gated by Koutecký and Brdička and Hanuš, the only important mechanism of proton transfer is indeed the reaction with hydronium ions as assumed by these authors. Therefore it is safe to assume that the deviation between experiment and theory in this region is caused by the difficulty to account precisely for the motion of the mercury drop in a solution containing concentration gradients. This difficulty of course does not exist when the concentrations of all components are constant, which are the conditions in the present work. In a recent communication which reached us after completion of this work Koutecký[9] has succeeded in accounting for the motion of the dropping electrode through the concentration gradients and has obtained excellent agreement between theory and experiment in the *p*H region in which i_k and i_d are of the same order of magnitude. His result is therefore in agreement with our conclusions. If the following values for the dissociation constants of water, hydronium ions and boric acid are accepted

$$K_{H_2O} = 10^{-14}/55.5;\ K_{H_3O^+} = 55.5;\ K_{BH} = 1.2 \times 10^{-9}$$

a logarithmic plot of the dissociation constant and the rate constant yields an approximately straight line for the three investigated proton donors. Thus it is seen that the Brönsted relation is reasonably well obeyed in this case. *This is the first time that the Brönsted relation has been verified for these primary proton transfer reactions.*

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NEW BRUNSWICK, CANADA

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NOTES

Solutions of Aluminum Chloride in Ethers

BY GORDON G. EVANS, THOMAS R. P. GIBB, JR., J. KEVIN KENNEDY AND FRANK P. DEL GRECO

RECEIVED MARCH 18, 1954

In connection with another problem, the conductivity of solutions of aluminum chloride in anhydrous ethyl ether and tetrahydrofuran has been studied. Since no further work is planned on these systems, the data are presented in their present form even though a full interpretation is not possible.

Experimental.—Pure solvent and concentrated stock solutions, dispensed from burets in an atmosphere of dry nitrogen, were run into a cylindrical vessel; conductances were measured by a pair of dipping electrodes, which were attached to a mercury-sealed, cam-driven shaft and served to stir the mixtures as well. The vessel was also provided with a rubber balloon, to accommodate the changes in gas volume due to the motion of the stirrer and the addition of liquid, and with a side-arm which permitted the removal of samples or insertion of a heavy rod to crush ampoules.

Commercial anhydrous ethyl ether was stored over sodium ribbon, decanted, refluxed overnight with a small amount of lithium aluminum hydride and distilled. Tetrahydrofuran was found to undergo significant decomposition when similarly treated, and was accordingly purified by fractional distillation from mineral oil to remove peroxides, storage overnight (not longer) over sodium and distillation from sodium. Aluminum chloride (Eimer and Amend reagent, anhydrous) was weighed out in a dry-box and dissolved under reflux (which the heat of solution of this powdered material necessitated); the resulting solutions were in the neighborhood of 0.3 *M*. Lithium chloride (Merck reagent, anhydrous) was dried overnight in a vacuum oven at 130° and loaded into ampoules in the dry-box. In operation, a known volume (usually 60 ml.) of solvent was run into the cell, the lithium chloride ampoule, if any, was broken under the surface of the solvent, and the aluminum chloride solution was then added gradually. Conductivities were measured at 1000 cycles with an Industrial Instruments conductivity bridge, model RC 16; for measurement of the lowest conductivities, it was necessary to extend the range of the instrument either by providing an additional fixed resistor in one arm of the bridge or by using a fixed resistor in parallel with the cell. The temperature was controlled within ±0.1° within any single run, but varied from 17 to 23° in different runs.

Results.—From a quantitative viewpoint, the data are not entirely reproducible, the conductances measured in ethyl ether solution showing variations up to about ±15%. (In tetrahydrofuran the variation is even more pronounced; see below.) The shapes of the curves, however, are quite uniform. The results of typical experiments are shown graphically in Figs. 1 and 2, and the conclusions reached may be stated as follows.

(1) The curve of specific conductance *vs.* concentration for solutions of aluminum chloride in ethyl ether is concave *upward*. Correspondingly, the equivalent conductance increases with increasing concentration, a fact which indicates that the ionization process is a complicated one involving at least two molecules of aluminum chloride and probably the solvent as well.

(2) The conductivity of a suspension of anhydrous lithium chloride in ethyl ether is very low, little greater than that of the ether itself. The addition of an aluminum chloride solution to such a suspension, however, results in specific conductances much higher than those observed with aluminum chloride alone, and the curvature of the graph is more pronounced. Presumably the equilibrium $AlCl_3 + LiCl\ (solid) \rightleftarrows Li^+ + AlCl_4^-$ is established; but, inasmuch as only a small part of the lithium chloride is brought into solution by the addition of an equimolar amount of aluminum chloride, it appears that the left-hand side of the equilibrium is strongly favored. (The arrow in

