Table V. Density Data For Ammonia–Lithium Thiocyanate Solutions

47.5 Wt % salt[a]		62.6 Wt % salt[b]	
Temp, °F	Density, g/cc	Temp, °F	Density, g/cc
128.1	0.895	98.1	1.010
139.2	0.891	117.9	1.005
149.7	0.887	133.4	1.000
161.1	0.883	150.0	0.992
171.3	0.879	184.9	0.984
189.5	0.873	200.6	0.979
207.8	0.866	226.3	0.971
226.5	0.858	253.0	0.968
234.3	0.856		

[a] 98.46 Wt % lithium thiocyanate + 1.54 wt % water. [b] 99.27 Wt % lithium thiocyanate + 0.77 wt % water.

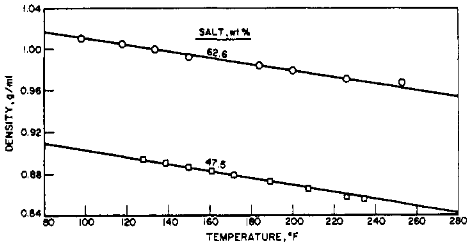

Figure 6. Density data for ammonia–lithium thiocyanate solutions

the kinematic viscosity was converted to absolute viscosity, μ. In this form the data obtained in the range of 75–200°F were extrapolated to 300°F in a log plot of μ vs. $1/T$ (Figure 5).

Density. Density measurements on two solutions were carried out in a specially built glass tube cell, entirely immersed in a temperature-controlled bath. At each temperature the volume occupied by a known quantity of solution was obtained by measuring the level of the solution in the upper capillary by means of a cathetometer. The cell had been previously calibrated by filling to different heights in the capillary with carefully weighed amounts of mercury. The volume of the cell was approximately 4 ml. The cell consisted of a 6-in. long $^1/_4$-in. i.d. lower portion, to which a $^1/_{16}$-in. i.d. and 6-in. long capillary was attached.

The solutions investigated contained 47.5 and 62.6 wt % salt. Densities were obtained in the 80–280°F temperature range, under the solution vapor pressure at each temperature (Table V and Figure 6).

Density data for the two solutions reported were linearly interpolated to obtain densities at four other concentrations: 48.0, 53.0, 56.2, and 60.8 wt % salt.

NOMENCLATURE

H_{vap} = heat of vaporization, 1000 Btu/lb-mol ammonia
p = total pressure, psia
T = absolute temperature, °R
X_s = mole fraction salt
X_{s_1} = initial mole fraction salt
X_{s_2} = final mole fraction salt
μ = absolute, viscosity, cP

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Effect of Aqueous–Ethanol and Aqueous–Dimethylsulfoxide Solvent Systems on Transference Numbers and Mobilities of H^+, K^+, and Cl^-

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The enhancement of the rate of nucleophilic reactions by aprotic solvents has been attributed to decreased solvation and, hence, increased activity of the nucleophile. The verification of this assumption and the evaluation of solvent effects on the anion are complicated by the fact that activity measurements are the average values for the cation and anion. Decreased solvation of the anion may well be accompanied by increased solvation (and decreased activity) of the cation so that the measured activity remains essentially constant. It occurred to us, after trying to evaluate solvent effects on anion activity by emf (*4*) and conductance (*3*) studies, that transference numbers and mobilities were properties which could be determined for individual ions and which would reflect changes in the ion's environment caused by solvent changes. Transference numbers and mobilities were determined for cations and anions of KCl and HCl in aqueous–ethanol and aqueous–dimethylsulfoxide (DMSO) in which the organic portion was varied from 0–60% (v/v). These two organic solvents were chosen as contrasting protic and aprotic solvent types.

EXPERIMENTAL

Apparatus. A modified moving-boundary transference number apparatus was developed which measured the move-

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Transference numbers and mobilities have been determined for the cations and anions of KCl and HCl in aqueous organic solvent systems. The solvents varied from 0–60% (v/v) ethanol of dimethylsulfoxide. The transference number of Cl⁻ generally showed a minimum at 20% organic solvent. Cation mobility decreased in a near-linear fashion with increasing concentration of organic solvent. The Cl⁻ mobility showed considerable variation between the HCl and KCl solutions—indicative of some form of association. No significant difference was observed between the effects of the protic ethanol and the aprotic DMSO.

