[Contribution from the Sterling Chemistry Laboratory, Yale University]

The Activity Coefficient of Calcium Nitrate in Aqueous Solution at 25° from Isopiestic Vapor Pressure Measurements

By R. A. Robinson[1]

The literature records two calculations of the activity coefficient of calcium nitrate which are not in agreement with each other. Redlich and Rosenfeld[2] obtained the activity coefficient between 0.001 M and 4.58 M from freezing point data and made a small correction to 25°, using the thermal data of Lange and Streeck[3]; their activity coefficient curve lies below that of barium chloride, indicative of the small "distance of closest approach" of the ions which would be expected if calcium nitrate is an incompletely dissociated electrolyte[4] exhibiting ion-pair formation of the Bjerrum type.

Pearce and Blackman[5] also have given values for the activity coefficient of this salt from dynamic vapor pressure measurements. They give a value of $\gamma = 0.3894$ at 0.1 M which compares badly with $\gamma = 0.48$ from freezing point measurements; as they did not make measurements at concentrations less than 0.1 M it is probable that the value given by Redlich and Rosenfeld is a better estimate of the activity coefficient at 0.1 M but even if the data of Pearce and Blackman are referred to $\gamma = 0.48$ at 0.1 M there is a big discrepancy between the two determinations, especially above 1 M. Thus at 3 M concentration Pearce and Blackman obtained 0.4556 or 0.562 referred to $\gamma = 0.48$ at 0.1 M, whereas Redlich and Rosenfeld obtained 0.37. It was therefore a useful task to make some isopiestic measurements on this salt by the method already described.[6]

Experimental

Baker c. p. calcium nitrate was recrystallized twice and employed in the form of a solution whose concentration was determined by calcium analysis. A second stock solution was prepared from separately recrystallized material. The solutions of calcium nitrate were equilibrated with solutions of potassium chloride and the concentrations of the isopiestic solutions are recorded in Table I.

Table I

Concentrations of Isopiestic Solutions of Potassium Chloride and Calcium Nitrate

Molality		Molality		Molality	
KCl	$Ca(NO_3)_2$	KCl	$Ca(NO_3)_2$	KCl	$(CaNO_3)$
0.08238	0.06118	0.8845	0.6332	3.482	2.258
.1348	.1003	1.109	.7890	3.652	2.356
.1496	.1112	1.370	.9590	3.750	2.415
.1966	.1460	1.634	1.134	3.803	2.446
.2574	.1894	1.745	1.198	3.915	2.514
.2964	.2186	2.083	1.411	4.128	2.633
.4758	.3481	2.581	1.722	4.181	2.665
.5205	.3785	2.705	1.792	4.603	2.902
.5950	.4320	2.916	1.920	4.673	2.939
.7222	.5216	3.034	1.995	4.829	3.026
		3.118	2.044		

From this experimental material the osmotic and activity coefficients of calcium nitrate were evaluated, using the data for potassium chloride given by Robinson.[7] These coefficients are recorded in Table II; since the data do not suffice to fix the activity coefficient at 0.1 M the value of $\gamma = 0.48$, given by Redlich and Rosenfeld,[2] was used as a reference value at this concentration. Table II also contains the activity coefficients

Table II

Osmotic and Activity Coefficients of Calcium Nitrate at 25°

m	φ	γ	(From f. pt.)	(Pearce and Blackman)
0.1	0.826	(0.480)	(0.480)	(0.480)
.2	.818	.421	.42	.401
.3	.819	.391	...	...
.4	.822	.373	...	.339
.5	.826	.360	.38	...
.6	.832	.351	...	.319
.7	.840	.344	...	...
.8	.846	.339	...	.318
.9	.854	.336	...	...
1.0	.862	.334	.35	.326
1.2	.880	.332	...	...
1.4	.899	.333	...	...
1.6	.917	.335	...	...
1.8	.937	.339	...	...
2.0	.956	.343	.35	.426
2.5	1.005	.359	...	.489
3.0	1.055	.379	.37	.562

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(1) Sterling Fellow, Yale University, 1940.

