gratitude to Dr. Milton D. Harris and Mr. A. M. Sookne for supplying them with the cellulose acetate fractions and for kindly consulting them throughout this investigation.

Summary

1. The specific viscosities of cellulose acetate fractions were determined at various concentrations (up to 0.5 volume per cent. of the solute). The slopes of the η_{sp}/c_v *versus* c_v curves can be represented by a single constant $k' = 0.70$.

2. The osmotic pressures of the same fractions were measured at various concentrations (up to 0.8 weight per cent. of the solute). The slopes of the π/c_2 *versus* c_2 curves can, within reasonable limits, be represented by one single constant $\mu = 0.43$.

3. The $[\eta]$-values for all fractions can be expressed by M_2 according to equation $[\eta] = 1.04 \times 10^{-2} \times M_2\,0.67$.

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

Activity Coefficients of Lead Chloride Determined from E. m. f. and Solubility Data at 25° in Ethylene Glycol–Water Solutions

BY A. B. GARRETT, RUSKIN BRYANT AND GEORGE F. KIEFER

The dihydric character of ethylene glycol, together with the moderately low value of its dielectric constant and its total miscibility with water, make it an interesting solvent in which to study solvation effects and to measure certain thermodynamic properties of solutes.

The cell data are used in this paper to evaluate the reciprocal of the mean molality at ionic strength of zero, $(1/m_{\pm})_{\mu=0}$, and the value of the activity coefficient, γ, to saturation; the solubility data are used to give a qualitative idea of the degree of dissociation and to evaluate γ above saturation.

Experimental

The experimental procedure is similar to that previously described.[1,2]

The cell Pb(Hg), $PbCl_2$, AgCl, Ag was used.[3]

All solutions were made on a weight basis. The work was done in an atmosphere of nitrogen. Conductivity water was used throughout the work. Three grades of ethylene glycol were used: namely, (a) Eastman Kodak Co. purest grade, (b) C. P. grade redistilled and (c) C. P. grade dried over sodium sulfate and redistilled; in each of the latter two cases, the center cut was used. The amalgam contained approximately 5% lead and was prepared thermally. The silver–silver chloride electrodes were prepared by the method previously described.[1] All chemicals were reagent quality or purified to that standard. The temperature was 25.00 ± 0.01°.

Data

The data are collected in Table I, and are shown in Figs. 1 and 2. The values of m_{PbCl_2} at saturation are those published earlier.[2] The

TABLE I

E. M. F. VALUES FOR THE CELL $Pb\text{-}Hg/PbCl_2[H_2O\text{-}C_2H_4(OH)_2]/AgCl/Ag$ AND SOLUBILITY DATA FOR THE SYSTEM $PbCl_2$–ETHYLENE GLYCOL–H_2O–KCl

Solution concentrations given in % by wt. water-ethylene glycol; *D*, dielectric constant; $PbCl_2$ and KCl as moles in 1000 g. of solvent.

I. 78.25%–21.75%, $D = 72.2$			II. 57.43%–42.57%, $D = 65.8$		
$PbCl_2$	*E*. obs.	γ	$PbCl_2$	*E*. obs.	γ
0.003124	0.5573	0.737	0.00206	0.5695	0.751
.006248	.5351	.656	.00619	.5345	.620
.007727	.5287	.626	.00845	.5254	.576
.01225	.5151	.562	.01238	.5147	.519
.02450	.4959	.463	.02476	.4961	.420
.03821*	.4842†	.402	.02728	.4936	.407
*(satn.)	†(extrap.)		.04016*	.4842†	.356
			*(satn.)	†(extrap.)	
$PbCl_2$	KCl	γ	$PbCl_2$	KCl	γ
0.03187	0.0196	0.402	0.03440	0.0192	0.355
.02690	.0392	.395	.02882	.0382	.354
.01951	.0783	.377	.02158	.0765	.336
.01733	.0995	.359	.01456	.1534	.289
.01080	.1968	.304	.01288	.1922	.268
.00682	.4972	.201	.00700	.3868	.219
.00482	.8098	.165	.00400	.7837	.167
.00402	1.222	.134	.00345	1.194	.133
.00496	2.096	.087	.00395	2.054	.089
$(1/m_{\pm})_{\mu = \text{satn.}} = 16.49$			$(1/m_{\pm})_{\mu = \text{satn.}} = 15.69$		
$(1/m_{\pm})_{\mu = 0} = 41.1$			$(1/m_{\pm})_{\mu = 0} = 44.1$		

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[1] Black and Garrett, THIS JOURNAL, **65**, 862 (1943).

[2] Garrett, Noble, Bryant and Kiefer, *ibid.*, **65**, 293 (1943).

[3] Carmody, *ibid.*, **51**, 2905 (1929).

