

CCLII.—*The Viscosities and Densities of Anhydrous Methyl Alcohol and of Solutions of some Halides of Sodium and Potassium in this Solvent.*

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RAIKES.

THE work detailed in this paper forms part of an investigation of the properties of solutions of electrolytes in methyl alcohol which is being carried on in this laboratory.

Although there are several values for the density of the pure solvent to be found in the literature, there are no data concerning the densities of solutions of electrolytes in methyl alcohol. Values for the viscosity of the pure alcohol are notably those of Dunstan (J., 1914, **105**, 784) and of Thorpe and Rodger (*Phil. Trans.*, 1894, A, **185**, 531). The only previous systematic work on the viscosities of halide solutions is that of Tower (*J. Amer. Chem. Soc.*, 1916, **38**, 833).

EXPERIMENTAL.

The preparation of the pure alcohol is described by Hartley and Raikes (J., 1925, **127**, 524). The only departure from their procedure was that the present authors avoided the use of drying agents altogether, relying entirely on repeated fractionation under the most careful conditions. It was shown by determinations of the density and viscosity of this alcohol that it was equally as pure and dry as that obtained by any of the other workers who used aluminium amalgam as a dehydrating agent.

Owing to the rapidity with which viscosity determinations could be carried out it was decided early in the course of the work to utilise this property as a routine method for testing the dryness of samples of alcohol. Table I shows the effect of increasing water content on the time of flow.

TABLE I.

Viscometer No. 2. Pipette A. Temperature 18°.

| Water added %. | Time of flow (secs.). | Increase. |
|----------------|-----------------------|-----------|
| 0.0 | 220.8 | — |
| 0.14 | 222.0 | 1.2 |
| 0.18 | 222.2 | 1.4 |
| 0.29 | 223.2 | 2.4 |
| 0.645 | 225.8 | 5.0 |
| 0.93 | 228.0 | 7.2 |
| 0.99 | 228.4 | 7.6 |
| 1.47 | 232.8 | 12.0 |

TABLE II.

| Acetone added %. | Time of flow (secs.). | Decrease. |
|------------------|-----------------------|-----------|
| 0.0 | 220.8 | — |
| 0.1 | 220.6 | 0.2 |
| 0.18 | 220.4 | 0.4 |
| 0.4 | 220.2 | 0.6 |
| 1.25 | 218.4 | 2.4 |

Table II gives similar figures for the addition of acetone. In the early stages of the work it was necessary to consider its presence, but later the alcohol supplied did not contain a detectable amount of this impurity.

The presence of water therefore increases the viscosity, whereas acetone has the opposite effect. One could be confident that similar results would be obtained at a higher temperature than 18° and when it was later decided to work at 25° the values were not redetermined since they had served their original purpose.

The Preparation of the Solutions.

Most of the salts used were Merck's "puriss." recrystallised. The specimens were heated at 150° until their weight was constant. Silica crucibles were used and the solutions made up in wide-necked Jena glass flasks.

With the weaker solutions, the addition of the methyl alcohol was carried out in a dry-box (Tutton, J., 1897, **71**, 865). Instead of drying the inside of the box with desiccating agents, as suggested by Tutton, a current of pure dry air was blown through the box for about an hour before any flasks were opened. The box was also fitted with suction apparatus for filling pyknometers.

Since the solution in no case approached saturation, no difficulty was experienced in dissolving the salts, the most obstinate, potassium chloride, passing into solution on standing with periodic shaking. In order to minimise the risk of introducing solid impurities, the solution after preparation was immediately transferred to a Jena flask with an externally ground stopper, further additions of alcohol being made to this when it was desired to dilute the solution. The greatest number of dilutions carried out with any one original solution was four.

The Determination of Density.

The densities were determined in two pyknometers which had a capacity of about 25 c.c. and were of the design described by Applebey (J., 1910, **97**, 2000) and by Hartley and Barrett (J., 1911, **99**, 1072). Two caps were used, one having a capillary head for use when filling the instrument and when it was suspended in the bath, and one closed for use when weighing. The use of the closed cap on the balance lessened the possibility of loss of solvent through evaporation by closing one of the openings to the air.

The filling of the pyknometer with alcohol or a solution was always carried out in the dry-box, since it was found by experiment that filling in the air with an ordinary water-pump introduced sufficient water seriously to affect the density. When the filling was effected

in the dry-box, the only likely error was that due to possible evaporation of part of the solvent. Since, however, the filling was a rapid process, taking not more than 3 minutes or so at the most, the loss of solvent would be small, and this was confirmed by the excellent agreement obtained when the density of the same solution was determined in two pycnometers of slightly different capacities and times of filling.

