

pretation of this region was further complicated by a medium strength absorption band for the CCl_4 between 960 and 1030 cm^{-1} . The general appearance of this band does seem to imply that its probable cause is a change in the P—O—C stretch frequencies. This would be in contrast to the findings of Miles (9) who found this band unaffected by inorganic acids and water in TBP.

If the sulfur dioxide were bonded at the sulfur atom, then it would be expected that the asymmetric stretch would show a larger shift than the symmetric stretch which appears to be the case here. On this basis, it seems reasonable to conclude that there is an interaction between the phosphoryl oxygen on the TBP and the sulfur atom of the sulfur dioxide.

Conclusions

Equations 1 and 3–5 give a good fit for measured vapor-liquid equilibrium data over the range $6\text{--}70^\circ\text{C}$ and vapor compositions from 10 to 650 mm Hg in SO_2 . Although this model was semiempirical, it was a convenient method of correlating the experimental data. Spectroscopic evidence of an interaction of the sulfur atom of the sulfur dioxide and the phosphoryl oxygen of the TBP was also presented.

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We are grateful to F. Frantisak (Peabody Engineering Co., Toronto, Canada) for his help in this work.

Nomenclature

- H = Henry's law constant, mm Hg
 K, K' = liquid-phase equilibrium constants
 P = pressure, mm Hg
 T = temperature, K
 x = liquid-phase mole fraction
 γ = liquid-phase activity coefficient

Subscript

i = refers to component i in mixture

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Diffusion Coefficients of n -Heptane and n -Decane in n -Alkanes and n -Alcohols at Several Temperatures

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The diffusion coefficients of the solutes n -heptane and n -decane were measured in the series of alkane solvents n -hexane through n -decane and in the alcohol solvents n -hexanol and n -heptanol. Mutual and self diffusivities in most cases were measured at the temperatures of 20° , 25° , 30° , and 40°C . Concentrations of the diffusion species were in the infinitely dilute region. An unsteady-state porous frit technique was used with carbon-14 tagged diffusion species. The diffusion coefficients measured were compared with various liquid diffusivity prediction correlations.

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The diffusion coefficients measured in this work add new information to the existing literature data for normal alkane diffusivities which in large part have been ob-

tained by Bidlack et al. (1), Douglass and McCall (2), and McCall et al. (11). The diffusion of n -alkanes in the normal alcohols hexanol and heptanol, also studied in this work, makes it possible to study the effects of solvent hydrogen bonding. Regularities in these homologous series permit data extension correlations to be proposed. The measured diffusion coefficients are also useful in examining some of the existing liquid diffusivity prediction correlations.

An unsteady-state porous frit technique developed in this laboratory was used to measure the diffusion coefficients. A detailed discussion of this method is given elsewhere (12). In this technique, the unsteady-state buildup of a diffusing tagged species from a nonglazed porcelain frit into a thermostated pure solvent bath is monitored. The diffusion coefficient is obtained by a least-squares curve fit of the experimental solvent bath solute concentration vs. time profile to the analytic expression describing this process.

Model of Diffusion in Frit

The unsteady-state porous frit method employs the diffusion of a tagged or otherwise analytically identifiable species from the confines of an enclosed volume, the frit, into a surrounding homogeneous volume, the stirred sol-

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vent bath. Mass transfer within the frit is assumed to be solely by molecular diffusion. The edges of the slab-like frit are sealed; hence, diffusion is only in one direction. The relations describing this diffusional process within the frit are:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

$$C(x, 0) = C^\circ \quad (2)$$

$$C(\infty, t) = C^\circ \quad (3)$$

$$C(0, t) = C_f(t) \quad (4)$$

where D is a constant owing to the infinitely dilute nature of the system or is approximated as some constant average value.

