Electrical Conductance and Density in Certain Fused Tungstate Systems

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The densities and electrical conductances of the three molten salt systems, Li_2WO_4–Na_2WO_4, Li_2WO_4–K_2WO_4, and $PbWO_4$–$Bi_2(WO_4)_3$, have been determined over a temperature range of approximately 200° above the melting points of the various compositions. Strong similarities are observed between the conductance-composition diagrams at corresponding temperatures and the phase diagrams for the Li_2WO_4–Na_2WO_4 and $PbWO_4$–$Bi_2(WO_4)_3$ systems. The similarity is less pronounced for the third system.

During the past two decades, an increasingly large amount of research has been concerned with the precise measurement of physical properties of fused salt systems. The data from such research are of importance not only to those researchers whose primary interest involves theoretical structural studies of fused salts, but also to those individuals who use the data in an effort to find interrelationships between physical properties of molten systems. A long-range goal of the senior author is that of finding fused salt systems in which for each system the property-composition diagram at corresponding temperatures is similar to the phase diagram for the system. Ultimately, it is hoped that the data for either type of diagram may be used in predicting data of reasonable reliability for the other type diagram. The present report is concerned with the properties of density and electrical conductance for the molten tungstate systems, Li_2WO_4–Na_2WO_4, Li_2WO_4–K_2WO_4, and $PbWO_4$–$Bi_2(WO_4)_3$. Density and electrical conductance data for molten mixtures of these salts have not been reported. However, data for pure Li_2WO_4, Na_2WO_4, and K_2WO_4 have been reported previously by Jaeger (*5–8*) and by Morris and Robinson (*12*). No density and electrical conductance data for pure $PbWO_4$ and $Bi_2(WO_4)_3$ appear in the literature.

EXPERIMENTAL

Materials. The anhydrous salts for the measurements were obtained from the A. D. Mackay Chemical Co., New York, N. Y. The purity of $Bi_2(WO_4)_3$ was 99.0%. The other salts ranged in purity from 99.5–99.8%. Each salt was dried in an atmosphere of argon gas for 6 hr at 225° C and then stored in a desiccator until ready for use. To establish purity of the salts, independent analyses for the cation and the anion of each salt were performed by two companies, Schwarzkopf Chemical Laboratory of New York and Du-Good Chemical Laboratory of St. Louis.

Apparatus. The procedure used for density measurements was that described by Janz and Lorenz (*9*) and adapted to this research by Brown and Morris (*2*). For the electrical conductance studies, the basic equipment was essentially the same as outlined by Morris and Robinson (*13*) and improved by Morris and Brown (*2*). Dip-type conductance cells of clear fused quartz, similar to those described by Van Artsdalen (*17*), were used for the resistance measurements. Cell constants, ranging from 200 to 525 cm^{-1}, were determined before and after each use because of the corrosive nature of the alkali tungstate salts and their mixtures. Although the cells were attacked only slightly by molten mixtures of $PbWO_4$–$Bi_2(WO_4)_3$, the difficulties involved in cleaning those cells made it necessary to use a new cell for each mixture studied. Other experimental techniques were the same as employed by the authors for the molybdate systems (*2*).

RESULTS AND DISCUSSION

Systems, Li_2WO_4–Na_2WO_4, Li_2WO_4–K_2WO_4, and $PbWO_4$–$Bi_2(WO_4)$. Density and specific conductance data for these systems as functions of temperature are represented, respectively, by equations available as easily read supplementary material (Tables I and II) from the American Chemical Society Microfilm Depository Service (*1a*). Over the temperature ranges studied, density varies inversely, as expected, and linearly with temperature. Specific conductances for all of the pure tungstate salts studied and for the $PbWO_4$–$Bi_2(WO_4)_3$ mixtures are best represented by the linear equation, $k = a + bt$. The slopes for the different compositions in the Pb–Bi tungstate system differ only slightly. This is due primarily to the fact that the temperature coefficients of the specific conductances of the pure components are fairly close to each other. Specific conductance data for the other systems have been fitted to quadratic equations. Density data for Na_2WO_4 and K_2WO_4 agree within 0.1 to 0.3% with those reported by Jaeger (*6*). The density data for Li_2WO_4 are about 1% lower than the values reported earlier by Morris and Robinson (*12*). Specific conductance data for the alkali tungstates are essentially in agreement with those reported in the literature (*5, 7, 8*).

