paper, in which the internal rotatory diffusion of long chain molecules will be treated.[16]

Summary

1. A method is given whereby the distribution of times of relaxation of a polar system can be calculated from the observed loss factor–frequency curve.

2. The reduced polarization is introduced as a simplification in calculating a. c. properties of polar systems.

3. Experimental loss factor–frequency curves for systems containing polyvinyl chloride can be represented empirically by the approximate equation

$$\epsilon'' = \epsilon''_m \operatorname{sech} [\alpha (\ln f/f_m)]$$

where α is the distribution parameter.

4. The average moment per monomer unit of a linear polar polymer of the type $(\text{—CH}_2\cdot\text{CHX—})_m$, assuming free rotation, is found to be $\sqrt{3}\,\mu_0/2$, where μ_0 is the moment of the equivalent group in free space.

5. Application of the theoretical results to data on polyvinyl chloride–diphenyl systems gives a value of 2.0 to the C–Cl moment in polyvinyl chloride.

6. Previous empirical conclusions concerning chain interaction in polymeric systems receive further support from the present theoretical treatment.

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(16) Relations between the real and imaginary parts of the dielectric constant similar to those presented here have been discussed by Kronig, *J. Optical Soc. Am.*, **12**, 547 (1926), and Kramers, *Atti Congr. dei Fisici, Como*, 545 (1927). Their use in connection with magnetic relaxation phenomena is treated by Gorter and Kronig, *Physica*, **3**, 1009 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YENCHING UNIVERSITY]

Solubility Studies. II. The Activity Product and Standard Electrode Potential of Silver Iodate from 10 to 35°

BY NORMAN C. C. LI AND YING-TU LO

In the first part of this series[1] it was shown that the heat of solution and standard electrode potential of silver chromate derived with the aid of solubility data for silver chromate agree closely with the values determined directly from calorimetric and potential measurements. This paper describes solubility determinations with silver iodate in solutions of potassium nitrate from 10 to 35°. The experimental values are compared with those calculated from the Debye–Hückel equation and the activity product of silver iodate is combined with the standard potential of the silver electrode to obtain the standard potential of the Ag(s), AgIO_3(s), IO_3-electrode at 10, 20, 25, 30 and 35°.

Experimental

Silver iodate was prepared by mixing dilute solutions of C. P. silver nitrate and twice-recrystallized potassium iodate. The finely-divided precipitate obtained was aged for several days in the mother solution, washed repeatedly with conductivity water and dried in a vacuum oven at 60°. The potassium nitrate solutions, used as solvents, were prepared by weight directly from thrice-recrystallized salt, followed by proper dilutions for the various concentrations.

The solubility determinations were carried out as described by Kolthoff and Lingane[2] using brown glass bottles, coated inside with paraffin and closed with paraffined corks. The temperature was regulated to ±0.05° for each temperature and three determinations were made for each point of the reported solubility curves.

The analysis of the saturated solutions consisted in the iodimetric determination of the iodate in 100-ml. samples by means of 0.01 *N* sodium thiosulfate solutions, using a calibrated microburet. The sodium thiosulfate solutions were standardized frequently against pure potassium dichromate and appropriate corrections made for blanks in each case. The titrations were accurate to ±0.3%.

Results

The data obtained are listed in Table I. The first column gives the molarity m of potassium nitrate, the second the solubility s in moles per liter averaged, in each case, from three closely agreeing results; the third column lists the square root of the ionic strength assuming that all the substances are completely ionized.

Using the Debye–Hückel equation in the form

$$\log f_{\pm} = -B\sqrt{\mu}/1 + A\sqrt{\mu} \tag{1}$$

in which the activity coefficient

$$f_{\pm} = S_0/S_{\mu} \tag{2}$$

the following equation can be obtained

$$\log S_0 - \log S_{\mu} = -B\sqrt{\mu}/1 + A\sqrt{\mu} \tag{3}$$

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(1) Li, *J. Chinese Chem. Soc.*, in press.

