

Properties of Aqueous Mixtures of Pure Salts. Thermodynamics of the Ternary System: Water-Sodium Chloride-Calcium Chloride at 25 °C

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Isopiestic vapor pressure measurements have been made to determine some thermodynamic properties of the system: water-sodium chloride-calcium chloride at 25 °C. Equations are derived for the activity coefficient of each salt in the presence of the other when the total ionic strength is kept constant. The limiting conditions in very dilute solutions are considered and "trace" activity coefficients calculated. A comparison with previous work is made. The excess free energy of mixing is calculated.

Key Words: Calcium chloride, isopiestic measurements, mixed salt solutions, sodium chloride, vapor pressure of aqueous solutions.

1. Introduction

The application of the isopiestic vapor pressure method of determining the activity coefficients of two salts in a mixed salt solution has been described in two previous papers. In one of these [1]¹ the system water-sodium chloride-barium chloride was described and in the other [2] the system water-potassium chloride-barium chloride. This paper is concerned with the system water-sodium chloride-calcium chloride.

2. Definitions

The definitions and symbols of the previous paper [1] will be retained except that C now designates calcium chloride.

3. Experimental Procedure

The sodium chloride was a portion of that used in earlier work [1]. Calcium chloride was purified in the manner already described [3]; the following impurities were detected by flame photometry:² sodium, 10 ppm; potassium, 10 ppm; strontium, 300 ppm. A stock solution of sodium chloride was made by dissolving a known weight of the salt in a known weight of water. The stock solution of calcium chloride was made by dissolving the salt in water to give a solution approximately 4*m* in concentration; its exact composition was then determined by coulometric titration.³

The stock solutions were used to prepare solutions containing both sodium chloride and calcium chloride in known amounts. These solutions were equilibrated in an isopiestic apparatus contained in a thermostat at 25 ± 0.01 °C. The time of equilibration varied from 3 days for the most concentrated solutions ($M_B \sim 5.8$) ($M_C \sim 2.9$) to 7 days for the most dilute solutions ($M_B \sim 0.5$) ($M_C \sim 0.4$). After equilibration, the composition of the solutions at equilibrium was determined from the loss or gain of water by each solution.

4. Isopiestic Data

The experimental results are given in table 1. The second column gives the molality (M_B) of the reference solution of sodium chloride. The next two columns give the molalities of sodium chloride (m_B) and of calcium chloride (m_C), respectively, in the mixed solutions. The fifth column gives values of the ionic fraction, y_C of calcium chloride in the mixed solution, defined as $y_C = 1.5m_C/m$, where $m = m_B + 1.5m_C$. The sixth column gives values of the isopiestic ratio, defined as $R = M_B/m$.

Figure 1 is a plot of isopiestic ratio versus the ionic fraction of calcium chloride for some sets of results in table 1. These isopiestic ratios are much higher than those encountered in the sodium chloride-barium chloride system. For example, in the latter system, a solution of 2.7147*m* sodium chloride was found to be in isopiestic equilibrium with a solution of 1.7610*m* barium chloride, $R = 1.0277$; we now find that a solution 2.7546*m* sodium chloride has the same vapor pressure as a solution of 1.5498*m* calcium chloride,

¹ Figures in brackets indicate the literature references at the end of this paper.

² Analysis by R. W. Burke of the Analysis and Purification Section.

³ Analysis by G. Martineau of the Analysis and Purification Section.

TABLE 1. Isopiestic ratios for the system water-sodium chloride-calcium chloride at 25°C