The relation, $\Lambda = k\bar{E}/(\text{density})$ has been used to calculate the equivalent conductance, Λ, for the mixtures. The mean equivalent weight of a mixture, $\bar{E}_{mix}$ is defined as $\bar{E}_{mix} = f_1E_1 + f_2E_2$, where f_1 and f_2 are the equivalent fractions of components 1 and 2 and E_1 and E_2 are their equivalent weights. For the general mixture consisting of y mole fraction of $PbWO_4$ and $1 - y$ mole fraction of $Bi_2(WO_4)_3$, respectively,

$$\bar{E}_{mix} = \frac{yE_1}{y + 3(1 - y)} + \frac{3(1 - y)E_2}{y + 3(1 - y)}$$

The idea of a "corresponding temperature" of 100° above the melting point for each composition has been used previously for the comparison of electrical conductance in molten materials (*11, 13*). Van Artsdalen and his associate (*18*) used the same fraction of the melting point ($\theta = T^\circ K/T^\circ_m K$, $T > T_m$) as "corresponding temperature" in their studies. Morris and Robinson (*13*) observed that both systems of corresponding states were satisfactory for alkali molybdate melts.

Figure 1 shows plots of both specific conductance and equivalent conductance as functions of composition for the Li_2WO_4–Na_2WO_4 system. It is interesting to observe that the conductance-composition curves bear a strong resem-

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blance to the phase diagram (Curve I) of Hoermann (*4*) for this system. The same similarity is observed between the conductance-composition curves and the phase diagram for the Pb-Bi tungstate system (Figure 3). Morris and his associates (*2, 11, 13*) have observed these similarities in five other systems. Molar conductance-composition isotherms presented by Riebling and Erickson (*15*) for the molten salt system, gallium monoiodide-gallium triiodide, show a maximum at the diiodide composition. Boston et al. (*1*) studied conductance for the molten system, aluminium chloride-potassium chloride, and presented conductance-composition isotherms showing a maximum at 50 mol % KCl. The maximum corresponds to the congruently melting 1 to 1 compound, $KAlCl_4$, indicated by the phase diagram. Delimarskii and Markov (*3*) studied isothermal plots of conductance vs. composition for several systems and concluded that some correlation appeared to exist between the conductance-composition plot and the phase diagram for a given system. The shape of the conductance-composition diagram for any system actually depends on the nature of the ionic species in the melt. Because of this factor, the phase diagram cannot be used to predict the behavior of every molten salt mixture since factors such as spatial conditions present in the solid may not necessarily apply to the liquid.

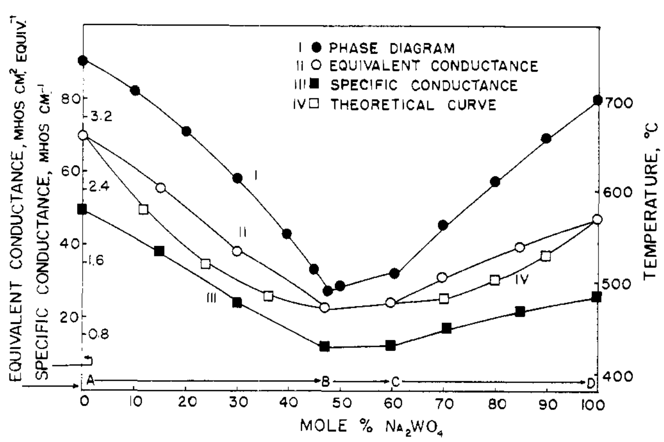

Figure 1. Specific conductance, equivalent conductance, and temperature as functions of composition for the molten system, Li_2WO_4–Na_2WO_4

