and 4.8 atom % of Tl obtained during the vaporization and estimated at the same temperature of 1010 K directly from the slopes reported in Figure 4.

From the $\Delta\alpha$ values measured with the cell illustrated in Figure 5 the activity values of the analized alloys are derived using the relation

$$a = 1 - 2[\exp(A_x' - B_x'/T)/\exp(A_0' - B_0'/T)] \qquad (4)$$

where the A_x', B_x', A_0', and B_0' are the constants reported in Table III. The values obtained with this procedure are also reported in Figure 6.

In agreement with Kundys and Terpilowsky's activity data measured at 723 K from emf measurements (*6*), the results here obtained show that the In–Tl solution has a quasi-ideal behavior with a small positive deviation.

This quasi-ideal behavior is not surprising if one considers that the differences in the atomic radii and in the electronegativity of thallium and indium are very small (*9*).

As the activity values derived from both mass spectrometric and torsion–effusion measurements at 830 and 1010 K are comparable within the reported errors, we have chosen the midrange temperature, 920 K, to derive the activities and the free energy of mixing for both elements in the different alloys.

The activity of indium has been derived in the usual way by a graphical integration of the Gibbs–Duhem equation (*10*). The β values $\beta = \ln \gamma_{\mathrm{Tl}}/(1 - N_{\mathrm{Tl}})^2$ necessary for this integration were evaluated for the investigated alloys by using the relation

$$\beta = [(A_x - A_0) - (B_x - B_0)/T](1 - N_{\mathrm{Tl}})^{-2} \qquad (5)$$

The activity values of both components so calculated at 920 K and the corresponding partial molar free energies are reported in Table IV at 0.1 mole fraction intervals across the system. The mixing enthalpy of Tl can be estimated by the equation

$$\Delta H_{\mathrm{mix}} = (1 - N_{\mathrm{Tl}}) \int_{N_{\mathrm{Tl}}=0}^{N_{\mathrm{Tl}}=N_{\mathrm{Tl}}} 4.5758(B_0 - B_x)(1 - N_{\mathrm{Tl}})^{-2}\, dN_{\mathrm{Tl}} \qquad (6)$$

The results of these calculations, even if they are not particularly meaningful as the associated errors are greater than the ΔH_{mix} values obtained, show that the $\Delta H_{\mathrm{mix,s}}$ are almost null and this is a further confirmation of the solution ideality.

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Some Data on Phase Equilibria in the System Benzene–$FeCl_3$–H_2O–HCl at 20 °C

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The solubility of iron trichloride in benzene (B) as a function of the water content of benzene has been determined quantitatively. At all values of the molar ratio $FeCl_3$:B a good solubility is guaranteed if the ratio H_2O:$FeCl_3$ in the mixture of $FeCl_3$, H_2O, and benzene amounts to 1. Maximum solubility (in the form of the $FeCl_3$–H_2O complex) amounts to 0.075 M at a HCl concentration of 0.02 M. By the addition of HCl up to a concentration of 0.70 M, this solubility increased to 0.10 M. The solubility in dry benzene and the solubility of the higher hydrates are comparatively small.

This study on the phase equilibria of B–$FeCl_3$–H_2O–HCl (B = benzene) was carried out to contribute to a better insight into the industrial process of the chlorination of benzene. The coordinative conclusions on phase equilibrium data, on kinetics measured in a homogeneous liquid mixture of the reactants, and on chlorinations carried out in a bubble column have been collected (*2*, *3*). In orientating experiments we found that the solubility of iron trichloride depends strongly on the water content of the medium. To determine quantitatively the solubility of iron trichloride as a function of the water content of the system, we carried out the following experiments.

Experimental Section

We prepared heterogeneous systems of iron trichloride and H_2O in 250 mL of B with overall compositions lying between the successive hydrates: thus between 0 and 2, 2 and 2.5, 2.5 and 3.5, 3.5 and 6 hydrate. The existence of these hydrates has been measured by Bakhuis Roozeboom (*1*, *6*). These mixtures were obtained by addition of anhydrous $FeCl_3$ and $FeCl_3 \cdot 6H_2O$ (U.C.B., tout pure) or by addition of anhydrous $FeCl_3$ and H_2O to benzene. In all these experiments so much iron trichloride is added that a precipitate is formed. In some experiments a gentle stream of HCl gas, dried on a molecular sieve, was bubbled through the mixture for 25 min. All mixtures were magnetically stirred. After the precipitate had settled we took samples of the liquid. We then

