CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Mössbauer Study of Tin(II)–Oxygen Heterocycles

BY A. J. BEARDEN, H. S. MARSH,[1a] AND J. J. ZUCKERMAN[1b]

Received February 7, 1966

Sn^{119m} Mössbauer spectra of *o*-phenylenedioxytin(II), 3-methyl-1,2-phenylenedioxytin(II), 2,3-naphthalenedioxytin(II), and 2,2′-biphenylenedioxytin(II) were measured, and from isomer-shift values the presence of stannous tin in these compounds is confirmed. Slow hydrolysis in air over prolonged periods results in the formation of stannic oxide, but in the absence of oxygen the expected stannous oxide was obtained. Observability of the Mössbauer effect for *o*-phenylenedioxytin(II) at ambient temperatures is interpreted in terms of the strength of lattice forces in the solid, and correlations are drawn between lattice force constants, isomer-shift values, and the strength of intermolecular (p→d) π bonding in these solids. The structures of the compounds are discussed.

Few organotin(II) compounds are known.[2] The unstable organotin compounds of empirical formula R_2Sn, known for over 100 years as examples of divalent organotin systems, have recently been shown by chemical[3] and X-ray evidence[4] to contain tetravalent tin. Mössbauer spectra of $[(C_6H_5)_2Sn]_n$ and $[(C_4H_9)_2Sn]_n$ show singlet resonances of isomer shift 1.42 and 1.55 ± 0.08 mm/sec,[5] respectively, using an $Sn^{119m}O_2$ source. This compares with the singlet resonance of isomer shift 1.35 ± 0.08 mm/sec measured for both $(C_6H_5)_4Sn$ and $(C_4H_9)_4Sn$.[6] In general the isomer shift of white tin can be taken as the dividing line between the two tin valences (+2.8 ± 0.1 mm/sec):[7] all tin(IV) compounds fall below and all tin(II) compounds above. There are no known exceptions to this rule. White tin itself (also called the β or tetragonal form) reacts with hydrochloric acid at $-17°$ to give stannous compounds.[8] Thus white tin can be said to be the stannous tin compound with the lowest isomer shift.

We were, therefore, interested to examine the Mössbauer spectra of the tin(II)–oxygen heterocycles first prepared by direct reaction between dihydric phenols and tin metal.[9] These compounds can also be obtained through reaction of dihydric phenols with a slurry of anhydrous stannous chloride and sodamide powders in ether,[10] by the action of dihydric phenols on stannous oxide in the presence of copper, either in a melt of the organic starting material or a suspension of the powders in refluxing xylene,[11] or from *o*-methoxy phenols and stannous oxide under similar conditions.[12] Cyclic esters thus obtained are notable chiefly for their low volatility and very high thermal stability (*e.g.*, in air to *ca.* 500°). This paper reports the Sn^{119m} Mössbauer spectra of the four known examples of this new class of compounds and the results of a study of their hydrolysis.

Experimental Section

Compounds examined were prepared by action of the appropriate diol upon stannous oxide or tin metal. Purification was by sublimation. Measurements reported here were carried out using an Sn^{119m}-equipped cam-drive spectrometer which utilizes recoilless γ radiation from the first excited state (23.8 kev) of Sn^{119m}, fabricated as $Sn^{119m}O_2$ in a lucite matrix (3.0 mcuries) (New England Nuclear Corp.) as a $^5/_8$-in. thick disk. Isomer shift and quadrupole splitting are studied by the usual Mössbauer technique of supplying the emitted radiation with a Doppler energy sufficient to restore the resonance condition. γ-Ray intensity is observed with a NaI scintillator and photomultiplier tube as a function of velocity on passing through resonance. Velocity requirements are met by a velocity sweep system consisting of an off-center circular cam which provides a skewed sinusoidal velocity *vs.* time curve.[13] Approximately 100° of the cycle corresponds to a nearly linear velocity curve, and it is this portion of the curve which is used in conjunction with a multichannel analyzer. The analyzer time base is triggered once each sweep by a magnetic pickup such that γ-ray intensities for a small fixed range of velocities are stored in the analyzer, an RIDL 400-channel pulse-height analyzer operating in the "timemode." Collimation length is approximately 1 m from source to detector. Lead collimators are used to minimize angular dispersion of γ-ray trajectories. Information from the analyzer is refined for solid-angle correction, accounting for changes in counting rate due to movement of the source relative to the detector, by computer (program written by P. Mattern), which also assigns uncertainties to the data and is read out as a plot of transmission *vs.* velocity. Since low temperatures increase the probability of the recoilless process, absorbers are mounted in a liquid nitrogen cryostat. A 1-mil Pd foil window is placed between the source and the absorber (approximately 1 m from the detector) to remove X-rays from the beam of γ and X-rays which is emitted from the Sn^{119m} source. Absorbers are tin compounds containing Sn^{119} in natural abundance (8.58%). Because of differences in the Debye temperature and the percentage of tin in the compounds, absorber thicknesses varied from 50 to 150 mg/cm² of total compound. The resonances observed were of strengths ranging between 6 and 10%. A statistically reliable number of counts (approximately 54 × 10^3 counts per channel) was used, yielding an error of about ±0.4% in the number of counts per

