Table II. Constants for Pure Solvents

Solvent	Exptl fp, °C	K_f, deg kg/mol	ΔH_f, kcal/mol[a]
NMA	30.6	6.65 (*3*)	2.02
DMSO	18.5	4.07 (*6*)	3.24
EC	36.5	7.03 (*8*)	2.39

[a] $\Delta H_f = \text{MR}\ T_f^2/10^3 K_f$.

and molar enthalpies of fusion, used in calculating the limiting slopes of the freezing point curves, are summarized in Table II.

NOMENCLATURE

NMA = *N*-methylacetamide
DMSO = dimethyl sulfoxide
EC = ethylene carbonate
ϵ = dielectric constant
η = viscosity, cP
ρ = density, g/cc
n_D = refractive index (sodium D line)
V = molar volume, cc/mol
ΔV^E = molar excess volume, cc/mol
ϕ = volume fraction
X = mole fraction
M = molecular weight, g/mol
ΔH_f = molar enthalpy of fusion, kcal/mol
R = molar gas constant, kcal/(mol deg)
MR = molar refraction, cc/mol
T = temperature, °K
T_f = freezing point, °K
K_f = cryoscopic constant, deg kg/mol

Subscripts

i, j = generalized components

LITERATURE CITED

(1) Addison, C. C., Sheldon, J. C., *J. Chem. Soc.*, **1956**, p 1941.
(2) Bass, S. J., Nathan, W. T., Meighan, R. M., Cole, R. H., *J. Phys. Chem.*, **68**, 509 (1964).
(3) Bonner, O. D., Jordan, C. F., Bunzl, K. W., *ibid.*, **68**, 2450 (1964).
(4) Dawson, L. R., Vaughn, J. W., Lester, G. R., Pruitt, M. E., Sears, P. G., *ibid.*, **67**, 278 (1963).
(5) Decroocq, D., *Bull. Soc. Chim. France*, **1964**, p 127.
(6) Garnsey, R., Prue, J. E., *Trans. Faraday Soc.*, **64**, 1206 (1968).
(7) Gopal, R., Rizvi, S. A., *J. Indian Chem. Soc.*, **43**, 179 (1966).
(8) Gross, S. K., Schuerch, C., *Anal. Chem.*, **28**, 277 (1956).
(9) Hoover, T. B., *J. Phys. Chem.*, **73**, 57 (1969).
(10) Kempa, R. F., Lee, W. H., *J. Chem. Soc.*, **1958**, p 1936.
(11) Malmberg, C. G., Maryott, A. A., *J. Res. Natl. Bur. Std.*, **56**, 1 (1956).
(12) Schläfer, H. L., Schaffernicht, W., *Angew. Chem.*, **72**, 618 (1960).
(13) Sears, P. G., Jurch, G. R., Jr., Sands, D. E., *Trans. Ky. Acad. Sci.*, **28**, 10 (1967).
(14) Seward, R. P., Vieira, E. C., *J. Phys. Chem.*, **62**, 127 (1958).
(15) Singh, R. D., Rastogi, P. P., Gopal, R., *Can. J. Chem.*, **46**, 3525 (1968).

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Density and Viscosity of Aqueous Solutions of Methanol and Acetone from the Freezing Point to 10°C

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The viscosities and densities of aqueous solutions of methanol and acetone are presented. Compositions studied ranged from 50–100 wt % for methanol solutions and 60–100 wt % for acetone solutions. Data were taken from the freezing points of the solutions up to +10° C at 10-degree intervals. A Cannon-Ubbelohde viscometer and a glass cell pycnometer were used to make the experimental measurements. The estimated precision of the measurements was ±1.9% for viscosity and 0.0002 gram/ml for density. No data have been previously reported for these systems below room temperature.

Growing industrial interest in cryogenic processing has greatly increased the need for reliable physical property data of fluid systems at low temperatures. Associated with such cryogenic processes are related processes which are carried out at moderately low temperatures. These moderately low temperatures can often be achieved more economically by refrigeration without the use of cryogens.

