Conductance of Sodium Perchlorate in Water-N-Methylacetamide (NMA) Solvent System

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The densities, partial molal volume, viscosities, and dielectric constants were determined for 0.000-0.9998 mole fraction, x, of N-methylacidamide in water at 30.00° (30.50°), 40.00°, and 50.00°C. These properties of the solvent system were discussed in relation to the making and breaking of structure in the solvent components and especially the NMA component of the mixed solvent as the proportions of the components continually changed. The equivalent conductance of sodium perchlorate at infinite frequency and infinite dilution $\Lambda_0(\infty)$ was obtained for 0.0000-0.9998 mole fraction, x, of NMA in water at 30.00° (30.50°), 40.00°, and 50.00°C. The dependence of the value of $\Lambda_0(\infty)$ on the viscosity of the solvent system is clearly evident, but $\Lambda_0(\infty)$ is also apparently very much affected by the structure making and breaking in the solvent components, and especially the NMA component, as the proportion of components continuously change, and also to the degree of and the selective solvation of the ions by the different components and by the different structural units of the NMA component as the composition of the solvent changes.

In the past half century most conductance studies have involved the investigation of electrolytes in solvents of relativity low dielectric constants. Therefore, the interest in association of electrolytes has been the primary objective of most theoretical efforts. However, within the last decade, relativity new solvents which have very high dielectric constants have become available in sufficient quantities to enable complete conductance studies of various electrolytes in aqueous solutions of these solvents. Yet, to date, there has not been a complete density viscosity and conductance study of an electrolyte in mixtures of water and a high dielectric solvent at different temperatures.

Certain amides are among solvents which have strikingly high dielectric constants; this is true in particular for N-methylacetamide (NMA) which has a dielectric constant of approximately 180 at room temperature (35). This solvent is suitable for conductance studies for many electrolytes. NMA is highly unusual with respect to many of its physical properties and especially when water mixtures are considered. Dawson et al. (11–14) have characterized NMA and also measured the conductance of many electrolytes in NMA.

Some of the unusual properties which make this solvent exceedingly attractive for a conductance study over the entire range of solutions from pure water to pure NMA are summarized. The density of water-NMA mixtures shows a maximum and a minimum with respect to composition at 30°C. The plot of viscosity vs. composition of water-NMA mixtures exhibits a large maximum at approximately 0.5 mole fraction (x) at 30°C. An oscillatory effect of chemical shifts in NMR spectrum of water-

NMA solutions has been observed (25). In regard to the solvation power of NMA, it has been suggested to be a solvent more "universal" than water (10). Strangely, its power of solvation on the alkaline earth sulfates, such as magnesium sulfate, is practically negligible (10); this is somewhat disappointing since the alkaline earth sulfates are largely used in ion association experiments.

Experimental

The conductivity measurements were made by measuring the resistances of the solutions at various standardized temperatures with a Jones and Josephs conductivity bridge (31) built by Leeds and Northrup. A Dumont 304 H oscilloscope was used to detect the balance point which was the minimum height of the Lissajous figure displayed on the oscilloscope screen (7, 8). The conductivity bridge, oscilloscope, frequency generator, and amplifier were each grounded by shielded cable to copper-coated lightning rods placed 3-ft deep in the earth outside the building. The stirring motors and electronic relays were grounded to water pipes to help eliminate background noise.

The accuracy of the conductivity bridge was checked by the use of U.S. Bureau of Standards certified resistors. The conductance measurements were made at frequencies of 0.5, 1.0, 2.0, 5.0, and 10 kHz. The frequency generator was a Heath sine-square audio generator IG-18 which was driven at 5-V rms. The Heath generator was beat against a General Radio 1000-Hz audio oscillator type 813A. The G.R. oscillator was calibrated and found accurate and highly stable within ±0.01% of the specified frequency by observing the Lissajous pattern displayed on the oscilloscope screen. The accuracy of the conductivity measurements is ±0.1%.

The solutions were made up by weight corrected to vacuum with a Seederer and Kohlbush 3-kg capacity balance with an average sensitivity of one division per 10 mg. All weights were calibrated by comparison with weights having a U.S. Bureau of Standards certificate. The conductivity cells were calibrated by preparing standard solutions of 0.1 and 0.01 "demal" (29) KCl. The cell constants were obtained by using the values for the specific conductance given by Jones and Bradshaw (29). The conductivity cells were also calibrated by the method proposed by Lind et al. (36). The results from both methods agreed within ±0.01%.

The densities were obtained with calibrated Lipkin (37) arm-type pycnometers. The accuracy of the density measurements is ±0.024%, or even a less percentage deviation. The viscosities were determined with size 100 and 150 Ostwald-Fenske viscometers which were calibrated by the Cannon Instrument Co. The changes in the viscometer constant with respect to temperature were computed by the method recommended by Cannon and Fenske (5). The appropriate corrections were made for kinetic energy effects which were usually less than ±0.1%. The accuracy of the viscosity measurements is estimated as ±0.2%.

The dielectric constants of water-NMA mixtures were obtained from Hovermale et al. (27, 28) and were only

available over the entire range of solvents at 30°C. To find the dielectric constants at 40° and 50°C, symmetric curves were computed which seem to give reasonable values for the higher temperatures. Symmetric curves were computed by interpolation of the data of Dawson et al. (12), Leader and Gormley (35), Hovermale (27), Hovermale et al. (28), and Bass et al. (2) with a computer.

The conductivity water was obtained by passing laboratory distilled water through a Barnsted standard ion-exchange column which reduced the specific conductance to 3–5 $\times$ 10^{-7} mho. This water was then piped directly to a Barnsted high-purity-type M ion-exchange column which further reduced the specific conductance to 0.8–1.0 $\times$ 10^{-7} mho.

