[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Viscosity of the Sodium–Potassium System

BY CURTIS T. EWING, JOSEPH A. GRAND AND R. R. MILLER

A closed viscometer technique was developed and applied to reactive metals with unusually high surface tension ranges. Viscosities were measured for sodium, potassium and several alloys from 60° (or the m.p.) to 200°. The values for the alloys were observed to vary uniformly between those for the metals, and a mixture equation was applied to satisfy the data. It was also shown that the temperature variation of the viscosity values could be adequately expressed by the equation set forth by Andrade.

The properties of liquid metals are becoming increasingly important for basic theoretical studies because of the simplicity and ideality of their atomic structure.

Viscosity coefficients have been reported in the literature for sodium and potassium by Chiong[1] and Sauerwald.[2] The values presented in this article for sodium show excellent agreement with those reported by Chiong. On the contrary, the values for potassium, though coinciding with those by Chiong at 70°, diverge as the temperature is increased and differ by as much as 10% at 200°. The viscosities measured by Sauerwald near the melting point were apparently intended only as rough approximations, and are several per cent. higher than corresponding values in this article.

Kremann, Pestemer and Schreiner[3] measured viscosities for several sodium–potassium alloys—the data, admittedly, having no absolute significance. Moreover, even the relative values when plotted against composition show a definite minimum at 25 weight per cent. potassium and a sharp maximum at 77 weight per cent., which is completely out of accord with the data here presented.

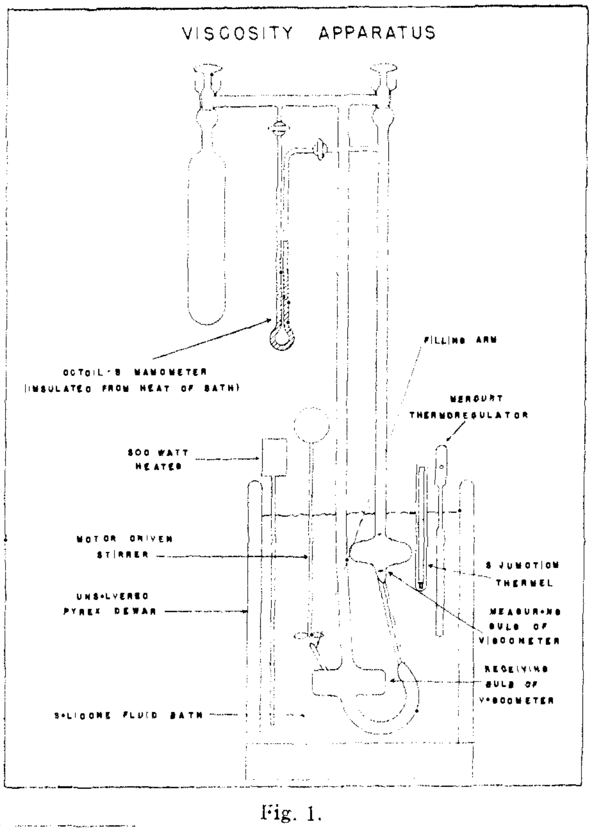

Fig. 1.

Experimental

Apparatus and Materials.—The modified Ostwald viscometer, the attached glass system, and the temperature-bath are schematically presented in Fig. 1. The glass viscometer unit was portable, designed for operation as a closed system, and for direct distillation of the metal sample into the receiving bulb. Octoil-S was used as the manometer fluid, to allow evacuation of the manometer arms. Readings were made with a cathetometer, with the manometer immersed in an insulated liquid-bath.

The portability of the viscometer facilitated the operations involved in cleaning and introducing the metals. When distilling the metal sample, the filling arm of the viscometer was sealed directly to the arm of the still below a sintered glass filter, such that the receiving bulb of the viscometer served as the receiver of the still. Preceding the distillation of each sample, the viscometer unit and the still were maintained at 250° under high vacuum for approximately 30 minutes. Each distillation was performed in a nickel still, and no distillation was made unless the initial pressure was less than 0.1 micron. After the desired volume of metal had been distilled into the bulb and the filling arm sealed off under a slight positive pressure of purified nitrogen, the viscometer unit was ready for removal to the temperature-bath and subsequent viscosity determinations.

Movement of the liquid into the measuring bulb was accomplished by manipulating the two vacuum seal stopcocks while alternately cooling and heating the expansion bulb. Then to observe the time of transpiration between the two marks, it was necessary simply to equalize the pressure of gas in the two limbs of the viscometer.

