

The Electrical Conductance of Rubidium Iodide in Water-Acetonitrile Solvent Mixtures at 25 °C

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The conductance of rubidium iodide in the concentration range 10^{-2} to 10^{-3} M has been measured in water-acetonitrile solvent mixtures. The solvent compositions covered the whole range from pure water to pure acetonitrile. The viscosities and the densities of the solvent mixtures were also determined.

The data were analysed according to the Fuoss-Onsager conductance equation. A graph of the limiting molar conductance, Λ° , versus solvent composition showed a pronounced minimum at about 20 mol percent acetonitrile, while the viscosity, η , had a maximum at about 10 mol percent. The Walden product, $\Lambda^\circ\eta$, decreased steadily when going from pure water to pure acetonitrile.

The study of transport processes in general, and of conduction and diffusion in particular, is one of the many approaches to elucidate the structure of electrolyte solutions. This has been extensively used for aqueous solutions for which a large body of experimental data is available.

Classical theory tended to regard the solvent as merely providing the viscous and dielectric medium for the movement of the ions and for the long range ion-ion interactions. The interaction between the ions and the solvent molecules was often neglected. If there had been no such interaction — *i.e.* if the model of the ion as a charged sphere in a continuous medium had been valid — the Walden product (the limiting conductance times the viscosity of the solvent) for any given ion should be constant. This, however, is very often not the case. It is found

to vary from solvent to solvent and also in the same solvent at different temperatures. In water, for instance, the Walden product for a given salt or ion varies considerably with temperature, having a positive temperature coefficient for some ions and a negative one for others, the latter being the most usual for simple ions. This has been interpreted in terms of the effect of the ions on the hydrogen bond structure of water. This interpretation is supported by the observation that in acetonitrile, which can be regarded as a non structural liquid, there seems to be very little variation in the Walden product with temperature for any given ion.¹

In this respect, then, acetonitrile is close to an ideal solvent, while water is highly non-ideal. This raises the question of mixtures of water and acetonitrile. To the authors' knowledge no conductance data in these solvent mixtures have been reported. A project has therefore been started in these laboratories to investigate the conductances of the alkali- and the halide ions in water-acetonitrile mixtures. The measurements reported in this paper are part of this project.

Acetonitrile (methyl cyanide, CH_3CN , abbreviated, MeCN) is a non-associated liquid with a relatively high dielectric constant, 36.0 at 25 °C, due to the high dipole moment of the acetonitrile molecule (3.9 Debye in the gas phase, 3.4–3.5 in solutions).² For water the high dielectric constant, 78.5 at 25 °C, is, to a large extent, due to its associated structure through hydrogen bonds. The dipole moment of the water molecule is 1.8 D.

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Conductance data for salts in mixed solvents also provide a test of the extended conduction equations commonly used. The data presented in this paper have been analyzed according to the Fouss-Onsager equation.^{3,4} For completely dissociated electrolytes it has the form

$$A = A^\circ - Sc^{\frac{1}{2}} + Ec \log c + Jc \quad (1)$$

S , the limiting Onsager slope, and E are given by

$$S = \alpha A^\circ + \beta \quad \text{and} \quad E = E_1 A^\circ - E_2$$

where α , β , E_1 and E_2 are constants depending on solvent properties only (dielectric constant and viscosity), and on temperature.

The coefficient of the linear term, J , is similarly given by

$$J = \sigma_1 A^\circ + \sigma_2$$

where σ_1 and σ_2 are functions of the ion size parameter a (the distance of closest approach or the mean ionic diameter), in addition to viscosity, dielectric constant and temperature.