Table I. Density of Water–N-Methylacetamide Mixtures at 30.00°, 30.50°, 40.00°, and 50.00°C

Mole fraction, x	Wt %	Temperature, °C		
		30.00, g/ml	40.00, g/ml	50.00, g/ml
0.0000	0.0000	0.99567	0.99224	0.98807
0.00107	0.4334	0.99547	0.99216	0.98805
0.01511	5.860	0.99542	0.99212	0.98754
0.06509	22.02	0.9974	0.9925	0.9873
0.08042	26.19	0.9979	0.9929	0.9874
0.1639	44.39	1.0005	0.9938	0.9867
0.3355	67.20	0.9936	0.9858	0.9774
0.3869	71.91	0.9898	0.9818	0.9736
0.5833	85.03	0.9749	0.9668	0.9583
0.6013	93.24	0.9602	0.9519	0.9434
		30.50°C	40.00°C	50.00°C
0.9879	99.70	0.9500	0.9423	0.9337
0.9914	99.86	0.9499	0.9422	0.93366
≥0.9997	≥99.86	0.9496	0.9419	0.9336
≥0.9998	≥99.995	0.9496	0.9419	0.9336
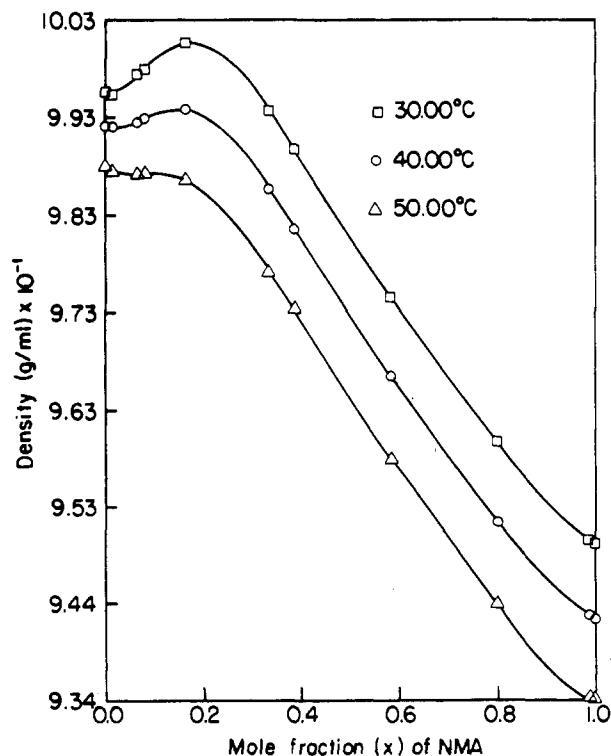
Figure 1. Density of water–NMA at 30.00°, 40.00°, and 50.00°C

Purified Aldrich NMA was distilled in a single-stage vacuum still at a pressure of 5 mm or less. The middle two thirds of the distillate was placed in a double stage still and redistilled at reduced pressure under dry nitrogen. This middle fraction was then placed in a fractional freezing flask (15) and fractionally frozen repeatedly until melting points of 30.2°C or greater were reached. The entire fractional freezing apparatus was maintained under an atmosphere of dry nitrogen inside a modified glove bag (6). Typically, the melting point of the pure NMA was 30.28°C. Higher melting points for NMA have been obtained by others (3, 34); however, these involved zone refining, and this method was impractical for this research problem owing to the large amounts of solvent needed and the prohibitive cost of the zone refining apparatus.

The amount of water in the NMA was determined by Karl Fischer titration with an Auto Aquatrator made by the Precision Scientific Co. A Perkin-Elmer 900 gas chromatograph with a 10-ft by ⅛-in. stainless-steel column packed with 80–100 mesh Porapak Q-S at a column temperature of 240°C revealed no detectable water on the most sensitive setting, although there was some tailing of the peak for NMA. The pure NMA used in the work was 99.997 ± 0.0004 wt % (0.9998 mole fraction) or even a higher percentage NMA. The specific conductance of the solvent was typically 5.0 $\times$ 10^{-8} mho at 30.50°C to 2.4 $\times$ 10^{-7} mho at 50°C (15, 10).

The sodium perchlorate was obtained from the G.F. Smith Co. and precipitated from 1-butanol and washed with reagent-grade anhydrous ethyl ether (32). It was then heated in vacuum at 120°C for 2–4 hr, placed in a furnace for 2 hr at 250–270°C, replaced in the heated vacuum desiccator and maintained at 120°C in vacuo for 12–24 hr prior to use. The desiccator was disconnected from the vacuum and allowed to cool under an atmosphere of dry nitrogen inside a dry box.

The temperatures read from thermometers calibrated against a thermometer calibrated by the U.S. Bureau of Standards are accurate to ±0.01°C.

Results and Discussion

Density. The densities of the water–NMA system are listed in Table I and are shown by Figure 1. This plot is quite unusual owing to the maxima and minima exhibited by the curves 30°, 40°, and 50°C. There is a slight minimum occurring at 0.01511 x NMA. This minimum was also noted previously (28) for the 30°C temperature. The solid line in Figure 1 is the line calculated by the polynomial fit of the data. The data agree well with other investigators (28, 1) at 30°C, with the exception of pure NMA which had to be measured at 30.50°C.

The polynomial fit was obtained by a linear least-squares program which involved equations of degree n in the variable x defined below:

$$Y = \Sigma C_n x^n \qquad (1)$$

with Y = density in g/ml, C_n = constant, x = mole fraction NMA, and n ≤ 9. The constants for C_n are listed in Table II with the standard deviation of the experimental points from the calculated regression line. The constants are listed as C_i/C_j which means the ith constant is directly over the jth constant. This does not mean a ratio of C_i/C_j.

The curves show slight minima which indicate that at 30°, 40°, and 50°C a small amount of NMA added to water produced a slight structure-breaking effect which disappears after 0.01511 x NMA was added. The 0.01511 x NMA solvent was also the most conducting of the various solvents having a specific conductance of 1.0

Table II. Constants for Calculated Densities, Viscosities, and Limiting Conductances of Water-N-Methylacetamide Mixtures at 30.00°, 40.00°, and 50.00°C