Temperature was noted with a five-junction iron constantan thermel. This thermel was calibrated against standard temperature reference points, a platinum resistance thermometer, and standard platinum–platinum rhodium couples (NBS). The calibration is accurate to ± 0.1 to 150° and ± 0.2 to 200°. The silicone bath would control the temperature to ± 0.03 at 50° and ± 0.2 at 200°.

Effective Head and Surface Tension.—The liquid metals differed greatly from the calibration fluid as to contact

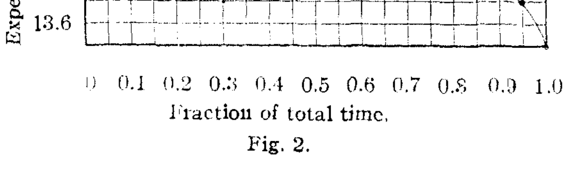

Fig. 2.

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[1] Y. S. Chiong, *Proc. Roy. Soc.* (*London*), **A157**, 264 (1936).

[2] F. Sauerwald, *Metallkunde*, **26**, 259 (1934).

[3] R. Kremann, Max Pestemer and H. Schreiner, *Rec. trav. chim.*, **51**, 557 (1932).

angles and surface tension ranges. Thus, surface tension effects assumed important proportions, necessitating an experimental determination of mean effective head. A value for the liquid head at any position of the menisci between the two extremes could be accurately determined by noting the actual balanced hydrostatic head as registered by the attached manometer. To obtain the mean effective head, hydrostatic heads were noted for successive positions of the menisci between the upper and lower extremes, together with the time required for each position to be reached as the liquid moved down under its own head. Then from a plot of the experimental heads at successive positions of the falling menisci against the fraction of the total time required to reach each position during the run, the mean hydrostatic head was determined by graphical integration. A typical head determination is shown graphically in Fig. 2. It is noted that the shape of the curve at the two extremes is not critical and does not appreciably influence the integrated value. Mean head values were reproducible to better than 0.2%.

Under certain conditions, even the experimental method for head determinations can be subject to appreciable error if there is any change in the curvature of the menisci as the moving column comes to a stationary equilibrium. This was demonstrated with preliminary experiments in an attempt to measure hydrostatic heads using a Fenske viscometer. With the small measuring bulb (3-ml. volume) and receiving bulb (3-cm. diameter), the head values as observed with the attached manometer were continually fluctuating. This was attributed to change in curvature of the menisci as equilibrium was reached, resulting in an increase in head, allowing the liquid to move down and repeat the cycle. The solution of the difficulties experienced in efforts with this viscometer lay in the use of the modified Ostwald viscometer with a larger measuring bulb (30 ml. with a mean diameter of 5 cm.) and a receiving bulb with an average diameter of 6 cm. With these large diameters, error from either capillary or drainage effects was not appreciable.

Calibration and Kinetic Energy.—For relative measurement by a calibration of the viscometer with a fluid of known viscosity, the Poiseuille equation for streamline flow, which includes the correction for kinetic energy, reduces to: $\eta = APt - Bd/t$, in which η is the absolute viscosity, P is the mean effective pressure, d is the density, t is the time, and A and B are constants for the viscometer. The constants were determined with water by a method similar to that previously described.[4] Viscosity coefficients were obtained from NBS,[5] and densities from the "Int. Critical Tables." A calculation of Reynold's numbers indicated that all flow rates were well below the turbulent region.

Data for the water calibration are presented in Table I. The values of A and B were determined to be 3.763×10^{-10} and 1.503×10^{-1}, respectively, by the method of least squares. The last column in the table gives the water viscosity as calculated from these empirical constants. The maximum deviation of any value, so calculated, from the corresponding NBS value was only 0.12%. A recheck of the calibration after the alkali metal investigation showed that there had been no change in the viscometer during the measurements.

TABLE I

WATER CALIBRATION DATA

Temp., °C.	Density, g./ml.	Viscosity, centipoises NBS	Viscosity, centipoises Calcd.
38.65	0.9928	0.6699	0.6699
		.6699	.6699
38.75	.9927	.6686	.6694
48.2	.9889	.5640	.5638
		.5640	.5639
58.4	.9840	.4784	.4781
		.4784	.4784
69.6	.9780	.4066	.4069
		.4066	.4069

Results and Discussion

Experimental results for sodium, potassium and three alloys are recorded in Tables II–VI. In all data tables, the number of significant places is consistent with relative accuracy. Density values used for the metals were obtained from data of this Laboratory and the Mine Safety Appliances Company, Pittsburgh, Pa.[6] The accuracy of the densities in this range is better than ±0.2%. Each composition figure represents analysis of the metal

