lengths of 6438 Å and 5875 Å and 24.8°C, and for the data reported here for 6328 Å and 25°C. The data given here and those of Waxler et al. (*6*) are in agreement to the curve within experimental error (0.00006 and 0.0001, respectively). For low pressure, atmospheric to 700 kg/cm^2, the data of all authors are within agreement but at higher pressures the data of Rosen (*2*) vary significantly from the results reported here and those of Waxler et al. (*6*). No reasons for these differences can be given without a detailed examination of the experimental instrumentation and procedures used. However, not having to correct for the distortion of the optical windows in the pressure vessel and measurement with an interferometer, which is very sensitive, suggest that the experimental data reported here and the data of Waxler and Weir (*5*) and Waxler et al. (*6*) are the more accurate.

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Determination of Activity Coefficients of Thiocyanic Acid and Salting-Out Effects in Mixture of Electrolytes from Extraction Data

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Activity coefficients of aqueous HSCN, determined in a previous publication, were used to determine activity coefficients of HSCN in the presence of foreign electrolytes. Determinations, made in systems containing an electrolyte with a common ion ($HClO_4$ and NaSCN) and in a system containing no common ion ($NaClO_4$), were derived from distribution data using a nonpolar organic solvent, xylene. Salting-out capacities of the three foreign electrolytes were compared by determining Harned's coefficients for each system.

Extractions of metal thiocyanate complexes from aqueous solutions into water-immiscible solvents have extensive uses in separation of metals with similar chemical properties, such as zirconium and hafnium (*3*, *8*). In most of these systems, the metal thiocyanates are extracted from highly salted solutions, but the extraction behavior of HSCN in such solutions has always been difficult to explain. HSCN does extract from an aqueous solution into a polar solvent, isobutyl methyl ketone (IBMK), and into a nonpolar solvent, xylene (*6*). The activity coefficients of aqueous HSCN have been determined by Bartlett et al. (*2*).

Using the above data, the author has determined the activity coefficients of HSCN in the presence of foreign electrolytes. These results could be useful in the elucidation of the role played by HSCN in the extraction of metal thiocyanates. Xylene was used for the extraction of HSCN since the dissociation of HSCN in a nonpolar solvent is negligible. Similar work has been conducted on HNO_3 in the presence of HCl (*9*), $HClO_4$ (*7*), and $CaCl_2$ (*1*) and on HCl in the presence of NaCl (*4*).

EXPERIMENTAL

Thiocyanic acid was prepared by mixing equivalent amounts of sodium thiocyanate and hydrochloric acid and was extracted into IBMK. Any HCl or NaSCN mechanically entrapped in the IBMK was completely removed by washing the IBMK three times with water. Upon back-extraction of the IBMK with water, aqueous HSCN was obtained. Any IBMK entrapped in the aqueous phase was removed by extraction with benzene which, in turn, was removed by bubbling nitrogen through the solution. The final concentration of aqueous HSCN was determined volumetrically.

During determination of activity coefficients by Bartlett et al. (*2*), the presence of H_2S could be detected above the solution when left overnight, indicating aqueous HSCN decomposition which was prevented by preparing fresh samples every 4 hr.

The activity coefficients of HSCN, in the presence of a second electrolyte, were determined from distribution data. The HSCN was distributed between an aqueous solution containing variable concentrations of the electrolyte and xylene. Extraction experiments were carried out by the batch extraction method in a thermostat bath kept at 25.0 ± 0.5°C. Equilibrium in the extraction of HSCN into xylene was reached within 2 min. Separation of the two phases was aided by centrifugation.

Equilibrium concentrations of HSCN in both phases were determined by direct titration with standard sodium hydroxide, using bromocresol green as indicator. In the titration of HSCN in xylene with aqueous NaOH, distribution of HSCN between xylene and water is an equilibrium reaction. Since NaOH neutralizes HSCN in the aqueous phase, the equilibrium reaction at the end point is shifted over completely to the aqueous phase. To ensure that the end point had been reached, the xylene–water mixture was shaken well for a further 3 min.

Extraction of $HClO_4$, NaSCN, and $NaClO_4$ into xylene was determined in a preliminary experiment with concentrations covering a range from 0–2.0 in the electrolyte. NaSCN and $NaClO_4$ were determined using a flame photometer with an accuracy of ±5%, and $HClO_4$ was determined volumetrically.