Temp,°C	C1/C5	C2/C6	C3/C7	C4/C8	SD
Density, g/ml					
30.00	0.99552	-0.76142×10^{-2}	0.85074	-5.6970	0.0001
	14.38168	-18.0892	11.33183	-2.81639	
40.00	0.99225	-0.26171×10^{-1}	0.75667	-4.9445	0.0001
	12.45366	-15.70469	9.88801	-2.47256	
50.00	0.98804	-0.33425×10^{-1}	0.53614	-3.45968	0.0001
	9.25923	-0.60689	5.41878	-1.16862	
Viscosity, cP					
30.00	0.80730	7.36586	65.76143	-302.53247	0.002
	562.80225	-578.70215	330.5613	-82.25348	
40.00	0.65822	6.18172	32.64204	-155.9278	0.002
	287.8198	-300.4404	179.2295	-47.1608	
50.00	0.5500	4.89976	18.7817	-89.7490	0.002
	144.6368	-113.1789	41.2159	-4.75893	
Limiting equivalent conductances					
30.00	129.148	-1164.960	5830.363	-15692.109	0.05
	22440.363	-15964.387	4441.594		
40.00	154.746	-1300.212	6351.449	-16945.672	0.05
	24163.910	-17181.086	4781.820		
50.00	182.00	-1427.345	6795.129	-17934.834	0.05
	25453.836	-18060.684	5022.695		

$x\ 10^{-6}$ mho at 50°C. The curves then began to turn upward and reached maxima at approximately 0.1639 x NMA; this implies there is a structure-making effect taking place. This effect may be due to the water molecules hydrogen bonding with the NMA molecules or chains of molecules, drawing the solvent molecules more tightly together, and thus enhancing the density of the solution. After the maximum is passed, the density falls fairly rapidly, perhaps because of the reduced rate of structuring of NMA chains (25) at lower water content, to the density of pure NMA.

Note the small deviation of the plot at 0.9998 x NMA arising from the temperature increase from 30.00° to 30.50°C, necessary to melt the practically pure NMA. Also the maximum in density has nearly disappeared at 50°C. This is probably because the structure-breaking effect arising from the increase of energy of the molecules owing to the increased temperature practically nullified the structure-making effect because of the binding by water of the NMA molecule chains.

Partial molar volumes and relative partial molar volumes. The volume changes on mixing the water–NMA solvents were determined as milliliters per mole and labeled by ΔV_{mix}.

$$\Delta V_{\mathrm{mix}} = (x_1 M_1 + x_2 M_2)/d_{12} - (x_1 V_1^\circ + x_2 V_2^\circ) \quad (2)$$

The first term represents the mean molar volume of the solution; the second term is the ideal volume additivity; M_1, M_2, x_1, x_2, V_1°, V_2° are the molecular weight, mole fraction, and molar volume of components 1 and 2, respectively; and d_{12} is the density of the mixture.

The partial molar volumes were calculated by the following method (42). The density data were used to calculate the mean molar volume, v_m, and a least-squares fit was obtained of the mean molar volume.

$$v_m = (x_1 M_1 + x_2 M_2)/d_{12} \quad (3a)$$

or

$$v_m = (M_2 + x_1(M_1 - M_2))/d_{12} \quad (3b)$$

The partial molar volumes, $\bar{V}$, were then calculated by

$$\bar{V}_1 = v_m + x_2 \partial v_m/\partial x_1 \quad (4a)$$

and

$$\bar{V}_2 = v_m - x_1 \partial v_m/\partial x_1 \quad (4b)$$

The relative partial molar volumes, $\bar{V}_r$, were obtained by the formulas:

$$\bar{V}_{1r} = \bar{V}_1 - V_1^\circ \quad (5a)$$

and

$$\bar{V}_{2r} = \bar{V}_2 - V_2^\circ \quad (5b)$$

where V_1° and V_2° were the molar volumes of the pure components 1 and 2.

A plot of the values is shown in Figure 2 for water–NMA at 40°C. Table III gives the values of ΔV_{mix}, $\bar{V}_1$, $\bar{V}_2$, $\bar{V}_{1r}$, and $\bar{V}_{2r}$ for the various temperatures at several mole fractions of water. The plots show minima for the relative partial molar volumes at low mole fraction for both solvents, such as those found by Frank and Ives (19) for water–ethanol mixtures.

Viscosity. Figure 3 shows the relative viscosity of the water–NMA system at 30°, 40°, and 50°C. The data are in good agreement with the viscosity given by Dawson et al. (12) for NMA at 40° and 50°C. The values are listed in Table IV. The viscosity values listed are not in very good agreement with the absolute viscosity values given by Assarsson and Eirich (1) for water–NMA mixtures at 30°C. This may be due to the difference in the type of viscometers used, i.e., Ubbelhode vs. Cannon-Fenske.

The viscosity data were fitted with Equation 1, and the constants and standard deviations are given in Table II. From the plot of viscosity vs. x NMA, one might believe that there is a net structure-making effect of intermolecular hydrogen bonding between water and NMA which causes the viscosity to increase rapidly with increasing mole fraction of NMA. A maximum in the viscosity x NMA curve appears at about 0.5 x NMA for each temperature. The maximum decreases rapidly with increasing temperature, perhaps because increased thermal energy of the molecules lessens solvent structuring. After
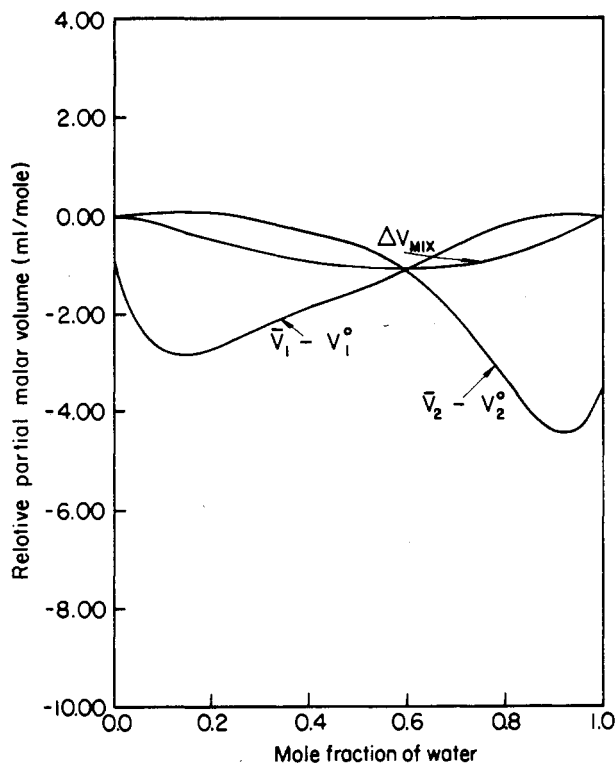
Figure 2. Relative partial molar volume of water–NMA mixtures at 40.00°C
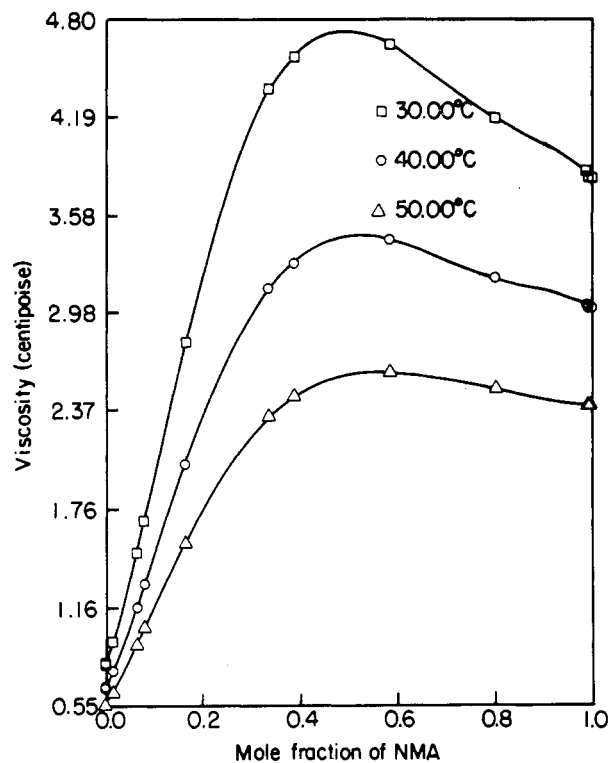

