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# Relative Determination of Soret Coefficients of Alkaline Earth Chlorides

Toshio IKEDA, Hidefusa OHE and Saburo KAWAMURA

*Department of Chemistry, Faculty of Science, Shizuoka University, Oiwa, Shizuoka*

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The Soret coefficients of aqueous solution of alkaline earth chlorides were determined indirectly using combined thermocells. "Combined thermocell" refers to a cell system of a back to back combination of two thermocells made of common electrodes and different electrolytes without liquid junction. The values are $-2.79$ for $MgCl_2$, $-3.43$ for $CaCl_2$, $-4.09$ for $SrCl_2$, and $-4.73$ for $BaCl_2$, respectively (in the unit of $10^{-3}$ deg$^{-1}$) at 0.005 M and 25°C. These agree with reported values found by the direct method.

## General Scheme

The Soret coefficients of a series of the alkaline earth chlorides, $MCl_2$, solution were determined by using combined thermocells of the following system:

$$\begin{array}{llll} \underset{T}{\text{Hg-HgCl}}, & \text{LiCl}(m), & \underset{T+\Delta T}{\text{HgCl-Hg-HgCl}} & \\ & \text{MCl}_2\left(\frac{1}{2}m\right), & \underset{T}{\text{HgCl-Hg}} & (1) \end{array}$$

where the concentrations of chloride ion are taken common in both left and right halves of the cell. Lithium chloride was taken as a standard reference because it shows a very slight Soret effect. The initial thermoelectric powers, $\varepsilon_0{}^{\mathrm{LiCl}}$ and $\varepsilon_0{}^{\mathrm{MCl_2}}$ for the left and right halves of (1) are expressed respectively as follows:[1]

$$\boldsymbol{F}\varepsilon_0{}^{\mathrm{LiCl}} = S_{\mathrm{Hg}} - S_{\mathrm{HgCl}} + 2\boldsymbol{R}Tt_{\mathrm{Li^+}}^{\mathrm{LiCl}}B^{\mathrm{LiCl}}\sigma^{\mathrm{LiCl}} + \overline{\overline{S}}{}_{\mathrm{Cl^-}}^{\mathrm{LiCl}} - \overline{\overline{S}}_{\mathrm{el}}$$

$$\boldsymbol{F}\varepsilon_0{}^{\mathrm{MCl_2}} = S_{\mathrm{Hg}} - S_{\mathrm{HgCl}} + \frac{3}{2}\boldsymbol{R}Tt_{\mathrm{M^{2+}}}^{\mathrm{MCl_2}}B^{\mathrm{MCl_2}}\sigma^{\mathrm{MCl_2}} + \overline{\overline{S}}{}_{\mathrm{Cl^-}}^{\mathrm{MCl_2}} - \overline{\overline{S}}_{\mathrm{el}}$$

where $\sigma$'s are the Soret coefficients, $t$'s the ionic transport numbers for ions indicated by the subscripts. Superscripts, LiCl or $\mathrm{MCl_2}$, indicate the solution phases, and so forth. $B$'s are defined by

$$B^{\mathrm{LiCl}} = (1 + \mathrm{d}\ln\gamma_{\pm}^{\mathrm{LiCl}}/\mathrm{d}\ln m)_{T,P}$$

$$B^{\mathrm{MCl_2}} = (1 + \mathrm{d}\ln\gamma_{\pm}^{\mathrm{MCl_2}}/\mathrm{d}\ln m)_{T,P}$$

where $\gamma_{\pm}$'s are the mean activity coefficients in the molality scale. $\overline{\overline{S}}_{\mathrm{el}}$ is the transported entropy of electrons in the metallic phase, and $\overline{\overline{S}}_{\mathrm{Cl^-}}$'s represent the transported entropies of the chloride ions. $\boldsymbol{F}$, $\boldsymbol{R}$ and $T$ have their usual significances. The temperature coefficient of the resultant thermoelectromotive force, $E$, of (1) at the initial state, or the initial thermoelectric power, $(\mathrm{d}E/\mathrm{d}T)_0$, of (1) is given by the relation, $(\mathrm{d}E/\mathrm{d}T)_0 = \varepsilon_0{}^{\mathrm{MCl_2}} - \varepsilon_0{}^{\mathrm{LiCl}}$. Then we have

