EFFECT OF TEMPERATURE ON THE ELECTRICAL CONDUCTANCE OF HYDROGEN CHLORIDE IN DIMETHYLSULPHOXIDE*

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Abstract—The electrical conductance of solutions of hydrogen chloride in dimethylsulphoxide at temperatures from 25 to 45°C has been studied. Results have been interpreted with the Fuoss theory for associated 1–1 type electrolytes. Values of the association constant K_A and the J parameter have been computed at each temperature. The temperature dependence of the molar conductance is inferred from the theoretical equation and related to the temperature dependence of viscosity.

Résumé—La conductance électrique des solutions de chlorure d'hydrogène dans le diméthylsulfoxyde à des températures de 25 a 45°C a été étudiée. Les résultats ont été inteprétés par la théorie de Fuoss pour des electrolytes associées du type 1–1. Les valeurs de la constante d'association K_A et du paramètre J ont été calculées à chaque température. La dépendance de la conductivité molaire avec la température est déduite de l'équation théorique et référée a la dépendance de la viscosité avec la température.

Zusammenfassung—Die elektrische Leitfähigkeit der Lösungen von Chlorwasserstoff in Dimethylsulfoxyd bei Temperaturen von 25 bis 45°C wurde studiert. Die Ergebnisse wurden mittels der Theorie von Fuoss für Electrolyte des 1–1 assoziarten Typs gedeutet. Die Werte der Assoziationskonstante K_A und der Parameter J wurden für jede Temperatur berechnet. Die Temperaturabhängigkeit des Molarenkonduktanz ist von der theoretischen Gleichung abgeleitet und auf die Temperaturabhängigkeit der Viskosität bezogen.

INTRODUCTION

In earlier papers the electrical conductance of solutions of hydrogen chloride in DMSO has been studied at 25°C.[1,2] It has been observed that HCl behaves in this solvent as a markedly associated 1–1 type electrolyte, its association constant K_A being 115·7 l/mole. This behaviour is dissimilar with that of other electrolytes of the same type in DMSO,[3] which are completely dissociated strong electrolytes over a rather large range of concentration. It is then of interest to extend previous work on this matter to other temperature and viscosity ranges, to discover the energetic peculiarities of the mechanism of electrical conduction.

EXPERIMENTAL TECHNIQUE

Experimental techniques for the measurement of the electrical conductance and viscosity, purification of the solvent and preparation of solutions have been described elsewhere.[2,4] Experiments were made in the range 10^{-1}–10^{-5} M, at temperatures from 25° to 45°C.

RESULTS

The experimental results of the electrical conductance are assembled in Tables 1–5. κ is the specific conductance and C the molar concentration. At each temperature, concentrations were corrected for density changes and the molar conductances Λ were calculated accordingly.

The dependence of the molar conductance with concentration is shown in Fig. 1, where it is plotted vs $C^{1/2}$ at different temperatures. Figure 2 shows results of viscosity measurements, in a plot of the viscosity coefficient η vs $C^{1/2}$, for each temperature.

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TABLE 1. CONDUCTANCE DATA AT 25°C

C M	κ int.ohm⁻¹/cm⁻¹	Λ int.ohm⁻¹. cm².mol⁻¹	γ	$\eta \times 10^2$ g/cm per s	$\Lambda\eta$ g cm int. ohm⁻¹.s⁻¹. mole⁻¹
$5\cdot383 \times 10^{-2}$	$7\cdot294 \times 10^{-4}$	13·55	0·450	2·085	0·283
$4\cdot306 \times 10^{-2}$	$6\cdot317 \times 10^{-4}$	14·67	0·477	2·080	0·305
$2\cdot153 \times 10^{-2}$	$3\cdot972 \times 10^{-4}$	18·45	0·568	2·061	0·380
$1\cdot724 \times 10^{-2}$	$3\cdot348 \times 10^{-4}$	19·42	0·589	2·053	0·399
$1\cdot036 \times 10^{-2}$	$2\cdot373 \times 10^{-4}$	22·91	0·675	2·045	0·469
$8\cdot305 \times 10^{-3}$	$1\cdot987 \times 10^{-4}$	23·93	0·697	2·042	0·489
$6\cdot648 \times 10^{-3}$	$1\cdot724 \times 10^{-4}$	25·93	0·749	2·038	0·528
$4\cdot297 \times 10^{-3}$	$1\cdot160 \times 10^{-4}$	27·00	0·765	2·032	0·549
$3\cdot327 \times 10^{-3}$	$9\cdot835 \times 10^{-5}$	29·56	0·830	2·030	0·600
$1\cdot664 \times 10^{-3}$	$5\cdot411 \times 10^{-5}$	32·52	0·896	2·027	0·659
$8\cdot585 \times 10^{-4}$	$2\cdot927 \times 10^{-5}$	34·10	0·925	2·023	0·690
$8\cdot337 \times 10^{-4}$	$2\cdot844 \times 10^{-5}$	34·11	0·925	2·022	0·690
$4\cdot179 \times 10^{-4}$	$1\cdot507 \times 10^{-5}$	36·06	0·968	2·020	0·728
$1\cdot716 \times 10^{-4}$	$6\cdot349 \times 10^{-6}$	37·00	0·983	2·020	0·747
$8\cdot350 \times 10^{-5}$	$3\cdot154 \times 10^{-6}$	37·77	0·998	2·018	0·762