Figure 3. Viscosities of water–NMA mixtures at 30.00°, 40.00°, and 50.00°C

the maximum is passed, the rate of change of viscosity of the solvents with respect to increasing mole fraction NMA tends to slow down, owing perhaps to the decreasing rate of structuring of the solvent by hydrogen bonding between water and NMA as the proportion of NMA increases.

Dielectric constant. Table V gives the values of the dielectric constants used in evaluating the equivalent conductance data with the equation of Fuoss and Kraus (*23*) and the Onsager-Shedlowsky (*40*) approach.

Stability of solvent. Preceding any equivalent conductance measurements, a check of the stability of the solvent with respect to the specific conductance was made. The specific conductance changed only 0.21% in 33½ hr at 50°C. For a like period of time the error this would cause in Λ for a solution whose resistance is 20,000 ohms and in a cell whose cell constant in unity would be less than 0.001%. The solvent drift at the lower temperatures would be even less. There also was not any significant change in the equivalent conductance of solution of sodium perchlorate in NMA at all temperatures for time intervals as long as 280 hr. Thus, any observed (*4*) slight instability of NMA did not affect our data.

Resistance at infinite frequency. The two-parameter equation given by Jones and Christian (*30*) in their classical study of polarization in conductivity measurements was used to find the resistance at infinite frequency. This equation is

$$R = R_\infty + \delta f^{-1/2} \qquad (6)$$

where R is resistance in ohms, R_∞ is the high-frequency limit of resistance, f is the frequency in Hz, and δ is a constant. There have been several other methods listed for obtaining the high-frequency limit of resistance. These have been summarized by Hoover (*26*). However, for the relatively slight frequency dependence found in this investigation, Equation 6 seems to give the best results. Equivalent conductance at infinite frequency $\Lambda(\infty)$ was

calculated from the determined $R(\infty)$ for each solution at each temperature; the equivalent conductance at infinite frequency and at infinite dilution of NaClO$_4$, $\Lambda_0(\infty)$, in each solvent at each temperature was found by the extrapolation to infinite dilution of plots of $\Lambda(\infty)$ values for each particular solvent and each particular temperature vs. the correct function of NaClO$_4$ concentration.

Limiting equivalent conductance. The limiting equivalent conductances of the various dilute solutions of sodium perchlorate in water–NMA solvents were obtained by several different methods. The first was a Kohlraush plot of the linear portion of the equivalent conductance curve, i.e.,

$$\Lambda = \Lambda_0 - \gamma c^{1/2} \qquad (7)$$

The values for Λ_0 and the constants γ were obtained by linear least-squares analysis, and the constant γ is compared to the theory of Onsager for the limiting slope.

$$\gamma = (\alpha \Lambda_0 + \beta) \qquad (8)$$

The second method is that of Fuoss and Kraus (*23*). The equations used in this method and the calculation procedure were previously described in detail (*7*). They are

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{c\Lambda f^2}{K\Lambda_0^2 F(z)} \qquad (9)$$

$$z = \gamma \sqrt{c\Lambda}/\Lambda_0^{3/2} \qquad (10)$$

$$F(z) = 1 - z(1 - z(1 - z(1 - \dots)^{-1/2})^{-1/2})^{-1/2})^{-1/2} \qquad (11)$$

$\alpha = \Lambda/(\Lambda_0 F(z))$; α is the degree of dissociation. The activity coefficient f was calculated by the Debye-Huckel limiting law. The function $F(z)/\Lambda$ was plotted vs. the function $c\Lambda f^2/F(z)$ by using $Y = F(z)/\Lambda$ and $X = c\Lambda f^2/F(z)$. The value of the limiting equivalent conductance is

Table III. ΔV_{mix}, $\bar{V}_1$, $\bar{V}_2$, $\bar{V}_{1r}$, $\bar{V}_{2r}$, V_1°, and V_2° of Water-N-Methyl—acetamide System at 30.00°, 40.00°, and 50.00°C

Mole fraction water	ΔV_{mix}	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_{1r}$	$\bar{V}_{2r}$
		30.00°C			
NMA	0.000	16.875	76.972	−1.219	−0.005
(30.50°C)					
0.100	−0.210	15.081	77.037	−3.013	0.060
0.200	−0.550	15.319	76.980	−2.776	0.003
0.300	−0.787	15.809	76.812	−2.285	−0.165
0.400	−0.980	16.222	76.592	−1.872	−0.385
0.500	−1.098	16.547	76.325	−1.548	−0.652
0.600	−1.147	16.944	75.830	−1.150	−1.147
0.700	−1.093	17.450	74.877	−0.644	−2.100
0.800	−0.858	17.916	73.474	−0.178	−3.503
0.900	−0.424	18.127	72.350	0.033	−4.626
Water	0.000	18.097	73.603	0.003	−3.374