$$\sigma^{\mathrm{MCl_2}} = \frac{4t_{\mathrm{Li^+}}^{\mathrm{LiCl}}B^{\mathrm{LiCl}}}{3t_{\mathrm{M^{2+}}}^{\mathrm{MCl_2}}B^{\mathrm{MCl_2}}}\sigma^{\mathrm{LiCl}} + \frac{2\boldsymbol{F}(\mathrm{d}E/\mathrm{d}T)_0}{3\boldsymbol{R}Tt_{\mathrm{M^{2+}}}^{\mathrm{MCl_2}}B^{\mathrm{MCl_2}}} - \frac{2(\overline{\overline{S}}{}_{\mathrm{Cl^-}}^{\mathrm{MCl_2}} - \overline{\overline{S}}{}_{\mathrm{Cl^-}}^{\mathrm{LiCl}})}{3\boldsymbol{R}Tt_{\mathrm{M^{2+}}}^{\mathrm{MCl_2}}B^{\mathrm{MCl_2}}} \tag{2}$$

## Experimental Results and Discussion

All aqueous solutions were prepared from Wakô Guaranteed Reagent grade chemicals (99.8% purity) for a concentration of 0.01 M with respect to the chloride ion. Accuracy of the concentration was within ±0.4%. Experimental equipments are entirely the same as those reported in the previous paper.[2] The measurements were begun after allowing cells to stand at a medium temperature near 25°C for more than 10 days, because, in the early stage, usually during several days after the set up of cell, the stability of electrode system was not sufficient to get reproducible results in measuring such a minute change in emf as the case the present work. Emf of the cell (1) was measured by using a precision Yokogawa potentiometer (New type P-7 for low voltage use) by the aid of Yokogawa sensitive galvanometer, and was accurate within ±0.1 $\mu$V. The range of $\Delta T$ was about 10° around a mean temperature 25°C, while the temperature on the terminal electrodes was kept constant at 25°C. Measurements were repeated for every possible combination of four or five well-conditioned $\mathrm{MCl_2}$ thermocells with four or five well-conditioned reference LiCl thermocells. Some of the typical results are represented in Fig. 1. The values of $(\mathrm{d}E/\mathrm{d}T)_0$, the initial thermoelectric power of the combined thermocells of type (1), were determined at 25°C with the least squares method, and are listed in Table 1. The data are reproducible, mostly within ±1% of fluctuation.

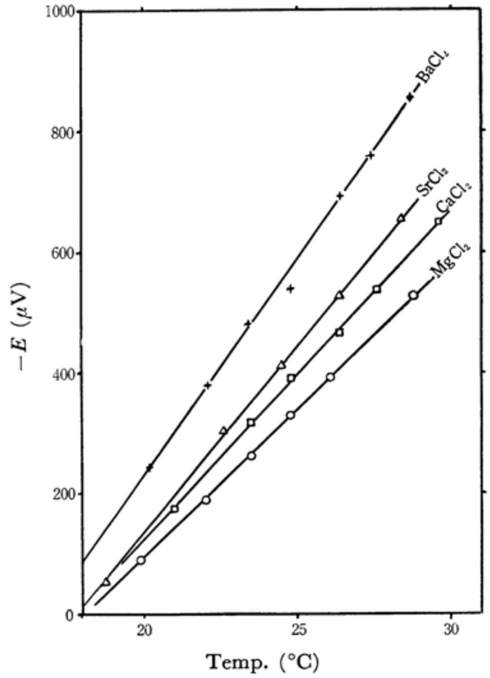

Fig. 1. Emf plots of combined thermocells of the type (1) against the temperature, $(T+\Delta T)$, around the mean temperature 25°C, where the temperature on two terminal electrodes was kept at 25°C constantly. The concentration of solutions was adjusted to 0.01 M with respect to the chloride ions.

