Electrical Conductance and Density in the Fused Molybdate Systems, Li_2MoO_4–Na_2MoO_4 and Li_2MoO_4–K_2MoO_4

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The densities and electrical conductances have been determined in the two molten systems, Li_2MoO_4–Na_2MoO_4 and Li_2MoO_4–K_2MoO_4. Measurements were made generally over a temperature range up to nearly 200° above the melting points. Certain correlations have been observed between the shape of the conductance-composition diagram at corresponding temperatures and the phase diagrams for these two molybdate systems. Density data and conductance data for both systems have been fitted to linear and quadratic equations, respectively, by using the method of least squares.

Accurate measurements of electrical conductance of molten salt systems are essential because such data are useful in understanding the ionic nature of melts. In this report, density and electrical conductance data for the two molten molybdate systems, Li_2MoO_4–Na_2MoO_4 and Li_2MoO_4–K_2MoO_4, have been determined. No density and electrical conductance data on these two systems have been reported in the literature. However, data for the pure salts have been reported by Jaegar (*3*) and by Morris and his associates (*8, 9*).

EXPERIMENTAL

Chemicals. The anhydrous molybdate salts were obtained from the S. W. Shattuck Co., Denver, Colo. The compounds were dried in a vacuum oven for 6 hr at 225° C and then were stored in a desiccator until ready for use. Independent analyses for Li, Na, K, and MoO_4 performed by two companies, Schwarzkopf Chemical Laboratory of New York and Du-Good Chemical Laboratory of St. Louis, revealed these purities: Li_2MoO_4, 99.8%; Na_2MoO_4, 99.8%; and K_2MoO_4, 99.7%.

Apparatus. The apparatus and the experimental details used were essentially the same as those described by Morris and Robinson (*9*). The samples were melted in a platinum-rhodium cylindrical crucible, 3 in. high and 2½ in. in diameter. A Marshall tubular furnace was used to melt the samples. An atmosphere of argon gas was maintained during the heating, melting, and cooling processes. An alumina core wound with platinum–40% rhodium alloy wire gave a resistance suitable enough for a maximum operating temperature of 1500° C. The furnace temperature was controlled to within 0.1° C by an assembly that consisted of the following units: a Pt–Pt 13% Rh thermocouple located in a well near the furnace windings; a Leeds and Northrup Speedomax H recorder (operated in the 5-mV range) used in conjunction with a saturable core reactor and a Leeds and Northrup current-adjusting-type controller. The temperature of the samples was measured with a calibrated Pt–Pt 10% Rh thermocouple used in conjunction with a Leeds and Northrup Type K-3 potentiometer.

Density. The density measurements were basically the same as described by Janz and Lorenz (*4*). A platinum bob weighing approximately 27 grams was suspended from a single-pan Mettler analytical balance by means of a platinum–10% rhodium wire of 0.01 in. diameter (B&S gage 30). Volume and surface tension corrections were made for the bob in the density calculations.

Electrical Conductance. Resistance measurements were made with a Leeds and Northrup No. 4666 Jones Bridge at a frequency of 2000 Hz. It was established with randomly chosen compositions that the use of frequencies greater than 2000 Hz and the traditional extrapolation to infinite frequency, measured resistance vs. $(\text{frequency})^{-2}$, did not improve the inductance-free resistances obtained at 2000 Hz. A Hewlett-Packard oscillator (Model 201-C, 20 Hz to 20,000 Hz) and a General Radio Amplifier and Null Detector (Model 1231-BMA) used in conjunction with a DuMont cathode ray oscilloscope were principal accessories. The conductance cells of clear fused quartz were similar to those described by Van Artsdalen (*10*). The technique of Jones and Bradshaw (*5*) was used to calibrate the cells. Cell constants ranged from 200–525 cm^{-1}. Because of the corrosive nature of the alkali molybdate salts and their mixtures, each conductance cell was discarded after one to three "runs." Whenever a redetermination of the cell constant *after a run* gave a different value for the *same cell*, the cell was discarded. Since the use of temperature-cycling for the property measurements on randomly chosen compositions gave the same results for a given composition, it was concluded that the technique of using rising temperatures for the measurements was satisfactory.

RESULTS AND DISCUSSION

The density and specific conductance data for the molten systems as functions of temperature have been fitted, by the method of least squares, to equations. NOTE: These equations are available as Tables I and II from the American Chemical Society Microfilm Depository Service (*1*).

Density data for the molybdates and their mixtures vary linearly and inversely with temperature over the temperature range studied. Specific conductance data for the pure molybdate salts are best represented by the linear equation, $k = a + bt$. Specific conductance data for the molybdate mixtures follow the quadratic equation, $k = a + bt + ct^2$. The specific conductance data for Na_2MoO_4 and K_2MoO_4 agree within 1% with the data reported by Morris and his associates (*8, 9*). Specific conductance data for Li_2MoO_4 are about 25% higher than the data reported by Kvist and Lunden (*6*). Morris and Robinson (*9*) obtained earlier in this laboratory specific conductance data for Li_2MoO_4 which were almost twice the values of Kvist and Lunden. The discrepancies between the data of this report and those obtained by others for this substance may be attributed to one or more of the following factors: the type of conductance cell employed (Kvist and Lunden used Alsint cells of different design), the difference in purity and composition of lithium molybdate, the preciseness of temperature control, and the possible migration of lithium

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ions through quartz. Morris and Robinson (9) discussed the Li_2MoO_4 data with Kvist and Lunden (6) in a private communication about five years ago. It is the belief of the present authors that the data of this report are the best available now for the lithium molybdate.