$V_1^\circ = 18.094$; $V_2^\circ = 76.977$

		40.00°C			
NMA	0.000	17.227	77.600	−0.930	−0.006
0.100	−0.210	15.392	77.670	−2.764	0.064
0.200	−0.506	15.426	77.654	−2.731	0.048
0.300	−0.749	15.883	77.500	−2.274	−0.106
0.400	−0.943	16.293	77.280	−1.864	−0.326
0.500	−1.056	16.649	76.986	−1.507	−0.620
0.600	−1.105	17.062	76.474	−1.095	−1.132
0.700	−1.048	17.548	75.559	−0.608	−2.047
0.800	−0.819	17.979	74.263	−0.177	−3.343
0.900	−0.422	18.177	73.208	0.020	−4.398
Water	0.000	18.157	74.160	0.000	−3.446

$V_1^\circ = 18.157$; $V_2^\circ = 77.606$

		50.00°C			
NMA	0.000	18.143	78.300	−0.090	0.007
0.100	−0.177	15.449	78.406	−2.784	0.112
0.200	−0.484	15.389	78.401	−2.844	0.108
0.300	−0.719	15.959	78.209	−2.274	−0.085
0.400	−0.915	16.450	77.946	−1.784	−0.347
0.500	−1.042	16.808	77.653	−1.425	−0.640
0.600	−1.078	17.220	77.131	−1.014	−1.163
0.700	−1.008	17.626	76.350	−0.608	−1.943
0.800	−0.781	18.047	75.082	−0.187	−3.211
0.900	−0.414	18.251	73.988	0.017	−4.306
Water	0.000	18.233	74.930	−0.000	−3.364

$V_1^\circ = 18.234$; $V_2^\circ = 78.294$

Table IV. Viscosity of Water-N-Methylacetamide Mixtures at 30.00°, 30.50°, 40.00°, and 50.00°C

Mole fraction x NMA	Wt %	30.00, cP	40.00, cP	50.00, cP
0.0000	0.0000	0.801	0.656	0.549
0.00107	0.4344	0.814	0.665	0.556
0.01511	5.860	0.944	0.762	0.629
0.06509	22.02	1.488	1.155	0.921
0.08042	26.19	1.688	1.302	0.030
1.1639	44.39	2.793	2.035	1.553
0.3355	67.20	4.365	3.126	2.328
0.3869	71.91	4.569	3.285	2.450
0.5833	85.03	4.644	3.433	2.602
0.8013	94.24	4.187	3.194	2.501
		30.50°C	40.00°C	50.00°C
0.9879	99.70	3.863	3.034	2.399
0.9914	99.86	3.820	3.006	2.400
≥0.9997	≥99.993	3.814	3.005	2.397
≥0.9998	≥99.995	3.814	3.005	2.397

then given by $\Lambda_0 = 1/(\text{intercept})$ and $K_d = 1/((\text{slope})\Lambda_0^2)$. K_d is the dissociation constant.

The values of Λ_0 obtained by the Fuoss-Kraus method generally agree with the values obtained by several other methods even though there may not be much ion association, but values of K_d are not always the same (21). However, the values of K_d do not tend to be correct for electrolytes that are nearly or completely dissociated; therefore, the K_d for any highly dissociated electrolyte should be viewed only as a general guide to the amount of dissociation. In this case, some of the dissociation constants were negative which is not uncommon for highly dissociated electrolytes evaluated by this method and indicate the difficulty of determining K_d with any precision at high dielectric constants (21). Typically, an absolute value of 0.2 or greater for K_d implies virtually complete dissociation.

The data were also evaluated by the rearrangement of the Onsager equation suggested by Shedlovsky (40). This method worked quite well (14) for solutions of high degrees of dissociation and especially those solutions of high dielectric constant. This method consists of using

$$\Lambda_0' = (\Lambda_0 + \alpha c^{1/2})/(1.0 - \alpha c^{1/2}) = \Lambda_0 + BC \quad (12)$$

The values of Λ_0' are plotted vs. c. Thus, a plot of Λ_0' vs. c should yield a straight line of intercept Λ_0 and slope B. The values for Λ_0 obtained by this method are those shown in the figures.

The equivalent conductance data were also evaluated by several methods which, in some cases, gave positive values for the dissociation constant (9, 16, 17, 22, 33, 38). However, some of these methods also gave negative dissociation constants which may be in part due to the highly precise data required to use the more extensive theories. The values of Λ_0 obtained by the Shedlovsky plot and those by Fernandez-Prini and Prue (17), Pitts et al. (38), Fuoss-Hsia (22), extended Fuoss-Hsia (16), and the Justice version (33) of the Fuoss-Hsia plot were all within the experimental error listed for a given set of data.

Limiting equivalent conductance and mole fraction, x, of NMA. Table VI gives sample data for sodium perchlorate in the 0.01511 x NMA solvent. The data are graphically represented in Figure 4. Table VII gives the values obtained by various methods of the limiting equivalent conductances at infinite frequency and infinite dilution of $NaClO_4$. Also listed are the theoretical Onsager slopes and the observed slopes, the Walden product, $\Lambda_0(\infty)\eta_0$, and the constant B from the Shedlovsky equation. Figure 5 shows a plot of the limiting equivalent conductance at infinite frequency and at infinite dilution of $NaClO_4$ obtained by the Shedlovsky method vs. x NMA. The continuous line is the calculated curve of the limiting equivalent conductance obtained by a least-squares fit of the data. The constants for the equation are listed in Table II.

