Influence of the Minimum-Approach Distance between Free Ions in Predicting Small Association Constants. A Reassessment of the Bjerrum Theory

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Abstract: Electrical conductance data of KCl in methanol–*n*-butyl alcohol, methanol–methylcellosolve, and water–methylcellosolve at 25° have been examined by different forms of the conductance theory. The 1959 Fuoss–Onsager equation does not predict any association if the distance R, the minimum-approach distance between free ions, is left as an adjustable parameter. On the other hand, association is predicted if, according to Justice, the position $R = q$ for the parameter J is assumed. Calculations by the Fuoss–Hsia–Fernandez-Prini equation confirm the above for $R = q$, revealing internal consistency. The inclusion of the influence of the relaxation field on the electrophoretic effect suggested by Chen has little influence on the numerical values of the determined association constants. When these association constants are correlated with the dielectric constant of the solvent, the data comply better with the functional form of the Bjerrum theory rather than with that of Fuoss.

Electrical conductance has been widely used to calculate the degree of dissociation α of weak electrolytes. The first approximation for such purpose may be to express $\alpha = \Lambda/\Lambda_0$, namely as the ratio of the experimental conductance Λ over the limiting value Λ_0 at infinite dilution. In the above expression, the conductance of the electrolyte taken as completely dissociated, at the concentration to which α refers, is approximated to Λ_0. In other words, when the conductance of the hypothetical completely ionized electrolyte is taken as Λ_0, the variation of the ionic mobilities with concentration is neglected.

α is also related to the association constant of the electrolyte by the expression $K_A = (1 - \alpha)/\alpha^2cf_\pm^2$, where c is the stoichiometric concentration of the electrolyte and $f_\pm$ is the mean ionic coefficient.

A far better approximation results from taking the Onsager tangent[2] as the reference function to compute the degree of association. This corrects Λ_0 by the $S\sqrt{c\alpha}$ term which expresses the contribution of relaxation and electrophoretic effects at high dilution.[2] In the correction term $S\sqrt{c\alpha}$, α may be taken as Λ/Λ_0 in a first approximation, then recycled. Then

$$\alpha = \Lambda/\Lambda_i = \Lambda/(\Lambda_0 - S\sqrt{c\alpha}) \qquad \text{(I)}$$

In eq I, Λ_i is the conductance of the hypothetical completely dissociated electrolyte.

More recent conductance expressions[3] introduce transcendent terms of the concentration $Ec_i \log c_i$ and linear terms Jc_i (c_i is the ionic concentration; $c_i = c\alpha$ for a symmetrical electrolyte). Then one has

$$\alpha = \frac{\Lambda}{\Lambda_0 - S\sqrt{c\alpha} + Ec\alpha \log c\alpha + J_1c\alpha} \qquad \text{(II)}$$

The coefficient J_1 depends on the minimum distance of approach of free ions R (sometimes called d by the English school).[4] Therefore, an element of ambiguity is introduced into the calculation of α, namely the choice of R or, in other words, the definition of the distance below which ions are considered to be paired. Mathematically, since J_1 depends on R, changing R means changing the reference function that should represent the conductance of the completely dissociated electrolyte, from which α is calculated.

Numerically, the dilemma was circumvented[3] by expressing α by the two arbitrary parameters Λ_0 and R and recycling the calculations until numerical convergence was achieved. If the expression in the denominator of (II) accurately represented the functional form of the conductance, it was expected that the correct value of α would be obtained.

Recently, however, two developments have appeared which put the above method of calculation under serious challenge especially for small associations (α close to one).

First it has appeared necessary[5] to introduce a $J_2 \cdot (c\alpha)^{3/2}$ term into the conductance equation to calculate Λ_i more precisely. Therefore

$$\alpha = \frac{\Lambda}{\Lambda_0 - S\sqrt{c\alpha} + Ec\alpha \log c\alpha + J_1c\alpha - J_2(c\alpha)^{3/2}} \qquad \text{(III)}$$

where J_2 is also a function of the parameter R.

Second, it has been claimed[6a] that in computing J_1 and J_2 one should set $R = q$, namely the Bjerrum[6b] parameter $q = |Z_+Z_-|e^2/2DkT$, where Z_+ and Z_- are the ionic valences, e is the electronic charge, D is the dielectric constant of the solvent, k is the Boltzman constant, and T is the absolute temperature.

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[1] (a) This work was part of the thesis of Claudio DeRossi in partial fulfillment of the requirements for the Doctorate in Chemistry, University of Rome. (b) University of Rome; (c) Polytechnic Institute of Brooklyn.

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The use of the parameter q as the minimum-approach distance of free ions means that ions which are somewhat further apart than the "contact distance"[3] a would be counted as ion pairs. This is especially true for solutions of low dielectric constants, in which q becomes far larger than ionic dimensions. The model for ionic association is also modified. In the 1959 edition of the conductance theory[3], the parameter R was defined as the contact distance a. Ions further apart than this distance were considered as free. The Justice approach reintroduces the Bjerrum model. By setting $R = q$ as the minimum distance of free ions (or the maximum distance of existence of ion pairs), it becomes necessary to define a contact distance a between ion pairs which would then exist in the distance range $q - a$.

This modification, however, increases the "excluded volume" not available to free ions. At any concentration, the association constant calculated on this basis would then be expected to be numerically much larger.

The introduction of the J_2 term into the conductance equation corresponding to the retention of $c^{3/2}$ terms in the theoretical derivation[5] improves the precision of the determination of small association constants which might otherwise be masked in a fitting procedure by eq II. The same conclusions have been reached by Prue, *et al.*,[7a] in reanalyzing aqueous Me(II)-benzene-*m*-disulfonates. These electrolytes, classified[7b] as basically unassociated on the basis of analysis by eq II, were found to give association constants between 40 and 80 M^{-1} by eq III, including the J_2 term. The parameter R gave the best fit to the data for the value $R = 11.0 \pm 1.5$ Å, being little changed by imposing $R = q = 14.3$ Å according to Justice. On the other hand, using eq II with $J_2 = 0$, the same systems gave[7b] $K_A = 0$ and $R \cong 6$ Å.

From the above it may seem, therefore, that the classification of electrolytes as weakly associated may depend somewhat on the equations and parameters (R) chosen as references.

