plots of σ_t^2 vs. arrest time are shown in Figures 1 and 2. Taking into account all the precautions discussed above the maximum possible error in the experimental results can be of the order of error in the peak width measurements.

Conclusion

Arrested flow technique has been used to measure binary gas diffusion coefficients of organic vapors in nitrogen. This technique is the quickest and reasonably accurate method available to the experimentalists today. The observed values of the diffusion coefficients are in excellent agreement with values predicted from Fuller's correlation, and for the four systems N_2–acetone, N_2–chloroform, N_2–carbon tetrachloride, and N_2–nitrobenzene, the experimental values match nicely with those reported in the literature. Experiments are in progress to extend the data base for other organic vapors with nitrogen and hydrogen as the carriers. It is also proposed to conduct experiments covering a wider range of temperatures.

Glossary

A	cross-sectional area, cm^2
D_{AB}	binary diffusion coefficient, cm^2/s
F, F_c	volumetric flow rates, cm^3/s
P_{fm}, P_W	flow meter and water-vapor pressure at T_{fm}, atm
t	arrest time, s
T, T_{fm}	temperatures of column and flow meter, K
P_i, P_o	column inlet and outlet pressures, atm
V	linear velocity, cm/s
W	peak width at base, cm

Greek Letters

σ_t	standard deviation, s^2
μ	micro

Registry No. 1-Propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; acetone, 67-64-1; methyl isobutyl ketone, 108-10-1; chloroform, 67-66-3; carbon tetrachloride, 56-23-5; nitrobenzene, 98-95-3; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; *o*-nitrotoluene, 88-72-2; tetrachloroethane, 79-34-5.

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Activity Coefficients of Hexaamminecobalt(III) Iodate in Aqueous Solutions of Different Electrolytes

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The solubility of hexaamminecobalt(III) iodate in aqueous solutions of NaCl, KCl, NH_4Cl, $NaNO_3$, KNO_3, NH_4NO_3, NaBr, KBr, NH_4Br, $(CH_3)_4NBr$, $(C_2H_5)_4NBr$, $(C_3H_7)_4NBr$, and $(C_4H_9)_4NBr$ has been determined over an ionic strength range of 0.032–0.20 mol kg^{-1} at 298.15 K by a spectrophotometric method. The solubility results were treated to yield the relative activity coefficients.

Introduction

Investigations of the thermodynamic properties of aqueous solutions of mixed electrolytes are interesting because they serve to study ion–ion interactions. A detailed examination of activity coefficients, especially by means of solubility measurements, has shown (*1–3*) the activity of ions to depend markedly on their individual natures and also to be influenced by the nature of the ions of the salt solutions serving as solvents.

The present investigation is designed to complement the previous study of the effect of different electrolytes on the solubility of $(Co(NH_3)_6)_2(C_2O_4)_3$ and of $Co(NH_3)_6Fe(CN)_6$. The relative activity coefficients of hexaamminecobalt(III) iodate in the presence of different electrolytes were evaluated from solubility determinations and are reported in this work.

Experimental Section

Materials. Hexaamminecobalt(III) iodate was prepared by precipitation of hexaamminecobalt(III) chloride with an aqueous solution of sodium iodate (Carlo-Erba RPE), as described in the literature (*3*, *4*) and was recrystallized. Analysis gave the following mass percentages: Co, 8.4 and NH_3, 15.0. The calculated values for $Co(NH_3)_6(IO_3)_3$ are Co, 8.6 and NH_3, 14.9. Hexaamminecobalt(III) chloride was the same as that used in previous work (*1*, *2*). All the other salts were Merck, Riedel,

