[A CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

A Thermodynamic Study of Lead Chloride in Dioxane–Water by Means of Electromotive Force and Solubility Data at 25°; The Acetone-, Ethanol-, Dioxane-, Glycerol–Water–Lead Chloride Systems[1a]

BY M. V. NOBLE AND A. B. GARRETT

This paper presents data on a study of the activity coefficients of lead chloride in dioxane–water solutions by means of electromotive force and solubility data. Data are also included on the solubility of lead chloride in acetone-, ethanol-, dioxane- and glycerol–water mixtures.

The general procedure is similar to that of other work[1] on the thallous chloride–ethylene glycol–water system.

The experimental procedure was (1) to measure the electromotive force of the cell Ag/AgCl/dioxane–water/$PbCl_2$/(Hg)Pb in 20, 40, and 60% dioxane over the concentration range of approximately 0.0004 molal lead chloride to saturation, and (2) to measure the solubility of lead chloride in these solutions in the presence of potassium chloride.

The cell data are used to evaluate the activity coefficients of lead chloride below the saturation point, and the solubility data are used for this evaluation above saturation. Solubility measurements in alcohol–water, acetone–water, and glycerol–water mixtures supplement the dioxane–water data and give an interesting picture of the effect of dielectric constant *versus* the solvent character upon the solubility of lead chloride.

The activity coefficients are evaluated by the method of Carmody.[2]

In a cell without liquid junction

$$E = E_0 - \frac{RT}{NF} \ln a_{AB_2} \text{ or} \tag{1}$$

$$E_0 - E_{\text{obs.}} = \frac{3RT}{Nf} \ln (4a_{\pm}) = \frac{3RT}{Nf} \ln 4(\gamma_{\pm} m_{\pm}) \tag{2}$$

where $E_{\text{obs.}}$ is the measured e. m. f., E_0 is the standard potential and the other quantities have their usual meaning.[1]

After rearranging, introducing values for the constants, and changing to Briggsian logarithms, we obtain

$$-\log \gamma_{\pm} = \left[\frac{E_{\text{obs.}}}{0.08873} + 0.2007 + \log m\right] - \frac{E_0}{0.08873} \tag{3}$$

Plotting the quantity in brackets against the square root of the ionic strength, the limit approached at infinite dilution gives $E_0/0.08873$ which when subtracted from $[(E_{\text{obs.}}/0.08873) + 0.2007 + \log m]$, gives the value of $(-\log \gamma_{\pm})$.

Using the value $(1/m)_{\mu=0}$ obtained in this manner, the accuracy of the values of γ obtained from solubility measurements are greatly increased.

III. Experimental Procedure

Conductivity water was used to prepare the solvent mixtures. Dioxane was purified[3,4] by refluxing it for two days with concentrated hydrochloric acid and then for two days over metallic sodium. The purified dioxane was stored over sodium until time to be used, at which time it was redistilled from the sodium and stored under nitrogen.

Glycerol was prepared by distilling at reduced pressure Merck C. P. grade glycerol; only the middle portion was used.

Acetone was prepared for use by fractionating C. P. grade acetone as in the case of glycerol.

Alcohol was purified by refluxing over silver oxide and fractionating.[5]

The solvent mixtures were all prepared on weight basis.

Lead chloride was prepared by dropping Coleman and Bell C. P. lead nitrate (1 *N* solution) simultaneously with 1 *N* hydrochloric acid solution into a two-liter flask. During the precipitation a current of nitrogen was passed through the solution to exclude air and to stir the mixture. The precipitate of lead chloride was then washed by decantation, recrystallized three times from conductivity water, dried on a porous plate, and stored in a desiccator until used.

Hydrochloric acid was prepared by distillation of Grasselli C. P. grade of hydrochloric acid in an all-glass still; the middle fraction was taken for use.

Potassium Chloride and Potassium Nitrate.—Baker Analyzed was used without futher purification.

