Density measurements on Li_2CO_3-Na_2CO_3-K_2CO_3-Rb_2CO_3-Cs_2CO_3-$CaCO_3$-$SrCO_3$-$BaCO_3$ liquids: systematic trends with composition

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The densities of 15 liquids in the Li_2CO_3-Na_2CO_3-K_2CO_3-Rb_2CO_3-Cs_2CO_3-$CaCO_3$-$SrCO_3$-$BaCO_3$ system were measured at 1 bar with the Pt double-bob method between 758 and 1455 K. They were combined with similar measurements from the literature on 9 liquids in the Li_2CO_3-Na_2CO_3-K_2CO_3-$CaCO_3$ system and used to calibrate a new linear volume equation. The results of the regression lead to partial molar volumes (± 1σ cm^3/mol) at 1100 K for Li_2CO_3 (41.22 ± 0.09), Na_2CO_3 (53.27 ± 0.11), K_2CO_3 (71.59 ± 0.13), Rb_2CO_3 (80.78 ± 0.11), Cs_2CO_3 (94.00 ± 0.09), $CaCO_3$ (40.18 ± 0.16), $SrCO_3$ (44.33 ± 0.22) and $BaCO_3$ (50.99 ± 0.19). At 1100 K, the thermal expansion coefficients of all alkali carbonate liquid components are indistinguishable within 1-sigma error (22.07 ± 1.66 x 10^{-5} K^{-1}), but differ from the thermal expansion coefficients of all alkaline-earth carbonate liquid components, which are also indistinguishable within 1-sigma error (16.40 ± 2.85 x 10^{-5} K^{-1}). The linear volume equation recovers the measurements within analytical error (± 0.3 %). The partial molar volumes of all eight carbonate components increase linearly along two different trends, one for the alkali carbonates (R^2=0.999) and another for the alkaline earth carbonates (R^2=0.999) as a function of cation volumes, where cation-oxygen coordination numbers are obtained from molecular dynamic simulations in the literature (ranging from 4- to 6-fold among the alkali metals and 7- to 8-fold among the alkaline-earth metals). The linear fits lead to two different partial molar volumes (~38 and ~31 cm^3/mole) for the carbonate ion (CO_3^{2-}) at 1100 K, depending on its coordination (4-fold and 6-fold, respectively), with the respective cations. The results permit the partial molar volume of $MgCO_3$ and $FeCO_3$ liquid to be estimated. If Mg^{2+} and Fe^{2+} are in 6-fold coordination with both oxygen and carbonate, the estimated partial molar volumes at 1100 K are 34.4 (± 0.1), and 35.1 (± 0.1) cm^3/mol, respectively, with a thermal expansion of 16.40 (± 2.85) 10^{-5} K^{-1}