

Pressure Effect on Conductivity in Solution of Two Quaternary Ammonium Iodides

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Conductance data are reported for methyl pyridinium iodide in acetone as a function of concentration at 50°C and pressures up to 9000 atm. Similar data, all at 30°C, are presented for tri-*n*-propyl methyl ammonium iodide in acetone to 9000 atm in dichloromethane, cyclohexanone, propionitrile, and nitromethane to 2000 atm, and in nitrobenzene to 1000 atm. The limiting equivalent conductance has been calculated and the Walden products determined for both salts in acetone and for the latter salt in three additional solvents. The Walden product was relatively constant from solvent to solvent at 1 atm, but decreased somewhat with increasing pressure.

The effect of solvent properties on conductance in ionic solutions has long been an important subject of investigation. In this work we present new experimental data for the conductivity in solution of two quaternary ammonium salts in nonaqueous solvents as a function of pressure and concentration. Measurements were made for methyl pyridinium iodide and tri-*n*-propyl methyl ammonium iodide in acetone up to 9000 atm at concentrations up to about 0.02*N*. For the latter salt the behavior in five other aprotic solvents was investigated over a similar range of concentrations but a smaller pressure range.

These data were obtained in conjunction with the development of a conductivity technique for investigating the kinetics of Menshutkin reactions under pressure (17), but they should also prove quite useful for investigators studying theories of ionic conduction in solution at high pressures. Recently, similar work on related systems has been reported by several authors (2-4, 19, 20).

EXPERIMENTAL

Materials. *Methyl pyridinium iodide (MPI)* was prepared by refluxing purified pyridine with purified methyl iodide in acetone for 48 hr and precipitation from the solution on chilling. The MPI was then recrystallized twice from acetone, dried under vacuum at 30°C for two days, and stored in a desiccator in the dark. No melting point could be measured since this salt decomposes on heating, but microanalysis gave C, 33.06%; H, 3.90%; N, 6.22%; I, 57.08%. Theoretical: 32.60, 3.65, 6.34, 57.41. This result, well within the limits of precision of the microanalysis, certified that the compound prepared was MPI as expected but did not give a good quantitative measure of its purity.

The best available criterion of purity for this salt was titration of gravimetrically prepared solutions of the salt for the iodide ion. The method described by Perrin et al. (16) was used. First, any organic molecular iodide compound present, such as residual methyl iodide, was extracted from the solution, and titration with AgNO₃ followed. The end point was observed potentiometrically, using the second derivative method, on a Sargent-Malmstadt titrator. In every case the result of the titration agreed with the nominal concentration determined from the weighing within experimental error, estimated to be $\pm 0.5\%$.

*Tri-*n*-propyl methyl ammonium iodide (TPMAI)* was pre-

pared by reacting purified tri-*n*-propyl amine with purified methyl iodide in nitrobenzene and recovering the product by filtration. The product was washed several times with acetone to remove the nitrobenzene, recrystallized from acetone, and dried in a vacuum oven. Before use, TPMAI was again recrystallized from acetone and dried under vacuum at 60°C for 24 hr. The melting point of the final product was 204.5°C. However, the melting point was not sharp as the product began to decompose. The TPMAI was stored in the dark at 0°C. Microanalysis of this salt gave C, 42.54%; H, 8.61%; N, 4.84%; I, 43.74%. Theoretical: 42.11, 8.48, 4.91, 44.50.

The purity was verified by titration in the same manner as the MPI.

Acetone was treated with 4 grams of AgNO₃ in 30 ml H₂O for each liter. Then 30 ml of 1*M* NaOH were added, and the acetone was shaken for 10 min, filtered, and predried with CaSO₄ while stirring overnight. The acetone was distilled from fresh CaSO₄ in a 1-m column packed with nichrome helices (about 36 theoretical plates), and the middle 60% kept had a boiling point range of 0.2°C. The acetone was stored in a glass bottle sealed with a rubber stopper.