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(1) (a) Department of Physics. (b) To whom all inquiries should be addressed, at the Department of Chemistry, Cornell University, Ithaca, N. Y.

(2) See J. D. Donaldson, "A Review of the Chemistry of the Tin(II) Compounds," Tin Research Institute, Greenford, England, 1964.

(3) W. P. Neumann, *Angew. Chem.*, **75**, 225 (1963).

(4) D. H. Olsen and R. E. Rundle, *Inorg. Chem.*, **2**, 1310 (1963).

(5) Values are listed with respect to an $Sn^{119m}O_2$ source throughout. Positive velocity indicates relative motion of the source toward the absorber.

(6) V. I. Goldanskii, V. Ya. Rochev, and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, **156**, 909 (1964).

(7) M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, **26**, 915 (1964).

(8) T. Gela, *J. Chem. Phys.*, **24**, 1009 (1956).

(9) J. J. Zuckerman, *J. Chem. Soc.*, 1322 (1963); *Advan. Inorg. Chem. Radiochem.*, **6**, 383 (1964).

(10) H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.*, **1**, 328 (1964).

(11) G. T. Cocks and J. J. Zuckerman, *Inorg. Chem.*, **4**, 596 (1965).

(12) T. B. Harvey, III, and J. J. Zuckerman, unpublished results.

(13) A. J. Bearden, M. G. Hauser, and P. L. Mattern in "Mössbauer Effect Methodology," I. J. Gruverman, Ed., Plenum Press, New York, N. Y., Vol. 1, 1965.

channel, negligible when compared with the total size of the resonance.

The computer-corrected curves were in the case of doublets decomposed by hand into separate Lorentzian curves which could be added to reproduce the original spectrum. Decomposition was accomplished by first choosing the "center of gravity" of the doublet as the "center of gravity" of the two-component Lorentzians and proceeding to find these Lorentzians by an iterative process which is completed when the peaks cease to move. This process yields peaks which are symmetric and Lorentzian except in the "tail" sections. Further iteration produces better curves, but does not shift the peak maxima; thus for most of the data the iteration is carried out only until the peak maxima become invariant.

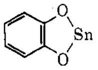
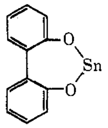
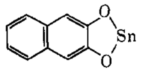
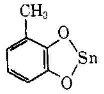
As might be expected, the quadrupole splitting is greater after the separation is carried out than it appears upon first inspection. Due to variations in line broadness and in separation of doublets, Δ values were measured after the decomposition rather than before. The errors in δ and Δ are estimated to be of the order of 0.06 mm/sec.

Results and Discussion

Isomer-shift (δ) and quadrupole-splitting (Δ) values and their ratio ($\rho = \Delta/\delta$) for the four known members of this class of compounds are listed in Table I. In all cases the isomer shift is higher than the white tin value of 2.8 mm/sec, and we conclude that these compounds are indeed carbon-containing derivatives of tin in the divalent state, in agreement with the suggestion based on chemical evidence (mercury(IV) reduction) put forward in the original paper which described their preparation.[9] Thus, with the possible exception of dicyclopentadienyltin,[14] the heterocyclic tin(II) compounds form the only members of the organotin(II) class.

