242. *The Solubility of Aluminium Chloride in Some Hydrocarbons.*

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A new experimental method has been developed for the measurement of the solubilities of hygroscopic metal halides in non-aqueous solvents. The solubility of anhydrous aluminium chloride in a number of hydrocarbons has been measured in the range 20° to 70°. The results give evidence of a weak complex formation in aromatic hydrocarbons, at room temperature, which disappears as the temperature is raised.

THE question of the existence of solution complexes between aromatic hydrocarbons and aluminium halides has, on account of its importance to a knowledge of the mechanism of Friedel–Crafts reactions, attracted the attention of a number of workers as has also the formation of ternary complexes involving also hydrogen halides and giving rise to the so-called "red-oils." The existence of a chemical solvent–solute interaction, in a strictly binary aluminium chloride–hydrocarbon system, involving neither hydrogen chloride nor moisture has hitherto, however, not been satisfactorily established. Even in the case of the more soluble aluminium bromide and benzene, which form a solid complex melting incongruently at 37°,[1] the interaction in solution is so weak as to lead to the conclusion, from the lowering of the vapour pressure of the solvent, that the aluminium bromide in concentrated solution is present mostly as the unsolvated dimer Al_2Br_6.[2]

In the case of the much more widely used catalyst, aluminium chloride, a study of complex formation by lowering of vapour pressure or the formation of univariant two-component systems is quite impracticable in hydrocarbon solutions on account of the low solubility. It is well known, however, that such complex formation in solution may be reflected in the temperature dependence of the solubility. We have therefore determined the solubility of aluminium chloride in a number of hydrocarbons, by an analytical technique under very rigidly anhydrous conditions, from 20° to 70°. The results give evidence of weak complex formation at room temperature in aromatic hydrocarbons, which becomes greater as the electron-donating character of the hydrocarbon increases and less as the temperature is raised.

In spite of the obvious relevance to widely-used reactions, few measurements have been made of the solubility of aluminium chloride in hydrocarbons. Menschutkin[3] reported a solubility in benzene of 0·12% at 17° and 0·72% at 80°; also in toluene of 0·26% at 17° and 0·92% at 73°. The context shows that these are in weight per cent of solution. Bruner[4] reported that it is insoluble in benzene and Thomas[5] that it was slightly soluble in benzene and toluene with a small rise of temperature and the production of an olive green or greenish-yellow colour, respectively, and slightly soluble in xylene with a temperature rise of 5° and the production of a heavy red oil after one hour. In none of this previous work does there appear to have been any rigorous exclusion of moisture. The only determinations hitherto carried out under anhydrous conditions are those of Eley and King[6] who measured the solubility in benzene by a synthetical method in closed ampoules from 108·6° to 192·0°. Between these temperatures, which are far above the boiling point of benzene under atmospheric pressure, the solubility is almost ideal and therefore indicates the absence of complex formation in this region. The present results give some indication of an appreciable, though not extensive, complex formation at room temperature even in the case of benzene. In the more donor or "basic" hydrocarbons the chemical interaction is greater, but in all cases as the temperature is raised the complex formation decreases, the solutions becoming regular. For comparison, the solubility

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[1] Plotnikov and Gratsianskii, *Chem. Abs.*, 1939, **33**, 2432; Van Dyke, *J. Amer. Chem. Soc.*, 1950, **72**, 3619; Eley and King, *Trans. Faraday Soc.*, 1951, **47**, 1287.

[2] Brown and Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 6265.

[3] Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1089 (*Chem. Zent.*, 1910, **81**, 167).

[4] Bruner, *Z. phys. Chem.*, 1902, **41**, 513.

[5] Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold, New York, 1941, 25.

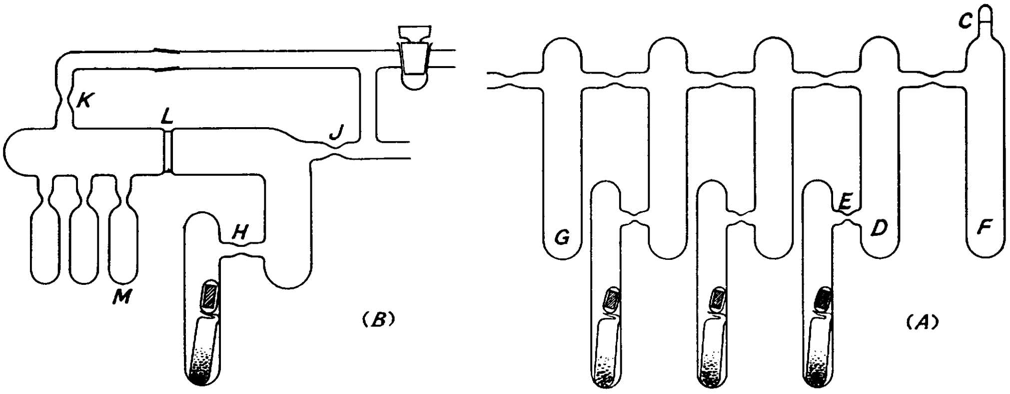
[6] Eley and King, *Trans. Faraday Soc.*, 1951, **47**, 1287.

has also been measured in *cyclo*hexane, methyl*cyclo*pentane, and *n*-hexane in which no complex formation occurs.

