Since practically all metallic impurities are soluble in concentrated hydrochloric acid solutions, it is reasonable to assume that these trace impurities will similarly result in high distribution ratios.

It is quite apparent that the effectiveness of any chemical purification scheme will be limited by the purity of the reagents employed. Thus, according to the A.C.S specifications for reagent grade hydrochloric acid (sp. gr. 1.188–1.192) used in this study, the maximum limit of arsenic impurity present is 8×10^{-7} per cent. Consequently, the use of this solvent without further purification imposes a lower limit for the removal of arsenic impurity from germanium tetrachloride, this limit being equal to or more than 5×10^{-4} parts of arsenic per million parts of germanium.

It is obvious that single batch extractions are very effective in removing the impurities under investigation from germanium tetrachloride, particularly when these impurities are present in very low concentrations. Repeated batch extractions with fresh hydrochloric acid will no doubt reduce the residual impurity considerably. Undoubtedly, a continuous system of solvent extraction could be employed with very successful results.

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Densities of Polyethylene Solutions[1]

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To obtain an estimate of the density of the amorphous regions in polyethylene at temperatures below the crystalline melting point, it is possible to extrapolate to these temperatures the (approximately) linear relation between the melt density and temperature. Confidence in this extrapolation would be increased if the resulting density could be obtained by a second independent method. To this end we have developed a precise method for measuring the densities of polyethylene solutions. The desired amorphous density is obtained by appropriate extrapolation of the specific volume–composition curve. The limited solubility of polyethylene restricts the experiments to temperatures not far below the crystalline melting point.

Previous measurements[2] of the densities of polyethylene solutions were restricted to relatively dilute solutions and were uncertain in the third decimal place. We have obtained a precision of about ±0.0002 density unit at the 95% confidence level. This is comparable to the precision attained on solid polyethylene samples at room temperature.[3]

Experimental

The polyethylene sample used in this work was that designated A-40 by others.[2,4,5] The solvent was Eastman Kodak Co. #277 *p*-xylene, m.p. 12–13°. Reischauer pycnometers (A. H. Thomas Co., #9023) were calibrated with mercury at several temperatures in the range under consideration. Corrections were applied for meniscus shape and for the buoyancy of air.

Solutions containing less than 30% polyethylene by weight were made up in glass stoppered flasks which were agitated by slow side-to-side rocking in an air oven at 90° for 12 hours. The homogeneous solutions were then poured into a 50-ml. hypodermic syringe whose barrel was wrapped with glass heating tape and maintained at 90°. An improvised needle with a 2-mm. bore was used to inject the solution into the heated pycnometer.

More concentrated solutions were too viscous to flow through the needles. They were made up directly in the pycnometers. Finely divided polyethylene and enough xylene to fill the pycnometer $^3/_4$ full at 90° were weighed in. Mixing was accomplished by slow rocking as before at 125° to reduce the viscosity of the solution. The pycnometer was then brought to 90° and filled to the graduated section. It was then cooled until the liquid level fell below the neck and rocked at this temperature until the solution was homogeneous.

Final measurements were carried out in a constant temperature bath at 90.0 ± 0.02°. The experimental data for several solutions of polyethylene A40 are listed in Table I.

Crude cloud point observations were made on the more dilute solutions by allowing them to cool in a test-tube while stirring them with a thermometer. The temperature at which the first sign of a precipitate appeared was recorded as the cloud point.

TABLE I

DENSITIES OF SOLUTIONS OF POLYETHYLENE A40 AT 90°

Wt. % polyethylene	Density	Specific vol.	Cloud point, °C.
0[a]	0.7982	1.2528	..
10.000	.8001	1.2498	68
20.000	.8020	1.2469	72
30.000	.8038	1.2441	77
44.138	.8065	1.2399	..
100	.8172	1.2237[b]	114[c]

[a] Pure *p*-xylene. [b] Obtained by least squares extrapolation. [c] Crystalline melting point by polarized light with hot stage microscope.

Discussion

Amorphous Density of Polyethylene.—A plot of specific volume against weight composition of the polyethylene solutions was a straight line with a maximum deviation of experimental points of less than 0.0002 cc./gram. This linear relationship suggests strongly that polyethylene and *p*-xylene mix without change in volume at least up to 44% polyethylene by weight. We therefore felt justified in extrapolating the line to 100% polyethylene. A least squares analysis gave a specific volume of 1.2237 ± 0.0005 (95% confidence limits) and a corresponding density of 0.8172 for amorphous polyethylene at 90.0°. This value may be compared with 0.8153 obtained by linear extrapolation to 90° of the melt density–temperature curve of another polyethylene.[6]

Estimated Heat of Fusion.—Bueche[7] has recently expressed Flory's relation[8] for the depression

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(1) A joint contribution of the Department of Chemistry, University of Delaware, and the Polychemicals Department, E. I. du Pont de Nemours & Co. Research performed by Robert Roberts in partial fulfillment of the requirements for the degree of Bachelor of Science at the University of Delaware. Presented at the Fifth Delaware Chemical Symposium, Delaware Section, A.C.S., January 17, 1953.