TABLE I

MÖSSBAUER PARAMETERS

	$\rho = \Delta/\delta$	δ, mm/sec	Δ, mm/sec
	0.60[a]	+2.95 ± 0.06	1.76 ± 0.06
	0.52[b]	+2.95 ± 0.06	1.53 ± 0.06
	0.63	3.13 ± 0.06	1.98 ± 0.06
	0.57	3.08 ± 0.06	1.82 ± 0.06
	0.61	3.09 ± 0.06	1.89 ± 0.06

[a] Liquid nitrogen temperature. [b] Room temperature.

The isomer-shift values listed lie in the range 2.95–3.13 ± 0.06 mm/sec with the five-membered heterocycle *o*-phenylenedioxytin(II) at the low end and the seven-membered 2,2′-biphenylenedioxytin(II) at the high end of the scale. The two more highly substituted five-membered ring systems take positions near the middle of the scale and are within experimental error of each other. The inorganic tin(II) compounds which have been examined show isomer-shift values which range to +4.6 mm/sec with respect to $Sn^{119m}O_2$ sources. The isomer-shift values reported here fall near the lower end of the tin(II) compound range, and we can conclude that the s-electron density at the tin nucleus in the cyclic tin esters resembles that found in stannous oxide (isomer shift $\delta = 2.93$ mm/sec).[15]

In fact, the cyclic tin(II) esters can be synthesized by a simple reaction directly from stannous oxide. In the stannous oxide structure tin lies at the apex of a square pyramid whose base is formed by its four nearest-neighbor oxygen atoms with each oxygen atom tetrahedrally coordinated to four tin atoms. In addition there are adjacent layers of tin atoms with rather short tin–tin distances (3.07 A) which may indicate some degree of metal–metal bonding.[4,16] While the exact nature of bonding in blue-black SnO is not clear, some sort of d-orbital hybridization of tin is probable. Further evidence for the relation between the cyclic tin(II) esters and stannous oxide comes from studies in a furnace-equipped mass spectrometer. Here 2,2′-diphenylenedioxytin(II) gave a cracking pattern which showed no tin-containing fragments. The sole cation fragment in the vapor was found to be $C_{12}H_8O$, and the cracking pattern was consistent with the dibenzofuran structure, which would result from the abstraction of stannous oxide from 2,2′-diphenylenedioxytin(II).

The square pyramidal structure of stannous oxide can be described in terms of sp^3d hybridization of the available orbitals to give four bonds to oxygen and a fifth orbital occupied by an unshared pair of electrons. The lone-pair orbital would prevent the close approach of oxygen atoms along the direction in which it pointed and would give rise to the layer structure. In the cyclic tin esters the oxygen atoms are bonded either through organic groups whose carbon atoms are required to be in the same plane as the two oxygen atoms (as in *o*-phenylenedioxytin(II), its 3-methyl derivative, and 1,3-naphthalenedioxytin(II), for example) or through groups whose carbon atoms could easily be forced into a planar conformation with the oxygens (as is the case with 2,2′-diphenylenedioxytin(II)). We propose that these cyclic tin esters crystallize in an essentially stannous oxide structure where the planar organic moieties occupy interlayer positions.

We have subjected this hypothesis to test by examining the cyclic tin esters in the Mössbauer spectrometer at ambient temperatures. It is generally known that some tin compounds exhibit strong Mössbauer resonances at room temperature, while others give weak resonances or show no Mössbauer effect at all. In addition the strength of the resonance at liquid nitrogen temperature varies from compound to compound. The magnitude of the resonance effect in the absorber is a function of such factors as the number of Sn^{119} nuclei in the γ-ray beam, but for a

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(14) L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959). The synthesis of dimethoxytin(II) has been reported [E. Amberger and M. R. Kula, *Angew Chem.*, **75**, 476 (1963); *Chem. Ber.*, **96**, 2562 (1963)].

(15) O. C. Kistner, V. Jaccarino, and L. R. Walker in "The Mössbauer Effect," D. M. J. Compton and A. H. Schoen, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p 264.

(16) W. J. Moore and L. Pauling, *J. Am. Chem. Soc.*, **63**, 1392 (1941).