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Table I. Solubility of Iron Trichloride or Its Hydrates in Benzene at 20 °C [b]

	10^{-3} kg added to 250 mL of B			overall compn, mole ratio		Compn of the solution					
Expt	$FeCl_3$	H_2O	$FeCl_3 \cdot 6H_2O$	$[FeCl_3]/([FeCl_3] + [H_2O])$	$[FeCl_3]/([FeCl_3] + [B])$	$[H_2O]$	Mole ratio $[H_2O]/([H_2O] + [B])$	$[FeCl_3]$	Mole ratio $[FeCl_3]/([FeCl_3] + [H_2O])$	$[H_2O]/[FeCl_3]$	[HCl]
1	3.92	0.34		0.56	0.0086	0.081	0.0073	0.075	0.48	1.10	0.02
2[a]	4.33	0.48		0.50	0.0094	0.104	0.0093	0.10	0.49	1.05	0.70[a]
3	3.95	0.98		0.31	0.0086	0.013	0.0012	0.0017	0.12	7.5	0.006
4[a]	4.00	1.00		0.29	0.0087	0.050	0.0044	0.016	0.24	3.0	0.41[a]
5	8.7		16.8	0.24	0.039	$<5 \times 10^{-4}$	$<5 \times 10^{-5}$	~0.001	1		
6	6.0		23.1	0.19	0.041	$<5 \times 10^{-4}$	$<5 \times 10^{-5}$	0.0006	1		
7		1	6	0.11	0.008	$<5 \times 10^{-4}$	$<5 \times 10^{-5}$	~0.0003	1		
$FeCl_3 \cdot 2H_2O$				0.333							
$FeCl_3 \cdot 2.5H_2O$				0.287							
$FeCl_3 \cdot 3.5H_2O$				0.222							
$FeCl_3 \cdot 6H_2O$				0.143							

[a] HCl is added. [b] Concentrations are given in M (kmol/m^3).

measured the concentrations of iron and H_2O using atomic absorption analysis and Karl-Fischer titration. Before we took samples we made sure that the mixture was in equilibrium. We found that after heating of the mixtures to the melting point of the solids (about 50 °C) for 5–10 min and magnetically stirring for 5 h after preparation of the mixtures, no changes in concentrations can be observed. Before the measurements we made sure that the mixtures had cooled to 20 °C. The results are based on samples taken at least 6 h after the preparation. Saturated solutions have been obtained, in all experiments undissolved iron trichloride or its hydrates have been found at the bottom of the flask. HCl has been determined by mixing of a 1–10-mL sample with water and titration of this mixture against 0.1 M NaOH.

In all our experiments we used benzene chemical pure, Ph.Ned.VI. The conditions and the results have been collected in Table I.

Results

The solubility of iron trichloride proved to be very much dependent on the H_2O content of the mixture. We measured a maximum value, 0.1 M, in experiment 2, to which HCl gas was added. A comparison of experiment 2 with experiment 1 shows that, by addition of HCl, the solubility of $FeCl_3$ is increased by 33% for an increase of [HCl] from 0.02 to 0.7 M. Since the estimated error in the determination of $[FeCl_3]$ and $[H_2O]$ amounts to 3 and 3%, respectively, we found that in both experiments the same ratio of $[H_2O]:[FeCl_3]$, which is practically 1, is measured in the solutions.

At an overall composition between the 2 and 2.5 hydrate the solubility of iron trichloride is considerably lower, 0.0017 M. Then nearly a tenfold increase is observed if HCl is added. When the overall composition lies between the 2.5 and 3.5 between the 3.5 and 6 hydrate, or between the 6 hydrate and H_2O, a still further decrease of the iron concentration in the solution is measured. The H_2O concentration decreases below its detection level.

In experiments 3–7 the amounts of iron trichloride and water in the solid phase are very large in comparison to the amounts dissolved. So the ratio $FeCl_3:H_2O$ in the solid phase is not altered substantially by the dissolution process. Thus weighing iron trichloride and water added to benzene is a reliable method to measure its composition. The preparation of the samples has been carried out in a drybox. In experiments 1 and 2 the amounts of iron trichloride and water constitute a major part of the quantities added. We observed that by the addition of water a part of the solid is converted into a precipitate having a structure quite different from that of dry $FeCl_3$. A part of the precipitate remains in its original form. Owing to its hygroscopic character, we could not determine the quantities of iron and water in the solid phase by chemical analysis.