To design systems for achieving these moderately low temperatures, transport properties of fluids to be used as heat transfer media must be known. A search of the literature showed that these types of data are virtually nonexistent. Therefore, this study was undertaken to obtain reliable viscosity and density data for aqueous solutions of methanol and acetone from the freezing point to 10° C.

PREVIOUS WORK

Howard and McAllister (*3*) report the viscosity of acetone–water over the entire composition range from 20° C to the boiling point. Thomas and McAllister (*8*) report the densities of the same compositions and temperatures. Kurtz et al. (*4*) report the densities over the entire composition range at 20° and 25° C. These three articles represent the bulk of all previous work done on the acetone–water

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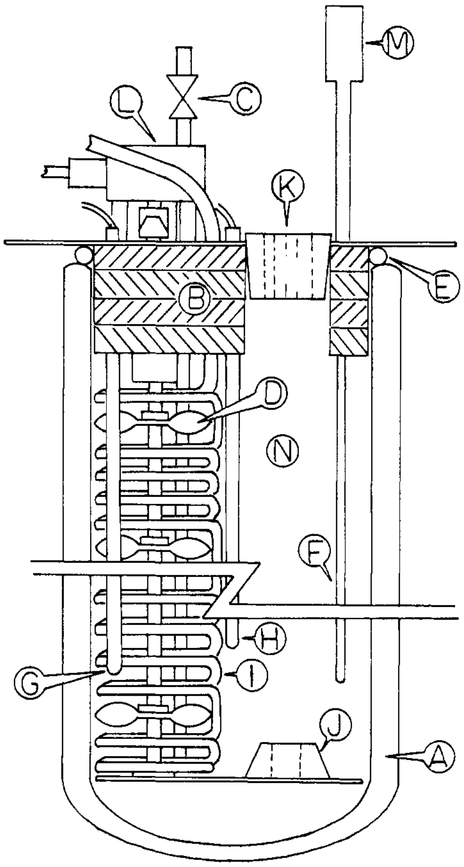

Figure 1. Low-temperature bath

system. A plot of viscosity vs. composition for this system shows that the viscosity at room temperature and above exhibits a maximum at a composition of about 36 wt % acetone. This maximum is a result of complex molecular bonding. Freezing points of the acetone–water system have been examined only by Benjamin (*1*) in 1932.

The viscosities and densities of the methanol-water system are reported by Mikhail and Kimel (*5*) from 25–50° C over the entire composition range. These authors also indicate that the inconsistencies in earlier work are probably due to inaccuracies in solution compositions. The viscosities of the methanol-water system above room temperature, like the acetone–water system, exhibit a maximum. For methanol–water, this maximum occurs at about 41 wt % methanol. The freezing point curve of the methanol–water system is complex, exhibiting eutectic and peritectic points (*1, 2, 6, 9*).

EXPERIMENTAL

The controlled temperature bath (Figure 1) provides temperature control within ±0.01° C in the range from −110° to +10° C. The bath fluid is approximately the eutectic composition of the methanol-water system—88 wt % methanol. A glass Dewar flask (*A*) with diametrically opposed unsilvered viewing strips serves as an adiabatic shield for the bath; a fluorescent lamp is positioned behind the Dewar to illuminate the contents. The Dewar is held against the top plate of the bath by a spring-tensioned platform and a large O-ring (*E*) forms a tight seal between the top plate and the Dewar. The top plate of the bath is made of layers of phenolic resin board (*B*) held together with nylon bolts. Four stirrers (*D*) mounted on a shaft driven by an air motor (*L*) circulate the bath fluid. Cooling is provided by liquid nitrogen which passes through a copper coil (*I*). The nitrogen flow rate is controlled by valve (*C*) mounted on the top plate. Control heat is supplied by heater (*G*), and an auxiliary heater (*H*) is used for rapid bath warm-up. Temperature is measured with platinum resistance thermometer (*F*) protected by copper tube shield (*M*). The open area of the bath (*N*) contains the viscometer and the density cell secured in a rubber stopper (*K*) held in position by another rubber stopper (*J*) mounted on the bottom plate.

