Density, Viscosity, and Conductivity of Lithium Trifluoromethanesulfonate Solutions in Dimethylsulfite

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The density, viscosity, and conductivity of solutions of lithium trifluoromethanesulfonate in dimethylsulfite at 25° C have been measured. CF_3SO_3Li was found to behave as a weak electrolyte, obeying the Ostwald dilution law. The equilibrium constant and equivalent conductance at infinite dilution obtained for CF_3SO_3Li in DMSU were found to be 4.87×10^{-4} mol/l. and 70.2 mho cm^2/equiv, respectively. The maximum specific conductance was 1.458×10^{-3} mho/cm.

Continuing research into the feasibility of using dimethylsulfite (DMSU) as a possible nonaqueous battery solvent (*13*) has led to the study of the DMSU–CF_3SO_3Li system. The deposition of Li from solutions of DMSU–CF_3SO_3Li has already been demonstrated in this laboratory (*3*). The density, viscosity, conductance, and solubility of DMSU–CF_3SO_3Li solutions are needed to characterize more fully this system. Measurements have been made from dilute solution to near saturation at 25° C.

EXPERIMENTAL

Reagents. DMSU was obtained from Eastman Kodak and purified by a batch vacuum distillation at 53° C under about 5.7 mm Hg pressure. The initial charge of 1 liter of DMSU to the still was refluxed for 1 hr. The first fraction of 100 ml was discarded. The second fraction of about 400 ml was used in these experiments. The specific conductance of redistilled DMSU was determined to be 1.4×10^{-7} mho/cm. The water in DMSU was found to be 50 ± 10 ppm by the Karl Fischer titration method (*1, 10*).

Nuclear magnetic resonance (nmr) spectra were obtained for DMSU before and after distillation. Using carbon 13 as a calibration reference, two impurity peaks were observed at 18 and 85 Hz displaced from the principal DMSU peak for the unpurified DMSU. Each of these peaks represented just under 0.5% impurities. For the purified DMSU, the peak at 18 Hz disappeared, but the peak at 85 Hz remained the same.

Conductance water for potassium chloride solution was prepared by double distillation in the presence of a nitrogen atmosphere. The specific conductance of the water used was 0.6×10^{-6} mho/cm.

Potassium chloride, Matheson, Coleman and Bell reagent, ACS crystals, was recrystallized from redistilled water and vacuum dried at 180° C for four days.

Dibutylphthalate was redistilled at $T = 173.5°C$, $P = 3.9$ mm Hg, and the middle cut (about 70% of the total charge) was retained for experimentation.

The $(CF_3SO_3)_2Ba$ was obtained from the 3M Co. and recrystallized from redistilled water. The CF_3SO_3Li was prepared by reacting a solution of $(CF_3SO_3)_2Ba$ and water with dilute H_2SO_4. The resulting solution was filtered and then neutralized with LiOH to give CF_3SO_3Li and water. The water was evaporated, and CF_3SO_3Li was recrystallized twice from acetone and then vacuum-dried at 110° C for two days. The ir spectrum obtained for a sample of $(CF_3SO_3)_2Ba$ corresponded to that reported by Gramstad and Haszeldine (*6*). The ir spectrum was also measured for CF_3SO_3Li with peaks occurring at the same positions as CF_3SO_3Ba. The only apparent impurity found in the ir spectrum of CF_3SO_3Li was water due to the extreme hygroscopic nature of the salt.

The salt was exposed to air during the ir analysis. The vacuum-dried salt only contacted dry argon in actual experiments. Karl Fischer titration of the DMSU–$LiCF_3SO_3$ solution showed 50 ± 10 ppm water, the same as the purified solvent.

Apparatus. Potassium chloride solutions were made up by weight. The molar concentrations were determined, and the equivalent conductances were calculated from the Lind et al. (*8*) equation. Two solutions of different concentrations were used to determine the cell constants. The agreement of the cell constants as determined by the two calibrating solutions was better than 0.1%. The cell constants for two cells were 0.6698 cm^{-1} and 0.008809 cm^{-1}.

