Greek letters

Δ_{123} = function defined by Equation 4

α_{ij}, α_{ji}, η_{ij}, η_{ji} = parameters in Equation 2

λ_{ij}, λ_{ji}, ψ_{ij}, ψ_{ji} = parameters in Equation 1

σ = standard deviation

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Conductances, Viscosities, and Densities of Solutions of Tetra-*n*-pentylammonium Thiocyanate in Nitrobenzene at 52°C

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The equivalent conductance of solutions composed of tetra-*n*-pentylammonium thiocyanate in nitrobenzene is measured from the fused salt region to 0.005410*N* at 52°C. Viscosity coefficients and densities are obtained over the range from the fused salt to pure solvent. The results show that the value of the $\Lambda\eta$-product at infinite dilution is approximately equal to the value for the fused salt. Contrary to our previous communication, the $\Lambda\eta$-product passes through a minimum as the concentration of the solution changes from $N = 0$ to $N = 2.513$ (fused salt).

In the early 1960's Kenausis, Evers, and Kraus (*2, 3*) (KEK) suggested that the product of the equivalent conductance and viscosity coefficient, $\Lambda\eta$, was a measure of ion dissociation in ultraconcentrated solutions of organic electrolytes. They proposed that the fused organic electrolytes were completely dissociated and that addition of solvent molecules caused aggregation by distorting the symmetrical fields about the ions. They used this hypothesis to explain the observation that $\Lambda\eta$ drops when solvent is added to the fused salt.

The ultraconcentrated region was defined roughly as the region between a solvent to electrolyte mole ratio (*N/n*) of 0.0–2.0. The ion fraction, F_i, was defined as $\Lambda\eta/(\Lambda\eta)_0$ where $(\Lambda\eta)_0$ is the value of the equivalent conductance-viscosity coefficient product for the fused salt. Kraus, Evers, and their students (*1–3, 8*) found that plots of $1 - F_i$ vs. *N/n* are linear up *N/n* ~ 2.0. These results were interpreted as support for two thermal mechanisms proposed to explain the conductance-viscosity behavior of concentrated and ultraconcentrated solutions.

In 1967 we communicated what we believed to be the anomalous behavior of the $\Lambda\eta$-product for the tetra-*n*-pentylammonium thiocyanate–nitrobenzene system at 52°C (*5*): We reported that the $\Lambda\eta$-product goes through a maximum in the ultraconcentrated region. Since that time we have convinced ourselves that we made an error in the calculation of the $\Lambda\eta$-product for this system, that it is quite normal, and, in fact, our observations may be interpreted to support the main KEK hypothesis, that the fused organic electrolyte is completely ionized.

Experimental

Preparation and purification of tetra-*n*-pentylammonium thiocyanate were accomplished by the methods of Longo et al. (*6*). The specific conductance obtained for this salt at 52.00° ± 0.01°C was 0.3102 mmho/cm, which agrees, within experimental error, with the value reported by Kenausis et al. (*2, 3*). Nitrobenzene (Matheson Coleman & Bell) was purified by a precedure described elsewhere (*7*). This method produced a solvent having a specific conductance of 1×10^{-10} ohm^{-1} cm^{-1}, which is good agreement with previously reported values (*6*).

Solution conductances were measured in two different cells. A conical cell having a cell constant 13.43 was utilized for the concentration range 2.417–0.005410*N*. A U-cell having a cell constant of 26.44 was used for the fused salt study and the ultraconcentrated solutions. This cell was designed to permit nitrogen gas mixing of the solution. All conductance measurements were made with a Wayne Kerr universal bridge Model No. B211. The cell constants were determined by the method of Lind et al. (*4*). Viscosities were determined with precalibrated Cannon-Ubbelohde viscometers with flow times measured by an electric timer to ±0.05 sec. Density values were obtained with a Christian-Becker specific gravity balance to ±0.0002 density units. All measurements were made in oil baths at 52°C with the temperature controlled to ±0.01°C. Temperature was monitored with a Beckmann dif-

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ferential thermometer calibrated vs. an NBS certified resistance thermometer used with a Mueller bridge. Solutions were prepared by weighing and were diluted to vary the concentrations. At least two complete runs were made over the same concentration range for each kind of measurement.

