Title
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Publication Date
1967-10-01

UCRL-17858

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University of California

Ernest O. Lawrence Radiation Laboratory

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(M. S. Thesis)

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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

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ABSTRACT

THE VISCOSITY OF CONCENTRATED SOLUTIONS OF CALCIUM IN LIQUID AMMONIA IN THE TEMPERATURE INTERVAL OF -40°C TO -70°C

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ABSTRACT

The viscosity of concentrated solutions of calcium in liquid ammonia was determined in the concentration interval from 3.4 to 8.9 mole-percent calcium at temperatures from -40 to -70°C. The modified cross-arm viscometer used for the measurements was calibrated at each of the temperatures at which measurements were made. A minor surface tension correction was made using the surface tension of sodium-ammonia solutions in the absence of such data for calcium-ammonia solutions. An analysis of possible errors indicates that the results are accurate to ±5 percent.

The viscosity of concentrated solutions at concentrations near the two phase region (about 40% of saturation) are nearly equal to the viscosity of pure liquid ammonia at the same temperature. At -40°C a solution with a concentration of 8.9 mole-percent calcium (83 percent of saturation) has a viscosity more than twice that of the pure solvent. Similar increases in viscosity with increasing concentration were found at all temperatures between -40 and -70°C. This is the opposite of the effect in sodium- and potassium-ammonia solutions where the viscosity decreases with increasing concentration. A possible explanation for these results is offered.

I. INTRODUCTION

Metals with high oxidation potentials should form solutions in water because of the excellent ionizing properties of this solvent. There have been several reports of short-lived alkali metal-water solutions;[1,2] however the reaction producing hydrogen and the metal hydroxide is so rapid that quantitative measurements in these solutions are very difficult. Liquid ammonia also possesses the ionizing power necessary to dissolve these metals, but in this case the reaction forming hydrogen and the metal amide proceeds at a slow enough rate to allow quantitative examination.

The alkali metals, alkaline earth metals, aluminum, europium, and ytterbium are known to dissolve to varying extents in liquid ammonia. In general the solutions which are formed show typically ionic properties at low concentration and metallic properties at high concentration. Below a certain critical temperature the division between these two concentration ranges is accented by the separation of two immiscible liquid phases, in the cases of lithium, sodium, potassium, calcium, strontium, and barium. The more dense phase is an inky, non-reflective blue color and is less concentrated in metal while the lighter more concentrated phase possesses a metallic, bronze color. Schettler and Patterson[3] report that the consolute temperature for sodium, lithium, and potassium are -41.6°C, -63.5°C, and -70.0°C, respectively. The consolute composition is about 4 mole-percent metal in these three cases. Apparently no such phase separation occurs for rubidium[3] or cesium solutions.[4] Vapor pressure measurements on calcium, strontium, and barium solutions[5] indicate that all three metals also show phase separation. More recent data on solutions of calcium[6,7] indicate that the consolute temperature is near or above room temperature and that the consolute composition is less (1 to 2 mole-percent metal) than for the alkali metal solutions. Phase separation for europium- and ytterbium-ammonia solutions has not yet been reported; however it is likely that the phase diagrams of these metals in liquid ammonia are similar to those of the alkaline earth metals.[8]

As the concentration of metal is increased, eventually saturation is reached. Vapor pressure measurements at -35°C have shown that the alkali metals are soluable to an extent of 15 to 22 mole-percent metal in the following order of increasing solubility: sodium, potassium, rubidium, cesium, lithium.[9] At -36°C Jolly et al.[6] report a solubility of 10.7 mole-percent calcium. All of these metals show little change in solubility with temperature, indicating a small differential heat of solution for the precipitate dissolving into the saturated solution.

The form of the solid which precipitates as ammonia is removed from saturated solutions differs for different metals. Kraus[10] applied the phase rule to his vapor pressure measurements to show that the free metals precipitated from solutions of sodium, potassium, and lithium but that the solid formed from solutions of calcium was approximately the hexammoniate. Biltz and Hüttig[11] confirmed the existence of the calcium hexammoniate and found similar hexammoniates for strontium and barium. Vapor pressure measurements at -75.9°C also indicate the existence of europium and ytterbium hexammoniates.[12] Recent vapor pressure measurements on calcium, strontium, and barium have led to the postulate that the ratio of ammonia to metal may not be integral.[5] From vapor pressure measurements Benoit[13] suggested that the compound $Li(NH_3)_4$ existed at -38.5°C, but Kraus and

Johnson[14] were unable to reproduce his results. Later data[15,16] at much lower temperatures have shown that the compound $Li(NH_3)_4$ does exist, but that it melts in contact with solid ammonia at -185°C.

Kraus[17] originally observed that when a direct current is passed through dilute, blue solutions of alkali metals in liquid ammonia, the blue color became more intense near the cathode and disappeared near the anode. He also found that no new products were formed at the anode. When a potassium amide solution was similarly electrolyzed, gas evolved at the anode and blue color appeared at the cathode. Based on these results, he correctly deduced that the negative carrier of current is the solvated electron, which also accounts for the blue color. Subsequently many experiments have been performed and many models have been introduced in an attempt to explain the results. The current status of metal ammonia solutions was recently reviewed in depth by Jolly[18] and Das[19] and will not be repeated here. However, a brief discussion of the currently accepted models for dilute metal-ammonia solutions will be useful in interpreting measurements in more concentrated solutions. Following this, discussion will be centered on the main subject of this report, the physical properties of concentrated solutions, although the great majority of research in metal-ammonia chemistry has been concerned with dilute solutions.

Many early investigators had suggested models to explain the results of their individual measurements, but the first attempt to devise a model to explain most of the previous experimental measurements in dilute metal-ammonia solutions was suggested by Becker, Lindquist, and Alder.[20] They proposed that four species exist in equilibrium as follows:

(1) The metal atoms are strongly associated with approximately six ammonia molecules oriented around the atoms with the negative end of their dipoles pointing inward. The valence electron moves around the metal ion in an expanded s-like orbital on the protons of the ammonia molecules. The complex, which they called a monomer, M, then is similar in some respects to a large hydrogen atom.

(2) The electron can escape from the immediate vicinity of the monomer leaving the metal ion, M^+. This species then exists in solution exactly as a metal ion formed by the dissociation of a metal salt.

(3) When the electron escapes from the monomer it polarizes the solvent to form an electron cavity, e^-.

(4) Just as with two hydrogen atoms, two monomers can associate to form a dimer, M_2. The energy of binding of the dimer arises both from exchange energy, as with a hydrogen molecule, and from van der Waals attraction. The equilibria between species are then represented by

$$M^+ + e^- \rightleftharpoons M \qquad (1)$$

and

$$M \rightleftharpoons \frac{1}{2} M_2 \qquad (2)$$

Arnold and Patterson[21] later conclusively showed that to account quantitatively for both the electrical and magnetic properties, it is necessary to postulate the existence of an additional diamagnetic species. Catterall and Symons[22] have included recent data on dilute europium solutions with many of the previous data on dilute metal-ammonia solutions in an analysis to determine which of the many models is most probable. They conclude that in extremely dilute solutions the main species present are the metal ion, the electron cavity, and an ion-pair resulting from their association. This latter species is equivalent to the monomer. As the total metal concentration is increased there is a spin-pairing of electrons. This results in a negatively charged species equivalent to an ion-pair formed from the association of a metal ion with an electron cavity containing two electrons of opposite spin. This is the additional diamagnetic species required by Arnold and Patterson's analysis. As the total concentration of metal is further increased, the association of this negatively charged species with another metal ion results in the equivalent of the dimer proposed by Becker, Lindquist, and Alder. A representation of these equilibria is given by

$$M^+ + e^- \rightleftharpoons M^+ \cdot e^- \quad . \tag{3}$$

$$M^+ \cdot e^- + e^- \rightleftharpoons M^+ \cdot (e_2^=) \tag{4}$$

$$M^+ \cdot (e_2^=) + M^+ \rightleftharpoons M^+ \cdot (e_2^=) \cdot M^+ \quad . \tag{5}$$

This model is very similar to that of Becker, Lindquist, and Alder except for the $M^+ \cdot (e_2^=)$ species and for the detailed structure of each species. For concentrated metal-ammonia solutions no such detailed model has been proposed. Instead numerous models have been suggested to explain individual measurements.

The equivalent conductance of solutions of sodium, potassium, and lithium show similar change with concentration at -33.6°C.[23] The value of the equivalent conductance decreases from its limiting value at infinite dilution, passes through a minimum at approximately 0.1 mole-percent metal, and then increases to very high values in concentrated solutions. For sodium-ammonia solutions, the limiting value at infinite dilution is 1022 cm^2/ohm-equivalent, the value at the minimum is 475 cm^2/ohm-equivalent, and the value for a saturated solution is 1.016×10^6 cm^2/ohm equivalent.[23-25] The equivalent conductance of a saturated sodium-ammonia solution is about 20 percent greater than that of a potassium-ammonia solution at the same concentration.[25] More recent data show that the equivalent conductance of a concentrated calcium-ammonia solution is about half that of a concentrated sodium-ammonia solution with the same number of equivalents metal per liter of solution.[7]

The temperature coefficient of conductance of sodium-[24] and potassium-ammonia[26] solutions shows a sharp maximum at concentrations near 2.5 mole-percent metal. The temperature coefficients at these maxima are 3.6 and 4.55 %/°C for sodium- and potassium-ammonia solutions, respectively. At lower concentrations the value decreases, passes through a broad minimum, and then increases slightly to a value near the temperature coefficient of viscosity. This is in accord with the ionic nature of dilute solutions. At higher concentrations the temperature coefficient of conductance decreases continuously from the maximum to a small, positive value. The temperature coefficients of conductance of saturated sodium- and potassium-ammonia solutions are 0.066 and 0.044 percent per °C, respectively, at a temperature near -34°C.[24,26] The temperature coefficient of conductance of metals is negative and it appears from the shape of the curve for solutions of sodium and potassium that if the concentration could be increased slightly beyond saturation, the temperature coefficient of conductance of these solutions would also become negative. The temperature coefficient of conductance increases with decreasing temperature at concentrations from about 1 mole-percent metal to saturation.[24,26] The temperature coefficient of conductance of concentrated calcium-ammonia solutions at temperatures between -35°C and -70°C, much below the consolute temperature, shows a somewhat different change with concentration.[7] The value at a concentration near the two phase region (about 4 mole-percent calcium) is 0.4 percent per °C. The temperature coefficient of conductance decreases with increasing concentration to 0.2 percent per °C at 5 mole-percent calcium, and then remains constant at this value up to a concentration of 7 mole-percent calcium.