Table I. Transference Numbers and Mobilities of Cations of HCl and KCl Solutions in Aqueous Organic Solvent Systems

Solvent system	Electrolyte	n^+	$\mu^+ \times 10^{-3}$
Water	KCl	0.490	5.72
10% Ethanol	KCl	0.502	4.54
20% Ethanol	KCl	0.514	3.60
40% Ethanol	KCl	0.490	2.26
60% Ethanol	KCl	0.417	1.39
10% DMSO	KCl	0.506	4.80
20% DMSO	KCl	0.512	3.86
40% DMSO	KCl	0.472	2.22
50% DMSO	KCl	0.412	1.47
Water	HCl	0.831	28.2
10% Ethanol	HCl	0.867	24.0
20% Ethanol	HCl	0.846	18.7
40% Ethanol	HCl	0.684	9.94
60% Ethanol	HCl	0.552	4.83
10% DMSO	HCl	0.827	23.2
20% DMSO	HCl	0.854	19.4
30% DMSO	HCl	0.850	15.2
40% DMSO	HCl	0.832	11.3
50% DMSO	HCl	0.703	6.69

ment of the boundary past sets of electrodes by the change in conductance on either side of the boundary. The apparatus, described in detail elsewhere (*6*), uses the familiar cadmium anode and silver, silver chloride cathode. The detecting unit consisted of several sets of platinum probes attached by a switching device to a conductance monitor (Industrial Instruments "Solumeter," Cedar Grove, N.J.), which in turn, was connected to a 10-in. recorder. As a boundary passed a set of electrodes, the conductance decreased sharply as evidenced by a signoid trace by the recorder. The inflection point, located with the aid of a solid glass rod, was used as the definitive time of passage. The time interval required for the boundary to pass between two sets of probes was taken from the time axis of the recorder trace. The volume between the set of electrodes was obtained by calibration using solutions of known transference numbers (e.g., 0.10*N* KCl).

A Heathkit IP-17 high-voltage power supply was used to give a potential of 400 V across the cell at 3, 4, or 5 mA.

The conductance measurements necessary for mobility determinations were made in a Jones-Bollinger-type cell (cell constant 1.3175) in conjunction with a conductivity bridge (Industrial Instruments Model No. RC-18).

Materials. Deionized water was used in the preparation of all solutions. DMSO was purified by successive freezing, partial thawing, and decantation. Reagent-grade absolute ethanol, potassium chloride, and hydrochloric acid were used without further purification. (The purity of these compounds was commensurate with the accuracy of apparatus used.) The potassium chloride was dried at 110°C prior to use. Hydrochloric acid solutions were prepared by dilution of standardized stock solutions.

Procedure. Solutions, approximately 0.10*N* in KCl and HCl, were prepared carefully in the solvent system being investigated. The solutions and apparatus were thermostated for an hour at 25°C in a constant-temperature air bath (*5*) prior to use. The cell was rinsed several times with the solution. A vacuum catheter tube was used to remove the rinse solution so that the cell was not moved from its vertical position. The cell was filled with the solution, all bubbles were removed, and the electrolysis began. The conductance between the lowest set of probes was measured until the boundary passed. Then the detecting circuit was switched to the next set of probes and the procedure was duplicated.

Each solution was run several times to obtain data of confidence. The data were reproducible within 0.05% for the KCl solutions and 1.0% for the HCl solutions. Maximum

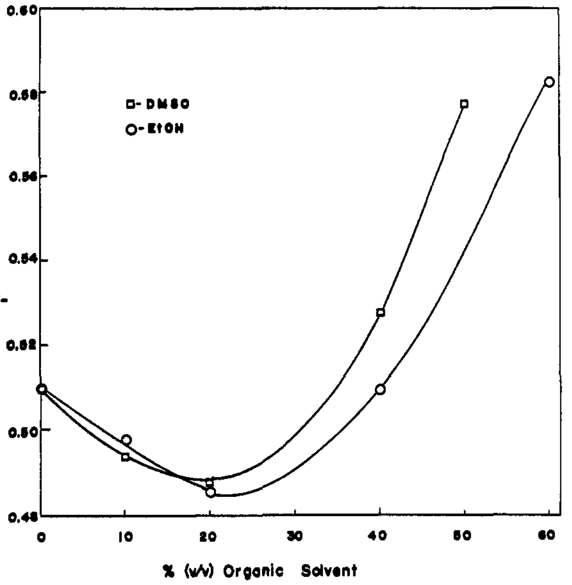

Figure 1. Variation of transference number of the Cl⁻ of KCl with change in solvent system

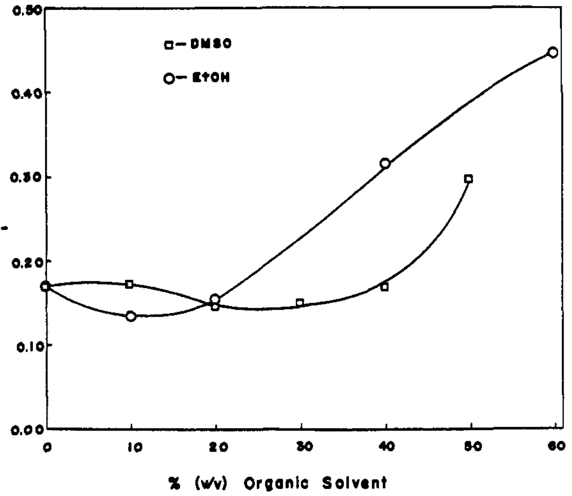

Figure 2. Variation of transference number of the Cl⁻ of HCl with changes in solvent system