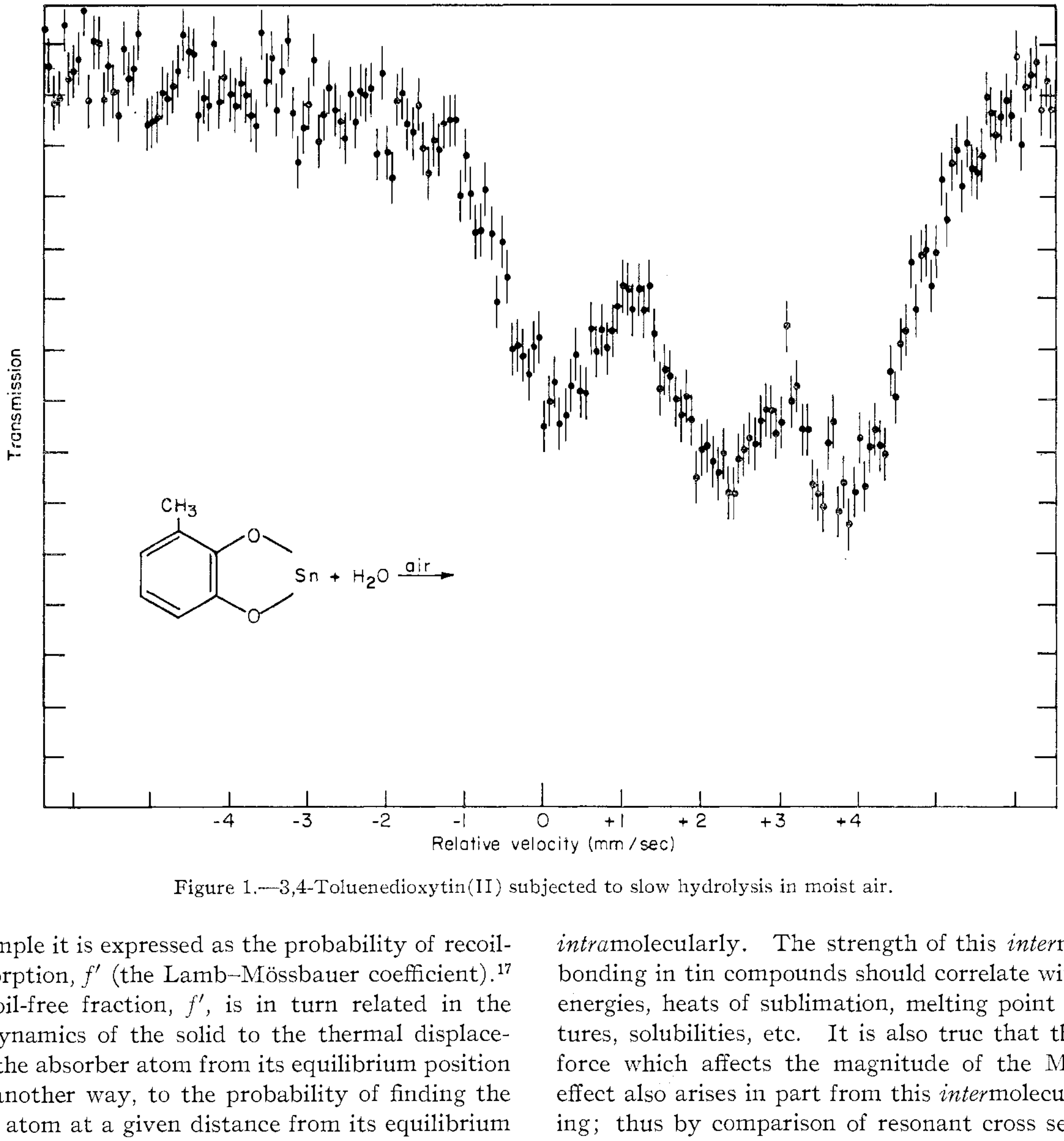

Figure 1.—3,4-Toluenedioxytin(II) subjected to slow hydrolysis in moist air.

given sample it is expressed as the probability of recoil-free absorption, f' (the Lamb–Mössbauer coefficient).[17] The recoil-free fraction, f', is in turn related in the lattice dynamics of the solid to the thermal displacement of the absorber atom from its equilibrium position or, put another way, to the probability of finding the absorber atom at a given distance from its equilibrium position. The Lamb–Mössbauer coefficient is then also a function of the binding force constants which hold the absorber atom in the lattice, being larger the more rigid the binding in the lattice.

