dried in a vacuum oven at 120° for 48 hours. The chlorine analysis was 21.39 per cent.

Procedure.—The method of saturation and removal of solution was the same as reported by Vernon and Sheard.[2] The solute was extracted with water and, after evaporation to a volume of 50 cc., was analyzed by the modified Volhard procedure described by Swift, Arcand, Lutwack and Meier.[3] Ferric ammonium sulfate was used as an indicator.

Results

The solubility results given in Table I are the averages of two to four determinations.

TABLE I

SOLUBILITY OF TETRAETHYLAMMONIUM CHLORIDE IN ETHYLENE DICHLORIDE–BENZENE MIXTURES AT 25°

Volume, %, ethylene dichloride	Dielectric constant	Moles per liter of chloride × 10^3
100.0	10.36	243.1 ± 3.2
93.5	9.02	159.8 ± 0.60
80.0	7.26	33.13 ± 0.22
69.0	6.09	7.27 ± 0.06
59.5	5.32	2.62 ± 0.01
43.0	4.25	0.576 ± 0.0025

The average deviation is no greater than 1.4% for any solvent mixture. Figure 1 shows a plot of the log of solubility against the log of dielectric constant. The values of dielectric constant were interpolated from the data reported by Vernon, Wyman and Avery.[4]

Discussion

As pointed out by Vernon and Sheard,[2] it is quite likely that at least triple ion formation exists in the solutions here studied and that straight line extrapolation to pure benzene might be justified if such conditions exist in pure benzene. Such an extrapolation gives a value of 4.0×10^{-11} mole per liter. Since this value is below that at which triple ions might be expected to exist, its value is doubtful.

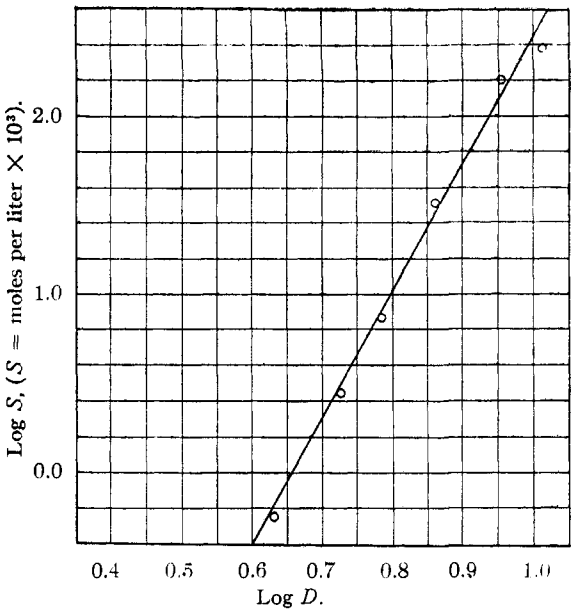

Fig. 1.

The slope of the log S–log D plot is about 7 as compared to a slope of about 5 for tetraethylammonium iodide reported by Vernon and Sheard.[2]

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(3) Swift, Arcand, Lutwack and Meier, *Analytical Chemistry*, **22**, 306 (1950).

(4) Vernon, Wyman and Avery, THIS JOURNAL, **67**, 1422 (1945).

[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES OF NORTHEASTERN UNIVERSITY]

The Solubility of Quaternary Ammonium Salts in Methanol–Benzene Mixtures. The Anomalous Behavior of Tetraethylammonium Iodide

BY GERSHON M. GOLDBERG[1] AND ARTHUR A. VERNON

Solubilities of tetramethylammonium bromide, tetraethylammonium bromide and iodide and tetrabutylammonium iodide were determined in methanol-benzene mixtures. Tetraethylammonium iodide shows a maximum in the solubility—mole fraction plot which may be due to solvent interaction.