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Table I. Solubility of Hexaamminecobalt(III) Iodate in Solutions of Different Electrolytes[a]

added electrolyte	$10^2 m/m^0$	$10^3 S/m^0$	$10^2 m/m^0$	$10^3 S/m^0$	$10^2 m/m^0$	$10^3 S/m^0$
NaCl	2.541	6.277	2.575	6.322	6.875	7.688
	7.290	7.751	9.881	8.461	12.246	8.947
	13.753	9.379	15.448	9.739		
KCl	1.299	5.819	2.749	6.465	4.847	7.148
	7.150	7.849	9.374	8.479	11.335	8.929
	13.292	9.361	14.131	9.613		
NH_4Cl	2.992	6.520	5.472	7.310	7.182	7.822
	11.271	8.893	11.413	8.965	14.224	9.612
	14.425	9.649				
$NaNO_3$	2.713	6.484	3.158	6.664	5.170	7.310
	7.635	8.047	9.207	8.434	10.692	8.848
	12.658	9.415	15.119	9.955		
KNO_3	1.966	6.125	3.289	6.609	5.087	7.184
	6.917	7.742	8.165	8.065	9.450	8.443
	12.775	9.217	14.824	9.649		
NH_4NO_3	2.726	6.556	3.373	5.807	6.202	7.688
	7.313	8.065	8.583	8.425	11.735	9.253
	12.683	9.523	15.474	10.145		
NaBr	2.444	6.466	3.179	6.699	5.159	7.364
	7.096	7.957	8.591	8.353	10.382	8.785
	12.690	9.361	15.788	10.151		
KBr	2.175	6.340	2.630	6.556	4.831	7.274
	7.133	7.966	8.944	8.497	11.203	9.072
	12.667	9.414	14.848	10.012		
NH_4Br	1.898	6.259	2.887	6.663	5.668	7.571
	6.946	7.957	9.519	8.677	11.061	9.055
	11.619	9.235	16.584	10.513		
$N(CH_3)_4Br$	2.685	6.349	5.324	6.978	9.746	7.904
	12.788	8.173				
$N(C_2H_5)_4Br$	2.850	6.304	3.302	6.394	6.135	6.969
	8.915	7.382	12.857	7.832		
$N(C_3H_7)_4Br$	2.845	6.161	5.103	6.475	8.252	6.861
	10.760	7.113	14.080	7.310		
$N(C_4H_9)_4Br$	3.199	6.071	5.440	6.376	7.805	6.556
	10.390	6.771				

Table II. Coefficients A_i[a] and Standard Deviation $\sigma(S)$ Corresponding to Eq 1, Relating S with m

added electrolyte	A_0	A_1	A_2	A_3	A_4	$10^5\sigma(S)$
NaCl	0.005 317	0.042 370	−0.144 38	0.361 54		3.4
KCl	0.005 317	0.045 197	−0.159 34	0.383 91		3.4
NH_4Cl	0.005 317	0.042 984	−0.134 39	0.309 74		2.0
$NaNO_3$	0.005 317	0.045 242	−0.119 76	0.149 60		1.3
KNO_3	0.005 317	0.042 519	−0.126 09	0.244 13		1.7
NH_4NO_3	0.005 317	0.053 825	−0.373 08	2.511 10	−6.7721	2.2
NaBr	0.005 317	0.050 169	−0.235 29	0.705 17		2.3
KBr	0.005 317	0.049 656	−0.171 13	0.316 19		1.8
NH_4Br	0.005 317	0.050 398	−0.223 72	0.650 72		3.5
$N(CH_3)_4Br$	0.005 317	0.038 746	−0.129 34			6.3
$N(C_2H_5)_4Br$	0.005 317	0.040 133	−0.262 35	0.795 16		3.0
$N(C_3H_7)_4Br$	0.005 317	0.033 22	−0.230 54	0.673 64		5.8
$N(C_4H_9)_4Br$	0.005 317	0.025 025	−0.110 52			5.9

[a] $0.005 < m/(\text{mol kg}^{-1}) < 0.15$.

or Carlo-Erba products of analytical purity and were recrystallized. The salts were dried to constant mass. Triply distilled water was used throughout.