Dichloromethane, shaken with portions of concentrated H₂SO₄ until the acid layer remained colorless, was washed with distilled water, 5% Na₂CO₃ solution, and again with distilled water. The dichloromethane was predried with CaCl₂ and distilled from CaSO₄ in the same column used for acetone. The boiling point range of the fraction kept was 0.2°C.

Cyclohexanone was treated with portions of dilute KMnO₄ solution, filtered, dried with Linde 13X Molecular Sieves, and distilled at atmospheric pressure in the same column used for acetone. The fraction kept had a boiling point range of 0.2°C.

Propionitrile, shaken with concentrated HCl until the smell of isonitrile had gone, was washed with distilled water, a 5% solution of K₂CO₃, and again with water. After preliminary drying with Linde 4A molecular sieves, it was stirred with CaH₂ until the evolution of hydrogen ceased. The propionitrile was decanted from the CaH₂, distilled from P₂O₅ (5 g/l.), and finally refluxed with and distilled from CaH₂ (5 g/l.) while under nitrogen to ensure exclusion of water. Only the middle 60% was retained for use.

Nitrobenzene was extracted with 2*M* NaOH, washed with distilled water, shaken with dilute HCl, again washed with distilled water, and dried with CaSO₄. Distillation was in a 1.5-m column packed with nichrome helices (50 theoretical plates) at 4-5 mm Hg (65-72°C) under nitrogen, and heating lasted no more than 8 hr. The first 10% and last 30% of the distillate were discarded. The nitrobenzene was stored in brown glass bottles at 0°C in contact with CaH₂.

Nitromethane, washed with portions of concentrated H₂SO₄ until the acid layer remained colorless, was then washed with

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Table I. Equivalent Conductance of Methyl Pyridinium Iodide at 50.00°C

P = Pressure, atm
 Λ = Equiv conductance, mho-cm²/mol
 c = Concn, mol/l. $\cdot 10^4$

Pressure	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ
Acetone										
1	9.55	198.3	19.11	175.7	47.78	145.4	95.57	196.9		
500	10.13	137.2	20.27	127.5	50.69	107.2	101.4	152.1		
1000	10.52	104.2	21.05	99.75	52.63	90.24	105.3	116.2		
1500	10.82	90.05	21.64	81.74	54.12	72.88	108.2	89.73		
2000	11.06	82.92	22.13	67.18	55.34	69.66	110.7	70.79		
3000	15.78	78.10	38.71	64.82	67.63	57.12	121.8	49.74	169.4	39.48
4000	16.22	63.05	39.79	52.85	69.51	46.69	125.2	36.86	174.1	32.89
5000	16.59	52.63	40.69	43.64	71.09	38.76	128.0	30.54	178.1	26.48
6000	16.91	44.25	41.47	35.53	72.46	32.83	130.5	23.02	181.5	19.83
7000	17.19	32.10	42.17	26.16	73.67	22.66	132.6	17.80	184.6	14.98
8000	17.45	26.00	42.80	20.46	74.77	16.48	134.6	13.89	187.3	11.86
9000	17.69	20.00	43.37	14.67	75.77	12.11	136.4	11.24	189.8	9.79

distilled water, 5% aqueous Na₂CO₃, and again with water. By stirring overnight, the nitromethane was predried with MgSO₄ and then distilled from CaSO₄ in the column used for acetone. The boiling point range of the fraction kept was 0.4°C. Nitromethane was stored at 0°C in brown glass bottles.

Apparatus. The high-pressure apparatus included an autofretted pressure vessel and pressure-generating system made by Harwood Engineering Co. The vessel, rated at 200,000 psi, had a working volume 6 in. long by 1.5 in. diameter and was thermostated in a 25-gal oil bath with temperature controlled and measured to $\pm 0.02^\circ\text{C}$. The pressure-generating system consisted of two Enerpac hand pumps, an intensifier, and check valves. Pressures were measured by a calibrated Heise gauge at lower pressures and a manganin coil with a Carey-Foster bridge at higher pressures. Measured pressures are accurate to ± 2 atm up to 2000 atm, to ± 3 atm up to 6000 atm, and to ± 7 atm at higher pressures. A more detailed description of the high pressure system has been given elsewhere (18).

