TABLE III

Compound	Yield, %	Metal, % Calcd.	Metal, % Found	Melting point, °C.
$Zr(CCA)_4$	75	18.7	18.9	190–193
$Hf(CCA)_4$	76	31.0	31.2	188–190
$Zr(CTA)_4$	97	13.0	13.2	128–130
$Hf(CTA)_4$	80	22.5	22.3	125–128
$Zr(FCA)_4$	81	13.1	13.1	198–201
$Hf(FCA)_4$	80	22.7	22.6	200–202
$Zr(FTA)_4$	95	10.0	10.0	199–201
$Hf(FTA)_4$	82	17.8	17.4	195–197
$Zr(PTA)_4$	93	10.1	10.0	184–185
$Hf(PTA)_4$	83	17.9	17.8	185–186
$Zr(TCA)_4$	81	12.0	11.95	244–245
$Hf(TCA)_4$	82	21.0	21.1	239–242
$Zr(TTA)_4$	80	9.3	9.3	225–226
$Hf(TTA)_4$	96	16.7	16.6	220–223

tained. This was evaporated to near dryness on a steam-bath, a few drops of concentrated H_2SO_4 along with a few ml. of concentrated nitric acid was added to the residue, again evaporated to near dryness, and the sulfuric acid fumed off. The charred samples were then ignited to constant weight over a Meker burner. The data in Table III represent average values of at least duplicate samples. The hafnium was assumed to have the corrected atomic weight of 177.94.

Melting Points (Table III).—The melting points were determined in a capillary melting point tube with a thermometer calibrated to an accuracy of 0.5°.

Densities and Molecular Volumes.—The densities of all the chelates were determined by the standard pycnometric method in which the volume of immersion liquid displaced by a known weight of a solid sample is measured. The immersion liquid here was boiled distilled water or petroleum ether (100–140°) saturated with the chelate. The HCCA derivatives were all run in petroleum ether. The measurements were all made at 25 ± 0.02° and the samples were degassed in a vacuum desiccator before weighing in the immersion liquid. The results along with the calculated molecular volumes are given in Table I. The molecular volume is simply the molecular weight of the compound divided by the density.

Absorption Spectra.—The ultraviolet absorption spectra were determined for each of the β-diketones and their corresponding zirconium and hafnium chelate compounds both in purified dry cyclohexane and in dry benzene. The data for the benzene solutions were determined using a Beckman DU quartz spectrophotometer, and the data for the cyclohexane solutions were obtained on a Carey model 11 recording quartz spectrophotometer. One-cm. cells were used in each case. Several of the solutions were run on both instruments with essentially identical results. The solutions were all about 10^{-5} M and were always run within a few hours of preparation. The diketones used were freshly distilled.

MADISON, WISC.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF SOUTH CAROLINA]

Activity Coefficient Ratios of Nitric Acid and Mercurous Nitrate and the Standard Potential of the Mercury, Mercurous Ion Electrode at 25°

BY OSCAR D. BONNER AND FRANCIS A. UNIETIS[1]

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Electromotive force measurements on cells of the type Ag, AgCl, HCl(0.2 m)/glass/$HNO_3(m_1)$, $Hg_2(NO_3)_2(m_2)$, Hg have been used for the calculation of the ratios of activity coefficients at 25° of nitric acid and mercurous nitrate. From extrapolations to infinite dilution, the standard potential of the mercury, mercurous ion electrode has been found to be −0.7961 v.

Introduction

Activity coefficient ratios of nitric acid and silver nitrate have previously been determined[2] from measurements of the electromotive force of the cell without liquid junction

Ag, AgCl, HCl(0.2 m)/glass/$HNO_3(m_1)$, $AgNO_3(m_2)$, Ag

Similarly, activity coefficient ratios of nitric acid and mercurous nitrate may be determined from measurements of the electromotive force of the cell

Ag, AgCl, HCl(0.2 m)/glass/$HNO_3(m_1)$, $Hg_2(NO_3)_2(m_2)$, Hg

In this instance also, the glass electrode must be used instead of the hydrogen electrode as the mercurous ion is reduced by hydrogen in the presence of platinum. For this cell the equation

$$E = E^0{}_{\text{glass}} - E^0{}_{\text{Hg.Hg}_2{}^{++}} - \frac{RT}{2F}\ln\frac{a^2{}_{\text{HNO}_3}}{a_{\text{Hg}_2(\text{NO}_3)_2}} =$$

$$E^0 - \frac{RT}{2F}\ln\frac{m^2{}_{\text{HNO}_3}}{m_{\text{Hg}_2(\text{NO}_3)_2}} - \frac{RT}{2F}\ln\frac{\gamma^4{}_{\text{HNO}_3}}{\gamma^3{}_{\text{Hg}_2(\text{NO}_3)_2}} \quad (1)$$

is applicable where $E^0 = E^0{}_{\text{glass}} - E^0{}_{\text{Hg.Hg}_2{}^{++}}$.