According to Snowdon and Turner,[3] the Soret coefficient of LiCl is $0.02\times10^{-3}\,\mathrm{deg}^{-1}$ at 25.3°C and 0.01 M. This value was adjusted to the 25°C

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[1] *E. g.*, H. J. V. Tyrrell, "Diffusion and Heat Flow in Liquid, "Butterworths and Co., Ltd., London (1961); T. Ikeda, *Report Liberal Arts Sci. Fac. Shizuoka Univ.*, **2**, 153 (1959).

[2] T. Ikeda, This Bulletin, **38**, 407 (1965); T. Ikeda and H. Kimura, *J. Phys. Chem.*, **69**, 41 (1965); T. Ikeda and M. Matsumoto, *ibid.*, **69**, 3755 (1965).

[3] P. N. Snowdon and J. C. R. Turner, *Trans. Faraday Soc.*, **56**, 1409 (1960).

TABLE 1. SORET COEFFICIENTS OF ALKALINE EARTH METAL CHLORIDES AT 25°C AND 0.005 M
(The $\sigma$-value in parentheses is adopted as the standard for the relative determination of $\sigma^{\mathrm{MCl_2}}$.)

| Chloride | $m$ | $t_+$ [a] | B [b] | $(\mathrm{d}E/\mathrm{d}T)_0$ $\mu$V/deg | $-\sigma\times10^3$ deg$^{-1}$ This work | $-\sigma\times10^3$ deg$^{-1}$ Literature value |
|---|---|---|---|---|---|---|
| LiCl | 0.01006 | 0.3289 | 0.969 | — | (−0.01) | −0.01 [c] |
| $MgCl_2$ | 0.00501 | 0.394 | 0.917 | −38.8±0.4 | 2.79 | 2.80 [d] |
| $CaCl_2$ | 0.00501 | 0.4264 | 0.905 | −51.0±0.3 | 3.43 | 3.17 [d] |
| $SrCl_2$ | 0.00502 | 0.424 | 0.923 | −61.6±0.6 | 4.09 | 3.99 [e] |
| $BaCl_2$ | 0.00502 | 0.439 | 0.898 | −71.2±0.5 | 4.73 | 4.65 [e] |

a) E. Conway, " Electrochemical Data," Elsevier Publishing Co., Amsterdam (1952).
b) Graphical determination from Landolt-Börnstein, " Physikalische Chemische Tabellen," Erg. II (1931) and III (1936).
c) Adjusted to the value for 0.01 M at 25°C (Ref. 3).
d) The value for 0.0050 M at 25.1°C (Ref. 4).
e) The value for 0.0051 M at 24.9±0.1°C (Ref. 4).

value, $0.01\times10^{-3}\,\mathrm{deg}^{-1}$, and was used as the standard in the present calculation. $B$-Values were determined graphically at a concentration $m=0.01$ M in the case of LiCl and at 0.005 M in the case of $MCl_2$, respectively, at 25°C. These values and the present data on $(\mathrm{d}E/\mathrm{d}T)_0$ were used to get the relative values of the Soret coefficients, $\sigma^{\mathrm{MCl_2}}$, at 25°C and 0.005 M by the aid of (2). In this treatment $\overline{\overline{S}}{}^{\mathrm{MCl_2}}_{\mathrm{Cl^-}}=\overline{\overline{S}}{}^{\mathrm{LiCl}}_{\mathrm{Cl^-}}$ was assumed. The results agree very well with those obtained by the direct method by Payton and Turner,[4] except calcium chloride. According to the theory of Helfand and Kirkwood,[5] $\overline{\overline{S}}_{\mathrm{Cl^-}}$'s should differ from solution to solution involving different cation species, particularly of high ionic valency, however, the present studies indicate that the difference between $\overline{\overline{S}}_{\mathrm{Cl^-}}$'s is practically negligible. This fact seems to indicate that our combined thermocell method is applicable extensively to determine the Soret coefficients of bivalent metal chlorides in water at low concentration by assuming $\overline{\overline{S}}{}^{\mathrm{MCl_2}}_{\mathrm{Cl^-}}=\overline{\overline{S}}{}^{\mathrm{LiCl}}_{\mathrm{Cl^-}}$.

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[4] A. D. Payton and J. C. R. Turner, *ibid.*, **58**, 55 (1962).

[5] E. Helfand and J. G. Kirkwood, *J. Chem. Phys.*, **32**, 857 (1960)