We measured $[H_2O]$ and $[FeCl_3]$ in these experiments but also in two saturated solutions of $FeCl_3$ in B which contained a small quantity of H_2O, so that the overall ratio of $H_2O:FeCl_3$ was considerably less than 1: $[H_2O] = 0.024$ and $[FeCl_3] = 0.026$, $[H_2O] = 0.023$ and $[FeCl_3] = 0.024$. A water:iron ratio of 1 was measured again.

In view of these results and the literature data about complex formation of $FeCl_3$ and solvent, we conclude that only a monocomplex of $FeCl_3$ and H_2O, $FeCl_3–H_2O$, is relatively soluble in benzene.

Discussion

We shall now give a semiquantitative description of the total phase diagram, B–$FeCl_3$–H_2O, based on the phase rule, on the hydrates measured by Bakhuis Roozeboom, and on the solubility data given above. A triangle diagram in which, for the sake of clearness, the coordinates are not proportional to the values of the actual occurring compositions is given in Figure 1. Thus Figure 1 is nonquantitative. Figure 2, which is an enlargement of the uppermost part of Figure 1, is semiquantitative, however. The solubility of H_2O in B is known from literature data (*4*, *7*) and has been confirmed by measurements. The points representing the compositions of the benzene phase in equilibrium with two solid phases have been measured. The solubility-lines connecting these points have been drawn as straight lines, usually these lines are slightly curved. According to the phase rule, $f = n - r + 2$, $5 - r$ degrees of freedom exist in our system. At a given temperature and pressure $3 - r$ compositions can be chosen independently. The system contains five zones where three phases exist, viz, $FeCl_3$ (solid)–B′–$FeCl_3 \cdot 2H_2O$ (solid), zone II (the overall composition of experiments 1 and 2 (Table I) lies in this zone and point B′ refers to the composition of the liquid); $FeCl_3 \cdot 2H_2O$ (solid)–C–$FeCl_3 \cdot 2.5H_2O$ (solid), zone IV (point C indicates the liquid composition for experiments 3 and 4); $FeCl_3 \cdot 2.5H_2O$ (solid)–D–$FeCl_3 \cdot 3.5H_2O$ (solid), zone VI (point D is the liquid composition for experiment 5); $FeCl_3 \cdot 3.5H_2O$ (solid)–E–$FeCl_3 \cdot 6H_2O$ (solid), zone VIII; $FeCl_3 \cdot 6H_2O$ (solid)–F–K, zone X (points E and F indicate liquid compositions for experiments 6 and 7).

Secondly the system contains seven zones of two coexisting phases, viz., (1) $FeCl_3$ (solid)–A–B′, zone I ("A" indicates the solubility of $FeCl_3$ in B. The curve A–B′ describes the change in solubility of $FeCl_3$ in B, when increasing amounts of H_2O are added to the system); (2) $FeCl_3 \cdot 2H_2O$ (solid)–B′–C, zone III (in this zone an equilibrium exists between a liquid whose composition lies on the line B′–C, and solid $FeCl_3 \cdot 2H_2O$). Mutatis mutandis the same holds for zones V, VII, and XI: (3) $FeCl_3 \cdot$

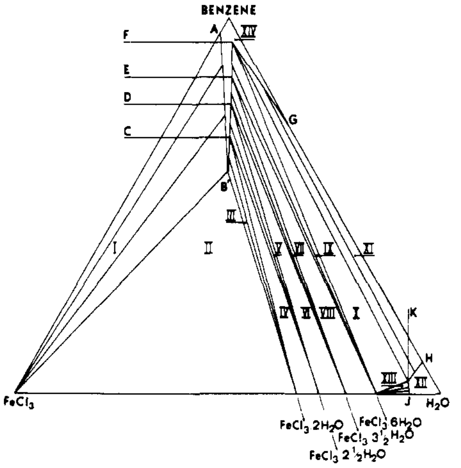

Figure 1. The semiquantitative phase diagram B–$FeCl_3$–H_2O.