In order to probe into the above points, the electrolyte KCl in the solvent mixtures water–methylcellosolve, methanol–methylcellosolve, and methanol–n-butyl alcohol at 25° has been studied. In particular, the effects of taking R either as a variable parameter or equal to q and the effect of retaining the $J_2c^{3/2}$ term into the conductance equation have been examined.

Experimental Part

Materials. KCl (Merck, reagent grade) was recrystallized from conductance water five times and dried under 10^{-4} mm at 250° for 1 week. H_2O was bidistilled according to the specifications of Kraus.[8] Its average specific conductance was $X_0 = 2 \times 10^{-7}$ ohm^{-1} cm^{-1} at 25°.

Methanol was distilled three times over aluminum amalgam and used shortly after the last distillation.

n-Butyl alcohol was kept over P_2O_5 for 24 hr, filtered in a drybox in a dry N_2 atmosphere, and distilled twice in a 5-ft all-Pyrex column.

Methylcellosolve was distilled under vacuum twice (1–2 mm), taking the middle portions only.

Equipment. The conductance cell was of the erlenmeyer type of 1-l. capacity. The cell constant was measured with KCl solutions using the equation given by Fuoss.[9] Its value was $0.15565 \pm 5 \times 10^{-5}$ over ten determinations. No concentration dependence was detectable.

The bridge was of the Jones model (Leeds and Northrup). A tuned oscillator gave frequencies of 1000, 2000, 3000, and 4000 cps. The output signal was amplified and displaced on a Dumont oscillograph. The zero method was of the phase-shift type.

The oil-filled thermostat (Leeds and Northrup) had a galvanometer–photocell–thyratron thermoregulator and kept the temperature constant within $\pm 2 \times 10^{-3}$°. The temperature was measured as 25.000 ± 0.002° by a Mueller bridge connected to a Pt thermometer as a sensor device.

Procedure. The solvent mixtures were prepared by weight directly in the conductance cell. Weighed amounts of salt were added after each resistance determination was performed at the various frequencies.

The resistance results for the various mixture were plotted *vs.* $f^{-1/2}$ and extrapolated at infinite frequency in the range between 10^5 and 3×10^2 ohms. The plots were linear, indicating only polarization effects to be present. No data were taken outside these limits.

Physical Properties of the Solvent Mixtures. Densities were measured by pycnometers calibrated with water at 25.00°. The same solution was repeatedly checked (two to three times), and the average reproducibility was $\pm 5\ 10^{-5}$ g/cm^3.

Viscosities were measured by a Cannon-Ubbelohde suspended-level viscometer at 25.00 ± 0.01°. The flux times were between 200 and 500 sec and were measured with a chronometer up to 0.1 sec. The viscometer was calibrated with water and methanol to obtain the A and B constants of the equation

$$\eta = A\rho t - B(\rho/t)$$

where ρ = density and t = time of flux. $B(\rho/t)$ is the kinetic correction factor that amounted to 3–5% of the total viscosity. With the so-calibrated viscometer literature data[10] of binary mixtures, methanol–n-butyl alcohol, were reproduced to within ±0.2%.

Dielectric constants were measured by the heterodyne method (Dekatometer DK-6) at the frequency of 1 MHz. The cells were calibrated at 25° with methanol ($D = 32.63$) and nitrobenzene ($D = 34.82$).

Results and Calculations

The results for equivalent conductance Λ (ohm^{-1} centimeters^2 equivalent^{-1}) at the concentrations (moles/liter) studied are reported in Table I. The physical constants, dielectric constant, viscosity (poise), and density (grams/cubic centimeter) of the solvent mixtures are also reported in Table I.

The conductance data were tentatively analyzed by the Fuoss–Onsager equation[3] for associated electrolytes

$$\Lambda = \Lambda_0 - S\sqrt{c\alpha} + Ec\alpha \log c\alpha + J_1 c\alpha - K_A c\alpha f_\pm^2 \Lambda \quad \text{(IV)}$$

where the symbols have their usual significance.

No association was detectable by the "y–x" method,[3] the plots being parallel to the abscissa for the value of Λ_0 that linearized the function.

The analysis then proceeded by the equation for unassociated electrolytes[3]

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \log c + J_1 c \quad \text{(V)}$$

Plots of the quantity Λ' ($\Lambda + S\sqrt{c} - Ec \log c$) *vs.* c are linear, J_1 being the slope and Λ_0 the intercept with the ordinate. The results of this analysis are reported in Figure 1. Λ_0 and J_1 calculated by least-squares

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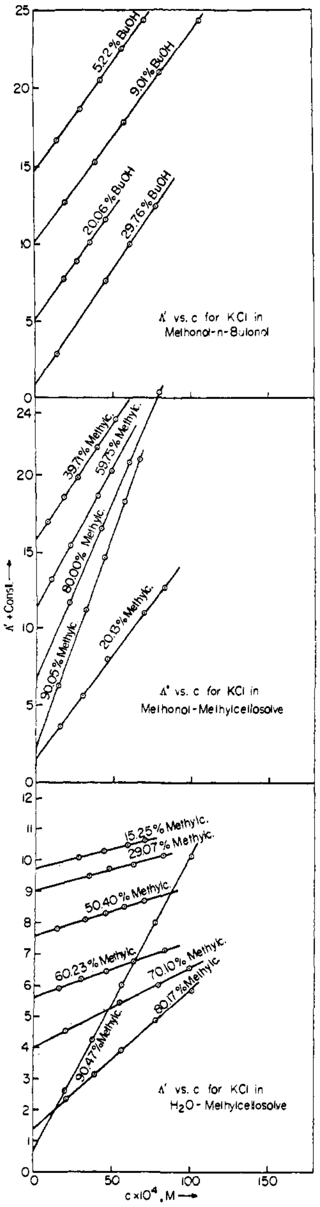

Figure 1. Plot of Λ' ($=\Lambda + S\sqrt{c} - Ec\log c$) *vs.* c for KCl in the solvent mixtures investigated at 25°.

