[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Conductance of Mixtures of Lead Abietate and Tributylammonium Chloride in Toluene

BY VICTOR DEITZ WITH RAYMOND M. FUOSS

I. **Introduction.**—While the properties of a number of 1–1 salts in solvents of low dielectric constant have been determined,[1–4] the properties of higher salt types in such solvents have not been investigated. One difficulty in the way of a study of the problem is the low solubility of most 2–1 salts in the hydrocarbon solvents. Two classes of salts are, however, soluble: the higher quaternary salts of dicarboxylic acids and the salts of heavy metals with the higher carboxylic acids. In this paper will be presented the results of an investigation of the properties of lead abietate in benzene and toluene solution.

II. **Materials, Apparatus and Method.**—**Benzene** was purified by washing with concentrated sulfuric acid, water, dilute caustic and water. It was then dried with calcium chloride and refluxed with potassium. Samples for use in the conductance experiments or analyses were distilled from potassium just before using. **Toluene** was treated in the same way, except that the potassium was replaced by sodium.

Tributylammonium picrate was prepared by adding a nearly saturated hot alcoholic solution of picric acid to a slight excess of tributylamine in alcohol. The crude product, which separates on cooling, was recrystallized once from alcohol, m. p. 106.9° (corr.).

Tributylammonium chloride was precipitated by *dry* hydrogen chloride from a solution of tributylamine in *dry* petroleum ether. It is advisable to precipitate less than half of the available amine, in order to prevent the coprecipitation of impurities which are difficult to separate. The precipitate was washed with dry petroleum ether, and then pumped dry over phosphorus pentoxide in a desiccator. Samples for use were dried to constant weight at 70–75° in weighing bottles in a miniature vacuum oven.

Several samples were analyzed by titration in 50% acetone solution with sodium hydroxide, using phenolphthalein as indicator. A small blank correction for acid in the acetone was made. Equivalents of $(C_4H_9)_3HNCl$ calculated from weight of salt taken: 0.001384, 0.001725, 0.001896; equivalents sodium hydroxide found by titration: 0.001390, 0.001749, 0.001896.

Lead Abietate.—Considerable difficulty was encountered in preparing pure lead abietate. Precipitation from lead nitrate or lead acetate solutions gives basic or double salts, whose composition depends on concentration, sequence and relative amounts of reagents.[5] It also proved useless to try to purify lead abietate made from impure abietic acid; it is essential that the abietic acid be in the highest state of purity initially. We obtained nearly colorless abietic acid, completely free from tacky impurities, by recrystallizing a good commercial grade (from Hercules Powder Co.) from methyl alcohol and washing the crystals with cold methyl alcohol. The crystallization yield was poor, but the quality of the product was compensation for the loss of raw material. The abietic acid was then dissolved in an equivalent amount of sodium hydroxide in water and this (very slightly yellow) solution was slowly added in turn to a hot dilute aqueous solution of an equivalent amount of lead chloride. The lead abietate formed as a pure white crystalline precipitate. This was recrystallized from ethyl acetate (2 g./100 cc.) which had been purified by shaking with aluminum oxide and distilling just before use. The final product consisted of small twinned needles. It was necessary to store the lead abietate in an evacuated phosphorus pentoxide desiccator, because exposure to air converted it into a product (presumably one of oxidation) insoluble in ethyl acetate and aromatic hydrocarbons. Heating to 100° in air causes the crystals to darken.

Of several new methods of analysis for lead in lead abietate, we found the most reliable to be the precipitation of the lead as lead chloride from a toluene solution of the abietate by means of dry hydrogen chloride. Moisture was excluded by working in a dry box; this precaution is necessary, because any water which condenses into the solution containing hydrogen chloride separates and preferentially wets the lead chloride precipitate, causing it to adhere so firmly to the walls of the vessel that quantitative transfer is very tedious.

The dry box was fed with air passed over activated aluminum oxide. At the start of an analysis, several weighed samples of lead abietate in capped weighing bottles, several weighed Gooch crucibles with fine asbestos mats, toluene wash bottle, toluene supply bottle, suction flask, hydrogen chloride generator and hot plate were placed in the dry box, which was swept out overnight with dry air. The next day, the abietate was dissolved in toluene (*ca.* 1 mg./cc.) in an Erlenmeyer flask which had a tea-kettle spout attached to the bottom. Hydrogen chloride from sulfuric acid and potassium chloride was passed slowly in through the spout, after which the precipitate was digested for about thirty minutes. Then the lead chloride was transferred to the Gooch crucible by sluicing it through the spout. (This procedure entirely eliminated the necessity of policing the precipitate.) After washing, the precipitate was sucked dry. After all the precipitations were complete, the dry box was opened and the crucibles were transferred to an oven at 110° where they were dried to constant weight. In some of the preliminary work, the crucibles were next washed with hot water and again dried to constant weight. The water insoluble resi-

---

(1) C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933).