An ac Wheatstone bridge was used to measure resistance. It is described in detail elsewhere (*11, 12*). A Wagner earth ground was used along with shielded cable and BNC connectors to reduce noise. General Radio-type 510A through 510F precision-decade resistors were used in all of the arms. Frequencies of 1–10 KHz were generated by a General Radio-type 1302-A oscillator using about 4 V peak to peak. The null point was detected using a Lissajous pattern on a Tektronix-type 503 oscilloscope. The accuracy in measuring the resistance of various precision resistors was better than 0.1% in the range of 100–100,000 Ω. Bright platinum electrodes were used in the cells. The frequency dependence of the solution resistance was determined in each experiment and extrapolated to infinite frequency. R vs. $1/\omega$ produced a straight line (frequency range 1–10 KHz.)

The viscometers were of the Cannon-Ubbelohde type. They were calibrated by Manning and Lloyd of the Cannon Instrument Co. The viscosity standards used in the calibrations have been described by Cannon (*4*). The corrections in the viscometer constant due to change in the gravitational constant with location, the kinetic energy correction, the surface tension correction, and error due to viscometer misalignment were all estimated to be less than 0.1%. The viscometer constants were 0.001836, 0.003910, 0.00774, and 0.01469 cSt/sec. A cell giving an efflux time between 500 and 900 sec was selected for each measurement. A few modifications were made to ensure an inert atmosphere in the apparatus (Figure 1).

The volume of solution for each experiment was of necessity small because of the availability of only limited quantities of $LiCF_3SO_3$. A method to measure the density which required only 1–2 ml of solution was, therefore, employed (*9*) (Figure 2). U-tube *A* contains solution of unknown density and U-tube *B* contains a well-known

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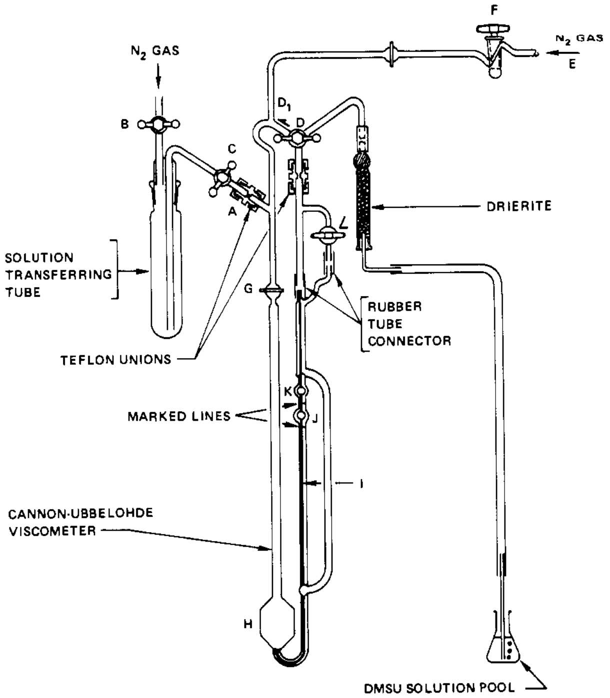

Figure 1. Modified viscometer cell

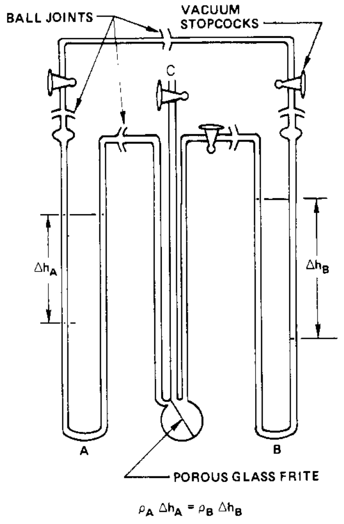

Figure 2. Density cell

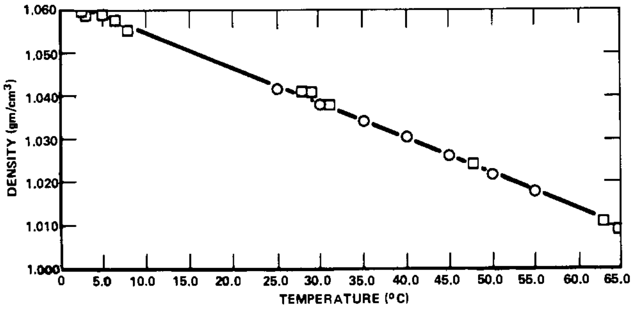

Figure 3. Density of dibutylphthalate

□ Kemppinen and Gokcen (7)

○ This work

standard. Pressure is applied at C to create a difference in the heights of the liquids in U-tubes A and B. A cathetometer was used to measure the difference in height of the solution in each U-tube. From the simple relation $\rho_A \Delta h_A = \rho_B \Delta h_B$, the density of the unknown solution can be determined. The accuracy of the cathetometer was 0.002 cm. The nominal measured height difference was 20.000 cm.