| Set | M_2 | m_2 | m_1 | y_c | $R(\text{obs})$ | $R(\text{calc})$ | Δ^* |
|--------|--------|--------|--------|--------|-----------------|------------------|------------|
| 1 | 0.5339 | 0.3735 | 0.1110 | 0.3083 | 0.9887 | 0.9892 | +0.05 |
| | | 0.2495 | 0.1968 | 0.5419 | 0.9802 | 0.9805 | +0.03 |
| | | 0.1258 | 0.2816 | 0.7691 | 0.9721 | 0.9717 | -0.04 |
| | 0.5406 | 0.4190 | 0.0842 | 0.2316 | 0.9917 | 0.9920 | +0.03 |
| | | 0.3146 | 0.1561 | 0.4267 | 0.9855 | 0.9849 | -0.06 |
| | | 0.1832 | 0.2470 | 0.6691 | 0.9767 | 0.9757 | -0.10 |
| | | 0.3746 | 1.0 | 0.9624 | 0.9623 | -0.01 | |
| 2 | 0.7980 | 0.6832 | 0.0769 | 0.1446 | 1.0003 | 1.0000 | -0.03 |
| | | 0.4544 | 0.2297 | 0.4312 | 0.9999 | 0.9997 | -0.02 |
| | | 0.2241 | 0.3842 | 0.7200 | 0.9960 | 0.9968 | +0.08 |
| | 0.8005 | 0.5729 | 0.0846 | 0.2846 | 0.9996 | 0.9999 | +0.03 |
| | | 0.3405 | 0.1672 | 0.5750 | 0.9990 | 0.9994 | +0.04 |
| | | 0.1271 | 0.2497 | 0.8414 | 0.9986 | 0.9983 | -0.03 |
| | | | 1.0 | 0.9980 | 0.9975 | -0.05 | |
| 3 | 1.0420 | 0.6887 | 0.2294 | 0.3332 | 1.0089 | 1.0092 | +0.03 |
| | | 0.4475 | 0.3929 | 0.5739 | 1.0148 | 1.0152 | +0.04 |
| | | 0.2166 | 0.5567 | 0.7880 | 1.0199 | 1.0201 | +0.02 |
| | 1.0524 | 0.7891 | 0.1706 | 0.2449 | 1.0246 | 1.0247 | +0.01 |
| | | 0.5393 | 0.3333 | 0.4810 | 1.0271 | 1.0268 | -0.03 |
| | | 0.3250 | 0.4725 | 0.6855 | 1.0283 | 1.0278 | -0.05 |
| | | 0.6846 | 1.0 | 1.0248 | 1.0247 | -0.01 | |
| 4 | 1.5186 | 0.9755 | 0.3348 | 0.3399 | 1.0277 | 1.0279 | +0.02 |
| | | 0.5078 | 0.4256 | 0.5489 | 1.0501 | 1.0517 | +0.16 |
| | | 0.2665 | 0.7736 | 0.8132 | 1.0645 | 1.0637 | -0.08 |
| | 1.5523 | 0.9414 | 1.0 | 1.0 | 1.0754 | 1.0770 | +0.16 |
| | | 1.2831 | 0.1656 | 0.1622 | 1.0436 | 1.0435 | -0.01 |
| | | 0.5750 | 0.6029 | 0.5113 | 1.0494 | 1.0489 | -0.05 |
| | 0.3506 | 0.7412 | 0.7603 | 1.0615 | 1.0599 | -0.16 | |
| | | 0.9601 | 1.0 | 1.0778 | 1.0770 | -0.08 | |
| 5 | 1.7785 | 1.2568 | 0.3258 | 0.2832 | 1.0307 | 1.0303 | -0.04 |
| | | 0.7203 | 0.6377 | 0.5709 | 1.0595 | 1.0601 | +0.06 |
| | | 0.2557 | 0.9204 | 0.8438 | 1.0869 | 1.0874 | +0.05 |
| | 1.7899 | 1.0762 | 1.0 | 1.0 | 1.1017 | 1.1027 | +0.10 |
| | | 1.5227 | 0.1600 | 0.1362 | 1.0154 | 1.0147 | -0.07 |
| | | 1.0256 | 0.4603 | 0.4024 | 1.0330 | 1.0328 | -0.02 |
| | 0.5579 | 0.7427 | 0.6666 | 1.0705 | 1.0698 | -0.07 | |
| | | 1.0822 | 1.0 | 1.1026 | 1.1027 | +0.01 | |
| 6 | 2.7546 | 1.9144 | 0.4751 | 0.2716 | 1.0497 | 1.0516 | +0.19 |
| | | 1.2728 | 0.8302 | 0.4945 | 1.0939 | 1.0935 | -0.04 |
| | | 0.5209 | 1.1974 | 0.7431 | 1.1597 | 1.1596 | -0.01 |
| | 2.7925 | 1.5498 | 1.0 | 1.0 | 1.1849 | 1.1870 | +0.21 |
| | | 1.6266 | 0.6524 | 0.3756 | 1.0719 | 1.0713 | -0.06 |
| | | 0.9691 | 1.0206 | 0.8124 | 1.1170 | 1.1153 | -0.17 |
| | 0.3633 | 1.3619 | 0.8490 | 1.1606 | 1.1593 | -0.13 | |
| | | 1.5679 | 1.0 | 1.1873 | 1.1870 | -0.03 | |
| 7 | 3.4285 | 2.2476 | 0.6360 | 0.2900 | 1.0709 | 1.0712 | +0.03 |
| | | 1.2284 | 1.1877 | 0.5919 | 1.1590 | 1.1404 | -0.14 |
| | | 0.3794 | 1.6464 | 0.8668 | 1.2034 | 1.2042 | +0.08 |
| | 3.4631 | 1.8530 | 1.0 | 1.0 | 1.2335 | 1.2348 | +0.13 |
| | | 2.8877 | 0.3111 | 0.1392 | 1.0325 | 1.0333 | +0.08 |
| | | 1.7012 | 0.9474 | 0.5551 | 1.1091 | 1.1083 | -0.08 |
| | 0.8440 | 1.4101 | 0.7148 | 1.1701 | 1.1690 | -0.11 | |
| | | 1.8677 | 1.0 | 1.2361 | 1.2348 | -0.13 | |
| 8 | 4.5821 | 3.4474 | 0.5772 | 0.2007 | 1.0624 | 1.0627 | +0.03 |
| | | 2.1539 | 1.2356 | 0.4625 | 1.1434 | 1.1433 | -0.01 |
| | | 1.2666 | 1.6382 | 0.6426 | 1.1983 | 1.1980 | -0.03 |
| | 4.6196 | 3.7520 | 0.4410 | 0.1499 | 1.0467 | 1.0469 | +0.02 |
| | | 2.9372 | 0.8548 | 0.3039 | 1.0948 | 1.0946 | -0.02 |
| | | | 2.3610 | 1.0 | 1.3044 | 1.3047 | +0.03 |
| 9 | 5.4851 | 3.8795 | 0.7994 | 0.2338 | 1.0832 | 1.0835 | +0.03 |
| | | 2.8929 | 1.3051 | 0.4067 | 1.1451 | 1.1453 | +0.02 |
| | | 1.4784 | 1.9724 | 0.6668 | 1.2362 | 1.2352 | -0.10 |
| | | | 2.7106 | 1.0 | 1.3490 | 1.3495 | +0.05 |
| | 5.8385 | 3.5953 | 1.0884 | 0.3123 | 1.1168 | 1.1169 | +0.01 |
| | | 2.2752 | 1.7306 | 0.5329 | 1.1986 | 1.1981 | -0.05 |
| 1.0796 | | 2.5162 | 0.7629 | 1.2820 | 1.2816 | -0.04 | |
| | | 2.8500 | 1.0 | 1.3657 | 1.3663 | +0.06 | |