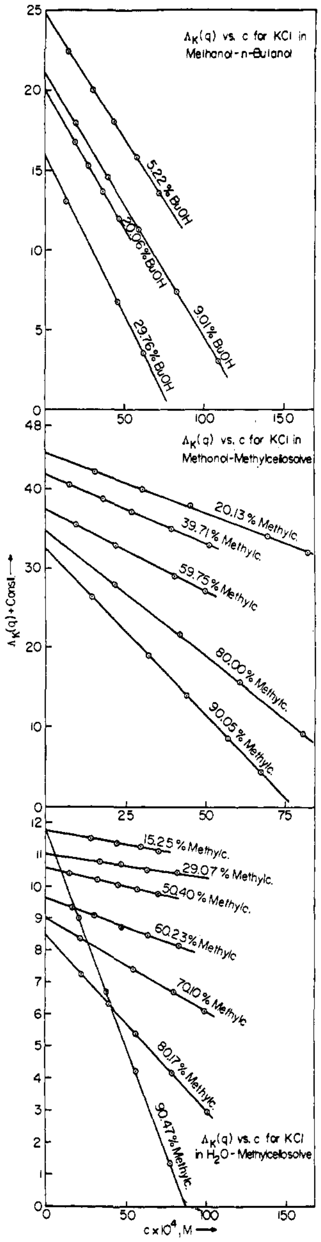

Figure 2. Plot of Λ_K ($=\Lambda' - J_1(q)c$) *vs.* c for KCl in the solvent mixtures investigated at 25°.

analysis are reported in Table II for all the systems studied.

One may notice that the R_{J_1} values are on the average of the same order of magnitude of the crystallographic distance of 3.14 Å. The difference from this figure, however, is not so large as to judge the parameter R_{J_1} to be unreasonable. Clearly, on the basis of analysis by eq IV and V, one might conclude that association in these systems is negligible.

However, by setting $R_{J_1} = q$, the situation changes. From eq IV one may write

$$\Lambda_K = \Lambda' - J_1(q)c\alpha = \Lambda_0 - K_A c\alpha\Lambda f_\pm^2$$

where $\Lambda' = \Lambda + S\sqrt{c\alpha} - Ec\alpha\log c\alpha$.

In practice for small associations, one may approximate $\alpha \approx 1$ and write[3]

$$\Lambda_K = \Lambda' - J_1(q)c = \Lambda_0 - K_A\Lambda_0 c \qquad \text{(Va)}$$

where in the last term on the right it has been approximated so that $f_\pm^2 \approx 1$ and $\Lambda \approx \Lambda_0$[3].

Plots of the quantity Λ_K *vs.* c are shown in Figure 2 for the various systems investigated.

It may be seen that the slopes of the plots are invariably different from zero. Λ_0 and K_A, calculated by least-squares analysis, are reported in Table II and called $\Lambda_0(q)$ and $K_A(q)$ for clarity.

Numerically, $K_A(q) \neq 0$ was to be expected, J_1 being an increasing function of R. By setting $R = q$, a larger quantity is subtracted from Λ' and $K_A \neq 0$. Physically the considerations of the increased excluded volume, already exposed, lead to the same expectancy, namely $K_A \neq 0$.

It seems, therefore, that it is possible to numerically fit the present data by eq V without assumptions on the value of R or by eq IV by assuming $R = q$ and $K_A \neq 0$.

However, because of the numerical approximations involved in eq Va and because of the neglect of the $J_2c^{3/2}$ term, it was our concern that the measured

Table I. Equivalent Conductance Λ ($\text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$) and Corresponding Concentration *c* (*M*) for KCl in Methanol–*n*-Butyl Alcohol, Methanol–Methylcellosolve, and Water–Methylcellosolve at 25°[a]

	Λ	$c \times 10^4$		Λ	$c \times 10^4$
		KCl in MeOH–BuOH			
5.22% BuOH			9.01% BuOH		
$D = 31.87$	90.131	14.688	$D = 31.10$	84.371	19.083
$10^2\eta = 0.572$	86.293	29.835	$10^2\eta = 0.600$	80.135	39.156
$\rho = 0.7876$	83.895	43.295	$\rho = 0.7882$	77.268	58.300
	81.878	57.160		74.713	81.941
	80.161	71.251		72.402	107.828
20.06% BuOH			29.76% BuOH		
$D = 29.40$	75.027	18.691	$D = 27.62$	67.500	13.453
$10^2\eta = 0.668$	73.150	26.692	$10^2\eta = 0.746$	61.136	45.312
$\rho = 0.7900$	71.459	35.472	$\rho = 0.7917$	59.103	61.542
	69.914	45.532		57.395	78.286
		KCl in MeOH–Methylcellosolve			
20.13% methylcellosolve			39.71% methylcellosolve		
$D = 30.75$	79.499	15.623	$D = 28.12$	68.982	7.5142
$10^2\eta = 0.648$	76.194	30.423	$10^2\eta = 0.767$	65.775	18.169
$\rho = 0.8199$	73.858	45.603	$\rho = 0.8531$	63.927	26.924
	71.087	69.676		61.935	39.607
	69.854	82.631		60.487	51.464
59.75% methylcellosolve			80.00% methylcellosolve		
$D = 25.02$	55.400	9.4101	$D = 21.05$	39.539	21.392
$10^2\eta\ 0.938$	52.313	21.935	$10^2\eta = 1.178$	36.483	41.720
$\rho = 0.8879$	49.400	40.257	$\rho = 0.9241$	34.682	60.321
	48.399	49.105		33.233	80.510
				32.252	97.679
90.05% methylcellosolve					
$D = 18.80$	34.458	14.201			
$10^2\eta = 1.344$	30.905	31.841			
$\rho = 0.9420$	29.385	43.921			
	28.145	56.852			
	27.372	66.935			
		KCl in H_2O–Methylcellosolve			
15.25% methylcellosolve			70.10% methylcellosolve		
$D = 71.20$	101.042	27.653	$D = 38.90$	35.393	20.875
$10^2\eta = 1.380$	100.192	44.233	$10^2\eta = 2.865$	33.894	54.516
$\rho = 1.007$	99.422	59.195	$\rho = 0.9955$	33.125	79.669
	99.036	70.138		32.632	99.391
29.07% methylcellosolve			80.17% methylcellosolve		
$D = 64.25$	72.787	34.379	$D = 32.00$	32.065	21.355
$10^2\eta = 1.923$	72.306	47.346	$10^2\eta = 2.595$	30.974	38.704
$\rho = 1.0047$	71.707	63.220	$\rho = 0.9865$	30.161	56.142
	71.208	82.179		29.350	78.623
				28.721	100.769
50.40% methylcellosolve			90.47% methylcellosolve		
$D = 52.10$	47.781	14.101	$D = 24.70$	29.781	20.304
$10^2\eta = 2.695$	46.916	32.118	$10^2\eta = 2.105$	28.131	37.472
$\rho = 1.0060$	46.443	45.110	$\rho = 0.9742$	26.903	56.115
	46.094	57.347		25.863	77.376
	45.755	70.180		24.999	100.804
60.23% methylcellosolve					
$D = 45.85$	40.646	15.790			
$10^2\eta = 2.885$	39.917	30.307			
$\rho = 1.0027$	39.243	46.941			
	38.737	63.849			
	38.253	83.631			

[a] The dielectric constant *D*, viscosity η (poise), and density (g/cm^3) for the various solvent mixtures (composition in wt %) are reported.