The standard potential of the glass electrode was determined from measurements of the e.m.f. of the cell Ag, AgCl, HCl(0.2 m)/glass/HCl(m), AgCl, Ag, since the activity coefficients of the standardizing hydrochloric acid solutions are known. This standard potential varied slightly with acid concentration, and in each subsequent calculation the potential corresponding to that of an acid solution of equal concentration was used.

Experimental

Electrodes and Auxiliary Apparatus.—The glass electrodes were prepared and calibrated, and the silver chloride electrodes were prepared in the manner described previously.[2] Triply distilled mercury was used for the mercury electrode. A galvanometer having a sensitivity of 5 × 10^{-4} microampere per mm. was used for the potentiometric measurements. Due to the high resistance of the glass electrode, a Leeds and Northrup thermionic amplifier was included in the circuit.

Standardization of Solutions.—Since mercurous nitrate is only slightly soluble in pure water, it was necessary to prepare those solutions having higher concentrations of mercurous ion by dissolving solid mercurous nitrate in nitric acid solutions. These stock solutions were then diluted to the desired ionic strength and kept in contact with metallic mercury.

The mercurous nitrate concentration was determined potentiometrically by titration with standard potassium chloride. The nitric acid concentration was determined potentiometrically with standard base after the mercurous ion had been removed by precipitation. Specific gravity measurements were then made in order to convert these concentrations to a molal basis. As the concentrations of these

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(1) From a thesis submitted by Francis A. Unietis in partial fulfillment of the requirements for the degree of Master of Science, University of South Carolina.

(2) O. D. Bonner, A. W. Davidson and W. J. Argersinger, Jr., THIS JOURNAL, **74**, 1047 (1952).

solutions were observed to change slowly with time, all e.m.f. measurements were made within 24 hours after the solutions were standardized.

Discussion

The Standard Potential of the Mercury, Mercurous Ion Electrode.—Substitution of e.m.f. data in equation 1 should permit calculation of activity coefficient ratios if the quantity $E^0_{\text{glass}} - E^0_{\text{Hg,Hg}_2^{++}}$ is known. The extrapolation to infinite dilution of a plot of the function $E + \frac{RT}{2F} \ln \frac{m^2_{\text{HNO}_3}}{m_{\text{Hg}_2(\text{NO}_3)_2}}$ *vs.* some function of the ionic strength (μ) might be expected to furnish this value. It was found, however, that the slope of this curve was too great to obtain an extrapolated value with any degree of certainty. Another alternative is to assume reasonable values for the activity coefficients of nitric acid and mercurous nitrate and calculate values for $E^0_{\text{glass}} - E^0_{\text{Hg,Hg}_2^{++}}$ for various values of the ionic strength. These values may be slightly in error due to errors in the assumed values for the activity coefficients. The extrapolated value at infinite dilution should, however, be correct. The activity coefficients of nitric acid which were used in the calculations were those which were obtained by Robinson and Stokes.[3] The activity coefficients of mercurous nitrate solutions are unknown. Trial extrapolations using the coefficients for uni-divalent electrolytes, which are given by Harned and Owen,[4] showed those of calcium nitrate solutions to be most satisfactory. Therefore, the activity coefficient ratio, $\gamma^4_{\text{HNO}_3}/\gamma^3_{\text{Ca(NO}_3)_2}$, was used in computing the data presented in Table I. The value of the standard potential obtained for the mercury, mercurous ion electrode is different from the National Bureau of Standards[5] accepted value of -0.7975 ± 0.0010 v. calculated by Bray and Hershey[6] from Linhart's data, and from the value of -0.7986 v. calculated by Lewis[7] from these data. Therefore, the data of Linhart[8] have been recalculated using the above activity coefficients which are believed to be more nearly correct. These calculations are presented in Table II. The average of these values, $E^0 = -0.7969$ v., is in fair agreement with the values obtained in Table I.

Table I

E.M.F. Data for the Calculation of the Standard Potential of the Mercury, Mercurous Ion Electrode

$\frac{m_{\text{H}^+}}{m_{\text{Hg}_2^{++}}}$	μ	$E + \frac{RT}{2F} \ln \frac{m^2_{\text{HNO}_3}}{m_{\text{Hg}_2(\text{NO}_3)_2}}$	$\frac{RT}{2F} \ln \frac{\gamma^4_{\text{HNO}_3}}{\gamma^3_{\text{Ca(NO}_3)_2}}$	$E^0_{\text{glass}} - E^0_{\text{Hg}}$	$-E^0_{\text{Hg}}$
0.815	0.728	0.4370	0.0178	0.4548	0.7952
.815	.364	.4417	.0133	.4550	.7955
.815	.182	.4452	.0101	.4553	.7959
.815	.0910	.4478	.0075	.4553	.7959
.815	.0455	.4496	.0058	.4554	.7960
	.0000 (extrapolated)				.7961