Introduction.—In continuation of work in progress in these laboratories on the general problem of solubility in low dielectric constant solvents, the methanol-benzene system was studied. Dielectric constant data for these mixtures were reported by Vernon and LaRochelle.[2]

Experimental

Materials.—C.P. thiophene-free benzene was stored over anhydrous calcium chloride for several days and distilled from phosphorus pentoxide in a fractionating column, discarding the first and last fifths. The refractive index was 1.4978 at 25.2° compared to the "International Critical Tables" value of 1.49779.

C.P. absolute methanol was dried over activated alumina and distilled from fresh activated alumina in the same way as benzene. The refractive index at 25° was 1.3269 compared with the "International Critical Tables" value of 1.32773.

Tetraethylammonium iodide, prepared by the method of Vernon and Sheard[3] analyzed 49.3% of iodine compared to the theoretical value of 49.4%.

The other salts were obtained from the Eastman Kodak Company. Tetrabutylammonium iodide was dissolved in ethanol, cooled and ether was added to cause crystallization. After drying the % of iodine was 34.3 compared to the theoretical 34.4%. Tetraethyl- and tetramethylammonium bromides were crystallized from ethanol. The former had a bromide content of 38.0% compared to the theoretical 38.1%; the latter salt analyzed 51.8% compared to a theoretical value of 51.9%.

Procedure.—The thermostat consisted of a glass jar 12″ deep and 12″ in diameter placed in an insulated container. A water motor with a 6″ Alnico bar magnet mounted on the shaft was fixed in the bottom of the container while flat bottom flasks containing solute, solvent and a bar magnet stirrer were supported in the bath. When the motor was

(1) Dougherty Refinery, Petrolia, Pa.

(2) Vernon and LaRochelle, THIS JOURNAL, **72**, 3293 (1950).

(3) Vernon and Sheard, *ibid.*, **70**, 2035 (1948).

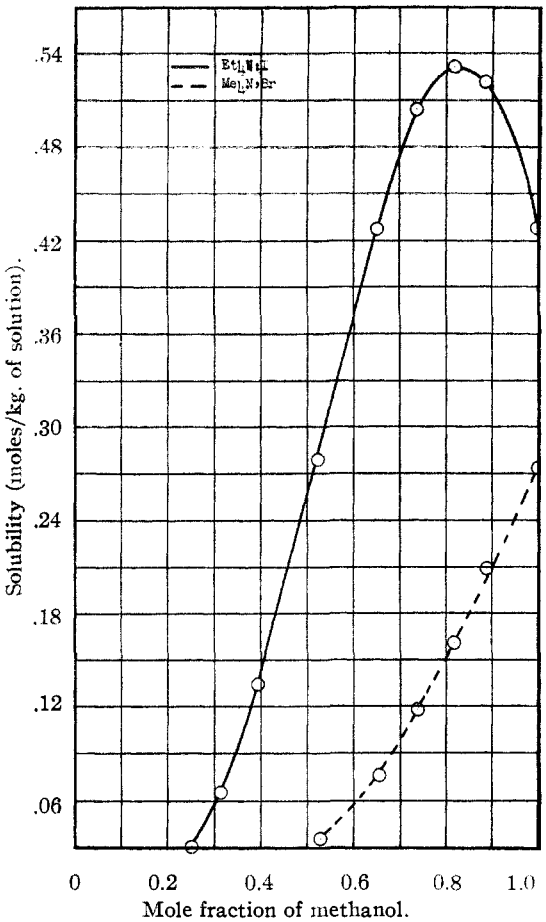

Fig. 1.—Et_4NI, ——; Me_4NBr, — — —.

