A smaller percentage than this would be found if K_2, determined from data at ionic strengths of 0.025 and 0.060, was corrected for the lower ionic strength of 0.015 involved here.

Ionic strength was not maintained at a constant value since it would have been impossible to do so over the range of H^+ and Cl^- concentrations employed without addition of other anions which would have introduced additional complexes.

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[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

Solution Viscosity Behavior of Some Metal Schiff Base Chelates

BY ROBERT G. CHARLES

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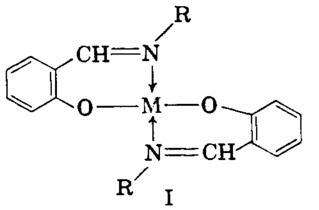
Viscosity measurements are suggested as useful adjuncts to other physical methods for the study of metal chelate compounds dissolved in organic solvents. In favorable instances such measurements can give information relative to the steric configuration of the dissolved molecules and to the degree and type of interaction of the solute molecules with the solvent. The viscosities of dilute solutions derived from the members of three homologous series of Cu(II), Ni(II) and Zn(II) N-(*n*-alkyl)-salicylaldimine chelates have been studied, using as solvents toluene, dioxane and pyridine. With the exceptions of the results obtained for the nickel chelates in pyridine the viscosity results ($\eta_{sp/c}$ as defined in the text) were found to be roughly independent of the solvent employed and of the nature of the bonded metal. The magnitude of $\eta_{sp/c}$ increased, however, with increasing chain length in all the solvents and for all three homologous series. Values of $\eta_{sp/c}$ for the nickel chelates in pyridine were higher than those for the corresponding Cu and Zn compounds due to the interaction of the nickel compound with the solvent to form hexacoördinated complexes. The values of $\eta_{sp/c}$ for the one copper compound studied having an enforced planar *cis* configuration about the metal were higher than those found for corresponding alkyl substituted chelates, evidently as the result of the permanent dipole moment associated with the *cis* configuration.

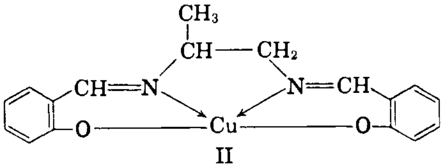
Solution viscosity measurements have been used but little in the study of metal coördination compounds. In an earlier paper[1] it was shown that significant information concerning the ethylenediaminetetraacetate chelates could be obtained by such measurements on aqueous solutions. It might be expected that, in favorable instances, useful information regarding the degree of solvation and the configuration of metal chelate compounds might be obtained also for solutions in organic solvents.

The present work is concerned largely with the N-(*n*-alkyl)-salicylaldimine chelates I, where R is a straight chain alkyl group and M is Cu, Ni or Zn.


I

We have chosen this group of compounds because of their adequate solubilities in organic solvents and, more particularly, because other data are available regarding the solution properties of some of these chelates.[2-7]

For comparison with the chelates I we have made a few measurements also with the copper chelate II, where the *cis* planar configuration about the metal atom is enforced by the N–N bridging group.


II

Experimental

Materials.—The preparation and properties of the N-alkylsalicylaldimine chelates have been described elsewhere.[2,3,8] All of these compounds were recrystallized and dried, *in vacuo*, over $CaCl_2$.

Bis-(salicylaldehyde)-propylenedimine-copper(II)[9] was prepared by condensing salicylaldehyde with propylenediamine in methanol solution and then reaction with copper acetate in the presence of sodium acetate. The yield was 97%. The violet compound was recrystallized from methanol and dried at room temperature in a vacuum desiccator; m.p. 238–243°. *Anal.* Calcd. for $C_{17}H_{16}O_2N_2Cu$: C, 59.4; H, 4.7; N, 8.2. Found: C, 59.2; H, 4.5; N, 7.9.

Carbide and Carbon 1,4-dioxane was purified by refluxing for 12 hr. over sodium and fractionating through an efficient column. Reagent grade pyridine and reagent grade toluene were used without additional purification.

Procedure.—Solutions were prepared by weighing the compound into a 10-ml. volumetric flask and diluting to volume with the solvent. All measurements were completed within a few hours of preparing the solutions.