RESULTS AND DISCUSSION

Activity coefficients of HSCN are assumed to remain constant in xylene since HSCN is unlikely to dissociate in a nonpolar solvent. No $HClO_4$, NaSCN, or $NaClO_4$ was extracted into xylene within the concentration ranges used. Consequently, the activity coefficients of HSCN could be determined on the basis that the activities of HSCN in two different aqueous phases, in equilibrium with organic phases containing the same concentration of HSCN, are equal. If a_1 is equal to the activity of HSCN in a mixture of electrolytes, and a_o is equal to the activity of pure HSCN

$$a_o = a_1 \tag{1}$$

Table I. Molal Activity Coefficients of HSCN in Foreign Electrolytes

Aqueous phase		Organic phase,				
M $NaClO_4$	M HSCN	M HSCN	$\chi°$, m	$\gamma_\pm°$	χ', m	$\gamma_\pm'$
0M	0.1562	0.0004	0.200	0.745		
	0.2388	0.0009	0.400	0.730		
	0.2980	0.0013	0.500	0.730		
	0.4884	0.0034	0.600	0.730		
	0.6836	0.0069	0.700	0.732		
	0.8090	0.0100	0.800	0.734		
	0.9850	0.0149	0.900	0.736		
0.25M	0.2550	0.0011	0.200	0.745	0.200	0.745
	0.3420	0.0019	0.400	0.730	0.387	0.755
	0.5120	0.0043	0.500	0.730	0.475	0.768
	0.5950	0.0060	0.600	0.730	0.568	0.771
	0.6628	0.0072	0.700	0.732	0.660	0.776
	0.7600	0.0101	0.800	0.734	0.751	0.782
	0.8940	0.0137	0.900	0.736	0.841	0.787
0.50M	0.2540	0.0010	0.200	0.745	0.200	0.745
	0.3840	0.0024	0.400	0.730	0.387	0.755
	0.5060	0.0045	0.500	0.730	0.470	0.777
	0.5960	0.0064	0.600	0.730	0.550	0.796
	0.6320	0.0061	0.700	0.732	0.645	0.794
	0.6620	0.0079	0.800	0.734	0.738	0.795
	0.7350	0.0099	0.900	0.736	0.810	0.817
1.0M	0.2096	0.0008	0.200	0.745	0.191	0.780
	0.3124	0.0019	0.400	0.730	0.356	0.820
	0.4192	0.0034	0.500	0.730	0.436	0.837
	0.5370	0.0061	0.600	0.730	0.521	0.841
	0.6240	0.0082	0.700	0.732	0.593	0.863
	0.6710	0.0099	0.800	0.734	0.669	0.877
	0.7360	0.0122	0.900	0.736	0.742	0.891
1.5M	0.1910	0.0009	0.400	0.745	0.308	0.968
	0.2860	0.0020	0.500	0.730	0.380	0.961
	0.3820	0.0037	0.600	0.730	0.454	0.965
	0.4750	0.0059	0.700	0.730	0.528	0.968
	0.5690	0.0089	0.800	0.732	0.593	0.988
	0.6660	0.0126	0.900	0.734	0.655	0.993
2.0M	0.1370	0.0006	0.200	0.745	0.129	1.155
	0.2050	0.0013	0.400	0.730	0.273	1.070
	0.2720	0.0024	0.500	0.730	0.284	1.285
	0.3400	0.0039	0.600	0.730	0.344	1.273
	0.4080	0.0058	0.700	0.732	0.454	1.128
	0.4540	0.0074	0.800	0.734	0.514	1.142
	0.5420	0.0110	0.900	0.736	0.560	1.165
M NaSCN						
0.25M	0.1650	0.0010	0.200	0.745	0.119	1.252
	0.2300	0.0016	0.400	0.730	0.282	1.035
	0.2970	0.0024	0.500	0.730	0.382	0.955
	0.3600	0.0032	0.600	0.730	0.485	0.903
	0.4556	0.0048	0.700	0.732	0.581	0.881
