[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

The Dissociation Constant of Lithium Bromide in Acetone[1]

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The conductances at 25 and 35° of a series of lithium bromide solutions in acetone water mixtures, and the viscosities of these solvents at 35° have been measured. From these measurements and from the published values of the solvent viscosities at 25°, as well as the dielectric constants, the ionization constant of lithium bromide in aqueous acetone has been calculated by the Fuoss method.

The dissociation constant of lithium bromide in acetone at 18° was calculated by Kraus and Bray[2a] from the conductance measurements of Dutoit and Levrier.[2b] Their value agrees as well as could be expected with that obtained by Dippy, Jenkins and Page.[3] Neither of these groups made corrections for ionic effects.

We could find no information in the literature concerning the change in the constant as water is added to the system. Since such information was needed to interpret some kinetic experiments, we have extended the work to aqueous acetone solvents containing up to 23 weight per cent. of water.

Preparation of Materials.—Acetone was shaken intermittently for 48 hours with potassium permanganate and potassium hydroxide and then distilled, rejecting all but the middle fraction. The water content, determined in the micro laboratory of this university using the Fischer reagent, was found to be approximately 0.2 *M*.

Lithium bromide was recrystallized three times from distilled water, dried under high vacuum for two days at room temperature and then for two days at 100°. The salt was dried again at 100° immediately prior to its use. Titration of the bromide gave a result within 0.2% of the theoretical. Twice distilled water was used.

Apparatus and Experimental Procedure.—Resistances were measured with a Jones–Josephs bridge. The cell electrodes were made of bright platinum. The two cells used in this work were calibrated against each other and then against a reference cell with a large cell constant.

The 35° viscosities were measured with a Hoppler viscosimeter which was calibrated with water as a reference liquid. The temperature was controlled to 0.01°.

A conventional pycnometer fitted with a thermometer was used for the density determinations.

Stock solvents in the acetone-rich range were prepared by weighing some water into a volumetric flask and filling up to the mark with acetone, mixing, and determining the density. The water content of the acetone was taken into account in calculating the composition. The composition of the water-rich solvents was calculated directly from the weights of water and acetone used in their preparation.

Dilute lithium bromide stock solutions were prepared by weighing some salt into a volumetric flask and then adding the stock solvent to the mark.

In the conductance measurements stock salt solution and stock solvents were added to the cell and mixed. After the cell had come to the thermostat temperature, the resistance was measured. Successive increments of stock solvent were then added, the resistance being determined after each addition. The concentration of the lithium bromide was computed from the weights of the solvent and that of the dilute LiBr solution originally added. The conductance of the solvent increased from 4×10^{-8} reciprocal ohm centimeter, for the dry acetone, to 5×10^{-7} for the acetone containing 23% of water.

Experimental Results and Discussion

The calculation of the ionization constants by the Fuoss method[4] involves the dielectric constants and the viscosities of the solutions. We have used Akerlof's[5] 25° dielectric constants. The 35° constants were obtained from his results by interpolation.

The viscosities at 25° were obtained from the "International Critical Tables"; the 35° viscosities were measured in this Laboratory. Table I is a summary of these data as used in our calculations.

TABLE I

Wt. % H_2O	Density 25°	Density 35°	Viscosity × 10^3 25°	Viscosity × 10^3 35°	Dielectric constant 25°	Dielectric constant 35°
0.45	0.7849	0.7731	3.20	2.93	19.2	18.3
2.89	.7922	.7809	3.49	3.12	20.3	19.4
5.35	.7997	.7884	3.78	3.31	21.5	20.5
12.48	.8204	.8101	4.73	4.12	25.2	24.5
23.67	.8523	.8419	6.90	5.77	31.6	30.2

The dielectric constant and the viscosity for dry acetone reported in the above publications differ from the values given by Reynolds and Kraus[6] who took particular care to dry their acetone. Their density (0.7845) agrees with our measured value and is lower by about 0.4% than the value given in the "Landolt-Börnstein Tabellen." Although Reynolds and Kraus' values for the viscosity and dielectric constant of acetone are probably the more reliable, we have used the data from the "International Critical Tables" and those of Akerlof[5] for the sake of consistency.

Using the Fuoss method of calculation, F/Λ and $cf^2\,\Lambda/F$ were computed from the measured conductances and graphed in Figs. 1 and 2. From these linear plots the limiting conductances and the ionization constants were determined.

The product $\Lambda_0\eta$ is almost independent of temperature. The results are summarized in Table II.