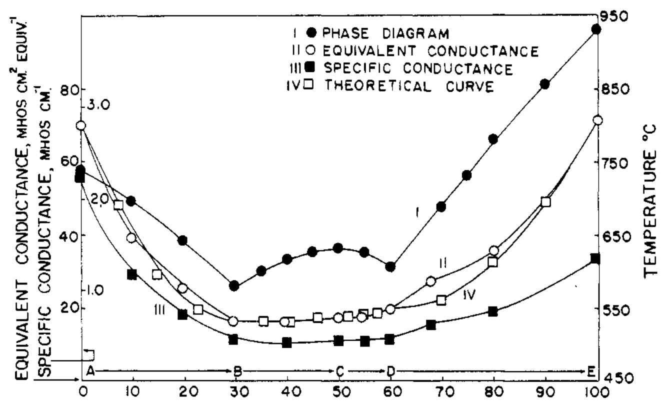

Figure 2. Specific conductance, equivalent conductance, and temperature as functions of composition for the molten system, Li_2WO_4–K_2WO_4

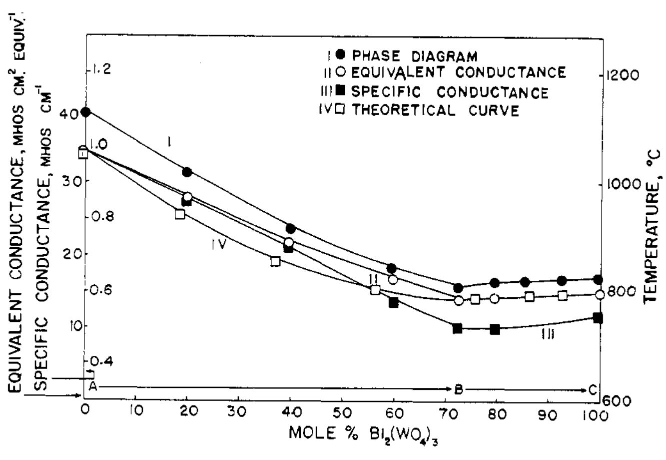

Figure 3. Specific conductance, equivalent conductance, and temperature as functions of composition for the molten system, $PbWO_4$–$Bi_2(WO_4)_3$

X-ray diffraction studies have shown that the average interionic distance between the structure units and their average arrangement in ionic liquids is similar to that in the solid. A treatment of melting and crystal structure of ionic melts is given throughout the text by Ubbelohde (*16*). Experimental observations based on thermodynamic parameters have supported the Ubbelohde viewpoint that a quasicrystalline arrangement exists in ionic melts. The structure of melts in the Li-Na tungstate system is envisioned as a highly disordered quasicrystalline arrangement in which the entities are ions, ion pairs, holes, and molecules.

A qualitative model which can account for the variation of conductance with composition for the Li-Na tungstate system is one in which the current-carrying species, in order of decreasing conductance, are $Li^+ > Na^+ > LiWO_4^- > NaWO_4^-$. This kind of approach, in which one postulates the presence of certain current-carrying ionic species and an order of the ionic conductances in the melts, can be used satisfactorily in a qualitative interpretation of the variation of conductance with composition for all three systems.

The quasitheoretical equation, $\Lambda_{mix} = X_1^2\Lambda_1 + X_2^2\Lambda_2 + 2X_1X_2\Lambda_1$ (where $\Lambda_1 < \Lambda_2$ and Λ_{mix} is the equivalent conductance of the mixture, X_1 and X_2 are the mole fractions of components 1 and 2 whose equivalent conductances are, respectively, Λ_1 and Λ_2) has been derived by Markov and Shumina (*10*) for the concentration dependence of the conductance of *simplest melts*. This equation has been applied to the Li-Na tungstate system in order to examine the deviations of the conductance in this system from theoretical values. Values for Λ_{mix} along the composition axis *AB*, where *A* refers to 100 mol % Li_2WO_4 and *B* refers to 100 mol % eutectic mixture, have been calculated (Figure 1, Curve IV) for this system. Positive deviations up to 32% are observed for the experimental curve. The Λ_{mix} values calculated along *CD* show positive deviations up to 21% existing in this composition region. Such large deviation ranges may be ascribed to the expansion of the quasicrystalline lattice which thereby permits increased mobility for the conducting species. Some support for this viewpoint is contained in the report by Riebling (*14*) in which a gradual change from tetrahedral to octahedral configuration occurs for GeO_2 with the addition of alkali metal oxides. The idea of expansion of the quasicrystalline lattice can be employed for the Li-K tungstate system of Figure 2 and the Pb-Bi tungstate system of Figure 3.

