An ESR Study of Mn(II) Complexes in Water-Methanol Mixed Solvents*

JAMES R. BARD

Penn Valley Community College, Kansas City, Missouri 64111

and

JAMES O. WEAR

Veterans Administration Hospital and Department of Physiology and Biophysics, University of Arkansas Medical Center, Little Rock, Arkansas

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0.01 M solutions of \( \text{Mn(ClO}_4\text{)}_2 \), \( \text{MnCl}_2 \) and \( \text{MnSO}_4 \) in water-methanol mixtures were studied at 25 °C to determine the effect of these anions and of solvent composition on the ESR intensity and linewidth of Mn(II). A significant feature of the data was the large difference between the intensity of \( \text{Mn(ClO}_4\text{)}_2 \) and that for \( \text{MnCl}_2 \) and \( \text{MnSO}_4 \) in solutions containing greater than about 0.5 mole fraction methanol. A plot of linewidth versus mole fraction methanol shows little difference between \( \text{Mn(ClO}_4\text{)}_2 \) and \( \text{MnCl}_2 \) but an increasingly greater difference between these salts and \( \text{MnSO}_4 \) with increasing methanol content. These results are interpreted as being due to first coordination sphere complex formation in solutions containing \( \text{Cl}^\circ \), while the \( \text{SO}_4^{2\circ} \) data are affected by both first and second coordination sphere complexes depending upon the solvent dielectric constant. The \( \text{Mn(ClO}_4\text{)}_2 \) data were interpreted as showing that the primary solvation sphere of the Mn(II) ions was changing as the composition of the bulk solvent changed. These results are compared with similar data in aqueous solution and confirm that complex formation involving \( \text{Cl}^\circ \) or \( \text{SO}_4^{2\circ} \) ions and Mn(II) is extensive in water-methanol mixtures.

There has been a limited study1–3 of Mn(II) in water-alcohol mixtures by ESR. In each case \( \text{MnCl}_2 \) was used as the source of Mn(II) ion which is subject to error for solvent interaction studies due to the formation of chloro complexes which cause line broadening4. With increasing alcohol content, there is a reduction in the intensity and an increase in linewidth of the Mn(II) signal. These results were interpreted as being due to a change in the primary solvation sphere of the Mn(II) ion as the composition of the bulk solvent changed. Yordanov3 also considered some influence of the \( \text{Cl}^\circ \) competing with alcohol molecules for coordination sites.

The influence of solvent dielectric constant on ion-pair association is well known5, and the formation of Mn(II)-chloro complexes has been demonstrated both in aqueous solution6,7 when the dielectric constant is lowered by increasing the temperature, and in several non-aqueous solvents of relatively low dielectric constant8–10 including methanol. Although the solvent dielectric constant per se does not determine the extent of ion association, the nature of the solvent also being important, evidence has been presented illustrating that the relationship between ESR signal intensity and linewidth for Mn(II) and extent of ion association is valid because of the ability of the complexing anion to alter the symmetry of the hexa-aquo Mn(II) ion9. In the present paper a distinction is made between the effects of solvent composition, and ion association as a function of solvent dielectric constant on the ESR spectrum of Mn(II) in water-methanol mixtures.

Requests for reprints should be sent to Dr. J. E. Wear, Veterans Administrationospital and Dept. of Physiology and Biophysics, Univ. of Arkansas, Medical Center, Little Rock, Arkansas 72201, U.S.A.

1 B. R. McGarvey, J. physic. Chem. 61, 1232 [1957].
7 D. C. McCain and R. J. Myers, J. physic. Chem. 72, 4115 [1968].
Experimental

Materials: Mn(ClO₄)₂·6H₂O and MnSO₄·H₂O were purchased from G. F. Smith Chemical Company and dried under vacuum over P₂O₅ before use. Anhydrous MnCl₂ was purchased from K and K Laboratories. Anhydrous Na₂SO₄ was purchased from the Mallinckrodt Chemical Works, and spectroquality reagent methanol from Matheson, Coleman and Bell was used as received.

Apparatus: A Varian V 4500 100-Kc ESR spectrometer operating in the X-band region near 9.5 KMc was used. The magnetic field sweep was calibrated using a Harvey-Wells proton resonance probe and frequency counter.