TABLE II

Wt. % H_2O	$k_{25°}$	$k_{35°}$	$\Lambda_{0\,25°}$	$\Lambda_{0\,35°}$
0.45	2.56×10^{-4}	2.25×10^{-4}	206.6	225.7
2.89	8.52×10^{-4}	7.73×10^{-4}	159.2	179.2
5.35	1.76×10^{-3}	1.62×10^{-3}	138.9	159.5
12.48	9.5×10^{-3}	9.1×10^{-3}	102.6	119.7
23.67	8×10^{-2}	5×10^{-2}	77.9	94.9

In the water-rich solvents the limiting conductance at 25° was obtained by plotting the equivalent conductance against the square root of the LiBr concentration. The results are summarized in Table III.

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[1] This work was supported in part by the Office of Naval Research under contract 222(02) with the University of California.

[2] (a) C. A. Kraus and W. C. Bray, THIS JOURNAL, **35**, 1315 (1913). (b) P. Dutoit and A. Levrier, *J. chim. phys.*, **3**, 435 (1904).

[3] J. F. Dippy, H. O. Jenkins and J. E. Page, *J. Chem. Soc.*, 1386 (1939).

[4] R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935).

[5] G. Akerlof, *ibid.*, **54**, 4125 (1932).

[6] M. B. Reynolds and C. A. Kraus, *ibid.*, **70**, 1709 (1948).

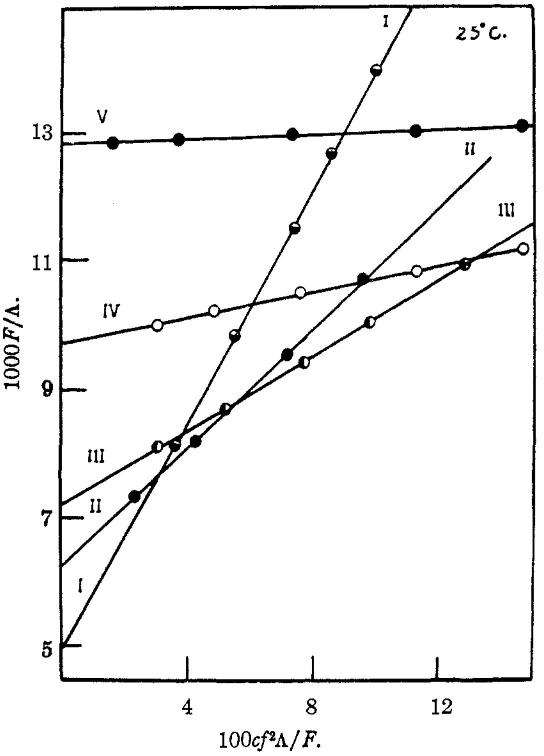

Fig. 1.—Fuoss plots for lithium bromide in aqueous acetone mixtures at 25°.

TABLE III			
Wt. % H_2O	100.0	84.0	57.8
Λ_0	118.5	86.2	64.5

In these systems the conductance of the solvent was large and the errors arising from it were appreciable. The limiting conductance of lithium bromide in water was about 1% too high.

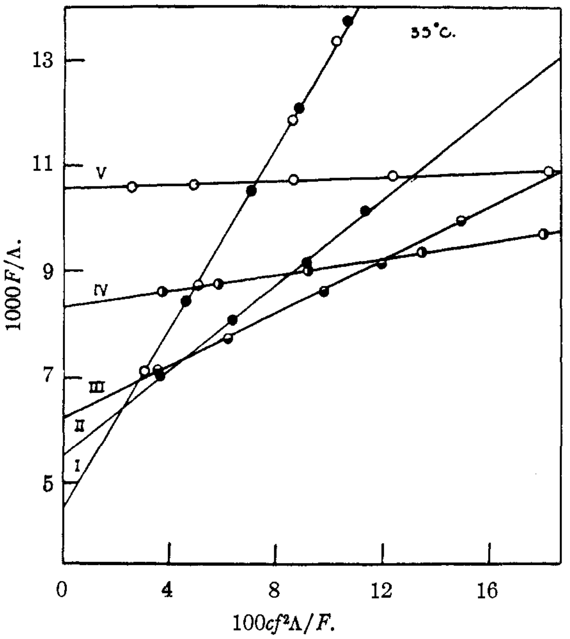

Fig. 2.—Fuoss plots for lithium bromide in aqueous acetone mixtures at 35°.

Using Bjerrum's[7] method of calculation we have determined the sum of the ionic radii, *a*, as shown in Table IV.

TABLE IV

Wt. % H_2O	$a_{25°}$	$a_{35°}$
0.45	2.28	2.50
2.89	2.50	2.73
5.35	2.62	2.79
12.48	3.33	3.61
23.67	6.17	5.59

The *a* values change gradually from slightly less than the sum of the ionic crystal radii[8] to the sum of the fully hydrated radii.

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(7) N. Bjerrum, *K. Kgl. Dansk., Vid. Selsk. Medd.*, **7**, No. 9 (1926).

(8) L. Pauling, THIS JOURNAL, **49**, 765 (1927).