The compounds under consideration form molecular solids; the crystal consists of molecules which retain their identity when assembled in the solid. Sublimation leaves the molecules intact, and the compounds dissolve as monomeric units and recrystallize from the solvent unchanged.[9,11] The tin compounds under study with similar heterocyclic tin(IV) oxygen compounds differ from their carbon, silicon, and germanium analogs, however, by the physical properties of their solids, all of which point to a very stable, high lattice energy crystal structure. It is interesting to note that these associated solids are apparently utilizing (p→d) π bonding between oxygen and tin atoms *inter*molecularly, while for silicon and germanium the overlap is said to take place along the σ-bond direction *intra*molecularly. The strength of this *inter*molecular bonding in tin compounds should correlate with lattice energies, heats of sublimation, melting point temperatures, solubilities, etc. It is also true that the lattice force which affects the magnitude of the Mössbauer effect also arises in part from this *inter*molecular binding; thus by comparison of resonant cross sections in compounds of similar structure and molecular weight it should be possible to draw conclusions as to the relative strengths of this *inter*molecular binding.

Of the compounds studied, only *o*-phenylenedioxytin(II) exhibits a Mössbauer resonance at room temperature, and as can be seen from Table I, while the isomer shift stays constant with temperature, the quadrupole splitting decreases markedly (by *ca.* 15%) for this compound. Other organotin compounds which exhibit Mössbauer resonance at room temperature include the dialkyl- and diphenytin oxides[18] and bis(3,4-toluenedithiolate)tin.[19] In both cases structures involving *inter*molecular O→Sn[20] and S→Sn[21] (p→d) π bonding have been proposed which would give tin a coordination number higher than four. It is interesting that bis(1,2-ethanedithiolate)tin, in which the organic lacks the requirement for planarity, apparently

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[17] H. Frauenfelder, "The Mössbauer Effect," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 34, 78; G. K. Wertheim, "Mössbauer Effect: Principles and Applications," Academic Press Inc., New York, N. Y., 1964, Chapter 4.

[18] V. I. Goldanskii, "The Mössbauer Effect and its Applications in Chemistry," Consultants Bureau, New York, N. Y., 1964, p 59.

[19] L. M. Epstein and D. K. Straub, *Inorg. Chem.*, **4**, 1551 (1965).

[20] V. I. Goldanskii, E. F. Marakov, R. A. Stukan, V. A. Trukhtanov, and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, **151**, 357 (1963).

[21] R. C. Poller, *Proc. Chem. Soc.*, 312 (1962).

also shows a much weaker Mössbauer resonance at room temperature than its toluene analog,[19] as do our compounds where additional substitution on the phenyl ring or incorporation of a biphenylene ring system apparently serves to disrupt the layer structure.[22]

The stronger (p→d) π *inter*molecular O→Sn bonding in *o*-phenylenedioxytin(II) is shown as well in the lower isomer shift of this compound relative to the others in Table I. Ionic stannous compounds have the electronic configuration Sn[Kr]$4d^{10}5s^2$, while covalent stannous compounds should have an intermediate s-electron density at tin depending upon the nature of their hybridization and the partial ionic character of their bonds. In a homologous series the amount of d-orbital involvement in the tin hybrid may be seen with reference to the Mössbauer isomer shift which measures s-electron density at the tin nucleus: the greater the d-orbital character the less the s character of the hybrid and the lower the Mössbauer isomer shift. The higher isomer shifts of the other five- and seven-membered heterocycles correlate with greater solubility, lower thermal stability, greater ease of hydrolysis, and lower temperatures of sublimation.[9-12]