(2) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 3614 (1933).

(3) G. S. Bien, C. A. Kraus and R. M. Fuoss, *ibid.*, **56**, 1860 (1934).

(4) W. F. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, *ibid.*, **58**, 255 (1936).

(5) Wolff and Rabinowicz, *Fettchem. Umschau*, **41**, 66 (1934).

due (of the order of 0.1 mg.) was probably abietic acid adsorbed on the lead chloride. The results of several typical analyses by this method are given below: wt. lead abietate, 0.2165, 0.2471, 0.1420; wt. $PbCl_2$ found, 0.0751, 0.0854, 0.0485; % Pb, 25.84, 25.75, 25.46; calcd. for $Pb(C_{20}H_{30}O_2)_2$, 25.61%.

As a control on the method, a sample of recrystallized silver perchlorate, which is toluene soluble, was analyzed by the same method: wt. $AgClO_4$, 0.1644, 0.3211; wt. AgCl found, 0.1138, 0.2218; wt. AgCl calcd. 0.1137, 0.2221.

Conductance Cells.—For the preliminary conductimetric titrations, several types of cells were used. The simplest and most convenient consisted of a beaker containing two concentric cylindrical platinum gauze electrodes, at the center of which was a motor driven glass stirrer.

For the final work, a three terminal cell was used. Figure 1 is a simplified sketch of the cell. The inner (test) electrode was a platinum cylinder 6.5 cm. long and 2.0 cm. in outside diameter. To each end of this cylinder and on the same axis, by means of platinum wires and lead glass beads, were attached two cylinders of the same diameter, 5 mm. long, and separated from the test electrode by about 1 mm. These end cylinders were the guard electrodes. The guard-test combination was then mounted by more platinum wire supports with lead glass insulators inside a platinum cylinder 7.7 cm. long and 2.3-cm. diameter, which served as the high potential electrode. The seams on the cylinders were soldered with gold. The electrode assembly was then sealed into an electrode capsule of Corning 332 glass by means of platinum tube supports coated with Corning 707 glass.[6] The capsule (40-cc. volume) was in turn sealed to a Pyrex mixing chamber (300-cc. volume), the inlet tube of which was equipped with a ground glass cap carrying a stopcock. The stopcock permitted rapid drying of the cell, by exhausting the cell after washing and heating. The three lead wires (high potential, test and guard) were brought up beside the neck of the cell in small glass tubes. (For simplicity, only one of these is shown in Fig. 1.) These, as well as the electrode capsule, were coated with gold by firing on at 500° a layer of Dupont "Liquid Bright Gold ZW." The gold screening was connected to the guard line. The bridge cable, which consisted of the test lead, sheathed with an insulated copper screen attached to the guard circuit, was plugged into the end of the test lead from the cell, so that the test electrode and its lead to the bridge were unbrokenly shielded.

The cell constant was determined by measuring the capacity of the empty cell on a Schering bridge[7] at 60 cycles; since the cell contains guard electrodes, the cell constant k can be obtained from the capacity by the relationship

$$C = 0.08842 \times 10^{-12}/k$$

(For an ideal cell consisting of parallel plates of area A separated by a distance d, $k = d/A$, if fringing is eliminated.) For the cell of Fig. 1, $k = 0.004423$.

The conductance determinations were made either at 60 cycles on the Schering or resistance bridge[8] which have been used for other work in this Laboratory, or on a d. c. bridge which has also been described previously.[8]

Method.—In the preliminary titrations, a solution of tributylammonium chloride in benzene or toluene was delivered in successive portions from a buret into the gauze electrode cell, which contained the lead abietate solution. The resistance was determined on the d. c. bridge after each portion. It was observed that both moisture and oxygen affected the results; titrations in the dry box gave steadier conductances.

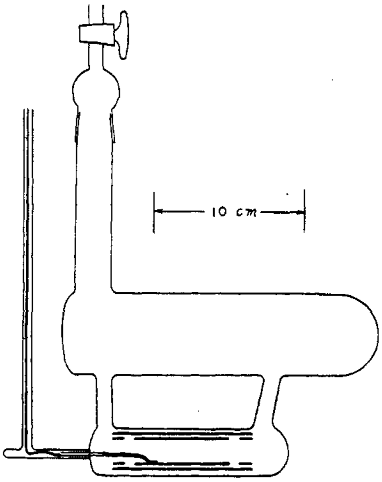

Fig. 1.—Conductance cell.