* $\Delta = R(\text{calc}) - R(\text{obs})$, where $R(\text{calc})$ is obtained with the aid of eq (1) and the parameters in table 2.

$R = 1.1849$. Moreover, a plot of isopiestic ratio versus ionic fraction of barium chloride gave a straight line, within experimental error; the plot of isopiestic ratio versus ionic fraction of calcium chloride (fig. 1) may appear to be linear but a closer examination, by the method of least squares, reveals a slight curvature.

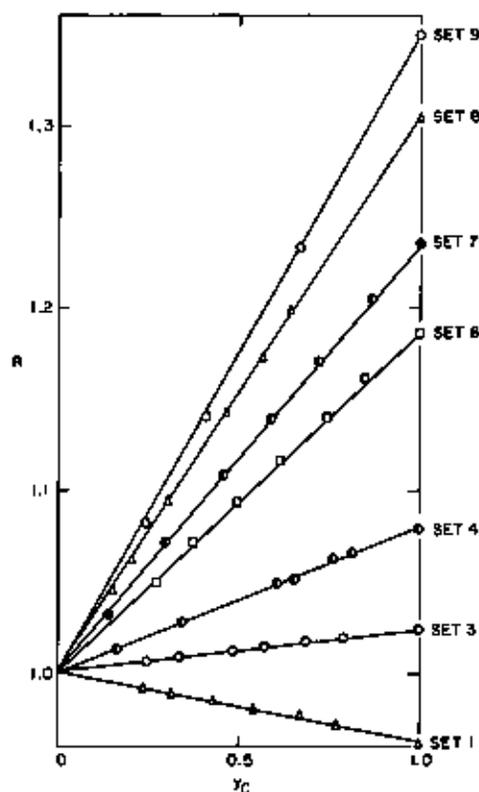


FIGURE 1. Isopiestic ratio of sodium chloride (B)-calcium chloride (C) solutions versus ionic fraction. $R = M_2/m, m = m_2 + 1.5 m_1, y_c = 1.0 m_2/m$.

The isopiestic results can be represented by the equation

$$R = M_2/m = 1 - ay_c - by_c^2 \quad (1)$$

The parameters of this equation were obtained by the method of least squares. The seventh column of table 1 gives values of R calculated by this equation, using the values of a and b given in table 2. The last column of table 1 gives the differences between the observed isopiestic ratios and those calculated using eq (1).