The determinations were carried out in a thermostat at 25°. The bath was electrically regulated, and the temperature, which was constant to 0.01°, was determined by reference to a thermometer standardised by the Reichsanstalt.

The weights used were standardised by Richards's method (*J. Amer. Chem. Soc.*, 1900, **22**, 144).

The formula used in the calculation of density was a reduced form of that recommended by Hartley and Barrett (*loc. cit.*), viz.,

$$\delta_l = \delta_w \{w_3 - (w_p - w_c)\} / \{w_2 - (w_p - w_c)\}.$$

δ_l = density of the liquid at the temperature of the determination referred to that of water at 4°.

δ_w = density of water at the temperature of the determination.

w_2 = apparent weight in air of the pycnometer when filled with water (corrected for air displaced by weights).

w_3 = apparent weight in air of the pycnometer when filled with the liquid (corrected for air displaced by weights).

w_p = true weight of the empty pycnometer in a vacuum.

w_c = true weight of the counterpoise in a vacuum.

This formula only requires the determination of w_3 , since the correction for the change in density of air is beyond the limits of accuracy of this work (compare Barr, J., 1924, **125**, 1042).

The Determination of Viscosity.

The viscometers, of the U-shaped Ostwald type, were held in the thermostat in an apparatus designed to ensure that they always occupied the same relative position in the bath, and were adjusted to the vertical by means of a plumb-line. The openings to the air were guarded by soda-lime tubes so that the liquid came into contact with dry air only. The water values were frequently redetermined and were found not to change; when the instruments were not in use they were kept filled with conductivity water.

Filling was carried out by means of a 5 c.c. pipette, a method found satisfactory by Applebey (*loc. cit.*) and by Washburn and Williams (*J. Amer. Chem. Soc.*, 1913, **35**, 737). The filled viscometer was left in the bath for at least 10 minutes before any times were taken, the liquid being sent through the capillary at least twice in order to

wet the sides. The usual number of times of flow taken was seven. If any time varied by more than one-fifth of a second from the mean, the readings were abandoned and the viscometer was cleaned. This was seldom necessary.

The viscosity values were calculated from the formula

$$\eta_l = \eta_w \delta_l t_l / \delta_w t_w$$

η_l = viscosity of the liquid at the temperature of the determination.

η_w = viscosity of water at the temperature of the determination.

δ_l, δ_w = densities of the liquid and of water, respectively, at the temperature of the determination, referred to that of water at 4°.

t_l, t_w = observed times of flow of the liquid and of water respectively, in the same viscometer.

No correction for loss of kinetic energy was applied and no allowance was made for the air-column (Merton, J., 1910, 97, 2454; Gruneisen, *Wiss. Abhandl. Physikal.-Tech. Reichsanst.*, 1905, 4, 151; Applebey, *loc. cit.*). The value of δ_w^{25} for water was taken as 0.997071, and that of the viscosity at 25° as 0.00895 (Goodwin and Mailey, *Physical Rev.*, 1908, 26, 47).

The results obtained are set forth in the tables below, Table III containing the values for the density and viscosity of pure methyl alcohol, Table IV giving the values obtained for the solutions investigated, and Tables V and VI the viscosity increments and changes of volume on solution.

Densities are referred to water at 4° and viscosities are in absolute units. Concentrations are expressed in g.-mols. of salt per 1000 g. of solution.

TABLE III.

Density and viscosity of pure methyl alcohol at 25°.

| Density. | | Viscosity. | |
|-----------------|----------|-----------------|----------|
| Pyk. 1. | Pyk. 2. | Visc. 3. | Visc. 4. |
| 0.78640 | 0.78641 | 0.005442 | 0.005456 |
| | 0.786405 | | |
| | 0.78641 | | |
| Mean = 0.78641. | | Mean = 0.00545. | |

The density figures are each the mean of several adjustments of different fillings with different samples of alcohol. The density value interpolated from those given in Landolt and Bornstein's tables is 0.7866.

Dunstan (*loc. cit.*) gives the viscosity as 0.00546 and the value interpolated from the work of Thorpe and Rodger (*loc. cit.*) is 0.00553.

TABLE IV.