Arnold and Patterson[27] have been quantitatively successful in explaining the concentration dependence of conductivity of sodium-ammonia solutions throughout the entire range of concentrations. The conductivity of dilute solutions was calculated from the Onsager-Kim theory, adjusted for the effective concentration of species according to equilibria similar to Eqs. (3) to (5). They postulate that at concentrations from near the conductance minimum up to about 2.5 mole-percent sodium, a mechanism where the electrons jump from neutral metal ion-electron cavity-pairs to the metal ions is important. This results in an increase in conductivity and accounts for the minimum in the equivalent conductance curve. In more concentrated solutions they account for the high conductivity by assuming a scattering of conduction electrons by screened metal ions. From the observed dependence of the temperature coefficient of conductance on concentration they suggest that a narrow conduction band begins to form at about 2.5 mole-percent sodium but that its structure is not complete except possibly at saturation. This model could also account for the lower conductance of concentrated potassium solutions if the screened potassium ions are larger than for the case of sodium. The conductivity and temperature coefficient of conductance of the calcium-ammonia solutions might also be explained by assuming that the second valence electron is not so easily promoted to the conductance band because of its deeper potential well.

The conductivity measurements provide information mainly concerning the interaction of electrons with the solvent and with the species in solution which contain metal nuclei. Two specific properties which have been interpreted in terms of the nature of metallic species in concentrated solutions are the result of the reflection spectra and small angle x-ray scattering data.

Beckman and Pitzer[28] have measured the reflection spectra of sodium ammonia solutions at -40°C covering a concentration range from 0.6 to 15.3 mole-percent sodium. The authors report the reflectivity as a ratio, ρ, of the reflectivity of the sodium-ammonia solution to the reflectivity of mercury at the same temperature. For the most concentrated solution, ρ is about 0.9 for a wave length of 1μ, increases to a maximum of 1.2 at a wavelength of 7μ, and then decreases slightly at higher wavelengths. At slightly lower concentrations ρ is smaller and shows a sharper decrease for higher wavelengths. The authors were able to explain the data quantitatively by using a model which includes dimers, conduction electrons and a high concentration of species of the type Na_n, where n is greater than two. Thus in concentrated solutions there may be clusters of monomers as well as dimers.

Schmidt[29] has measured small angle x-ray scattering by concentrated solutions of lithium, sodium, and potassium at -75°C. He found evidence of scattering centers with dimensions of the order of 32 Å for lithium, 16 Å for sodium, and 13 Å for potassium. He showed that there was no evidence of a center greater than 3 Å which was independent of the type of metal. From measurements at -45°C on lithium solutions, he determined that the concentration of these centers increases with increasing temperature. He concluded that these results indicate the existence of clusters containing at least two atoms of metal.

Heats of solution of the alkali metals and of calcium, strontium, and barium have been measured at concentrations near 1 mole percent metal at -33°C.* The heats of solution for potassium, cesium, and rubidium are essentially zero, while that of sodium is +1.4 kcal/mole. Lithium and the above alkaline earth metals evolve large amounts of heat on dissolving. The heat of solution of lithium is -9.65 kcal/mole, and that of the alkaline earth metals is about -20 kcal/mole. This is in agreement with the formation of solid hexammoniates of the alkaline earth metals and indicates that lithium is also strongly ammoniated even at temperatures much above where $Li(NH_3)_4$ has been observed. Recently Gunn and Green[30] have measured the heats of solution of alkali metals as a function of concentration and found that for concentrations above about 1.5 mole-percent metal there is no change in the heat of solution with increasing concentration. One of the authors has attempted to explain the results for sodium-ammonia solutions using the equilibria of Eqs. (1) and (2) with some success for dilute solutions.[31] This theory however failed to predict their result that the heat of

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* These measurements are summarized by Jolly[18] where the original references are given.

solution is not a function of concentration for concentrations greater than 1.5 mole-percent metal. He postulated that this could be explained by an exothermic dissociation of higher clustered species, a conclusion which agrees with the x-ray scattering data.

The densities of alkali metal-ammonia solutions have been measured by many investigators (see Jolly[18] for original references). The densities of lithium, sodium, and potassium solutions are less than that of pure liquid ammonia at all concentrations while the density of concentrated cesium-ammonia solutions increases with concentration. The results are usually discussed in terms of the excess volume. This quantity is defined as the net change in total volume associated with the dissolution of one gram atom of metal in a volume of liquid ammonia. The excess volume of all metal-ammonia solutions is positive, indicating a net increase in volume. Both sodium- and potassium-ammonia solutions show a broad maximum in excess volume at a concentration between 8 and 9 mole-percent metal. The excess volume of concentrated lithium-ammonia solutions decreases continuously with increasing concentration while that of concentrated cesium-ammonia solutions increases with concentration. Recent density measurements[7] show that the excess volume of calcium-ammonia solutions is somewhat higher than any of the alkali metal-ammonia solutions.[*] The excess volume of concentrated calcium-ammonia solutions decreases with increasing concentration, and the rate of decrease is

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[*] However if one assumes that two valence electrons are released when calcium dissolves, the excess volume per electron of calcium-ammonia solutions is less than that of lithium-, potassium-, or sodium-ammonia solutions at the same concentration.

much faster than for sodium, potassium, or lithium solutions. Wong[7] postulates that this decrease indicates that any higher order clusters that may be formed are more stable in calcium-ammonia solutions than in alkali metal-ammonia solutions.

Maybury and Coulter[32] determined the adiabatic compressibility of concentrated solutions of lithium, sodium, and potassium iodide in liquid ammonia as a function of concentration by measuring the velocity of sound through these solutions. They also determined the adiabatic compressibility of a nearly saturated solution of calcium. The compressibility of the salt solution was found to decrease with increasing concentration in a manner typical of ionic solutions. The compressibility of the metal-ammonia solutions was found to increase with increasing concentration. At concentrations greater than 3 mole-percent metal, the compressibility of a sodium-ammonia solution was slightly greater than that of a lithium-ammonia solution at the same concentration. The difference between the adiabatic compressibility of the calcium-ammonia solution and that of pure liquid ammonia was only about half the equivalent difference of lithium and sodium at the same concentration. The authors suggested that this increase of adiabatic compressibility with concentration was indicative of the metallic nature of these solutions and that the difference between the calcium- and the alkali metal-ammonia solution was due to the fact that calcium has two valence electrons.

Kikuchi[33] has measured the viscosity of sodium-ammonia solutions over the entire range of concentrations at temperatures between +30 and -30°C. The viscosity was found to decrease with increasing concentration at all temperatures. The effect was most pronounced at lower temperatures.

At the higher temperatures the viscosity was almost independent of concentration at concentrations near saturation, though at a value much below the viscosity of pure liquid ammonia at the same temperature. O'Reilly[34] has measured the viscosity of potassium-ammonia solutions up to concentrations of about 8-mole percent potassium and found that these solutions also have viscosities below that of the pure solvent.

We can conclude from the above measurements that concentrated solutions of alkali metals in liquid ammonia are metallic in nature. This is clearly shown by their high electrical conductivity and their high reflectivity to light. The increase in adiabatic compressibility and the decrease in viscosity with increasing metal concentration indicates that the forces of interaction between species in concentrated solutions are considerably smaller than the forces of interaction between ammonia molecules in the pure solvent. In addition the reflection spectra, the small angle x-ray scattering data, and the heat of solution data have led to the suggestion that a higher order clustering of species takes place in concentrated solution than in dilute solutions.

The physical properties of concentrated solutions of alkaline earth metals in liquid ammonia often show considerably different behavior than the alkali metal-ammonia solutions. The alkaline earth metals form solid compounds with ammonia unlike the alkali metals. The temperature coefficient of conductance, the excess volume and the adiabatic compressibility of concentrated calcium-ammonia solutions are different from the analogous alkali metal-ammonia solutions. From these results we would expect that the viscosity of concentrated alkaline earth metal-ammonia solutions would also be different from the case of alkali metal-ammonia solution, and a knowledge of this property might help to explain some of the previously measured physical properties of concentrated metal-ammonia solutions.

For these reasons measurements of the viscosity of concentrated calcium-ammonia solutions were undertaken. This report presents the results of the study. The experimental procedure is described in section II, and the results are presented and discussed in sections III and IV.

II. EXPERIMENTAL PROCEDURE

Experimental techniques quite different from the techniques used with higher boiling solvents are necessary when working with a solvent such as liquid ammonia, which boils at -33.35°C. It becomes necessary to work at reduced temperatures or, alternately, to use apparatus capable of withstanding the high pressures associated with such solvents at room temperature. Since metal-ammonia solutions are thermodynamically unstable with respect to the reaction of the metal with the solvent, the low temperature approach has the advantage of reducing the rate of this decomposition. However it is not possible to make measurements over the full range of concentrations at temperatures below the consolute temperature because of the coexistence of two liquid phases. For calcium-ammonia solutions this two phase region extends from about 0.05 to about 3.6 mole-percent calcium[7] at -50°C. The solution of calcium in liquid ammonia is saturated at about 10.4 mole-percent calcium,[6] so about one third of the total concentration range is unavailable for measurements on a single phase. Since this study is concerned with the properties of concentrated solutions, this latter objection is not very important. Therefore measurements were made in the temperature range from -40°C to -70°C at 10 degree intervals. Significantly, the density data necessary to interpret the results of viscosity measurements with a capillary viscometer have been measured in this temperature range.[7]

This chapter will be divided into two sections. In the first section the apparatus and procedure used to determine the viscosities of concentrated solutions of calcium in liquid ammonia will be described.