Temperature control in the bath is effected by setting the resistance corresponding to the desired temperature on the Mueller bridge connected to the platinum resistance thermometer. This resistance and the actual resistance measured by the thermometer are compared by a null detector. The error signal generated by this comparison is fed to a dc amplifier which provides electrical power for the heater.

The platinum resistance thermometer employed was calibrated against the laboratory's standard platinum resistance thermometer which was, in turn, calibrated by the National Bureau of Standards (1948 IPTS). Temperature measurements over the range −110 to 10° C are accurate to ±0.03° C.

Five Cannon-Ubbelohde viscometers covering the viscosity range from 0.3–500 cSt were used. These instruments were calibrated by the Cannon Instrument Company at 100° F. The manufacturer stated that the viscometer constant was independent of temperature; this was checked in our laboratory. By use of Phillips Pure Grade (99 mol % minimum) *n*-heptane with physical properties taken from Rossini (*7*), calibration checks were made on the viscometers at temperatures to −90° C. The calibration constants so determined varied randomly over the temperature range with an average error of ±1.5% and no significant trend with temperature. Since there is some question as to the accuracy of the *n*-heptane density and viscosity data used, the calibration constants determined by the manufacturer were employed and considered independent of temperature. A minimum of three determinations were made for viscosity

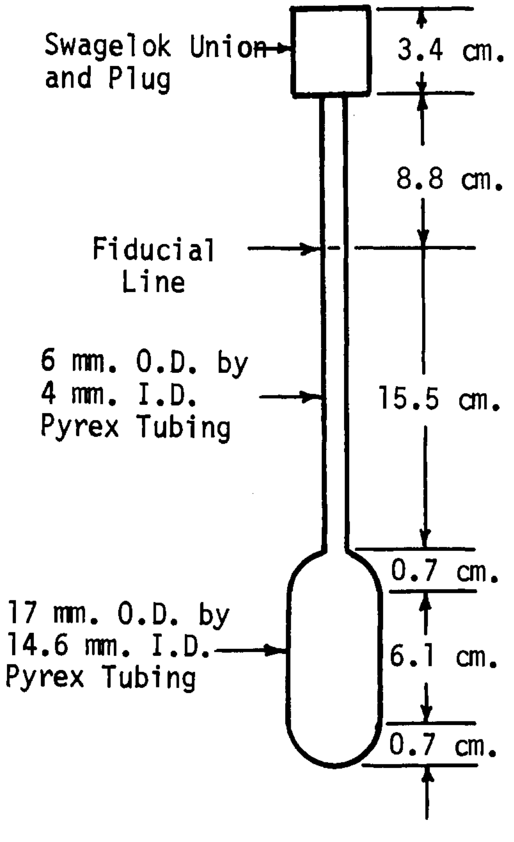

Figure 2. Density cell

Table I. Low-Temperature Densities (G/Ml) and Viscosities (CP) Methanol–Water System

Wt % methanol	99.95		90.01		79.98		70.00		60.07		50.04	
Mol % methanol	99.91		83.51		69.20		56.75		45.82		36.03	
Temp, °C	Density	Viscosity	Density	Viscosity	Density	Viscosity	Density	Viscosity	Density	Viscosity	Density	Viscosity
10.0	0.8008	0.6795	0.8283	1.023	0.8548	1.394	0.8791	1.760	0.9016	2.103	0.9229	2.388
0.0	0.8104	0.7966	0.8372	1.250	0.8631	1.772	0.8868	2.320	0.9085	2.865	0.9291	3.349
–10.0	0.8197	0.9425	0.8459	1.556	0.8712	2.302	0.8943	3.144	0.9156	4.043	0.9353	4.912
–20.0	0.8289	1.134	0.8544	1.971	0.8793	3.074	0.9019	4.420	0.9223	5.961	0.9413	7.587
–30.0	0.8383	1.380	0.8630	2.546	0.8871	4.231	0.9092	6.478	0.9288	9.261	0.9474	12.46
–40.0	0.8479	1.715	0.8716	3.384	0.8952	6.061	0.9163	9.991	0.9354	15.34	0.9530	22.10
–50.0	0.8574	2.184	0.8804	4.665	0.9031	9.124	0.9236	16.46	0.9420	27.55	0.9587	42.74
–60.0	0.8673	2.868	0.8893	6.705	0.9111	14.65	0.9311	29.56	0.9486	54.43	...	...
–70.0	0.8768	3.899	0.8983	10.22	0.9195	25.68	0.9389	58.96	0.9552	121.8	...	...
–80.0	0.8867	5.596	0.9075	16.90	0.9282	50.24	0.9466	135.3	...	...	...	...
–90.0	0.8968	8.624	0.9172	31.32	0.9370	115.3	0.9537	376.4	...	...	...	...
–100.0	...	...	0.9270	68.36	0.9461	333.3	...	...	...	...	...	...
–110.0	...	...	0.9371	189.7	...	...						