Diffusion within the porous frit can be related to the solute concentration of the well-stirred solvent bath by the following material balance expression:

$$V_f \frac{\partial C_f}{\partial t} = 2 A_T D \frac{\partial C(0, t)}{\partial x} \quad (5)$$

where

$$C_f(0) = C_f^\circ \quad (6)$$

The above equations can be solved simultaneously to yield the following equation for solute concentration in the solvent bath:

$$C_f(t) = C^\circ - (C^\circ - C_f^\circ) \exp(B^2 t) [1 - \operatorname{erf}(B \sqrt{t})] \quad (7)$$

where

$$B = 2 A_T \sqrt{D} / V_f = 2 \sqrt{D} / L_{\text{eff}} \quad (8)$$

The semi-infinite nature of the boundary condition, Equation 3, used to obtain Equation 7 limits the applicability of this solution to diffusion times so that the solute concentration at the effective centerline of the frit remains constant at its initial value of C° . In practice, limiting the diffusion data to times less than $0.30 L_{\text{eff}}^2 / D$ assures the conformity of Equation 7 with the short-time restriction of Equation 3. Estimates of L_{eff} were obtained in a previous study (23).

The experimental solvent bath solute concentration vs. time data can be curve fit to Equation 7 by an iterative nonlinear least-squares procedure. In the case of calibration runs where the diffusivity D is known, C_f° and A_T become the curve-fit parameters. Once the frit constant, A_T , has been determined, Equation 7 can be similarly fit to the experimental data employing D and C_f° as the variable curve-fit parameters.

The initial solute concentration of the solvent bath, C_f° , is employed as a curve-fit parameter to account for potential irregular start-up effects. The solvent bath concentration is influenced by two factors in addition to molecular diffusion at the startup of a diffusion run. A small quantity of binary solution is unavoidably transferred to the solvent bath from the outside surfaces of the frit. This material is swept immediately into the surrounding solvent when the run is begun. A limited erosion of binary solution at the entrances to the frit's capillary passages can be expected during startup owing to the convective action of the stirred solvent. These essentially zero-diffusion-time effects are accounted for by considering C_f° a curve-fit parameter.

The solvent bath volume, V_f , in Equation 7 is not constant. The initial 300-ml solvent volume is reduced by sampling during the course of the diffusion run. A time averaged volume,

$$V_f = \frac{\sum_{i=1}^N (t_i - t_{i-1}) V_{f,i-1}}{\sum_{i=1}^N (t_i - t_{i-1})} \quad (9)$$

where N is the number of samples taken during the diffusion run, is used in Equation 7.

Experimental

The porous frits were calibrated by diffusing a 0.5*N* aqueous sodium chloride solution from the frits into an initially pure water solvent bath at 25°C. An integral NaCl diffusion coefficient of 1.480×10^{-5} cm²/sec was used for the frit calibration based upon the data of Harned and Owen (6), Stokes (20), and Vitagliano and Lyons (21). Justification for the use of this value and the calibrated mass transfer areas of the frits is given elsewhere (13). Average experimental precision of the calibrated frit area is better than $\pm 4\%$.

The normal alkanes used in this diffusion study were obtained in pure grade (99+ mol %) from the Phillips Petroleum Co. After chromatographic analysis had confirmed this purity specification, the alkanes were used without further processing. The normal alcohols were obtained from both Fisher and Matheson Scientific Companies. Both the *n*-hexanol and *n*-heptanol were purified by distillation. A Nester-Faust spinning band distillation unit was used for this purpose. The purified alcohols were free of significant impurities by chromatographic analysis. A Karl-Fisher analysis showed all solvents to be free of significant traces of moisture. The tagged tracers used in this study, *n*-heptane-1-C14 and *n*-decane-1-C14, were obtained from Mallinckrodt Nuclear. The manufacturer's certificates of analysis were accepted as proof of solute purity.

Experimental techniques were systematized as much as possible. An initial solvent volume of 300.0 ml was employed. All diffusion temperatures were controlled to within $\pm 0.01^\circ\text{C}$. A solvent bath stirrer assembly speed of about 320 cpm was used throughout this work. Similar sampling schemes, employing about 20 1-ml sample withdrawals, were used for each run. Tracer samples were analyzed on a Nuclear Chicago Mark II scintillation counter. All samples within a given diffusion run were counted for the same number of total counts, with a minimum of 10,000 counts recorded for each sample.