The values of $\Lambda_0(\infty)$ at infinite frequency were not available at the temperatures specified in water; however, the value of $\Lambda_0(\infty)$ at 25°C calculated by plotting ln $\Lambda_0(\infty)$ vs. $1/T$ using the data in Table VII and extrapolating to $1/298.15$ gave 117.49 compared to 117.48 (32) and 117.32 (9). This agreement shows that the $\Lambda_0(\infty)$ values calculated for water and given in Table VII are accurate. The small amount of NMA was, in the solutions where $x = 0.001074$, added to see what effect a trace amount of a second solvent would have on $\Lambda_0(\infty)$. The change in $\Lambda_0(\infty)$ is quite striking when one considers that only 0.001074 x NMA (0.4344 wt %) causes a decrease using the Shedlovsky calculation in $\Lambda_0(\infty)$ of 1.10, 1.12, and 1.06 conductance units at 30°, 40°, and 50°C, respectively.

The equivalent conductance of sodium perchlorate at infinite frequency in 0.01511 x NMA was studied since this particular mole fraction of NMA corresponds to the slight minimum exhibited in the density of NMA–H₂O solvent vs. composition plot shown by Figure 1. The decrease in $\Lambda_0(\infty)$ from that of NaCO₄ in water using the Shedlovsky calculation is 16.66, 18.58, and 20.32 at 30°, 40°, and 50°C (Table VII). The decrease in $\Lambda_0(\infty)$ for the 0.08042 x NMA solvent is approximately one half of the water value at corresponding temperatures. The equivalent conductance continues to decrease for the 0.1639 x NMA and the 0.3869 x NMA solvents compared to solvents containing less NMA or to pure water, but the rate

of change of $\Lambda_0(\infty)$ with respect to solvent composition has slowed considerably. The 0.3869 x NMA solvent is approaching the solvent composition having the maximum viscosity as shown by Figure 3. Equivalent conductance. $\Lambda_0(\infty)$, of NaClO₄ in 0.8013 x NMA decreases only slightly compared to that of the salt in the 0.3869 x NMA solvent. This decrease amounts to 8.02 conductance units at 50°C. This solvent is well past the maximum in viscosity.

The $\Lambda_0(\infty)$ for NaClO₄ in 0.9879 x NMA solvent was measured at 30.50°, 40°, and 50°C. The temperature of 30.50°C was used so that the data could be compared to data at 0.9998 x NMA solvent. The 0.9879 x NMA cor-

Table V. Dielectric Constant for Water–N-Methylacetamide Solvents at 30.00°, 40.00°, and 50.00°C

Solvent	Temperature, °C		
	30.00	40.00	50.00
Water	75.75	73.28	69.94
0.001074	76.80	73.32	69.99
0.01511	77.75	74.13	70.63
0.08042	81.5	77.2	73.1
0.1639	85.8	80.7	75.7
0.3869	85.7	88.4	81.4
0.8013	143.5	132.1	120.4
	30.50°C	40.00°C	50.00°C
0.9879	175.6	163.0	149.4
0.9998	178.2	165.5	151.8

Table VI. Equivalent Conductance of Sodium Perchlorate at Infinite Frequency in 0.01511 Mole Fraction N-Methylacetamide at 30.00°, 40.00°, and 50.00°C

	30.00°C		40.00°C		50.00°C	
Solution	C × 10⁴ eq/L	Λ_∞	C × 10⁴ eq/L	Λ_∞	C × 10⁴ eq/L	Λ_∞
a	134.691	104.83	134.211	126.62	133.639	150.16
b	102.147	105.69	101.775	127.70	101.321	151.30
c	88.565	106.09	88.250	128.10	87.874	151.74
d	52.985	107.30	52.792	129.66	52.557	153.73
e	48.208	108.58	48.036	130.00	47.831	153.97
f	13.561	109.87	27.526	131.45	27.409	155.71
g	27.625	108.71	20.986	131.91	20.892	156.43
h	21.062	109.07	13.513	132.84	13.455	157.50
i	6.309	110.48	6.286	133.55	6.258	158.56
j	2.571	111.03	2.562	134.22	2.550	159.49

Table VII. Limiting Equivalent Conductances at Infinite Frequency, Limiting Slopes, Theoretical Onsager Slope for Kolhraush, Fuoss-Kraus and Shedlovsky Extrapolations, and Walden Product