(2) Kolthoff and Lingane, *J. Phys. Chem.*, **42**, 133 (1938).

TABLE I

SOLUBILITY AND ACTIVITY COEFFICIENT OF SILVER IODATE IN POTASSIUM NITRATE SOLUTIONS

m_{KNO_3}	$S \times 10^4$	$\sqrt{\mu}$	$f_{obsd.}$	$f_{calcd.}$
		10 °C.		
	0.9605[a]		(1.000)	(1.000)
0	.97	0.0099	0.990	0.989
0.001326	1.0016	.0378	.958	.958
.003263	1.023	.0580	.939	.937
.006464	1.054	.0811	.911	.912
.01404	1.104	.119	.870	.874
.07032	1.279	.266	.754	.740
		20 °C.		
	1.442[a]		(1.000)	(1.000)
0	1.463	.0121	.986	0.986
.001326	1.508	.0384	.957	.957
.003263	1.543	.0585	.935	.935
.006464	1.582	.0814	.912	.911
.01404	1.656	.119	.871	.872
.07032	1.943	.266	.742	.736
		25 °C.		
	1.748[a]		(1.000)	(1.000)
0	1.785	.0133	.980	0.984
.001301	1.827	.0386	.957	.956
.003252	1.868	.0587	.937	.934
.006503	1.913	.0818	.914	.910
.01410	2.002	.120	.873	.870
.07050	2.304	.266	.759	.734
.1213	2.454	.349	.712	
.2528	2.793	.503	.626	
.5050	3.330	.711	.526	
.8738	3.904	.935	.447	
		30 °C.		
	2.119[a]		(1.000)	(1.000)
0	2.152	.0147	0.984	0.983
.001326	2.212	.0393	.957	.955
.003263	2.263	.0591	.936	.933
.006464	2.324	.0817	.912	.909
.01404	2.419	.120	.875	.869
.07032	2.844	.266	.745	.732
.1213	3.041	.349	.697	.664
.2528	3.428	.503	.618	.554
.5050	4.035	.711	.525	.434
		35 °C.		
	2.541[a]		(1.000)	(1.000)
0	2.587	.0160	.982	.981
.001326	2.663	.0399	.953	.954
.003263	2.714	.0595	.935	.932
.006464	2.786	.0822	.912	.907
.01404	2.920	.120	.871	.868
.07032	3.381	.266	.752	.730
.2003	3.908	.448	.650	.588
.4987	4.803	.707	.530	.433

[a] Extrapolated value, S_0.

In these equations S_0 is the solubility at zero ionic strength, S_μ is the observed solubility in the ionic strength μ and A is a parameter involving the ion size.

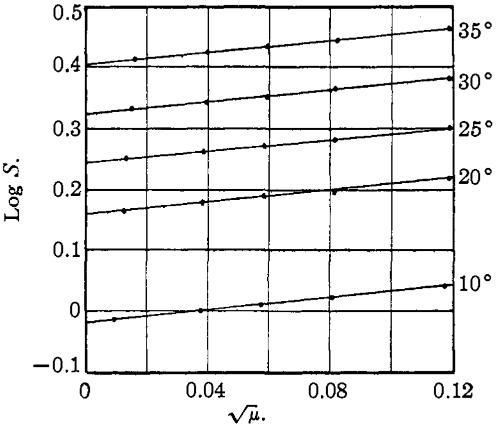

Fig. 1.—Solubility of silver iodate in potassium nitrate solutions at different temperatures.

By plotting log S against $\sqrt{\mu}$ as in Fig. 1 and extrapolating to zero ionic strength the values of S_0 at different temperatures are obtained. These extrapolated values are given at the top of column 2 in Table I for each temperature. Activity product, K, is S_0^2 and its values at different temperatures are listed in Table II.