Experimental Procedure: Stock solutions of Mn(ClO₄)₂·6H₂O, MnSO₄·H₂O, MnCl₂ and Na₂SO₄ in water and Mn(ClO₄)₂·6H₂O and MnCl₂ in methanol were prepared in the usual manner. All water-methanol solutions were prepared by weight as follows. A constant aliquot of the aqueous Mn(II) salt to be studied was added to the desired weight of methanol in a volumetric flask, diluted to the mark with water and weighed. The resulting solutions were 0.01 M in Mn(II). For solutions containing sulfate, the desired aliquot of the Na₂SO₄ solution was added prior to the final dilution. Ordinary melting point capillary tubing was used as sample containers. The spectra were recorded as the first derivative of the absorption curve, and the peak height for each of the six peaks was taken to be the vertical distance between the maximum and the minimum amplitudes of the derivative. The linewidth of the $M_1 = 1/2$ transition was taken as the peak to peak separation of the derivative.

Results

Since linewidth varied with solvent composition, intensity was measured as the summation of the peak height times linewidth squared for each of the six hyperfine lines. Fig. 1 is a plot of the intensity, in arbitrary units, versus mole fraction methanol for Mn(ClO₄)₂, MnCl₂, and MnSO₄. All of these solutions were 0.01 M Mn(II) and contained no other salts.

From this plot it can be seen that Mn(ClO₄)₂ and MnCl₂ are very similar if not identical up to a mole fraction of 0.8 but after this the intensity of MnCl₂ is considerably less than for Mn(ClO₄)₂. Between 0.4 and 0.8 mole fraction there appears to be a difference between the MnCl₂ and Mn(ClO₄)₂ intensities but since the technique is subject to errors of the order of $10 - 20\%$ this may not be real. However, since the plotted points are averages of several measurements the trends should be significant. Since the shape of the curves for these two salts are almost identical, the lower intensity for MnCl₂ is probably due to the formation of MnCl₆.

The intensity plot of the MnSO₄ has a different shape from the other two and also is considerably lower. This difference is due to the formation of MnSO₄ and a different solvent-solute interaction.

If it is assumed that the change in intensity for Mn(II) is only due to solvent effects for Mn(ClO₄)₂, the other two salts can be corrected for the solvent effect by plotting relative intensity. Here the relative intensity must be relative to the intensity of Mn(ClO₄)₂ in each solvent mixture, i.e.

$$I = I_n, s_i \left/ I_{ClO_4}, s_i \right.$$ where $a_i$ is the anion and $s_i$ is the i-th solvent mixture. A plot of this relative intensity is shown in Fig. 2. The curves for MnCl₂ and MnSO₄ are considerably different which indicates different rates...
of outer-sphere complex formation. The decrease of intensity is indicative of inner-sphere complexing since this type of complex does not contribute to the ESR signal provided that the symmetry of the complex is strongly distorted. Above a methanol mole fraction of 0.5, MnCl₂ is formed in increasing amounts but up to this point the Mn(II) is either present as Mn²⁺ or the outer-sphere complex with their appropriate solvation.

DOHRMANN¹¹ has reported that MnCl₂ and Mn(ClO₄)₂ can be used as primary standards for spin concentration in methanol-water media. His conclusion is based on a methanol-water mixture of equal weight which is a methanol mole fraction of 0.36, and for measurements in this region of solvent composition his conclusion is apparently valid. However, above a methanol mole fraction of 0.5, MnCl₂ should not be used as a primary standard.

The relative intensity of MnSO₄ solutions starts decreasing with the first addition of methanol. The outer-sphere complex is formed in a near logarithmic manner with respect to methanol mole fraction. A plot of the relative intensity of MnSO₄ versus mole fraction of methanol yields a line of the equation:

\[ \log I_R = -0.067N_{\text{MeOH}} + 0.053 \]

with only the point at \( N_{\text{MeOH}} = 0.11 \) falling off the line.

The data for MnSO₄ could only be collected up to solutions containing a methanol mole fraction of 0.80. Above this point MnSO₄ was not sufficiently soluble.