At 25°C the constants in the conduction equation are given by

$$\alpha = 159.35/D^{3/2}$$

$$\beta = 4.7779/\eta D^{1/2}$$

$$E_1 = 2.5559 \times 10^6/D^3$$

$$E_2 = 1122.3/\eta D^3$$

$$\sigma_1 = 0.4343E_1(7.133 \times 10^5 aD + 1.274 \times 10^{11} a^2 D^2 - 1.137 \times 10^{16} a^3 D^3 + 3.953 - \ln D + 2 \ln 10^8 a)$$

$$\sigma_2 = \alpha\beta + 12.757 \times 10^8 a - 0.4343E_2(4.172 - \ln D + 2 \ln 10^8 a)$$

The extended conduction equation (1) is the well-known Onsager limiting equation $A = A^\circ - Sc^{\frac{1}{2}}$, to which have been added the terms $Ec \log c$ and Jc . These represent mainly the higher terms of the relaxation effect, the leading term of which is αA° .

A convenient way to analyse the data is to use the function A' defined by

$$A' = A + Sc^{\frac{1}{2}} - Ec \log c \quad (2)$$

It follows from eqns. (1) and (2) that

$$A' = A^\circ + Jc \quad (3)$$

A plot of A' versus concentration should give a straight line with intercept A° and slope J .

In order to calculate the value of A' for each concentration, one must, however, know the value of A° (to find S and E). A simple procedure is to find a preliminary value of A° — usually by a straight line extrapolation by hand of a A versus $c^{\frac{1}{2}}$ plot — and to use this to calculate preliminary values of S and E . An extrapolation of the A' versus c plot to zero concentration then gives a more accurate value of A° , which in turn is used to calculate more accurate values of S and E . This procedure is then repeated until one gets no further change in A° . Usually two iterations are sufficient.

If the electrolyte is associated, an additional term — the association term — must be added to the conduction equation:

$$A = A^\circ - Sc_1^{\frac{1}{2}} + Ec_1 \log c_1 + Jc_1 - K_A A f_{\pm}^2 c_1 \quad (4)$$

Here K_A is the association constant, f_{\pm} is the mean ionic activity coefficient, and it can be calculated from the Debye-Hückel theory: $\log f_{\pm}^2 = -708.85 c_1^{\frac{1}{2}}/D^{3/2}$. c_1 is the concentration of ions: $c_1 = \gamma c$ where γ is the degree of dissociation. K_A and γ are related through $K_A = (1 - \gamma)/c\gamma^2 f_{\pm}^2$. When the degree of association is small, one can approximate c_1 by c .

The need to include an association term in the conduction equation is indicated by the A' plot becoming curved upwards. A graph of A'' versus c_1 , however, should be linear when A'' is defined by

$$A'' = A + Sc_1^{\frac{1}{2}} - Ec_1 \log c_1 + K_A A f_{\pm}^2 c_1 \quad (= A^\circ + Jc_1) \quad (5)$$

Fitting the experimental data to these conduction data is most conveniently done by computer. A program was developed that is essentially a modified version of the one suggested by Kay.⁵ By a least squares method the data were first fitted to the three parameter eqn. (5), and then, if the association constant is small, to the two parameter eqn. (1). From the values of the root mean square deviations one could then see which of the two conduction equations gave the better fit.

EXPERIMENTAL

Materials. Acetonitrile. Baker's reagent grade acetonitrile with a maximum water content of 0.2 % was stored over calcium hydride of mixed mesh for at least one day with intermittent shaking. After refluxing it was distilled onto phosphorus pentoxide, from which it was redistilled at once. The middle fraction of a final distillation gave a constant boiling product with a density of 0.7768 g/cm³ and a specific conductivity in the range $(0.3-1) \times 10^{-7}$ ohm⁻¹ cm⁻¹.

Water. After distillation and deionising, the water used had a specific conductivity of $(0.8-1) \times 10^{-6}$ ohm⁻¹ cm⁻¹.

The salts. Merck's suprapure rubidium iodide and potassium chloride were used without further purification, except for drying at about 400 °C in a stream of dry nitrogen.