TABLE 2. Values of the parameters of eq (1) and of the integral in (5)

| Set | M_2 (mean) | a | b | b/M_2 | v_2 | M_{2v2} | \int^* |
|-----|--------------|---------|--------|---------|--------|-----------|----------|
| 1 | 0.5374 | +0.0327 | 0.0040 | 0.0074 | 0.9217 | 0.4953 | 0.0015 |
| 2 | 0.7997 | -0.0007 | 0.0032 | 0.0040 | 0.9288 | 0.7428 | 0.0022 |
| 3 | 1.0472 | -0.0267 | 0.0040 | 0.0038 | 0.9372 | 0.9614 | 0.0036 |
| 4 | 1.5355 | -0.0828 | 0.0076 | 0.0051 | 0.9583 | 1.4715 | 0.0098 |
| 5 | 1.7842 | -0.1087 | 0.0050 | 0.0034 | 0.9715 | 1.7334 | 0.0141 |
| 6 | 2.7736 | -0.1909 | 0.0059 | 0.0021 | 1.0304 | 2.8579 | 0.0399 |
| 7 | 3.4458 | -0.2496 | 0.0058 | 0.0017 | 1.0759 | 3.7073 | 0.0666 |
| 8 | 4.6009 | -0.3141 | 0.0094 | 0.0020 | 1.1609 | 5.3412 | 0.074 |
| 9 | 5.4851 | -0.3595 | 0.0100 | 0.0018 | 1.2298 | 6.7456 | 0.082 |
| 10 | 5.8385 | -0.3781 | 0.0110 | 0.0020 | 1.2578 | 7.3437 | 0.086 |

* This column gives values of the integral $0.4348 \int_0^{y_c} (b/M_2) d(M_{2v2})$.

5. Calculation of Activity Coefficients

The immediate result of an isopiestic experiment is the information that a set of solutions, one of which contains only sodium chloride, another contains only calcium chloride, and the remainder contain both sodium chloride and calcium chloride in different proportions, all have the same vapor pressure and the same water activity, a_w . It follows that:

$$2M_B\varphi_B = (2m_B + 3m_C)\varphi = 3M_C\varphi_C \quad (2)$$

where φ_B is the osmotic coefficient of the solution containing sodium chloride only at molality M_B , φ_C is the osmotic coefficient of the solution containing calcium chloride only at molality M_C , and φ is the osmotic coefficient of the solution containing both sodium chloride at molality m_B and calcium chloride at molality m_C .

It is the activity coefficients of these two salts in the mixed solution that are required. These are obtained by means of the McKay-Perring equation [4]:

$$\ln \gamma_B = \ln \Gamma_B + \ln R + \int_0^{M_B\varphi_B} f(m, M_B, \gamma_C) d(M_B\varphi_B) \quad (3)$$

where γ_B is the activity coefficient of sodium chloride in the mixed solution and Γ_B that of sodium chloride in the reference solution at molality M_B . In eq (3),

$$f(m, M_B, \gamma_C) = \frac{1}{m^2} \left(\frac{\partial m}{\partial \ln \gamma_C} \right)_{a_w} + \frac{1}{m} - \frac{1}{M_B} \quad (4)$$

There are similar equations for $\ln \gamma_C$. It can be shown that, if the isopiestic ratio can be represented by eq (1), then the integral term in eq (3) reduces to:

$$\gamma_C^2 \int_0^{M_B\varphi_B} (b/M_B) d(M_B\varphi_B) \quad (5)$$

Figure 2 is a plot of (b/M_B) against $(M_B\varphi_B)$. The smooth curve is that of the equation

$$b/M_B = 0.0075 - 0.00243(M_B\varphi_B) + 0.000234(M_B\varphi_B)^2 \quad (6)$$

The integral in eq (3) now becomes:

$$\gamma_C^2 \{ 0.0075 - 0.00122(M_B\varphi_B) + 0.000078(M_B\varphi_B)^2 \} (M_B\varphi_B) \quad (7)$$

or

$$\gamma_C^2 \{ 0.0033 - 0.00053(M_B\varphi_B) + 0.00034(M_B\varphi_B)^2 \} (M_B\varphi_B) \quad (8)$$

if eq (3) is to be used with decadic logarithms.