NaClO₄	Kolhraush		Fuoss-Kraus			Shedlovsky		Onsager slope	$\Lambda_0\eta_0$	$\sigma\Lambda_0$	$\sigma\Lambda$
	$\Lambda_0(\infty)$	Slope	$\Lambda_0(\infty)$	$|K|$	Slope	$\Lambda_0(\infty)$	B				
					30.00°C						
Water	128.80	76.41	129.12	−0.382	96.66	129.18	209.41	67.02	1.034	0.07	0.14
0.001074	127.94	85.92	128.00	−0.541	95.26	128.08	121.83	65.90	1.042	0.03	0.07
0.01511	112.15	65.99	112.40	−0.417	81.78	112.52	143.38	56.48	1.061	0.06	0.12
0.08042	65.85	37.11	65.96	−0.494	44.69	66.04	67.51	30.85	1.113	0.02	0.04
0.1639	39.79	17.38	40.00	−0.382	25.94	40.08	54.42	18.17	1.117	0.04	0.07
0.3869	21.72	12.93	21.67	−0.514	14.09	21.70	23.87	10.52	0.990	0.02	0.04
0.8013	18.95	10.19	18.97	−2.363	11.08	18.99	4.38	9.37	0.794	0.01	0.02
0.9879	20.04	11.67	19.98	2.657	10.50	19.97	−4.59	9.18	0.772	0.03	0.05
0.9998	20.05	11.95	20.01	3.168	10.52	20.00	−3.52	9.22	0.763	0.01	0.02
					40.00°C						
Water	154.25	93.86	154.65	0.372	118.61	154.73	255.43	82.37	1.014	0.09	0.18
0.001074	153.56	109.64	153.51	−0.526	117.18	153.51	148.61	81.23	1.021	0.04	0.09
0.01511	135.68	81.70	136.00	−0.396	101.83	136.15	180.13	70.50	1.036	0.08	0.16
0.08042	83.38	49.52	83.46	−0.446	58.50	83.56	93.37	40.42	1.086	0.03	0.06
0.1639	52.74	25.28	52.98	−0.374	36.03	53.08	71.82	25.30	1.078	0.04	0.08
0.3869	29.59	18.06	29.54	−0.449	20.20	29.58	35.97	14.98	0.970	0.02	0.05
0.8013	24.45	13.47	24.49	−1.816	14.97	24.52	7.13	12.60	0.782	0.02	0.02
0.9879	25.00	14.70	24.95	3.908	13.70	24.94	−3.82	11.94	0.757	0.04	0.06
0.9998	24.98	14.35	24.95	5.279	13.69	24.94	−2.58	11.96	0.750	0.02	0.03
					50.00°C						
Water	181.31	111.69	181.80	0.344	142.69	181.90	321.51	99.10	0.999	0.10	0.20
0.001074	180.83	133.64	180.72	0.510	141.17	180.84	178.55	97.89	1.005	0.06	0.15
0.01511	161.17	103.26	161.40	0.375	124.26	161.58	224.34	86.14	1.015	0.06	0.11
0.08042	102.86	65.22	102.87	0.424	74.82	103.01	118.74	51.72	1.060	0.05	0.09
0.1639	67.46	33.99	67.76	0.342	48.14	67.90	97.90	33.70	1.052	0.05	0.09
0.3869	38.88	25.01	38.80	0.395	28.10	38.87	51.60	20.64	0.951	0.03	0.06
0.8013	30.76	17.67	30.80	1.367	19.86	30.85	11.448	16.59	0.770	0.02	0.04
0.9879	30.83	18.31	30.80	12.296	17.90	30.80	1.448	15.53	0.739	0.05	0.07
0.9998	30.81	18.06	30.80	11.638	17.73	30.80	−1.408	15.42	0.738	0.02	0.04
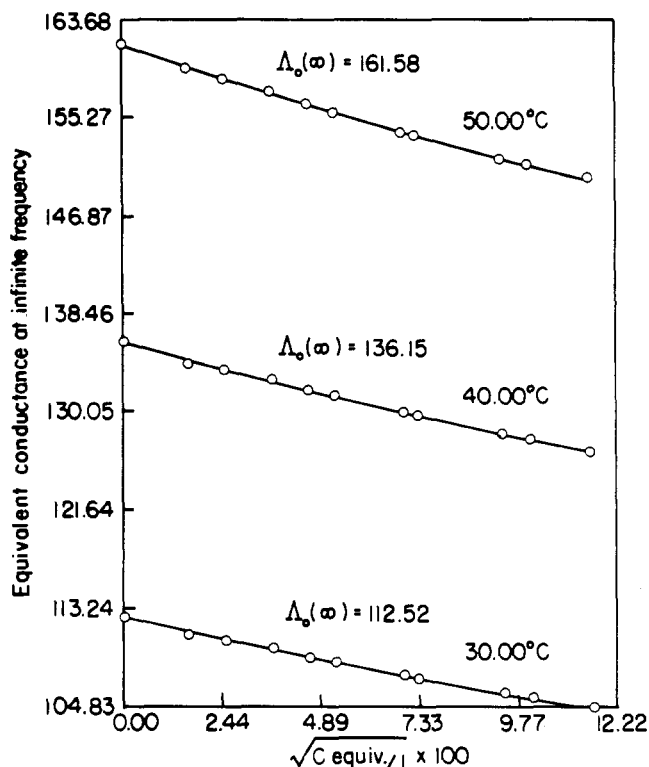
Figure 4. Sodium perchlorate in 0.01511 x NMA at 30.00°, 40.00°, and 50.00°C

Figure 5. $\Lambda_0(\infty)$ for water–NMA mixtures at 30.00°, 40.00°, and 50.00°C

responds to 99.70 x % NMA. It was hoped to observe a sharp drop or increase in $\Lambda_0(\infty)$ comparable to the precipitous decrease in $\Lambda_0(\infty)$ for HCl observed by Shedlovsky (39) in water–methanol solvents and by Goldenberg and Amis (24) in $\Lambda_0(\infty)$ for $HClO_4$ in water–ethanol solvents when trace amounts of water were added to the pure alcohol solutions. No such drastic change in $\Lambda_0(\infty)$ was observed in the present case. However, there was a slight decrease in $\Lambda_0(\infty)$ when corrected to 30.00°C compared to that in 0.9998 x NMA. The value of $\Lambda_0(\infty)$ in the 0.9998 x NMA solvent of 24.94 at 40.00°C compares well with the value of 24.96 given by Dawson et al. (12).

Limiting equivalent conductance and viscosity of solvent. Figure 6 shows a plot of $\Lambda_0(\infty)$ vs. the viscosity of the solvent. This "finger" curve has been found by others in water–ethanol and water–methanol (7, 24, 41, 18). These particular curves show a very sharp break compared to most other salts observed in water–ethanol solvents. This type of plot is usually expected from the nature of the solvent composition-viscosity curve.

The difficult part of the interpretation is the explanation of the broadness or narrowness of the angles between the branches of the plots. In the lower ranges of NMA composition of the NMA–water system, this effect seems to be principally a viscosity effect with the $\Lambda_0(\infty)$ decreasing at all temperatures as the viscosity increases up to the maxima of viscosity. However, in this range of NMA composition, the structure of NMA is markedly increasing as shown by the upfield chemical shift of the amide proton with increasing mole fraction of NMA (25). The rapid fall of $\Lambda_0(\infty)$ in this region up to about 0.6 mole fraction NMA could also partially arise from the selective solvation of the Na^+ or ClO_4^- or both by the increasingly larger agglomerates of the solvent. Beyond the viscosity maximum, the decrease in viscosity offsets any further ion size increase produced by either further solvation of the ions or increase in size of the solvating agglo-