The observed values of activity coefficient, $f_{obsd.}$, given in the fourth column of Table I, were computed by eq. (2). The fifth column lists the values of $f_{calcd.}$ computed by the Debye–Hückel limiting expression which is

$$-\log f = B\sqrt{\mu} \qquad (4)$$

The values of B, calculated to be 0.491, 0.500, 0.505, 0.510, 0.515 for 10, 20, 25, 30 and 35°, respectively, were obtained with the help of the dielectric constant data of Drake, Pierce and Dow.[3]

It will be observed that the activity coefficient calculated from the limiting Debye–Hückel equation is accurate up to an ionic strength of about 0.01 molar. At higher ionic strengths the more extended equation (1) must be used.

The standard potential of the silver–silver iodate electrode can be calculated from the values of activity product K and the standard electrode potential of silver by means of the equation

$$E^0_{AgIO_3} = E^0_{Ag^+, Ag} + \frac{RT}{F} \ln K \qquad (5)$$

The standard electrode potential of silver from 5 to 45° has been determined by Owen and Brinkley.[4] The values of $E^0_{AgIO_3}$ were computed by means of eq. (5) and listed in Table II. Our values at 25° check well with those reported by Kolthoff and Lingane[2] who gave 3.04 × 10^{-8} and

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[3] Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

[4] Owen and Brinkley, THIS JOURNAL, **60**, 2233 (1938).

0.3551 v. for K and $E^0_{AgIO_3}$, respectively. From our results we derive the following empirical equation relating $E^0_{AgIO_3}$ and temperature

$$E^0_{AgIO_3} = 0.3551 - 0.00051\,(t - 25) - 6 \times 10^{-7}(t - 25)^2 \qquad (6)$$

Values computed from this equation are listed in Table II, column 4 and are to be compared with the values given in column 3.

TABLE II

ACTIVITY PRODUCT, STANDARD ELECTRODE POTENTIAL OF SILVER IODATE AND RELATED THERMODYNAMIC QUANTITIES FOR THE ELECTRODE REACTION $AgIO_3 = Ag + IO_3^-$

t, °C.	K	$E^0_{AgIO_3}$, v.	$E^0_{AgIO_3}$ from eq. (6)	$-\Delta S^0$	$-\Delta H^0$	$-\Delta C^0_p$
10	0.923	0.3625	0.3626	11.35	11,579	7.84
20	2.078	.3576	.3576	11.63	11,657	8.11
25	3.055	.3550	.3551	11.77	11,699	8.25
30	4.490	.3524	.3525	11.90	11,740	8.39
35	6.456	.3498	.3499	12.04	11,782	8.53

Differentiation of eq. (6) gives

$$-\mathrm{d}E^0_{AgIO_3}/\mathrm{d}T = 0.00051 + 1.2 \times 10^{-6}(t - 25) \qquad (7)$$

The standard change in entropy of the reaction $AgIO_3 = Ag + IO_3^-$

$$\Delta S^0 = F(\mathrm{d}E^0_{AgIO_3}/\mathrm{d}T) \qquad (8)$$

the standard change in heat content

$$\Delta H^0 = F(T\mathrm{d}E^0/\mathrm{d}T - E^0) \qquad (9)$$

and the standard change in heat capacity

$$\Delta C^0_p = \mathrm{d}\Delta H^0/\mathrm{d}T = F(T\mathrm{d}^2E/\mathrm{d}T^2) = -23{,}070 \times 1.2 \times 10^{-6}T \qquad (10)$$

are computed readily and listed in Table II, columns 5, 6, 7, respectively.

By substitution of eq. (6) from this paper and the equation for the temperature variation of the standard electrode potential of silver given by Owen and Brinkley[4] into eq. (5), the following expression for $RT/F \ln K$ is obtained

$$RT/F \ln K = -0.4442 + 0.000478(t - 25) + 1 \times 10^{-7}(t - 25)^2 \qquad (11)$$

This equation reproduces the values of K given in Table II to ±0.6%. The experimental accuracy of K is also of this degree, so that the corresponding error in $E^0_{AgIO_3}$ due to this small uncertainty in K is

$$\Delta E^0_{AgIO_3} = 2.303RT/F \log \frac{K_2}{K_1} = 2.303RT/F \log 1.006 = \pm 0.15 \text{ mv.}$$

The uncertainty in $E^0_{Ag^+, Ag}$ reported by Owen and Brinkley is of the same order of magnitude.