	0.5487	0.0064	0.800	0.734	0.676	0.868
	0.6840	0.0095	0.900	0.736	0.774	0.855
0.50M	0.1310	0.0012	0.100	0.774	0.026	2.962
	0.2310	0.0024	0.200	0.745	0.067	2.224
	0.2960	0.0034	0.400	0.730	0.212	1.377
	0.4390	0.0062	0.500	0.730	0.304	1.201
	0.5699	0.0097	0.600	0.730	0.397	1.103
	0.6370	0.0116	0.700	0.732	0.482	1.062
M NaSCN	M HSCN	M HSCN	$\chi°$, m	$\gamma_\pm°$	χ', m	$\gamma_\pm'$
0.50M (*Contd.*)	0.7086	0.0139	0.800	0.734	0.566	1.037
	0.8720	0.0211	0.900	0.736	0.650	1.018
1.00M	0.1556	0.0028	0.200	0.745	0.036	4.139
	0.2083	0.0039	0.400	0.730	0.124	2.355
	0.3108	0.0064	0.500	0.730	0.191	1.911
	0.3626	0.0079	0.600	0.730	0.261	1.679
	0.4124	0.0096	0.700	0.732	0.279	1.835
	0.4699	0.0115	0.800	0.734	0.406	1.446
	0.5631	0.0154	0.900	0.736	0.485	1.365
1.50M	0.0850	0.0022	0.200	0.745	0.024	6.208
	0.1710	0.0048	0.400	0.730	0.086	3.395
	0.2319	0.0075	0.500	0.730	0.132	2.765
	0.2761	0.0092	0.600	0.730	0.182	2.407
	0.3394	0.0120	0.700	0.732	0.232	2.207
	0.4139	0.0156	0.800	0.734	0.287	2.045
	0.5070	0.0211	0.900	0.736	0.343	1.930
2.00M	0.1579	0.0073	0.200	0.745	0.015	9.933
	0.1794	0.0088	0.400	0.730	0.050	5.984
	0.2380	0.0118	0.500	0.730	0.080	4.563
	0.2701	0.0144	0.600	0.730	0.117	3.744
	0.3334	0.0179	0.700	0.732	0.153	3.346
	0.4944	0.0309	0.800	0.734	0.194	3.027
M $HClO_4$						
0.249M	0.0752	0.0003	0.200	0.745	0.165	0.902
	0.2252	0.0016	0.400	0.730	0.284	1.028
	0.3073	0.0023	0.500	0.730	0.395	0.924
	0.3778	0.0033	0.600	0.730	0.503	0.871
	0.4314	0.0043	0.700	0.732	0.604	0.848
	0.5434	0.0058	0.800	0.734	0.697	0.841
	0.6887	0.0092	0.900	0.736	0.787	0.835
0.498M	0.2559	0.0028	0.300	0.745	0.091	1.637
	0.3075	0.0039	0.400	0.730	0.193	1.513
	0.4720	0.0074	0.600	0.730	0.382	1.147
	0.5290	0.0089	0.700	0.732	0.465	1.101
	0.6314	0.0121	0.800	0.734	0.545	1.077
	0.8871	0.0233	0.900	0.736	0.624	1.062
0.996M	0.2152	0.0046	0.200	0.745	0.052	2.865
	0.2900	0.0073	0.400	0.730	0.124	2.355
	0.3667	0.0094	0.500	0.730	0.173	2.110
	0.4630	0.0138	0.600	0.730	0.235	1.864
	0.5300	0.0016	0.700	0.732	0.299	1.712
	0.6140	0.0202	0.800	0.734	0.366	1.604
1.494M	0.0474	0.0017	0.200	0.745	0.029	5.138
	0.0988	0.0035	0.400	0.730	0.062	4.710
	0.1442	0.0055	0.500	0.730	0.098	3.724
	0.1795	0.0071	0.600	0.730	0.139	3.151
	0.2475	0.0102	0.700	0.732	0.181	2.829
	0.2796	0.0132	0.800	0.734	0.225	2.609
	0.3456	0.0156	0.900	0.734	0.277	2.386
1.992M	0.1157	0.0076	0.200	0.745	0.015	9.933
	0.1541	0.0099	0.400	0.730	0.036	8.111
	0.1716	0.0130	0.300	0.730	0.057	6.404
	0.2321	0.0157	0.600	0.730	0.085	5.153
	0.3122	0.0223	0.700	0.732	0.114	4.491