$K_A(q)$ values were numerical artifacts without physical significance.

It was then decided to reanalyze the present data by more recent and complete forms of the conductance equation, namely by the Fuoss–Hsia[5a] equation expanded by Fernandez-Prini.[5b] This form of the conductance equation when combined with the mass action law becomes

$$\Lambda = \Lambda_0 - S\sqrt{c\alpha} + Ec\alpha \log c\alpha + J_1 c\alpha - J_2(c\alpha)^{3/2} - K_A c\alpha \Lambda f_\pm^{\,2} \quad \text{(VI)}$$

Table II. Results of the Calculation for Λ_0, J_1, and R_{J_1} According to the Fuoss–Onsager Equation (Eq I)[a]

	Λ_0 (ohm^{-1} cm^2 equiv^{-1})	J_1	R_{J_1}	$\Lambda_0(q)$	$K_A(q)$
			Methanol–*n*-Butyl Alcohol		
% BuOH					
5.22	99.73 ± 0.03	1346 ± 6	3.16 ± 0.01	99.73 ± 0.03	15.66 ± 0.07
9.01	95.12 ± 0.07	1327 ± 10	3.04 ± 0.02	95.12 ± 0.07	17.64 ± 0.09
20.06	85.11 ± 0.04	1417 ± 13	3.15 ± 0.02	85.11 ± 0.04	21.23 ± 0.14
29.76	75.84 ± 0.05	1489 ± 9	3.08 ± 0.01	75.84 ± 0.05	26.47 ± 0.12
			Methanol–Methylcellosolve		
% methylcellosolve					
20.13	88.55 ± 0.16	1360 ± 29	3.30 ± 0.08	88.55 ± 0.16	17.13 ± 0.04
39.71	74.82 ± 0.03	1508 ± 9	3.42 ± 0.02	74.82 ± 0.03	23.19 ± 0.12
59.75	61.60 ± 0.03	1757 ± 8	3.51 ± 0.02	61.60 ± 0.03	35.46 ± 0.13
80.00	49.10 ± 0.18	2260 ± 3	3.33 ± 0.01	49.10 ± 0.18	66.18 ± 0.53
90.05	42.31 ± 0.04	2809 ± 9	3.52 ± 0.02	42.31 ± 0.04	98.91 ± 0.21
			Water–Methylcellosolve		
% methylcellosolve					
15.25	104.72 ± 0.08	135 ± 16	2.4$_4$ ± 0.2$_6$	104.72 ± 0.08	0.71 ± 0.15
29.07	76.02 ± 0.06	138 ± 9	2.82 ± 0.06	76.02 ± 0.06	0.95 ± 0.12
50.40	49.57 ± 0.01	160 ± 2	3.01 ± 0.03	49.57 ± 0.01	2.16 ± 0.04
60.23	42.63 ± 0.02	179 ± 3	2.76 ± 0.03	42.60 ± 0.24	3.5 ± 1.1
70.10	38.01 ± 0.02	258 ± 3	2.84 ± 0.02	38.01 ± 0.03	7.66 ± 0.07
80.17	35.42 ± 0.01	438 ± 2	3.00 ± 0.01	35.42 ± 0.01	15.30 ± 0.05
90.47	34.71 ± 0.03	944 ± 4	3.12 ± 0.01	34.71 ± 0.03	38.58 ± 0.11

[a] Results for $\Lambda_0(q)$ and $\Lambda_K(q)$ according to eq Va.

Table III. Results of the Calculations for Λ_0, J_2, R_{J_2}, and K_A According to the Fuoss–Hsia Equation in the Form Developed by Fernandez-Prini with the Position of Setting $J(q)$ and $f_{\pm}(q)$[a]

Solvent, %	$(xq\cdot\alpha^{1/2})_{\max}$	$q \times 10^8$ cm	$J_1(q)$	Λ_0, ohm^{-1} cm^2 equiv^{-1}	J_2	$R_{J_2} \times 10^8$ cm	K_A, M^{-1}	$a_K{}^B \times 10^8$ cm
				MeOH-BuOH				
5.22[b]	0.38	8.79	2908	99.93 ± 0.06	8,108 ± 262	8.3 ± 0.2	22.3 ± 0.6	4.4
9.01	0.49	9.01	3004	95.56 ± 0.20	7,748 ± 450	8.1 ± 0.5	27.8 ± 1.6	4.1
20.05	0.33	9.53	3224	85.78 ± 0.23	8,094 ± 1375	8.3 ± 1	36.4 ± 3.4	4.1
29.76	0.46	10.14	3498	76.25 ± 0.04	11,077 ± 159	9.5 ± 0.1	42.3 ± 0.6	4.4
				MeOH–Methylcellosolve				
20.13[c]	0.44	9.11	2877	88.60 ± 0.04	8,105 ± 151	8.5 ± 0.1	23.8 ± 0.5	4.7
39.71	0.39	9.96	3243	75.13 ± 0.09	9,391 ± 733	9.0 ± 0.4	36 ± 2	4.7
59.75	0.43	11.20	3886	61.81 ± 0.08	14,464 ± 591	10.9 ± 0.2	50.5 ± 2.1	5.3
80.00	0.70	13.31	5510	50.26 ± 0.09	18,251 ± 264	11.3 ± 0.1	145 ± 2	4.5
90.05	0.67	14.90	6995	44.25 ± 0.13	26,768 ± 665	12.8 ± 0.2	246 ± 5	4.6
				H_2O–Methylcellosolve				
15.25[c]	0.11	3.94	209.1	104.71 ± 0.09	(246.0)	(3.94)	0.66 ± 0.21	3.2
29.07	0.14	4.36	209.9	76.00 ± 0.06	(273.1)	(4.36)	0.84 ± 0.19	3.6
50.40	0.18	5.38	272.1	49.56 ± 0.03	451 ± 185	5.43 ± 1	2.2 ± 0.6	4.0
60.23	0.24	6.11	357.5	42.67 ± 0.08	537 ± 351	5.5 ± 2	5.4 ± 1.6	3.7
70.10	0.33	7.20	548.9	38.00 ± 0.01	1,289 ± 39	7.36 ± 0.11	8.9 ± 0.3	4.4
80.18	0.43	8.76	980	35.54 ± 0.05	2,380 ± 121	8.2 ± 0.2	23 ± 1	4.4
90.47	0.59	11.34	2283	35.31 ± 0.10	6,574 ± 252	9.9 ± 0.2	76 ± 3	4.2