The molar conductance increases monotonously with decreasing concentration at all temperatures, as already reported for 25°C,[2] while at constant concentration it increases with the temperature, following as a first approximation an Arrhenius equation. On this basis average values of the experimental activation energy for conductances, $\Delta H_\Lambda{}^*$, are calculated. These values lie between $3\cdot2 \pm 0\cdot3$ and $2\cdot4 \pm 0\cdot3$ Kcal/mole. $\Delta H_\Lambda{}^*$ tends to decrease with increasing concentration, as shown in Fig. 3. Viscosity also decreases with concentration and temperature. Figure 4 shows these results. In a plot of log η vs $1/T$ slightly bent curves are obtained for all concentrations, but the average experimental activation energy for viscosity, $\Delta H_\eta{}^*$, is $3\cdot0 \pm 0\cdot1$ kcal/mole, for the pure solvent and for all the range of concentrations studied, can be calculated.

These results indicate that at least at infinite dilution, where $\Delta H_\Lambda{}^*$ and $\Delta H_\eta{}^*$

TABLE 2. CONDUCTANCE DATA AT 30°C

C M	κ int.ohm⁻¹cm⁻¹	Λ int.ohm⁻¹cm² mole⁻¹	γ
$5\cdot361 \times 10^{-2}$	$7\cdot885 \times 10^{-4}$	14·71	0·445
$4\cdot288 \times 10^{-2}$	$6\cdot820 \times 10^{-4}$	15·90	0·470
$2\cdot144 \times 10^{-2}$	$4\cdot297 \times 10^{-4}$	20·04	0·561
$1\cdot717 \times 10^{-2}$	$3\cdot632 \times 10^{-4}$	21·15	0·584
$1\cdot032 \times 10^{-2}$	$2\cdot572 \times 10^{-4}$	24·92	0·670
$8\cdot271 \times 10^{-3}$	$2\cdot163 \times 10^{-4}$	26·15	0·695
$6\cdot621 \times 10^{-3}$	$1\cdot876 \times 10^{-4}$	28·33	0·747
$4\cdot279 \times 10^{-3}$	$1\cdot265 \times 10^{-4}$	29·56	0·764
$3\cdot313 \times 10^{-3}$	$1\cdot074 \times 10^{-4}$	32·42	0·843
$1\cdot657 \times 10^{-3}$	$5\cdot866 \times 10^{-5}$	35·40	0·890
$8\cdot550 \times 10^{-4}$	$3\cdot204 \times 10^{-5}$	37·47	0·929
$8\cdot303 \times 10^{-4}$	$3\cdot123 \times 10^{-5}$	37·61	0·932
$4\cdot162 \times 10^{-4}$	$1\cdot655 \times 10^{-5}$	39·76	0·974
$1\cdot709 \times 10^{-4}$	$7\cdot068 \times 10^{-6}$	41·36	
$2\cdot316 \times 10^{-5}$	$3\cdot507 \times 10^{-6}$	42·17	
$1\cdot663 \times 10^{-5}$	$7\cdot309 \times 10^{-7}$	43·95	

TABLE 3. CONDUCTANCE DATA AT 35°C

C M	κ int.ohm^{-1}cm^{-1}	Λ int.ohm^{-1}cm^2 mole^{-1}	γ
$5\cdot339 \times 10^{-2}$	$8\cdot436 \times 10^{-4}$	15·80	0·436
$4\cdot271 \times 10^{-2}$	$7\cdot307 \times 10^{-4}$	17·11	0·466
$2\cdot135 \times 10^{-2}$	$4\cdot602 \times 10^{-4}$	21·56	0·546
$1\cdot710 \times 10^{-2}$	$3\cdot910 \times 10^{-4}$	22·87	0·570
$1\cdot027 \times 10^{-2}$	$2\cdot780 \times 10^{-4}$	27·07	0·655
$8\cdot237 \times 10^{-3}$	$2\cdot336 \times 10^{-4}$	28·36	0·678
$6\cdot593 \times 10^{-3}$	$2\cdot012 \times 10^{-4}$	30·52	0·726
$4\cdot262 \times 10^{-3}$	$1\cdot373 \times 10^{-4}$	32·21	0·747
$3\cdot300 \times 10^{-3}$	$1\cdot162 \times 10^{-4}$	35·21	0·810
$1\cdot650 \times 10^{-3}$	$6\cdot371 \times 10^{-5}$	38·61	0·868
$8\cdot514 \times 10^{-4}$	$3\cdot491 \times 10^{-5}$	41·00	0·907
$8\cdot268 \times 10^{-4}$	$3\cdot410 \times 10^{-5}$	41·24	0·912
$4\cdot145 \times 10^{-4}$	$1\cdot795 \times 10^{-5}$	43·31	0·963
$1\cdot702 \times 10^{-4}$	$7\cdot770 \times 10^{-6}$	45·65	0·988
$8\cdot281 \times 10^{-5}$	$3\cdot898 \times 10^{-6}$	47·07	
$1\cdot656 \times 10^{-5}$	$7\cdot979 \times 10^{-7}$	48·18	

