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Molar Volume Equations of Several Molten Binary Systems

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Synopsis. The molar volumes of YCl_3–KCl, YCl_3–NaCl, YCl_3–$CaCl_2$, $PrCl_3$–KCl, $PrCl_3$–NaCl, $PrCl_3$–$CaCl_2$, $NdCl_3$–KCl, $NdCl_3$–NaCl, and $NdCl_3$–$CaCl_2$ systems in molten state were measured. The results are represented by empirical equations as functions of both temperature and composition. The calculations were carried out by using the methods of least squares and Powell's procedure.

It is important to know the molar volumes of molten salts, since they are used for the calculation of molar values in thermodynamics. The molar volume equation has been customarily expressed as a function of temperature for a fixed mole fraction. If empirical equations for the molar volumes of molten mixture systems are obtained as functions of temperature and mole fraction, they are convinient for the estimation of molar volumes at any temperature and composition over the measured range. Since the molar volume is given as a linear function of temperature, the empirical equation is given as follows.

$$V_m = \sum_0^n a_n x^n + \left(\sum_0^n b_n x^n\right) T$$

where V_m is the averaged molar volume of the molten mixture system in cm^3/mol, a_n and b_n the parameters, x the mole fraction of rare-earth chlorides, and T the temperature in K. The parameters were calculated by the method of least squares, and Powell's method.[1,2] The latter is considered to be effective for finding the minimum value of function containing several variables. The molar volumes calculated from the resulting empirical equations are in agreement with the observed values within 2%.

Experimental

Materials. Rare-earth chlorides were prepared by a procedure similar to that reported.[3] KCl, NaCl, and $CaCl_2$ were dried by heating at a temperature 50 °C below their melting points *in vacuo*.

Measurement. The dilatometer method was used. The volume of the dilatometer, which was made of transparent silica, was determined by use of distilled water at room temperature since the thermal expansion coefficient of quartz is much smaller than that of molten salts. The meniscus of melt in the dilatometer was read with a cathetometer.

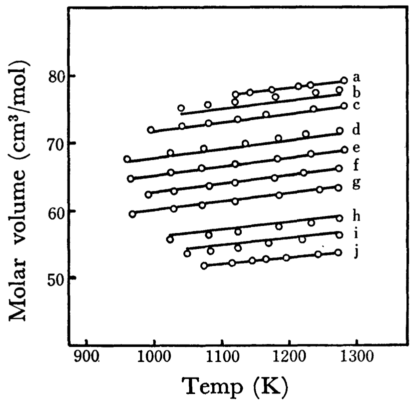

Fig. 1. Molar volumes of YCl_3–$CaCl_2$ system in molten state; ○: observed values, —: calculated values by empirical equation (n=2), a: mole fraction of YCl_3 1.0, b: 0.929, c: 0.849, d: 0.700, e: 0.599, f: 0.500, g: 0.398, h: 0.221, i: 0.125, j: 0 ($CaCl_2$: 1.0).

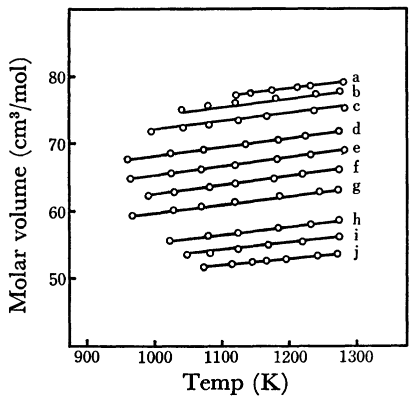

Fig. 2. Molar volumes of YCl_3–$CaCl_2$ system in molten state; ○: observed values, —: calculated values by empirical equation (n=3), a: mole fraction of YCl_3 1.0, b: 0.929, c: 0.849, d: 0.700, e: 0.599, f: 0.500, g: 0.398, h: 0.221, i: 0.125, j: 0 ($CaCl_2$: 1.0).

TABLE 1. PARAMETERS OF EMPIRICAL EQUATIONS FOR MOLTEN BINARY SYSTEMS (n=3)

System	a_0 (×10)	a_1 (×10)	a_2 (×10)	a_3 (×10)	b_0 (×10^{-2})	b_1 (×10^{-2})	b_2 (×10^{-2})	b_3 (×10^{-2})
YCl_3–KCl	2.5133	8.4872	−13.0034	8.1121	2.2033	−4.6025	10.6857	−6.8596
YCl_3–NaCl	2.1124	4.9782	−3.1680	2.1865	1.5030	−0.9367	2.7031	−1.8426
YCl_3–$CaCl_2$	4.1616	0.2464	3.2924	−1.3030	0.9483	1.2902	−1.1699	0.1151
$PrCl_3$–KCl	2.5547	7.3695	−10.3620	5.1980	2.1675	−3.1106	7.4261	−3.9764
$PrCl_3$–NaCl	2.1124	3.0262	2.3676	−2.7460	1.5030	0.5474	−1.7208	2.1769
$PrCl_3$–$CaCl_2$	4.0348	1.9796	−1.5171	0.2628	1.0851	1.5488	−2.4048	2.2774
$NdCl_3$–KCl	2.5547	4.1783	−3.2497	1.9470	2.1675	−0.8841	1.9325	−1.3067
$NdCl_3$–NaCl	2.1124	3.1752	0.6594	−0.5344	1.5030	0.6079	−0.8599	0.6721
$NdCl_3$–$CaCl_2$	4.0348	−0.0979	3.4814	−1.9880	1.0851	2.5231	−4.3237	2.6247

Results and Discussion

Comparisons between the observed molar volumes and the values for the molten YCl_3–$CaCl_2$ system obtained by means of empirical equations are given in Figs. 1 and 2 for $n=2$ and $n=3$, respectively. Fitting of the resulting equation for the observed molar volumes is better in the case of $n=3$ than that of $n=2$. The molar volumes of the respective pure component salts in molten state can be obtained from the values at $x=0$ or $x=1$. The parameters for these molten binary systems are given in Table 1. All the excess molar volumes calculated by means of the equations are small. The intersections between experimental curves and additivity lines in the molar volume isotherms were observed except for $PrCl_3$–KCl and $NdCl_3$–KCl systems.

Calculations were carried out with the computers in the University of Tokyo and Chiba University.

References

1) M. J. D. Powell, *Computer J.*, **7**, 155 (1964).
2) M. J. D. Powell, *Computer J.*, **5**, 147 (1962).
3) J. Mochinaga, and K. Irisawa, *Bull. Chem. Soc. Jpn.*, **47**, 364 (1974).