Hydrolysis of the tin(II) heterocycles on standing either in air (where differential thermal analysis shows about 10% hydrolysis per month) or in alcoholic potassium hydroxide[9] regenerates the dihydric organic phenol starting material. The black refractory material frequently found in sublimation residues was assumed to be stannous oxide. Figure 1 shows the Mössbauer spectrum of a sample of 3,4-toluenedioxytin(II) allowed to hydrolyze over a long period in air. The resonance at zero isomer shift is due to *stannic* oxide. Separation by sublimation *in vacuo* nets the dihydric phenol and pure 3,4-toluenedioxytin(II), which hydrolyzes under a nitrogen atmosphere to give the expected stannous oxide according to the equation

$$CH_3C_6H_3O_2Sn + H_2O \longrightarrow CH_3C_6H_3(OH)_2 + SnO$$

Acknowledgment.—Our work is supported by the Advanced Research Projects Agency. We thank Professor R. F. Porter of this department for examining our compounds in the furnace-equipped mass spectrometer.

[22] Preliminary studies on tin(IV) derivatives of these heterocyclic compounds where tin is substituted with methyl, butyl, and octyl groups show these systems fail to exhibit room-temperature resonances as well [H. S. Marsh, H. S. Sage, and J. J. Zuckerman, unpublished results].

CONTRIBUTION NO. 1814 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

An Electromotive Force Study of Lower Oxidation States of Lead, Cadmium, and Tin in Molten $NaAlCl_4$[1]

BY THEODORE C. F. MUNDAY AND JOHN D. CORBETT

Received November 1, 1965

Sealed cells of the type

$$Ag|Ag^+ \text{ in } NaAlCl_4|\text{glass}|M^{2+}, M_m{}^{m(2-n)+} \text{ in } NaAlCl_4|Ta$$

have been studied for lead, cadmium, and tin at 277°. The initial concentration of the dipositive state was ≤ 5 mole %, and the reduced ion $M_m{}^{m(2-n)+}$ was produced coulometrically in conjunction with a third electrode separated by a glass frit. A one-electron reduction found for lead indicates the formation of Pb^+ (or generally, $Pb^+ \cdot nPb^{2+}$). With cadmium, larger reductions were possible and the product $Cd_2{}^{2+}$ could be distinguished from Cd^0, $Cd_3{}^{4+}$, etc. A tentative result for the reduction of tin is $Sn_2{}^+$ ($Sn_3{}^{2+}$, etc.). Further evidence for the enhanced stability of lower oxidation states in acidic melts is presented. Preparation of $Ni(AlCl_4)_2$ was not possible, contrary to a recent report.

Introduction

Studies of the apparent solution of cadmium, tin, and lead in their respective molten halides all suggest, but in some cases do not prove, that the process takes place through the formation of a lower oxidation state in the melt. For the better studied $CdCl_2$–Cd system, recent magnetic,[2] emf (oxidation–reduction),[3,4] Henry's law,[4] and cryoscopic[5] studies are all consistent with the formation of a solute in the series Cd^0, $Cd_2{}^{2+}$, $Cd_3{}^{4+}$, $Cd_4{}^{6+}$, etc. The uncertainty in the solute here arises from the general inability to determine the amount of $CdCl_2$ consumed in dilute solutions of metal where ideal solution laws may be expected to apply, although the solute mobility[6] in this system suggests that it is charged. A similar result pertains to cadmium solution in the melt $CdCl_2$–KCl–NaCl,[7] where the metal solubility is markedly less. In opposition, a specific solute is indicated by studies in the $CdCl_2$–

[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] N. H. Nachtrieb, *J. Phys. Chem.*, **66**, 1163 (1962).

[3] L. E. Topol, *ibid.*, **67**, 2222 (1963).

[4] M. Okada, K. Yoshida, and Y. Hisamatsu, *J. Electrochem. Soc. Japan*, **32**, 99 (1964).

[5] L. E. Topol and A. L. Landis, *J. Am. Chem. Soc.*, **82**, 6291 (1960).

[6] W. Herzog and A. Klemm, *Z. Naturforsch.*, **15a**, 1100 (1960); C. A. Angell and J. W. Tomlinson, *Discussions Faraday Soc.*, **32**, 237 (1961).

[7] S. Karpachev and A. Stromberg, *Zh. Fiz. Khim.*, **13**, 397 (1939).