Dibutylphthalate (Matheson, Coleman and Bell) was used as the standard in the density measurements. The density of dibutylphthalate has been determined as a function of temperature by Kemppinen and Gokcen (*7*). However, to determine the accuracy of the new apparatus, the density of redistilled dibutylphthalate was measured independently, using freshly redistilled water as a standard. Figure 3 shows the results of the determination of the density of dibutylphthalate.

The conductance, viscosity, and density cells were cleaned in a HNO_3-H_2SO_4 acid solution and washed repeatedly with acetone and redistilled water and then vacuum dried at 100° C for 24 hr. Temperature control to $\pm 0.005°$ C was achieved with a Fisher 15-452W2 Isotemp bath filled with light mineral oil. This temperature control is needed because of the type of density apparatus used. Variations in temperature of 0.01° C will not cause significant changes in the density of the solution, but changes of this magnitude will cause changes in the density and pressure of the argon over the solution. This will produce oscillations in the levels of the liquids. This problem was eliminated with the above temperature control.

Procedure. All weighings and transfers were performed in a dry box (nitrogen or argon atmosphere). Distilled DMSU was weighed into a flask containing a known weight of recrystallized CF_3SO_3Li. The concentration was determined in moles per kilogram of solution and converted to moles per liter after the density had been measured. Solutions of varying concentrations were prepared by transferring a known weight of DMSU to a flask containing a known weight of the above solution. All weights were corrected for air buoyancy. After a desired solution had been prepared, the conductance cell, viscometer, and density U-tube were filled in the dry box. The cells were placed in the temperature bath and allowed to reach thermal equilibrium. At least 6 hr were allowed to ensure equilibration. However, no fluctuations in readings were observed after 1 hr. The conductance, viscosity, and density readings were recorded.

RESULTS AND DISCUSSION

Conductance data were obtained for DMSU-$LiCF_3SO_3$ solutions over a concentration range 10^{-4} to 1*M* at 25° C. The lower limit of the concentration was taken such that the specific conductance of the solvent would be less than 2% of the specific conductance of the most dilute solution. The solvent correction was made by subtracting the specific conductance of the solvent from the measurement of the solution being tested.

Bellobono and Favini (*2*), who studied conductances of electrolytes in ethylenediamine, obtained satisfactory values of Λ_0 (equivalent conductance) and K (equilibrium constant) by plotting a variation of the Ostwald dilution equation

$$\frac{1}{\Lambda} = \frac{\Lambda C}{\Lambda_0^2 K} + \frac{1}{\Lambda_0} \qquad (1)$$

The same approach was applied to the system presently being studied, and satisfactory results were obtained (Figure 4). It was not necessary to use the more complicated form of the Ostwald dilution equation stated by Fuoss and Shedlovsky as was the case for Caruso et al. (*5*), where the dielectric constant of their solvent was only 11.0. In general,

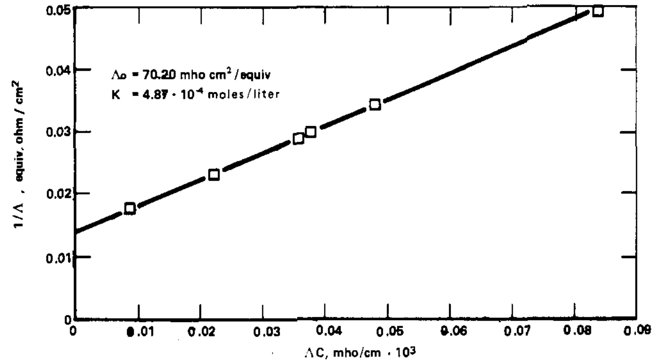

Figure 4. Ostwald dilution plot to determine limiting equivalent conductance

Table I. Density, Viscosity, and Conductivity of DMSU–CF_3SO_3Li Solutions at 25° C