Viscosities were determined with a Cannon–Fenske capillary viscometer having an efflux time greater than 200 seconds. Efflux times were determined with a stopwatch. Each solution was compared with the corresponding solvent run under the same conditions. All solvents and solutions were filtered through a sintered glass pressure filter before the viscosity runs were begun. Densities of solutions and solvents were determined concurrently with the viscosity measurements, using a 5-ml. Weld pycnometer. All determinations were made at 30° in a water-bath which could be maintained constant to ±0.01°.

Viscosities were calculated in the usual manner from the efflux times and densities. Results were expressed in Table

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(1) R. G. Charles, THIS JOURNAL, **78**, 3946 (1956).

(2) R. G. Charles, *J. Org. Chem.*, **22**, 677 (1957).

(3) R. G. Charles, *J. Inorg. Nucl. Chem.*, accepted for publication.

(4) F. Basolo and W. R. Matoush, THIS JOURNAL, **75**, 5663 (1953).

(5) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955).

(6) H. C. Clark and A. L. Odell, *ibid.*, 520 (1956).

(7) L. Sacconi, P. Paoletti and G. Del Re, THIS JOURNAL, **79**, 4062 (1957).

(8) R. G. Charles and W. D. Johnston, *Anal. Chem.*, **29**, 1115 (1957).

(9) P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, *Ann.*, **503**, 81 (1933).

TABLE I

SOLUTION VISCOSITY RESULTS FOR SALICYLALDIMINE CHELATES

R[a] Solvent:	Toluene			Dioxane			Pyridine		
Metal:	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn
Methyl				0.69			0.74	1.17	
Ethyl	0.72			.74				1.15	
n-Propyl	.78	0.77		.77	0.78	0.89	.81	1.27	0.80
n-Butyl	.86	.86		.87	.88		.89	1.33	
n-Amyl	.95	.97		.95	.96		.98	1.44	
n-Hexyl		1.06	1.05		1.05	1.05		1.50	1.08
n-Heptyl	1.18	1.19		1.13	1.13		1.14	1.60	
n-Octyl	1.26	1.29		1.25	1.28		1.26	1.71	
n-Decyl	1.54	1.59	1.56	1.49	1.53	1.54	1.47	2.00	1.52
n-Dodecyl	1.87	1.94		1.80	1.81		1.80	2.38	
n-Tetradecyl-	2.26	2.38	2.29	2.17	2.29	2.11	2.13	2.69	2.21
$-CH(CH_3)-CH_2-$[b]				1.01			1.06		

[a] See formula I in text. [b] Formula II in text.

I as $\eta_{sp/c}$, where $\eta_{sp} = (\eta_{soln}/\eta_{solv}) - 1$ and c = moles chelate/l. solution.

The quantity $\eta_{sp/c}$ was determined as a function of concentration for several of the chelates, employing all three solvents. The quantity was found to be constant, in the concentration range 0.05–0.1 *M*, within experimental error for all the systems investigated. For the remaining chelates, determinations were made at only one concentration. Where possible 0.1 *M* solutions were used. For a few of the less soluble compounds it was necessary to employ 0.07 or 0.05 *M* solutions.

Absorption spectra were determined at 25° with a Cary recording spectrophotometer model 14, employing 1 cm. quartz cells and 6.4×10^{-5} *M* solutions. Molar extinction coefficients were calculated from the formula

$$\epsilon = \frac{\text{O.D.}}{lc}$$

where O.D. is the optical density, l is the cell thickness and c is the molar concentration.

Results and Discussion

The values of $\eta_{sp/c}$ for the compounds corresponding to formula I are listed in Table I. For all three homologous series, in all three solvents, $\eta_{sp/c}$ increases with increasing length of the alkyl chain (R in I). All of the compounds studied here were found to obey the empirical relationship 1, where

$$\log (\eta_{sp/c}) = a + bn \qquad (1)$$

n is the number of carbon atoms in the alkyl chain and a and b are constants characteristic of a given series and solvent. The extent of the agreement to this relationship is shown for the nickel chelates in Fig. 1.