Diphenylthiocarbazone.—Eastman Kodak Co. diphenylthiocarbazone was purified by repeated extraction between water and chloroform as recommended by Wilkins, Willoughby, Kramer and Smith.[6]

Preparation of Electrodes.—Silver–silver chloride electrodes were prepared by different methods,[7–12] several of which involve plating of platinum with silver and subsequent chloridization, or baking silver oxide on platinum followed by chloridization. Due to several chemical and mechanical difficulties involved, it was decided to investigate the possibility of simply chloridizing pure silver wire as described in previous work.[12] This gave a firm white coating of silver chloride in a solution free from impurities such as are present in a silver plating bath (particularly the cyanide ion). These electrodes gave the required potential reproducible to 0.1 mv. against a calomel half-cell. Electrodes were prepared in this manner only a short time in advance of making up the cell and were stored in distilled water until ready for use.

Preparation of Amalgam.—The amalgam was prepared thermally[13] by dissolving enough freshly cleaned Baker Reagent stick lead in carefully purified mercury to make a 6% amalgam. The amalgam was run through a capillary tube and stored in a sealed Pyrex tube under nitrogen pressure until used.

(1a) Original manuscript received August 14, 1941.

(1) Black and Garrett, THIS JOURNAL, **65**, 862 (1943); *cf.* also Garrett, Bryant and Kiefer, *ibid.*, **65**, 1905 (1943).

(2) Carmody, *ibid.*, **51**, 2905 (1929).

(3) Scatchard and Benedict, *ibid.*, **58**, 837 (1936).

(4) Eigenberger, *J. prakt. Chem.*, **130**, 73 (1931).

(5) Gross, Kuzmany and Wald, THIS JOURNAL, **59**, 2692 (1937).

(6) Wilkins, Willoughby, Kramer and Smith, *Ind. Eng. Chem., Anal. Ed.*, **7**, 33 (1935).

(7) Smith and Taylor, *J. Research Natl. Bur. Standards*, **20**, 837 (1938), and **22**, 307 (1939).

(8) Harned, THIS JOURNAL, **51**, 416 (1929).

(9) MacInnes and Parker, *ibid.*, **37**, 1445 (1915).

(10) Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

(11) Carmody, *ibid.*, **51**, 2901 (1929).

(12) Black and Garrett, *ibid.*, **65**, 862 (1943).

(13) Crockford and Thomas, *ibid.*, **55**, 568 (1933).

Preparation of Cells.—The cell was a modification of the one used by Carmody.[1,2]

Purification of Nitrogen.—Tank nitrogen was purified by successively passing it through soda lime, calcium chloride, reduced copper at 700°, calcium sulfate, alkaline pyrogallol, and a solution of the same composition as that in the cell. All work was done in an atmosphere of nitrogen.

Measurement of e. m. f.—The e. m. f. of the cells was measured with a Leeds and Northrup type K-2 potentiometer. The standard cell used was checked at regular intervals against another cell certified by the National Bureau of Standards which was kept for that purpose only. The galvanometer used was a Type R (Leeds and Northrup) with a sensitivity of 3 × 10^{-9} ampere per millimeter with scale at one meter. All leads were shielded.

Preparation of Solubility Samples.—These were prepared by the method described in earlier work.[1,14]

Sampling and Analysis.—After equilibration, the samples were sedimented for a day in the 25° bath, and were then filtered by means of nitrogen pressure through a Jena glass filter into a dry flask. The sample was weighed, density determinations were then made and the weighed sample analyzed by the chromate method given by Scott[15] (test analyses by this method gave results reproducible to two parts in one thousand) or by the colorimetric method of Craig and Vinal.[16]