There is some scatter of the points in figure 2 because it is not easy to get precise values of the b coefficient, especially from measurements on the more dilute solutions. But the maximum value of the integral that will

be used in subsequent calculations is only 0.0060; this occurs in the computation of the activity coefficient of calcium chloride in a mixture of total ionic strength $I=4$. Here the logarithm of the isopiestic ratio is -0.0691 and is therefore more important than the integral term. Consequently, we can tolerate some uncertainty about the exact form of the curve in figure 2. For example, had we considered the data best represented by the dashed straight line shown in figure 2, and carried out the integration of b/M_B with respect to $(M_B\varphi_B)$ accordingly, the value of the integral would still have been 0.0060.

The calculation of an activity coefficient can be illustrated by the following example. The mean of two results in set 6 of table 1 shows that a solution of 2.7736*m* sodium chloride was in isopiestic equilibrium with a solution of 1.5589*m* calcium chloride; the isopiestic ratios of the mixed solutions could be expressed as:

$$R = 1 + 0.1909\gamma_C - 0.0039\gamma_C^2 \quad (9)$$

It has been shown [eq (15) of ref. 2] that the composition of a mixed solution of total ionic strength I in isopiestic equilibrium with a solution of sodium chloride of molality M_B can be obtained by solving the quadratic equation:

$$bI\gamma_C^2 + (aI + M_B)\gamma_C = I - M_B \quad (10)$$

Putting $a = -0.1909$, $b = 0.0039$, $I = 4.5$, we find that $\gamma_C = 0.8944$ and hence, by eq (9), $R = 1.1676$, $\log R = 0.0673$. But $m = m_B + 1.5m_C = M_B/R = 2.3755$ and therefore $m_B = 0.2509$, $m_C = 1.4164$. At $M_B = 2.7736$, $\log \Gamma_B = -0.1542$ [5]; $\log R$ is 0.0673 and, from eq (8), the integral contributes 0.0052. Hence, by eq (3) $\log \gamma_B = -0.0817$. This is the logarithm of the activity coefficient of sodium chloride in the mixed solution at $I = 4.5$, $\gamma_C = 0.8944$.

The equation

$$\log \gamma_B = \log \gamma_B^0 - \alpha_B I_C \quad (11)$$

is often valid for systems at constant ionic strength.

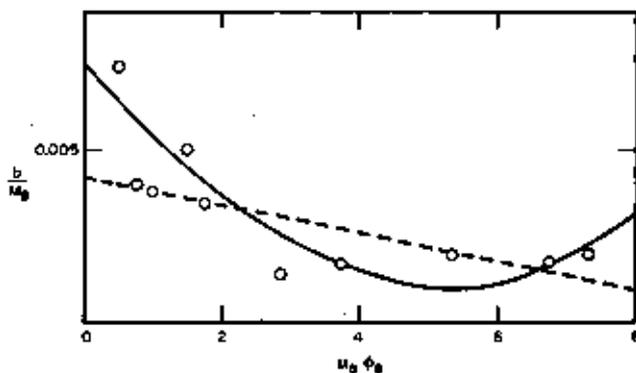


FIGURE 2. b/M_B versus $(M_B\varphi_B)$.

Here $\log \gamma_{\pm}^0 = -0.0830$ [5] is the logarithm of the activity coefficient of sodium chloride in its own solution at a total ionic strength (or molality) of 4.5 and $I_C = 3m_C = 4.2492$. Substituting in eq (11), $\alpha_B = -0.0013$.

Similar calculations show that the activity coefficient of calcium chloride in this mixture is given by $\log \gamma_C = -0.2065$. But for a solution of calcium chloride only at this total ionic strength ($I = 4.5, 1.5m$), $\log \gamma_C^0 = -0.1222$ [6]. Substituting in the equation

$$\log \gamma_C = \log \gamma_C^0 - \alpha_C I_B, \quad (12)$$

with $I_B = m_B = 0.2509$, gives $\alpha_C = -0.0047$.

In this way, values of α_B and α_C have been calculated at other values of the total ionic strength. They are given in table 3. The figures in parentheses indicate the set number in table 1 corresponding to the data from which the calculations were made. The values of α_B and α_C are plotted in figure 3. They lie on a smooth curve except for the values at $I = 0.75$ and 1.0; in these cases $\log \gamma_B$ and $\log \gamma_B^0$ are very close together and α_B is the result of dividing a small quantity by I_C , so that it is not surprising that there is some scatter. The same holds for the α_C values. "Best" values of α_B and α_C , read from figure 3, are given in the latter part of table 3 (the significance of the values at $I = 0$ in fig. 3 is explained in sec. 6). Table 3 also gives values of $(2\alpha_B + \alpha_C)$. It has been shown that for a system of this valence type $(2\alpha_B + \alpha_C)$ is independent of I if eq (11) and eq (12) are valid, that is to say, no terms in higher powers of I_B or I_C are needed. Values of $0.5(2\alpha_B + \alpha_C)$ are plotted in figure 3; there is a small variation of $(2\alpha_B + \alpha_C)$ with I . It could be explained by introducing $\beta_B I_C^2$ and $\beta_C I_B^2$ terms into eq (11) and eq (12), respectively, but β_B and β_C would be so small that their effect on $\log \gamma_B$ and $\log \gamma_C$ would be beyond the experimental error.