The solute concentration of the binary solution in which the frits were initially soaked varied from run to run. The initial solute concentration never exceeded 1.98×10^{-4} mol/l. and was usually in the range 1.0×10^{-6} mol/l.

Viscosities were measured with a Cannon-Fenske viscometer, and densities were measured with a standard Weld pycnometer. Agreement with available literature values is good.

Results and Discussion

The experimentally measured diffusion coefficients are listed in Table I. The pure solvent density and viscosity data measured in this laboratory are given in Table II. In most cases, the reported diffusivities represent an average of two experimental measurements. Generally, experimental reproducibility was 5–10%. For some systems, *n*-heptane-*n*-alkanes, experimental error at times masked the slight temperature dependency of the diffusion coefficient.

Comparison of data to reported values. The experimental data listed in Table I can in several instances be compared to previously reported values. The self-diffusion

coefficient of *n*-heptane at 25°C of $3.12 \times 10^{-5} \text{ cm}^2/\text{sec}$ obtained in this work compares to the value of $3.04 \times 10^{-5} \text{ cm}^2/\text{sec}$ obtained by interpolating Fishman's capillary cell data (4) and to the value of $3.12 \times 10^{-5} \text{ cm}^2/\text{sec}$ (spin-echo method) reported by Douglass and McCall (2). Douglass and McCall also measured a *n*-decane self-diffusivity (25°C) of $1.31 \times 10^{-5} \text{ cm}^2/\text{sec}$ (spin-echo method), compared to the value of $1.55 \times 10^{-5} \text{ cm}^2/\text{sec}$ obtained in this work.

A more significant disagreement of values exists for the mutual diffusivity of the solute *n*-decane in the solvents *n*-hexane (25°C) and *n*-heptane (20°C). Using interferometric techniques, Bidlack et al. (7) and Rossi and Bianchi (17) measured diffusivities of 3.02×10^{-5} and $2.06 \times 10^{-5} \text{ cm}^2/\text{sec}$, respectively, for these systems.

Table I. Experimental Diffusion Coefficients

Solute	Solvent	$D \times 10^5, \text{ cm}^2/\text{sec}$			
		20°C	25°C	30°C	40°C
<i>n</i> -Heptane	<i>n</i> -Heptane	3.10	3.12	3.22	...
<i>n</i> -Heptane	<i>n</i> -Octane	2.33	2.50	2.35	2.74
<i>n</i> -Heptane	<i>n</i> -Nonane	1.84	2.02	1.97	...
<i>n</i> -Heptane	<i>n</i> -Decane	1.52	1.61	1.58	...
<i>n</i> -Heptane	<i>n</i> -Hexanol	0.46	0.48	0.51	0.65
<i>n</i> -Heptane	<i>n</i> -Heptanol	0.41	0.43	0.48	0.50
<i>n</i> -Decane	<i>n</i> -Hexane	4.20	4.63	5.00	...
<i>n</i> -Decane	<i>n</i> -Heptane	2.97	3.08	3.48	3.82
<i>n</i> -Decane	<i>n</i> -Octane	2.12	2.40	2.52	2.96
<i>n</i> -Decane	<i>n</i> -Nonane	1.60	1.90	2.05	2.22
<i>n</i> -Decane	<i>n</i> -Decane	1.44	1.55	1.68	1.86
<i>n</i> -Decane	<i>n</i> -Hexanol	0.42	0.48	0.50	0.57
<i>n</i> -Decane	<i>n</i> -Heptanol	0.32	0.37	0.44	0.50