An increase in $\eta_{sp/c}$ with increasing chain length is also characteristic of other homologous series of compounds.[10,11] It is striking, however, that the data for other homologous series do not obey equation 1. Staudinger[10,11] has found instead that, for a number of homologous series, plots of $\eta_{sp/C}$ (where here C is in grams per unit volume) *vs.* alkyl chain length are linear. When the data of Table I are recalculated and plotted in this manner, curves are obtained which are concave toward the the $\eta_{sp/c}$ axis.

These facts suggest that a progressive change in structure or change in ability to interact with the solvent, of a type not found for other homologous series, occurs as the alkyl groups of I are lengthened. These effects cannot be due to association of solute molecules since molecular weight determinations,[2,3] using similar concentrations, indicate that all the compounds I are monomolecular in solution, at least in dioxane. It appears that additional data will be necessary before any logical explanation for relation 1 can be advanced. In particular it would be of interest to have solution viscosity data for the series of Schiff base chelating agents from which compounds I are derived.

It will be noted from Table I that, for a given R group, $\eta_{sp/c}$ is, to a first approximation, independent of both the nature of the metal present in the molecules and the solvent employed, if one omits the data for the nickel chelates in pyridine. The value of $\eta_{sp/c}$ for a particular chelate should be determined by a number of factors including the size and shape of the molecule and the degree and type of interaction of the solute molecules with the solvent. For a given R group the size of the molecule I should be nearly independent of which of the three metals is present since all have similar ionic radii. The very similar values of $\eta_{sp/c}$ obtained for a given R group suggest that the shape of the molecules and their degree of interaction with the solvent are also largely independent of the nature of the metal.

Sacconi, Paoletti and Del Re[7] have presented evidence that copper and nickel chelates of type I have planar *trans* configurations about the metal in solution. It appears from the very similar values of $\eta_{sp/c}$ obtained for the zinc chelates that these (in contrast to some other zinc complexes which have been studied)[12] may also have the *trans* planar configuration. A tetrahedral, or a *cis* planar configuration about the metal would result in a permanent dipole moment for the molecule. This should give rise to increased interaction with the solvent and a higher value of $\eta_{sp/c}$.

To demonstrate the effect of enforcing the *cis* planar configuration about the metal atom we have determined $\eta_{sp/c}$ for the copper chelate II in dioxane and in pyridine. The values of $\eta_{sp/c}$ are much larger than those for compounds I, R = methyl or ethyl, as predicted from the above.[13]

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[10] H. Staudinger, "Die hochmolekulare organischen Verbindungen," Julius Springer, Berlin, 1932, p. 63.

[11] H. Staudinger, *Trans. Faraday Soc.*, **29**, 18 (1933).

[12] J. C. Bailar, Jr., Editor, "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., 1956, p. 372.

[13] A better comparison would be with bis-(salicylaldehyde)-ethylenediamine-copper(II). This compound was found to be too insoluble, however, to permit measurements to be made.

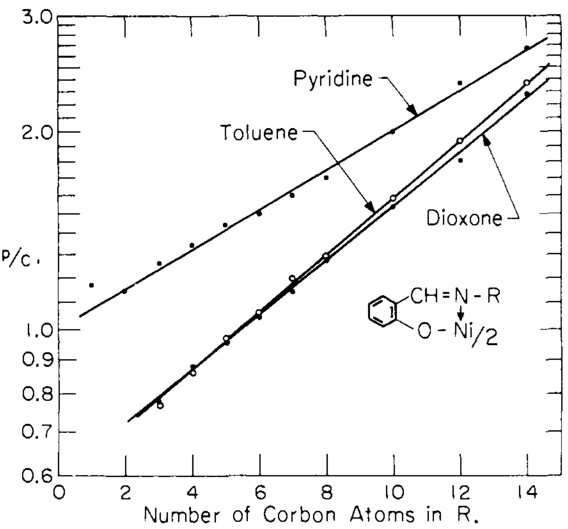

Fig. 1.—$\eta_{sp/c}$ as a function of chain length for nickel(II)-salicylaldimine chelates in the solvents indicated.