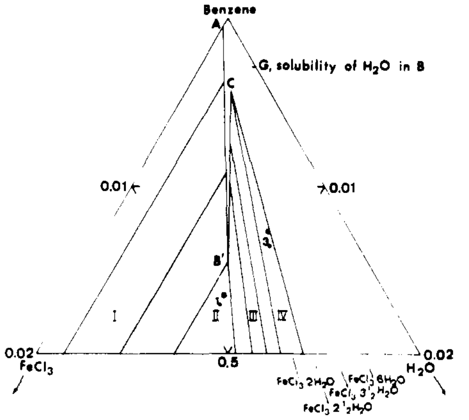

Figure 2. Some phase equilibria of the system B–$FeCl_3$–H_2O.

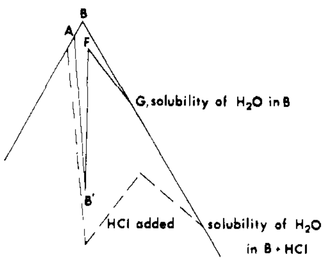

Figure 3. The effect of HCl.

2.5H_2O (solid)–C–D, zone V; (4) $FeCl_3$·3.5H_2O (solid)–D–E, zone VII; (5) $FeCl_3$·6H_2O (solid)–E–F, zone IX; (6) F–G–H–K, point H has been given by ref 5; (7) $FeCl_3$·6H_2O (solid)–K–J, zone XIII.

In the system occur two zones of one phase, viz., benzene–A–B'–C–D–E–F–G and H_2O–H–K–J. In the former, zone XIV, B is unsaturated with both $FeCl_3$ and H_2O. In the latter, zone XII, H_2O is unsaturated with iron trichloride and B.

Zone XIV, benzene–A–B'–C–D–E–F–G, has a remarkable shape; it consists of two wedges. Due to this shape the solubility of H_2O decreases sharply (according to line G–F) if small quantities of $FeCl_3$ are added to B which is saturated with H_2O. It should be pointed out that for all solutions the compositions of which lie on the line F–E–D–C–B', the ratio $[H_2O]/[FeCl_3]$ remains practically one.

We observe that if HCl is added to the system the solubility of iron trichloride increases; the solubility of H_2O in B also increases when HCl is present. The percentage increase of the solubility is much larger for the solutions given by points C, D, E, and F than for point B'. The wedges are thus broadened by addition of HCl. This effect is qualitatively demonstrated by the interrupted line in Figure 3. Only in the presence of HCl it is possible to prepare solutions containing sizable iron trichloride concentrations at a ratio $[H_2O]/[FeCl_3] > 1$; see, e.g., experiment 4.

In Figure 2 our data, the hydrates and the solubility of H_2O in B, are quantitatively given. It should be borne in mind that the area of the diagram given in Figure 2 gives only 1/2500 of the total area of the diagram B–$FeCl_3$–H_2O.

For the preparation of solutions containing the highest concentration of the monocomplex $FeCl_3$–H_2O, the overall composition must lie in zone II. If the quantity of water present in the mixture of experiment 1 is increased till the ratio $FeCl_3$:(H_2O + $FeCl_3$) is only slightly more than 0.5, the overall composition will be found in zone III and the solubility decreases (point 1_0 moves horizontally to the right and the line $FeCl_3$–H_2O (complex) to $FeCl_3$·2H_2O (solid) is intersected).

From the above it may be clear that under equilibrium conditions the solubility of iron trichloride greatly depends on the overall water content of the system and on [HCl]. Summarizing the results of our experiments we may conclude the following. Dry iron trichloride is practically insoluble in dry benzene. $FeCl_3$ is only reasonably well soluble in B, if both $FeCl_3$ and $FeCl_3$·2H_2O are present in solid phase. When this condition is fulfilled a monocomplex $FeCl_3$–H_2O will be formed in the solution. If the solution is not in equilibrium with the two solids mentioned, but with $FeCl_3$·2H_2O and $FeCl_3$·2.5H_2O or with two higher hydrates, the solubility decreases sharply. For any overall ratio of $FeCl_3$:B (kmol/kmol), a good solubility is guaranteed if the overall ratio H_2O:$FeCl_3$ is 1. The presence of HCl increases the solubility of iron trichloride. Generally, the percentage increase of the solubility is larger as the overall ratio H_2O:$FeCl_3$ in the system is larger. The shape of the solubility curve represented as a part of the diagram B–$FeCl_3$–H_2O remains essentially the same, however.

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