In the final work, toluene was distilled in a nitrogen stream from sodium directly into the carefully dried three terminal conductance cell. Access of moisture was prevented by a drying tube. After determining the solvent conductance,[9] a sample of lead abietate was weighed into the cell, and the solution was allowed to come to equilibrium in an oil thermostat held at 35.00 ± 0.03°. The conductance was determined and then a small portion of a solution of tributylammonium chloride in toluene was added from a weight buret. A conductance run consisted in adding several stoichiometrical equivalents of chloride to the lead salt in successive portions, and determining the conductance at 60 cycles at each point. The field strength was kept below one kilovolt per centimeter, in order to minimize both heating effects and a possible Wien effect.[10,11]

Polarization.—A very marked dependence of apparent resistance on voltage was noted when solutions were measured on the d. c. bridge. An analysis of the results indicates that a fairly high polarization e. m. f. is responsible. The bridge is shown schematically in Fig. 2, where R_1 is the cell resistance, R_2 and R_3 are Shallcross high resistance coils and R_4 is a variable decade box. Suppose the voltage applied to the bridge is V and

---

(6) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

(7) Fuoss, THIS JOURNAL, **59**, 1703 (1937).

(8) Fuoss, *ibid.*, **60**, 451 (1938).

(9) The solvent conductance was of the order of 10^{-14} and represented a negligible correction.

(10) M. Wien, *Physik. Z.*, **29**, 751 (1928); L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

(11) An appreciable dissociation effect in accordance with Onsager's theory appears in solvents of low dielectric constant at fairly low field strengths. (Unpublished observations of D. J. Mead and R. M. Fuoss, made in this Laboratory.)

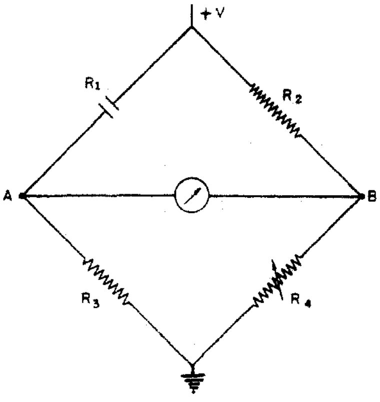

Fig. 2.—Diagram of d. c. bridge.

the back e. m. f. of the cell is E. Then at balance, $V_a = V_b$ and we have

$$V = I_a(R_1 + R_3) - E = I_b(R_2 + R_4) \qquad (1)$$

$$(I_aR_1 - E)/I_aR_3 = R_2/R_4 \qquad (2)$$

Combining (1) and (2), and noting that $R_1 >> R_3$, we find

$$\frac{R_1R_4}{R_2R_3} = 1 + \frac{E}{V} \qquad (3)$$

A typical result for a 5.85×10^{-3} molar solution of lead abietate in benzene at 25° in a cell with chromium plated brass electrodes is shown in Fig. 3. According to (3), if we plot R_4V against V, we should obtain a straight line whose slope determines R_1, and whose intercept determines E. Having determined R_1, a plot of R_1R_4/R_2R_3 against $(1/V)$ should give a straight line with slope E and intercept unity at infinite voltage $(1/V) = 0$. The data satisfy these requirements, and give, for this example, $E = 10$ v. Lack of time unfortunately forced us to postpone a detailed study of this phenomenon. A study of the rates of decay of these polarization voltages should give useful information concerning the diffusion coefficients and mobilities of the ions involved.

Subsequent d. c. titrations were made at a fixed cell voltage (100 v.) and the final titrations were made with alternating current. Since the latter was low frequency (60 cycles), some polarization error undoubtedly is present, but experiments made at several frequencies between 60 and 500 cycles showed that the effects were considerably less than with d. c. and our a. c. results at 60 cycles are no more than several per cent. in error in absolute value due to polarization. Since we were primarily interested in relative values, the study of polarization effects was dropped.

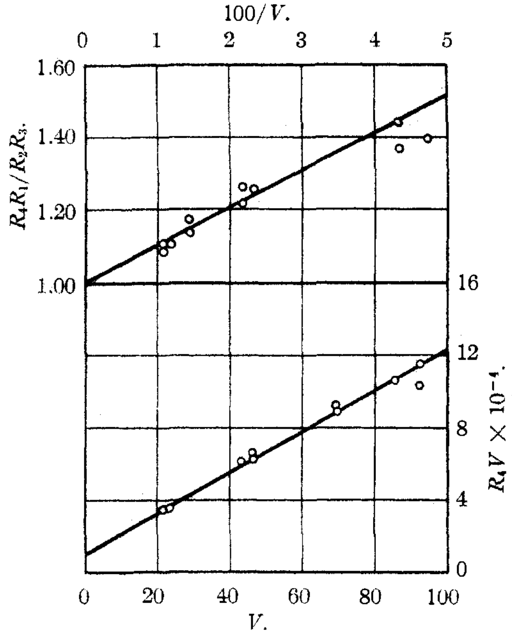

Fig. 3.—Polarization curves.

III. Experimental Results and Discussion.—In order to test the reliability of the conductance methods, the conductance of tributylammonium picrate in toluene at 35° was determined. Three dilution runs were made. The results are given in Table I.