The values of $\eta_{sp/c}$ for the nickel chelates I in pyridine are larger than those for the corresponding copper and zinc chelates in this solvent and also much larger than the $\eta_{sp/c}$ values found for the nickel chelates in the other two solvents. A ready explanation for these observations is found in the fact that the nickel–methyl compound I forms with pyridine a hexacoördinated complex in which two pyridine molecules are bonded to the metal.[4,5] The larger volume of the hexacoördinated complex compared to I accounts for the higher value of $\eta_{sp/c}$ in pyridine. The viscosity results (Table I and Fig. 1) indicate (a) that the other nickel compounds I form similar hexacoördinated complexes to that formed by the methyl chelate in pyridine and (b) that neither the copper nor the zinc chelates I form complexes of this type in pyridine.

Supporting evidence for these conclusions is given by the absorption spectra of the nickel and copper chelates in the three solvents (Fig. 2).[14] The spectra for the two nickel compounds in pyridine are very similar to each other and to the spectrum of the corresponding N-methyl compound,[6] which is known to form a hexacoördinated complex with pyridine. On the other hand the spectra of the two nickel chelates in dioxane and toluene are quite dissimilar from the pyridine spectra and resemble the spectrum of the N-methyl chelate in chloroform[6] where no hexacoördinated complexes are formed.

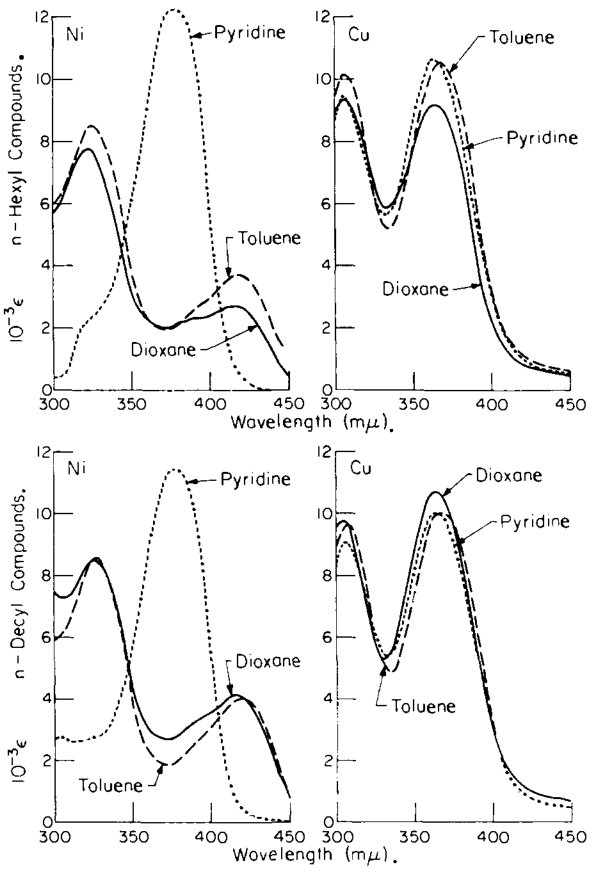

Fig. 2.—Absorption spectra of *n*-alkylsalicylaldimine chelates at 25°.

The spectra for the two copper chelates in Fig. 2 are nearly independent of the solvent employed, confirming the conclusion from the viscosity data that no specific interaction (to form hexacoördinated complexes) between the copper compounds and pyridine occurs.

The results obtained in the present work suggest that solution viscosity measurements may be of some general utility in studying the solution structure of those metal coördination compounds which are sufficiently soluble in organic solvents. More ready interpretation of the results obtained should become possible as additional data are accumulated.

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(14) Spectra for the corresponding zinc compounds are not shown in Fig. 2. These spectra were found to change fairly rapidly with time, eventually (1 or 2 days) becoming nearly identical with the spectra of the corresponding chelating agents from which the zinc compounds were derived. Evidently, at the low concentrations necessary for the determinations of the spectra, the zinc chelates are hydrolyzed by traces of water present in the solvent to form zinc hydroxide and the corresponding chelating agents. This explanation is consistent with the fact that zinc chelates are, in general, less stable to dissociation in solution (and hence more susceptible to hydrolysis) than are the copper and nickel chelates derived from the same chelating agents.