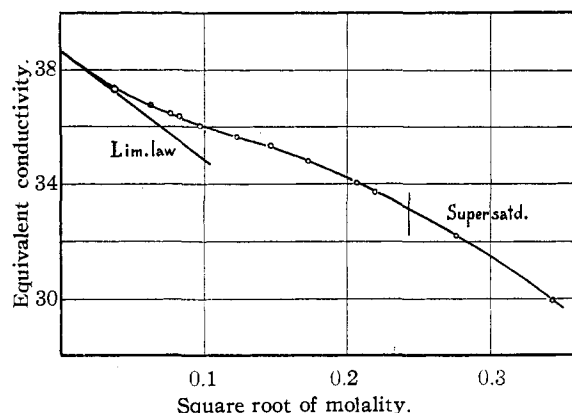


Fig. 3.—Equivalent conductivity of sodium dipicrylamine in water at 0°.

The large conductivity of the dipicrylamine at intermediate concentrations, together with the very low activity coefficients given above, must probably be interpreted as a pronounced association of anions, increasing with increasing concentration.

At about 0.025 N , however, we have an inflection point of the conductivity curve, perhaps caused by the interaction between associated anions and the cations.

Ion Mobilities.—The extrapolation to infinite dilution was made by the method of Shedlovsky.²⁴ The plotting of $\Lambda'_0 = (\Lambda_c + 29.5c^{1/2})/(1 - 0.219c^{1/2})$ against c gave a straight line below $c = 0.025$, with the result $\Lambda_0 = 38.7$ for sodium dipicrylamine. If 25.85 be taken²⁵ as Λ_0 for

(24) Shedlovsky, *THIS JOURNAL*, **54**, 1405 (1932).

(25) Landolt-Börnstein-Roth, "Physikalisch-chemische Tabellen," 5 Aufl., 111 Erg. bd., Verlag von Julius Springer, Berlin, 1936, p. 2059.

sodium ion at 0°, one obtains the limiting equivalent conductivity for the dipicrylamine anion at 0° equal to 12.8, which is a fairly probable figure (compare the known figure for picrate anion, 15.2).

Mobility values at other temperatures may be computed from the empirical Johnston-Angel²⁶ formula

$$\Lambda_0(t) = \Lambda_0(t_1) \times [\varphi_1/\varphi t_1]^m \quad (7)$$

where φ denotes the fluidity of water; $m = c/a$, where c equals the temperature coefficient of ion mobility, and a that of the fluidity of water. Since m represents the deviation from Stokes' law, a deviation which decreases with decreasing mobility and also with increasing size of the hydrated ions, we have from plottings of c against mobilities extrapolated to a probable figure $m = 0.98 \pm 0.01$ for the dipicrylamine anion. Then we have

$$\Lambda_0 = 21.5 [1 + 0.0251(t - 18) + 0.000125(t - 18)^2]^{0.98} \quad (8)$$

Heat of Solution

The integral heat of solution of sodium dipicrylamine in water was determined at 0.005 and 0.01 N , also the heat of dilution of a 0.125 N solution. The measurements were carried out at 20° in a Dewar vessel of 1.5-liter capacity, with 2- to 4-g. samples of sodium dipicrylamine crystals. The temperature curves were taken with the platinum resistance thermometer described above. Calibration of the calorimeter was made with potassium chloride, the heat of solution of which was obtained from the tables of Bichowsky and Rossini.²⁷ The results are seen from Table VII (in the last column is shown the error caused by an uncertainty of 3×10^{-4} degree in the original temperature measurements).

TABLE VII
INTEGRAL HEAT OF SOLUTION OF SODIUM DIPICRYLAMINATE IN WATER

| Concn., moles per liter | Heat of soln., kcal. per mole |
|-------------------------|-------------------------------|
| 0.005 | -12.35 \pm 0.06 |
| .010 | -12.32 \pm 0.04 |
| .125 | -10.9 \pm 0.1 |

The absorption of heat is seen to be fairly high, reaching about twice the figure for sodium picrate.

(26) Angel, *Z. physik. Chem.*, **170**, 81 (1934).

(27) Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

Discussion.—The figures above indicate a relative partial molal heat content at 0.05 N equal to $\bar{L}_2 \doteq -0.8$ kcal., while the non-ideal free energy change is calculated to $\bar{F}_2 \doteq -0.5$ kcal. Hence,²⁸ we can conclude that in such solutions some molecule-molecule effect must be quite overwhelming. Taking into consideration also the results of the activity and conductance measurements, we see that, owing to strong van der Waals forces between the two large organic, polarizable anions, considerable association occurs between ions of equal sign, in spite of electrostatic repulsion. A more quantitative treatment of the degree of association will appear elsewhere.²⁹

Phase Phenomena

The writer recently happened to make some interesting observations, a preliminary report of which might be mentioned here.

On mixing at room temperature perhaps 1 g. of sodium dipicrylamine crystals with 10 ml. of a 1 N aqueous sodium chloride solution, part of the crystal mass is dissolved, while the remainder sinks to the bottom, still in the crystalline state. Making the same experiment with calcium chloride instead of sodium chloride, part of the crystals dissolve readily, but the remainder after some minutes will have changed into a *heavy, clear and red colored liquid*. Heating to 53° causes complete miscibility. On cooling below 52°, the dark colored liquid phase again separates as a turbidity which soon collects to larger drops, subsiding to the bottom. As an example may be mentioned that the separated liquid phase from one of the experiments had a specific gravity of 1.33 and contained about 45% of water, the rest being calcium dipicrylamine together with some chloride.

Such systems, with definite temperatures of complete miscibility (the same result obtained by increasing as by decreasing the temperature), were also observed at other normalities of calcium chloride, as well as with different weights of dipicrylamine added. The results of these preliminary experiments, carried out in sealed glass tubes of 1-ml. capacity, are given in Fig. 4.

(28) Scatchard, *Chem. Rev.*, **13**, 23 (1933).

(29) Kjeliland, to be published in *J. Chem. Education*.

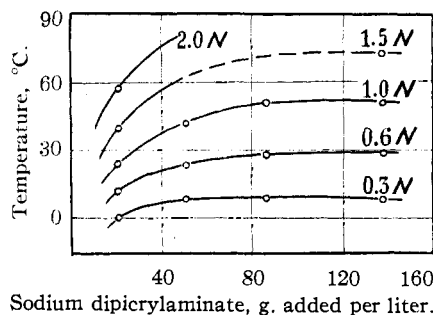


Fig. 4.—Curves of complete miscibility of dipicrylamine in calcium chloride solutions of different normalities.

At present the writer is not able to give a satisfactory explanation of the astonishing distribution of the electrolyte dipicrylamine on *two* aqueous solutions in equilibrium with each other, though it is in accordance with the phase rule. An extensive and thorough study of the problem seems very desirable, particularly because, on account of the strong specific forces observed in dilute solutions, interesting structural relationships are likely to occur in such concentrated solutions as obtained during the miscibility experiments.

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Summary

1. A short color analysis of dipicrylamines is given.
2. The molal volume of sodium dipicrylamine in water has been determined, and density figures of aqueous solutions are reported.
3. Freezing point depressions and equivalent conductivities of sodium dipicrylamine have been measured at 0°, also its heat of solution.
4. Strong association effects due to van der Waals forces have been found to exist between the dipicrylamine anions even in dilute aqueous solutions.
5. An interesting case of partial miscibility has been discovered in mixtures of dipicrylamines with aqueous calcium chloride solutions.