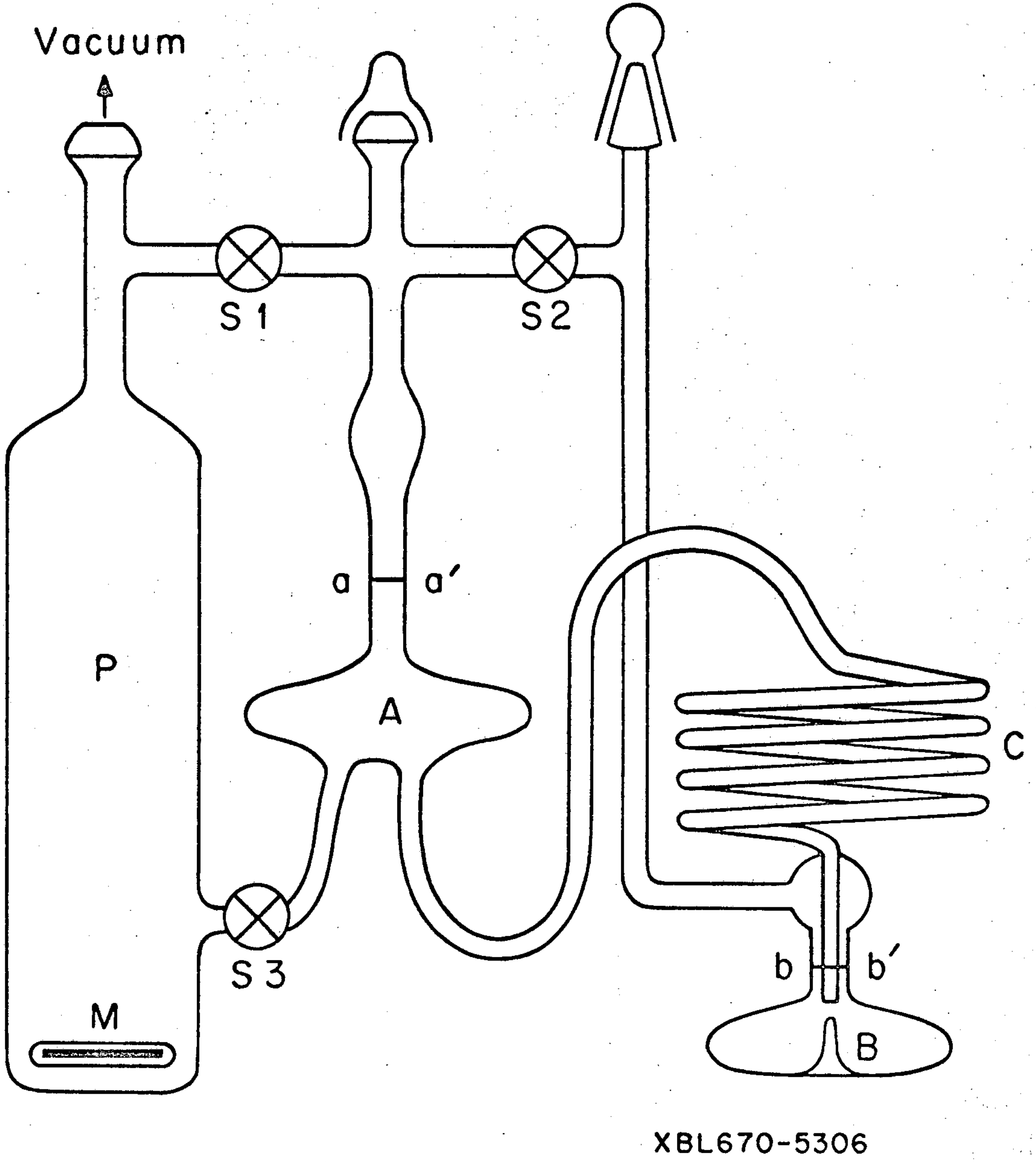
The second section will discuss the method of calibration of the viscometer.

A. Viscosity Measurements in Concentrated Solutions

The viscosities of concentrated calcium-ammonia solutions were determined by measuring the time for a fixed volume of solution to flow through a length of capillary tubing. The viscometer is a modification of the cross-arm viscometer developed by Johnson, Tourneau, and Matteson[35] and is shown in Figs. 1 and 2. The apparatus was fabricated entirely of Pyrex glass with high vacuum stopcocks.

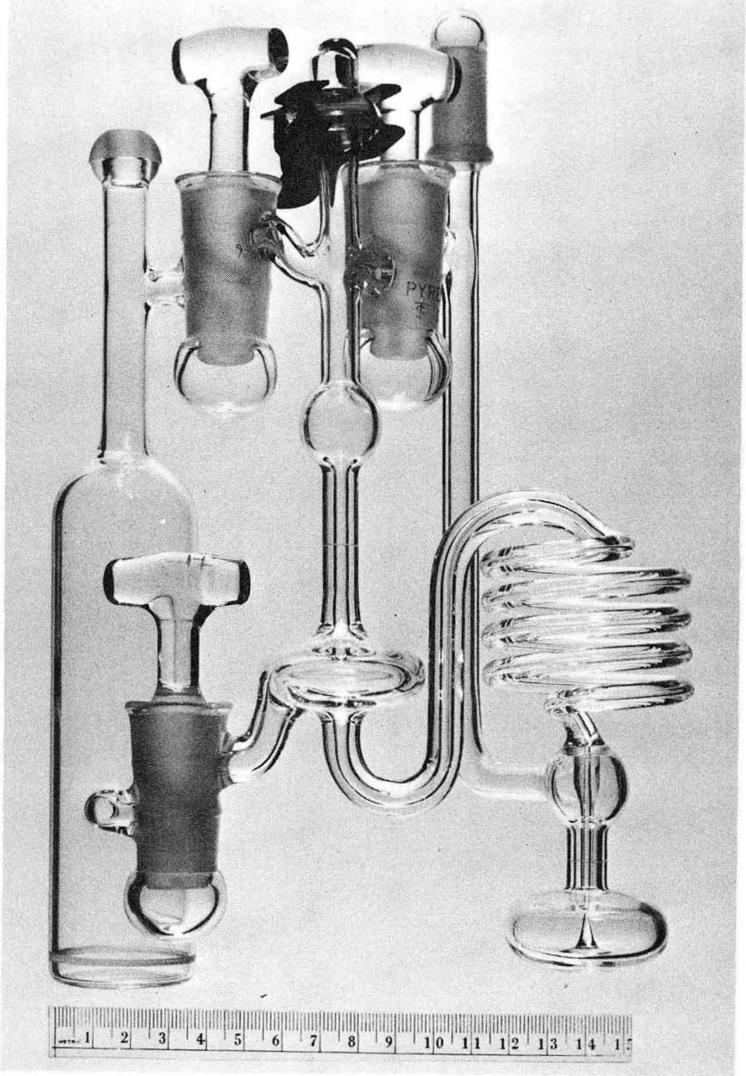
Prior to a viscosity measurement, the apparatus was thoroughly cleaned by the following procedure: The viscometer was soaked in an aqueous solution of sodium hydroxide (2 N) for approximately four hours to remove any stopcock grease or other organic material. Since hydroxide is known to be an excellent catalyst for the decomposition reaction,[36] this was followed by an extended aging of the apparatus in 2 N hydrochloric acid for about twenty hours. Finally the apparatus was thoroughly rinsed with distilled water and dried in an oven at 120°C for at least ten hours.

The above cleaning procedure was adopted after trying several techniques. A small apparatus was built of Pyrex glass in which very dilute solutions of calcium in liquid ammonia (about 10^{-3} M) could be prepared. This apparatus was used to study the effectiveness of the cleaning procedures by visually observing the rate of discoloration of the blue solutions and by measuring the pressure over the solution to detect any hydrogen that would be formed by the reaction. Appreciable



P:	Preparation Cell	C:	Coiled Capillary Tubing
M:	Magnetic Stirring Bar	S:	Stopcocks
A:	35 ml Inlet Reservoir	a-a' b-b':	Etched Lines
B:	18 ml Receiving Bulb		

Fig. 1 Modified cross-arm viscometer



XBB 679-5163

Fig. 2 Modified cross-arm viscometer

reaction was found to occur when the apparatus was cleaned with hot, concentrated chromic acid only. However if this procedure was followed by soaking first in sodium hydroxide, then in hydrochloric acid, the solution could be kept for more than five hours with no appreciable decomposition. Stable solutions could also be prepared after cleaning the apparatus with a solution of 5 percent HF, 33 percent HNO_3, 2 percent Alconox, and 60 percent water (all by volume)* followed by a soak in aqua regia, but this procedure was found to lead to appreciable dissolution of the glassware. For these reasons the first cleaning procedure described was used throughout this study.

When the apparatus was removed from the oven, the stopcocks were greased with a low viscosity silicone lubricant (Dow Corning, Type 33, light consistency) while the apparatus was still warm. This lubricant is functional at temperatures down to -70°C and does not dissolve in liquid ammonia or in metal-ammonia solutions. The magnetic stirring bar and a weighed amount of metal** were placed in the preparation cell (Fig. 1) and the apparatus was immediately attached to the vacuum line and exhausted to a pressure less than 10^{-3} mm mercury. The apparatus was then immersed in a low temperature bath held at a temperature near -60°C and 50 to 60 grams of ammonia were condensed into the preparation cell.

The dissolution of calcium is slower than the dissolution of sodium in liquid ammonia. Therefore, up to one hour was necessary before all the metal had dissolved, depending upon the amount of calcium present.