at each temperature and composition. Wherever possible, different-sized viscometers were employed for replication. The agreement between such replications was, in general, within 0.1%. In some instances, where the second viscometer employed for replication gave an efflux time of less than 200 sec (minimum required to render the kinetic energy correction insignificant), agreement without making the kinetic energy correction was within 0.4%—at efflux times, as low as 168 sec. Data obtained at efflux times less than 200 sec were not included in the results reported. Data obtained at efflux times greater than 200 sec were not corrected for kinetic energy effects. The magnitude of this correction at such times is less than 0.1% of the reported value. Since the viscometers were open to the atmosphere, there existed the possibility of concentration change due to the pickup of water. This was checked by placing a sample of given composition in the bath at low temperature for 8 hr, measuring the viscosity, recharging the viscometer with a fresh sample of the same composition, and remeasuring the viscosity. These measurements agreed within 0.1%.

The density cell used is shown in Figure 2. It was designed such that 20% of the total volume of the cell was contained in the small-bore neck of the tubing. Distilled water was used to calibrate the density cell volume relative to the fiducial line scribed on the neck. A cathetometer was used to measure the height of the liquid level to ±0.001 cm, and a Mettler H-15 balance was used to weigh the cell and its contents to within 0.0001 gram. The usual corrections for the buoyancy of air were made during this procedure. To do the experimental density measurements, the cell was filled to the top with a mixture of known composition, sealed by inserting and tightening the plug

