Osmotic Coefficients of Aqueous Solutions of Calcium Chloride and Calcium Perchlorate at 25° C

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The osmotic coefficients of solutions of calcium chloride and calcium perchlorate at 25° C have been measured. The binary interaction coefficient (Cl^-–ClO_4^- interaction) is found to have the comparatively high value of b_{01} = 0.0444 mole^{-1} kg.

Scatchard's equations (*10, 11*) for the excess free energy of a mixed electrolyte solution containing two salts of the same charge type can be expressed in the form:

$$\Delta \equiv \nu(\phi - y_A\phi_A^0 - y_B\phi_B^0) = y_Ay_Bb_{01}I \qquad (1)$$

where b_{01} is a measure of binary ionic interaction. This simplified equation suffices for the system now to be described but the complete equation contains additional terms, $b_{02}I^2$, $b_{03}I^3$... and skew terms such as $y_Ay_B(y_A - y_B)b_{12}I^2$. An examination of the literature suggests that, for a mixture with a common ion, b_{01} may be small; for example, it is 0.0038 mole^{-1} kg for the NaCl–NaBr system (*2*), indicating that Cl^-–Br^- interaction is weak; on the contrary, for the NaCl-KCl system (*4, 9*), b_{01} = −0.0253 mole^{-1} kg, corresponding to comparatively strong Na^+–K^+ interaction. That the anion–anion interaction is not always weak is demonstrated by the work of Yoest (*8, 13*) who found b_{01} = 0.1225 mole^{-1} kg for the $CuCl_2$–$Cu(ClO_4)_2$ system, showing that Cl^-–ClO_4^- interaction, in contrast to that of Cl^-–Br^- is strong. This paper presents measurements on the $CaCl_2$–$Ca(ClO_4)_2$ system.

MATERIALS

A stock solution of calcium chloride was made from calcium carbonate and hydrochloric acid by the method of Stokes (*12*). A stock solution of calcium perchlorate was prepared from calcium carbonate and perchloric acid by a method already described (*6*). Portions of these solutions were mixed and diluted for isopiestic vapor pressure measurements.

METHOD

The application of the isopiestic vapor pressure method to mixed salt solutions was essentially that described in earlier publications (*4, 7*).

RESULTS

The experimental data are given in Table I, where m_{ref} is the molality of a solution containing calcium chloride only and m that of a mixed salt solution of the same vapor pressure. Two mixtures were used, in one of which y_B was 0.3064 and in the other 0.6344. Table I gives the osmotic coefficients of these mixed salt solutions and values of $\Delta/(y_Ay_BI)$.

DISCUSSION

The osmotic coefficients given in the third and sixth columns of Table I are probably reliable to within 0.001; an error of this magnitude corresponds to an uncertainty of 0.003 in Δ and of 0.0025 in $\Delta/(Iy_Ay_B)$ for the most dilute solution and correspondingly less for the more concentrated solutions.

The average value of $\Delta/(y_Ay_BI)$ is 0.0477 mole^{-1} kg at y_B = 0.3064 and 0.0412 mole^{-1} kg at y_B = 0.6344; this difference is not sufficient to justify the use of the $(y_A - y_B)$ skew term in Equation 1. Moreover, there seems to be no significant trend in the values of $\Delta/(y_Ay_BI)$ with a change in I and, therefore, there is no need for additional terms such as $b_{02}I^2$ in Equation 1. The average of all 26 determinations, b_{01} = 0.0444 mole^{-1} kg, is a measure of Cl^-–ClO_4^- interaction in this system. It is much larger than that for Cl^-–Br^- interaction in the NaCl-NaBr system (*2*) but smaller than that found by Yoest (*13*) for Cl^-–ClO_4^- interaction in the $CuCl_2$–$Cu(ClO_4)_2$ system.

If b_{01} is a measure of binary interaction between two anions, it should be independent of the cations, Ca^{2+} and Cu^{2+} in this case. However, for these two systems, b_{01} has very different values. The reason for this, it is suggested, lies in the peculiar properties of cupric chloride. There is considerable evidence that this salt forms $CuCl^+$, either a contact ion-pair or as the first stage in the formation of higher complexes such as $CuCl_4^{2-}$. Two lines of evidence are now quoted. Figure 1 shows the osmotic coefficients of calcium perchlorate (*6*), calcium chloride (*12*), cupric

Table I. Osmotic Coefficients of Aqueous Solutions of Calcium Chloride and Calcium Perchlorate at 25° C

