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

$$(1/T_m - 1/T_m^\circ)/v_1 = R/dv_sH_f - C(v_1/T_m)$$

where T_m and T_m° 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.

Acknowledgment.—We wish to acknowledge the guidance of W. M. D. Bryant, who directed this work on behalf of the du Pont Company.

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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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(6) *Cf.* W. Klemm, ref. 4a, p. 111; P. W. Selwood, ref. 5, p. 62.

TABLE I

MAGNETIC SUSCEPTIBILITY OF HYDROCHLORIC SOLUTIONS OF MOLYBDENUM(V) IONS

No.	Mo, %	Cl, %	H_2O, %	HCl, moles/l.	ρ	$\chi_g \times 10^6$	$\Sigma\delta$	$\chi_A \times 10^6$	Mo(V) monomer, %
1	2.670	33.13	64.20	10.29	1.209	−0.3138	−0.6712	+1284	100
2	2.736	31.08	66.18	9.46	1.196	− .3106	− .6733	+1272	100
3	2.752	27.08	70.17	7.99	1.178	− .3155	− .6778	+1263	99.2
4	2.767	24.94	72.30	7.19	1.166	− .3182	− .6795	+1253	98.4
5	2.783	22.79	74.43	6.39	1.154	− .3494	− .6815	+1146	90.0
6	2.835	20.55	76.62	5.61	1.142	− .4387	− .6838	+830	64.8
7	2.859	18.24	78.90	4.82	1.134	− .5723	− .6862	+382	29.1
8	2.900	16.03	81.07	4.05	1.120	− .6560	− .6882	+107	7.2
9	2.929	13.73	83.34	3.27	1.111	− .6740	− .6910	+52.4	2.8
10	2.958	11.21	85.83	2.45	1.098	− .6876	− .6930	+17.5	0.0

TABLE II

MAGNETIC SUSCEPTIBILITIES OF MOLYBDENUM-BLUE SOLUTIONS

	Solution I containing Mo(V) and Mo(VI) ions				95% ethanol	% (wt.) of sol. I	Molybdenum-blue solution	
o.	Mo(V), %	Mo(VI), %	Cl, %	$\chi_g \times 10^6$	$\chi_g \times 10^6$		Calcd. $\chi_g \times 10^6$	expt. $\chi_g \times 10^6$
1	1.59	2.98	11.57	−0.6585	-0.7276^a	41.10	−0.6992	-0.7001 ± 5.10^{-4}
2	1.50	4.32	9.87	− .6583	$- .7281^a$	41.19	− .6993	$- .6989 \pm 5.10^{-4}$

[a] These values refer to samples from two different standard 95% ethanol.

lybdenum atoms linked by an electron-pair bond. The little value of $+17.5 \times 10^{-6}$ for χ_A at 2.45 N HCl, can be considered as due to a small temperature independent paramagnetism usual in the molybdenum compounds.[7] At lower acid concentration, the values of χ_A remain roughly constant but such values are scarcely accurate since the diamagnetic contribution of the solvent reaches nearly the value of the susceptibility of the solution.

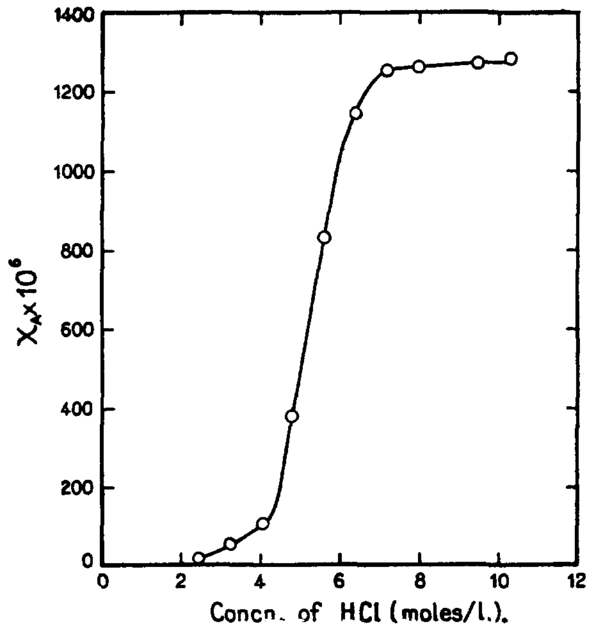

Fig. 1.—χ_A of molybdenum(V) ion as a function of HCl concentration.

Both monomer and dimer forms of molybdenum(V) ions are in equilibrium, as is confirmed by the reversible change in color from green to brown and *viz.*, of the solutions.

It must be remembered, at least, that the sharing of a pair of electrons by two molybdenum(V) atoms was already assumed by Klemm[8] in order to explain the diamagnetism or the feeble paramagnetism of certain complexes of quinquevalent molybdenum.

Present investigations correlate with those on amorphous molybdenum-blue which was found to be diamagnetic.[9] In fact, the measurements above reported show that, in hydrochloric solutions of quinque- and sexavalent molybdenum ions, the disappearance of paramagnetism of molybdenum(V) ions, at concentration of HCl near 2 N, precedes the formation of molybdenum-blue which, as is well known, takes place in solution less than 2 N in hydrochloric acid content.[3]

As a confirmation the susceptibilities of colloidal solutions of molybdenum-blue, obtained by mixing the brown solutions containing quinque- and sexavalent molybdenum ions with 95% ethanol,[10] are found to be, within the experimental errors, strictly additive to the susceptibilities of both the mixed solutions. This affords evidence that the diamagnetism which accompanies the appearance of Mo(V)–Mo(V) electron-pair bonds takes place before molybdenum blue is formed.

Table II reports the data referring to these measurements carried out with a very sensitive torsion balance already described elsewhere.[11]

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[7] *Cf.* P. W. Selwood, ref. 5, p. 150; W. Klemm, ref. 4a, p. 151.

[8] W. Klemm and H. Steinberg, ref. 4b, p. 211.

[9] L. Sacconi and R. Cini, *J. Chem. Phys.*, **18**, 1124 (1950); L. Sacconi and R. Cini, *Ann. chim.* (*Rome*), **42**, 706 (1952).

[10] 95% ethanol was used as diluent since in aqueous alcoholic solution it can be reached a concentration in molybdenum-blue larger than in aqueous one before flocculation takes place.

[11] R. Cini and L. Sacconi, *J. Sci. Instr.*, **31**, 56 (1954).