Fig. 3 is a plot of the fourth linewidth versus methanol mole fraction for the three salts. Mn(ClO₄)₂ and MnCl₂ follow a near symmetrical curve with a maximum linewidth at \( N_{\text{MeOH}} \approx 0.5 \). Methanol is competing with water for the solvation sphere sites around Mn²⁺ and the exchange is merely a statistical problem. At \( N_{\text{MeOH}} = 0.5 \) there are as many methanol molecules as water molecules in the solution so three methanol and three water molecules are in the solvation sphere of Mn²⁺ which is the most asymmetric mixture. The maximum asymmetry of the solvated ion results in a maximum linewidth. The slight difference between the MnCl₂ and Mn(ClO₄)₂ points may be due to the formation of MnCl₂ in small amounts. The linewidth value of 17.6 gauss for Mn(MeOH)₅²⁺ is in good agreement with the 17 gauss value reported by LEVANON and LUZ.⁹ The linewidth of 23.2 gauss for Mn(H₂O)₆²⁺ compares favorably with the values obtained by MCCAIN and MYERS.

The linewidth for MnSO₄ is broader in all solvent mixtures including water. This linewidth continues to broaden with increase in methanol mole fraction and does not reach a maximum. The formation and equilibrium for the outer-sphere MnSO₄ complex is the cause of this line broadening.

For all the solutions \( g = 2.00 \) and the hyperfine coupling constant, \( A \), was \( 96\pm1 \) gauss which is what one would expect for a oxygen coordinating ligand and octahedral coordination.

**Discussion**

The interactions of Mn²⁺ and the anions to form outer-sphere and inner-sphere complexes can be described by the following equilibrium:

\[
\text{Mn}^{2+} + A^{n-} \rightleftharpoons \text{Mn}^{2+}\text{(sol)}(\text{sol}) A^{n-} \rightleftharpoons \text{Mn}^{2+}\text{(sol)} A^{n-} \rightarrow \text{MnA}^{(2-n)}
\]

where \( A^{n-} \) is some anion. This system has been well studied in water by EIGEN and ATKINSON for MnSO₄. ESR will not distinguish between the two ion pairs that are separated by solvent molecules so the following equilibrium is more appropriate:

\[
\text{Mn}^{2+} + A^{n-} \xrightarrow{k_{\text{on}}} \text{Mn}^{2+} A^{n-} \xrightarrow{k_{\text{on}}} \text{MnA}^{(2-n)} \quad (1)
\]


¹³ G. ATKINSON and S. K. KOR, J. physic. Chem. 69, 128 [1965].
where $\text{Mn}^{2+}$, $A^{n-}$ represents outer-sphere complexes.

$$K_{ab} = \frac{k_{ab}}{k_{bu}} = \frac{[\text{Mn}^{2+}, A^{n-}]}{[\text{Mn}^{2+}][A^{n-}]}$$  \hspace{1cm} (2)

$$K_{bc} = \frac{k_{bc}}{k_{bc}} = \frac{[\text{Mn}^{2+}, A^{n-}]}{[\text{Mn}A^{(2-n)}]}$$  \hspace{1cm} (3)

where [] indicates activity rather than concentration.

Inner-sphere complexes of $\text{Mn}^{2+}$ lacking cubic symmetry have line broadening that is sufficiently large to cause the ESR spectra to go undetected. This line broadening is a result of molecular tumbling modulating the zero field splitting interaction. Under these conditions the concentration of this inner-sphere complex can be calculated from the decrease in intensity. The mole fraction of outer-sphere complex can be calculated from the modified Bloch equation 14.

$$1/T_2 = (1 - X)/T_{2a} + X/T_{2b}$$  \hspace{1cm} (4)

where $T_2$ is the observed transverse relaxation time, $T_{2a}$ and $T_{2b}$ are the relaxation times for the free ion and the outer-sphere complex respectively, and

$$X = \frac{[\text{Mn}^{2+}, A^{n-}]}{[\text{Mn}^{2+}] + [\text{Mn}^{2+}, A^{n-}]}$$  \hspace{1cm} (5)

$T_{2a}$ can be calculated from the Mn(ClO$_4$)$_2$ linewidth in each solvent mixture from

$$T_2 = \frac{\lambda (\sqrt{3} \pi g \beta)^{-1}}{\Delta H_{pp}} = 1/(1.5228 \cdot 10^7) \Delta H_{pp}$$  \hspace{1cm} (6)

where $\lambda$ is Planck’s constant, $g$ is the spectroscopic splitting factor, $\beta$ is the Bohr magneton and $\Delta H_{pp}$ is the peak to peak linewidth.