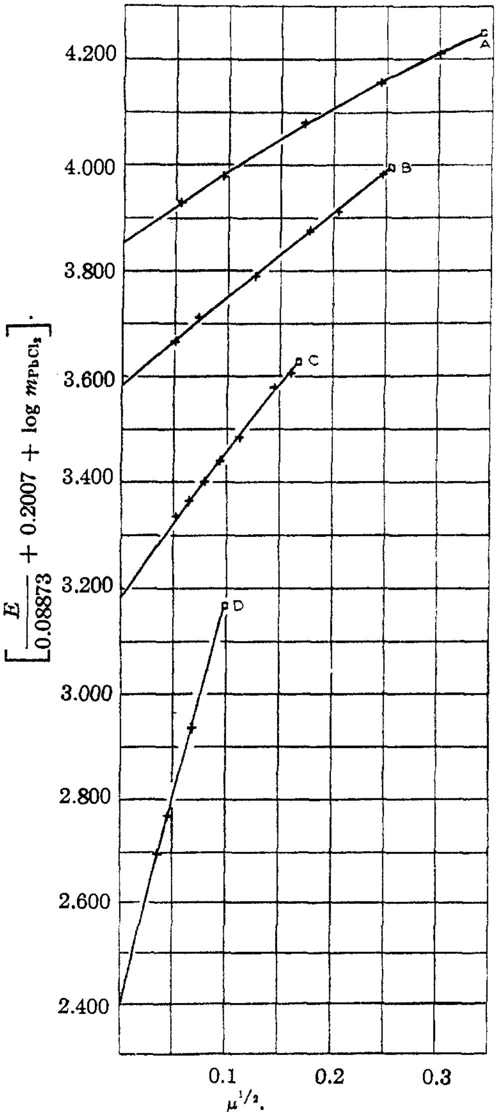

Fig. 1.—A, Water; B, 20% dioxane; C, 40% dioxane; D, 60% dioxane.

The Data

A. Electromotive Force Data; Activity Coefficients to Saturation (at 25 ± 0.02°).—The apparatus and techniques of the cell measurements were first studied in the lead chloride–water system previously reported by other investigators;[2,17] the values of E and γ obtained were in agreement with their data. The mixed solvent system was then investigated.

The activity coefficients of lead chloride were calculated from cell data in 20, 40 and 60% dioxane–water mixtures which are given in Table I.

Table I

Activity Coefficients of Lead Chloride from E. M. F. Data

Moles of $PbCl_2$ per 1000 g. solvent	20% dioxane–80% water $E_{obs.}$	γ	40% dioxane–60% water $E_{obs.}$	γ	60% dioxane–40% water $E_{obs.}$	γ
0.02173 (s)[a]	0.4842[a]	0.387				
.02013	.4857	.397				
.01399	.4938	.470				
.01049	.5017	.511				
.00932 (s)			0.4842[a]	0.358		
.00856			.4855	.374		
.00699			.4909	.401		
.00525	.5209	.619				
.00428			.5016	.496		
.00323 (s)					0.4842[a]	0.173
.00293			.5120	.546		
.00214			.5201	.604		
.00175	.5561	.745				
.00153					.4929	.295
.00142			.5334	.656		
.000951			.5462	.702		
.000874	.5788	.828				
.000694					.5081	.434
.000424					.5207	.511
	$\left(\frac{1}{m_\pm}\right)_{\mu \text{ at s}} = 29.0$		$\left(\frac{1}{m_\pm}\right)_{\mu \text{ at s}} = 67.6$		$\left(\frac{1}{m_\pm}\right)_{\mu \text{ at s}} = 195$	
	$\left(\frac{1}{m_\pm}\right)_{\mu = 0} = 75.0$		$\left(\frac{1}{m_\pm}\right)_{\mu = 0} = 187$		$\left(\frac{1}{m_\pm}\right)_{\mu = 0} = 1127$	

[a] s = saturation.

The extrapolations used to obtain values of E_θ are reproduced in Fig. 1. The values of γ were obtained by means of equation (3) described above and referred to the standard state of infinite dilution in the particular solvent mixture used.

The reproducibility of the cells was within ±0.1 mv. except in solutions less than 0.0004 molal where the deviations became greater (0.5 mv.) as is expected for cell measurements at such solutions.[18]

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[14] Garrett, Noble, Kiefer and Bryant, This Journal, **65**, 293 (1943).

[15] Scott "Standard Methods of Chemical Analysis." D. Van Nostrand Company, New York, N. Y., 1927, p. 275.

[16] Craig and Vinal, *J. Research Natl. Bureau of Standards*, **22**, 55 (1939).

[17] Allmand and Hunter, *Trans. Faraday Soc.*, **24**, 300 (1928).

[18] Early work on these cells was discouraging due to the difficulty experienced in reproducing the data. However, this was almost entirely eliminated as a result of the observation that even small traces of oxygen will apparently cause rapid oxidation of the organic solvent in the presence of the solute. Consequently, standard solutions prepared and stored under nitrogen were discarded and the general policy adopted was to prepare the lead chloride–dioxane–water solution just before it was to be used.