[a] q is the Bjerrum parameter. $(xq\alpha^{1/2})_{\max}$ is the ratio between the Bjerrum q parameter and the Debye–Hückel radius of the ionic atmosphere at the maximum concentration studied for the various solvent mixtures. [b] Numbers represent % BuOH. [c] Numbers represent % methylcellosolve.

In particular, the parameter R was set equal to q. Equation VI is a four-parameter equation, $\Lambda = \Lambda(\Lambda_0, J_1, J_2, K_A)$. One parameter, $J_1(q)$, was fixed to its theoretical value for $R = q$. The three remaining parameters, Λ_0, J_2, and K_A, were adjusted up to convergence and best fit with the experimental value. The activity coefficient was calculated from the Debye–Hückel theory for $R = q$. An initial value of Λ_0 had to be taken to calculate preliminary values of S, E, $J_1(q)$, and α in the correction terms. An iteration process was used up to convergence. For the two water-rich mixtures, 15.25 and 29.07% methylcellosolve, values were imposed on both $J_1(q)$ and $J_2(q)$, leaving Λ_0 and K_A as adjustable parameters. A computer was used for the iteration process.

In Table III the results of this calculation are reported together with the values of q and $J_1(q)$ used for each mixture. In particular, the calculated Λ_0, J_2, and K_A are reported. It may be seen by comparing Tables II and III that the values of K_A are in fair agreement when less than ~20 M^{-1}, rapidly diverging for larger values because of the approximations in eq Va. Before proceeding with discussion of the results of Table III, however, some further comments must be made.

The question may arise of whether association would

Table IV. Results of the Same Calculation Shown in Table III with a Modified Version of the Conductance Equation Including the Chen Effect (See Text)

Solvent, %	$(xq\cdot \alpha^{1/2})_{\max}$	$q \times 10^8$ cm	$J_1(q)$	Λ_0, ohm^{-1} cm^2 equiv^{-1}	J_2	$R_{J_2} \times 10^8$ cm	K_A, M^{-1}	$a_K{}^B \times 10^8$ cm
				MeOH–n-BuOH				
5.22[a]	0.37	8.79	2449	99.86 ± 0.05	6,739 ± 208	8.4 ± 0.1	23.8 ± 0.5	4.2
9.01	0.46	9.01	2537	95.46 ± 0.14	6,456 ± 326	8.2 ± 0.2	29.1 ± 1.2	4.0
20.06	0.33	9.53	2741	85.73 ± 0.23	6,583 ± 1370	8.2 ± 0.8	38.2 ± 3.4	4.0
29.76	0.46	10.14	2991	76.17 ± 0.03	9,549 ± 137	9.7 ± 0.1	43.8 ± 0.5	4.3
				MeOH–Methylcellosolve				
20.13[b]	0.41	9.11	2442	88.53 ± 0.04	6,795 ± 137	8.6 ± 0.1	25.2 ± 0.4	4.5
39.71	0.37	9.96	2782	75.09 ± 0.06	7,770 ± 488	9.1 ± 0.3	38.2 ± 1.3	4.5
59.75	0.43	11.20	3371	61.76 ± 0.07	12,659 ± 547	11.1 ± 0.2	52.5 ± 1.9	5.2
80.00	0.70	13.31	4872	50.14 ± 0.05	16,141 ±153	11.4 ± 0.1	144 ± 1.3	4.5
90.05	0.67	14.90	6259	44.17 ± 0.09	23,983 ± 436	13.0 ± 0.1	245 ± 3.5	4.6
				H_2O–Methylcellosolve				
15.25[b]	0.11	3.94	(188.4)	104.69 ± 0.1	(202.7)	(3.94)	0.82 ± 0.2	3.0
29.07	0.14	4.36	(189.3)	75.99 ± 0.06	(228.9)	(4.36)	1.02 ± 0.2	3.4
50.40	0.18	5.38	245.6	49.55 ± 0.02	362 ± 132	5.3 ± 0.9	2.6 ± 0.4	3.8
60.23	0.24	6.11	322.4	42.66 ± 0.06	431 ± 247	5.3 ± 1.5	5.9 ± 1.1	3.6
70.10	0.33	7.20	494.1	37.98 ± 0.01	1,142 ± 36	7.5 ± 0.1	9.5 ± 0.2	4.2
80.17	0.43	8.76	879.2	35.51 ± 0.03	2,101 ± 80	8.3 ± 0.2	23.3 ± 0.7	4.3
90.47	0.59	11.34	2044	35.27 ± 0.06	5,845 ± 165	10.1 ± 1.8	76.7 ± 0.8	4.2

[a] Numbers represent % n-BuOH. [b] Numbers represent % methylcellosolve.

have appeared if instead of setting $R = q$ one would have left R as an adjustable parameter. This type of analysis on the conductance data of alkali halides in methanol–n-butyl alcohol has been carried by Singh and Aggarwal[11a] by the use of the Onsager–Fuoss–Skinner[11b] equation of 1965. In this equation the exponential of the relaxation term was fully retained without a truncated series expansion. Terms up to the first power of c were retained. It is worthwhile noting that these authors found association for KCl in these mixtures with values comparable with the ones obtained by eq Va as shown above and R = 4.5 ± 0.4 Å.