have practically the same absolute value, the Walden product $\Lambda_0\eta_0$, where Λ_0 is the limiting molar conductance and η_0 the solvent viscosity, should be temperature-independent as observed in Table 6. On the contrary, from Table 1 it is seen that the product $\Lambda\eta$, at constant temperature, depends on concentration. This shows that the mechanisms of the above processes are differently affected by ionic interactions, which must play an increasing role at higher concentrations, particularly in the mechanism of electrical conduction.

DISCUSSION

On the basis of the interpretation advanced in a previous paper,[2] the results are now discussed with the Fuoss theory for associated 1–1 type electrolytes.[5] The following general equation applies in the range from 25 to 45°C,

$$\Lambda_\eta = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log (C\gamma) + JC\gamma - K_A C\gamma f^2 \Lambda_\eta. \tag{1}$$

TABLE 4. CONDUCTANCE DATA AT 40°C

C M	κ int.ohm^{-1}cm	Λ int.ohm^{-1}cm^2 mole^{-1}	γ
$5\cdot317 \times 10^{-2}$	$8\cdot919 \times 10^{-4}$	16·77	0·425
$4\cdot253 \times 10^{-2}$	$7\cdot778 \times 10^{-4}$	18·29	0·459
$2\cdot126 \times 10^{-2}$	$4\cdot923 \times 10^{-4}$	23·16	0·543
$1\cdot703 \times 10^{-2}$	$4\cdot183 \times 10^{-4}$	24·56	0·567
$1\cdot023 \times 10^{-2}$	$2\cdot978 \times 10^{-4}$	29·11	0·654
$8\cdot203 \times 10^{-3}$	$2\cdot506 \times 10^{-4}$	30·55	0·678
$6\cdot566 \times 10^{-3}$	$2\cdot170 \times 10^{-4}$	33·05	0·727
$4\cdot244 \times 10^{-3}$	$1\cdot476 \times 10^{-4}$	34·78	0·749
$3\cdot286 \times 10^{-3}$	$1\cdot249 \times 10^{-4}$	38·01	0·813
$1\cdot643 \times 10^{-3}$	$6\cdot895 \times 10^{-5}$	41·97	0·878
$8\cdot479 \times 10^{-4}$	$3\cdot774 \times 10^{-5}$	44·51	0·917
$8\cdot234 \times 10^{-4}$	$3\cdot695 \times 10^{-5}$	44·87	0·924
$4\cdot128 \times 10^{-4}$	$1\cdot965 \times 10^{-5}$	47·60	0·969
$1\cdot695 \times 10^{-4}$	$8\cdot362 \times 10^{-6}$	49·33	0·994
$8\cdot247 \times 10^{-5}$	$4\cdot214 \times 10^{-6}$	51·10	
$1\cdot649 \times 10^{-5}$	$8\cdot707 \times 10^{-7}$	52·80	