TABLE I

CONDUCTANCE AND DIELECTRIC CONSTANT OF TRIBUTYLAMMONIUM PICRATE IN TOLUENE AT 35°

Series	$C \times 10^3$	$\Lambda \times 10^6$	ϵ'
1	13.04	2.650	...
	8.12	1.500	...
	5.03	0.957	...
	2.82	.603	...
	1.62	.442	...
2	2.65	.597	2.391
	1.21	.370	2.368
3	4.88	.926	2.428
	3.05	.548	2.400
	0.0	..	2.347

For comparison with earlier work, the only available data are those of Kraus and Fuoss[1] on tri-*i*-amylammonium picrate in benzene at 25°. These data, multiplied by the ratio of the viscosity of benzene at 25° to that of toluene at 35° are shown as the dotted curve in Fig. 4, where the present data are given as the circles on curve IV. It will be noted that the behavior of the two systems is, as expected, very similar.

The conductance of tributylammonium chloride as a function of concentration was determined by adding successive portions of an approxi-

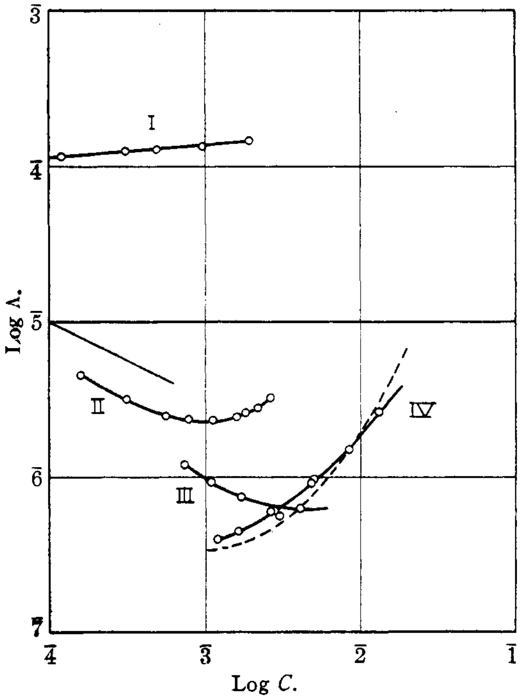

Fig. 4.—Conductance curves: I, PbAbCl in C_6H_6; II, Bu_3HNCl in $C_6H_5CH_3$; III, $PbAb_2$ in $C_6H_5CH_3$; IV, Bu_3HNPi in $C_6H_5CH_3$.

mately 0.01 normal solution of the salt in toluene to 66 g. of pure solvent in the conductance cell. The results are given in Table II, and are shown as curve II in Fig. 4, where the logarithm of the equivalent conductance Λ is plotted against the logarithm of the concentration. The appearance of a characteristic minimum in the equivalent conductance[12] near thousandth normal will be noted.

TABLE II

CONDUCTANCE AND DIELECTRIC CONSTANT OF TRIBUTYLAMMONIUM CHLORIDE IN TOLUENE AT 35°

$C \times 10^3$	$\Lambda \times 10^6$	ϵ'
0.000	..	2.347
.159	4.49	2.348
.290	3.13	2.348
.568	2.45	2.352
.790	2.32	2.352
1.116	2.30	2.356
1.575	2.38	2.359
1.819	2.58	2.362
2.203	2.76	2.365
2.692	3.22	2.368

The conductance and dielectric constants of a series of lead abietate solutions in toluene at 35° are given in Table III. Each solution was made up by weighing a definite amount of salt and solvent.

TABLE III

CONDUCTANCE AND DIELECTRIC CONSTANTS OF LEAD ABIETATE IN TOLUENE AT 35°

$C \times 10^4$	$\Lambda \times 10^6$	ϵ'	ϵ_0'
4.083	0.626	2.349_5	2.348_2
1.686	0.762	2.348_8	2.348_2
1.073	0.936	2.349_0	2.347_8
0.740	1.213	2.348_6	2.348_2

No dilution runs were made for this salt; the solutions of Table III were the initial solutions for the conductimetric titrations to be described later. In the last column, the dielectric constant ϵ_0' of the solvent, as measured before addition of the salt, is given for each solution.

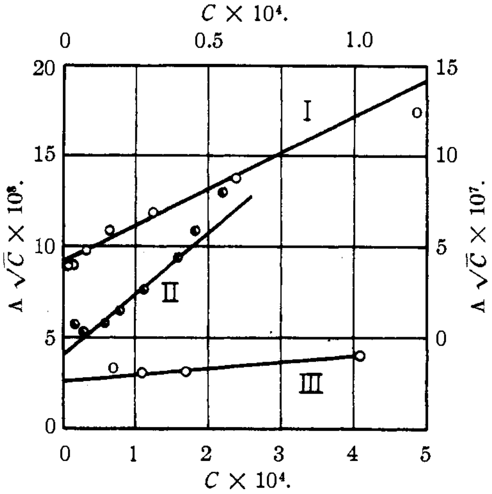

Fig. 5.—Triple ion test plots: I, PbAbCl in C_6H_6 (coördinates, top and right); II, Bu_3HNCl in $C_6H_5CH_3$ (coördinates, bottom and left); III $PbAb_2$ in $C_6H_5CH_3$ (coördinates, bottom and left).