Bridge and accessories. The bridge was a Tinsley, LCRF, type 4725 conventional a.c. bridge with an accuracy of better than 0.1 %, with a separate Wagner earth device. The signal generator (Hewlett Packard model 201 oscillator with continuous frequency control) and the oscilloscope, used as a null detector, were connected so as to display the signal as an ellipse for easy distinction between capacitative and resistive imbalance.

The cells were of pyrex glass and of conventional design.

Experimental procedure. The electrodes were of bright platinum which made the resistance markedly frequency dependent. Frequencies between 770 and 10 000 Hz were used. Plots of resistance versus frequency⁻¹ were rectilinear and could easily be extrapolated to infinite frequency. This extrapolated resistance was used to calculate the conductivity of the solution. Correction was made for the conductivity of the pure solvent, which for the solvent mixtures was about 10^{-6} ohm⁻¹ cm⁻¹.

Calibration of the cells was made with aqueous potassium chloride solutions in the concentration range 0.002 to 0.01 M. The conductivities of these solutions were calculated using the equation given by Lind, Zwolenik and Fuoss,⁸

$$\Lambda = 149.93 - 94.65c^{\frac{1}{2}} + 58.71 c \log c + 198.4c$$

All solutions were made up by weight reduced to vacuum. The concentrations in mol/

liter were calculated, assuming the densities of the solutions to be that of the pure solvent.

The densities of the solvent mixtures were determined by the conventional pycnometer method, and the viscosities by measuring the

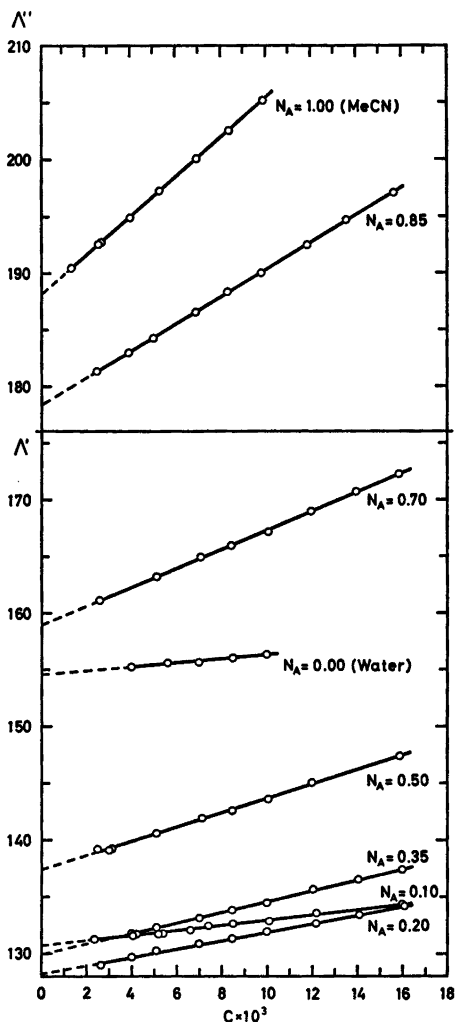


Fig. 1. A' and A'' versus c for RbI in water-acetonitrile mixtures.

Table 1. The dielectric constant (D), the viscosity (η) and the density (d) of water-acetonitrile mixtures at 25 °C.

N _A	0.00	0.10	0.20	0.35	0.50	0.70	0.85	1.00
D	78.5	70.6	62.2	53.2	47.0	41.5	38.5	36.0
η (cp)	0.890	0.970	0.864	0.698	0.552	0.431	0.371	0.347
d (g/cm ³)	0.9971	0.9611	0.9232	0.8791	0.8445	0.8080	0.7905	0.7768

Table 2. The equivalent conductance of RbI in water-acetonitrile mixtures. c in mol/l, Λ in $\text{ohm}^{-1} \text{cm}^2$.