TABLE 5. CONDUCTANCE DATA AT 45°C

C M	κ int.ohm^{-1}cm^{-1}	Λ int.ohm^{-1}cm^2 mole^{-1}	γ
$5 \cdot 295 \times 10^{-2}$	$9 \cdot 422 \times 10^{-4}$	$17 \cdot 79$	$0 \cdot 416$
$4 \cdot 235 \times 10^{-2}$	$8 \cdot 229 \times 10^{-4}$	$19 \cdot 43$	$0 \cdot 444$
$2 \cdot 122 \times 10^{-2}$	$5 \cdot 217 \times 10^{-4}$	$24 \cdot 59$	$0 \cdot 529$
$1 \cdot 696 \times 10^{-2}$	$4 \cdot 447 \times 10^{-4}$	$26 \cdot 22$	$0 \cdot 554$
$1 \cdot 019 \times 10^{-2}$	$3 \cdot 170 \times 10^{-4}$	$31 \cdot 11$	$0 \cdot 638$
$8 \cdot 169 \times 10^{-3}$	$2 \cdot 674 \times 10^{-4}$	$32 \cdot 73$	$0 \cdot 662$
$6 \cdot 539 \times 10^{-3}$	$2 \cdot 314 \times 10^{-4}$	$35 \cdot 39$	$0 \cdot 709$
$4 \cdot 226 \times 10^{-3}$	$1 \cdot 581 \times 10^{-4}$	$37 \cdot 41$	$0 \cdot 734$
$3 \cdot 272 \times 10^{-3}$	$1 \cdot 335 \times 10^{-4}$	$40 \cdot 80$	$0 \cdot 794$
$1 \cdot 640 \times 10^{-3}$	$7 \cdot 315 \times 10^{-5}$	$44 \cdot 60$	$0 \cdot 866$
$8 \cdot 444 \times 10^{-4}$	$4 \cdot 039 \times 10^{-5}$	$47 \cdot 83$	$0 \cdot 896$
$8 \cdot 200 \times 10^{-4}$	$3 \cdot 974 \times 10^{-5}$	$48 \cdot 46$	$0 \cdot 906$
$4 \cdot 110 \times 10^{-4}$	$2 \cdot 121 \times 10^{-5}$	$51 \cdot 61$	$0 \cdot 953$
$1 \cdot 688 \times 10^{-4}$	$9 \cdot 238 \times 10^{-6}$	$54 \cdot 73$	$0 \cdot 999$
$8 \cdot 213 \times 10^{-5}$	$4 \cdot 614 \times 10^{-6}$	$56 \cdot 18$	
$1 \cdot 643 \times 10^{-5}$	$9 \cdot 564 \times 10^{-7}$	$58 \cdot 21$	
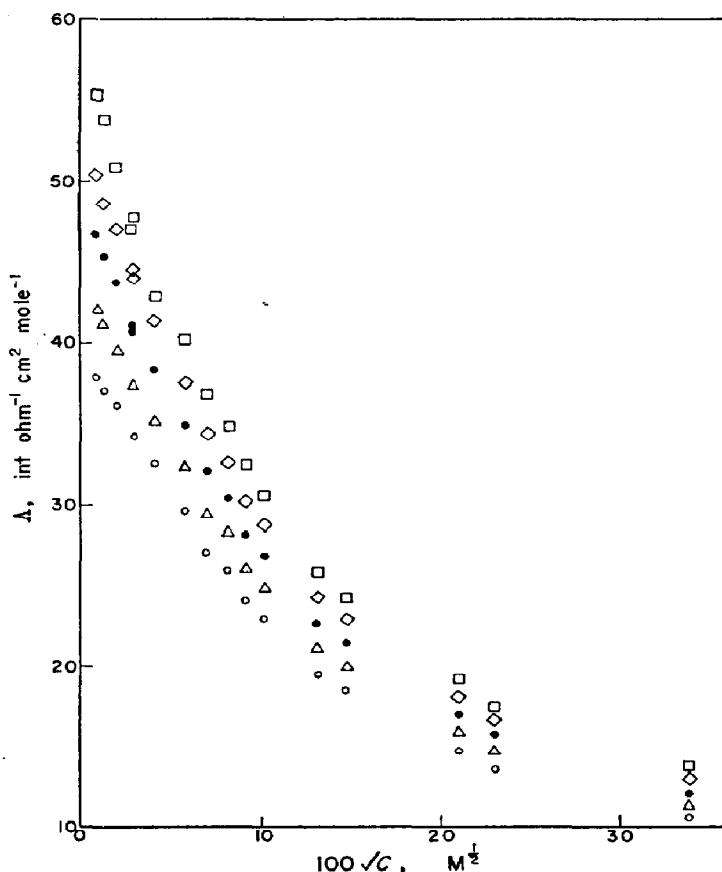
FIG. 1. Plot of the molar conductance Λ vs $\sqrt{C}$ at different temperatures.
○, 25°C; △, 30°C; ●, 35°C; ◇, 40°C; □, 45°C.
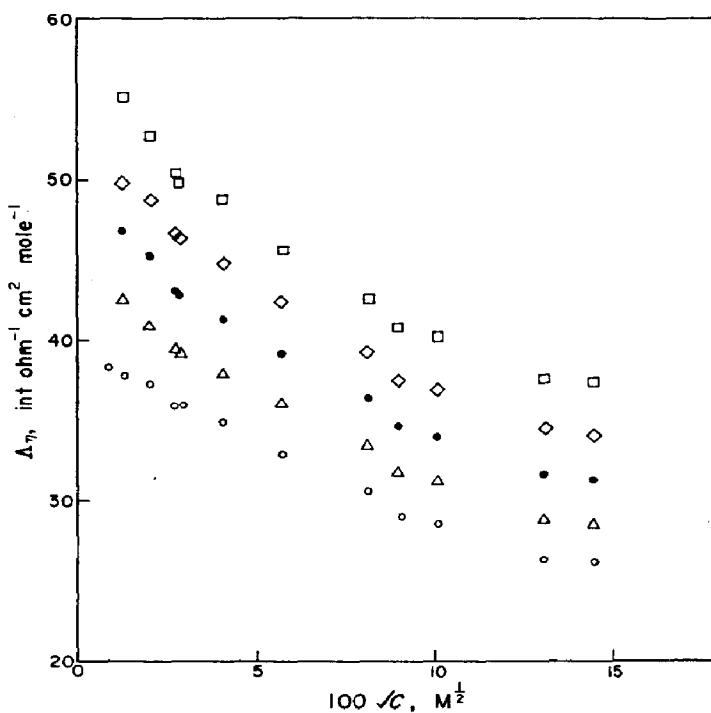
FIG. 2. Plot of $\Lambda'\eta$ vs $\sqrt{C}$ at different temperatures.
$\Lambda_\eta' = \Lambda_\eta + S(C\gamma)^{1/2} - EC\gamma \log(C\gamma)$. $\bigcirc$, 25°C; $\triangle$, 30°C; $\bullet$, 35°C; $\Diamond$, 40°C; $\square$, 45°C.