If $\Lambda\sqrt{c}$ is plotted (Fig. 5, curve II) against concentration for the tributylammonium chloride,[11] a straight line is obtained, whose intercept at $c = 0$ gives $K\Lambda_0^2 = 3.8 \times 10^{-8}$ for this salt. If we set Λ_0, the limiting conductance, equal to 100 in order of magnitude (a reasonable value, assuming Walden's rule to apply), we find for the dissociation constant $K \approx 1.5 \times 10^{-19}$. This is of the order expected.[2] For lead abietate, a value about one half as large is obtained. The dissociation constant of lead abietate refers, of course, to the initial dissociation

$$PbAb_2 \rightleftarrows PbAb^+ + Ab^-$$

because it seems impossible that the second abietate ion should be free in any appreciable amount in solvents of low dielectric constant. Confirmation of this opinion is furnished by the numerical

---

(12) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 2387 (1933).

value of the dissociation constant of silver perchlorate in benzene,[4] 8×10^{-20}, which is a 1–1 salt with a metallic cation.

The dependence of the dielectric constants of the solutions on concentration is shown in Fig. 6.

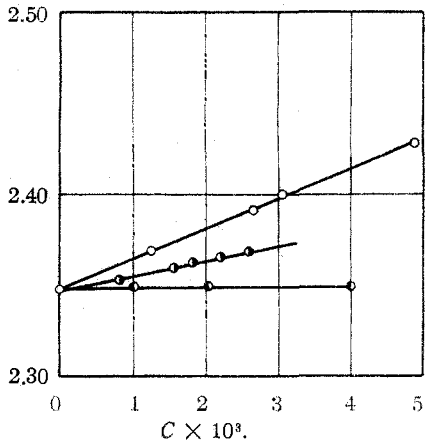

Fig. 6.—Dielectric constant–concentration curves for salts in toluene at 35°: ○, Bu_3HNPi; ◑, Bu_3HNCl; ◐, $PbAb_2$.

It is seen at once that the tributylammonium picrate has a higher dipole moment than the chloride and that the lead abietate has zero moment. Calculation of the moments from the data gives $\mu\,(Bu_3HNP_i) = 11.7 \times 10^{-18}$ and $\mu\,(Bu_3HN{\cdot}Cl) = 7.3 \times 10^{-18}$. These are of the expected order of magnitude and agree very well with Geddes' values,[13] $\mu\,(Bu_3HNP_i) = 13.1 \times 10^{-18}$, $\mu\,(Bu_3HNCl) = 7.2 \times 10^{-18}$. It should be pointed out that our values were determined by bridge measurements at 60 cycles, while Geddes' values were determined by Wyman's resonance method[14] at several megacycles. The value of zero for the moment of lead abietate is entirely in agreement with the theory of ion association[15] because one naturally assumes the abietate ions symmetrically located with respect to the lead ion.

We shall next consider a few of the preliminary conductimetric titrations. The examples chosen are shown in Fig. 7; in order to save space, no tabulation of data will be presented. The vertical scale is specific conductance; as abscissas are chosen the ratio r of equivalents of chloride to the equivalents of lead present in the cell. At $r = 0.5$, the empirical composition is $(Bu_3HNCl + PbAb_2)$; at $r = 1$, it is $(2Bu_3HNCl + PbAb_2)$. Curve I represents the conductance curve obtained on the d. c. bridge when successive portions of 0.01 normal tributylammonium chloride solution in benzene were added to a 6.84×10^{-4} N solution of lead abietate in benzene. It will be seen that the conductance rises to a very high peak near the point where one mole of chloride has been added to one mole of lead, after which the conductance rapidly drops. Beyond the equivalence point, the conductance slowly rises again. The appearance of the maximum was entirely unexpected and its presence suggested that some hitherto unsuspected reaction was taking place. If the titration is carried out using hydrogen chloride in benzene, curve II, where the initial lead concentration was 7.64×10^{-4}, is obtained. It is similar to curve I in that a maximum appears, but the maximum is not nearly so high. Finally, curve III represents the reverse titration in which lead abietate was added to a solution of the amine hydrochloride. (The initial point of the titration here corresponds to $r = \infty$, of course.) As more and more lead is added (moving from right to left in Fig. 7), the conductance goes through a shallow minimum and then rises, going through