Analysis of the lithium molybdate obtained from A. D. Mackay Co. revealed 100% Li_2MoO_4. Specific conductance measurements made on this grade of Li_2MoO_4 gave values in good agreement with the data of Morris and Robinson. However, the melt corroded the quartz cell to such an extent that it was impossible to make a complete run using the same conductance cell. The only explanation for the Shattuck Li_2MoO_4 being less corrosive than the Mackay chemical is that the former probably contained traces of some nonconducting impurity that inhibited the action of the chemical on clear fused quartz. For this reason, the Li_2MoO_4 of 99.8% purity from the Shattuck Co. was used in the present study. It was considerably less corrosive than the other product. Density data for all of the pure salts are in very good agreement with those reported in the literature.

The equivalence conductance, Λ, for the molybdate mixtures has been calculated from the relation, $\Lambda = k\bar{E}/d$. The quantity $\bar{E}$ is the mean equivalent weight of the mixture and is defined as, $\bar{E} = f_1E_1 + f_2E_2$, 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. A "corresponding temperature" of 100° above the melting point for each composition was used, as in previous studies, for the comparison of mixtures with respect to both density and electrical conductance.

Justification for the suitability of our system of defining corresponding temperature are reported elsewhere (9). Plots of the equivalent conductance and the specific conductance at corresponding temperatures as functions of composition for the Li_2MoO_4-Na_2MoO_4 system are shown in Figure 1. Curve I is the phase diagram of Hoermann (2) for this system. Both the specific conductance and equivalent conductance vs. composition plots are found to be similar in shape to the phase diagram. This suggests that the structures of the melts do not differ very greatly from the structures of their respective solids.

Figure 2 shows the conductance-composition plots for the Li_2MoO_4-K_2MoO_4 system. Curve I is the phase diagram of Hoermann (2) for this system. In this system, there are also similarities between the conductance-composition plots and the phase diagram. The shapes of the conductance-composition curves for the molybdate systems appear to depend upon the nature of the ionic species available for the conduction process and on the cation mobilities. Apparently, the large anions contribute very little to the conduction process. Whenever ionic transport numbers become available in the future for these molten systems, such data should provide information on the mobilities of the ionic species.

The quasitheoretical equation, $\Lambda_{mix} = X_1^2\Lambda_1 + X_2^2\Lambda_2 + 2X_1X_2\Lambda_1$ (where $\Lambda_1 < \Lambda_2$), has been derived by Markov and Shumina (7) for the concentration dependence of the conductance of noninteracting mixtures. Symbols X_1 and X_2 represent the mole fractions of components 1 and 2 whose equivalent conductances are Λ_1 and Λ_2, respectively. The quantity Λ_{mix} is the equivalent conductance of the mixture. This equation has been used in the molybdate systems to see whether conductances in these systems deviate from the conductances predicted for simple noninteracting melts. Calculations of Λ_{mix} values have been made for the composition ranges represented by *AB*, *BC*, and so forth in both figures. The experimental equivalent conductance values (Curve II) for the Li_2MoO_4-Na_2MoO_4 system in Figure 1 show positive deviations from the Markov-Shumina values (Curve III). Positive deviations are also observed in the Li_2MoO_4-K_2MoO_4 system (Figure 2, Curve II) for compositions greater than 60 mol % K_2MoO_4. These deviations may be due to the increased mobility of the conducting species as a result of an expanded lattice that possibly accompanies the mixing process.

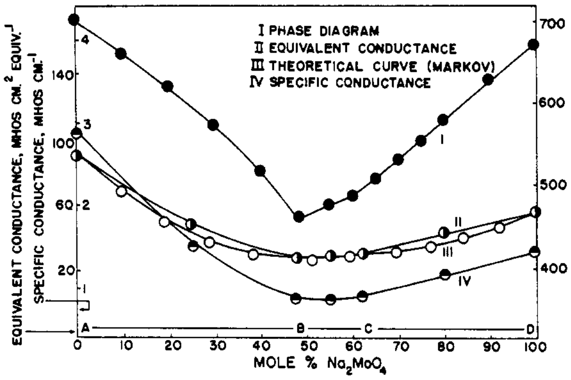

Figure 1. Specific conductance, equivalent conductance, and temperature as functions of composition in molten system, Li_2MoO_4–Na_2MoO_4

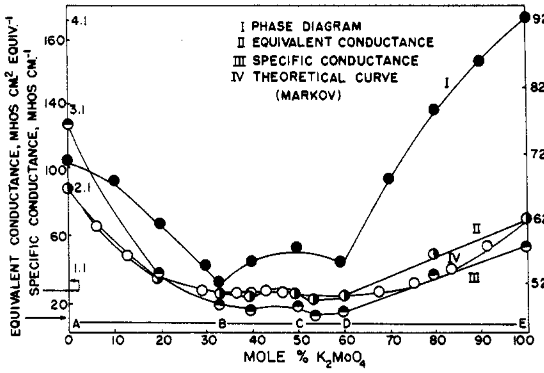

Figure 2. Specific conductance, equivalent conductance, and temperature as functions of composition in molten system, Li_2MoO_4–K_2MoO_4

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