The meaning of each term is given in Fuoss' original paper.[5] From (1), the equilibrium constant of the ionic association process, K_A, and the J parameter, are determined. J is directly related to a, the mean distance of nearest approach of the pairs of ions.

As already indicated, the evaluation is made by successive approximations. An initial value of Λ_0 calculated by Shedlovsky's equation is chosen.[6] The procedure indicated by Fuoss is then followed until a set of x, y values representing a straight line is found. If the plot bends downward, a new lower value is chosen, and the procedure repeated until necessary. If the plot bends upward, a higher value of Λ_0 is selected. The constants for using (1) at different temperatures are assembled in
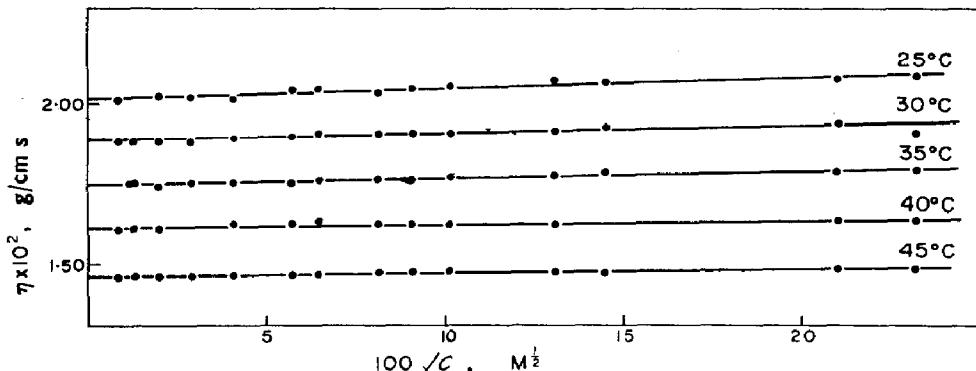
FIG. 3. Plot of the viscosity coefficient η vs $\sqrt{C}$ at different temperatures.

Tables 6 and 7. Table 7 also includes values of the dielectric constant of the solvent, D, the limiting molar conductance calculated with Shedlovsky's equation, and parameters obtained with (1).

From Table 7 two important facts are deduced. First, the dissociation constant decreases slightly with the temperature. This effect is similar to that observed for other 1-1 type electrolytes, such as acetic acid in water.[8] By applying the Kirchhoff
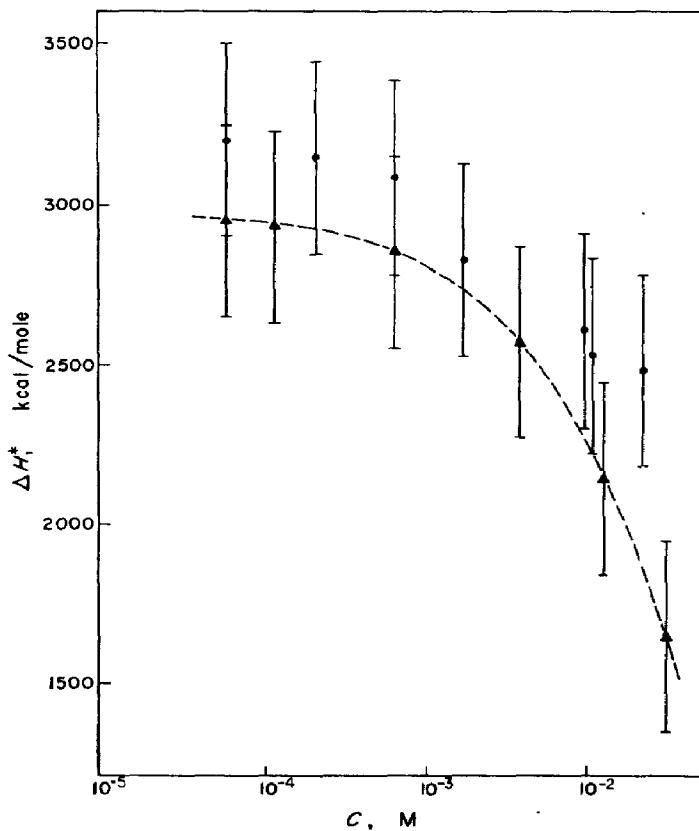