Solubility Measurements. The solubility measurements were carried out in the apparatus previously described (*2*). Details of the experimental procedure have been given elsewhere (*1*, *5*). Solid $Co(NH_3)_6(IO_3)_3$ was stirred for at least 3 h with a solution of the desired electrolyte in a vessel thermostated at 298.15 ± 0.01 K. Longer equilibration times (48 h) yielded the same results. The solubility of $Co(NH_3)_6(IO_3)_3$ was determined by measuring the absorbance at 475 nm, where $Co(NH_3)_6^{3+}$ has a broad maximum. The absorbance was determined by means of a Perkin-Elmer COLEMAN 55 UV/vis spectrophotometer. The spectrophotometer provides a precision of 10^{-3} in absorbance readings, and was calibrated with aqueous solutions of $Co(NH_3)_6Cl_3$. Occasional determinations of ammonia liberated by adding sodium hydroxide solution to a fixed quantity of saturated solution and then boiling gave identical results (*4*, *6*, *7*) within experimental error. The solutions of the different electrolytes were made up by mass in all cases.

Results and Discussion

The experimental solubilities of hexaamminecobalt(III) iodate in aqueous solutions of different electrolytes are reported in Table I where S represents the solubility of the saturating salt ($Co(NH_3)_6(IO_3)_3$) and m the molality of the inert electrolyte solutions. The solubility of $Co(NH_3)_6(IO_3)_3$ at 298.15 K in pure water was found to be $5.317 \pm 0.005 \times 10^{-3}$ mol kg^{-1} compared with the literature value of 5.270 mol m^{-3} (*3*).

Experimental results were fit to the polynomial of the type

$$S = \sum A_i(m/(\text{mol kg}^{-1}))^i \qquad (1)$$

where S is the solubility of hexaamminecobalt(III) iodate and

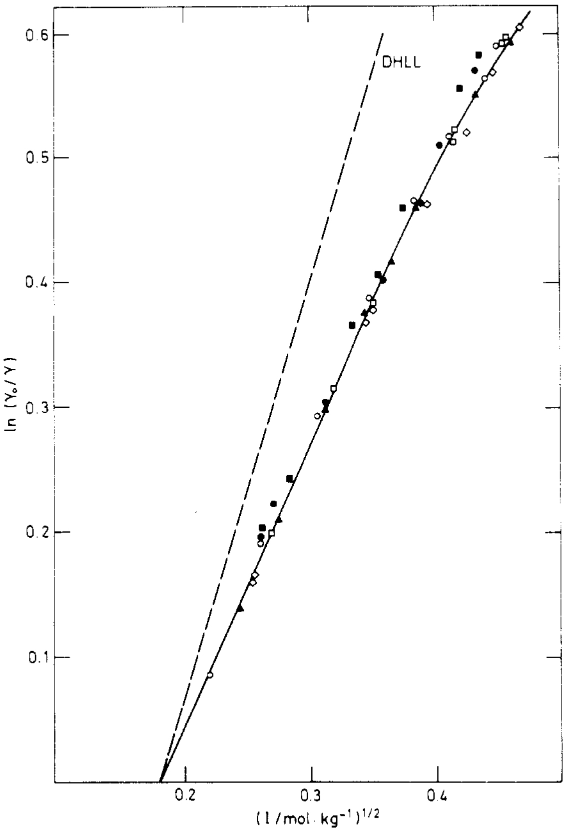

Figure 1. Relative activity coefficient (γ_0/γ) of $Co(NH_3)_6(IO_3)_3$ in the presence of different 1-1 electrolytes as a function of the square root of the total ionic strength I_m: ◇, NaCl; ○, KCl; □, NH_4Cl; ●, $NaNO_3$; ▲, KNO_3; ■, NH_4NO_3.