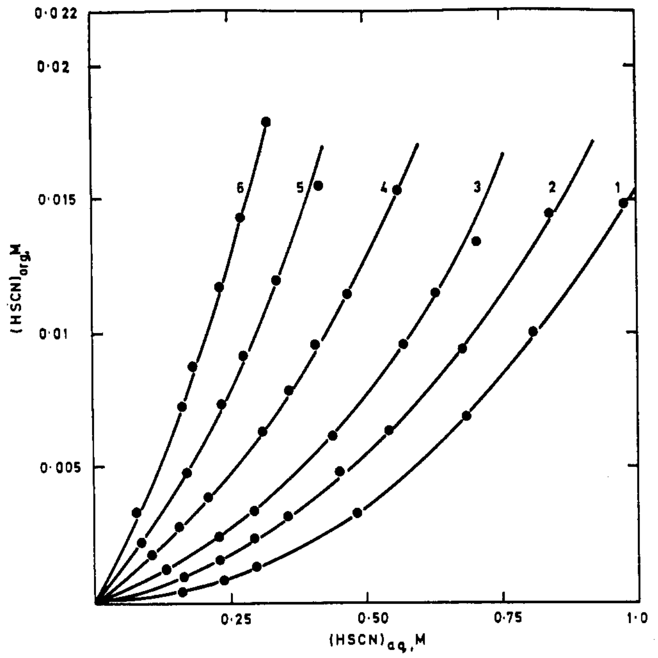

Figure 1. Extraction curves for HSCN at constant NaSCN concentrations

1. 0M NaSCN
2. 0.25M NaSCN
3. 0.50M NaSCN
4. 1.00M NaSCN
5. 1.50M NaSCN
6. 2.00M NaSCN

When activity coefficients are introduced into Equation 1, Equation 2 is derived:

$$\gamma_\pm' = \frac{\gamma_\pm^\circ m_0}{m_1} \qquad (2)$$

where m_0 is the molality of pure HSCN, m_1 is the molality of HSCN in the mixture, $\gamma_\pm^\circ$ is the molal activity coefficients of pure HSCN, and $\gamma_\pm'$ is the molal activity coefficients of HSCN in the mixture.

The extraction curves (Figure 1) for HSCN with variable NaSCN concentration, used in conjunction with Equation 2 to determine $\gamma_\pm'$, are typical of those found for the other two systems. The densities, determined at 25°C with a pycnometer, were necessary for the conversion of the concentration in molarity (M) to molality (m) for $HClO_4$ and NaSCN and were taken from the International Critical Tables (*5*).

The molal activity coefficients of HSCN in a mixture of electrolyte for all three systems are tabulated in Table I. Molal activity coefficients $\gamma_\pm^\circ$, determined by Bartlett et al. (*2*), have a precision of ± 0.005. Accuracy of the concentration of HSCN in the aqueous phase is limited by the accuracy of volumetric titrations of a strong base and strong acid. The duplicate titrations of HSCN in the organic phase in all three systems agreed within 1%, but the accuracy of the determination does not exceed 2%. $HClO_4$ increases the activity coefficients to the greatest extent, while $NaClO_4$ has the least effect.

The equation derived by Harned (*4*) for the system HCl–NaCl,

$$\log \gamma_\pm(\chi, m) = \log \gamma_\pm(\chi, o) - \alpha_B m_c \qquad (3)$$

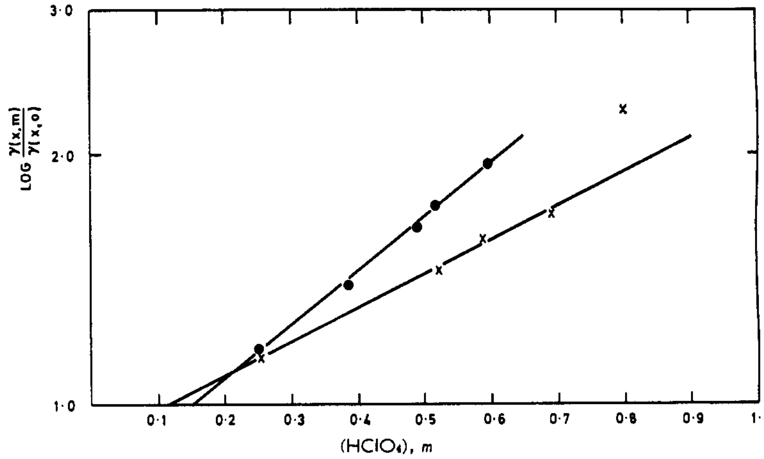

Figure 2. Variation of molal activity coefficients of HSCN with change in molality of $HClO_4$ at constant total molality (m)

x. $m = 1.0$
●. $m = 0.8$

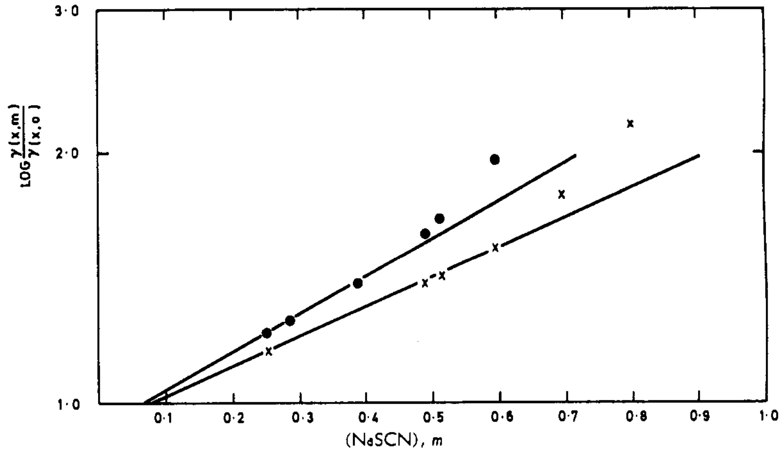

Figure 3. Variation of molal activity coefficients of HSCN with change in molality of NaSCN at constant total molality (m)