Results

In Table I are listed values of the equivalent conductance, Λ, and the product $\Lambda\eta$, computed at the normality, N, where Λ was determined. The parameter $\Lambda\eta$ was evaluated from the experimental value of Λ and a viscosity coefficient, η, calculated by the relationship

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 + 2.19089\, X_1 X_2 \ln \eta_1 \ln \eta_2 \quad (1)$$

where X_1, X_2, η_1, and η_2 represent mole fractions of the solvent and salt; the viscosity coefficients of the pure solvent and pure salt, respectively. We plan to explain the form of this function in a future paper. Differences between the experimental and calculated viscosities are presented in Table II. Plots of Λ vs. the square root of normality, $\sqrt{N}$, and of the $\Lambda\eta$-product vs. N are presented in Figures 1 and 2.

The density of the solution is adequately described by the equation

$$d = 1.1721 - 3.2788 \times 10^{-1}(W) + 5.2049 \times 10^{-4}(W)^2 \quad (2)$$

where (W) represents the mass fraction of the salt. This relationship was generated by a least-squares analysis of 18 density determinations between the fused salt region and infinite dilution. The average deviation between the calculated and experimental densities is 0.0006 density units.

Discussion

A plot of Λ vs. $\sqrt{N}$, Figure 1, becomes linear for the most dilute solutions investigated. Extrapolation to infinite dilution yields a value 52.02 for the equivalent conductance of infinite dilution, Λ_0. Although it may not be theoretically justifiable to obtain Λ_0 from our data because the solutions we examined

Table I. Conductance and Conductance-Viscosity Product for Tetra-*n*-pentylammonium Thiocyanate at 52°C

N	Λ	$\Lambda\eta \times 10^2$
2.513[a]	0.1236	41.93
2.513[a]	0.1235	41.89
2.417	0.1826	39.05
2.371	0.2165	37.31
2.356	0.2296	36.81
2.152	0.4681	31.46
2.132	0.4673	29.09
2.072	0.5558	27.55
1.993	0.6835	25.62
1.981	0.7009	25.22
1.905	0.8459	23.82
1.903	0.8460	23.67
1.841	1.005	23.23
1.807	1.056	22.07
1.763	1.156	21.35
1.689	1.348	20.41
1.584	1.656	19.29
1.500	1.733	19.11
1.429	2.191	18.03
1.380	2.386	17.76
1.347	2.521	17.56
1.190	3.246	16.86
1.085	3.808	16.60
0.9857	4.423	16.49
0.8736	5.184	16.40
0.7309	6.370	16.63
0.6305	7.360	16.95
0.5412	8.378	17.38
0.4260	9.993	18.24
0.3674	11.00	18.88
0.2942	12.52	19.94
0.2223	14.41	21.40
0.1036	18.44	24.53
0.06666	23.89	30.75
0.05123	26.28	33.37
0.03978	27.29	34.31
0.03003	29.82	37.22
0.02956	30.63	38.17
0.01790	34.02	41.97
0.01586	35.38	43.57
0.01418	35.81	44.04
0.009166	39.02	47.78
0.005410	42.24	51.56

[a] Fused salt.

Table II. Viscosity Coefficients for Tetra-*n*-pentylammonium Thiocyanate in Nitrobenzene at 52°C

N, mol/l.	η(exptl), cP	η(calcd), cP
2.532[a]	322	322
2.531[a]	339.2[b]	339.2
2.483	288.3	293.8
2.441	179.3	239.9
2.313	129.9	132.1
2.228	92.09	91.41
2.22	83.40	88.98
2.11	55.66	57.64
1.83	22.66	22.52
1.678	17.38	14.71
1.429	9.205	8.220
1.113	5.029	4.564
1.024	4.316	3.955
0.8335	3.132	2.993
0.5870	2.255	2.187
0.2253	1.561	1.538
0.0000	1.215[b]	1.215

[a] Different preparations of the fused salt. [b] Values used in Equation 1.

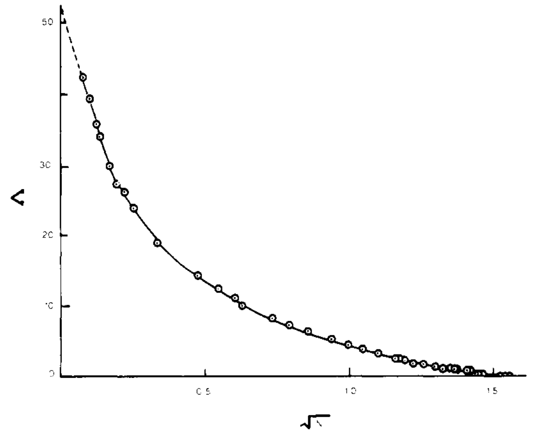

Figure 1. Plot of Λ vs. $\sqrt{N}$ for tetra-*n*-pentylammonium thiocyanate in nitrobenzene at 52°C