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* The use of this solution is described by Morgan, Schroeder and Thompson.[37]

** Preparation of the metal and the ammonia is discussed below.

It was not difficult to determine when all the metal had dissolved because up to that time the magnetic stirring bar would not rotate freely. When all the metal had dissolved, the bath was adjusted to the desired temperature and the solution was stirred for one-half hour to insure thermal equilibrium. The stirring was then stopped, and about ten minutes were allowed for any solid calcium amide present to precipitate. The solution was then ready to be used in the viscosity determinations.

Concentrated metal-ammonia solutions are not transparent and leave a thin mirror-like film on the glass walls as the solution level is depressed. For these reasons the viscometer was designed so that liquid levels could always be determined from a rising meniscus (Fig. 1). When the solution in the preparation cell was ready, stopcocks S1 and S2 were opened to bring the pressure in the entire apparatus up to the vapor pressure of the solution. Stopcock S3 was then opened, allowing the solution to fill the inlet reservoir up to line a - a'. Stopcock S2 and S3 were closed and a slight pressure of dry argon started the solution flowing through the capillary. The pressure was then equalized on either side of the capillary by opening S2 and flow continued by gravity. The efflux time was determined as starting when the solution passed line b - b' flowing inside the capillary and ending when the receiving bulk filled and the solution level raised in the annular space around the capillary tip to the same line, b - b'.

A series of preliminary measurements were made on concentrated calcium-ammonia solutions at -60.4°C. From these measurements it was concluded that the efflux times were reproducible to within ±1 percent. Part of this scatter may have been due to drop formation at the tip of the capillary. To eliminate this problem and to reduce any associated surface tension effects at the capillary tip, a solid glass rod was built into the receiving bulk. This caused the liquid to flow smoothly out of the capillary and down the surface of the solid rod. All of the data reported below were obtained with the viscometer so modified.

The ammonia used was anhydrous grade ammonia supplied by the Matheson Company, Inc. in a cylinder of five pound capacity. The principal impurity present in the ammonia was water (approximately 50 ppm, by weight). The ammonia from this cylinder was condensed into a smaller, stainless steel cylinder equipped with a Hoke needle valve and having a capacity of approximately 140 grams of liquid ammonia. The strainless steel cylinder contained about five grams of sodium to remove the moisture from the ammonia. Before an experiment was begun, about five grams of ammonia were bled from the cylinder in order to remove the hydrogen formed by the reaction of sodium with the moisture. The cylinder was then weighed and attached to the vacuum line. The rate of condensation was controlled by the needle valve. After a sufficient quantity of ammonia had been condensed into the preparation cell, the cylinder was removed from the vacuum line and reweighed. The amount of ammonia used was determined from the difference in the two weighings, making an allowance for the ammonia vapor remaining in the vacuum line. The accuracy in this determination was ±5 mg.

The metallic calcium was upplied by Bram Metallurgical-Chemical Company in the form of bars having dimensions 1/4 in. × 1/4 in. × 3 in. which were stored under oil. A thick oxide coating on the bars was removed by filing in air. The bars were washed free of oil using dry hexane, and this solvent was removed from the bars by evacuating in the antechamber of a glove box. The glove box was equipped with an antechamber, two glove ports and a vacuum pump capable of evacuating the antechamber and the working chamber to a pressure of less than 10^{-3} mm mercury. The working chamber was maintained at one atmosphere with dry oxygen-free argon. The argon which contained less than 2 ppm oxygen and which had a dew-point of -100°F (2 ppm) was passed successively through a tube of anhydrous magnesium perchlorate and a column of activated copper BTS catalyst (BASF Colors and Chemicals, Inc.) to remove these traces of water and oxygen, respectively. The atmosphere in the working chamber was renewed about once a week. After flushing the antechamber twice with fresh argon, the antechamber was filled with argon and the calcium was transferred into the working chamber. The surface of the calcium bars was carefully removed with a sharp knife until no traces of oxide could be seen on the surface. Enough calcium to perform three experiments was cleaned and placed in three small weighing bottles. These small weighing bottles were then placed in three larger weighing bottles, and only the outer weighing bottles were greased. These sealed containers were then removed from the glove box through the antechamber. One such sample of calcium stored for six months in a normal atmosphere was still apparently free from oxide, although the samples were usually used within a week.

When a sample was to be used, the inner weighing bottle was removed and weighed. The sample was quickly placed in the preparation cell, and the cell was immediately evacuated. The empty weighing bottle was then reweighed, and the amount of calcium used was determined from the difference in weights. A slight correction was made because the weighing bottle contained argon during the first weighing and air during the second weighing. The accuracy of this determination was ±0.2 mg.

As described in the following section, the viscosity of a solution of sodium in liquid ammonia was measured in order to check the calibration procedure. The preparation of the metallic sodium sample was considerably different from the preparation of calcium. Reagent grade sodium containing 99.994 weight percent sodium was used for this determination. Since the sodium was stored under its oxide coating, no inert organic liquid came in contact with the metal. Most of the oxide was cut from the surface of a single lump of metal weighing about 50 grams. This piece of sodium was transferred through and antechamber into the glove box. The surface was removed as with the calcium and the metal was placed in a glass container equipped with a stopcock and a long piece of 7 mm glass tubing sealed at the upper end. The container was removed from the glove box and was attached to the vacuum line through the stopcock and evacuated. The sodium was melted by heating the container until a pool of liquid metal was formed around the tip of the glass tubing. Dry argon was then used to force the metal up into the tubing where it was allowed to solidify. The apparatus was then returned to the glove box where the glass tubing was broken into 4 in. pieces. These lengths of sodium-filled tubing were then placed in preparation cell of the viscometer, and a stopcock was attached to the ball joint at the top of the preparation cell. The process was performed in the working chamber so that only the sodium at the ends of the glass tubing came in contact with the argon atmosphere. The viscometer with stopcocks greased and in place was weighed before and after the sodium was placed in the preparation cell. Following the viscosity measurement, which proceeded exactly as with the calcium-ammonia solutions, the empty glass tubing was cleaned and weighed to determine the weight of metallic sodium.

The insulated cooling bath was mounted on a heavy-duty jack adjacent to the vacuum line so that it could be raised to immerse the viscometer. Cold methanol was circulated between the cold bath and an Ultra Kryostat (Landa Company, Model UK-60D). The temperature of the methanol leaving the kryostat was adjusted to a value about one degree below the desired temperature. The temperature of the cooling medium was controlled by a resistance heater connected to a proportional temperature controller (Melabs Scientific Instruments, Model CTC-1A) and measured by a calibrated platinum resistance thermometer. The temperature was also checked by measuring the vapor pressure of pure liquid ammonia using the vapor pressure data of Cragoe, Meyers, and Taylor.[38] These two measurements differed by less than 0.1°C. The peak-to-peak fluctuation in temperature was also less than 0.1°C.

B. Calibration of the Viscometer

The determination of the viscosity of a liquid using a capillary viscometer requires either an exact knowledge of the dimensions of the viscometer or a calibration using liquids of known viscosity. As discussed in Appendix A, the relation between the kinematic viscosity, ν, and the time, t, required for a fixed volume of liquid to flow through a capillary can be expressed by

$$\nu = At - B/t \quad . \qquad (6)$$

A and B are constants depending on the dimensions of the viscometer and on two coefficients which do not vary with efflux time for a Reynolds number between 10 and 600. The Reynolds number was within these limits in all cases for the viscosity measurements described in this study. Theoretically, if the efflux times of two liquids of known kinematic viscosity are measured, the constants A and B can be determined from Eq. (6). However if the kinematic viscosity of one or both the calibration liquids is not the same as that given in the literature (because of differences in purity), the procedure can lead to erroneous values of the constants A and B. The efflux times then might be perfectly reproducible, but the value of the viscosity calculated from the efflux times using Eq. (6) would be in error.

Another practice often used is to determine the values of constants A and B at one temperature and then assume that their values do not change with temperature. From the dependence of the constants on the dimensions of the viscometer (See Appendix A) and from the thermal expansion coefficient of glass, this would seem to be a reasonable assumption. A 100° change in temperature can be calculated to produce a change in the viscometer constants of less than 0.01 percent. However Meranda,[39] among others, reports that it is more accurate to calibrate a capillary viscometer at each temperature at which it is to be used. If this statement is correct, either or both the viscometer constants must change significantly with temperature. Sklyarenko et al.[40] used a viscometer in which the second term in Eq. (6) ($-B/t$) was less than 0.1 percent of the first term to show that the constant A does not change with temperature. However if the constant B does vary with temperature, these authors would not have been able to detect such a change.

Equation (6) was derived for a viscometer with a straight capillary. In this study it was necessary to coil the capillary tubing to obtain a sufficient length of tubing while maintaining the overall dimensions of the viscometer such that it would fit into a reasonably sized constant temperature bath. The long capillary was necessary to obtain efflux times long enough that they could be measured accurately. In order to determine whether Eq. (6) can be used for a viscometer with a coiled capillary and whether the constants change with temperature, the Ubbelohde viscometer shown in Figs. 3 and 4 was carefully calibrated at 25°C and at temperatures between -40 and -70°C. The efflux times of the following six liquids were measured with an accuracy of better than 0.1 percent at 25°C (references refer to the source of kinematic viscosity data): ethyl bromide,[41] carbon tetrachloride,[41] benzene,[42] methanol,[43] water,[44] and acetic acid.[45] ACS reagent grade liquids were used without further purification. The differences between the viscosities of the calibration liquids reported in the literature and those calculated from Eq. (6) with $A = 3.774\times10^{-3}$ cs/sec and $B = 6.84$ cs/sec averaged 0.1 percent.* Equation (6) can therefore be used for a viscometer with a coiled capillary.