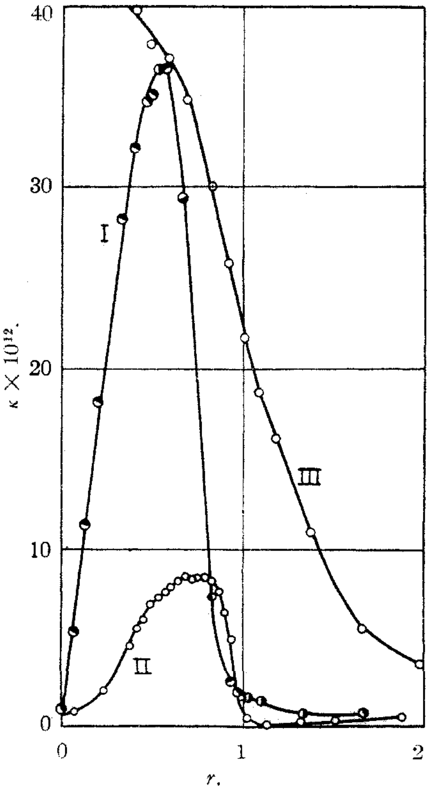

Fig. 7.—D. c. titrations in benzene.

---

[13] J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

[14] J. Wyman, *Phys. Rev.*, **35**, 623 (1930).

[15] Fuoss, *Chem. Rev.*, **17**, 27 (1935).

an inflection point at the equivalence point corresponding to lead chloride. The initial solutions were clear; then an opalescence appeared, and finally a precipitate formed as the amount of lead was increased.

The increase of conductance on adding tributylammonium chloride to lead abietate was certainly not due solely to the formation of tributylammonium abietate by metathesis: a 5×10^{-4} normal solution of abietic acid in benzene had a specific conductance of 0.07×10^{-12} and the addition of an equivalent amount of tributylamine raised this to only 0.15×10^{-12}, showing that the amine abietate is, as expected, an exceedingly weak electrolyte. An estimate from the above conductance gives it a dissociation constant of the order of 10^{-21} in benzene. Incidentally, it would be interesting to study the properties of acids and of their salts with weak bases in non-protonic solvents: this field is practically unexplored. In this particular case, the conductance of the tributylammonium abietate is completely negligible compared to the maximum specific conductance observed near $r = 0.5$ in the titration curves.

In Tables IV and V are given the results of the titrations in the closed cell, where moisture and oxygen were excluded and, as has been mentioned, where the determinations were made at 60 cycles on the Schering bridge.

TABLE IV

CONDUCTIMETRIC TITRATION OF LEAD ABIETATE WITH TRIBUTYLAMMONIUM CHLORIDE IN TOLUENE AT 35°. CONCENTRATION DATA

Series	10^3C_{Pb}	10^6C_{Cl}	w_0	w_{Cl}
1	4.083	13.29	74.85	27.86
2	1.686	9.51	79.27	16.62
3	1.073	9.51	69.50	12.99
4	0.740	9.51	73.89	14.43

In the second column of Table IV is given the initial concentration of lead abietate in equivalents per liter; in the third, the concentration of the tributylammonium chloride; in the fourth, the initial weight of toluene in the cell and in the last, the total weight of chloride solution added by the end of the titration. We used the density of the solvent (0.8538 g./cc. at 35°) as an approximation for the density of the solutions in calculating normalities from weight concentrations.

In Table V are given the conductances for the various solutions, corresponding to successive values of the ratio r of equivalents of chloride added to equivalents of lead initially present. For the most concentrated solution (Series 1), dielectric constants are also given.

Examples of the titration curves are shown in Fig. 8, where the logarithm of the specific conductance is plotted against r. It will be noted that the conductance rises by approximately two decades for the first half equivalent of chloride added. During the addition of the second half equivalent, the conductance drops to a very low value, and then rises again, corresponding to the conductance of the excess tributylammonium chloride now present in the solution.

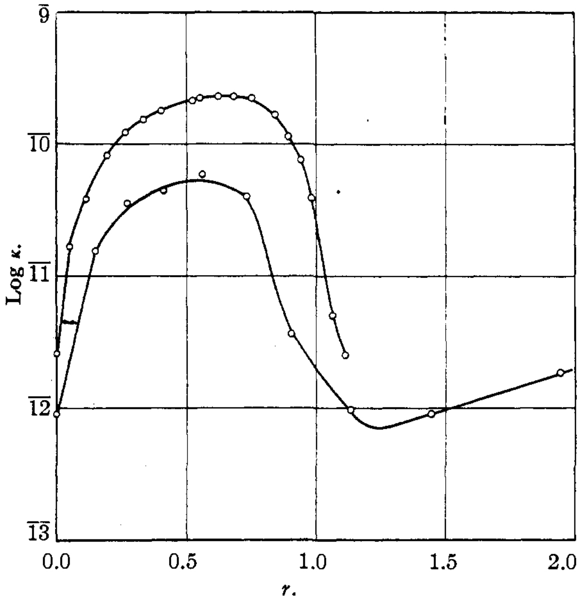

Fig. 8.—A. c. titrations in toluene.