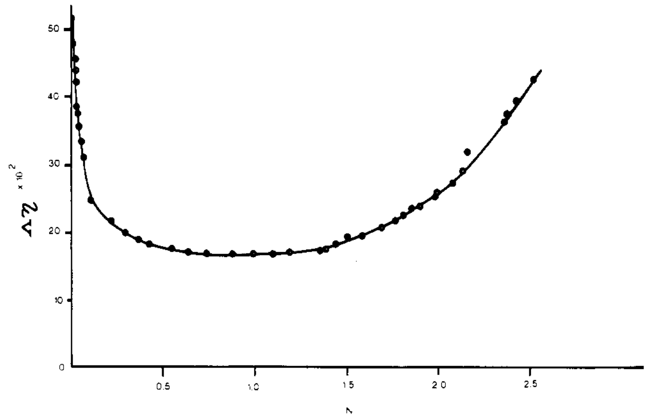

Figure 2. Plot of $\Lambda\eta$-product vs. *N* for tetra-*n*-pentylammonium thiocyanate in nitrobenzene at 52°C

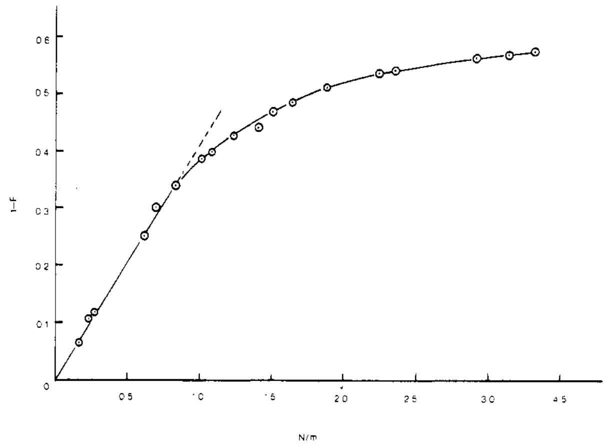

Figure 3. Plot 1 − F_i vs. *N/n* for tetra-*n*-pentylammonium thiocyanate in nitrobenzene at 52°C

were above the Debye-Huckel range, we gain some support for the validity of our Λ_0-value by comparing the Walden product, $\Lambda_0\eta_0$, at 52°C with the value for 25°C. We previously reported that Λ_0 and $\Lambda_0\eta_0$ are 33.44 ku and 0.6163, respectively, at 25°C (*6*). Using $\Lambda_0 = 52.02$ we obtain a value 0.6321 for $\Lambda_0\eta_0$ at 52°C. Since our value for the solvent viscosity is probably accurate and precise and since $\Lambda_0\eta_0$ should be relatively insensitive to temperature (*9, 10*), we feel our extrapolated value of Λ_0 at 52°C must be fairly accurate.

The Onsager slope determined at 52°C (using the values $\eta = 0.01215$; dielectric constant, $\epsilon = 30.395$; $T = 325.1\text{K}$, and $\Lambda_0 = 52.02$) is −111.7. The experimental slope of the plot of Λ vs. $\sqrt{N}$ is −145.0 ± 8 ku. Therefore, we can conclude that ion association is occurring in dilute solutions, but our data lack the precision required for the determination of the association constant.

Examination of Figure 2 shows that the values of $(\Lambda\eta)_0$ and $\Lambda_0\eta_0$ are not too different and that the $\Lambda\eta$ product passes through a broad minimum at *N* 0.9. This behavior for $\Lambda\eta$ has been reported for several other systems (*1–3, 8*).

The plot of 1 − F_1 vs. *N/n* (Figure 3) is linear in the region from $N/n = 0$ to $N/n \sim 0.9$. Hence, in solutions of nitrobenzene the linear portion is much smaller than in other systems which have been studied. The difference in this case may be due to the higher dielectric constant and very high dipole moment of the solvent nitrobenzene. We have previously suggested that the large nitrobenzene dipoles may very easily fit into the molten salt structure as electrical and volume substitutes for the cation and anion of the electrolyte (*5*). Therefore, the "doping" of the fused salt with a few nitrobenzene molecules may cause only a slight change in the electrical forces which are operative and the mechanism proposed by KEK which depends on a solvent molecule induced distortion may not be effective.

In any event, the KEK hypothesis (that the introduction of solvent molecules into the fused salt and ultraconcentrated solutions causes ions to aggregate) is not easy to test. In fact, the observation that the viscosity coefficient decreases upon addition of solvent molecules in the ultraconcentrated region appears to contradict the hypothesis.

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