The efflux times were then measured at the low temperatures for liquid ammonia,[40] liquid propane,[46] and acetone.[47] Liquid ammonia was prepared in the manner discussed in section II-A. Research grade propane was further purified by low temperature, vacuum distillation. Reagent

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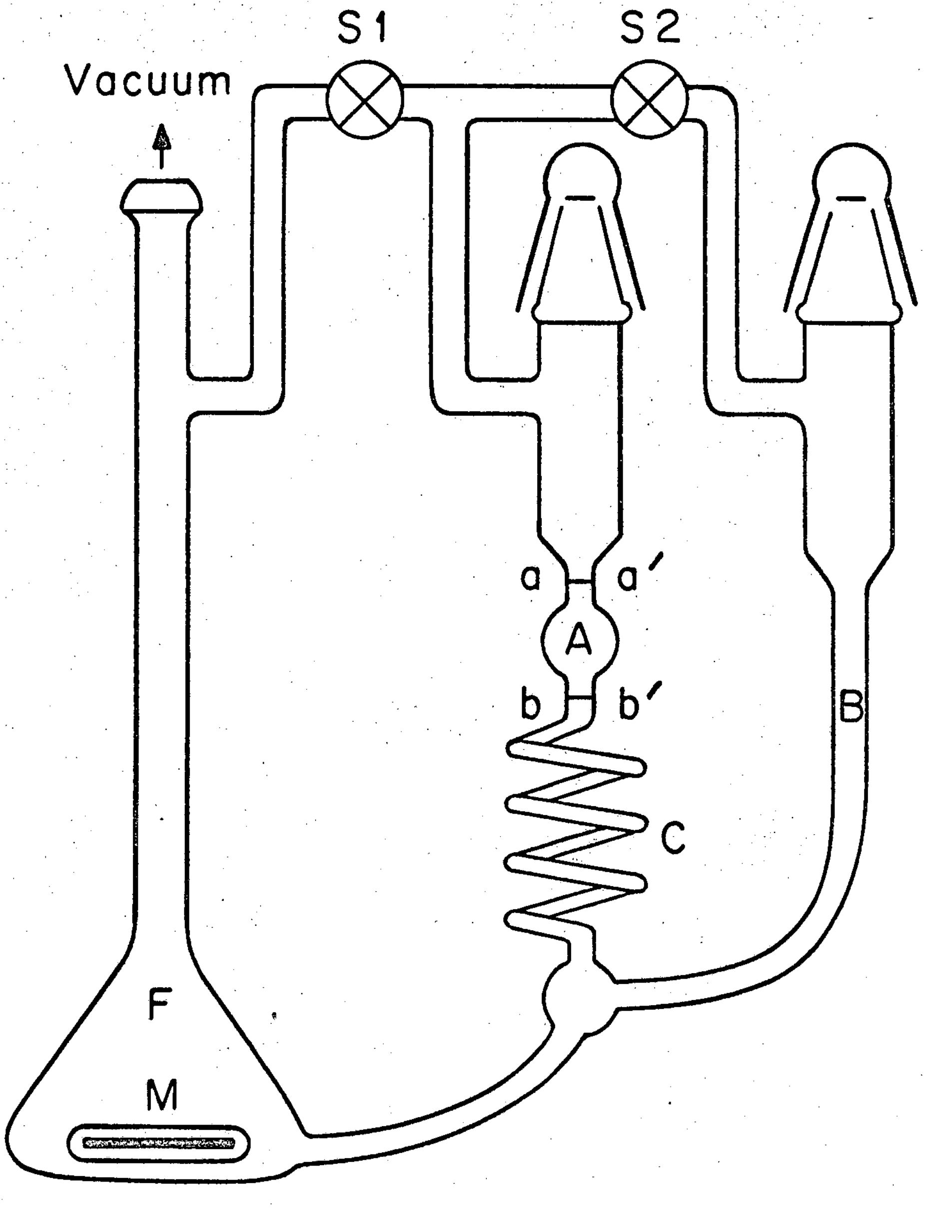
* See Appendix B for a more thorough discussion of these results.



XBL670-5307

F: 50 ml Flask

M: Magnetic Stirring Bar

A: 4.2 ml Bulb

B: 6 mm Tubing

C: Coiled Capillary Tubing

S: Stopcocks

a-a'
b-b' : Etched Lines

Fig. 3 Ubbelohde Viscometer

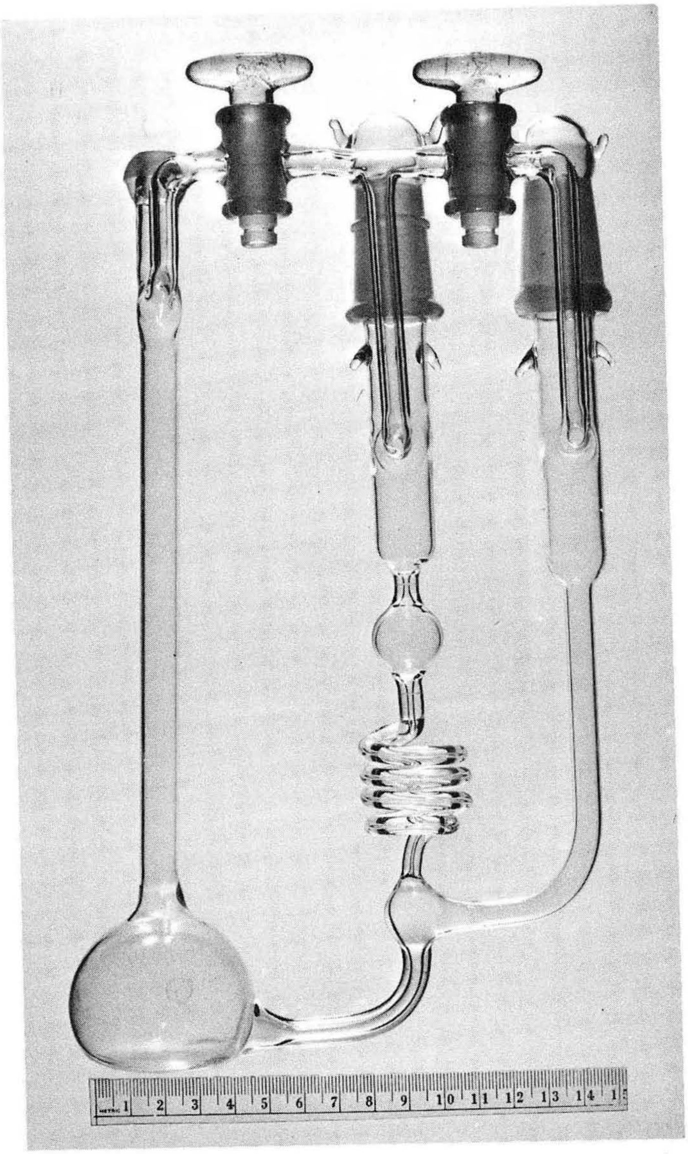


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Fig. 4 Ubbelohde viscometer

grade acetone was distilled at -40°C over molecular sieves to remove traces of moisture. The results indicate that the constant A is not a function of temperature but that B decreases nearly linearly with temperature. The differences between the viscosities of the calibration liquids reported and those calculated from Eq. (6) with $A = 3.774\times10^{-3}$ cs/sec and $B = 6.84 - 0.336\ (25-T)$, where T is the temperature in °C, averaged 0.8 percent (Appendix B). This difference is larger than at 25°C probably because of the lower accuracy of low temperature viscosity data.

When the efflux times were measured using the modified cross-arm viscometer for the same liquids at 25°C, it was found that Eq. (6) could not predict the viscosity data from the literature with such high accuracy. This was thought to be due to a surface tension effect either at the capillary exit or in the inlet reservoir. The situation was not completely corrected either by changing the dimensions of the inlet reservoir or by adding the solid glass rod in the receiving bulb to eliminate drop formation at the capillary tip. It was therefore necessary to account for the effect of surface tension by adjusting Eq. (6).

Johnson, Tourneau, and Matteson[35] have shown that surface tension effects can be accounted for by letting $A = A_o - a(\sigma/\rho)$, where A_o and a are constants and σ/ρ is the ratio of surface tension to density of the test liquid. With this modification, the differences between the viscosities calculated with Eq. (6), using $A_o = 2.574\times10^{-3}$ cs/sec and $a = 5.49\times10^{-6}$ cs-sec/cm^3, and the viscosities reported in the literature for the six liquids at 25°C averaged 0.2 percent with a maximum deviation of 0.4 percent (Appendix B). These differences are slightly larger than for the Ubbelohde viscometer because the efflux times were not as reproducible.

It would be necessary to measure the efflux times for at least three liquids having accurately known kinematic viscosities at low temperatures to determine a possible temperature dependence of all three constants. It was not possible to use liquid propane in the modified cross-arm viscometer because this liquid dissolved the stopcock grease in the one stopcock which was below the liquid level. This did not present a problem when using the Ubbelohde viscometer because no stopcocks were below the liquid level, nor did it present a problem when calibrating at 25°C because the measurements were made at atmospheric pressure and the stopcock could be used without grease. The efflux times were measured successfully for liquid ammonia and acetone at -40, -50, -60, and -70°C. By assuming that A_o and a do not change with temperature, the efflux times measured for liquid ammonia were used to calculate the values of B at each temperature. B was again found to decrease nearly linearly with decreasing temperature. Using the values of A_o and a determined at 25°C and the values of B determined from the results for liquid ammonia, the viscosity of acetone was calculated from its measured efflux time. The difference between these results and the viscosity reported in the literature for each temperature averaged 1.5 percent (Appendix B). The final equation relating the efflux time, the surface tension and the density to the kinematic viscosity is

$$\nu = (A_o - a(\sigma/\rho))t - B/t \tag{7}$$

where $A_o = 2.574\times10^{-3}$ cs/sec,

$a = 5.49\times10^{-6}$ cs-sec/cm^3, and

$B = 10.74$, 9.46, 8.41, and 6.29 at -40, -50, -60, and -70°C, respectively.*

As a final check on the validity of the calibration, the efflux time was measured for a concentrated sodium-ammonia solution at -40°C. The concentration was 12.14 mole-percent sodium for which the data of Kikuchi[33] predict a kinematic viscosity of 0.2589 cs and the data of Sienko[48] predict a surface tension of 47.1 dynes/cm. Using the measured efflux time and Eq. (7), the kinematic viscosity was calculated to be 0.2551 cs. The difference is only 1.4 percent, so we conclude that the calibration procedure is correct. The expected error in the kinematic viscosity of a liquid with accurately known surface tension and density calculated from a measured efflux time at low temperatures using Eq. (7) should be no larger than 2 percent.