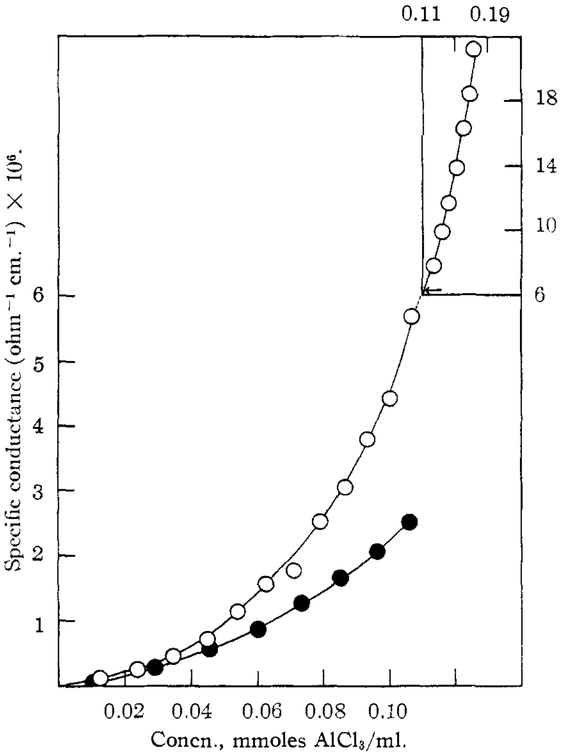

Fig. 1.—Conductivity of solutions of aluminum chloride in diethyl ether: ●, LiCl absent; ○, LiCl present.

Fig. 1 marks the point where equimolar amounts of the two chlorides were present.) We did not look for a change of conductivity with time in this experiment; but since none forced itself on our attention (which happened in the course of some related work), we consider that equilibrium is reached rapidly, during the period of not over one minute which is devoted to stirring before the taking of each reading.

(3) Solutions of aluminum chloride in tetrahydrofuran show much higher conductivities than do solutions in ethyl ether. The curve of specific conductance *vs.* concentration in tetrahydrofuran is almost a straight line when the solvent has been properly purified, but the slope of the line is different for different stock solutions even though the latter are freshly prepared. This variation does not show a systematic dependence on the concentration of the stock solution, and is probably to be traced to the combined effects of concentration, age, and temperatures attained in its preparation. It certainly indicates reaction between solute and solvent, which the following observation confirms.

(4) The addition of the first few ml. of the stock solution of aluminum chloride in tetrahydrofuran to a large volume of pure solvent causes the formation of an abundant white flocculent precipitate, which is gradually but completely dissolved by the addition of more stock solution. We propose for this substance the structure $Cl_2AlO(CH_2)_4Cl \cdot C_4H_8O$.

Anal. Calcd. for $C_8H_{16}O_2AlCl_3$: Al, 9.7; Cl (ionic), 25.6. Found: Al (by 8-quinolinol), 9.3; Cl (by Volhard), 26.2.

Such a structure could result from the attack of aluminum chloride, a Lewis acid, on the basic

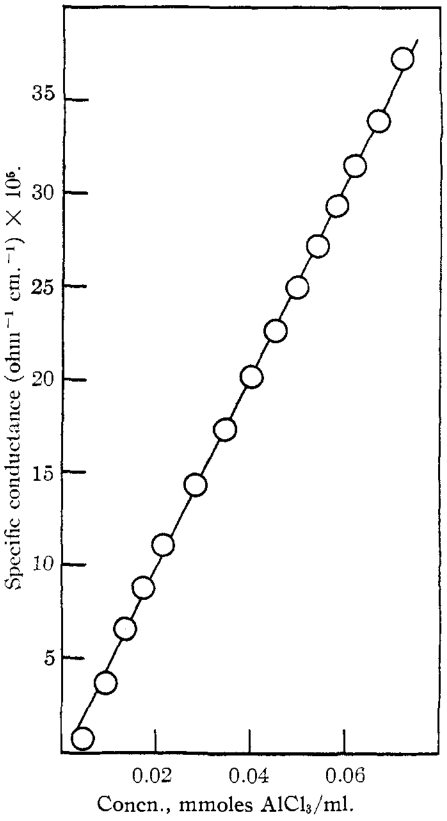

Fig. 2.—Conductivity of solutions of aluminum chloride in tetrahydrofuran.

oxygen atom of tetrahydrofuran, followed by a simple rearrangement. To the best of our knowledge, no material of comparable structure has previously been isolated; but such a substance may well be the intermediate in the formation of δ-chlorobutyl esters by the action of acid chlorides on tetrahydrofuran in the presence of zinc chloride[1] and stannic chloride,[2] both of which are likewise Lewis acids.

(5) Lithium chloride is soluble in tetrahydrofuran to the extent of approximately 2 g. per 100 ml. of solvent. The solubility is increased by the presence of aluminum chloride.

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Solid–Liquid Phase Equilibria in the Condensed System Bromine–Uranium Hexafluoride

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Investigation of the system bromine–uranium hexafluoride has shown that the system is a simple eutectic type. The solid phases are the pure