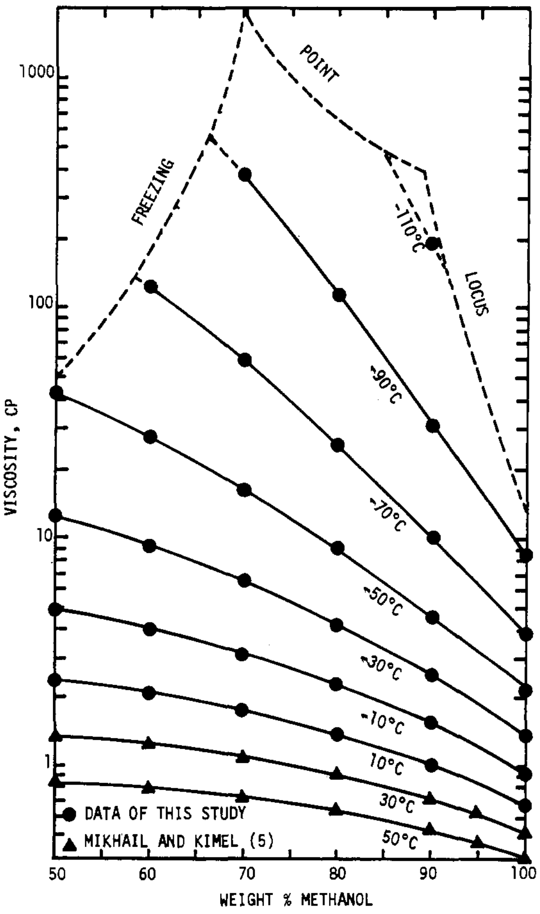

Figure 3. Viscosity of methanol–water system

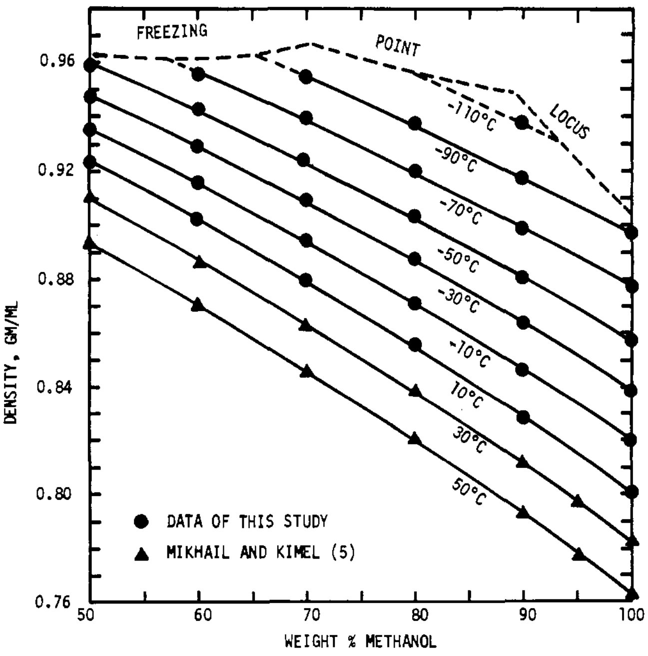

Figure 4. Density of methanol–water system

Table II. Low-Temperature Densities (G/Ml) and Viscosities (CP) Acetone–Water System

Wt % acetone	99.95		95.01		90.01		80.00		70.02		59.99	
Mol % acetone	99.84		85.52		73.65		55.37		42.01		31.74	
Temp, °C	Density	Viscosity	Density	Viscosity	Density	Viscosity	Density	Viscosity	Density	Viscosity	Density	Viscosity
10.0	0.8028	0.3562	0.8178	0.4286	0.8328	0.5343	0.8602	0.8168	0.8854	1.178	0.9089	1.575
0.0	0.8141	0.3976	0.8288	0.4876	0.8436	0.6246	0.8706	1.007	0.8954	1.535	0.9181	2.145
−10.0	0.8250	0.4457	0.8396	0.5607	0.8540	0.7391	0.8806	1.273	0.9050	2.067	0.9271	3.061
−20.0	0.8358	0.5050	0.8501	0.6527	0.8643	0.8895	0.8905	1.659	0.9143	2.907	0.9659	4.629
−30.0	0.8468	0.5783	0.8608	0.7701	0.8747	1.094	0.9003	2.237	0.9236	4.322	...	...
−40.0	0.8574	0.6708	0.8711	0.9246	0.8850	1.379	...	...	...	...	...	...
−50.0	0.8682	0.7897	0.8816	1.136	...	...	...	...	...	...	...	...
−60.0	0.8786	0.9495	...	...	...	...	...	...	...	...	...	...
−70.0	0.8893	1.171	...	...	...	...	...	...	...	...	...	...
−80.0	0.9002	1.497	...	...	...	...	...	...	...	...	...	...
−90.0	0.9104	1.993	...	...	...	...	...	...	...	...	...	...