Densities and Viscosities of Solutions at 25°.

| Salt. | Conc. | Density. | Viscosity. | | |
|-------|---------|----------|------------|----------|----------|
| | | | Visc. a. | Visc. b. | Mean. |
| KI | 0.4951 | 0.84660 | 0.00662 | 0.00670 | 0.00667 |
| | 0.2577 | 0.81701 | 0.00608 | 0.00610 | 0.00609 |
| | 0.1930 | 0.81018 | 0.00594 | 0.00595 | 0.005945 |
| | 0.1643 | 0.80601 | 0.00587 | 0.00590 | 0.00588 |
| | 0.0916 | 0.79830 | 0.00571 | — | 0.00571 |
| | 0.08116 | 0.79597 | 0.00568 | 0.00570 | 0.00569 |
| KBr | 0.10884 | 0.79650 | 0.00575 | 0.00577 | 0.00576 |
| | 0.09926 | 0.794895 | 0.00573 | 0.00575 | 0.00574 |
| | 0.07192 | 0.79343 | 0.00566 | 0.00568 | 0.00567 |
| | 0.04446 | 0.79027 | 0.00560 | 0.00561 | 0.00560 |
| | 0.02840 | 0.78991 | 0.00553 | 0.00555 | 0.00554 |
| | 0.04713 | 0.79150 | 0.00565 | 0.00565 | 0.00565 |
| NaI | 0.2753 | 0.81811 | 0.00628 | 0.00630 | 0.00629 |
| | 0.1306 | 0.80198 | 0.00586 | 0.00589 | 0.005875 |
| | 0.08303 | 0.79664 | 0.00572 | 0.00574 | 0.00573 |
| NaBr | 0.03870 | 0.79195 | — | — | — |
| | 0.6142 | 0.835624 | 0.00744 | 0.00745 | 0.007445 |
| | 0.3185 | 0.81169 | 0.00650 | 0.00651 | 0.006505 |
| | 0.15895 | 0.80027 | 0.00600 | 0.00602 | 0.00601 |

These results, when plotted, display no irregularities.

The values given by Tower (*loc. cit.*) for potassium iodide seem to agree with ours, but it is not possible to make a complete comparison, since he does not give the densities of his solutions, nor does it appear certain that his solvent was dry.

The viscosity increment is given by K/c , where c is the concentration and $K = (\eta_{\text{soltn.}} - \eta_{\text{alc.}})/\eta_{\text{alc.}}$.

TABLE V.

Viscosity Increments.

| Conc. | K. | K/c. | Conc. | K. | K/c. |
|--------------------------|--------|-------|---------------------------|---------|--------|
| <i>Potassium iodide.</i> | | | <i>Potassium bromide.</i> | | |
| 0.4951 | 0.224 | 0.452 | 0.1088 | 0.05688 | 0.5226 |
| 0.1643 | 0.079 | 0.480 | 0.09926 | 0.05321 | 0.5361 |
| 0.1930 | 0.0899 | 0.466 | 0.04446 | 0.02752 | 0.619 |
| 0.0916 | 0.0477 | 0.521 | 0.07192 | 0.0404 | 0.5631 |
| 0.08116 | 0.044 | 0.543 | 0.02840 | 0.01651 | 0.5813 |
| <i>Sodium bromide.</i> | | | <i>Sodium iodide.</i> | | |
| 0.6142 | 0.367 | 0.598 | 0.2753 | 0.1541 | 0.5598 |
| 0.3185 | 0.1936 | 0.607 | 0.1306 | 0.0789 | 0.6042 |
| 0.15895 | 0.1028 | 0.646 | 0.08303 | 0.0514 | 0.622 |

The volume change on solution (V) is calculated by the method adopted by Hartley and Barrett (*J.*, 1923, **123**, 398).

The figures for sodium iodide are omitted, since they display considerable discrepancies.

TABLE VI.

| Conc. | Density. | V. | Conc. | Density. | V. |
|--------------------------|----------|------|---------------------------|----------|------|
| <i>Potassium iodide.</i> | | | <i>Potassium bromide.</i> | | |
| 0.4951 | 0.84460 | 27.6 | 0.10884 | 0.79650 | 41 |
| 0.2577 | 0.81701 | 28.4 | 0.09926 | 0.794895 | 31 |
| 0.1930 | 0.81018 | 27.5 | 0.07192 | 0.79343 | 49.5 |
| 0.1643 | 0.80601 | 30.0 | 0.04446 | 0.79027 | 34 |
| 0.0916 | 0.79830 | 28.3 | 0.02840 | 0.78991 | 56 |
| 0.08116 | 0.79597 | 28.4 | | | |
| | | | <i>Sodium bromide.</i> | | |
| | | | 0.6142 | 0.835624 | 26.1 |
| | | | 0.3185 | 0.81169 | 26.8 |
| | | | 0.15895 | 0.80027 | 42.0 |

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