merates or both; the equivalent conductance changes a small amount with addition of further amounts of NMA.
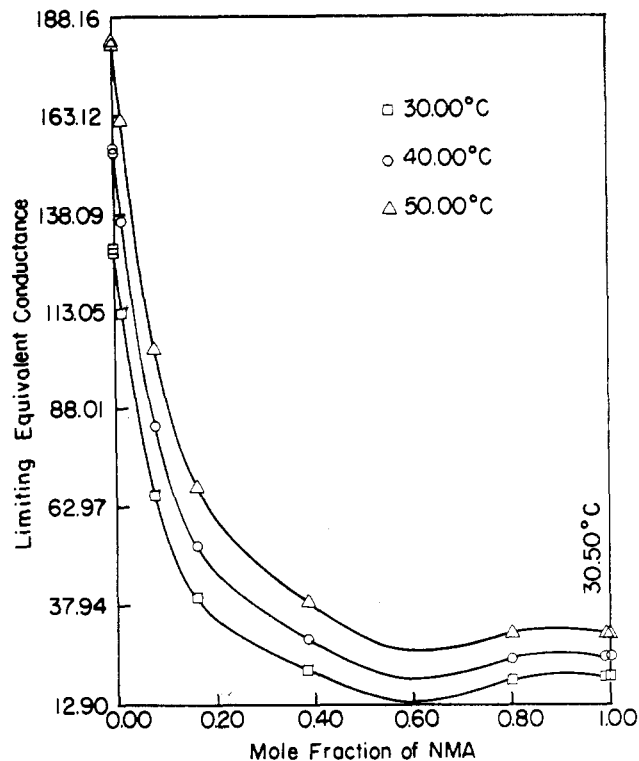
If only a viscosity effect prevailed, the equivalent conductance should increase rather sharply when the viscosity begins to decrease; however, the equivalent conductance does not show a marked steady increase after the maximum viscosity is passed. In fact, it shows a slight decrease at first after the maxima at all temperatures are passed and then becomes almost constant.

Equivalent conductance and dielectric constant of solvent. Figure 7 shows a plot of the limiting equivalent conductance for sodium perchlorate vs. the reciprocal of dielectric constant of water–NMA at the various temperatures. The curves have very slow curvature at the high dielectric solvents and then turn sharply upward at the lower dielectric constant solvents. The extreme change of curvature is unusual. Usually, the curves will continue to rise or fall throughout the range of dielectric constants of different solvents instead of having an initial flat portion and then a sharp upward break. The break in the curve corresponds approximately to the maximum in the viscosity of the various water–NMA solvents. This seems to imply that the viscosity of the solvent plays a most important role in determining the limiting equivalent conductance since the dielectric constant generally varies quite smoothly over the range of solvents studied.

Also, in the temperature range of these experiments, the structure of NMA increases rather rapidly with the first increments of NMA in water (25) where $\Lambda_0(\infty)$ is falling rapidly. If the ions attached themselves to these agglomerates of NMA or of $NMA-H_2O$, of continuously increasing size, the resulting solvated ions would be slower moving and fall more rapidly in conductance with increasing size, especially since the viscosity of the solvent is increasing in this region of increasing mole fraction of NMA. The rate of structuring falls with increasing amounts of NMA, and also the viscosity, after reaching a
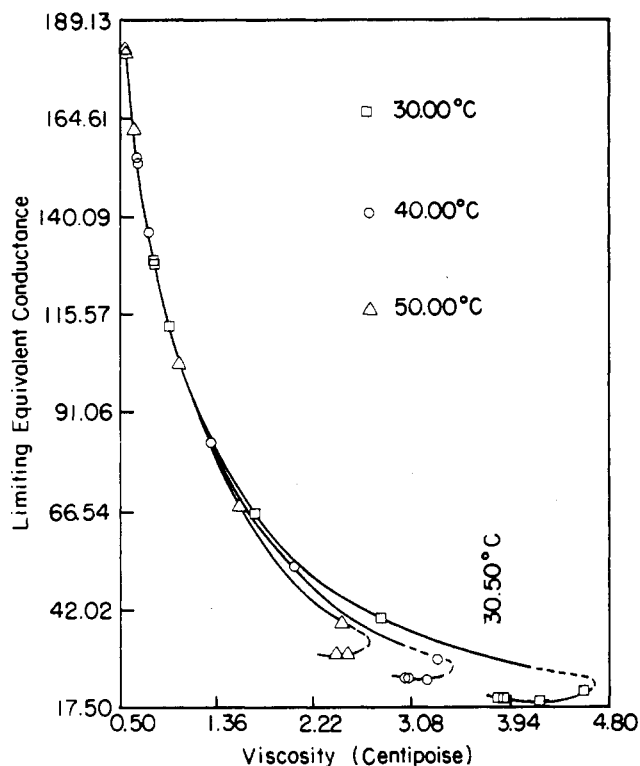
Figure 6. $\Lambda_0(\infty)$ vs. viscosity of solvent for sodium perchlorate in water–NMA mixtures
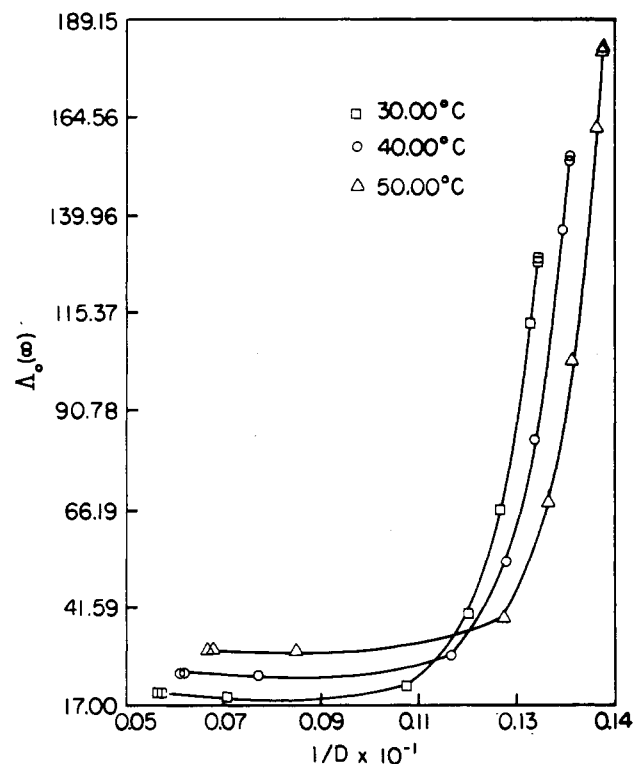

Figure 7. $\Lambda_0(\infty)$ vs. $1/D$ for sodium perchlorate in water–NMA mixtures

maximum, begins to fall. The decrease in viscosity tends to increase $\Lambda_0(\infty)$. The solvation of ions by increasingly larger solvent agglomerates and the decrease in viscosity of the solvent probably balance each other; hence, $\Lambda_0(\infty)$ reaches a fairly steady minimum conductance.

Acknowledgment

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