Where $X \lesssim 1$, $T_{2b}$ can be calculated from the limiting form of equation (4)

$$1/T_2 \approx X/T_{2b}.$$  \hspace{1cm} (6 a)

An overall equilibrium constant can be calculated for the complex formation by the following equation 13:

$$K_A = \frac{[\text{Mn}^{2+}, A^{n-}] + [\text{Mn}A^{(2-n)}]}{[\text{Mn}^{2+}](A^{n-})} \gamma_\pm^2$$  \hspace{1cm} (7)

where [] are activities and () are concentrations. The activity coefficients, $\gamma_\pm$, can be calculated for the MnCl$_2$ and MnSO$_4$ solutions in methanol-water mixed solvents by the use of an extended Debye-Hückel equation 5:

$$\log \gamma_\pm = \frac{-A(z_1 z_2) \sqrt{\mu}}{1 + B a \sqrt{\mu}} + b \mu$$  \hspace{1cm} (8)

$A = 0.5091/(dt)_{1/2}^2 $  \hspace{1cm} $B = 0.3286 \cdot 10^{8}/(dt)_{1/2}^{1/2}$


and $d = D/78.54$ and $t = T/298.16$ where $D$ is the bulk dielectric constant and $T$ is in degrees Kelvin. $a$ is the distance of closest approach for the ions and $b$ is an empirical parameter.

**Chloride**

The chloride does not appear to form an outer-sphere complex with $\text{Mn}^{2+}$ since there is no line broadening with added chloride except at higher temperatures. Therefore, for chloride only the overall equilibrium would be important:

$$K_{Cl} = \frac{[\text{MnCl}^{2+}]}{[\text{Mn}^{2+}][Cl^{-}]} = \frac{[\text{MnCl}^{2+}]}{[\text{Mn}^{2+}][Cl^{-}]} \gamma_+^2.$$  \hspace{1cm} (9)

Table I is a tabulation of equilibrium constants calculated from equation (9) using the decrease in intensity to calculate (MnCl$_2$) and equation (8) to calculate activity coefficients. It was assumed that $a = 4 \AA$ and $b = 0.1$ for these calculations. The $K_{Cl}$ for methanol agrees well with one calculated from LEVANON and Luz. Sillen 15 reports a $K_{Cl} \approx 1$, which agrees well with our value of 1.6. A plot of log $K_{Cl}$ versus $1/D$ is a linear plot with only the water and methanol points being significantly off the line.

**Sulfate**

Studies of SO$_4^{2-}$ interactions with $\text{Mn}^{2+}$ were complicated by solubility in higher methanol mixtures. Only where the mole fraction methanol was below 0.43 was it possible to add a large excess of SO$_4^{2-}$. At a methanol mole fraction of 0.26, a plot

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of excess linewidth versus initial sulfate concentration resulted in an inflection point at 1:1 ratio of initial sulfate and manganese. This would be expected if a 1:1 complex were formed since excess linewidth can be expressed as follows:

\[ Q = \frac{X_{\text{Mn}^{2+}} K_{ab} [\text{SO}_4^{2-}]_0}{[\text{Mn}^{2+}]_0} \left( \frac{1}{T_{2b}} - \frac{1}{T_{2a}} \right) \]  

(10)

where \( Q = 1.52 \times 10^{-7} \). If \([\text{SO}_4^{2-}]_0 < [\text{Mn}^{2+}]_0 \) and \( K_{ab} \gg 1 \) so that \([\text{Mn, SO}_4] \cong [\text{SO}_4^{2-}]_0 \) then

\[ X_{\text{Mn}^{2+}} K_{ab} [\text{SO}_4^{2-}]_0 \left( \frac{[\text{Mn}^{2+}]_0}{[\text{Mn}^{2+}]_0} \right) = \frac{[\text{Mn, SO}_4]}{[\text{Mn}^{2+}]_0} = \frac{[\text{SO}_4^{2-}]_0}{[\text{Mn}^{2+}]_0} \]

Equation 10 now becomes

\[ \Delta H_{\text{ex}} = \frac{[\text{SO}_4^{2-}]_0}{Q [\text{Mn}^{2+}]_0} \left( \frac{1}{T_{2b}} - \frac{1}{T_{2a}} \right) \]  

(11)

so that the excess linewidth increases linearly with increasing total sulfate concentration.