$N_A = 0.00$		$N_A = 0.35$		$N_A = 0.85$	
$10^3 c$	Λ	$10^3 c$	Λ	$10^3 c$	Λ
2.5847	149.70	3.9739	121.00	2.5384	160.38
3.9740	148.68	5.1023	119.97	3.9519	156.01
5.5665	147.75	7.0317	118.39	5.0577	153.16
7.0328	146.76	8.4642	117.48	6.9328	149.31
8.5037	146.16	9.9614	116.55	8.4040	146.77
10.027	145.57	12.065	115.70	9.9331	144.31
		14.072	114.82	12.005	141.50
		15.982	114.06	13.770	139.56
				15.922	137.25
$N_A = 0.10$		$N_A = 0.50$		$N_A = 1.00$	
$10^3 c$	Λ	$10^3 c$	Λ	$10^3 c$	Λ
2.3559	126.32	2.5370	127.79	1.4264	172.31
4.0631	124.95	2.9894	126.61	2.6559	166.80
4.2571	124.94	3.1644	126.44	2.7987	165.98
5.1723	124.14	5.1086	123.84	4.0428	161.71
5.4212	124.03	7.0778	121.86	5.3745	158.13
6.6328	123.55	8.4653	120.43	7.1170	154.09
7.3824	123.29	10.060	119.18	8.6520	151.13
8.5146	122.75	11.999	118.13	10.156	148.85
10.086	122.06	15.920	115.81		
12.210	121.55				
16.004	120.48				
$N_A = 0.20$		$N_A = 0.70$			
$10^3 c$	Λ	$10^3 c$	Λ		
2.6285	122.54	2.6070	144.74		
4.0042	121.63	5.1230	139.23		
5.0722	121.08	7.0761	136.15		
6.9983	120.00	8.4379	134.14		
8.4583	119.25	10.066	132.03		
9.9940	118.73	11.988	130.15		
12.184	117.91	14.035	128.25		
14.051	117.43	15.912	126.62		
16.101	116.95				

flow time in an Ostwald viscometer. In both cases water was used for calibration. The density and viscosity of pure water at 25 °C were taken to be 0.9971 g/cm³ and 0.890 centipoise, respectively.⁷

The temperature was kept at 25.0 ± 0.01 °C.

For each solvent composition, 8 to 12 solutions of different concentrations of RbI were used. These were made up from three independently prepared stock solutions. Only six different solutions were used in water, for which published data for the conductance of RbI were available. Our measurements in pure water were made as a quick check on the apparatus and experimental procedure.

RESULTS AND DISCUSSION

The dielectric constant, D , the viscosity, η , and the density, d , of the eight solvents used are shown in Table 1. The solvent composition is given in terms of N_A —the mol fraction of acetonitrile. The values of the dielectric constants have been interpolated from a large scale graph of the data of Douh ret and Mor nas.⁸ Our density data agree well with the ones reported by Maslan and Stoddard Jr.⁹ No viscosity data at 25 °C could be found in the literature.

The results of the conductance measurements of rubidium iodide in the eight solvents used

Table 3. Values of the parameters in the conduction equations for RbI in water-acetonitrile mixtures.

N_A	0.00	0.10	0.20	0.35	0.50	0.70	0.85	1.00
A°	154.56 ± 0.09	130.68 ± 0.06	128.24 ± 0.09	129.99 ± 0.06	137.39 ± 0.09	158.98 ± 0.07	178.31 ± 0.16	188.02 ± 0.16
J	181 ± 13	232 ± 7	371 ± 9	464 ± 5	629 ± 11	832 ± 7	1199 ± 31	1735 ± 66
$\alpha(\text{\AA})$	2.82 ± 0.19	3.31 ± 0.11	3.98 ± 0.10	3.28 ± 0.04	3.01 ± 0.06	2.43 ± 0.02	2.57 ± 0.07	3.02 ± 0.14
K_A	—	—	—	—	—	—	2.3 ± 0.7	6.2 ± 1.1
σA	0.08	0.09	0.12	0.06	0.14	0.08	0.06	0.07