FIG. 4. Dependence of the experimental activation energy for conductance on concentration.
●, experimental values. ▲, values calculated with equation (5).

equation the enthalpy change related to the ionic dissociation is obtained, $\Delta H_d = -(2 \pm 1)$ Kcal/mole. This figure is significantly higher than RT. Secondly, conclusions about mean ionic radius are derived from the J values. J is defined by

$$J = \sigma_1 \Lambda_0 + \sigma_2; \tag{2}$$

the expressions σ_1 and σ_2 are given in the literature.[5] Table 7 shows that J varies inversely with D at constant temperature. From J, the mean ionic radius calculated for the range of temperature and concentration of the present work results, $a = (2\cdot3 \pm 0\cdot3) \times 10^{-8}$ cm, this figure being practically temperature-independent. The degree of dissociation, γ, shown in the Tables was also calculated with Fuoss' procedure.

TABLE 6. BASIC VALUES FOR THE FUOSS EVALUATION

	25°C	30°C	35°C	40°C	45°C
$\dfrac{\kappa}{C^{1/2}} = \left(\dfrac{8\pi e^2 N}{1000k}\right)^{1/2} \cdot \dfrac{1}{(DT)^{1/2}}$	$2\!\cdot\!9126 \times 10^8 D^{-1/2}$	$2\!\cdot\!8885 \times 10^8 D^{-1/2}$	$2\!\cdot\!8650 \times 10^8 D^{-1/2}$	$2\!\cdot\!8420 \times 10^8 D^{-1/2}$	$2\!\cdot\!8195 \times 10^8 D^{-1/2}$
$\alpha = \left(\dfrac{8\pi N}{1000k^3}\right)^{1/2} \times \dfrac{e^3}{6\times 1\!\cdot\!7071} \cdot \dfrac{1}{(DT)^{3/2}}$	$159\!\cdot\!37 \times D^{-3/2}$	$155\!\cdot\!44 \times D^{-3/2}$	$151\!\cdot\!68 \times D^{-3/2}$	$148\!\cdot\!06 \times D^{-3/2}$	$144\!\cdot\!58 \times D^{-3/2}$
$\beta = \left(\dfrac{8N}{1000k\pi}\right)^{1/2} \cdot \dfrac{Fe^2}{3C} \cdot \dfrac{1}{\eta_0(DT)^{1/2}}$	$4\!\cdot\!7772 \times (\eta_0 D^{1/2})^{-1}$	$4\!\cdot\!7376 \times (\eta_0 D^{1/2})^{-1}$	$4\!\cdot\!6991 \times (\eta_0 D^{1/2})^{-1}$	$4\!\cdot\!6614 \times (\eta_0 D^{1/2})^{-1}$	$4\!\cdot\!6245 \times (\eta_0 D^{1/2})^{-1}$
$E_1 = \dfrac{2\!\cdot\!3026 e^6 \pi N}{3 \times 1000 k^3} \cdot \dfrac{1}{(DT)^3}$	$2\!\cdot\!5565 \times 10^5 D^{-3}$	$2\!\cdot\!4321 \times 10^5 D^{-3}$	$2\!\cdot\!3157 \times 10^5 D^{-3}$	$2\!\cdot\!2065 \times 10^5 D^{-3}$	$2\!\cdot\!1039 \times 10^5 D^{-3}$
$E_2 = \dfrac{2\!\cdot\!3026 Ne^5 F}{6 \times 1000 k^2 C} \cdot \dfrac{1}{\eta_0(DT)^2}$	$1122\!\cdot\!2 \times (\eta_0 D^2)^{-1}$	$1085\!\cdot\!5 \times (\eta_0 D^2)^{-1}$	$1050\!\cdot\!6 \times (\eta_0 D^2)^{-1}$	$1017\!\cdot\!3 \times (\eta_0 D^2)^{-1}$	$985\!\cdot\!5 \times (\eta_0 D^2)^{-1}$
$ab = \dfrac{e^2}{k} \cdot \dfrac{1}{DT}$	$560\!\cdot\!45 \times 10^{-8} D^{-1}$	$551\!\cdot\!21 \times 10^{-8} D^{-1}$	$542\!\cdot\!26 \times 10^{-8} D^{-1}$	$533\!\cdot\!61 \times 10^{-8} D^{-1}$	$525\!\cdot\!22 \times 10^{-8} D^{-1}$