(2) Landolt-Börnstein, "Tabellen," Dritter Ergänzungsband, p. 2142.

(3) E. Lange and H. Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

(4) E. C. Righelatto and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

(5) J. V. Pearce and L. E. Blackman, This Journal, **57**, 24 (1935); Pearce, *ibid.*, **58**, 376 (1936).

(6) R. A. Robinson and D. A. Sinclair, *ibid.*, **56**, 1830 (1934).

(7) R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).

recorded by Redlich and Rosenfeld and those determined by Pearce and Blackman,[5] the latter, for purpose of comparison, also being referred to $\gamma = 0.48$ at 0.1 *M*.

Discussion

The mean deviation between the activity coefficients determined by the isopiestic method and those obtained from freezing point data is 0.01 over the concentration range up to 3 *M*, the largest difference of 0.02 occurring at 0.5 *M*. The data of Pearce and Blackman are on the average only 0.024 lower than the isopiestic results up to 1 *M* but large deviations occur at 2, 2.5 and 3 *M* where the isopiestic and freezing point data yield good agreement. The isopiestic data therefore support the freezing point calculations of Redlich and Rosenfeld rather than the direct vapor pressure determination of Pearce and Blackman.

Up to 2.5 *M* the activity coefficient calculated by the equation

$$-\log\gamma = \frac{1.755\sqrt{c}}{1 + 2.222\sqrt{c}} - 0.0957\,c + \log(1 + 0.054\,m)$$

corresponding to a "distance of closest approach" of 3.9 Å., agrees with the observed values with a mean deviation of 0.002 and a maximum deviation of 0.004 in γ.

Summary

Isopiestic measurements have been made on solutions of calcium nitrate and potassium chloride at 25°. The osmotic and activity coefficients of the former have been evaluated over the range 0.1–3 *M*. Of two previous calculations of the activity coefficient from different data, that from freezing point measurements is in agreement with the activity coefficient now obtained.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Activity Coefficients of Sodium and Potassium Thiocyanate in Aqueous Solution at 25° from Isopiestic Vapor Pressure Measurements

BY R. A. ROBINSON[1]

If a comparison is made of the activity coefficients of alkali metal salts with a common anion at the same concentration, the activity coefficients are generally in the order Li > Na > K > Rb > Cs. This order holds for the chlorides, bromides, iodides, chlorates, perchlorates, etc. Less frequently salts are found in which the order is reversed, the best known examples being the hydroxides, formates and acetates. It has been noted[2] that this reversal in behavior usually occurs with salts possessing an unsymmetrical anion. The thermodynamic properties of the alkali thiocyanates have not been the subject of extensive investigation but they offer a further possibility of exploring the relation of the activity coefficient curves to the nature of the anion. The isopiestic vapor pressure method[3] has now been applied to sodium and potassium thiocyanate at 25°. The activity coefficient of the sodium salt, however, is found to be greater than that of the potassium salt at the same concentration; thus the order Na > K is found to hold in the case of an unsymmetrical anion; on the other hand, it is known[4] that reversal of the osmotic coefficient curves occurs with the fluorides where the anion is probably of the symmetrical noble gas type. Consequently, while the asymmetry of the anion may be one factor it is not the only one determining the order of the activity coefficient curves.

Experimental

Stock solutions of the thiocyanates prepared from Merck reagents were used, the potassium salt being recrystallized once. The solutions were analyzed for thiocyanate volumetrically, and equilibrated against solutions of potassium chloride, the thiocyanate solutions being contained in platinum dishes. The experimental results are given in Table I.

The osmotic and activity coefficients of the two thiocyanates have been evaluated with reference to the activity coefficient of potassium chloride given by Robinson.[5] They are recorded in Table II.

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(1) Sterling Fellow, Yale University, 1940.

(2) H. S. Harned, *Trans. Faraday Soc.*, **23**, 462 (1927).

(3) R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

(4) G. Scatchard and S. S. Prentiss, *ibid.*, **56**, 807 (1934).

(5) R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).