At the point where \([\text{SO}_4^{2-}]_0 > [\text{Mn}^{2+}]_0 \) and \( K_{ab} \gg 1 \) the following will occur:

\[ [\text{Mn, SO}_4] \cong [\text{Mn}^{2+}]_0 \]

and

\[ X_{\text{Mn}^{2+}} K_{ab} [\text{SO}_4^{2-}]_0 = \frac{[\text{Mn, SO}_4]}{[\text{Mn}^{2+}]_0} = [\text{Mn}^{2+}]_0 \]

so that equation 10 becomes

\[ \Delta H_{\text{ex}} = \frac{1}{Q} \left( \frac{1}{T_{2b}} - \frac{1}{T_{2a}} \right) \]  

(12)

If equations 11 and 12 hold then at the point \([\text{SO}_4^{2-}]_0 = [\text{Mn}^{2+}]_0 \) there would be an inflection point and the excess linewidth would remain constant with added sulfate and this is what occurs within a few percent.

In water and methanol-water solutions with less than a methanol mole fraction of 0.26 there is no sharp inflection point but there is a nonlinear increase in \( \Delta H_{\text{ex}} \) with \([\text{SO}_4^{2-}]_0 \). This nonlinearity would indicate that \( K_{ab} \) is not large.

In Table II are presented relaxation time and equilibrium constants for the manganese sulfate solutions. The \( T_{2a} \) values were calculated from equation (6) and they agree with literature values for water and methanol. The \( T_{2b} \) values were estimated from equation (6a) using the linewidth for the highest sulfate ratio which for higher alcohol mixtures was a 1:1 ratio. Values of \( T_{2b} \) were also calculated from slopes of excess linewidth versus \([\text{SO}_4^{2-}]_0 \) plots using equation (11).

Equilibrium constants were calculated by determining \([\text{Mn}^{2+}]_0 \), \([\text{Mn, SO}_4] \), and \([\text{MnSO}_4] \) from equations (4) and (5) and the decrease in intensity. Activity coefficients were calculated using equation (8) with values for \( a = 4.0 \) Å and \( b = 0.1 \). The following equations were used for the equilibrium constants:

\[ \text{Fig. 4. A Plot of Log Excess Line Width, } \Delta H_{\text{ex}}, \text{ for MnSO}_4 \text{ in Water-Methanol Versus } 1/D, \text{ the Dielectric Constant.} \]

<table>
<thead>
<tr>
<th>( N_{\text{MeOH}} )</th>
<th>( T_{2a} \times 10^9 )</th>
<th>( T_{2b} \times 10^9 )</th>
<th>( K_{ab} )</th>
<th>( K_{bc} )</th>
<th>( K_A )</th>
<th>( K_A' )</th>
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<tr>
<td>0</td>
<td>2.8</td>
<td>2.1</td>
<td>250 ± 10</td>
<td>0.21 ± 0.02</td>
<td>150 ± 25</td>
<td>133</td>
</tr>
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<td>0.11</td>
<td>2.2</td>
<td>1.6</td>
<td>400 ± 40</td>
<td>0.34 ± 0.03</td>
<td>530 ± 50</td>
<td>439</td>
</tr>
<tr>
<td>0.26</td>
<td>1.9</td>
<td>1.5</td>
<td>900 ± 200</td>
<td>1.0 ± 0.1</td>
<td>1600 ± 100</td>
<td>1710</td>
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<td>0.43</td>
<td>1.7</td>
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<td>0.54</td>
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<td>0.67</td>
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<tr>
<td>0.80</td>
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<td>1.0</td>
<td>3.7</td>
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</table>

Table II. Relaxation Times for \( \text{Mn}^{2+} \) and \( \text{Mn, SO}_4 \) and Equilibrium Constants for Manganese Sulfate in Methanol—Water Solutions. * Values of \( K_A' \) are from H. TSUBOTA and G. ATKINSON, J. physic. Chem. 71, 1131 [1967].