The conductivity cell was a Teflon piston and cylinder arrangement, the same used for kinetic measurements. The cavity was about 10 cm long by about 1.1 cm i.d., and platinum flags about 0.9 cm square rested in shallow (0.02 cm) grooves on opposite sides of the cylinder. Platinum wire leads were welded to these electrodes and pushed through undersized holes in the cylinder wall to give an excellent seal.

The pistons were carefully machined and fitted for each run to slide at an applied force between 200–300 grams, which was satisfactory to prevent leaks without any irreversible deformation of the conductivity cell. Each piston was tapped for a small Teflon-covered screw for convenience in loading.

Conductivities were measured by a Beckman Model RC-18 conductivity bridge equipped with a Wagner ground, and capacitance was added to balance the circuit. The manufacturer's claim of an accuracy of 0.1% or better, was valid throughout the range used in this work by calibrations with resistance standards.

The Teflon cell was definitely compressible, and the cell constant was a slight function of pressure. Calibration measurements were made for the conductance of 0.01N KCl in water, and the results compared with the recent data of Hensel and Franck (12). The cell constant decreased with pressure with a maximum change under the conditions used of less than 4%. The cells used had cell constants at 30°C, 1 atm, ranging from 0.961–0.993.

Procedure. Before each series of determinations, the electrodes in the cell were blacked by immersing them in a chloroplatinic acid solution and running a mild current between them.

For each solvent and salt, a series of about four solutions was

prepared gravimetrically (on a Mettler H6 single-pan balance) and stored in sealed glass flasks in a refrigerator until use. For each series the concentration range was chosen to maximize the accuracy obtainable from the cell and conductivity bridge. The concentration of each solution was verified by titration and was correct within experimental error, which served as an additional check on the purity of the salts.

Before each use the cell was thoroughly rinsed with pure acetone and dried with nitrogen. It was assembled and loaded by syringe through the small hole in the piston, care being taken to avoid air bubbles. After the loaded cell was sealed into the thermostated pressure vessel, readings were taken over a range of pressures, and ample time was allowed to dissipate the heat of compression after each pressure rise. The thermal characteristics of this high pressure vessel had previously been determined by putting a thermocouple inside a cell within the bomb and observing the rate of temperature decay after the heating from rapid compression. The thermal half-life was found to vary from about 3 min at low pressures to over 5 min at the highest pressures. Thus, for thermal equilibration 45–90 min, depending on pressure, was necessary.

RESULTS

Conductance measurements were made for MPI in acetone at 50.00°C at pressures to 9000 atm. Experimental results are given in Table I. Similar data were obtained at 30.00°C for TPMAI in acetone to 9000 atm, in propionitrile, nitromethane, cyclohexanone, and dichloromethane to 2000 atm, and in nitrobenzene to 1000 atm. Results are given in Table II.

The concentrations reported in Tables I and II are expressed as mol/l.; for each case the 1-atm value was determined by weight as already described, and the variation with pressure from the Tait equation, by assuming that the density, ρ , of these dilute solutions varied with pressure in the same manner as the pure solvents. This expression is

$$\left(1 - \frac{\rho_1}{\rho}\right) = C \log \left(\frac{B + P}{B + 1}\right) \quad (1)$$

where ρ_1 is the density at atmospheric pressure, ρ is the density at pressure P , and B and C are constants. The value of C was taken as 0.2159 for all solvents (8), and values of B were determined by least-square fits of reported densities (1, 9, 13, 18) where available. For nitromethane, B was found from the compressibility as determined by velocity of sound measurements (21).