Also, objections could be raised for having neglected in the above analysis[4] by eq VI some very recent developments in the conductance theory, namely the influence of the relaxation field on the elctrophoretic effect, discovered by Chen.[12] This effect modifies the coefficient $E = E_1\Lambda_0 - E_2$ of the transcendental term into $E = E_1\Lambda_0 - 2E_2$. It also affects the numerical values of both the J_1 and J_2 coefficients.[13] We have, therefore, used a third equation of conductance to analyze the data. This equation, which has been recently used by Treiner and Justice,[13] includes the above effects. (The authors are indebted to Dr. Justice for allowing its use, before publication, as a private communication.)

In this equation of the same functional form as formula VI, S is the same term as in the Fuoss–Onsager theory[3] and $E = E_1\Lambda_0 - 2E_2$, where E_1 and E_2 are the same terms as before.[3] $J_1 = \sigma_1\Lambda_0 + \sigma_2$ and $J_2 = \sigma_3\Lambda_0 + \sigma_4$, where

$$\sigma_1 = 2E_1'\left(\frac{2b^2 + 2b - 1}{b^3} + 0.9074 + \ln \frac{xR}{c^{1/2}}\right)$$

$$\sigma_2 = E_2'\left(\frac{35}{3b} + \frac{2}{b^2} - 2.0689 - 4 \ln \frac{xR}{c^{1/2}}\right)$$

$$\sigma_3 = \frac{xR}{c^{1/2}}E_1'\left(0.6094 + \frac{4.4748}{b} + \frac{3.8284}{b^2}\right)$$

$$\sigma_4 = \frac{xR}{c^{1/2}}E_2'\left(-1.3693 + \frac{34}{3b} - \frac{2}{b^2}\right)$$

where

$$E_1' = x^2R^2b^2/24c$$

$$E_2' = xRb\beta/16c^{1/2}$$

In the above, the symbols have the same significance as in the Fuoss monograph.[3] In particular, the parameter R has been set equal to q, the Bjerrum parameter, as done above for the analysis by the Fernandez-Prini equation.[5b]

The results of this analysis are reported in Table IV. It may be seen that the numerical values of the parameters Λ_0, R_{J_2}, and K_A are comparable to the ones reported in Table III within the reported standard errors in most of the cases.

The insensitivity of the parameters to the inclusion of the Chen effect[12] means that it is of little consequence to the numerical values of Λ_0, J_2, and K_A as determined by the Fernandez-Prini[5b] equation.

In the following a discussion of the calculated values of the parameter Λ_0, J_2, and K_A from Table III is presented.

Discussion

From a comparison of Table II with Tables III and IV, it may be seen that the value of Λ_0 is somewhat dependent by the equations and parameter R used. The changes are outside the experimental error in Λ.

Second, one may see that the R's calculated from J_2 found by the Justice method[6a] follow the trend of the numerical value of q with solvent composition (Tables III and IV), namely increasing with a decrease in dielectric constant, although the reproduction of

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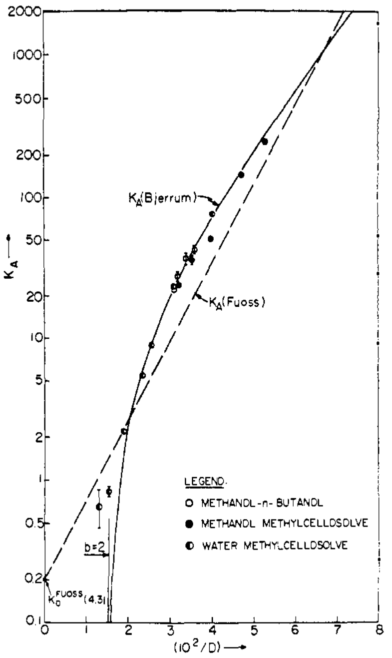

Figure 3. Log K_A *vs.* $1/D$ for KCl in the solvent mixtures investigated. The solid line is the calculated Bjerrum function for the contact distance $a = 4.3$ Å. The dashed line is the corresponding Fuoss function for $a = 4.3$ Å.

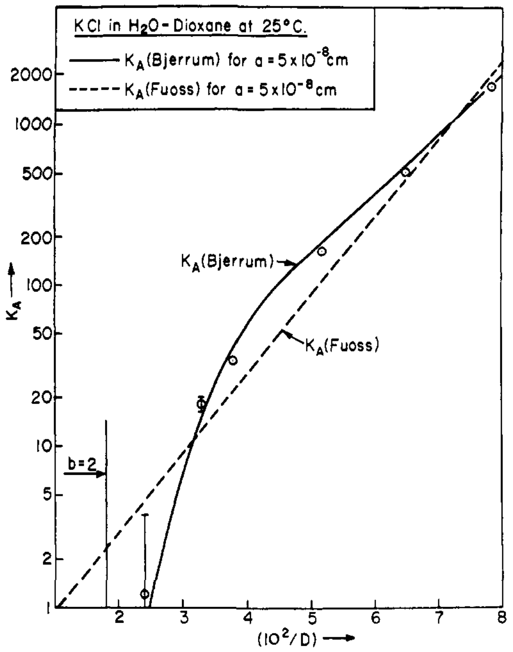

Figure 4. Log K_A *vs.* $1/D$ for KCl in H_2O-dioxane at 25°. The solid line is the calculated Bjerrum function for the contact distance $a = 5$ Å. The dashed line is the corresponding Fuoss function for $a = 5$ Å.

the value of q is poor. Objections could be raised on the theoretical consistency of having taken $R = q$ in the calculation of J_1. The equation of motion was integrated[3] with the boundary condition that the hydrodynamic radius had to be equal to a, the contact distance between ions. The above calculation shows, however, that, at least internally, there is consistency; namely, choosing $J_1 = J_1(q)$ one gets a numerical value of J_2 which gives $R_{J_2} \approx q$ within a large scatter.

It is also of interest to investigate whether the calculated association constants are internally consistent.

The results of K_A may be correlated in two ways. One may assume the validity of the Bjerrum theory,[6a] and from the reported K_A and the function

$$K_A(\text{Bjerrum}) = \frac{4\pi N}{1000}\int_{a_K{}^B}^{q} r^2 \exp\left(\frac{|Z_+Z_-|e^2}{rDkT}\right)dr \quad \text{(VII)}$$

calculate $a_K{}^B$, namely the minimum distance of approach of ion pairs, or the contact distance. These calculated values are reported in Tables III and IV. It may be seen that they are on the average equal to 4.3 ± 0.5 and 4.1 ± 0.5 Å, respectively, for the two forms of eq VI used in this analysis. These are reasonable values compared to the crystallographic distance between K^+ and Cl^- of 3.14 Å and compared to the results by eq V reported in Table II.