TABLE II

VISCOSITY OF SODIUM

Temp., °C.	Density, g./ml.	Viscosity, centipoises Exptl.	Viscosity, centipoises Calcd.	Diff., %
103.7	0.9252	0.6863	0.6806	−0.8
		.6858	.6806	−0.8
121.6	.9218	.6232	.6206	−0.4
		.6180	.6206	+0.4
		.6178	.6206	+0.5
147.0	.9160	.5477	.5504	+0.5
		.5477	.5504	+0.5
167.6	.9110	.5038	.5047	+0.2
		.5035	.5047	+0.2
192.7	.9052	.4603	.4585	−0.4

TABLE III

VISCOSITY OF SODIUM–POTASSIUM ALLOY (31.7 WEIGHT PER CENT. POTASSIUM)

Temp., °C.	Density, g./ml.	Viscosity, centipoises Exptl.	Viscosity, centipoises Calcd.	Diff., %
58.4	0.9094	0.7880	0.7648	−2.9
		.7881	.7648	−3.0
		.7884	.7648	−3.0
69.5	.9065	.7246	.7097	−2.1
		.7244	.7097	−2.0
103.8	.8979	.5816	.5807	−0.2
		.5811	.5807	−0.1
		.5815	.5807	−0.1
121.5	.8935	.5301	.5305	+0.1
		.5300	.5305	+0.1
147.1	.8871	.4696	.4718	+0.5
		.4710	.4718	+0.2
167.5	.8822	.4342	.4339	−0.1
		.4344	.4339	−0.1
193.0	.8758	.3956	.3947	−0.2

TABLE IV

VISCOSITY OF SODIUM-POTASSIUM ALLOY (49.0 WEIGHT PER CENT. POTASSIUM)

Temp., °C.	Density, g./ml.	Viscosity, centipoises Exptl.	Viscosity, centipoises Calcd.	Diff., %
58.3	0.8922	0.7228	0.6920	−4.3
		.7226	.6920	−4.2
65.2	.8905	.6843	.6622	−3.2
69.7	.8895	.6619	.6437	−2.7
		.6617	.6437	−2.7
103.9	.8810	.5324	.5308	−0.3
		.5325	.5308	−0.3
121.7	.8765	.4853	.4864	+0.2
		.4853	.4864	+0.2
147.2	.8702	.4336	.4346	+0.2
		.4339	.4346	+0.2
167.4	.8652	.4007	.4012	+0.1
		.4009	.4012	+0.1
192.9	.8590	.3679	.3662	−0.5

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(4) Guy Barr, "Viscometry," Oxford University Press, London, 1931.

(5) James F. Swindells, *J. Colloid Sci.*, **2**, 177–184 (1947).

(6) Naval Research Laboratory Report, No. C-3287 (1948).

TABLE V

VISCOSITY OF SODIUM–POTASSIUM ALLOY (78.6 WEIGHT PER CENT. POTASSIUM)

Temp., °C.	Density, g./ml.	Viscosity, centipoises Exptl.	Viscosity, centipoises Calcd.	Diff., %
58.3	0.8573	0.6193	0.5976	−3.5
		.6176	.5976	−3.2
69.6	.8545	.5637	.5580	−1.0
		.5641	.5580	−1.1
103.7	.8460	.4652	.4650	0.0
		.4652	.4650	0.0
120.8	.8420	.4304	.4295	−0.2
121.4	.8417	.4275	.4283	+0.2
147.0	.8355	.3841	.3848	+0.2
		.3840	.3848	+0.2
167.4	.8307	.3564	.3566	+0.1
		.3568	.3566	−0.1
192.7	.8245	.3275	.3273	−0.1
		.3275	.3273	−0.1

TABLE VI

VISCOSITY OF POTASSIUM

Temp., °C.	Density, g./ml.	Viscosity, centipoises Exptl.	Viscosity, centipoises Calcd.	Diff., %
69.6	0.8267	0.5158	0.5133	−0.5
		.5140	.5133	−0.1
		.5126	.5133	+0.1
103.7	.8187	.4304	.4281	−0.5
		.4259	.4281	+0.5
121.5	.8150	.3925	.3947	+0.6
		.3943	.3947	+0.1
147.0	.8087	.3538	.3547	+0.2
		.3520	.3547	+0.8
167.4	.8040	.3292	.3288	−0.1
		.3297	.3288	−0.3
192.7	.7984	.3033	.3020	−0.4
		.3030	.3020	−0.3