For propionitrile no density data were available, but the effect of pressure on the dielectric constant is known (10). The dielectric data can be fitted with a Tait-like expression

Table II. Equivalent Conductance of Tri-*n*-propyl Methyl Ammonium Iodide at 30.00°C

P = Pressure, atm
 Λ = Equiv conductance, mho-cm²/mol
 c = Concn, mol/l. $\cdot 10^4$

Acetone												
Pressure	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ
1	9.85	157.9	19.70	139.6	39.40	122.1	59.11	108.8	78.81	100.9	98.52	98.44
250	10.13	138.5	20.26	122.1	40.53	110.8	60.80	98.53	81.07	94.69	101.34	89.78
500	10.36	119.1	20.72	111.8	41.44	101.2	62.17	90.24	82.89	83.99	103.6	81.63
750	10.53	109.6	21.08	102.1	42.15	92.08	63.23	82.56	83.31	77.45	105.4	74.87
1000	10.71	98.17	21.43	91.60	42.87	82.91	64.30	74.96	85.74	70.80	107.3	68.13
2000	11.22	74.55	22.45	69.42	44.90	59.51	67.36	54.00	89.81	50.82	112.2	49.95
3000	22.03	57.56	43.74	51.52	86.33	47.47	138.3	41.94	171.1	39.45		
4000	22.61	48.36	44.90	40.51	88.61	37.81	142.0	33.51	175.6	31.69		
5000	23.10	38.61	45.87	31.96	90.53	30.53	145.0	27.22	179.4	25.43		
6000	23.53	32.25	46.72	26.83	92.21	25.70	147.7	22.50	182.8	21.01		
7000	23.90	25.89	47.47	21.66	93.69	20.47	150.1	17.78	185.7	16.78		
8000	24.25	20.34	48.15	17.92	95.04	16.31	152.3	13.72	188.4	13.28		
9000	24.56	16.39	48.78	14.58	96.27	13.00	154.2	11.08	190.8	10.70		
Cyclohexanone												
	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ
1	33.55	17.18	70.29	13.78	106.4	12.11	156.7	10.79				
125	33.91	15.27	71.04	12.30	107.5	10.84	158.4	9.67				
250	34.23	13.51	71.72	10.90	108.6	9.67	159.9	8.62				
500	34.81	10.61	72.93	8.59	110.4	7.70	162.6	6.88				
750	35.31	8.39	73.99	6.86	112.0	6.18	165.0	5.54				
1000	35.76	6.69	74.93	5.50	113.4	4.98	167.1	4.46				
1500	36.54	4.20	76.56	3.59	115.9	3.29	170.7	2.94				
2000	37.20	2.78	77.94	2.42	118.0	2.21	173.8	2.00				
Dichloromethane												
	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ
1	32.16	9.40	75.01	7.41	145.2	6.41	219.6	6.19	299.8	5.55		
125	32.66	9.16	76.16	6.96	147.5	6.24	228.7	5.88	304.4	5.46		
250	33.10	8.92	77.19	6.65	149.5	6.06	231.8	5.70	308.5	5.27		
682	34.31	7.78	80.02	5.91	154.9	5.18	240.3	4.86	319.8	4.33		
1000	35.02	6.58	81.66	5.28	158.1	4.44	245.2	4.12	326.4	3.90		
1500	35.93	4.63	83.80	4.06	162.3	3.40	251.6	2.96	334.9	2.98		
2000	36.69	3.79	85.57	3.27	165.6	2.78	256.9	2.10	341.9	2.47		
Nitrobenzene												
	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ
1	24.52	32.75	46.94	30.35	72.31	28.41	90.48	27.38				
125	24.66	29.21	47.22	27.16	72.74	25.51	91.02	24.56				
250	24.80	26.10	47.48	24.32	73.15	22.85	91.53	22.01				
500	25.06	20.93	47.98	19.49	73.91	18.39	92.48	17.69				
750	25.30	16.93	48.43	15.75	74.61	14.89	93.36	14.32				
1000	25.52	13.68	48.85	12.74	75.25	12.06	94.16	11.63				
Nitromethane												
	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ
1	14.43	106.4	29.60	102.2	42.63	100.1	58.28	97.78				
125	14.56	97.04	29.86	93.39	43.01	91.48	58.80	89.39				
250	14.68	88.74	30.11	85.34	43.36	83.73	59.29	81.70				
500	14.90	74.60	30.55	71.98	44.00	70.49	60.16	68.90				
750	15.09	63.45	30.95	61.09	44.57	60.01	60.94	57.93				
1000	15.27	54.39	31.30	52.33	45.08	51.45	61.64	49.79				
1500	15.57	40.83	31.92	39.49	45.98	38.77	62.86	37.44				
2000	15.83	32.23	32.46	30.83	46.75	30.49	63.91	29.32				
Propionitrile												
	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ	c	Λ
1	34.27	123.1	67.09	111.7	115.4	101.9	140.5	98.39				
125	34.82	111.2	68.17	101.3	117.3	92.48	142.8	89.39				
250	35.31	100.8	69.12	91.89	118.9	83.99	144.8	81.27				
500	36.13	83.60	70.74	76.48	121.7	70.17	148.2	67.86				
750	36.82	70.36	72.09	64.48	124.0	59.23	151.0	57.35				
1000	37.42	59.51	73.25	54.83	126.0	50.44	153.5	48.87				
1500	38.41	44.06	75.20	40.77	129.4	37.61	157.5	36.48				
2000	39.24	34.23	76.82	31.63	132.2	29.32	160.9	28.43				