Even more convincing evidence of the internal consistency of the calculated K_A's may be achieved by plotting the data for K_A as log K_A *vs.* $1/D$, as shown in Figure 3. Within the experimental error, all the points are on the same concave-down line. The data used are from Table III. Using the data from Table IV the same result is obtained.

This puzzling behavior of the concavity of the log K_A *vs.* $1/D$ plot has also been observed by other investigators in systems as different from the present one as 2:2 electrolytes.[14] It is noteworthy that such a result cannot be explained by the Fuoss association theory[15]

$$K(\text{Fuoss}) = \frac{4\pi Na^3}{3000}\exp(b) = \frac{4\pi Na^3}{3000}\exp\left(\frac{|Z_+Z_-|e^2}{aDkT}\right) \quad \text{(VIII)}$$

unless one assumes a continuous change of a with composition of the solvent, namely some solvation effect. (Alternatively, one may add an ion solvent term into eq VIII.)

It is also noteworthy that by retaining the Bjerrum function there is no need of invoking nonelectrostatic effects. Indeed, the solid line in Figure 3 has been calculated with the Bjerrum function setting $a_K{}^B = 4.3$ Å. It may be seen that the points conform to the required curvature and K_A seems to tend asymptotically to zero for a dielectric constant corresponding to $b = 2$, as indicated in Figure 3. It might be said that the argument is circular, since having set $R_J = q$ one has already bound the results for K_A to a model. However, if one plots, for instance, the data of Fuoss and Lind[16] for KCl in water–dioxane on a similar graph (Figure 4), one may see that the same curvature appears, the data for K_A being comparable to ours.

The fitting of the Bjerrum function in Figure 4 has been obtained with $a_K{}^B = 5$ Å. For this system, these authors[16] used an incomplete functional form for J_2 and dealt with R_J as an adjustable parameter. The numerical difference between our association constants and the one for this system is due to this different treatment. Justice,[17] in fact, reanalyzed these data by setting $R_{J_1} = q$ with the J_2 coefficient used as

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Table V. Experimental K_A, K_A(Fuoss), and K_A(Bjerrum) for $a = 4.3$ Å[a]

Solvent	D	K_A	K_A^F	$\Delta K_A^F/K_A$, %	K_A^B	$\Delta K_A^B/K_A$, %
MeOH–BuOH	31.87	22.3 ± 0.6	12.0	−46.2	23.4	+4.9
	31.10	27.8 ± 1.6	13.2	−52.5	26.1	−6.1
	29.40	36.4 ± 3.4	16.8	−53.8	33.5	−8.0
	27.62	42.3 ± 0.6	22.6	−87.1	44.9	−6.2
MeOH–methylcellosolve	30.75	23.8 ± 0.5	13.9	−41.6	27.4	+15.1
	28.12	36 ± 2	20.5	−43.1	40.7	+13.1
	25.02	50.5 ± 2.1	36.7	−27.3	69.7	+38.0
	21.05	145 ± 2	97.8	−32.5	160	+10.3
	18.80	246 ± 5	205	−16.7	280	+13.8
H_2O–methylcellosolve	71.20	0.66 ± 0.21	1.25	−89.5	0	−100
	64.25	0.84 ± 0.19	1.51	+79.7	0.10	−88.1
	52.10	2.2 ± 0.6	2.44	+10.9	1.65	−25
	45.85	5.4 ± 1.6	3.43	−36.5	3.86	−28.5
	38.90	8.9 ± 0.3	5.71	−35.8	9.28	+4.3
	32.00	23 ± 1	11.7	−49.1	23.1	+0.4
	24.70	76 ± 3	39.4	−48.1	74.2	−2.3

[a] $\Delta K_A/K_A$ (%), $\Delta K_A = K_A(\text{calcd}) - K_A(\text{obsd})$. K_A(calcd) is either K_A(Fuoss) or K_A(Bjerrum) for $a = 4.3$ Å.

an "experimental" parameter, as done in this work. He could fit the log K_A *vs.* $1/D$ plot by the Bjerrum equation with $a_K{}^B = 4.5$ Å, a value within the standard error of the ones obtained by us for the present systems; namely, $a_K{}^B = 4.3 \pm 0.5$ or 4.1 ± 0.5 Å.

One may also see from Figure 3 that if the Fuoss function (eq VIII) is retained as the valid correlation function between K_A and $1/D$ then a straight line would result, with slope

$$\frac{\text{d} \log K_A(\text{Fuoss})}{\text{d}(1/D)} = 0.4343\frac{|Z_+Z_-|e^2}{akT} \qquad \text{(IX)}$$

The intercept with the ordinate corresponding to a medium where $D \rightarrow \infty$ would be $K_0(\text{Fuoss}) = (4\pi Na^3/3000)$ (as indicated in Figure 3), namely the association constant due to molecular collision between neutral particles. In Figure 3, the Fuoss function (eq VIII) calculated for $a = 4.3$ Å is shown as a dashed line. It may be seen that the data for the present work seem on the average to comply better with the Bjerrum function than with the Fuoss one. The same seems to be true for the data shown in Figure 4 for KCl in H_2O–dioxane.[16]

This is also shown in Table V, where the quantities $(\Delta K_A/K_A)$ (%) are reported; $\Delta K_A = K_A(\text{calcd}) - K_A(\text{obsd})$. K_A(obsd) values are from Table III, whereas K_A(calcd) is either the Fuoss or the Bjerrum function calculated for $a = 4.3$ Å. The $(\Delta K_A/K_A)$ (%) values are on the average smaller for the Bjerrum function.

Although the two theories are based on different models, a mathematical comparison is possible. For large b one may write

$$K_A(\text{Bjerrum}) = \frac{4\pi Na^3}{1000}b^3Q(b) \approx \frac{4\pi Na^3}{1000}\frac{e^b}{b} \qquad \text{(X)}$$

Comparing this function with eq VIII, for large b, it has been suggested[3] that $(e^b/b) \approx e^b$. It has also been suggested[3] that for large b, or low dielectric constants, the two functions become numerically comparable given $(e^b/3) \approx (e^b/b) \approx e^b$.