The interesting part of the curve is, of course, the maximum. The following explanation is proposed. We know from the conductance curves of the tributylammonium chloride and lead abietate (Fig. 4, curves II and III) that these salts exist almost completely as ion pairs at the concentrations in question; only a minute fraction is present as free ions (singles or triples). The degree of dissociation involved is of the order of *one millionth* per cent. We also know that tributylammonium abietate is almost completely associated ($K \approx 10^{-21}$). In the first part of the titration, we therefore assume that the few free tributylammonium ions, present in the titrating solution added, combine with the abietate ions from the lead abietate solution in the cell, giving completely associated ion pairs of tributylammonium abietate.[16] This leaves $(PbAb)^+$ and

---

[16] We shall use the abbreviation "Ab" for $(C_{20}H_{30}O_2)^-$, the abietate ion.

TABLE V

CONDUCTIMETRIC TITRATION OF LEAD ABIETATE WITH TRIBUTYLAMMONIUM CHLORIDE IN TOLUENE AT 35°. ELECTRICAL DATA

Series 1			Series 2		Series 3		Series 4	
r	$10^{12}\kappa$	ϵ'	r	$10^{12}\kappa$	r	$10^{12}\kappa$	r	$10^{12}\kappa$
0.000	2.544	2.350	0.000	1.285	0.000	1.004	0.000	0.90
.050	16.44	2.349	.037	4.24	.050	5.20	.150	15.5
.113	38.0	2.351	.063	10.12	.101	9.40	.273	34.5
.191	80.4	2.364	.201	33.7	.247	38.2	.411	44.8
.338	153.3	2.370	.294	54.9	.352	50.7	.562	59.0
.404	176.6	2.371	.332	65.3	.464	65.5	.909	3.60
.557	225	2.380	.432	88.6	.599	77.0	1.136	0.96
.622	228	2.374	.534	106.6	.702	76.0	1.445	0.89
.684	227	2.375	.655	122.4	.859	18.7	1.945	1.88
.756	222	2.358	.766	136.2	.996	2.80	2.510	3.64
.848	168	2.360	1.048	18.0	1.186	0.72	...	...
.895	145	2.348	1.182	3.5	1.420	1.08	...	...
.941	75	2.353	...	....	1.656	1.74	...	...
.987	39	2.358	...	....	...	...	...	...
1.067	5	2.355	...	....	...	...	...	...
1.212	2.5	2.359	...	....	...	...	...	...

Cl^- ions in solution. But the ion pair $(PbAb)^+(Cl^-)$ has a smaller coulomb binding energy than the $(PbAb^+)(Ab^-)$ pair, because the negative oxygens of the carboxyl group in the abietate ion can approach the lead ion closer than the chloride ion, a fact which makes for higher conductance. The practically irreversible reaction

$$Bu_3HN^+ + Ab^- \longrightarrow Bu_3N{\cdot}HAb$$

eventually removes all the free abietate ions from solution, leaving the ion pair equilibrium

$$PbAb^+ + Cl^- \rightleftarrows (PbAb^+)(Cl^-)$$

Then as more chloride is added, we get the reactions

$$(PbAb^+)(Cl^-) + (Cl^-) \rightleftarrows (Cl^-)(PbAb^+)(Cl^-)$$
$$(Cl^-)(PbAb^+)(Cl^-) \rightleftarrows Ab^- + PbCl_2\downarrow$$

In other words, the triple ion[12] formed from the abietate–chloride ion pair and a chloride ion rearranges to give lead chloride, which is insoluble and precipitates out, leaving (Bu_3HN^+) and (Ab^-) ions in solution. But since this ion pair is much more highly associated than the $(Cl^-)(PbAb^+)$ pair, the conductance again drops. The final rise is simply due to increasing $Bu_3HN{\cdot}Cl$ concentration, after the available lead has been precipitated as lead chloride.

The assumption that a soluble mixed salt, lead chloride–abietate ($PbAb{\cdot}Cl$), is formed is in accordance with the observation that the initial additions of chloride to the lead solution produce no precipitate, and that the lead chloride only begins to precipitate in quantity as the $r = 0.5$ point is approached. The opalescence before this point corresponds to the formation of some lead chloride, and accounts for the displacement of the maximum to the right of the point where $r = 0.5$.

We also observed that lead chloride could be dissolved in a solution of tributylammonium chloride (evidence: increased conductance; black precipitate with hydrogen sulfide) which indicates that complexes can be formed in which lead is in the negative ion. This is in accord with the fact that the conductance minimum corresponds to a value of r somewhat greater than unity. We are inclined to ascribe the maximum in the preliminary HCl–$PbAb_2$ titration (Fig. 7) to the presence of moisture in the benzene; this experiment was made without exclusion of atmospheric moisture. Here the much weaker $H_3O^+{\cdot}Cl^-$ was probably the actual titrating solution.