Finally, the conductance-composition diagrams for the two alkali tungstate systems resemble the corresponding phase diagrams as determined by Hoermann (*4*) while the composition-conductance plot for the Pb-Bi tungstate resembles its phase diagram as obtained by Zambonini (*19*). As more data for fused salt systems become available in the future, it should be possible to offer reasonable explanations for the fact that property-composition diagrams at corresponding temperatures resemble, for certain systems, the phase diagrams of the corresponding fused systems.

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Gas Chromatographic Determination of Henry's Constants of 12 Gases in 19 Solvents

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Henry's constants determined by gas-liquid chromatography are reported for gaseous solutes in 16 polar solvents and 3 heavy hydrocarbons. A direct measurement of the solubility of air gives the best determination of the dead volume of the chromatographic system and increases the accuracy of the data for the light gases.

Efficient separation of gaseous mixtures by absorption requires that the solvent have a high selectivity for one gas relative to another. Henry's constants of gaseous solutes have been measured by gas-liquid chromatography for many polar and nonpolar solvents.

Chromatographic techniques, first suggested by Martin (*9*), have been considerably utilized by many authors (*1, 11, 14*) in attempting to measure activity coefficients at infinite dilution of liquid solutes. Nevertheless, the data of gas solubilities are relatively scarce (*13, 14*).

EXPERIMENTAL

The apparatus used is very similar to a conventional gas-liquid chromatographic unit. The chromatograph is an IGC 12 M Intersmat model, equipped with a thermal conductivity detector. The columns are immersed in a liquid bath, which allows control of the temperature within ±0.1° C. The pressure drop in the column is measured by means of a mercury manometer. Helium is used as carrier gas, and flow rate is regulated by needle valves and measured when it leaves the column by a soap-bubble flow meter at atmospheric pressure. The response impulse of the detector is recorded on a Sefram recorder.

The columns consist of coiled ¼-in. stainless steel pipe and are 2 or 3 m long. Fluoropak is used as inert solid support. A preliminary experiment has shown that all gases, especially polar gases, are not retained by a column filled only with Fluoropak.

Before the columns are loaded, acetone is added to the solvent. This provides a uniform dissolution of the solvent on the solid support. Acetone is evaporated slowly under the effect of a small nitrogen flow. Columns are weighed before and after the experimental runs to check any loss of solvent. The vapor pressure of the solvent never exceeds 2 mm Hg in the experimental conditions.

The carrier gas and all the gaseous solutes were provided by l'Air Liquide with a stated minimum purity of 99.9%. No further purification was deemed necessary.

The solvents were provided by Touzart & Matignon and Serlabo with a minimum purity of 99% and were further purified (by distillation) when necessary. Refractive index was measured for each of them as an indication of component purity. Maximum relative deviation with values of literature was 10^{-3}. All light impurities, especially water, were expected to be finally eliminated by elution of helium passing through the column during several hours before experimental runs.

In chromatographic measurements, the difference between the absolute retention volume of the solute and the dead volume of the apparatus must be determined. When this difference, generally called the reduced retention volume, is large, one can take the absolute retention volume of air as the value of the dead volume. But, if the solubility of the solute, for instance methane or ethane, is not large enough compared to the solubility of air, the reduced volume is very small, and the dead volume must be measured with a greater accuracy. All the methods (*2, 3*) proposed by authors for the direct determination of the dead volume are not precise enough.

In this work, the solubility of air is obtained at atmospheric pressure in a cell by measurement of the volume of air absorbed in degassed solvent. Another method consists of a quantitative chromatographic analysis of a solvent sample entirely saturated with air. The differences between the values given by the two methods do not exceed 10%. From the measurement of air solubility, the reduced retention volume of air is easily deduced and the dead volume obtained with great precision.

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