		$y_B = 0.3064$			$y_B = 0.6344$	
m_{ref}	m	ϕ	$\Delta/(Iy_Ay_B)$	m	ϕ	$\Delta/(Iy_Ay_B)$
2.017	1.905	1.464	0.0596	1.825	1.528	0.0496
2.202	2.078	1.540	0.0629	1.988	1.610	0.0601
2.483	2.344	1.654	0.0498	2.243	1.729	0.0377
2.795	2.641	1.791	0.0513	2.525	1.873	0.0410
3.210	3.035	1.971	0.0454	2.898	2.065	0.0451
3.656	3.460	2.159	0.0415	3.307	2.259	0.0365
4.118	3.901	2.353	0.0410	3.730	2.461	0.0369
4.771	4.521	2.624	0.0436	4.324	2.744	0.0445
5.321	5.037	2.834	0.0413	4.824	2.959	0.0377
6.074	5.709	3.083	0.0440	5.463	3.222	0.0335
6.795	6.327	3.275	0.0475	6.030	3.436	0.0366
7.385	6.794	3.388	0.0491	6.442	3.573	0.0420
7.970	7.247	3.464	0.0429	6.833	3.674	0.0341

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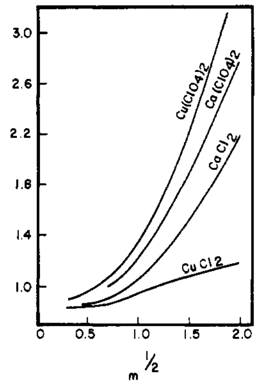

Figure 1. Dependence on concentration of the osmotic coefficients of cupric perchlorate (*3*), calcium perchlorate (*6*), calcium chloride (*12*), and cupric chloride (*5*)

perchlorate (*3*), and cupric chloride (*5*). The curves for the first three salts are typical of fully dissociated, highly solvated electrolytes; that for cupric chloride is such as to suggest incomplete dissociation. Spectrophotometric measurements of cupric chloride in lithium chloride solution (*1*) suggest that formation of $CuCl^+$ is likely. Any such reduction in the number of Cu^{2-} ions in a $CuCl_2$ solution suffices to explain, at least qualitatively, why b_{01} is different in the $CaCl_2$–$Ca(ClO_4)_2$ and $CuCl_2$–$Cu(ClO_4)_2$ systems.

NOMENCLATURE

ϕ = osmotic coefficient of a mixed salt solution
ϕ_A^0, ϕ_B^0 = osmotic coefficients of solutions of salts A and B, respectively, at ionic strength equal to the total ionic strength of the mixed salt solution, I
y_A = m_A/m, $y_B = m_B/m$
m_A and m_B = molalities (mole kg^{-1}) of A and B, respectively, in the mixed salt solution
m = $m_A + m_B$
Δ $\equiv$ $\nu(\phi - y_A\phi_A^0 - y_B\phi_B^0)$

In this paper, $A = CaCl_2$, $B = Ca(ClO_4)_2$, $\nu = 3$

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Densities of Some Nitrate and Sulfate Melts

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The densities of $NaNO_3$–KNO_3 (45:55 mol %), $LiNO_3$–KNO_3 (41:59), KNO_3–$LiNO_3$ (41:59), and $NaNO_3$–$LiNO_3$ (46:54) melts are reported for a temperature range of some 200° together with that of Li_2SO_4–Na_2SO_4–K_2SO_4 eutectic at 550° C. Molar volumes of the nitrate mixtures are additive to within 1.3%.

Although the densities of several molten nitrate mixtures are recorded in the literature, the data for four mixtures, employed in a series of electrochemical investigations, are not known. It was therefore necessary to make density measurements of these, and the values have been compared with those calculated upon the assumption of additivity of molar volumes. The density of a ternary sulfate eutectic, also a common solvent, was also measured and is recorded here.

EXPERIMENTAL

Densities were measured by the buoyancy method favored for its simplicity coupled with accuracy (*3*). A silver bob (about 2 cm length), suspended on a 1-mm diameter silver wire below an analytical balance, was immersed to 10 ± 1 mm below the surface of the melt in a glass container. The ±1-mm error represents a volume error of $\pm 8 \times 10^{-4}$ cc or ±0.02%. Temperatures were measured by a chromel-alumel thermocouple immersed in the melt and were controlled by a Proportio Null, 1300 Series, controller (Cole-Parmer Instrument and Equipment Co.) connected to the power circuit of a simple box furnace.

In making temperature measurements, the zero point was ice water, and recordings were taken from a Cropico Type P3 potentiometer. The thermocouples were calibrated against the fixed points (mp of ice, Sn, Cd, Pb, and Zn, bp of water) used to define the International Temperature Scale of 1948 (*4*), a pressure correction being included. In taking measurements, a constancy of ±0.0005 gram and ±0.25° C for 15 min was required, and both heating and cooling cycles were used for each system. The volume of the silver bob as a function of temperature from 325° to 475° C was obtained by measuring the density of sodium nitrate which is given by ref. *6*:

$$\rho = 2.125 - 7.15 \times 10^{-4}\ T\ (^\circ C)$$

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