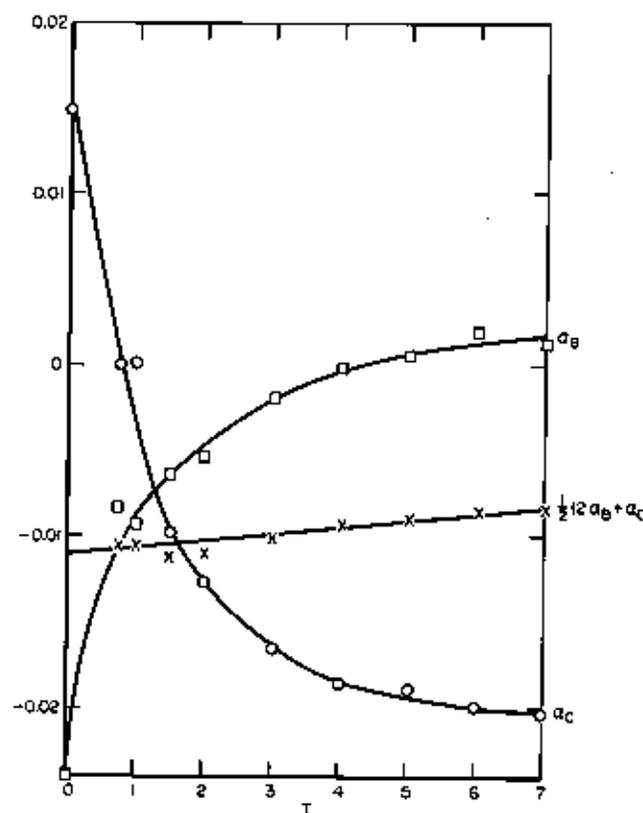


FIGURE 3. α_B , α_C , and $0.5(2\alpha_B + \alpha_C)$.

6. Values of α_B and α_C in Dilute Solutions

We now consider what values α_B and α_C might be expected to have when the total ionic strength becomes very small. For this purpose we write for the activity coefficient of the i th ion in a mixed solution [7, 8]:

$$\log \gamma_i = \log \gamma_i^0 + \sum_j B_{ij} m_j \quad (13)$$

Here γ_i^0 is the activity coefficient calculated on the assumption that the only interionic interaction is of the Debye-Hückel type; it can be expressed as

$$\log \gamma_i^0 = \frac{-z_i^2 A I^{1/2}}{1 + 1.5 I^{1/2}} \quad (14)$$

where z_i is the valence of the i th ion. B_{ij} is a coefficient characteristic of the interaction between an i th ion and a j th ion and, in accordance with the Brønsted Principle of Specific Interaction, the summation is to be made over all pairs of oppositely charged ions. Thus, in a solution containing both sodium chloride and calcium chloride,

$$\log \gamma_{Cl} = \log \gamma_{Cl}^0 + B_{Na,Cl} m_{Na} + B_{Ca,Cl} m_{Ca} \quad (15)$$

TABLE 3. Values of α_B and α_C calculated from data in table 1

| I | α_B | α_C | "Best" values | | $(2\alpha_B + \alpha_C)$ |
|------|------------|-------------|---------------|------------|--------------------------|
| | | | α_B | α_C | |
| 0.75 | -0.0073(1) | 0 | -0.0106 | 0.0025 | -0.0207 |
| 1.0 | -0.0022(2) | 0.0002(2) | -0.0092 | -0.0020 | -0.0204 |
| 1.5 | -0.0063(3) | -0.0089(3) | -0.0063 | -0.0048 | -0.0224 |
| 2.0 | -0.0052(4) | -0.0130(4) | -0.0047 | -0.0126 | -0.0220 |
| | -0.0054(5) | -0.0123(5) | | | |
| 5.0 | -0.021(5) | -0.0163(5) | -0.0018 | -0.0165 | -0.0201 |
| | -0.014(6) | -0.0165(6) | | | |
| 4.0 | -0.006(6) | -0.0186(6) | 0 | -0.0186 | -0.0186 |
| | -0.006(7) | -0.0185(7) | | | |
| 5.0 | -0.007(7) | -0.0190(7) | 0.0007 | -0.0192 | -0.0178 |
| | -0.006(8) | -0.0186(8) | | | |
| 6.0 | -0.016(8) | -0.0190(8) | 0.0016 | -0.0198 | -0.0166 |
| | -0.024(9) | -0.0200(9) | | | |
| 7.0 | -0.014(9) | -0.0204(9) | 0.0020 | -0.0208 | -0.0163 |
| | -0.014(10) | -0.0202(10) | | | |

