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.

New Haven, Conn. Received September 13, 1940

[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).

TABLE I

CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND SODIUM OR POTASSIUM THIOCYANATE

Sodium Thiocyanate

Molality		Molality		Molality	
KCl	NaCNS	KCl	NaCNS	KCl	NaCNS
0.1639	0.1608	0.9447	0.8832	2.896	2.555
.1647	.1616	1.097	1.018	3.122	2.745
.2840	.2757	1.298	1.192	3.124	2.746
.4053	.3911	1.428	1.307	3.373	2.938
.5170	.4923	1.506	1.374	3.717	3.228
.5170	.4930	1.887	1.705	3.895	3.384
.5929	.5627	1.970	1.776	4.229	3.641
.7354	.6910	2.226	1.993	4.249	3.650
.8624	.8045	2.621	2.326	4.622	3.982

Potassium Thiocyanate

KCl	KCNS	KCl	KCNS	KCl	KCNS
0.1639	0.1648	1.033	1.035	3.448	3.597
.3057	.3046	1.701	1.728	3.656	3.846
.5170	.5185	1.887	1.923	3.754	3.936
.5904	.5933	2.121	2.167	4.132	4.371
.6770	.6787	2.442	2.507	4.301	4.562
.8624	.8624	2.915	3.020	4.623	4.925

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM THIOCYANATE

m	NaCNS		KCNS	
	φ	γ	φ	γ
0.1	0.937	0.787	0.926	0.769
.2	.934	.750	.911	.716
.3	.935	.731	.904	.685
.5	.943	.715	.898	.646
.7	.954	.710	.896	.623
1.0	.969	.712	.896	.600
1.5	.998	.725	.894	.574
2.0	1.029	.751	.896	.558
2.5	1.061	.784	.901	.548
3.0	1.093	.820	.908	.542
3.5	1.126	.860	.913	.537
4.0	1.160	.911	.918	.533
4.5	...	...	.923	.531
5.0	...	...	.927	.529

There do not appear to be any data with which the results on sodium thiocyanate may be compared. Data on the potassium salt are also meager; Gibson and Adams[6] have made direct vapor pressure measurements over the concentration range 4.589 to 17.328 *M* at 20.28°. Redlich and Rosenfeld[7] have calculated activity coefficients from their results with reference to a value of $\gamma = 1$ at 4.589 *M*. Referred to $\gamma = 0.531$ at this concentration the data of Gibson and Adams lead to activity coefficients which decrease almost linearly with the concentration to a value of $\gamma = 0.486$ at 17.328 *M*. It may be shown graphically that the present data and those of Gibson and Adams are consistent.

The activity coefficient curves of these two thiocyanates are not symmetrical with those of the alkali halides. The curve given by potassium thiocyanate is lower than that for potassium chloride and intersects the curve for rubidium chloride at about 3.3 *M*. The curve for sodium thiocyanate is lower than that for sodium iodide and intersects the curve for sodium bromide at about 3 *M*.

Summary

Solutions of sodium and potassium thiocyanate have been compared with potassium chloride at 25° by isopiestic vapor pressure measurements and the activity coefficients have been evaluated.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 13, 1940

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[6] R. E. Gibson and L. H. Adams, THIS JOURNAL, **55**, 2679 (1933).

[7] Landolt-Börnstein, "Tabellen," Dritter Ergänzungsband, p. 2146.

[CONTRIBUTION NO. 202 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF TEXAS]

The Pressure–Volume–Temperature Relations of *n*-Hexane and of 2-Methylpentane

BY EDWARD A. KELSO[1] WITH W. A. FELSING

Object of the Investigation.—The increasing utilization of petroleum hydrocarbons for diversified purposes is demanding a more extended knowledge of the properties of the individual members. Numerous contributions have appeared in the chemical literature in the last few years on individual hydrocarbons. It was, therefore, one object of this investigation to determine the compressibilities of the hexanes; a report on *n*-hexane and 2-methylpentane is being made; work on 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane is being carried on now and will be reported later. It is hoped, at that time, to correlate structure with properties for all of the hexanes.

Method and Apparatus.—The apparatus for this investigation has been patterned after that described by Beattie.[2] The mercury injector was thermostated in a

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[1] Research Assistant, Project No. 1, University Research Institute.

[2] Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).