Table III. Solvent Properties

Solvent	T, °C	B, atm	ϵ_1 (11)	$C' \cdot 10^3$ (11)	B' (11) atm
Acetone	30	626 (1)	20.25	11.89	610
	50	507 (1)	18.34	12.35	443
Cyclohexanone	30	997 (13)	15.42	9.267	718
Dichloromethane	30	668 (18)	8.64	24.88	628
Nitrobenzene	30	1818 (9)	33.90	8.19	1517
Nitromethane	30	1185 (21)	35.78	8.168	1143
Propionitrile	30	636	27.90	5.995	636

(14, 15) to yield a value of B which for other polar solvents is quite close to the results of fitting density data (18); this value was used for propionitrile. The values of B used for all solvents are listed in Table III.

The concentration values given in Tables I and II represent values calculated by the Tait equation from the prepared concentration at 1 atm and for all solvents except acetone, the same solutions were used for the entire pressure range. However, a separate set of solutions was used for the higher pressure measurements on both salts in acetone, at 3000 atm and above.

A knowledge of the variation of the dielectric constant, ϵ , with pressure was required for analysis of the data and calculated from a Tait-like expression.

$$\frac{1}{\epsilon_1} - \frac{1}{\epsilon} = C' \log \left(\frac{B' + P}{B' + 1} \right) \quad (2)$$

The constants B' and C' were obtained by Hartmann et al. (11) from their experimental data, and the values used are listed in Table III.

DISCUSSION

The theory of Fuoss and Onsager for nonassociated ions in dilute solution in solvents of high dielectric constant is applicable to several of the systems reported here. From this treatment the limiting conductance Λ_0 may be found and used in conjunction with data on solvent viscosity η for comparison with Walden's rule, derived from the Stokes Law which states that for a given salt at a given temperature, the product W is a constant.

$$W = \Lambda_0 \eta = \text{constant} \quad (3)$$

By treating totally dissociated ions as charged spheres in a continuous medium undergoing hydrodynamic flow, Fuoss and Onsager (6, 7) expressed the conductance Λ as

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Jc \quad (4)$$

where c is the concentration. S and E are constants, which are functions of Λ_0 and the solvent properties, viscosity and dielectric constant. J is an adjustable parameter, a function of ion size.

Conductivity data in the four most polar solvents satisfy the assumptions of Equation 4, and values of the limiting equivalent conductance Λ_0 have been determined from Equation 4 by a trial-and-error solution (5). To verify the applicability of Equation 4, plots of Λ vs. \sqrt{c} were made and shown to be anabatic phoreograms. A typical set of data is shown in such a diagram for TPMAI in nitrobenzene, Figure 1. Unfortunately, data for the pressure dependence of viscosity of nitromethane and propionitrile are not available; therefore, the data at elevated pressures could be evaluated only for acetone and nitrobenzene solutions.