are given in Table 2. These data were analysed by the methods outlined in the introduction. For solvents with mol fraction of acetonitrile 0.70 or less, conduction eqn. (1), *i.e.* without association, gave the best fit. The Λ' plots for these systems are rectilinear and are shown in Fig. 1. For $X_A=0.85$ and 1.00, the Λ' plots showed a slight upward curvature. The deviations from straight lines were within the estimated limits of experimental errors, approximately 0.1 %, but they were systematic with positive deviations at high and low concentrations, and negative in the middle range. For these two systems, then, the data were fitted to the three parameter conduction eqn. (4), and it is the Λ'' plot that is shown on Fig. 1.

The values of Λ° , J , a , and K_A and their standard deviations are given in Table 3. The last row of the table gives the root mean square

deviation defined by $\sigma\Lambda = (\sum d_i^2/n - 2)^{\frac{1}{2}}$ and $\sigma\Lambda = (\sum d_i^2/n - 3)^{\frac{1}{2}}$, respectively, according to whether the data have been fitted to the two parameter or to the three parameter conduction equation. Here d_i is the difference between the observed Λ and the calculated Λ and n is the number of experimental points. It is seen that the $\sigma\Lambda$'s are 0.03 to 0.10 % of the values of Λ° . This shows that the self-consistency of the data is satisfactory. But there may be systematic errors (in viscosity, density, dielectric constant, bridge resistance, cell constant, *etc.*) in addition to the random errors that are reflected in the values of the root mean square deviations.

The only Λ° value which can be compared with previously reported data is the one in pure water. Robinson and Stokes⁷ have compiled a table of the most reliable (up to 1959) values of single ion conductances in water at 25°C. From their values of 77.8₁ and 76.8₄ for λ° of

Table 4. Values for the terms in the conduction equations for RbI in water-acetonitrile mixtures.

$N_A=0.10$	$\Lambda^\circ=130.68$	$S=93.74$	$E=71.7$	$J=231.5$	
10^3c (mol/l)	2.3559	5.1723	8.5146	12.210	16.004
Λ (ohm ⁻¹ cm ²)	126.32	124.14	122.75	121.55	120.48
$Sct^{\frac{1}{2}}$	4.55	6.74	8.65	10.36	11.86
$-Ec \log c$	0.44	0.85	1.26	1.68	2.06
Jc	0.54	1.20	1.97	2.83	3.71
d_i	+0.09	-0.15	+0.01	+0.08	+0.01
$N_A=0.70$	$\Lambda^\circ=158.98$	$S=266.98$	$E=417.2$	$J=832$	
10^3c (mol/l)	2.6070	5.1230	8.4379	11.988	15.912
Λ (ohm ⁻¹ cm ²)	144.74	139.23	134.14	130.15	126.62
$Sct^{\frac{1}{2}}$	13.63	19.11	24.52	29.23	33.68
$-Ec \log c$	2.81	4.90	7.30	9.61	11.94
Jc	2.17	4.27	7.02	9.98	13.25
d_i	+0.03	-0.01	-0.04	+0.03	+0.01
$N_A=1.00$	$\Lambda^\circ=188.02$	$S=368.1$	$E=780.5$	$J=1735$	$K_A=6.2$
10^3c (mol/l)	1.4264	2.7987	5.3745	7.1170	10.156
Λ (ohm ⁻¹ cm ²)	172.31	165.98	158.13	154.09	148.85
$Sct^{\frac{1}{2}}$	13.86	19.36	26.74	30.70	36.58
$-Ec_1 \log c_1$	3.15	5.52	9.38	11.71	15.46
Jc_1	2.46	4.80	9.16	12.07	17.13
$K_A \Lambda f_{\pm} c_1^{\frac{1}{2}}$	1.15	1.93	3.01	3.56	4.33
d_i	-0.01	+0.03	+0.08	-0.03	+0.07

