

become then $D(\text{B}-\text{S})=1.85 \text{ \AA}$ and $D(\text{B}-\text{Se})=1.99 \text{ \AA}$, i.e. about 0.05 \AA longer than the observed values in $\text{B}(\text{SCH}_3)_3$ and $\text{B}(\text{SeCH}_3)_3$, respectively. We conclude therefore that the

π -bond order is non-negligible in $\begin{array}{c} \diagup \quad \diagdown \\ \text{B}-\text{Se} \end{array}$

as well as in $\begin{array}{c} \diagup \quad \diagdown \\ \text{B}-\text{S} \end{array}$ bonds.

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1. Seip, H. M., Seip, R. and Siebert, W. *Acta Chem. Scand.* 27 (1973) 15.
2. Almendingen, A., Seip, H. M. and Vassbotn, P. *Acta Chem. Scand.* 27 (1973) 21.
3. Brendhaugen, K., Nilssen, E. W. and Seip, H. M. *Acta Chem. Scand.* 27 (1973) 2965.
4. Johansen, R., Nilssen, E. W., Seip, H. M. and Siebert, W. *Acta Chem. Scand.* 27 (1973) 3015.
5. Kroner, J., Nölle, D. and Nöth, H. Z. *Naturforsch. B* 28 (1973) 416.
6. Bock, H. and Ramsay, B. G. *Angew. Chem.* 85 (1973) 773.
7. Gropen, O., Nilssen, E. W. and Seip, H. M. *J. Mol. Struct.* 23 (1974) 289.
8. Zeil, W., Haase, J. and Wegmann, L. Z. *Instrumentenk.* 74 (1966) 84.
9. Bastiansen, O., Graber, R. and Wegmann, L. *Balzers' High Vacuum Report* 25 (1961) 1.
10. Andersen, B., Seip, H. M., Strand, G. T. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
11. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Lett.* 3 (1969) 617.
12. Hamilton, W. C. *Acta Crystallogr.* 18 (1965) 502.
13. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell, Univ. Press, New York 1960.
14. Bartell, L. S. and Carroll, B. L. *J. Chem. Phys.* 42 (1965) 3076.
15. Ryan, R. R. and Hedberg, K. *J. Chem. Phys.* 50 (1969) 4986.
16. Kuchitsu, K. and Cyvin, S. J. In Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972, Chapter 12.

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Density and Surface Tension of Molten Manganese—Cesium Chloride Mixtures

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Density and surface tension of molten MnCl_2 - CsCl were investigated to supplement absorption¹ and Raman spectroscopic² studies. The density and surface tension were determined from liquidostatic weighing and the pin detachment force, respectively. The principle and experimental details have been previously described.³⁻⁵

Anhydrous salts were obtained from $\text{MnCl}_2 \cdot x\text{H}_2\text{O}$ (p.a. Merck, Darmstadt, Germany) and

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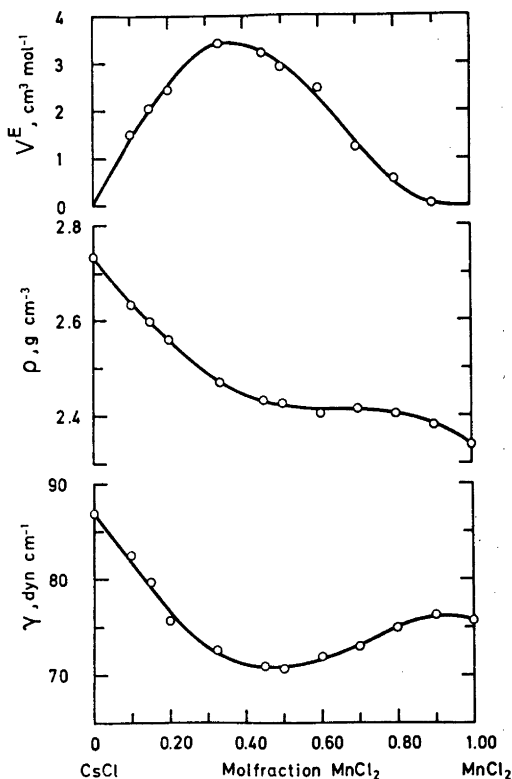


Fig. 1. Surface tension, γ ; density, ρ ; and molar excess volume, V^E , for molten mixtures of CsCl and MnCl_2 at 700°C .