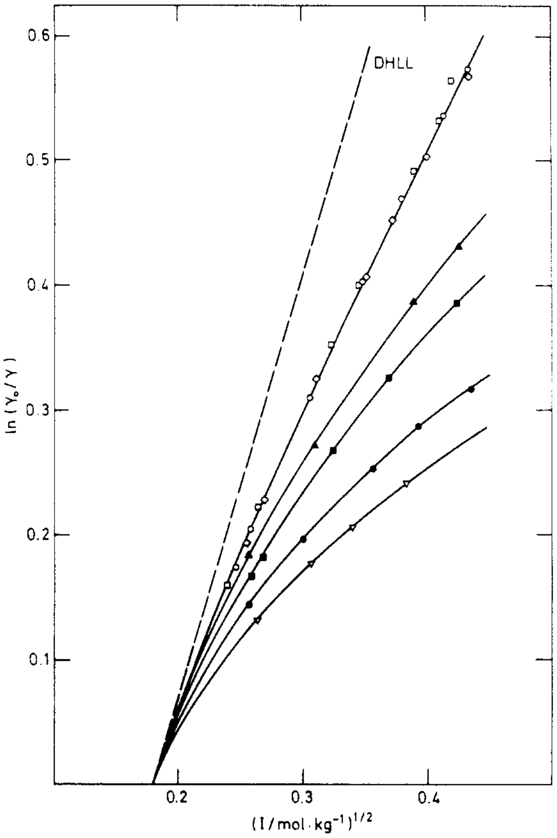

Figure 2. Relative activity coefficient (γ_0/γ) of $Co(NH_3)_6(IO_3)_3$ in the presence of different 1-1 bromides as a function of the square root of the total ionic strength I_m: ◇, NaBr; ○, KBr; □, NH_4Br; ▲, $(CH_3)_4NBr$; ■, $(C_2H_5)_4NBr$; ●, $(C_3H_7)_4NBr$; ▽, $(C_4H_9)_4NBr$.

m the molality of the added electrolyte solutions.

The coefficients of eq 1 and standard deviation are given in Table II. Judging from the scatter of values obtained when repeated measurements of the saturated solutions and of the calibration solutions are performed, we estimate a precision of $\pm 0.005 \times 10^{-3}$ mol kg^{-1} for our *S* values of Table I.

The relative activity coefficients γ_0/γ of the solute was calculated by using

$$\gamma_0/\gamma = S/S_0 \tag{2}$$

where γ_0 is the(molality-based) activity coefficient of the saturating salt, hexaamminecobalt(III) iodate, in pure water, γ is the activity coefficient of the saturating salt in the electrolyte solution under consideration, *S* is the solubility of the saturating salt in the electrolyte solution, and S_0 is in pure water.

Values of ln (γ_0/γ) derived from experimental solubility measurements are plotted against the square root of the ionic strength in Figures 1 and 2. As it can be seen the increase in solubility of $Co(NH_3)_6(IO_3)_3$ is smaller for sodium salts than for potassium or ammonium salts. This behavior was also observed in previous work (*2*) and can be related with the effective radii of the solvated ions in solution. In the case of chlorides, the solubility of the saturating salt increases in the order $Na^+ < NH_4^+ < K^+$ while for bromides and nitrates the solubility increases in the order $Na^+ < K^+ < NH_4^+$.

The tetraalkylammonium bromides R_4NBr are a set of homologous salts which can be used as model compounds to study the effect of the cation size and nonpolar groups on the activity coefficient of another electrolyte. Tetraalkylammonium salts give a much smaller increase in solubility as shown in Figure 2. The solubility of the saturating salt in the presence of organic salts increases in the order $(C_4H_9)_4N^+ < (C_3H_7)_4N^+ < (C_2H_5)_4N^+ < (CH_3)_4N^+$. As it is shown the larger the ionic size of the organic cation the smaller the increases in solubility. This behavior was also observed in previous works (*1*, *2*, *5*).

Registry No. $Co(NH_3)_6(IO_3)_3$, 14589-65-2; NaCl, 7647-14-5; KCl, 7447-40-7; NH_4Cl, 12125-02-9; $NaNO_3$, 7631-99-4; KNO_3, 7757-79-1; NH_4NO_3, 6484-52-2; NaBr, 7647-15-6; KBr, 7758-02-3; NH_4Br, 12124-97-9; $(CH_3)_4NBr$, 64-20-0; $(C_2H_5)_4NBr$, 71-91-0; $(C_3H_7)_4NBr$, 1941-30-6; $(C_4H_9)_4NBr$, 1643-19-2.

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