The data so calculated and the resulting values of the Walden products for the two salts are given in Tables IV and V. W

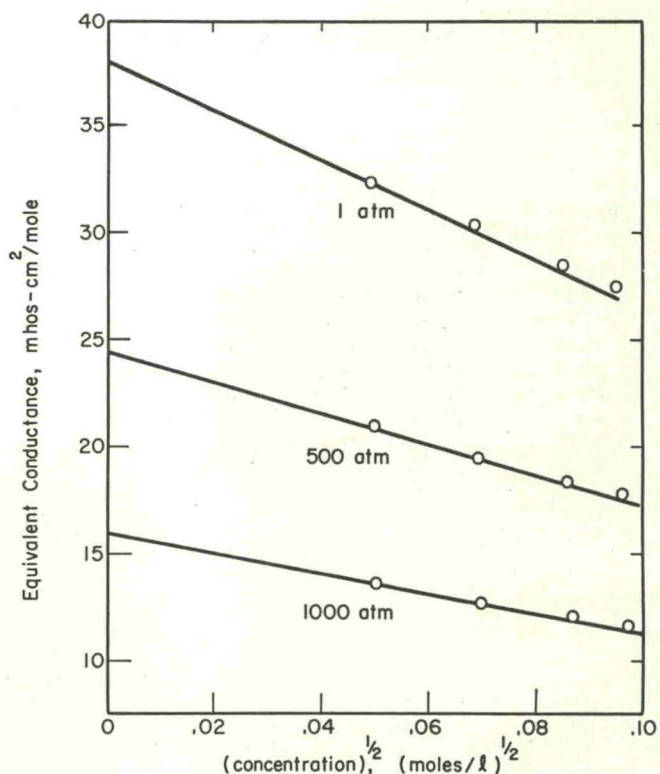
Figure 1. Anabatic phoreogram for tri-*n*-propyl methyl ammonium iodide in nitrobenzene at 30°C

Table IV. Walden Product of Methyl Pyridinium Iodide at 50°C in Acetone

Pressure, atm	Λ_0 , mho-cm²/mol	η , cP (1)	W
1	245	0.256	0.63
500	162	0.282	0.46
1000	113	0.309	0.35
2000	82.0	0.358	0.29

Table V. Walden Product of Tri-*n*-propyl Methyl Ammonium Iodide at 30°C

Solvent	Pressure, atm	Λ_0 , mho-cm²/mol	η , cP (1)	W
Acetone	1	195	0.295	0.58
	500	148	0.326	0.48
	1000	118	0.357	0.42
	2000	87.5	0.414	0.36
	3000	71.5	0.482	0.34
Nitrobenzene	1	38.0	1.634	0.62
	500	24.3	2.228	0.54
	1000	15.9	3.000	0.48
Nitromethane	1	115	0.595	0.68
Propionitrile	1	153	0.389	0.60

for TPMAI is relatively constant in four solvents in Table V, but W for MPI in acetone and for TPMAI in both acetone and nitrobenzene does decrease with increasing pressure. This variation is in the opposite direction from that noted in previous work (20) for tetrabutyl ammonium bromide in methanol. Perhaps this discrepancy is due to the associated nature (hydrogen bonding) of the solvent methanol compared to the aprotic solvents used here.

NOMENCLATURE

- B = Constant in Tait equation
 B' = Constant in dielectric constant equation
 C = Constant in Tait equation
 C' = Constant in dielectric constant equation
 c = Concentration
 E = Constant in Equation 4
 J = Constant in Equation 4
 P = Pressure
 S = Constant in Equation 4
 W = Walden product
 ϵ = Dielectric constant
 ϵ_1 = Dielectric constant at 1 atm
 η = Viscosity
 Λ = Equivalent conductance
 Λ_0 = Limiting equivalent conductance
 ρ = Density
 ρ_1 = Density at 1 atm

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