EXPERIMENTAL

Aluminium chloride was prepared by passing dry hydrogen chloride over high-purity aluminium wire at 400° to 500°, subliming the product four times *in vacuo* and sealing it into fragile hook-ended ampoules. The final product was a pure white solid which could be sublimed without residue. Pure commercial solvents were further purified, fractionated, and dried by appropriate conventional methods. The final drying was in all cases carried out by treatment with aluminium chloride, as described below. The course and success of this drying could be followed by observing the colour of the solutions. A solution of aluminium chloride in dry benzene or toluene is visually quite colourless. When cooled to −195° a lemon-yellow colour is produced, which disappears on warming the solution to room temperature. Solutions in the xylenes and in mesitylene, subjected to the same drying procedure, are lemon-yellow at room temperature and darken on cooling. This behaviour is reminiscent of the colour of iodine in these solvents, which is browner in mesitylene than in benzene and in any aromatic hydrocarbon becomes browner on cooling and more purple on heating, and it points like the case of iodine to the formation of weak complexes between solvent and solute. In both cases the complex formation can be regarded as an "acid–base" or "donor–acceptor" reaction.[7]

FIG. 1.



In the case of an aluminium halide, however, the amount of complex formation with the solvent can be increased by increasing the strength of the "acid" by the addition of hydrogen halide or water. In the first place there is obtained a deeply-coloured ternary complex which may be regarded as $Cl_3AlCl^-..^+HArH$ and gives rise to the so-called "red oils." There is no necessity, however, to suppose that colours due to traces of moisture are produced by the formation of the same ternary complexes. These are more probably due to hydrated aluminium chloride–hydrocarbon complexes, $Cl_3AlOH^-..^+HArH$, since they are formed under conditions where hydrolysis is very slow. Such colours, however, are an exceedingly sensitive test for the presence of moisture; *e.g.*, pinholes or minute cracks in the solubility apparatus quickly became evident by the development or deepening of the colour of the solutions. In these cases the results were discarded, although analysis of several such coloured solutions showed only a small difference from the solubility in the colourless solutions.

The solubility apparatus, Fig. 1, made of Pyrex glass, consisted essentially of two parts: the solvent pre-treatment line *A* and the saturation and sampling vessel *B*. Purified solvent was introduced, against a stream of dry nitrogen, through *C* into the previously outgassed apparatus. After removal of any dissolved gases by alternately freezing, pumping, and remelting, the solvent was frozen at −195°, the apparatus evacuated, and a sample of pure aluminium chloride sublimed into the first pre-treatment tube *D*. After the tube had been sealed-off at *E* the solvent was condensed at −195° on to the aluminium chloride, having been allowed to melt in the first tube *F*, which was then removed. This process was then repeated, three or four such treatments being usually sufficient. The purified frozen solvent was temporarily stored in the tube *G* whilst a sample of pure aluminium chloride was sublimed in a

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[7] Fairbrother, *J.*, 1948, 1051.

vacuum into the saturation vessel through *H*, which was then sealed. Finally the purified solvent was condensed on to this aluminium chloride and the apparatus sealed under vacuum at *J* and *K*. The vessel *B* was then suspended in a large water thermostat, controlled at the several temperatures to ± ≯ 0·1°, with the longer limb approximately vertical and rocked, for **24** hours at each temperature, about an axis normal to the plane of the diagram. It was then rotated about this axis until the saturated solution filtered through the sintered-glass disc *L* (porosity **3**) into the first of the sampling tubes *M*. Only three of these are shown in the diagram : a further set of three was arranged at the rear of the diagram. When sufficient solution had collected in the tube it was sealed off and the sampling side of *B* thoroughly cleaned by condensing small quantities of solvent from the solution, passing it as vapour through the sintered-glass disc, washing it round and returning it as liquid. This was repeated several times. The sample ampoules were weighed, cracked about the middle without separation, and broken under water by gentle shaking. After 2 hr. to ensure complete extraction and hydrolysis, the chloride content was determined by a differential electrometric method based on that of McInnes and Dole.[8] The solubility is given in the Table and plotted as the logarithm of mol. fraction of solute against $1/T$ in Fig. 2.

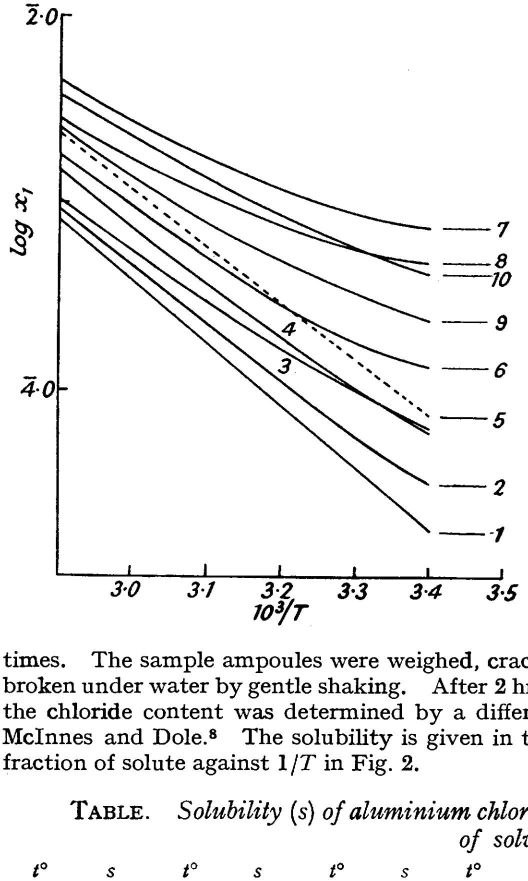

FIG. 2.