\[ ^{16} \text{H. TSUBOTA and G. ATKINSON, J. physic. Chem. 71, 1131 [1967].} \]
$K_A = (\text{Mn, } \text{SO}_4) + (\text{MnSO}_4)$

$K_{ab} = \frac{(\text{Mn, } \text{SO}_4)}{(\text{Mn}^{2+}) (\text{SO}_4^{2-})^{\gamma_2}}$

$K_{bc} = \frac{(\text{MnSO}_4)}{(\text{Mn, } \text{SO}_4)}$

Values of $K_A$, $K_{ab}$, and $K_{bc}$ could only be calculated for solutions up to $N_{\text{MeOH}} = 0.26$ due to problems in determining concentrations. The values of $K_A$ agree with the values found by TSUBOTA and ATKINSON by conductance.

Fig. 4 is a plot of the log excess linewidth for MnSO$_4$ versus $1/D$ where $D$ is the dielectric constant. This yields a typical plot that one might expect for the equilibrium constant as a function of dielectric constant. $\Delta H_{ex}$ is related to $K_{ab}$ by equation (10) and if all terms except $\Delta H_{ex}$ and $K_{ab}$ are approximately constant then log $\Delta H_{ex}$ can be used to show how $K_{ab}$ changes with dielectric constant.

**Darstellung von Schwermetallsulfiden durch Fällung aus organischen Lösungsmitteln.**

**IR-Spektren von Metallsalzen der Naphthensäure**

Preparation of Metal Sulphides from Organic Solvents.

IR-Spectra of Metal Salts of Naphthenic Acid

HEINZ DIETER LUTZ und HARTMUT HAEUSELER

Institut für Anorganische Chemie der Universität Köln


The following sulphides were precipitated with hydrogen sulphide from solutions of naphthenates in organic solvents: In$_2$S$_3$, CoS, NiS, CuS, ZnS, CdS, HgS, PbS, Ag$_2$S and the thiospinels NiIn$_2$S$_4$, CdIn$_2$S$_4$ and HgIn$_2$S$_4$. Not precipitated are chromium (II) and chromium (III). The ir-spectra of the naphthenates are discussed.

VELLER berichtete 1936 über die Fällung von Cr$_2$S$_3$ in Form graugrüner Plättchen durch Einleiten von H$_2$S in eine benzolische Lösung von Chromnaphthenat. Da die Darstellung von Chrmnaphthenat sowie anderer Schwermetallchalkogenide von präparativem Interesse ist, haben wir die Versuche von VELLER nachgearbeitet und Chromnaphthenat sowie eine Reihe weiterer Metallnaphthenate mit Schwefelwasserstoff in verschiedenen organischen Lösungsmitteln umgesetzt.

Charakterisierung der erhaltenen Metallsulfide


Die bei gemeinsamer Fällung von Metallnaphthenaten und Indiumnaphthenat anfallenden Sulfidniederschläge können durch Tempern bei einer relativ niedrigen Temperatur (ca. 270 °C) kristallin (Spinell) erhalten werden. Da in den Pulveraufnahmen der Fällungsprodukte die Reflexe der unter diesen Bedingungen kristallin anfallenden binären Metallsulfide (vgl. Tab. 1) nicht zu erkennen sind, nehmen wir an, daß bei der Fällung unmittelbar die ternären Phasen MeIn$_2$S$_4$, wenn auch nur in mikrokristalliner Form, entstehen. Im Laufe unserer Untersuchungen ist es uns nicht gelungen, die von VELLER beschriebene Fällung von Chromsulfid zu reproduzieren. Aus Lösungen von Chrom(II)- und Chrom(III)-naphthenat konnten keine Sulfide erhalten werden. Über die Darstellung von Chromsulfiden aus organischen Lösungsmitteln nach einem anderen Verfahren werden wir in einer folgenden Arbeit berichten.

IR-Spektren der Naphthenate

Die sehr unterschiedliche Fällungsverhalten der Naphthenate veranlaßte uns, die Stärke der „Kom-

1 H. HAEUSELER, Teil der Diplomarbeit, Köln 1970.

2 S. M. VELLER, Ukrain. chem. Jurnal 11, 23 [1936].