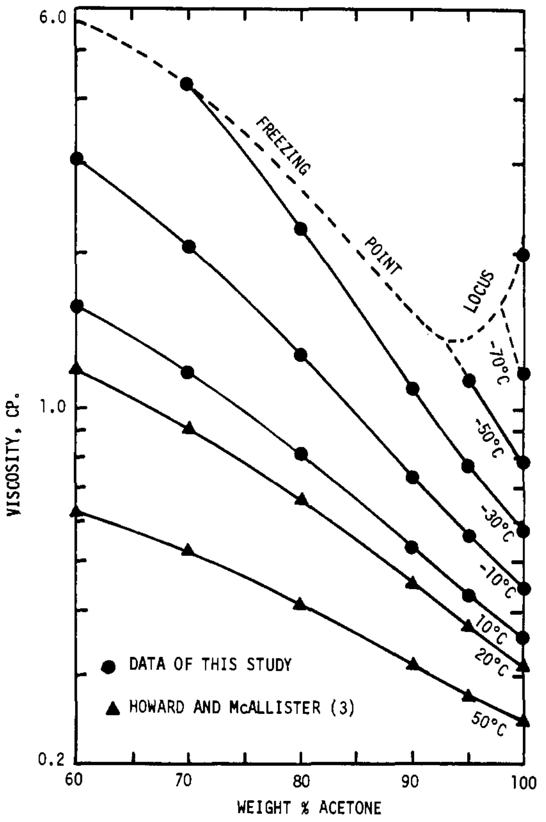

Figure 5. Viscosity of acetone–water system

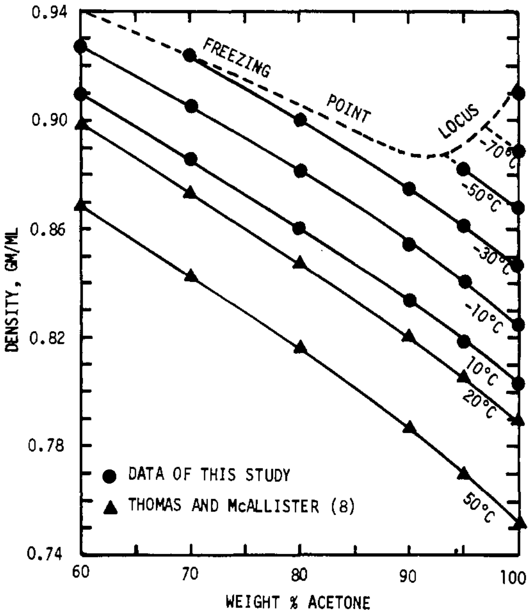

Figure 6. Density of acetone–water system

in the union at the top of the cell, and weighed. It was then placed in the temperature bath and, after thermal equilibrium was established at each of the experimental temperatures, the height of the meniscus relative to the fiducial line was measured with the cathetometer. Since 20% of the volume of the cell is contained in the neck, the meniscus remained in the neck even at the lowest temperatures, thereby giving excellent resolution on the measurement. In calculating experimental densities, corrections were made for differences in meniscus height between water and the solutions studied and also for the contraction of the glass cell with decreasing temperature.

The methanol and acetone used in this study were Fisher Certified Spectro-analyzed Reagents. Their purity was 99.95% with water as the main impurity in the methanol, and methanol as the main impurity in the acetone. The sample solutions were prepared by weighing and combining pure reagents. The compositions are accurate to ±0.01 wt %.

RESULTS

The experimental viscosities and densities of the methanol-water system are presented in Table I. Selected values from Table I are plotted on Figures 3 and 4, together with the data of Mikhail and Kimel (*5*). No overlap of experimental data from this study with that of Mikhail and Kimel was possible since our viscometers were not equipped with vapor pressure control devices. However, viscosity-temperature and density-temperature crossplots will show that our data and those of Mikhail and Kimel fall on the same curves.

The experimental viscosities and densities of the acetone-water system are presented in Table II, and selected values are plotted on Figures 5 and 6, together with the viscosity data of Howard and McAllister (*3*) and the density data of Thomas and McAllister (*8*). Again, no overlap of data was possible, but crossplots illustrate good agreement.

The results of an analysis for maximum error give:

composition, ±0.01 wt %, viscosity, ±1.9%, and density, ±0.0002 g/ml.

A complete description of the error analysis is given by Yergovich (*10*).

LITERATURE CITED

(1) Benjamin, R., Thesis Bruxelles, 1932.
(2) Ewert, M., *Bull. Soc. Chim. Belg.*, **46**, 90-103, 1937.
(3) Howard, K. S., McAllister, R. A., *AIChE J.*, 4 (3), 362-366, 1958.
(4) Kurtz, S. S., Wikingsson, S. E., Camin, D. L., Thompson, A. R., *J. Chem. Eng. Data*, **10** (4), 330-334, 1965.
(5) Mikhail, S. Z., Kimel, W. R., *ibid.*, **6** (4), 533-537, 1961.
(6) Miller, G. A., Carpenter, D. K., *ibid.*, **9** (3), 371-373, 1964.
(7) Rossini, F. D., "Selected Values of the Properties of Hydrocarbons and Related Compounds," Carnegie Press, 1958.
(8) Thomas, K. T., McAllister, R. A., *AIChE J.*, **3** (2), 161-164, 1957.
(9) Weast, R. C., "Handbook of Chemistry and Physics," D-145, D-162, F-35, 1968.
(10) Yergovich, T. W., MS Thesis, The University of Kansas, Lawrence, Kan., 1969.

