rotational isomers (*1*), even if they were made for the liquid state, suggests that the presented thermodynamic function values (Table I) may well be within the bounds of experimental accuracy.

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Densities of Molten Zinc Chloride and Its Mixtures with Cesium Chloride

W. EWEN SMITH and G. PEDRO SMITH
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830

Liquid state densities of $ZnCl_2$–CsCl mixtures are reported as functions of temperature. The excess molar volume is positive and large near 40 mole % $ZnCl_2$ and negative and small near pure $ZnCl_2$. Measurements on pure $ZnCl_2$ and 97 mole % $ZnCl_2$ were made by both the buoyancy and float methods. Measurements at other compositions were made by the buoyancy method alone.

MOLTEN mixtures of zinc chloride with alkali metal chlorides have unusual structural properties (*1, 2*) that make them of special interest as solvents for chemical reactions (*3–5*). To investigate such reactions by absorption spectrophotometry, it is necessary to have density data so that light absorption may be converted to molar absorptivity units. For this reason, the authors have measured the densities of $ZnCl_2$–CsCl mixtures as functions of temperature.

EXPERIMENTAL

Cesium chloride (99.9%) was recrystallized from water, solvent extracted to remove organic contaminants, and vacuum dried. It was finally purified by passing high-purity HCl followed by high-purity nitrogen through the melt. Zinc chloride was prepared from a very good grade of zinc metal and high-purity HCl and then distilled. These preparations were carried out in all-silica systems that were baked out and isolated from the atmosphere. Weighings and cell loadings were performed in a vacuum-type dry box under a nitrogen atmosphere with a measured water-vapor content of less than 2 p.p.m.

Most of the density measurements were made under dry nitrogen by the buoyancy method with an apparatus described previously (*6*). However, because of the hygroscopicity and volatility of zinc chloride, measurements on this material and the 97 mole % mixture were also made in sealed silica cells by the float method described by Boston (*7*). Results obtained by these two techniques were in agreement to within 0.1% for pure zinc chloride and 0.7% for the 97 mole % mixture.

RESULTS AND DISCUSSION

Results of the density measurements are summarized in Table I where the density, ρ, is given by the usual expression, $\rho = \alpha - \beta t$, and the temperature t is in °C. The present results for pure zinc chloride agree well with those of Wachter and Hildebrand (*8*), somewhat less well with those of Mackenzie and Murphy (*9*), and differ by about 1.5% from those of Duke and Fleming (*10*).

Molar volumes were calculated at several temperatures and the results are plotted in Figure 1. Values for CsCl,

Table I. Density Equations for $ZnCl_2$–CsCl Mixtures

Composition Mole %, $ZnCl_2$	$\rho = \alpha - \beta t$		Std. Dev. $\times 10^3$, Grams/Cc.	Exptl. Temp. Range, °C.
	α, grams/cc.	$\beta \times 10^3$, grams/cc. °C.		
10.0	3.378	1.001	1.1	616–795
25.0	3.190	0.880	1.6	616–792
40.0	3.137	0.957	3.3	598–743
58.0	3.031	0.882	1.9	310–603
66.6	2.991	0.851	1.0	311–602
80.0	2.870	0.718	6.6	400–603
95.0	2.765	0.611	7.8	310–602
96.0	2.724	0.534	0.6	362–488
97.0	2.738	0.571	2.5	362–500
98.0	2.750	0.620	. . .	400–500
99.0	2.684	0.515	0.1	358–496
100.0	2.683	0.511	1.8	357–595

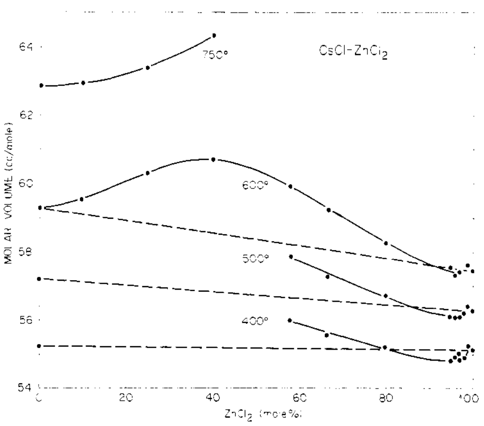

Figure 1. Molar volumes of molten CsCl–ZnCl$_2$ mixtures as functions of composition

Each curve is labeled with the temperature in ° C.

taken from the literature (*11*), were extrapolated below the melting point where necessary. The excess molar volume is large and positive near 40 mole % ZnCl$_2$ and small and negative near pure ZnCl$_2$. The general shape of the molar volume curve is similar to that for KCl-ZnCl$_2$ (*10*) and KCl-MgCl$_2$ mixtures (*12*).

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Temperature Dependence of Conductances and Viscosities for Some Moderately Concentrated Nonaqueous Electrolytic Solutions

PAUL G. SEARS and LYLE R. DAWSON
Department of Chemistry, University of Kentucky, Lexington, Ky. 40506

Conductance, viscosity, and density data at 10° intervals between −50° and 20° C. are reported for 28 nonaqueous electrolytic solutions ranging in concentration from 0.05 to 4.7 molal. Results are summarized also for the fitting of these data as a function of temperature to appropriate polynomial equations by digital computer methods. Conductance-viscosity products and activation energies of conductance and viscous flow are discussed.

THREE articles originating from this laboratory in 1955 described qualitatively and graphically the conductimetric and viscometric behavior of moderately concentrated solutions for three nonaqueous systems over the temperature range of −50° to 20° C. (*1, 9, 10*). These earlier investigations have yielded corresponding conductance and viscosity data at 10° intervals for eight to 10 solutions each of potassium thiocyanate in methanol, lithium perchlorate in a 50 to 50 weight % mixture of methanol and acetone, and lithium bromide also in the latter medium. Digital computer methods recently have been used to evaluate quantitatively these extensive experimental data in view of more appropriate conductance-temperature and viscosity-temperature relationships. Hence, the objectives of this article are to provide the original publication of the experimental data and to summarize the results of the recent quantitative calculations associated with them.

EXPERIMENTAL

The experimental equipment and procedures have been described thoroughly in the related previous articles (*1, 9, 10*). An IBM-360 digital computer has been used for the fitting of data by the method of least squares to various polynomial equations. The experimental conductance, viscosity, and density data are compiled in Table I. Densities were used in the calculation of absolute viscosities and in converting concentrations from a weight to volume basis.

RESULTS AND DISCUSSION

For nonassociated liquids and very dilute solutions of electrolytes in such media, viscous flow and conductance as rate processes can be related to the following equations (*3*):