C, mol/l.	ρ, g/cm^3	ν, cSt	κ, mho/cm	Λ, mho cm^2/equiv
1.483×10^{-4}	1.2040	0.6943	8.322×10^{-6}	56.10
5.102×10^{-4}	1.2040	0.6944	2.202×10^{-5}	43.20
1.050×10^{-3}	...	...	3.588×10^{-5}	34.25
1.140×10^{-3}	...	...	3.78×10^{-5}	33.10
1.646×10^{-3}	...	...	4.782×10^{-5}	29.02
4.087×10^{-3}	1.2044	...	8.373×10^{-5}	20.50
1.099×10^{-2}	1.2060	0.6996	1.527×10^{-4}	13.90
1.1278×10^{-1}	1.2141	0.7425	5.558×10^{-4}	4.94
3.035×10^{-1}	1.2234	0.8345	9.420×10^{-4}	3.11
9.866×10^{-1}	1.2703	1.3289	1.458×10^{-3}	1.48
1.002	1.2712	1.3572	1.444×10^{-3}	1.44
1.289	1.2893	1.7314	1.437×10^{-3}	1.12

the upper limit of concentration where one can expect a straight line to result from the plot of $1/\Lambda$ vs. ΛC as predicted by the Fuoss equation, $C_{\max} = 3.2 \times 10^{-7}\epsilon^3 M$ *(11)*, was found to be about $4 \times 10^{-3}M$ for the system under consideration. As can be seen from Figure 4, at about ΛC equal 0.08 mho/cm ($4.1 \times 10^{-3}M$), the experimental data begin to deviate from a straight line. However, below this concentration a satisfactory straight line is realized. The limiting equivalent conductance and overall equilibrium constant were 70.20 mho-cm^2/equiv and 4.87×10^{-4} mol/l., respectively.

The results of the density, viscosity, and conductivity of $LiCF_3SO_3$ solutions in DMSU measurements at 25° C are shown in Table I. As can be seen, the density and viscosity are relatively constant up to $0.1M$. Above $0.1M$, rapid increase in all three properties is observed.

The general experimental procedures and equipment used in this study are similar to those used by Yao *(12)*. The estimated errors are conductivity ±0.3%, viscosity ±0.1%, and density ±0.1%. Discussion of these error limits has been presented by Yao *(12)*.

NOMENCLATURE

R = resistance, ohm
ω = frequency, KHz
ρ = density, gm/cm^3
h = height, cm
c = concentration, mol/l.
Λ = equivalent conductance, mho cm^2/equiv
Λ_0 = equivalent conductance at infinite dilution, mho cm^2/equiv
k = specific conductance, mho/cm
K = equilibrium constant, mol/l.
ϵ = dielectric constant
u = kinematic viscosity, cSt

LITERATURE CITED

(1) Archer, E. E., Jeater, H. W., *Analyst,* **90**, 351 (1965).
(2) Bellobono, I. R., Favini, G., *Ann. Chim.* (Rome), **55**, 32 (1965).
(3) Bennion, D. N., "Nonaqueous Electrolyte Studies for High Energy Batteries," Final Report to U.S. Navy, Contract No. N123 (62738)-57439A (September 1969).
(4) Cannon, M. R., *Ind. Eng. Chem., Anal. Ed.*, **16**, 708 (1944).
(5) Caruso, J. A., Sears, P. G., Popov, A. I., *J. Phys. Chem.*, **71**, 1756 (1967).
(6) Gramstad, T., Haszeldine, R. N., *J. Chem. Soc.* (London), **173** (1956).
(7) Kemppinen, A. I., Gokcen, N. A., *J. Phys. Chem.*, **60**, 126 (1956).
(8) Lind, J., Zwolenik, J., Fuoss, R. M., *J. Amer. Chem. Soc.*, **81**, 1557 (1959).
(9) McAuly, W. J., Rhodes, E., Ubbelohde, A. R., *Proc. Roy. Soc., A.*, **289**, 151 (1966).
(10) Meyer, A. S., Boyd, C. M., *Anal. Chem.*, **31**, 215 (1959).
(11) Tiedemann, W. H., MS thesis, Department of Engineering, Univ. Calif., Los Angeles, Calif., June 1968.
(12) Yao, N. P., PhD Dissertation, *ibid.*, September 1969.
(13) Yao, N. P., D'Orsay, E., Bennion, D. N., *J. Electrochem. Soc.*, **115**, 999 (1968).

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