TABLE II

SOLUBILITY OF $PbCl_2$ IN KCl SOLUTIONS OF DIOXANE-WATER AT 25 ± 0.02°[a]

20% dioxane-80% water		40% dioxane-60% water		60% dioxane-40% water	
Moles KCl	Moles $PbCl_2$	Moles KCl	Moles $PbCl_2$	Moles KCl	Moles $PbCl_2$
0.000	2.173×10^{-2}	0.000	0.932×10^{-2}	0.000	0.323×10^{-2}
.01005	1.84	.0098	.660	.010	.208
.03016	1.33	.0294	.442	.030	.204
.0695	.874	.0688	.348	.050	.210
.0995	.725	.099	.336	.070	.207
.199	.537	.199	.335	.085	.198
.299	.509	.295	.312	.100	.154
.401	.437	.399	.252	.300	.135
.553	.353	.693	.225		
.711	.325	.859	.211		
.868	.314	1.008	.254		
.970	.312	1.224	.283		
1.180	.323				
1.455	.371				
1.674	.418				

[a] All concentrations are expressed as moles of solute for 1000 g. of solvent.

Considering the error in extrapolation to $\mu = 0$ and the reproducibility of the data, the maximum probable error is in the order of ±0.005.

From the value of $\gamma_{\pm}$ at saturation and $(1/m_{\pm})_{\mu \text{ at sat.}}$, the value of $(1/m_{\pm})_{\mu = 0}$ could be evaluated for use in evaluating γ from the solubility data.

B. Solubility Data in Potassium Chloride and in Potassium Nitrate Solutions.—The data in potassium chloride solutions are summarized in Table II. All solubility values are expressed in moles per 1000 g. of solvent. A plot of the solubility of lead chloride as a function of added chloride ion is shown in Fig. 2. The common ion effect, complex formation and relative degree of dissociation may be noted in this graph.

An indication of the degree of dissociation of lead chloride in these solvents is given by extrapolating the solubility curve to $m_{Cl^-} = 0$ to obtain the amount of undissociated lead chloride.[19] This value divided by the total amount of lead chloride in solution (solubility in the pure solvent) gives the per cent. of dissociated lead chloride; these values range for 5% in water through 6, 9 and 20% in the three mixtures studied. The data in water solubility are those obtained by Deacon in solutions of sodium chloride.[20] Fromherz[21] claims that absorption spectra data indicate the following relative ion concentrations in a saturated aqueous solution of lead chloride: 48% $PbCl^+$, 48% Pb^{++} and 4% $PbCl_2$. His conclusions are compatible with the above calculations.

TABLE III

ACTIVITY COEFFICIENTS OF LEAD CHLORIDE AT ROUNDED VALUES OF IONIC STRENGTH

Dioxane	20%	40%	60%
μ	γ	γ	γ
0.0005	0.919	0.870	0.662
.001	.887	.818	.562
.004	.782	.661	.318
.008	.705	.561	.202
.01	.678	.527	.173
.04	.471	.301	.060
.08	.356	.198	.039
.1	.323	.171	.035
.3	.176	.084	.020
.5	.117	.064	
.7	.080	.055	
.9	.053	.046	
1.0	.045		

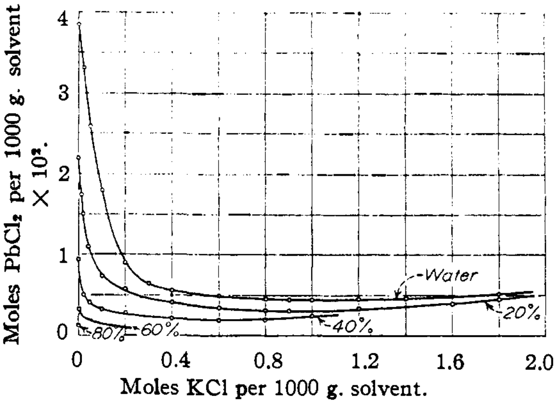

Fig. 2.

Values of γ at rounded values of m_{PbCl_2} are given in Table III.

The solubility of lead chloride as a function of added potassium nitrate (at 25°) is summarized in Table IV. The increased ionic strength due to the presence of potassium nitrate has the obvious and expected effect of increasing the solubility of lead chloride.