TABLE I (*Concluded*)

III. 37.56%–62.44%, $D = 50.3$			IV. 19.36%–81.64%, $D = 48.4$		
$PbCl_2$	E, obs.	γ	$PbCl_2$	E, obs.	γ
0.00263	0.5603	0.664	0.00360	0.5485	0.549
.00469	.5426	.589	.00720	.5294	.450
.00526	.5391	.575	.01440	.5114	.359
.00629	.5336	.555	.02880	.4952	.274
.00836	.5257	.512	.04635*	.4842†	.226
.01671	.5074	.412	*(satn.)	†(extrap.)	
.02517	.4967	.361			
.04296*	.4842†	.293			
*(satn.)	†(extrap.)				
$PbCl_2$	KCl	γ	$PbCl_2$	KCl	γ
0.02429	0.0756	0.277	0.04043	0.0185	0.226
.01518	.1879	.222	.03578	.0370	.220
.00524	.4750	.183	.02856	.0735	.212
.00336	.7678	.158	.01491	.1848	.189
.00323	1.1678	.121	.00493	.4668	.160

$(1/m_\pm)_{\mu = \text{satn.}} = 14.67$ $(1/m_\pm)_{\mu = \text{satn.}} = 13.59$

$(1/m_\pm)_{\mu = 0} = 50.1$ $(1/m_\pm)_{\mu = 0} = 60.1$

V. 0% H_2O–100%, $D = 37.75$

$PbCl_2$	E, obs.	γ	$PbCl_2$	KCl	γ
0.00245	0.5582	0.561	0.02506	0.0189	0.224
.00736	.5282	.407	.01999	.0440	.211
.01472	.5118	.311	.01672	.0727	.193
.02945	.4966	.231	.01566	.0910	.179
.03086*	.4963†	.225	.01319	.1452	.151
*(satn.)	†(extrap.)		.01227	.1821	.137

$(1/m_\pm)_{\mu = \text{satn.}} = 20.42$ $(1/m_\pm)_{\mu = 0} = 90.8$

values of the activity coefficients, γ, were calculated by the method given by Carmody,[3] who used the following method outlined by Randall.[4]

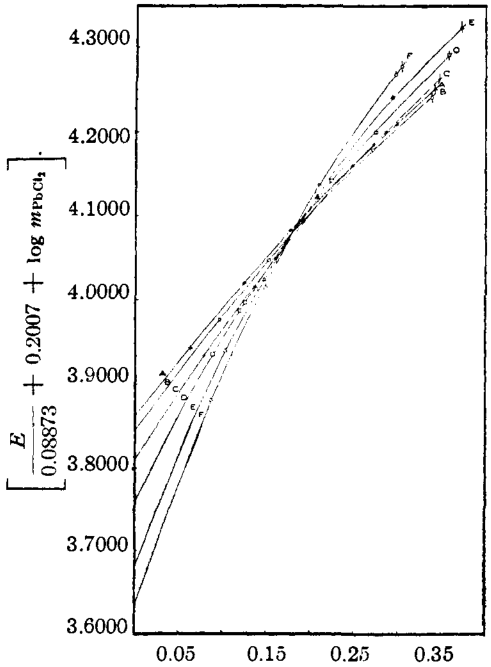

Fig. 1.—A, Water; B, 20% glycol; C, 40%; D, 60%; E, 70%; F, 100%.

For the cell Pb(Hg), $PbCl_2$, AgCl, Ag with the reaction $Pb + 2AgCl \rightarrow 2Ag + PbCl_2$: $E_{obs.} = E^0 - (RT/nF)\log a_{PbCl_2}$ where $E_{obs.}$ is the measured potential, E^0 is the potential at infinite dilution, and $a_{PbCl_2} = (a_{Pb^{++}})(a_{Cl^-})^2 = 4a^3 = 4\cdot(m\gamma)^3$. It follows that $\log \gamma = (E^0/0.08873) - (E/0.08873) + 0.2007 + \log m$.

TABLE II

VALUES OF ACTIVITY COEFFICIENTS (γ) OF LEAD CHLORIDE AT ROUNDED VALUES OF IONIC STRENGTH (μ)

Values from large scale graph; ethylene glycol–water system; temp., 25°.

	γ					
μ	H_2O^a	78.25% H_2O	57.43% H_2O	37.56% H_2O	19.36% H_2O	0% H_2O (pure etbylene glycol)
0.001	0.912	0.910	0.895	0.866	0.823	0.793
.003	.847	.844	.820	.775	.715	.677
.006	.791	.786	.755	.701	.637	.591
.008	.764	.758	.724	.666	.594	.553
.01	.740	.732	.697	.635	.562	.520
.03	.604	.593	.551	.483	.407	.364
.06	.505	.494	.450	.385	.316	.273
.08	.464	.452	.410	.348	.282	.241
.0926	.443	.431	.391	.330	.266	.225(s)
.1146	.413	.402(s)	.363	.305	.243	.202
.1172	.408(s)	.396	.360	.302	.241	.200
.1205	.405	.393	.356(s)	.299	.239	.197
.1289	.396	.384	.348	.293(s)	.232	.191
.1397	.385	.372	.336	.283	.226(s)	.182
.2	.335	.320	.290	.248	.196	.144
.4		.236	.217	.193	.166	
.8		.166	.60	.148		

[a] Data of Carmody (ref. 3) and ref. 5. (s) saturation.