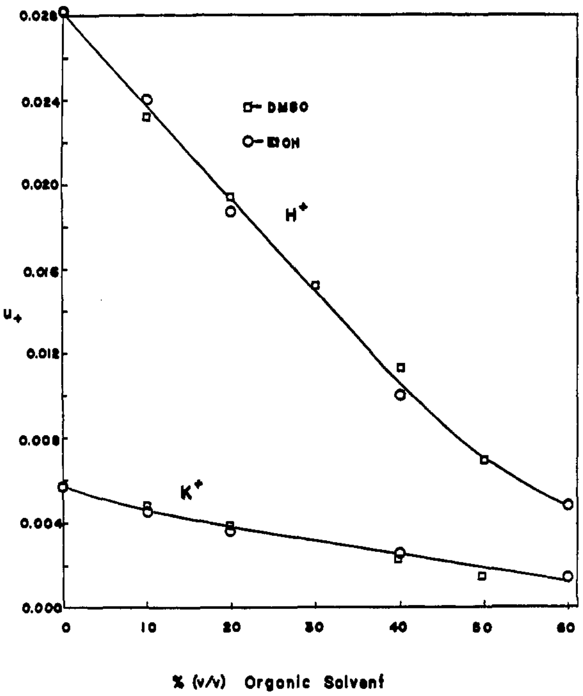

Figure 3. Variation of mobility of H^+ and K^+ of HCl and KCl with changes in solvent system

deviations, 1.6% for the KCl and 4.5% for the HCl solutions, occurred at high concentrations of organic solvents.

The transference numbers, n, and mobilities, μ, were calculated from the moving boundary and conductance data by the following equations (*1*):

$$n^+ = \frac{cFV}{It} \tag{1}$$

$$n^- = 1 - n^+ \tag{2}$$

$$\mu^+ = \frac{LV}{It} \tag{3}$$

$$\mu^- = \frac{n^-\mu^+}{n^+} \tag{4}$$

where c is concentration in equivalents/liter, F is Faraday's constant, I is the current in amperes, V is the volume (liters) displaced by the boundary in time t (seconds), and L is the specific conductance in cm^{-1} ohm^{-1}.

The data are tabulated (Table I) and displayed graphically in Figures 1–4. Figure 1 shows that the transference numbers of the Cl^- of KCl is affected in much the same manner by the addition of protic ethanol as by aprotic DMSO. (Note the expanded scale in Figure 1.) More variation is shown in Figure 2; the transference number of Cl^- of HCl is affected in an anomalous fashion by the addition of DMSO. The effect of the ethanol addition is similar to that in the KCl solutions.

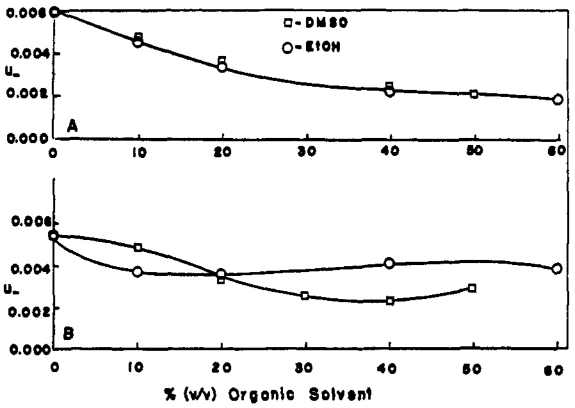

Figure 4. Variation of mobility of Cl^- of (A) KCl, (B) HCl with changes in solvent system

The mobility of the H^+ decreased in a near-linear fashion with added organic solvent. The effects of the two organic solvents were almost identical; both sets of data for the H^+ mobility fit one line acceptably (Figure 3). The mobility of the K^+ was affected similarly although the decrease was much less dramatic than for the H^+. Disruption of the Grotthus conductance is a possible explanation of the large decrease in H^+ mobility. The mobility of the Cl^- of KCl also was decreased in almost the identical manner by the two organic solvents (Figure 4A). Again the Cl^- of HCl shows anomalous behavior (Figure 4B).

The data, while preliminary in nature, are significant in several respects. First, the fact that the mobility of the chloride ion varies from HCl to KCl solutions indicates some interaction between the ions (incomplete ionization). Second, the parallel effect of the protic ethanol and aprotic DMSO on ionic mobilities is surprising in view of their different effects on reaction rates (*2*). Third, the ionic mobilities, in general, appear to be directly proportional to solvent dielectric constant and inversely proportional to viscosity. These parameters vary in a near-linear fashion over the range of solvent concentrations used in this study. These tentative conclusions naturally must be tested with a wide range of electrolyte concentrations and types and with a wide range of solvent concentrations and types.

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