$\dfrac{11}{12}\beta \dfrac{\kappa}{C^{1/2}} = \dfrac{22Fe^3N}{9 \times 1000 Ck} \cdot \dfrac{1}{\eta_0 DT}$	$12\!\cdot\!755 \times 10^8(\eta_0 D)^{-1}$	$12\!\cdot\!544 \times 10^8(\eta_0 D)^{-1}$	$11\!\cdot\!219 \times 10^8(\eta_0 D)^{-1}$	$11\!\cdot\!040 \times 10^8(\eta_0 D)^{-1}$	$10\!\cdot\!866 \times 10^8(\eta_0 D)^{-1}$
$2\beta'' = \left(\dfrac{8\pi N}{1000k^3}\right)^{1/2} \cdot \dfrac{e^3}{2\!\cdot\!3026} \cdot \dfrac{1}{(DT)^{3/2}}$	$708\!\cdot\!92 \times D^{-3/2}$	$691\!\cdot\!46 \times D^{-3/2}$	$674\!\cdot\!71 \times D^{-3/2}$	$658\!\cdot\!61 \times D^{-3/2}$	$643\!\cdot\!12 \times D^{-3/2}$
$\dfrac{0\!\cdot\!4343 e^3}{k} \cdot \dfrac{1}{T}$	$243\!\cdot\!40 \times 10^{-8}$	$239\!\cdot\!39 \times 10^{-8}$	$235\!\cdot\!51 \times 10^{-8}$	$231\!\cdot\!74 \times 10^{-8}$	$228\!\cdot\!10 \times 10^{-8}$
$\alpha\beta = \dfrac{4Fe^5N}{3 \times 1\!\cdot\!7071 \times 1000 \times 3Ck^3} \times \dfrac{1}{\eta_0(DT)^3}$	$761\!\cdot\!34 \times (\eta_0 D^3)^{-1}$	$736\!\cdot\!41 \times (\eta_0 D^3)^{-1}$	$712\!\cdot\!76 \times (\eta_0 D^3)^{-1}$	$690\!\cdot\!17 \times (\eta_0 D^3)^{-1}$	$668\!\cdot\!61 \times (\eta_0 D^3)^{-1}$
$\dfrac{1}{12}\dfrac{\kappa^2}{C} a^2b^3 = \dfrac{2\pi e^6 N}{3k^3 1000} \cdot \dfrac{1}{(DT)^3}$	$2\!\cdot\!2205 \times 10^5 D^{-3}$	$2\!\cdot\!1125 \times 10^5 D^{-3}$	$2\!\cdot\!0113 \times 10^5 D^{-3}$	$1\!\cdot\!9165 \times 10^5 D^{-3}$	$1\!\cdot\!8274 \times 10^5 D^{-3}$
$\dfrac{1}{8}\dfrac{\kappa}{C^{1/2}} ab\beta = \dfrac{e^5 NF}{3k^3 1000 C} \cdot \dfrac{1}{\eta_0(DT)^3}$	$974\!\cdot\!77 \times (\eta_0 D^3)^{-1}$	$942\!\cdot\!88 \times (\eta_0 D^3)^{-1}$	$912\!\cdot\!55 \times (\eta_0 D^3)^{-1}$	$883\!\cdot\!64 \times (\eta_0 D^3)^{-1}$	$856\!\cdot\!03 \times (\eta_0 D^3)^{-1}$

Values of fundamental constants are those accepted by the National Bureau of Standards. See *Handbook of Chemistry and Physics*, edited by CH. D. HODGMAN, p. F 158 (1967/68).

TABLE 7.

°C	$\Lambda_{0(S)}$	$\Lambda_{0(F)}$	D	$\eta_0 \times 10^2$	$\Lambda_{0(F)}\eta_0$	J	K_A	K_D	E
25	38·74	38·34	46·5	2·015	0·773	160 ± 20	115·7	8·64	71·67
30	43·50	41·80	44·3	1·886	0·788	190 ± 20	117·0	8·55	87·48
35	47·43	46·80	42·0	1·746	0·817	240 ± 20	128·0	7·81	112·05
40	51·41	50·00	39·7	1·609	0·804	320 ± 20	130·2	7·68	136·21
45	55·33	55·00	37·4	1·460	0·803	360 ± 20	147·2	6·79	172·93

The temperature coefficient

The expression for the molar conductance contains a number of terms depending on the temperature. In a general way, the molar conductance, corrected for the Falkenhagen–Dole viscosity factor, Λ_η, can be written[9]

$$\Lambda_\eta \approx \Lambda = \Lambda(\Lambda_0, S, E, J, K_A, C, \gamma, f). \tag{3}$$