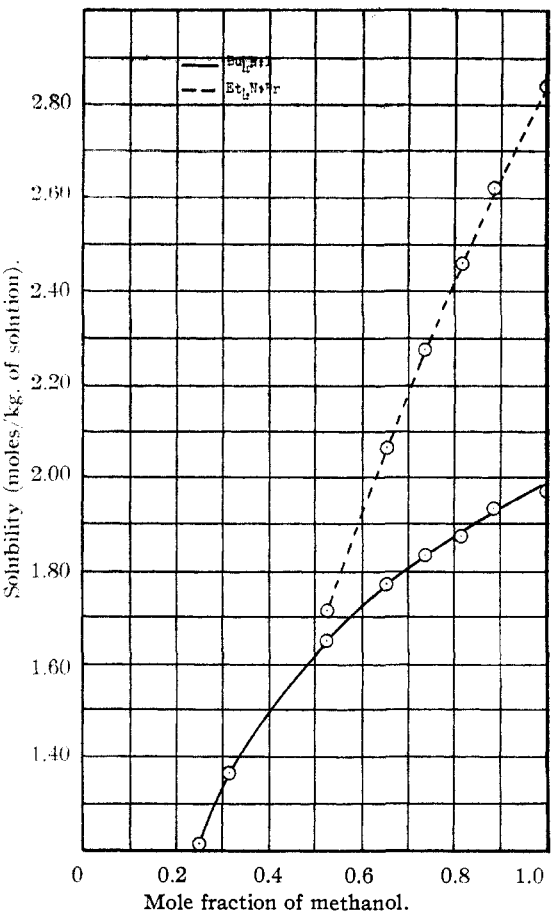

Fig. 2.—Bu_4NI, ——; Et_4NBr, — — —.

driven by air, the rotating bar magnet served both to agitate the bath and stir the solutions. By means of an electrical heater and regulator, the temperature was maintained at 25 ± 0.07°.

Some solutions were stirred at 30° for three to six hours and then at 25° long enough to reach equilibrium while others were stirred at 25° until saturation was obtained. The solutions were then forced out by dry air through glass wool filters into weighed glass-stoppered flasks. Afte weighing, the solutions were transferred to a beaker and the flasks washed with water or ethanol depending upon the salt solubility. An excess of silver nitrate solution was then added to the beaker and the solutions were acidified with nitric acid. The excess silver was titrated with standardized potassium thiocyanate solution using ferric ammonium sulfate indicator. The tetrabutylammonium iodide solutions containing silver nitrate were digested on a steam-bath for twenty minutes before titrating.

TABLE I

SOLUBILITY OF QUATERNARY AMMONIUM SALTS IN METHANOL–BENZENE MIXTURES AT 25°

Vol., % benzene	Solubility in moles per kg. of solution				M.f. methanol
	Me_4NBr	Et_4NBr	Et_4NI	Bu_4NI	
0	0.274	2.84	0.428	1.97	1.000
20.9	.209	2.62	.523	1.93	0.888
32.2	.161	2.46	.532	1.88	.816
42.9	.118	2.28	.502	1.84	.741
53.7	.0748	2.07	.427	1.78	.652
66.5	.0348	1.71	.279	1.65	.522
76.9			.134		.394
82.6			.0653	1.37	.312
86.6			.0293	1.21	.250
94.4				0.726	.123

Results

The results are shown in Table I in which the solubility values are averages of three or more determinations. Three of the values have average deviations from the mean of 1.5%; the rest are less than 1%.

The data are plotted in Figures 1 and 2, two graphs being necessary due to the different solubility ranges.

Discussion

The unusual behavior of tetraethylammonium iodide as shown in Fig. 1 may be due to solvent-solute ion interaction. Sadek and Fuoss[4] showed that methanol interacts with the bromide ion when tetrabutylammonium bromide is dissolved in methanol–nitrobenzene mixtures. If such an effect is present in the systems here reported, it does not seem to be significant for tetraethyl- or tetramethylammonium bromide and it is rather surprising that an effect should be evident for the larger iodide ion in tetraethylammonium iodide. Work is underway to determine the solubility behavior for other quaternary ammonium iodides to determine whether a maximum occurs with any other compound.

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(4) Sadek and Fuoss, THIS JOURNAL, **72**, 301 (1950).