1, n-*Hexane.*
2, cyclo*Hexane.*
3, *Methyl*cyclo*pentane.*
4, *Benzene.*
5, *Ideal.*
6, *Toluene.*
7, o-*Xylene.*
8, m-*Xylene.*
9, p-*Xylene.*
10, *Mesitylene.*

TABLE. *Solubility* (*s*) *of aluminium chloride, expressed in mg. of* Al_2Cl_6 in 100 g. *of solvent.*

t°	*s*	*t*°	*s*	*t*°	*s*	*t*°	*s*	*t*°	*s*	*t*°	*s*	*t*°	*s*
n-Hexane		*cyclo*Hexane		Methyl*cyclo*-pentane		Benzene		Toluene		*m*-Xylene		Mesitylene	
20·0	5·0	20·5	9·8	20·0	19·1	19·9	20·0	20·15	39·0	19·9	113·4	21·35	98·3
30·0	12·0	29·4	16·1	30·0	32·1	30·4	36·5	29·1	48·6	29·8	154·2	29·85	125·5
39·8	27·3	39·4	32·2	39·8	53·9	39·8	66·7	39·1	82·7	40·2	196·8	39·65	202·5
49·9	56·1	45·0	51·9	49·9	96·1	49·8	118·9	49·25	139·9	50·0	283·0	59·1	478·4
60·5	120·3	49·0	66·2	60·5	165·6	59·6	236·6	59·3	258·0	59·0	409·0	68·0	666·0
69·8	227·7	55·0	97·8	69·8	261·2	69·4	463·0	67·6	407·6	69·1	605·2		
		59·8	129·7										
		67·5	240·3										

In addition to the figures given, the solubility was also measured in pure *o*-xylene and *p*-xylene. The values were in the same general region as in *m*-xylene, but examination of the solvents by infrared absorption at the end of a run showed that in spite of the very rigorous

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[8] McInnes and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 1119.

drying, considerable (15 to 20%) isomerisation into *m*-xylene had occurred. Even in the case of *m*-xylene, more trouble was experienced with oil formation in the pre-treatment and with reproducibilty of results than with the other solvents, and the final results still show a small scatter about a smooth curve. There was, however, much less isomerisation, amounting to less than 5% after 6 days and a maximum temperature of 70°.

The ideal solubility curve of Fig. 2 has been calculated by the equation given by Hildebrand:[9]

$$\log_{10} x_1 = \frac{-\Delta H_{T_M}}{4{\cdot}575} \cdot \frac{(T_M - T)}{T_M \cdot T} + \frac{\Delta C_p}{4{\cdot}575} \cdot \frac{T_M - T}{T} - \frac{\Delta C_p}{1{\cdot}987} \log_{10} \frac{T_M}{T}$$

where x_1 = mol. fraction of solute (ideal); ΔH_{T_M}, heat of fusion, = 17·0 kcal. at m. p. $T_M = 466°$K;[10] ΔC_p = molar heat capacity change of solute on fusion = 35·9 − 0·056T kcal.[11]

The curves for the saturated hydrocarbons and for benzene lie below the ideal solubility, as does also that for toluene at the higher temperatures. At the lower temperatures there is a general increase of solubility as the donor character of the hydrocarbons becomes greater, though there is little difference between the solubility in *m*-xylene and in mesitylene. There is little evidence of complex formation at the higher temperatures, where all form regular solutions. The solute parameters of aluminium chloride have been calculated, according to Hildebrand's method,[12] from the solubilities at 65° (interpolated), using solvent parameters obtained by interpolation from the data given by Hildebrand and Scott and $(\Delta E/V)^{\frac{1}{2}} = 7{\cdot}3$ for methyl*cyclo*pentane. The results are as follows:

Solvent	Solvent parameter	10^3x	Solute parameter, Al_2Cl_6
n-Hexane	6·7	0·525	8·9
*cyclo*Hexane	7·6	0·603	9·6
Methyl*cyclo*pentane	7·3	0·679	9·2
Benzene	8·5	1·00	9·8
Toluene	8·4	1·23	9·4

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[9] Hildebrand and Scott, " The Solubility of Non-electrolytes," Reinhold, New York, 1950.
[10] Fisher and Rahlfs, *Z. anorg. Chem.*, 1932, **205**, 1.
[11] Landolt Börnstein, Tabellen.
[12] Ref. 9, p. 275.