The limiting slopes of $-\log \gamma_{\pm}$ *vs.* $\sqrt{\mu}$ are 1.69, 2.73 and 8.00 for the three mixtures studied; they are all larger than the theoretical slopes calculated from the limiting law, $-\log \gamma = C\sqrt{\mu}$.

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(19) See Johnston, Cuta and Garrett, THIS JOURNAL, **55**, 2320 (1933), who used this method for AgOH.

(20) Deacon, *J. Chem. Soc.*, 2063–2065 (1927).

(21) Fromherz, *Z. physik. Chem.*, **153**, 382 (1931).

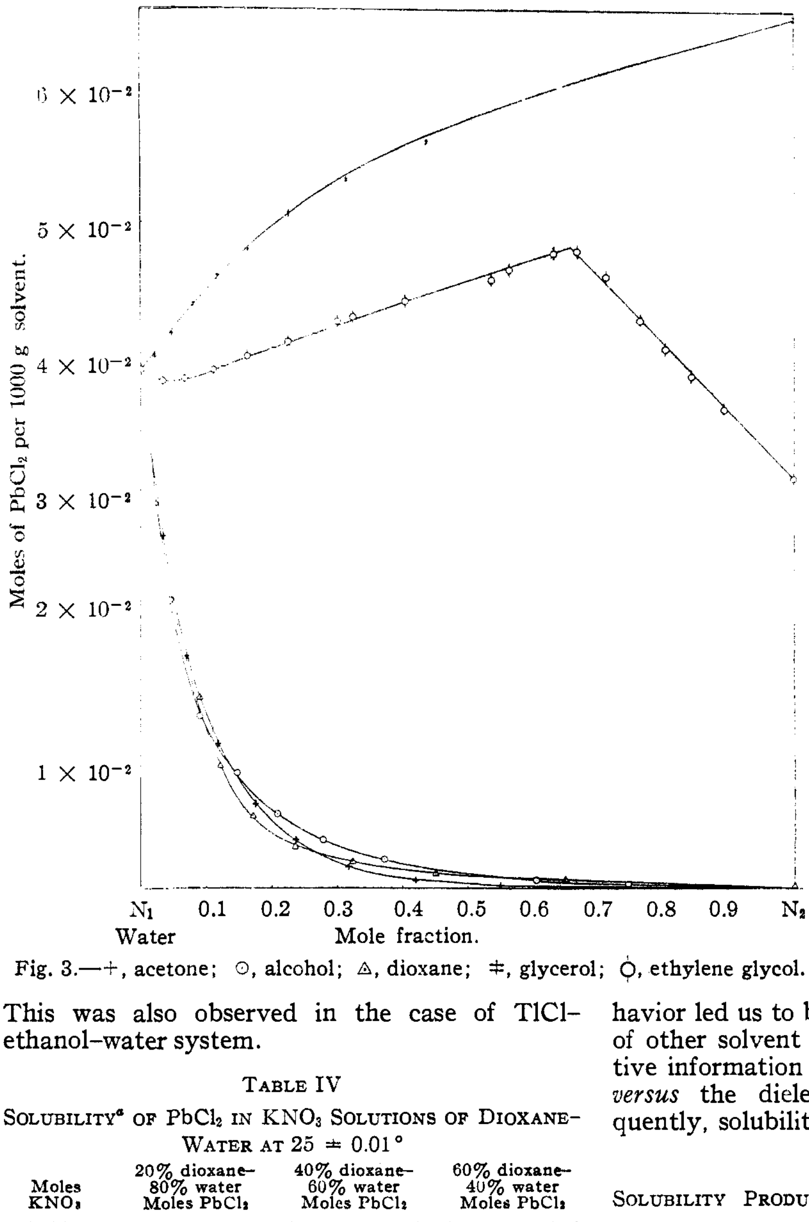

Fig. 3.—+, acetone; ○, alcohol; △, dioxane; ≑, glycerol; ⌽, ethylene glycol.

This was also observed in the case of TlCl-ethanol-water system.