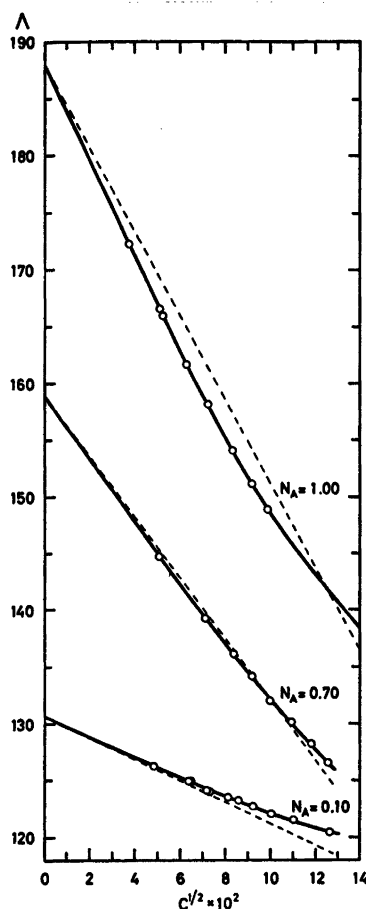


Fig. 2. Λ versus $c^{\frac{1}{2}}$ for RbI in water-acetonitrile mixtures. (---) Onsager limiting tangent. (—) Calculated from the conduction equation. (O) Experimental point.

Rb⁺ and I⁻, one gets $\Lambda^{\circ}_{\text{RbI}} = 154.6$, as compared with our 154.56. The excellent agreement — to within 0.06 % — is probably fortuitous since our measurements in water were made just as a quick check on the apparatus and experimental procedure. The value for $\Lambda^{\circ}_{\text{RbI}}$ as calculated from Kay's table,⁵ and the one reported by Fabry and Fuoss,¹⁰ are lower (about 154.1₅ and 154.0).

It is of interest to consider the magnitudes of the individual terms in the conduction eqns. (1) and (4). This is done in Table 4 for three solvent compositions, 10, 70, and 100 % acetonitrile. The first two of these have been chosen because

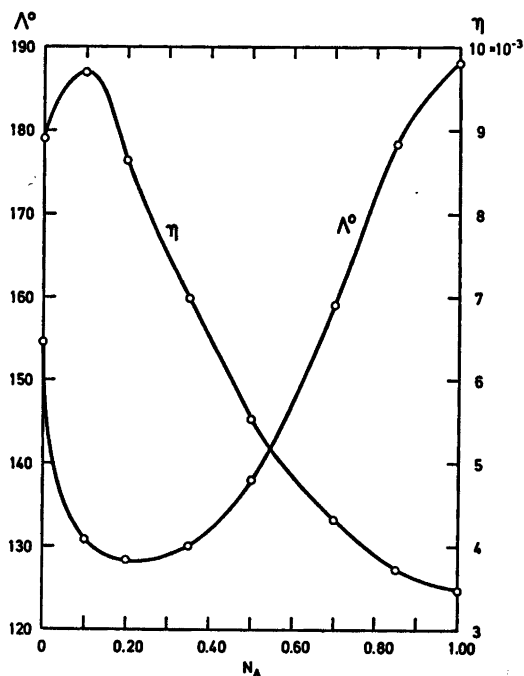


Fig. 3. Λ° for RbI and viscosity of solvent versus mol fraction of acetonitrile in water-acetonitrile solvent mixtures.

they clearly show the effect of the higher terms, *i.e.* the logarithmic and the linear terms, in the conduction eqn. (1). Of these terms, the logarithmic is negative while the linear is positive. At very low concentrations $Ec \log c$ will be numerically larger than Jc . This will be the case when $c < 10^{-4}J/E$. The points on a Λ versus $c^{\frac{1}{2}}$ plot will then lie below the Onsager limiting tangent represented by the line $\Lambda = \Lambda^{\circ} - Sc^{\frac{1}{2}}$. For $c > 10^{-4}J/E$ the points will lie above this line (see Fig. 2).