TABLE VII

EMPIRICAL CONSTANTS FOR ANDRADE FORMULAS

Compn., wt. % potassium	Constants, NRL data		Constants Chiong data	
	C	$A \times 10^{+3}$	C	$A \times 10^{+3}$
0.0	756.9	1.089	716.5	1.183
31.7	751.1	1.006		
49.0	735.5	0.9934		
78.6	721.8	.9727		
100.0	742.8	.9114	600.0	1.293

as removed from the viscometer at the conclusion of the measurements. Within the limits of the experimental method of analysis, the pure metals analyzed to 100.0% purity. Assuming that the absolute accuracy of the NBS viscosities for water is 0.2%, the over-all accuracy of the viscosity results will be stated as ±0.8%.

The temperature variation of viscosity for each of the five metal samples can be effectively expressed by the equation of Andrade[7]: $\eta v^{1/3} = Ae^{C/vT}$ in which η is the viscosity, v is the specific volume, T is the absolute temperature and A and C are constants for a given liquid. By the method of least squares the constants for this equation were determined for each metal and alloy. A summary of these constants and a comparison with similar values for the pure metals by Chiong[1] are presented in Table VII. As might be expected, the two metals being similar in structure, the constants are of the same magnitude. In order to show the conformity of the experimental values to the viscosity–temperature relationship, viscosities calculated from these constants and the Andrade equation are presented in Tables II to VI, along with the per cent. deviations from the corresponding experimental values. It is noted that the calculated values for all three alloys below 100° are definitely too low. This may be due to association or compound formation. In any event, the experimental values below 100° for the alloys were not used in deriving the constants for the equation. Chiong,[1] in fitting the equation to his experimental data for the metals, found a maximum deviation of 0.59% for potassium and 0.72% for sodium. Eliminating the values for the alloys below 100°, it follows that our data for sodium, potassium and the alloys fit an equation of this type equally well.

Data in the literature still leave the question of the true-ideal-mixture equation quite undecided. The mixture equation found to satisfy the variation of viscosity with composition was $\phi = x_{Na}\phi^0_{Na} + x_K\phi^0_K$ in which ϕ is the fluidity and x is the weight fraction. The applicability of this mixture equation to the experimental data for the pure metals is illustrated in Table VIII. An average experimental value was used for each temperature. The table shows the values derived by the mixture equation and, further, their per cent. deviation from the corresponding experimental values. The mean deviation is 0.4% with only one value deviating by as much as 1%.

TABLE VIII

VISCOSITY BY MIXTURE EQUATION

Viscosity in centipoises for compositions in weight per cent. potassium

Temp., °C.	103.7 ± 0.2	121.5 ± 0.2	147.0 ± 0.2	167.4 ± 0.2	192.8 ± 0.2
Sodium by exp.	0.6861	0.6197	0.5477	0.5037	0.4603
31.7% by exp.	.5814	.5301	.4703	.4343	.3956
by mixt. eq.	.5761	.5241	.4661	.4314	.3954
% diff.	−0.9	−1.1	−0.9	−0.7	−0.1
49.0% by exp.	.5325	.4853	.4338	.4008	.3679
by mixt. eq.	.5298	.4834	.4311	.4001	.3671
% diff.	−0.5	−0.4	−0.6	−0.2	−0.2
78.6% by exp.	.4652	.4275	.3841	.3566	.3275
by mixt. eq.	.4657	.4268	.3820	.3558	.3271
% diff.	+0.1	−0.2	−0.5	−0.2	−0.1
Potassium by exp.	.4282	.3934	.3529	.3295	.3032

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[7] E. N. daC. Andrade, *Phil. Mag.*, **17**, 698 (1934).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Hydrolysis and Polymerization of Zirconium in Perchloric Acid Solution[1]

BY ROBERT E. CONNICK AND WILLIAM H. REAS[2]

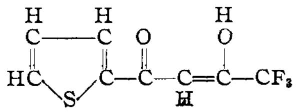
Because of its high charge and small radius, the ion Zr^{+4} exhibits a marked tendency to hydrolyze in aqueous solution. Normal compounds of zirconium, such as $ZrCl_4$, when dissolved in water, liberate hydrogen ion and even the zirconyl salts, *e.g.*, $ZrOCl_2 \cdot 8H_2O$, which are already half hydrolyzed, produce acidic solutions.