As for simple inorganic salts Λ_η and Λ are nearly equal and depend practically in the same way on T, in order to obtain a temperature-dependent equation we write the following general equation to express the temperature dependence of molar conductance,

$$\frac{d \ln \Lambda}{d(1/T)} = \frac{1}{\Lambda} \left(\frac{\partial \Lambda}{\partial \Lambda_0} \frac{d\Lambda_0}{d(1/T)} + \frac{\partial \Lambda}{\partial S} \frac{dS}{d(1/T)} \right.$$

$$+ \frac{\partial \Lambda}{\partial E} \frac{dE}{d(1/T)} + \frac{\partial \Lambda}{\partial J} \frac{dJ}{d(1/T)} + \frac{\partial \Lambda}{\partial K_A} \frac{dK_A}{d(1/T)}$$

$$\left. + \frac{\partial \Lambda}{\partial C} \frac{dC}{d(1/T)} + \frac{\partial \Lambda}{\partial \gamma} \frac{d\gamma}{d(1/T)} + \frac{\partial \Lambda}{\partial f} \frac{df}{d(1/T)} \right). \tag{4}$$

The partial derivatives are obtained from (1), assuming that the coefficient dC/dT is negligible. Furthermore, as the product $\Lambda_0\eta_0$ is independent of T, the following expression is deduced for the activation energy of the molar conductance,

$$\Delta H_\Lambda^* = -\Delta H_\eta^* + \frac{R}{\Lambda} u^{1/2} S \frac{d \ln S}{d(1/T)} - \frac{R}{\Lambda} u \log u \, E \frac{d \ln E}{d(1/T)} - \frac{R}{\Lambda} uJ \frac{d \ln J}{d(1/T)}$$

$$+ Ruf^2 K_A \frac{d \ln K_A}{d(1/T)} + \frac{R}{\Lambda} \frac{S}{2} u^{1/2} \frac{d \ln u}{d(1/T)} - 0.4343 \frac{R}{\Lambda} Eu \frac{d \ln u}{d(1/T)}$$

$$- \frac{R}{\Lambda} Eu \log u \frac{d \ln u}{d(1/T)} - \frac{R}{\Lambda} Ju \frac{d \ln u}{d(1/T)} + Rf^2 K_A u \frac{d \ln u}{d(1/T)}$$

$$+ 2RK_A f^2 u \frac{d \ln f}{d(1/T)}, \tag{5}$$

where $u = C\gamma$.

Equation (5) shows that the activation energy of the conduction process is practically equal in absolute value to the activation energy of the viscosity at infinite dilution. The terms involving C in (5) are due to ionic interactions participating in the electrical conduction. They are mainly related to the dependence of the dielectric constant of the solvent and the association constant of the electrolyte with temperature. Summing

TABLE 8

°C	$\dfrac{d \ln \eta_0}{d(1/T)}$	$E\dfrac{d \ln E}{d(1/T)} \times 10^{-5}$	$J\dfrac{d \ln J}{d(1/T)} \times 10^{-5}$	$K_A \dfrac{d \ln K_A}{d(1/T)} \times 10^{-5}$	$S\dfrac{d \ln S}{d(1/T)} \times 10^{-5}$
25	1510	−2·96	−6·80	−1·30	−1·14
30	1510	−3·61	−8·08	−1·31	−1·28
35	1510	−4·63	−10·20	−1·43	−1·42
40	1510	−5·63	−13·60	−1·46	−1·59
45	1510	−7·14	−15·30	−1·65	−1·82

up these contributions, they tend to diminish ΔH_A^* with respect to ΔH_η^*. This effect is illustrated in Fig. 4, although the scatter of the experimental results is somewhat pronounced. This fact does not encourage any further analysis of (5) but on the knowledge of $dS/d(1/T)$, $dJ/d(1/T)$, $dE/d(1/T)$, $dK_A/d(1/T)$, $du/d(1/T)$ and $df/d(1/T)$, previously calculated, the contribution of each term in that equation can be calculated and compared with experimental data. The dotted line in Fig. 4 corresponds to (5), which therefore explains quantitatively the experimental results reasonably well.

The non-coincidence of the activation energies for electrical conductance and viscosity over the whole range of concentrations is not surprising, as the mechanism of the two transport processes are not the same. As a matter of fact, ionic interactions predominate in the electrical conductance mechanism yielding a square root dependence of the conductance on concentration. On the other hand, the viscous process involves principally the participation of ion–solvent interactions. Thus, the dependence of the viscosity coefficient is mainly governed by terms that depend linearly on the concentration, in equations such as the Jones–Dole equation for the viscosity of ionic solutions.[10]

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