TABLE IV

SOLUBILITY[a] OF $PbCl_2$ IN KNO_3 SOLUTIONS OF DIOXANE-WATER AT 25 ± 0.01°

Moles KNO_3	20% dioxane-80% water Moles $PbCl_2$	40% dioxane-60% water Moles $PbCl_2$	60% dioxane-40% water Moles $PbCl_2$
0.000	2.173×10^{-2}	0.932×10^{-2}	0.323×10^{-2}
.005		1.011	.505
.010		1.052	.756
.030	2.323	1.222	
.050	2.445	1.352	
.070	2.584	1.486	
.085	2.772	1.539	
.100	2.869	1.605	
.300	3.145	2.382	

[a] All concentrations are expressed as moles of solute per 1000 g. of solvent.

Other situations where the experimental slopes are greater than the theoretical slopes have been observed in the $CdBr_2$-water system,[22] in which it is well known the cadmium bromide is a weak electrolyte; furthermore, it is observed in mixed solvent systems,[23] and in liquid ammonia system.[24] It may safely be concluded that the deviation from the limiting law can be accounted for primarily by the increased association at these low values of the dielectric constant. The changing a values should be considered but are probably of secondary importance.

Solubility Products.—The thermodynamic solubility products of lead chloride have been calculated in water, 20, 40 and 60% dioxane from the relationship $K_{s.p.} = 4(m\gamma)^3$, and are given in Table V.

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C. The Solubility of Lead Chloride in Dioxane-Water, Ethanol-Water, Acetone-Water, Glycerol-Water and Ethylene Glycol-Water Solutions.—Preliminary treatment of the lead chloride-dioxane-water data indicated that a plot of the log of the solubility of lead chloride *vs.* log D along with the data of Dunning and Shutt[25] taken in solutions of glycine and water of high dielectric constant, gave a break at the water point. This behavior led us to become interested in the behavior of other solvent pairs to obtain at least qualitative information about the specific solvent effect *versus* the dielectric constant effect. Consequently, solubility data were obtained in several

TABLE V

SOLUBILITY PRODUCTS OF $PbCl_2$ IN DIOXANE-WATER MIXTURE

$K_{s.p.} = 4(m\gamma)^3$

% Dioxane	D	m	γ	$K_{s.p.}$	ΔF, cal.
0	78	0.03905	0.409[a]	1.63×10^{-5}	6530
20	61	.0217	.387	2.37×10^{-6}	7680
40	43	.00932	.358	1.49×10^{-7}	9320
60	26	.00323	.173	7.0×10^{-10}	12500

[a] Carmody, ref. 2.

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(22) Bates THIS JOURNAL, **61**, 308 (1939).

(23) For HCl in water-dioxane see Harned and others, THIS JOURNAL, **61**, 49 (1939); for TlCl in water-ethanol see Hogge and Garrett; for alkali halides in water-methanol see Akerlof, *ibid.*, **51**, 2359 (1929). It is also of interest to note a recent paper by H. S. Frank, *ibid.*, **63**, 1789 (1941), in which he discusses the necessity to assume an association-solvation equilibrium at low values of the dielectric constant in order to correlate experimental data with deductions from his derivation for the Debye-Pauling equation, *cf.* *ibid.*, **47**, 2129 (1925).

(24) Hunt, *J. Phys. Chem.*, **45**, 351 (1941).

(25) Dunning and Shutt, *Trans. Faraday Soc.*, **34**, 1192 (1938).

pairs of mixed solvents; they are tabulated in Table VI and shown graphically in Fig. 3.[26]

TABLE VI

SOLUBILITY OF LEAD CHLORIDE IN MIXED SOLVENTS

Weight % water in solvent	Moles $PbCl_2 \times 10^{-2}$ per 1000 g. of solvent Dioxane–water	Alcohol–water	Acetone–water	Glycerol–water
100	3.905[a]	3.905	3.905	3.905
90	2.90	2.380	2.65	4.04
80	2.173	1.410	1.74	4.20
70	1.44	0.885	1.08	4.38
60	0.932	.568	0.640	4.57
50	.550	.360	.350	4.79
40	.323	.215	.164	5.04
30	.210	.111	.064	5.33
20	.120	.050	.016	5.66
10	.060	.021	.0091	6.07
0	.0013	.0077	.0038	6.55

[a] Carmody, ref. 2.

The plot of solubility *vs.* mole fraction (Fig. 3) gives an interesting comparison of relative solvation effects in mole for mole of solvent.