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Hittorf Transference Numbers in Aqueous Copper Sulfate at 25°C

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Hittorf transference numbers have been determined at 25° C for aqueous $CuSO_4$ solutions from 0.046*m* to 1.4*m* (saturation). All solutions were first equilibrated with Cu metal. The results, except at 0.046*m*, can be well represented by the equation:

$$t_+ = 0.4010 - 0.1426m^{1/2} + 0.0186m \qquad (\sigma = 0.005)$$

The results are in satisfactory agreement (<0.01) with Fritz and Fuget's moving boundary results over a more limited concentration range.

Recent interest in the Onsager transport coefficients (*4, 8, 19-21*), l_{ij}, has created a new need for experimental electrolyte transport properties over a large concentration range. Data for the l_{ij} of aqueous 2-2 electrolytes are particularly lacking, owing at least in part to the unavailability of the transference numbers necessary to calculate them (*19, 20*).

Transference measurements have been the subject of numerous investigations for more than a century. However, data available on 2-2 electrolytes are few, and when available, are often the results of studies made before 1910 at temperatures other than 25° C.

The principal purpose of this study is to provide transference data on an appropriate 2-2 electrolyte over a large concentration range, which would then be suitable for l_{ij} calculations. In addition, these data can be compared with the older measurements, thus serving as a basis for estimating the accuracy and suitability of other 2-2 electrolyte data reported by early workers.

Our experiments were carried out at 25° C on aqueous $CuSO_4$ solutions from 0.04*m* to 1.4*m* (saturation), where *m* is the molality. This system was chosen because $CuSO_4$ is a representative 2-2 electrolyte, there are relatively recent moving boundary measurements for comparison done by Fritz and Fuget (*6*) at 25° C over the limited range 0.15-0.5*m*, and there are limited data for comparison in the older literature (1853-1901) up to about 1*m* (*3, 10, 11, 13, 16*).

Despite its known difficulty, we selected the Hittorf method over the moving boundary and concentration cell methods for the following reasons. The Hittorf method is valid at any concentration. The moving boundary method, while accurate at low concentrations, becomes increasingly inaccurate at higher concentrations both because the correction for volume changes at electrodes becomes increasingly large and the assumptions for this correction become increasingly invalid (*1, 2, 7, 15, 18*). The concentration cell method, although valid over the complete concentration range, requires accurate activity coefficient data and either good copper or good sulfate electrodes. Previous experience with $CuSO_4$ concentration cells at LRL has been discouraging. (See appendix.) If good cell results are obtained in the future, they could be used in conjunction with the Hittorf measurements to provide a test of the Onsager Reciprocal Relations.

In order to obtain a successful electrode reaction without formation of Cu_2O, we found it necessary to *equilibrate our $CuSO_4$ solutions with Cu metal*, although previous workers (*3, 10, 11, 13*) either did not do or did not report this.

EXPERIMENTAL

The Hittorf apparatus used was identical to that described previously (*23*), except that high purity copper wire (99.999% pure) was used for the anode. The cell design was that of MacInnes and Dole (*14*). Two cells with 10-mm tubing were used, one with 12 ml and the other with 25-ml compartments. A P.A.R. Model TC-100.2BR voltage reference source provided a constant current to the cell. Standard resistors were used at each end to detect possible current leaks into the thermostat. The thermostat was controlled at 25.00° ± 0.01° C. The copper sulfate was purified by preparing a saturated solution at 35° C, using reagent grade copper sulfate, cooling to 0° C, and recovering the crystals. Copper sulfate solutions should not be boiled

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