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* See Appendix B for a sample calculation demonstrating the use of this equation.

III. RESULTS AND DISCUSSION OF ERRORS

The efflux times have been measured for concentrated calcium-ammonia solutions as a function of concentration at temperatures from -40 to -70°C at ten degree intervals. Measurements have been made at concentrations from very near the two phase region up to about 9 mole-percent calcium. In order to calculate the viscosity from the efflux time using Eq. (7) (Sec. II-B), it is necessary to know the density and surface tension as a function of concentration and temperature. The densities used are from a smooth curve through the data of Wong.[7] This data is believed to be accurate to 0.1 percent. The surface tension of calcium-ammonia solutions has not been measured; however the surface tensions of sodium-, lithium-, and potassium-ammonia solutions were reported by Sienko.[48] These data are reported as a percent increase in surface tension over that of the pure solvent, and they show only slight differences for the different metals. The surface tension of pure liquid ammonia has been measured by Stairs and Sienko,[49] so the surface tension of these solutions can be calculated. In the absence of surface tension data for concentrated calcium-ammonia solutions, the values of the surface tension of sodium-ammonia solutions were used as an approximation. As discussed below, this approximation is not expected to result in a large error in the reported viscosities. The results of this study are presented in Table I and are plotted in Fig. 5. The viscosities of pure liquid ammonia are also included for comparison with the results for calcium-ammonia solutions. The dashed lines in Fig. 5 represent the range of concentrations where two liquid phases coexist.

Table I. Viscosities of concentrated calcium-ammonia solutions.

Temp (°C)	Concentration (mole %)	Efflux Time (sec)	Density (gm/cc)	Surface Tension* (dyne/cm)	Viscosity (cp)
-40	0	198.8	0.6909	35.6	0.277
-40	3.439	226.9	0.6623	36.0	0.311
-40	5.283	238.1	0.6519	36.8	0.322
-40	7.335	320.8	0.6472	39.6	0.443
-40	8.263	413.8	0.6457	41.1	0.577
-40	8.888	559.3	0.6450	42.1	0.787
-50	0	221.1	0.7029	37.9	0.324
-50	3.755	242.4	0.6690	38.4	0.340
-50	5.548	258.6	0.6593	39.4	0.359
-50	7.444	358.1	0.6537	42.4	0.502
-60	0	254.2	0.7147	40.3	0.387
-60	4.005	269.8	0.6745	40.9	0.387
-60	5.739	288.7	0.6640	42.2	0.407
-60	7.102	354.9	0.6604	44.5	0.501
-60	7.574	406.7	0.6595	45.3	0.576
-70	0	296.1	0.7259	42.4	0.469
-70	4.197	298.2	0.6802	43.1	0.437
-70	5.714	325.3	0.6700	44.4	0.469
-70	7.008	388.0	0.6661	46.7	0.555
-70	7.801	495.2	0.6647	48.1	0.708

* Surface tension of a Na-NH_3 solution of same concentration (see text).

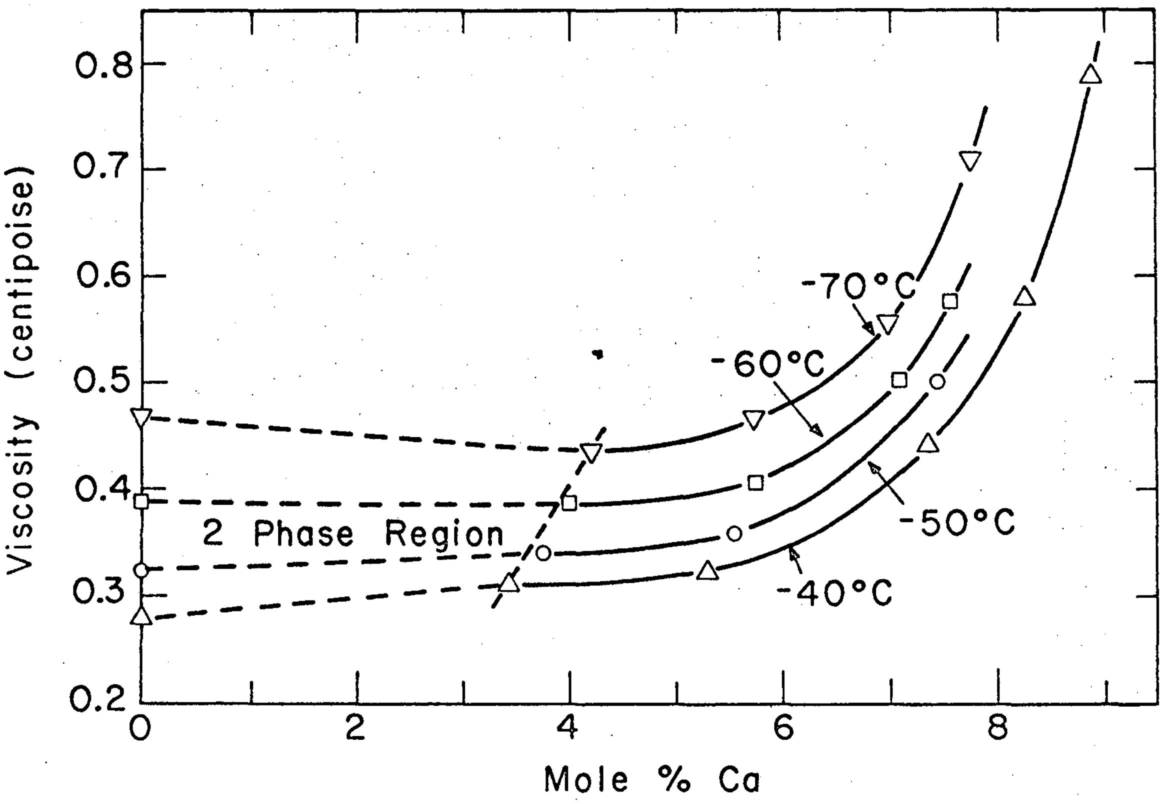

Fig. 5 Viscosity of calcium-ammonia solutions.

As is discussed in Sec. II-B, the error in the results due to the calibration of the viscometer is believed to be less than 2 percent. This value includes the inaccuracy in the measurement of the efflux time, which was estimated to be about 1 percent. The errors introduced by inaccuracies in the density data of Wong[7] will only introduce an error of approximately 0.1 percent. From inaccuracies in the weights of calcium and ammonia, the concentration is estimated to be accurate to better than 0.1 percent. From the temperature dependence of the viscosity (approximately 2.4 percent per °C) an error in temperature of ±0.1°C would introduce an error in the viscosity of 0.2 percent. The only other known source of error is that introduced by using the surface tension of sodium-ammonia solutions instead of calcium-ammonia solutions. An estimate of this error can be deduced from the following calculation:

For a concentration of 7.335 mole-percent sodium, the surface tension increment is 11.3 percent.[48] This leads to a surface tension of 39.6 dynes/cm. Using the measured efflux time, 320.8 sec, for a calcium-ammonia solution of the same concentration, the viscosity is calculated from Eq. (7) to be 0.443 cp. If the surface tension increment of the calcium-ammonia solution were 25 percent, the calculated viscosity would be 0.434 cp. This amounts to a 2 percent difference in viscosity. There is no reason to believe that the surface tension increment of a calcium-ammonia solution would be this much different from that of an alkali metal-ammonia solution. We conclude that an upper limit on the error of the data reported here is ±5 percent. Sufficient data are included to allow recalculation of the viscosities if the surface tension of calcium-ammonia solutions is measured.

IV. CONCLUSIONS

The results shown in Fig. 5 clearly show that the viscosity of concentrated calcium-ammonia solutions increases with increasing concentration of metal at all temperatures between -40 and -70°C. The viscosity of a concentrated solution is less than that of pure liquid ammonia only at -70°C and at concentrations near the two-phase region. At the higher temperatures, the viscosity of concentrated solutions is equal to or greater than the viscosity of the pure solvent at all concentrations. The viscosity of concentrated solutions of sodium in liquid ammonia is less than that of pure liquid ammonia at all concentrations.[33] The viscosities of concentrated solutions of sodium and calcium at -40°C are compared in Fig. 6. It has been found that the ratio of the mole fraction of solute to the mole fraction of solute at saturation at the same temperature is a useful measure of concentration when comparing the viscosity data of concentrated solutions of electrolytes.[50] This same measure of concentration is used in Fig. 6 to compare the viscosities of sodium- and calcium-ammonia solutions.[*] The solubility of sodium in liquid ammonia at -40°C is 15.6 mole-percent sodium[51] and that of calcium is 10.6 mole-percent calcium.[6]

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[*] Kikuchi's viscosity measurements[33] actually only covered the temperature range from +30 to -30°C at 10 degree intervals. However it was found that at constant values of the mole fraction of sodium divided by the mole fraction of sodium at saturation (at the same temperature), at plot of ln μ vs the reciprocal of the absolute temperature resulted in a straight line. It is surprising that this emperical result which is followed by concentrated solutions of electrolytes is also followed by concentrated sodium-ammonia solutions. For this reason the extrapolation to -40°C is probably accurate. The close proximity of the two-phase region (consolute point at -41.6°C) was assumed to have no effect on the viscosity of these sodium-ammonia solutions.