Differentiation of eq. (11) gives

$$2.303\ RT/F\ \mathrm{d} \log k/\mathrm{d}T = 0.000478 + 2 \times 10^{-7}(t - 25) \qquad (12)$$

The values of ΔF^0, ΔS^0, ΔH^0 and ΔC^0_p for the reaction $AgIO_3 = Ag^+ + IO_3^-$ can be calculated from the usual thermodynamic relations with the aid of equations (11) and (12). These values are listed in Table III.

TABLE III

DERIVED THERMODYNAMIC QUANTITIES FOR THE REACTION $AgIO_3 = Ag^+ + IO_3^-$

t, °C.	ΔF^0	ΔS^0	ΔH^0	ΔC^0_p
10	10,415	10.96	13,515	1.31
20	10,300	11.00	13,528	1.35
25	10,252	11.03	13,535	1.38
30	10,190	11.05	13,542	1.40
35	10,142	11.07	13,549	1.42

Kolthoff and Lingane derived from their data on the solubility of silver iodate at 25° and from Kohlrausch's data the following values: $\Delta F^0_{298.1} = 10{,}250$ cal. per mole and $\Delta H^0_{298.1} = 14{,}200$ cal. Greensfelder and Latimer[5] computed from Kohlrausch's data $\Delta F^0_{298.1} = 10{,}233$ and $\Delta H^0_{298.1} = 14{,}478$. Our value of $\Delta F^0_{298.1}$ is in good agreement with their values. Their values of $\Delta H^0_{298.1}$ however, were obtained from solubility data in pure water where the activity is not strictly unity. Latimer, Schutz and Hicks[6] recalculated from the solubility data and obtained $\Delta H^0_{298.1} = 13{,}200$, with which our value of 13,535 is in fair agreement. Latimer, Schutz and Hicks gave the value $\Delta S^0_{298.1} = 10.1$, as compared with our value of 11.03.

Entropy of Iodate Ion.—Using the convention that the entropy of hydrogen ion is zero at all temperatures, we can calculate the ionic entropy and heat capacity of the iodate ion from the reaction $AgIO_3 = Ag^+ + IO_3^-$ if we have supplementary values for the molal entropy and heat capacity of silver ion. We have obtained these supplementary values by interpolating the data of Greensfelder and Latimer[5] and of Owen and Brinkley.[4] The ionic entropy and heat capacity of iodate ion are calculated to be 29.6 e. u. and 13.6 cal./mole/deg., and are approximately constant over the temperature range 10-35°. Our value for the entropy of iodate ion compares well with the value $S^0_{298.1} = 27.1 \pm 1.0$ e. u. reported by Latimer, Schutz and Hicks,[6] in view of the difference in the values of $S^0_{Ag^+}$ used. They obtained 18.4 ± 0.2 cal./deg. mole for $S^0_{Ag^+}$ at 25° based on the heat of precipitation data of Lange and Fuoss[7] whereas we have used $S^0_{Ag^+} = 17.4 \pm$

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(5) Greensfelder and Latimer, THIS JOURNAL, **53**, 3813 (1931).

(6) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

(7) Lange and Fuoss, *Z. physik. Chem.*, **126**, 431 (1937).

0.2 cal./deg. mole, a value recommended by Owen and Brinkley[4] to be the most probable value at 25°.

Summary

The solubility and activity coefficient of silver iodate in potassium nitrate solutions have been determined at 10, 20, 25, 30 and 35°. The activity product of silver iodate and the standard potential of the silver–silver iodate electrode have been calculated at these temperatures. Values of ΔS^0, ΔH^0 and ΔC^0_p have been calculated for the electrode reaction and for the reaction $AgIO_3 = Ag^+ + IO_3^-$ at various temperatures. The ionic entropy and heat capacity of the iodate ion also are given.