x. $m = 1.0$
●. $m = 0.8$

describes the variation of the molal activity coefficient of HSCN in a mixture of electrolytes as a function of the molality (m_c) of the second electrolyte. $\gamma_\pm(\chi, m)$ is the molal activity coefficient of HSCN in a solution containing a second electrolyte at a certain molality, and $\gamma_\pm(\chi, o)$ is the molal activity coefficient of pure HSCN at the same total molality. Harned's coefficient, α_B, is a function of the total molality of the solution but is independent of the variation of m_c and can be used as an indication of the salting-out capacity of a foreign electrolyte in a system. Figures 2 and 3 show the validity of Equation 3 for the systems HSCN-$HClO_4$ and HSCN-NaSCN at a total molality of 0.8*m* and 1.0*m*. At NaSCN concentrations exceeding 0.5*m*, deviations from linearity exist but can be attributed to a limit in the accuracy of the experimental results at these concentrations. Extractions of HSCN in the presence of $NaClO_4$ were too low to derive an equation of type 3 to any accuracy.

The α_B value found for the systems HSCN-$HClO_4$ ($\alpha_B = -0.508$ at $m = 1.0$, and $\alpha_B = -0.627$ at $m = 0.8$) and HSCN-NaSCN ($\alpha_B = -0.486$ at $m = 1.0$, and $\alpha_B = -0.532$ at $m = 0.8$) illustrates that $HClO_4$ exerts a greater salting-out effect upon HSCN than NaSCN. The greater the hydration number of the salting-out agent, the less "free water" exists in the vicinity of HSCN, resulting in an increase in the effective concentration of HSCN. Since the hydration of H^+ is greater than Na^+, $HClO_4$ would increase the extraction of HSCN more than NaSCN.

Harned's coefficients determined for the systems HNO_3-$HClO_4$ (*3*) ($\alpha_B = -0.048$ at $m = 1.0$) and HCl-NaCl (*5*) ($\alpha_B = +0.0315$ at $m = 1.0$) show that $HClO_4$ and NaCl have less effective salting-out capacities in these systems than the salting-out effect of $HClO_4$ and NaSCN upon HSCN. If HSCN is less strongly hydrated than $HClO_4$ and NaSCN, the addition of either $HClO_4$ or NaSCN will cause a large increase in the effective concentration of the HSCN and, consequently, an increase in the activity coefficients.

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Radiometric Determination of Solubility and Excess Volume in Molten Systems of Cadmium–Cadmium Bromide and Cadmium–Cadmium Iodide

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Solubility limits and excess volumes in Cd–$CdBr_2$ and Cd–CdI_2 liquid solutions were determined by a γ-ray absorption method described previously. This method was modified and developed. For both systems the phase diagram reported by Topol and Landis was confirmed. The proportionality of the excess volumes of these systems, as well as Cd–$CdCl_2$ solution, to the product of the molar fractions of both components was sought. The excess volumes were positive in Cd–$CdCl_2$, nearly zero in Cd–$CdBr_2$, and negative in Cd–CdI_2 liquid systems.

Previously, we presented a radiometric method for the determination of the solubility limits and excess volumes in liquid binary solutions at high temperatures (*11–13*). This method, consisting of measurements of the absorption of γ-rays by these solutions, was successfully applied to the Cd-$CdCl_2$ molten system at 903–1073°K. The limiting solubility of the metal, as dependent on temperature, agreed with the results of classical measurements reported in the literature. The excess volume determination proved possible with an accuracy slightly lower than that obtained in molten salt systems by other methods (*2, 5, 9, 15*).

If we consider the results obtained for the Cd-$CdCl_2$ system, the radiometric method seems particularly appropriate for the determination of excess volume in liquid solutions of metals in their own molten salts. In the literature concerning those systems, few data exist on the excess volume, which has been determined in bismuth–bismuth halide solutions only (*6–8*).

Knowledge of excess volumes is important for structural investigations of liquid solutions. In this study excess volumes in Cd-$CdBr_2$ and Cd-CdI_2 liquid systems were determined.

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