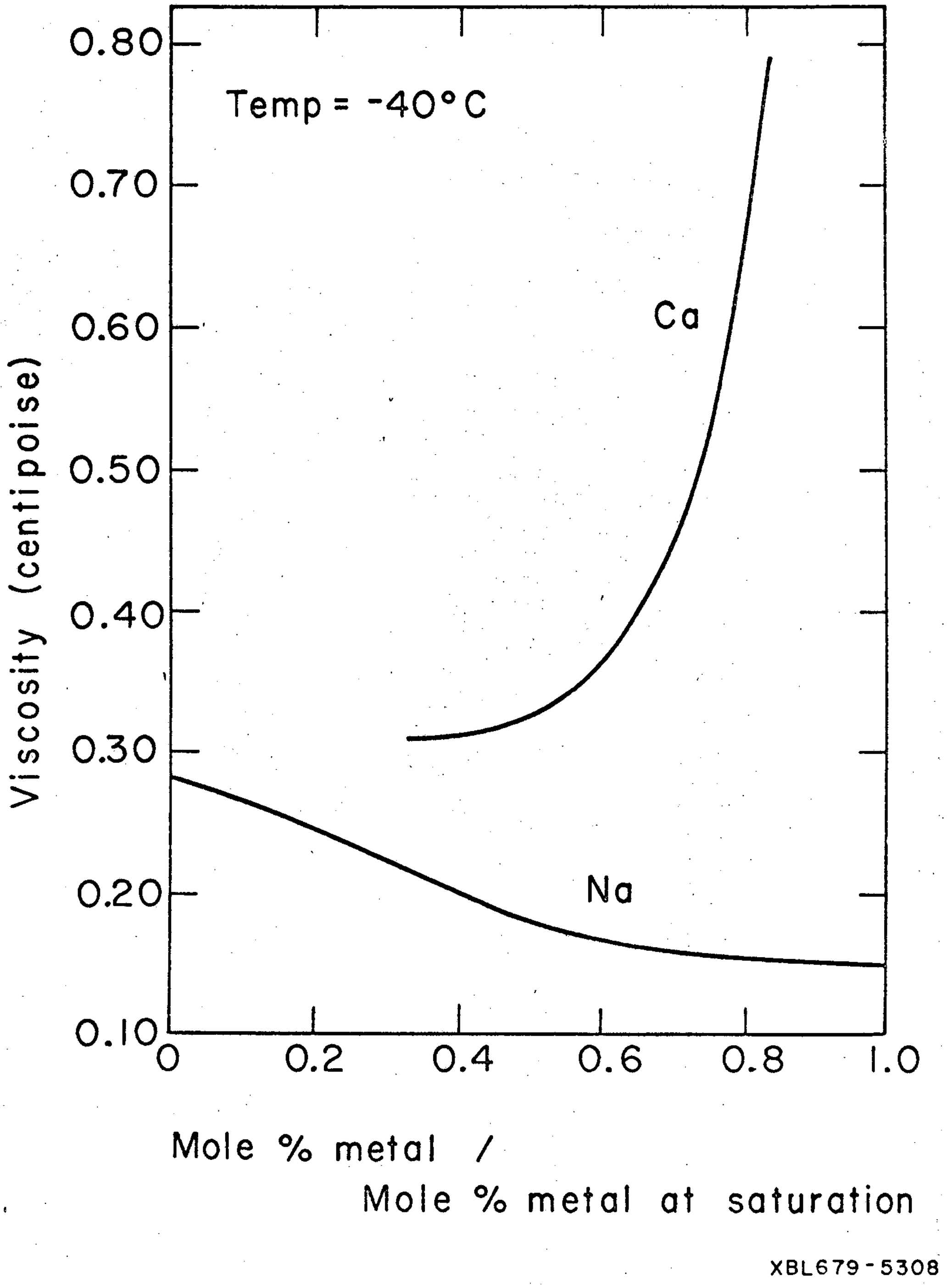

Fig. 6 Viscosity of metal-ammonia solutions.

The difference between the concentration dependence of viscosity of concentrated sodium- and calcium-ammonia solutions is striking. Clearly the forces of interaction between species in solution are much different in these two solutions. It is possible that the difference is caused by a greater stability of clusters in concentrated calcium-ammonia. This effect also leads to the formation of the solid hexammoniate in calcium-ammonia solutions, while the free metal is in equilibrium with saturated sodium-ammonia solutions. It is difficult to imagine that the rapid increase of viscosity for calcium-ammonia solutions is caused only by the greater volume of clusters in solution. Such a rapid increase of viscosity is reasonable, however, if there is a high degree of order in the solution even at concentrations much below saturation. Thus one may propose that in solutions of calcium in liquid ammonia at a concentration near the two-phase region, some degree of order is established, and as concentration increases, the ammoniated metallic species becomes more ordered. In the saturated solution the metallic species are very close to fitting into the crystal structure of solid calcium hexammoniate. This would account for the very rapid increase in viscosity at concentrations approaching saturation.

ACKNOWLEDGEMENTS

I wish to express my appreciation to Professor C. W. Tobias for his encouragement and guidance during the course of this study and to Professors D. N. Lyon and R. E. Powell for their suggestions during the preparation of the manuscript.

I am indebted to Doctors Wa-She Wong and F. G. K. Baucke for their suggestions and assistance during the experimental work.

Financial support was provided by the Inorganic Materials Research Division of the Lawrence Radiation Laboratory, Berkeley, California, under the auspices of the United States Atomic Energy Commission, and by the National Science Foundation.

APPENDIX A

Capillary Viscometers

The precise measurement of the coefficient of viscosity of fluids poses an experimental problem which has plagued researchers for many years. However techniques have been developed which allow this property to be determined for a range of fluids from gases to extremely viscous oils and asphalts. The configuration of the experimental apparatus for measurement of the coefficient of viscosity has assumed many shapes, depending mainly upon the viscosity of the fluid to be tested and the required accuracy of the result. The most common types of apparatus can be classified into three categories: 1) capillary tube viscometers based on Poiseuille's law for flow of a fluid through a cylindrical tube, 2) falling-body viscometers based on Stoke's law for the motion of a solid body falling through a fluid, and 3) rotational and oscillational viscometers having less well known hydrodynamic bases. For Newtonian liquids having a coefficient of viscosity in the range from 0.2 to 2.0 centipoise, the most widely used, most accurate, and most easily used type is the capillary tube viscometer.

All capillary viscometers are based on Poiseuille's law relating the volumetric flow rate, the radius of the tube, and the pressure drop per unit length of the tube to the coefficient of viscosity under conditions of laminar flow. In addition two major corrections must be made to account for effects at the entrance of the capillary where the test liquid must converge from the inlet reservoir into the capillary and possibly for effects at the end of the capillary where the stream diverges into the outlet reservoir.

The first and more important correction is the so-called "kinetic energy correction." The liquid entering the capillary must be accelerated at the expense of the measured pressure drop. The kinetic energy at the capillary exit is assumed to be dissipated as heat in the outlet reservoir. By making the assumption that the velocity in the inlet reservoir is zero, the correct form of this correction was derived by Wilberforce.[52] Since this assumption is never actually satisfied, the correction term is multiplied by a coefficient, m, known as the "kinetic energy coefficient," which is determined experimentally.

The second correction to the Poiseuille equation accounts for the viscous resistance encountered when the liquid stream converges from the inlet reservoir into the capillary tubing. Brillouin has shown that one can compensate for this effect by adding to the capillary length an amount proportional to the capillary radius.[53] The constant of proportionality is known as the Couette constant, n.

When the Poiseuille equation is modified by the above corrections, the following relation results:

$$\mu = \frac{\pi r^4 (\Delta P)}{8Q(l + nr)} - \frac{m \rho Q}{8 \pi (l + nr)} \qquad \text{(A-1)}$$

where

r = capillary radius

ΔP = pressure drop from the inlet reservoir to the capillary exit

Q = volumetric flow rate

l = length of capillary tubing

ρ = fluid density

μ = coefficient of viscosity.

The coefficient of viscosity of a liquid can then be determined if the values of m, n, and the other more easily measured quantities on the right are known.

The exact values of the two correction coefficients are still subject to some question. Many of the ingenious experiments which have been performed to determine the exact values have been reviewed by Barr.[53] Dorsey[54] has treated the problem extensively and concludes that for capillaries with square-cut ends, $m = 0$ and $n = 1.14$ up to a Reynolds number of 10; at higher Reynolds numbers $m = 1.0$ and $n = 0.57$. Barr agrees with Dorsey's conclusion concerning the value of n, but concluded that a value of $m = 1.12$ should be used for a Reynolds number greater than 10. Other workers have reported values of m ranging from 0.56 to 1.46 and of n from 0.0 to 1.7; these discrepancies may result in part from differences in the shape of the capillary ends.

Although the values of m and n are not precisely known, their effect on the measured coefficient of viscosity can be minimized by appropriate design of the viscometer. By making the ratio l/r very large, the effect of n is minimized. If at the same time the flow rate is very small, the kinetic energy term can be reduced to about one-thousandth of the first term. Using these specifications, the absolute viscosity of water at 20°C has been determined to be 1.0020 centipoise, a value which is now taken as the primary standard for viscosity determinations.[44]

Since the most difficult variable to measure in pressure-driven viscometers is the pressure drop itself, gravity-driven capillary tube viscometers are now in general use. In these instruments a column of the test liquid is used to provide the pressure-driving-force. In this case ΔP is replaced by the quantity ρgh. Also the average flow rate is determined by measuring the time, t, for the test liquid to flow into or out of a known fixed volume, V. Therefore, Eq. (A-1) becomes

$$\mu = \frac{\pi r^4 \rho g h t}{8V(1 + nr)} - \frac{m\rho V}{8\pi t(1 + nr)} \qquad \text{(A-2)}$$

where

h = log-mean average head of liquid[53]

g = gravity constant.

As long as the Reynolds number is greater than 10, but less than about 600, so that there is little or no turbulence, Eq. (A-2) may be rewritten

$$\mu/\rho = At - B/t \qquad \text{(A-3)}$$

where A and B are constants depending on m, n, and the dimensions of the apparatus. This equation is ideal for relative viscosity measurements. From this equation it is apparent that if the efflux times for two liquids of known, but different, kinematic viscosities ($=\mu/\rho$) are measured, the constants A and B can be determined.