In general, the e. m. f. values were easily reproducible to 0.1 mv. except at the high dilutions (below 0.002 M). The values of $E_{obs.}$ for 20, 40, 60 and 80% ethylene glycol–water solution extrapolate directly to the value of $E = 0.4842$, which is the value established in water for the cell involving the reaction $Pb(s)(Hg) + 2AgCl(s) = 2Ag(s) + PbCl_2(s)$ and which should be independent of the solvent at saturation (since all reactants and products are at unit activity) unless an additional reaction occurs. The value of $E_{obs.}$ at saturation in 100% ethylene glycol, however, is 0.4963. Presumably, here the reaction is

$$Pb(s) + 2AgCl(s) + xC_2H_4(OH)_2 = PbCl_2xC_2H_4(OH)_2(s) + 2Ag(s)$$

at saturation,[2] giving a free energy difference of −520 calories for the reaction

$$PbCl_2 + xC_2H_4(OH)_2 = PbCl_2{\cdot}xC_2H_4(OH)_2$$

The values of γ from the cell data have a maximum probable error of ±0.005 due principally to

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(4) Randall, *Trans. Faraday Soc.*, **23**, 498 (1927).

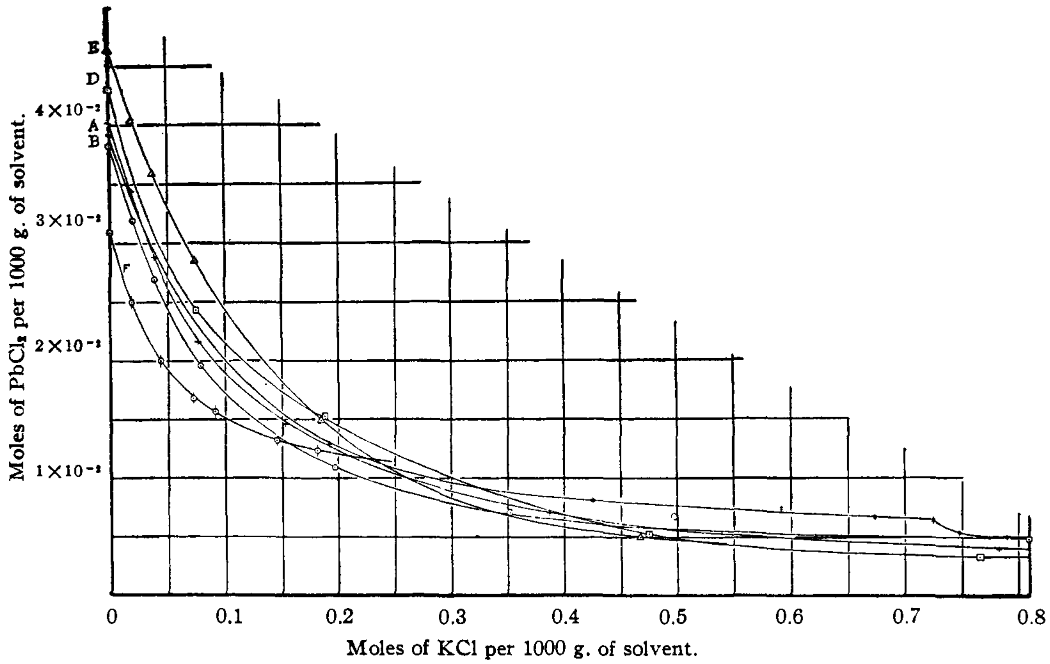

Fig. 2.—A, Water; B, 20% glycol; (unmarked) 40%; D, 60%; E, 80%; F, 100%.

the uncertainty in the extrapolation of $(1/m_{\pm})_{\mu=0}$; this error and the errors involved in evaluating $(1/m)_{\mu=\text{satn.}}$ from the solubility data give an estimated maximum probable error in the individual values of γ above saturation of ± 0.01. Table II gives smoothed values of γ at rounded values of μ taken from a large-scale graph. The values of γ of lead chloride in water were obtained from Carmody's data.[3]

A qualitative idea of the relative degree of dissociation of lead chloride in water, ethylene glycol and in the mixed solvents may be obtained from Fig. 2. The values for the lead chloride–potassium chloride–water system are those of Parton, Robinson and Matson.[5] They claim to have found evidence for change in solid phase to $PbCl_2 \cdot KCl$ at $m_{KCl} = 0.725$. Consequently, the data are compared only to this point. No evidence was observed for such compound formation in the ethylene glycol–water systems at the concentrations of potassium chloride used.

Summary

The solubility of lead chloride was determined in approximately 20, 40, 60, 80 and 100% ethylene glycol–water solutions containing potassium chloride.

The e. m. f. values of the cell Pb(Hg),$PbCl_2$, AgCl, Ag were determined in approximately 20, 40, 60, 80 and 100% ethylene glycol–water solutions of lead chloride.

The values of the activity coefficients of lead chloride were calculated from the solubility and the cell data in approximately 20, 40, 60, 80 and 100% solutions of ethylene glycol–water.

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[5] Parton, Robinson and Matson, *Trans. Faraday Soc.*, **35**, 402 (1939).