For the solvent mixture containing 10 % acetonitrile, we have $E_1 = 0.7263$, $E_2 = 23.22$, and $E = E_1\Lambda^{\circ} - E_2 = 71.70$. J was found to be 232. The concentration at which the Λ crosses the Onsager limiting tangent is then $10^{-232/71.70} = 5.8 \times 10^{-4}$ M. This is below the concentration range covered in this investigation. It becomes difficult to get accurate conductance data as one comes down to such low concentrations, because of the uncertainty in the correction for the conductivity of the pure solvent. For this solvent composition, then, all the experimental points lie above the Onsager limiting tangent.

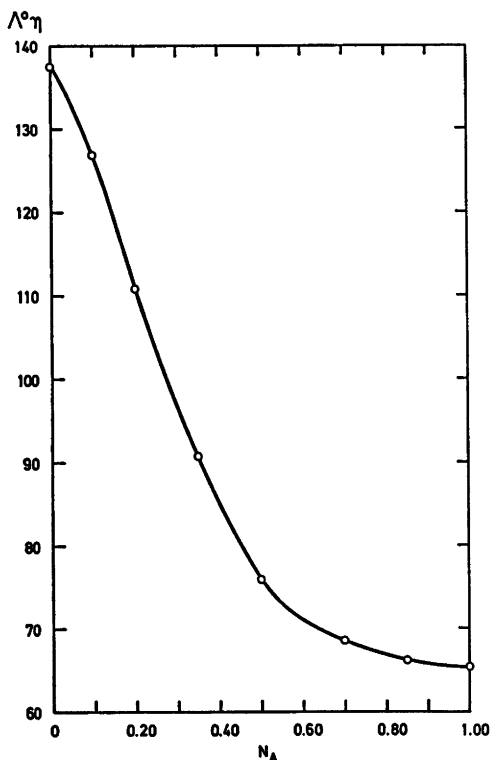


Fig. 4. $A^\circ\eta$ for RbI versus mol fraction of acetonitrile in water-acetonitrile mixtures.

For 70 % acetonitrile, however, the situation is different. Because of the lower dielectric constant and viscosity, the value of E is larger: $E = 417.2$. J was found to be 832 and the "crossing" concentration is then $10^{-832/417.2} = 1.0 \times 10^{-2}$ M, which is well within the actual working range. Fig. 2 clearly shows the difference between the 10 % and the 70 % acetonitrile mixtures in this respect.

For pure acetonitrile, a small association term had to be added to the conduction equation to get the best fit. The "crossing" concentration is still higher than in 70 % acetonitrile.

Fig. 3 shows how A° for rubidium iodide varies with solvent composition. The A° has a conspicuous minimum at about 20 mol percent acetonitrile, while the viscosity, shown in the same figure, has a maximum at about 10 mol percent. There is, then, no obvious direct relationship between A° and viscosity. The Walden product, $A^\circ\eta$, is plotted versus solvent composition in Fig. 4. It decreases

monotonically from pure water to pure acetonitrile. This shows that the model on which Stoke's law, and hence Walden's rule, is based — the sphere in a continuous viscous medium — is not valid for this system. The sharp decrease in the Walden product as acetonitrile is added to water, reflects a corresponding increase in the solute-solvent interaction (solvation). In terms of Stoke's law, the rubidium and/or the iodide ions (or rather the spheres that are hydrodynamically equivalent to these), become larger as the acetonitrile content increases. There is, however, no a priori reason why the mobilities of the two ions should be affected to the same extent by the change in solvent composition. In fact, known single ion conductances in pure water and pure acetonitrile¹¹ indicate that the rubidium ion is more affected than the iodide ion. Further comments on specific ion-solvent interaction will, however, have to wait until single ion conductances in this solvent system have been determined. Work on this is now in progress in this laboratory.

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