The behavior of the solutions on the addition of chloride during titration was particularly interesting. In the first part of the titration, the conductance increased with time, approaching an asymptotic value (the values given in Table V) exponentially. On the down-side of the titration, the conductance decreased exponentially to an asymptotic value. Approach to within a per cent. or so of the limiting value was reached in serveral hours. If reactions of the type postulated above occur, we would expect finite times to be required for their completion, because the dissociation constants of the two reagents are of the order of 10^{-19}. The marked contrast to electrolytic reactions in water, which take place almost instantaneously, is easily understood when we recall that association of ions in aqueous solutions is negligible for salts of low valence type. These observations suggest a study of the rates of electrolytic dissociation in solvents of low dielectric constant through their conductance–time curves. With dissociation constants of the order of 10^{-20}, there should exist a measurable rate of establishment of equilibrium when an electrolytic solution in benzene, for example, is diluted. We hope that further work on this phase of the problem will be done.

The dielectric constant–concentration curve (Fig. 9) for series 1 of Table V gives further evidence for the existence of a stable mixed salt $(PbAb^+)(Cl^-)$. The dielectric constant goes through a maximum at the same point as the conductance curve, and, after a following minimum, rises at a rate corresponding to the presence of free $Bu_3HN{\cdot}Cl$ ion pairs. From the dielectric constant at the maximum point for Series 1, we have the data $\epsilon' = 2.378$ at $C = 3.52 \times 10^{-3}$. From these, we calculate $\mu(PbAb{\cdot}Cl) = 8.6 \times 10^{-18}$. This value is of the same order as that of the ion pair $Bu_3HN{\cdot}Cl$, and since it is due to the vectorially opposed (Pb^+Ab^-) and (Pb^+Cl^-) moments, we conclude that either the $(Cl^-)(PbAb^+)$ ion pair is not linear, or that the Pb–Cl bond is much more polar than the lead–carboxyl bond. The latter view is more probable, if we compare the dissociation constants of the two ion-pairs $(PbAb^+)(Ab^-)$ and $(PbAb^+)(Cl^-)$.

Finally, we consider the conductance curve of the mixed salt $(PbAb^+)(Cl^-)$. To a solution of 1.314×10^{-4} equivalent (0.1063 g.) of lead abietate in benzene was added an equivalent amount of tributylammonium chloride in benzene, giving a solution 1.943×10^{-3} normal in PbAbCl. No precipitate appeared, although the solution became opalescent. A regular dilution run was made on this solution, giving the conductance curve I of Fig. 4, where the equivalent conductance was calculated as that of PbAbCl. A typical conductance curve for a 1–1 salt appears. In Fig. 4 is given a $\Lambda\sqrt{c} - c$ plot for these data. From the intercept at $c = 0$, we obtain for the reaction

$$PbAb^+ + Cl^- \rightleftarrows PbAbCl$$

$K = 1.5 \times 10^{-17}$, assuming $\Lambda_0 = 100$. This result confirms the assumption made above that a chloride ion is less firmly bound to a lead ion than an abietate ion. The value 1.5×10^{-17} is of the order as that of the strongest electrolytes previously studied in benzene: for example, K for tetra-*i*-amylammonium picrate in benzene at 25° is 1.0×10^{-17}.

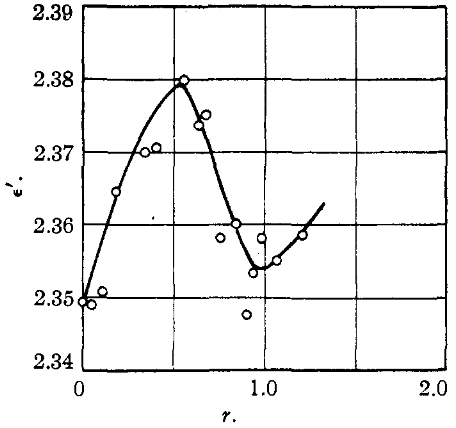

Fig. 9.—Change of dielectric constant during titration.

Summary

1. The conductances of lead abietate and of tributylammonium picrate and chloride in toluene at 35° have been determined at 60 cycles by means of the Schering bridge.

2. The polar moment of lead abietate in toluene is zero. Values for the other two salts check values in the literature.

3. The reaction between lead abietate and tributylammonium chloride in aromatic hydrocarbons has been studied. It is suggested that an intermediate soluble mixed salt, PbAbCl, is formed. The moment of the corresponding ion pair is 8.6×10^{-18} and its dissociation constant is approximately 1.5×10^{-17}.

4. An analytical method for the determination of lead in compounds soluble in aromatic hydrocarbons is described. The method depends on the fact that dry hydrogen chloride precipitates lead chloride quantitatively from benzene or toluene solutions of lead salts.

5. The preparation of pure lead abietate is described.

SCHENECTADY, N. Y. RECEIVED JUNE 24, 1938