Table II

Recalculation of Linhart's Data

m_{HClO_4}	$m_{\text{Hg}_2(\text{ClO}_4)_2}$	$-E^0_{\text{Linhart}}$	$\frac{RT}{2F} \ln \frac{\gamma^4_{\text{HNO}_3}}{\gamma^3_{\text{Ca(NO}_3)_2}}$	$-E^0_{\text{H}}$
0.0817	0.002750	0.7896	0.0075	0.7971
.0817	.00550	.7895	.0073	.7968
.0236	.00550	.7927	.0042	.7969

Activity Coefficient Ratios.—Six stock solutions of approximately unit ionic strength and varying ratios of nitric acid to mercurous nitrate were prepared and standardized. These stock solutions were then diluted and used to obtain the data given in Table III. The variation of the activity coefficient ratio with composition at rounded values

Table III

E.M.F. Data for Cells of the Type: Glass/$\text{HNO}_3(m_1)$, $\text{Hg}_2(\text{NO}_3)_2(m_2)$, Hg and the Corresponding Activity Coefficient Ratios

$\frac{m_{\text{H}^+}}{m_{\text{Hg}_2^{++}}}$	μ	$E^0 - E$	$\frac{\gamma^4_{\text{BNO}_3}}{\gamma^3_{\text{Hg}_2(\text{NO}_3)_2}}$
9.59	1.187	0.0554	8.68
	0.594	.0380	4.47
	.2968	.0226	2.91
	.1484	.0109	2.17
	.0742	$-$ .0005	1.78
7.41	1.209	.0516	8.76
	0.605	.0342	4.50
	.3022	.0200	2.98
	.1511	.0071	2.18
	.0756	$-$ .0044	1.78
4.11	1.267	.0415	8.40
	0.634	.0243	4.39
	.3168	.0101	2.91
	.1584	$-$ .0025	2.18
	.0792	$-$ .0142	1.75
1.913	1.357	.0267	7.89
	0.679	.0101	4.36
	.3392	$-$ .0040	2.91
	.1696	$-$ .0164	2.21
	.0848	$-$ .0282	1.79
1.147	1.420	.0161	7.77
	0.710	$-$ .0003	4.36
	.3550	$-$ .0141	2.98
	.1775	$-$ .0266	2.25
	.0888	$-$ .0382	1.82
0.815	1.456	.0088	7.77
	0.728	$-$ .0077	4.29
	.364	$-$ .0215	2.96
	.1820	$-$ .0340	2.23
	.0910	$-$ .0454	1.82

Table IV

Variation of Activity Coefficient Ratio with Composition

$\frac{m_{\text{H}^+}}{m_{\text{Hg}_2^{++}}}$	$\mu = 0.1$	0.2	0.5	1.0	1.2
9.59	1.88	2.45	3.94	7.18	8.80
7.41	1.88	2.45	3.94	7.07	8.66
4.11	1.87	2.38	3.76	6.49	7.88
1.913	1.85	2.36	3.62	5.78	6.91
1.147	1.85	2.34	3.56	5.55	6.54
0.815	1.84	2.30	3.45	5.42	6.38

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(3) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 567.

(5) National Bureau of Standards Circular 500, p. 199.

(6) W. C. Bray and A. V. Hershey, This Journal, **56**, 1889 (1934).

(7) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N. Y., 1923, p. 418.

(8) G. A. Linhart, This Journal **38**, 2356 (1916).

of the ionic strength, determined from a smoothed plot of the above data, is given in Table IV.

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NOTES

Long-chain Aliphatic Semicarbazides[1]

BY J. D. CHANLEY, STELLA KALICHSTEIN AND E. M. GINDLER

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We wish to report the synthesis of a few long-chain aliphatic semicarbazides: 4-pentadecyl- (I), 4-heptadecyl- (II), 4-octadecyl- (III) and 2-methyl-4-heptadecyl semicarbazide (IV). As far as we are aware there is no mention in the literature of any long-chain semicarbazides. The semicarbazone derivatives of ketones—obtained from them—are soluble in petroleum ether. This property may prove useful in the isolation of ketones. The combined hydrophilic and hydrophobic features of these semicarbazides render them suitable for spreading in monomolecular layers and present the possibility of employing them as carbonyl reagents at interfaces. The monomolecular film properties of these compounds and their derivatives, described below, have been investigated in these laboratories and will be the subject of a separate communication.