PEIPING, CHINA RECEIVED OCTOBER 10, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YENCHING UNIVERSITY]

Solubility Studies. III. The Ionization Constant of Iodic Acid at 25, 30 and 35°

BY NORMAN C. C. LI[1] AND YING-TU LO

In this study we have determined the solubility of silver iodate in solutions of nitric acid at 25, 30 and 35°. By using these results, together with the results we reported in our previous paper[2] on the solubility of silver iodate in potassium nitrate solutions, we have calculated the ionization constant of iodic acid.

Experimental

The nitric acid solutions were made by a series of dilutions from a stock solution standardized against pure sodium carbonate, using methyl orange as indicator. The solubility determination, method of analysis and per cent. accuracy were the same as reported in our previous paper.[2]

The results obtained are given in Table I. The first column gives the molarity m of nitric acid and the second column the solubility, S, in moles per liter at the different temperatures.

TABLE I

SOLUBILITY OF SILVER IODATE IN NITRIC ACID SOLUTIONS

	$S \times 10^4$		
m	25°	30°	35°
0	1.785	2.152	2.587
0.001301	1.829		
.006503	1.949	2.373	2.844
.01410	2.070	2.520	3.045
.07050	2.660	3.256	3.922
.1213	3.040	3.750	4.537
.2528	3.820	4.738	5.688
.5050	5.027	6.350	7.718
.8738	6.522		

Log S is plotted against $\sqrt{\mu}$ in Fig. 1. For comparison data in potassium nitrate solutions given in Table I of our previous paper[2] are also graphed. The increased solubility of silver iodate in solutions of nitric acid, as compared to its solubility in the corresponding solutions of potassium nitrate, is due to the incomplete dissociation of iodic acid formed by double decomposition between silver iodate and nitric acid.

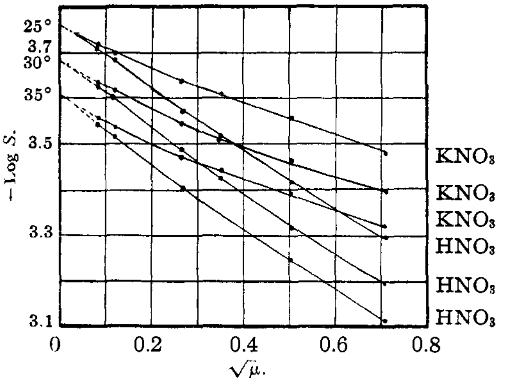

Fig. 1.—Solubility of silver iodate in electrolyte solutions.

Discussion

If we assume with Naidich and Ricci[3] that the mean activity coefficient of a slightly soluble salt is the same in solutions of the same total ionic strength, regardless of whether the electrolyte is the acid or the potassium salt of a given anion, we may set the solubility product of silver iodate in solutions of nitric acid to be equal to its solubility product in the potassium nitrate solution of the same ionic strength.

The various ionic concentrations in the acid solutions are calculated by means of the following equations

$$m_{IO_3^-} = K_{sp}/S_a = S_s^2/S_a \qquad (1)$$

$$m_{HIO_3} = S_a - m_{IO_3^-} \qquad (2)$$

$$m_{H^+} = m_{HNO_3} - m_{HIO_3} \qquad (3)$$

$$\begin{aligned} \mu &= S_a + m_{HNO_3} - m_{HIO_3} \\ &= m_{HNO_3} + m_{IO_3^-} \qquad (4) \end{aligned}$$

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[1] Present address: Department of Chemistry, The Catholic University, Peking, China.

[2] Li and Lo, THIS JOURNAL, **63**, 394 (1941).

[3] Naidich and Ricci, *ibid.*, **61**, 3270 (1939).