$$\log \gamma_{Na} = \log \gamma^{\#} + B_{Na, Cl} m_{Cl} \quad (16)$$

$$\log \gamma_{Ca} = 4 \log \gamma^{\#} + B_{Ca, Cl} m_{Cl} \quad (17)$$

Writing $B_{Na, Cl} = B_B$ and $B_{Ca, Cl} = B_C$ for brevity, and remembering that $2 \log \gamma_B = \log \gamma_{Na} + \log \gamma_{Cl}$ and $3 \log \gamma_C = \log \gamma_{Ca} + 2 \log \gamma_{Cl}$,

$$\log \gamma_B = \log \gamma^{\#} + (m_B + m_C)B_B + \frac{1}{2}m_C B_C \quad (18)$$

and

$$\log \gamma_C = 2 \log \gamma^{\#} + 2/3 m_B B_B + 1/3 (m_B + 4m_C) B_C \quad (19)$$

The activity coefficient of either salt in its own solution in the absence of the other salt, at a total ionic strength I , is now given as:

$$\log \gamma_B^0 = \log \gamma^{\#} + I B_B \quad (20)$$

$$\log \gamma_C^0 = 2 \log \gamma^{\#} + 4/9 I B_C \quad (21)$$

where $I_B = m_B$ and $I_C = 3m_C$. These equations enable us to evaluate B_B and B_C from data on dilute single salt solutions; using the values of Janz and Gordon [9] for sodium chloride and of McLeod and Gordon [10] for calcium chloride, we find $B_B = 0.007$ and $B_C = 0.176$.

By $\gamma^{\#}$ we designate the 'trace' activity coefficient of a salt, that is the activity coefficient of a salt when it is present in vanishingly small amount in a solution which contains virtually only the other salt. Equation (18) gives

$$\log \gamma_B^{\#} = \log \gamma^{\#} + 1/3 I (B_B + \frac{1}{2} B_C) \quad (22)$$

and eq (19)

$$\log \gamma_C^{\#} = 2 \log \gamma^{\#} + 1/3 I (2B_B + B_C) \quad (23)$$

Hence,

$$\alpha_B = 1/I \cdot \log \gamma_B^0 / \gamma_B^{\#} = 2/3 B_B - 1/6 B_C \quad (24)$$

and

$$\alpha_C = 1/I \cdot \log \gamma_C^0 / \gamma_C^{\#} = 1.9 B_C - 2/3 B_B \quad (25)$$

Substituting numerical values for B_B and B_C , we find $\alpha_B = -0.024$, $\alpha_C = 0.015$. These values are shown in figure 3 at $I=0$. It will be seen that they are consistent with a reasonable extrapolation of the experimental values at finite concentrations. But $(2\alpha_B + \alpha_C) = -0.0165$, which is in poor agreement with the value of -0.0110 extrapolated from the experimental values. This suggests that the behavior of this system may be more complicated in more dilute solutions.

7. Trace Activity Coefficients

In the case when $I_C \rightarrow I (m_B \rightarrow 0)$ in eq (11), the trace activity coefficient of sodium chloride is given by

$$\log \gamma_B^{\#} = \log \gamma_B^0 - \alpha_B I \quad (26)$$

and similarly

$$\log \gamma_C^{\#} = \log \gamma_C^0 - \alpha_C I \quad (27)$$

Using the values of α_B and α_C in table 3, values of the trace activity coefficients have been calculated. They are shown in figure 4 along with plots of the activity coefficients of each of the salts in its own solution (γ_B^0 , γ_C^0). This figure is used to emphasize the fact that, at constant total ionic strength, the addition of calcium chloride has only slight effect on the activity coefficient of sodium chloride. On the contrary, addition of sodium chloride has considerable effect on the activity coefficient of calcium chloride.