APPENDIX B

Details of Calibration

A most important part of any relative viscosity determination is the careful calibration of the viscometer to be used. As discussed in Appendix A, the relation between the kinematic viscosity, ν, and the efflux time, t, for a capillary viscometer is

$$\nu = At - B/t \tag{B-1}$$

Since A and B are constants (within the limitations discussed in Appendix A), a calibration consists of determining their values for a particular viscometer. In this appendix the results of a thorough calibration of two capillary viscometers is described. In each case the viscometer was first calibrated at 25°C, and then any temperature dependence of the "constants" A and B was determined by measurements at temperatures between -40 and -70°C.

Using an Ubbelohde viscometer, the efflux times were measured for six liquids. In each case at least three determinations of the efflux times were made. The times were reproducible to 0.1 second. From the efflux times the constants A and B were determined as follows:

Since water has been chosen as a primary standard, one of the constants was determined by requiring Eq. (B-1) to predict the kinematic viscosity of water exactly. The other constant was then chosen so as to minimize the sum of the percent differences between the values of the kinematic viscosity calculated by Eq. (B-1) and those from the literature for the other five liquids. This was accomplished by trial and error.

At 25°C the best (in the above sense) values of the constants are $A = 3.774 \times 10^{-3}$ cs/sec and $B = 6.84$ cs-sec. In Table B-1 the calculated

Table B-I. Calibration of Ubbelohde viscometer at 25°C.

Liquid	Efflux Time (sec)	ν_{CAL} (cs)	ν_{Lit} (cs)	% Diff.	Ref.
Ethyl bromide	89.4	0.2609	0.2611	+0.08	41
Carbon Tetrachloride	162.0	0.5692	0.5692	0.00	41
Benzene	191.6	0.6874	0.6878	+0.06	42
Methanol	192.9	0.6925	0.6923	-0.03	43
Water	244.2	0.8936	0.8936	0	44
Acetic Acid	295.4	1.0917	1.0888	-0.27	45

and literature values of the kinematic viscosity are shown. The percent difference is equal to $(\nu_{LIT} - \nu_{CAL})/\nu_{LIT}$. In the final column the literature reference from which ν_{LIT} was taken is given.

Only for acetic acid is the difference greater than would be expected from the error in the measured efflux time. In the present study, reagent grade acetic acid was used without further purification while the literature value was determined for liquid which was further purified.[45] Therefore the difference is probably due to the presence of some water in the acetic acid used here. For this reason, when calibrating the modified cross-arm viscometer, the value of the kinematic viscosity of acetic acid called ν_{LIT} is actually the value determined with the Ubbelohde viscometer.

The next step in the calibration procedure was to determine any temperature dependence of the values of constants A and B. The efflux times were measured for liquid ammonia, liquid propane, and acetone at the temperatures of -40, -50, -60, and -70°C. If Eq. (B-1) is multiplied through by t, there results

$$\nu t = At^2 - B. \qquad \text{(B-2)}$$

From this equation it is apparent that a plot of νt vs t^2 should be a straight line having a slope of A and an intercept of -B. When the data for measurements at any one low temperature were plotted in this manner, all the points were found to lie above the line determined by the calibration at 25°C. They could be best represented by a straight line having a slope the same as the line determined at 25°C, but having a different intercept (different value of B). When the values of B thus determined at each temperature were plotted against temperature, they fell approximately on a straight line represented by $B = 6.84 - 0.0336 (25-T)$ where T is the temperature in °C. Thus

$$\nu_{CAL} = (3.774 \quad 10^{-3})t - \frac{(6.84 - 0.0336\ (25-T)\ )}{t} \qquad \text{(B-3)}$$

The results are compared in Table B-II. The values of ν_{LIT} are from References 40, 46, and 47 for ammonia, propane, and acetone, respectively. The average deviation is 0.8 percent, larger than at 25°C, probably because of the lower accuracy of low temperature viscosity data. The main conclusion from these results is that B decreases nearly linearly with decreasing temperature. The measured viscosity of acetone is consistently lower than the value from the literature. This could be due to traces of water in the acetone used by the previous investigator.[47] In this study, research grade acetone was dried by low temperature, vacuum distillation over molecular sieves, a method which has been shown to give very dry acetone.[55]

Table B-II. Calibration of Ubbelohde viscometer at low temperatures.

Temp. (°C)	Ammonia[40]		Propane[46]		Acetone[47]	
	ν_{CAL}	ν_{LIT}	ν_{CAL}	ν_{LIT}	ν_{CAL}	ν_{LIT}
-40	0.403	0.405	0.341	0.336	0.759	0.778
-50	0.461	0.460	0.372	0.371	0.888	0.905
-60	0.541	0.544	0.406	0.407	1.057	1.074
-70	0.653	0.648	0.449	0.455	1.297	1.303

The modified cross-arm viscometer was calibrated in much the same manner as was used for the Ubbelohde viscometer. However a plot of νt vs t^2 at 25°C showed considerable scatter from any straight line drawn through the data. This was thought to be due to a surface tension effect. Johnson, Tourneau, and Matteson[35] have shown that surface tension effects can be corrected for by letting $A = A_o - a\,(\sigma/\rho)$, where A_o and a are constants and σ/ρ is the ratio of surface tension to density of the test liquid. Therefore Eq. (B-1) becomes

$$\nu = (A_o - a(\sigma/\rho))t - B/t. \qquad \text{(B-4)}$$

The values of the three constants in Eq. (B-4) were determined at 25°C as follows:

The equation was required to predict the literature value of the kinematic viscosity of water exactly. This gives the following equation:

$$(\nu t)_{H_2O} = A_o t^2_{H_2O} - a(\sigma t^2/\rho)_{H_2O} - B. \qquad \text{(B-5)}$$

If Eqs. (B-4) and (B-5) are combined to eliminate the constant B, the resulting equation can be rearranged to give

$$\frac{\nu t - (\nu t)_{H_2O}}{t^2 - t^2_{H_2O}} = A_o - a\,\frac{(\sigma t^2/\rho) - (\sigma t^2/\rho)_{H_2O}}{t^2 - t^2_{H_2O}} \quad . \qquad \text{(B-6)}$$

Therefore a plot of

$$\frac{\nu t - (\nu t)_{H_2O}}{t^2 - t^2_{H_2O}} \quad \text{vs} \quad \frac{(\sigma t^2/\rho) - (\sigma t^2/\rho)_{H_2O}}{t^2 - t^2_{H_2O}}$$

should be a straight line. This was found to be the case, giving $A_o = 2.574 \times 10^{-3}$, $a = 5.49 \times 10^{-6}$, and $B = 6.47$. The kinematic viscosities calculated using Eq. (B-4) and these values of the constants are compared to the literature values of the kinematic viscosity in Table B-III. The average percent difference is 0.2 percent.

Table B-III. Calibration of modified cross-arm viscometer at 25°C.

Liquid	Efflux Time (sec)	$(\sigma/\rho)^*$ (cm^3/sec^2)	ν_{CAL} (cs)	ν_{LIT} (cs)	% DIFF
Ethyl Bromide	126.1	16.2	0.2621	0.2611	-0.38
Carbon Tetrachloride	239.9	16.5	0.5687	0.5692	+0.09
Benzene	295.0	32.3	0.6852	0.6878	+0.38
Methanol	295.8	28.1	0.6939	0.6923	-0.23
Water	417.4	72.2	0.8936	0.8936	0
Acetic Acid	455.0	26.2	1.0910	0.0917	+0.06

* Surface tensions from Reference 56.

It was not possible to check the temperature dependence of all three constants in Eq. (B-4) for the modified cross-arm viscometer because the efflux time for liquid propane could not be measured. This solvent was found to readily dissolve the stopcock grease from the one stopcock below the liquid level in the modified cross-arm viscometer. Instead it was assumed that the constant A was not a function of temperature, as was found for the Ubbelohde viscometer. Based on this assumption, Eq. (B-4) was used to calculate the value of B at each temperature using the measured efflux times for liquid ammonia and the viscosity data of Sklyarenko et al.[40] B was again found to decrease nearly linearly with decreasing temperature. The final equation used for all subsequent viscosity determinations using the modified cross-arm viscometer at low temperatures is

$$= (A_o - a(\sigma/\rho))t - B/t \tag{B-7}$$

where

A_o = 2.574×10^{-3} cs/sec,
a = 5.49×10^{-6} cs-sec/cm^3, and
B = 10.74, 9.46, 8.41, and 6.29 at -40, -50, -60, and -70°C, respectively.

The efflux times were measured for acetone at each of the low temperatures. Using Eq. (B-7), the kinematic viscosity was calculated, and the results were compared with the kinematic viscosity data of Mitsukuri and Tonomura.[47] On the average these two values differed by 1.4 percent. As was found with the Ubbelohde viscometer, the results calculated from Eq- (B-7) were consistently lower than the values from the literature.

A sample calculation will now by given to illustrate the use of Eq. (B-7). The efflux time for a solution of acetone at -70°C was measured giving $t = 556.6$ seconds. The surface tension is obtained by extrapolating data[56] from higher temperatures, giving $\sigma = 35.2$ dynes/cm. The density is 0.8888 gm/cm^3.[57] Therefore, $\sigma/\rho = 39.6\ \text{cm}^3/\text{sec}^2$. This allows A to be calculated.

$$\begin{aligned} A &= 2.574 \times 10^{-3} - (5.49 \times 10^{-6})\ (39.6) \\ &= 2.357 \times 10^{-3}\ \text{cs/sec.} \end{aligned}$$

At -70°C $B = 6.29$ cs-sec. Therefore

$$\nu = At - B/t = 2.357 \times 10^{-3}(556.6) - 6.29/556.6$$

$$\nu = 1.3006\ \text{cs.}$$

The absolute viscosity can then be calculated:

$$\mu = \nu\ \rho = 1.3006 \times 0.8888 = 1.156\ \text{cp.}$$

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