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of the melting point of a polymer by added diluent in terms of the heat of fusion H_f of the polymer

$$(1/T_m - 1/T_m{}^\circ)/v_1 = R/dv_s H_f - C(v_1/T_m)$$

where T_m and $T_m{}^\circ$ are the melting temperatures of the solution and pure polymer, respectively; v_1 and v_s are the volume fraction and molar volume of the solvent; R is the gas constant; and d is the amorphous density of the polymer. C is a constant expressing the polymer–solvent interaction. Application of this equation to the crude cloud point data of Table I gave H_f = 1.68 kcal./mole C_2H_4. This may be compared with the value of 1.647 obtained by Parks and Mosely[9] by extrapolation of the heats of fusion of normal paraffin hydrocarbons. This agreement must be considered fortuitous in view of the long extrapolations involved in treating our dilute solution data.

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Magnetic Evidence of Monomer–Dimer Equilibrium of Molybdenum(V) Ions in Hydrochloric Solution

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The change in constitution of the quinquevalent molybdenum ions accompanying the change in color from green to brown of the hydrochloric solutions as the normality passes from 8 to 2 has not been yet completely elucidated.

After the researches of Chilesotti[1] and of Foerster, Fricke and Hausswald,[2] El-Shamy, *et al.*,[3] on the basis of results of electrometric and spectrophotometric measurements, established the most probable formulas for the quinquevalent molybdenum ions in 8–6 and 4–2 hydrochloric acid, and postulated the existence of two different forms within these two acid ranges and of other ionic species at intermediate acidities.

Since quinquevalent molybdenum has one unpaired electron, the carrying out of magnetochemical investigations seemed suitable for the purpose of obtaining information on the constitution of quinquevalent molybdenum ions in 10–2.4 N hydrochloric acid.

Experimental

Materials and Method.—Molybdic acid of "Anala R" grade was dissolved in pure concentrated hydrochloric acid and the solution (0.491 g./ml. in molybdenum) diluted 1:4 with concd. HCl and then submitted to electrolytic reduction.[2]

The total molybdenum content was determined by reduction with zinc amalgam in a Someya reductor and by subsequent titration with standard ceric sulfate. The reduced molybdenum was determined by titration against the same reagent.

The stock solution of exact quinquevalent molybdenum was prepared by mixing the solution containing molybdenum ions, reduced to an oxidation state <5, with the appropriate amount of the starting hydrochloric solution of molybdic acid, and the oxidation state checked again by analysis. The total chloride ion was determined by the Bunsen method.

Solutions for magnetic measurements were made by mixing 10 ml. of the stock solution of quinquevalent molybdenum with 20 ml. of an aqueous hydrochloric solution whose acid content ranged from 35.49% (density = 1.177 at 20°) to 0% (pure water). The weights of all the solutions were in each case determined. The composition of the solutions submitted to magnetic measurements was determined from the analytical data of the solutions mixed together. The amount of free hydrochloric acid was computed, according to previous work,[3] by subtraction of the amount supposed to be combined (three Cl^- for each MoO^{+++} group) from the total chloride ion. The eventual uncertainty in the results arising from such a calculation can be taken as inconsequential.

Magnetic susceptibility measurements on the solutions were carried out, with an accuracy of ±0.2%, using a Gouy balance at 20°.

Results

The measurements obtained and certain data necessary for the calculation of results are listed in Table I.

Correction for diamagnetism of the solvent (including ions) was made by subtraction of experimentally determined displacement for the hydrochloric solutions added to the stock solution of quinquevalent molybdenum and by further subtraction of the calculated contribution of Cl^-, H_2O, Mo(V) in the stock solution. The diamagnetic increments used were -22.9, -13.0, -14.0 ($\times 10^{-6}$), respectively, after Klemm.[4]

In Fig. 1, the values of χ_A for molybdenum(V) ion are plotted against the concentration of HCl in the solutions.

Discussion

In the case of molybdenum ions, as an exception to the ions of heavy transition metals, it is generally assumed that quenching of the orbital moment takes place.[5] Therefore the expected moment for the quinquevalent molybdenum ion, with one unpaired electron, is the "spin only" moment equal to the usual 1.73 Bohr magnetons. The atomic susceptibility corresponding to this moment is calculated to be $+1270 \times 10^{-6}$ at 20°.[6]

The observed values of χ_A at concentrations of HCl > 7 N agree quite closely with this value. This indicates that, in this range of HCl concentrations, molybdenum(V) ions exist as monomer entities. As the HCl concentration is lowered, the magnetic susceptibility begins to drop and approaches null value as the 2 N concentration of HCl is approached. This shows that at acid concentration lower than 7 N, electron pairing takes place, reaching the completion at HCl concentration near 2.5 N. Below this value, 100% of molybdenum(V) ions exist as dimers containing two mo-

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