The syntheses of compounds I, II and IV were accomplished in good yield by the addition of anhydrous hydrazine in the first two cases and anhydrous methylhydrazine in the latter instance to the appropriate isocyanate. The reaction sequence is

$$\text{R—CO—Cl} \xrightarrow{\text{NaN}_3} \text{R—CO—N}_3 \xrightarrow{\Delta}$$

$$\text{R—N=C=O} \xrightarrow{\text{R'NHNH}_2} \text{RNHCONR'NH}_2$$

$R = C_{15}H_{31}$ (I) or $C_{17}H_{35}$ (II, IV); $R' = H$ (I, II) or CH_3 (IV)

The synthesis of 4-octadecyl semicarbazide (III) was accomplished, albeit in very poor yield, by the interaction of anhydrous hydrazine on the ethyl carbamate derivative of octadecylamine. The reaction sequence is

$$\text{R—NH}_2 \xrightarrow{\text{ClCOOEt}} \text{RNHCOOEt} \xrightarrow{\text{NH}_2\text{NH}_2} \text{RNHCONHNH}_2$$

$R = C_{18}H_{37}$ (III)

The monosubstituted semicarbazide reacted readily with aldehydes and ketones to give the corresponding semicarbazone derivatives in high yield. In contrast the disubstituted semicarbazide, compound IV, although reacting readily and in high yield with benzaldehyde, is very sluggish in its reactivity toward ketones. We were able, however, to obtain the cyclohexanone derivative. This difference in behavior toward ketones has previously been described by Evans and Gillam in the instance of semicarbazide and 2-methyl semicarbazide.[2] A comparison of the ultraviolet absorption spectra in 95% ethanol of the benzaldehyde derivative of compound II, λ_{max} 285 mμ, ϵ_{max} 19,500 and of compound IV, λ_{max} 293 mμ, ϵ_{max} 20,800, shows a shift to longer wave length of 8 mμ, in the case of the 2-methyl-substituted semicarbazide. The same phenomenon has been observed by the above authors[2] for 2-methylsemicarbazone and semicarbazone derivatives of a variety of aromatic aldehydes.

Experimental

All spectra were obtained in 95% ethanol with a Beckman spectrophotometer, Model DU.

Stearoyl and palmitoyl chloride were distilled before use. Octadecylamine, m.p. 53.2°, was obtained from Armour and Company, Chicago 9, Ill. The preparation of compounds I, II and IV was essentially the same and is illustrated in the instance of 4-heptadecylsemicarbazide. The isocyanates were prepared essentially according to the method given for the preparation of undecyl isocyanate,[3] except that it was found desirable to isolate the intermediate acid azide.

4-Heptadecyl semicarbazide (II).—To a well cooled (5–15°), vigorously stirred solution of sodium azide (3.31 g., 0.051 mole) in 22 ml. of water and 16 ml. of acetone a solution of stearoyl chloride (11 g., 0.037 mole) in 11 ml. of acetone was added at such a rate that the temperature remained between 5 and 15°. The mixture was stirred for approximately 45 minutes and the heavy white precipitate of the azide was removed by filtration, washed thoroughly with water and pressed dry; yield 17 g. The azide is quite stable and may be dried in a vacuum desiccator overnight over calcium chloride. The slightly wet azide was dissolved in benzene (125 ml.), dried overnight over sodium sulfate at 15°, filtered, refluxed for one hour, cooled in ice and 7 ml. of anhydrous hydrazine was added rapidly with hand swirling. The solid reaction product was removed by filtration, washed with benzene and water and dried overnight *in vacuo* over calcium chloride; yield 9.0 g., m.p. 90–95°. Three recrystallizations from ethanol or methanol gave 5 g. of pure material; m.p. 100–100.5°.

Anal. Calcd. for $C_{18}H_{39}N_3O$: C, 68.95; H, 12.54; N, 13.40. Found: C, 69.03; H, 12.12; N, 13.70.

4-Pentadecylsemicarbazide (I) prepared as above from palmitoyl chloride, etc., after recrystallization from methanol or ethanol, melted at 100–101°.

Anal. Calcd. for $C_{16}H_{35}N_3O$: C, 67.32; H, 12.36; N, 14.72. Found: C, 67.30; H, 12.06; N, 15.02.

2-Methyl-4-heptadecylsemicarbazide (IV) was prepared essentially according to the method given above with the following modifications. To the benzene solution of heptadecyl isocyanate, anhydrous methylhydrazine was added. Since the semicarbazide is soluble in benzene, dry HCl was passed into the benzene solution and the precipitated mixture of semicarbazide hydrochloride and methylhydrazine hydrochloride was collected, dissolved in ethanol and decomposed with an excess of dilute aqueous sodium hydroxide

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(1) This work was supported by a Grant-in-Aid from the Permanent Science Fund of the American Academy of Arts and Sciences to Dr. Harry Sobotka.

(2) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

(3) *Org. Syntheses*, **24**, 94 (1944).