For small b, the two functions diverge, the Fuoss function leading to $(4\pi Na^3/3000)$, the Bjerrum function converging to zero for $b = 2$. One might also inquire about the theoretical reasons for the numerical agreements for large b between the two theories based on different models. According to Fuoss, following Denison and Ramsey,[18] ions are taken *either* at contact distance a as associated, *or* so distant that their Coulombic mutual potential $(|Z_+Z_-|e^2/rD)$ is small with respect to kT. This is also roughly true for the Bjerrum theory for small dielectric constants or large b. Indeed, Pikal[19] has calculated the average ion-pair distance $\langle r_{\text{ip}}\rangle$ according to the Bjerrum distribution function as shown in eq XI with $\beta = |Z_+Z_-|e^2/DkT$. For large b, $\langle r_{\text{ip}}\rangle \simeq a[1 + 1/b] \simeq a$.

$$\langle r_{\text{ip}}\rangle = \frac{\int_a^q e^{\beta/r}r^3\text{d}r}{\int_a^q e^{\beta/r}r^2\text{d}r} \qquad \text{(XI)}$$

This means that the ions are on the average close to their contact distance a in accord with Fuoss and Denison and Ramsey[18] only for large b, when in fact the Bjerrum and Fuoss theories are in rough agreement. The above is not true, however, according to (XI), for larger dielectric constants, where b decreases and the electrostatic energy $|Z_+Z_-|e^2/rD$ becomes comparable to kT. Denison and Ramsey[18] stated that under this last condition their theory was only an approximation to the more rigorous Bjerrum one.

Conclusions

The above conductance analysis shows the possibility of arriving at conflicting results about the state of association of an electrolyte in solution by using different equations and distance parameters R. In particular, the 1959 conductance equation seems particularly affected by these ambiguities. Because of its admitted incomplete theoretical derivation, it should be abandoned. All the other, more precise, equations, namely the 1965 equation by Fuoss, Onsager, and Skinner,[11b] the Fernandez-Prini[5b] equation, or the more recent equation[13] including the Chen effect,[12] predict association, although the exact value of it depends also on the chosen distance parameter R (either the one which gives the best fit or $R = q$).

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Only when the association is very large ($K_A \geqslant 1000$ M^{-1}) do the results become insensitive to the parameters used. On the other hand, in this case, one may resort to use of eq I or the corresponding Fuoss–Kraus[20] or Shedlowsky[21] methods without retention of the $Ec\alpha \log c\alpha$, $J_1 c\alpha$, and $J_2(c\alpha)^{3/2}$ terms.

Analysis by the Justice method,[6a] setting $R = q$, although inconsistent with some of the derivations of the theory, gives internally consistent results in terms of the model assumed. In particular, the significance of the Bjerrum parameter q is well founded on statistical mechanical grounds.[22] The ionic distribution function shows a minimum for $R = q$, a maximum for the distance x^{-1} (the Debye atmosphere distance or average distance), and increases at shorter distances toward a. If the positions $J_1(q)$, $J_2(q)$, and $f_\pm(q)$ are correct, this would make eq III a one-parameter equation in Λ_0 and the calculations of association constants through conductance data an unambiguous process.

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Theoretical Studies of the Low-Lying Electronic States of NH_2^+ and CH_2[1]

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Abstract: Nonempirical configuration-interaction wave functions constructed from Gaussian basis functions are used to study the $^3B_1$, $^1B_1$, $^1A_1$, and $^1A_1{}^*$ states of the isoelectronic systems NH_2^+ and CH_2. The $^3B_1$ state is predicted to have a minimum-energy configuration at a bond angle of 130° for CH_2 and 140° for NH_2^+. For the $^1A_1$ state, the optimal bond angle is predicted to be 120° for NH_2^+ and 100° for CH_2. The calculated singlet–triplet energy separation ($^3B_1 - {}^1A_1$) is 1.56 eV for NH_2^+ and 0.88 eV for CH_2. Investigation of the correlation diagrams for the formation of CH_2 from the photolysis of diazomethane suggest that CH_2 is probably formed initially in the $^1A_1{}^*$ state. Since this state is predicted to be only 1.92 eV above the lower $^1A_1$ state, the possibility that the $^1A_1{}^*$ state is responsible for the stereospecific addition of CH_2 to olefins is proposed.

The importance of carbonium ions in organic chemistry has been recognized for several years;[2] however, it is only recently that the nitrogen analog, the nitrenium ion, has been established as a useful intermediate in a variety of chemical reactions.[3] The purpose of this paper is to report nonempirical quantum mechanical studies of the low-lying electronic states of the simplest nitrenium ion, NH_2^+. To our knowledge there is no direct experimental information on these states, so it is hoped that these theoretical predictions will be valuable in providing a better theoretical basis for the understanding of nitrenium ion chemistry.

As with most quantum mechanical studies, one is faced with the problem of estimating the accuracy of the calculations. To minimize this difficulty, we have carried out parallel calculations for both NH_2^+ and CH_2. Comparison of these two systems should not be taken to imply that one should expect the chemistry of these two species to be the same. In fact, Gassman[3] has pointed out that nitrenium ion chemistry is similar to carbonium ion chemistry. It appears that the presence of the positive charge plays a significant role in the chemistry of these species. To our knowledge, nitrenium ions do not exhibit carbene-like behavior.[4] Nevertheless, the electronic structure of the low-lying states of NH_2^+ and CH_2 are quite similar, and for this reason it is felt that the earlier theoretical and experimental data on CH_2 could be used to calibrate our results for CH_2 and NH_2^+.

In the case of methylene, there have been numerous theoretical studies of the ground state and several low-lying states. It is interesting to note that the accuracy of the theoretical calculations on CH_2 is such that they prompted Herzberg and Johns[5] to reinterpret the vacuum ultraviolet spectrum in terms of the predicted bent form for the $^3B_1$ ground state. In the early work by Herzberg,[6] this state was thought to be linear or nearly linear. However, most theoretical studies of this state predicted a bond angle considerably less than 180°. In Table I a number of the theoretically predicted bond angles are presented. From this table, it is clear that most of these theoretical studies are in good agreement with the rather extensive configuration-interaction calculations of

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