Recently it has been shown[3] that in 2 *M* perchloric acid at 25° the average zirconium species at low zirconium concentrations has a charge somewhere between +3 and +4 and is not polymerized. This corresponds to a mixture of Zr^{+4} and $ZrOH^{+3}$, or possibly ZrO^{++}. At high zirconium concentrations there is abundant evidence that zirconium is polymerized and considerably more hydrolyzed in the polymers than when present as the monomer. Thus Jander and Jahr[4] found the diffusion coefficient of 0.1 *M* zirconium(IV) to be only half as great as that of uranyl nitrate at acidities ranging from 1.2 *M* perchloric acid to no added acid. Measurements[5,6] of the *p*H of aqueous solutions of zirconyl chloride indicate there are approximately three hydroxide ions per zirconium in the polymers. Freezing point studies[6] also indicate extensive polymerization and hydrolysis. In the above cited work the evidence for polymer formation was only qualitative or, if quantitative, could not be uniquely interpreted because of the variation of two or more conditions simultaneously.

The present research was undertaken to identify, if possible, the polymeric zirconium species which are formed at high zirconium concentrations in solutions of moderate acidity.

Experimental

Method.—The experimental method, which is similar to that used by Connick and McVey,[3] involves the measurement of the distribution of zirconium between an aqueous phase and a benzene phase containing a chelating agent, thenoyltrifluoroacetone (hereafter referred to as TTA). The formula of the enol form is



(1)

It forms a neutral chelate molecule with zirconium(IV), which is very soluble in benzene, but, under the extraction conditions, the TTA does not complex an appreciable fraction of the zirconium in the aqueous phase.[3] Assuming the zirconium species in the aqueous phase to be unhydrolyzed and unpolymerized, the extraction reaction is

$$Zr^{+4}_{(aq)} + 4HK_{(b)} = ZrK_{4(b)} + 4H^{+}_{(aq)} \qquad (2)$$

where HK is used to designate TTA. Any polymer formation by the zirconium in the aqueous phase is reflected quantitatively as a decrease in the extraction of zirconium into the benzene phase.

For more details as to the general method and of the properties of TTA and ZrK_4, see reference 3.

Procedure.—The distribution of zirconium between the benzene and water phases was measured in two series of experiments—one at 2 *M* perchloric acid and the other at 1 *M* perchloric acid and 1 *M* lithium perchlorate, the latter being added to maintain an ionic strength of 2. The zirconium concentration was varied over a 3000-fold range in each series.

Equal volumes of a benzene phase, containing a known concentration of TTA and radioactive zirconium tracer, and an aqueous phase, containing perchloric acid (and lithium perchlorate in the low acid series) and zirconium perchlorate, were shaken vigorously in a water thermostat at 25°. In every case two or more analyses were made at sufficiently long time intervals to demonstrate that equilibrium had been attained.

The zirconium concentration in each phase was determined by mounting known aliquots on glass cover slides, evaporating to dryness and counting, using a mica window Geiger tube.

It was necessary to know the TTA concentration in the benzene phase. This could not be obtained readily from the original concentration by difference because it was found, through spectrophotometric measurements, that a small, but unknown, fraction of the zirconium in the aqueous phase was being complexed by TTA in the experiments at high zirconium concentration. Although the fraction of zirconium complexed was quite small, the concentration of TTA in the benzene phase was appreciably altered because of the relatively high zirconium concentration.

The TTA in the benzene phase was determined spectrophotometrically after diluting the sample with benzene. Correction for the absorption of the zirconium chelate was necessary. Zebroski[7] has measured its spectrum. On repeating his measurements it was found that the molar extinction coefficient appeared to vary with time, probably because of hydrolysis of the chelate in these diluted samples. At 3300 Å. however the absorption remained constant. At this wave length the molar extinction coefficient of ZrK_4 is almost exactly four times that of TTA so that hydrolysis produces no change in the absorption.

From the absorption at 3300 Å. the sum of the TTA and four times the zirconium chelate concentrations was obtained. Subtraction of the zirconium chelate concentration, calculated from the measured extraction coefficient, yielded the TTA concentration.

In theory, it is possible with aid of the Beer law to calcu-

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[1] This research was carried out under the auspices of the United States Atomic Energy Commission.

[2] General Electric Co., Hanford Works, Richland, Washington.

[3] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

[4] G. Jander and K. F. Jahr, *Kolloid-Beihefte*, **43**, 295 (1935).

[5] A. W. Laubengayer and R. B. Eaton, THIS JOURNAL, **62**, 2704 (1940).

[6] M. Adolf and W. Pauli, *Kolloid-Z.*, **29**, 173 (1921).

[7] E. L. Zebroski. University of California Radiation Laboratory classified thesis, BC-63, 1947.