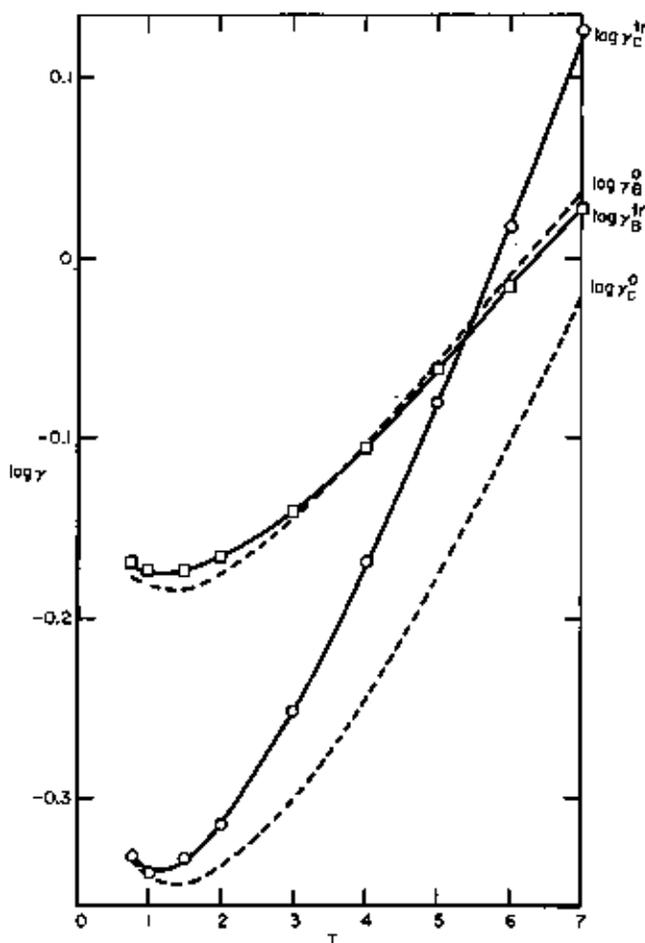


FIGURE 4. Activity coefficients of sodium chloride and calcium chloride.
 - - - - - Activity coefficient of a salt in its own solution.
 ——— Trace activity coefficient.

8. Comparison With Previous Work

Lanier [11] has used the sodium ion-sensitive glass electrode to measure the activity coefficient of sodium chloride in calcium chloride solutions. In table 4 we compare his values of α_B with those obtained in the present work, and also values of $\log \gamma_{\pm}^{\circ}$ calculated therefrom. The agreement is excellent at $I=3.0$ and $I=6.0$. The agreement between the two values of α_B at $I=1.0$ is not so good, but the values of $\log \gamma_{\pm}^{\circ}$ are in fair agreement.

TABLE 4. Comparison of α_B and $\log \gamma_{\pm}^{\circ}$ values

| I | α_B | | $-\log \gamma_{\pm}^{\circ}$ | |
|-----|------------|-------------|------------------------------|--------|
| | This work | Lanier [11] | This work | Lanier |
| 1.0 | -0.0092 | -0.0040 | 0.173 | 0.178 |
| 3.0 | -.0018 | -.0029 | .142 | .140 |
| 6.0 | .0016 | .0013 | .016 | .014 |

9. Excess Free Energy of Mixing

It has been shown [2] that the excess free energy of mixing 0.5 kg of water containing 0.5 I moles of a 1:1 salt and 0.5 kg of water containing 0.5($I/3$) moles of a 1:2 salt, giving a kilogram of water containing 0.5 I moles of the first salt and 0.5($I/3$) moles of the other, the total ionic strength of all three solutions being I , is given by the expression:

$$\frac{\Delta G^E}{2.303RT} = -\frac{I^2}{8}(2\alpha_B + \alpha_C) \quad (28)$$

provided that eq (11) and eq (12) hold. Using the values of α_B and α_C in table 3, the excess free energy of the sodium chloride-calcium chloride system can be calculated, giving the values shown in table 5.

TABLE 5. Excess free energy of mixing at 25 °C

| I | 0.75 | 1 | 1.5 | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------|------|---|-----|----|----|----|----|-----|-----|
| ΔG^E | 2 | 4 | 9 | 15 | 31 | 51 | 76 | 102 | 136 |

ΔG^E is expressed in calories per kilogram of water, 1 calvin = 4.1840 J.

These values of the excess free energy of mixing are opposite in sign but comparable in magnitude with those for the sodium chloride-barium chloride and potassium chloride-barium chloride systems.

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