It appears that the number and the character of polar groups on the solvent which is used with water is a factor that determines the direction of the solubility effect. Within the particular solvent pair the dielectric constant of the mixture plays an important role, but a minor one compared with the "solvent character" effect. This is in accord with the conclusions of Kraus.[27]

Summary

1. The electromotive force of the cell $Pb(Hg)/PbCl_2/AgCl/Ag$ has been measured at several concentrations in 20, 40, and 60% dioxane–water mixtures.

2. The solubility of lead chloride has been determined in dioxane–water mixtures with added potassium chloride and potassium nitrate. The solubility has also been determined in alcohol–water, glycerol–water and acetone–water mixtures with no added salt present.

3. From these data the activity coefficients of lead chloride are calculated over a wide range of concentrations. The divergence in the slope of $-\log \gamma$ *vs.* $\sqrt{\mu}$ is attributed to association.

4. The solubility product constants are calculated for the 20, 40, and 60% mixtures of dioxane and water and for pure water.

5. The data in the various mixed solvent pairs are discussed.

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[26] The data on the lead chloride–ethylene glycol–water system were published in THIS JOURNAL, **65**, 293 (1943). The data are tabulated here in weight per cent. rather than mole per cent. for the sake of condensing the tables. The data are shown in Fig. 3 as mole fraction which serves as a better basis of comparison of solvation effects.

[27] Kraus, *Science*, **90**, 381 (1939).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

The Dipole Moments of Friedelin, Cerin, Isomers of Friedelinol and Isomers of 3-α-Naphthyl-1-chloro-1-propene[1,2]

BY JOHN J. LANDER AND W. J. SVIRBELY

The presence of specific functional groups in friedelin, cerin and high and low melting friedelinol have been decided upon on the basis of chemical evidence.[3] While dipole moment determinations would not be able to locate the positions of the functional groups in these cases, nevertheless such measurements could be regarded as a check on the accepted structures since their magnitudes should be of about the same order as those usually attributed to those same functional groups. This investigation was undertaken to check the structures of the above compounds. Dipole moments were also determined for two compounds which were suspected of being *cis-trans* isomers of 3-α-naphthyl-1-chloro-1-propene to decide whether such isomerism was possible on the basis of their moments.

Materials

Benzene.—J. T. Baker thiophene-free benzene was refluxed over mercuric acetate, dried with calcium chloride, refluxed over sodium and fractionally distilled over sodium, collecting the middle fraction (b. p. 78.1° uncor.). Subsequent distillations of benzene solutions were made to recover the benzene for reuse. The benzene was stored over sodium wire in a glass bottle and used as required.

Friedelin.—Slightly impure friedelin was recrystallized twice from pyridine (m. p. 254–260°). This may be compared with the melting range of 256–262° for the pure material.

Low-melting Friedelinol.—Slightly impure compound was recrystallized twice from dioxane. The melting point range, 278–282°, was the same as for the pure material.

High-melting Friedelinol.—This compound was prepared by hydrogenating some of the pure friedelin in dioxane solution over a copper–chromium oxide catalyst at 200° and 2000 lb. pressure. The crude material was recrystallized once from dioxane. The melting point range, 299–301°, may be compared to the range 301–304° for the pure material.

Cerin.—Pure cerin was used,[4] m. p. 248–251°.

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[1] Presented in part at the Washington Section meeting of the A. C. S. held at the University of Maryland, May, 1942. Original version received March 15, 1943.

[2] A portion of this paper is abstracted from the Master's thesis presented by John J. Lander to the Graduate School of the University of Maryland, December, 1942.

[3] Drake and Jacobsen, THIS JOURNAL, **57**, 1570 (1935); Drake and Shrader, *ibid.*, **57**, 1854 (1935); Drake and Campbell, *ibid.*, **58**, 1681 (1936); Drake and Haskins, *ibid.*, **58**, 1684 (1936); Drake and Wolfe, *ibid.*, **62** 3018 (1940); G. K. Holmes, Thesis, University of Maryland 1940; J. Lann, Thesis, University of Maryland, 1941.

[4] Impure friedelin, impure low-melting friedelinol, and pure cerin were supplied us through the courtesy of Dr. N. L. Drake and his collaborators.