Table 1. Density, ρ , surface tension, γ , and excess molar volumes, V^E , for molten CsCl–MnCl₂ mixtures at 700 °C.

| Mol fraction MnCl ₂ | ρ g cm ⁻³ | $\alpha \times 10^{-4}$ g cm ⁻³ K ⁻¹ | γ dyn cm ⁻¹ | $-\alpha \times 10^2$ dyn cm ⁻¹ K ⁻¹ | V^E cm ³ mol ⁻¹ |
|--------------------------------|---------------------------|--|-------------------------------|--|---|
| 0 | 2.735 | 10.7 | 86.9 | 8.4 | 0 |
| 0.10 | 2.635 | 10.0 | 82.5 | 5.9 | 1.497 |
| 0.15 | 2.534 | 10.0 | 73.7 | 6.8 | 2.047 |
| 0.20 | 2.560 | 9.3 | 75.6 | 6.3 | 2.429 |
| 0.33 | 2.470 | 7.7 | 72.6 | 6.0 | 3.434 |
| 0.45 | 2.435 | 8.4 | 70.9 | 6.4 | 3.202 |
| 0.50 | 2.426 | 8.4 | 70.6 | 5.3 | 2.935 |
| 0.60 | 2.404 | 7.2 | 71.8 | 5.6 | 2.482 |
| 0.70 | 2.414 | 8.3 | 72.9 | 5.9 | 1.248 |
| 0.80 | 2.401 | 7.5 | 74.9 | 5.3 | 0.566 |
| 0.90 | 2.380 | 6.4 | 76.3 | 3.5 | 0.047 |
| 1.00 | 2.337 | 4.8 | 75.6 | 0.6 | 0 |

CsCl (Analar, Hopkin and Williams, England) by standard procedures.³

The experiments were performed in the temperature range 660–740 °C, and least-squares programs were used for determination of the temperature coefficient. The average standard deviation for the fitting was 0.15 % for the surface tension and 0.03 % for the density, except for the 60 mol % MnCl₂ mixture, where the standard deviation of the density was 0.13 %.

Table 1 gives the surfaces tension, density and calculated excess molar volume at 700 °C and the determined temperature coefficients. Fig. 1 shows the concentration variation at 700 °C graphically. The density and surface tension data for the pure salts are in good agreement with those reported in the literature (ρ for CsCl = 2.734,³ from this work ρ = 2.735. γ for CsCl = 87.4,⁴ from this work γ = 86.9. ρ for MnCl₂ = 2.332,⁵ from this work ρ = 2.337).

Excess molar volume as well as excess surface tension, defined as deviation from additivity, exhibit maxima near 33 mol % MnCl₂ (Cs₂MnCl₄), similar to observations made in the corresponding CsCl–MgCl₂ system.^{3,4} This supports the existence of the spectroscopically detected MnCl₄²⁻.^{1,2}

The properties of pure MnCl₂ also show similarities to those of pure MgCl₂. The temperature coefficient of the surface tension for MnCl₂ is abnormally low compared with the mixtures with CsCl, and close to that of pure MgCl₂: 0.6×10^{-2} versus 0.4×10^{-2} dyn cm⁻¹ K⁻¹ for MgCl₂. The thermal expansion coefficient is also considerably lower than for CsCl, although not as low as for MgCl₂: 4.8×10^{-4} versus 2.9×10^{-4} g cm⁻³ K⁻¹ for pure MgCl₂.

Consequently, the shape of the density and surface tension curves versus concentration shows great similarities to those of RbCl–MgCl₂ and CsCl–MgCl₂.^{3,4} The curves (Fig. 1) are

S-shaped, being convex upwards on the MnCl₂ side and concave on the CsCl side.

Apart from the existence of MnCl₄²⁻ configurations in these melts, one cannot draw any other definite conclusion concerning the structure. The postulated octahedral coordination of Mn²⁺ in MnCl₂-rich mixtures is,¹ however, not contradicted by this study, as a change from octahedral to tetrahedral coordination is expected to be accompanied by volume expansion, in agreement with the positive excess molar volume having a maximum close to 33 mol % MnCl₂.

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1. El-Sayed, L. and Øye, H. A. *To be published.*
2. Øye, H. A. and Bues, W. *To be published.*
3. Grjotheim, K., Holm, J. L., Lillebuen, B. and Øye, H. A. *Trans. Faraday Soc.* 67 (1971) 640.
4. Grjotheim, K., Holm, J. L., Lillebuen, B. and Øye, H. A. *Acta Chem. Scand.* 26 (1972) 2050.
5. Lillebuen, B. *Acta Chem. Scand.* 24 (1970) 3287.
6. Janz, G. J., Dampier, F. W., Lakshminarayanan, G. R., Lorenz, P. K. and Tomkins, R. P. T. *Molten Salts*, Vol. I, Electrical Conductance, Density and Viscosity Data, NSRDS-NBS 15, Washington 1968.

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