Table II. Solvent Properties

Solvent	Temp, °C	Density, g/cm ³	Viscosity, cp
<i>n</i> -Hexane	20	0.660	0.310
	25	0.655	0.296
	30	0.651	0.282
	40	0.642	0.258
<i>n</i> -Heptane	20	0.684	0.409
	25	0.680	0.388
	30	0.676	0.368
	40	0.667	0.333
<i>n</i> -Octane	20	0.703	0.537
	25	0.699	0.506
	30	0.695	0.478
	40	0.687	0.428
<i>n</i> -Nonane	20	0.718	0.702
	25	0.714	0.657
	30	0.710	0.616
	40	0.703	0.545
<i>n</i> -Decane	20	0.730	0.909
	25	0.726	0.843
	30	0.723	0.784
	40	0.715	0.686
<i>n</i> -Hexanol	20	0.820	5.069
	25	0.816	4.339
	30	0.813	3.735
	40	0.806	2.807
<i>n</i> -Heptanol	20	0.822	6.999
	25	0.819	5.898
	30	0.815	5.005
	40	0.808	3.676

This may be compared with values of 4.63×10^{-5} and $2.97 \times 10^{-5} \text{ cm}^2/\text{sec}$, respectively, for these systems, which were determined in this study. On the basis of the limited discussion of experimental procedure furnished by these authors (1, 17), it is difficult to speculate on a cause for this discrepancy. However, it is probable that these interferometric diffusivity measurements were made at a considerably higher solute (*n*-decane) concentration than the diffusivity measurements of this study.

Some, but not all, of the deviation noted above may be attributed to isotopic effects of the carbon-14 tagged tracers used in this study. Eppstein (3) has suggested that diffusivities determined with carbon-14 tagged tracers need to have the following mass correction applied:

$$\frac{D}{D(\text{C-14})} = \left[\frac{M(\text{C-14})}{M} \right]^{1/2} \quad (10)$$

where D and $D(\text{C-14})$ and M and $M(\text{C-14})$ are the diffusivities and molecular weights of the untagged and tagged species, respectively. For both *n*-heptane/*n*-heptane-1-C14 and *n*-decane/*n*-decane-1-C14, this ratio is about 1.01 or less. Even the need for this small correction is put in doubt by the findings of Harris et al. (7). By measuring the self-diffusion of benzene with varying degrees of carbon-14 substitution, these workers concluded that the isotope effect is minimal, and Equation 10 tends to overcorrect for it.

Data extension relationships. Hayduk and Cheng (8) have recently reviewed the relationship of diffusivity to solvent viscosity. These workers have found that for a given solute the following empirical relation closely approximates the diffusional behavior of very dilute mixtures:

$$D = K_1 \mu^{K_2} \quad (11)$$

where K_1 and K_2 are parameters characteristic of the diffusing species. Figures 1 and 2 are logarithmic plots of the diffusivity and viscosity data obtained in this investigation for the diffusion of *n*-heptane and *n*-decane. The solid lines on these plots were fitted by standard least-squares techniques. The parameters for Equation 11 are listed in Table III, where viscosity is in centipoise, and diffusivity has the units cm^2/sec .

Diffusivity estimation methods. The experimental diffusivity coefficients are compared in Table IV to the predictions of several diffusivity correlations which appear in the literature. The average absolute percent deviations, AAPD, were computed by comparing the predicted diffusivities to all the experimental data given in Table I for each respective solute-solvent system.

The diffusivity correlation of Wilke and Chang (22) yielded comparatively good results for the *n*-heptane-*n*-alkane systems. The prediction accuracy decreased significantly, however, for the other systems studied. The rather large 53% AAPD experienced by the Wilke-Chang equation for the alcohol solvent solutions may in part be due to the value of 1.0 used for the association parameter in this equation. The AAPD is reduced to 42% if a solvent association parameter of 1.5 is used; this is the association parameter suggested by Wilke and Chang for ethanol. The lack of a suitable technique for estimating the association parameter limits this equation's effectiveness for hydrogen-bonded solvent systems.

In a review of diffusion coefficient correlations, Reid and Sherwood (16) recommend the use of the relation developed by Scheibel (18) for nonaqueous binary systems. The Scheibel equation was comparable in accu-

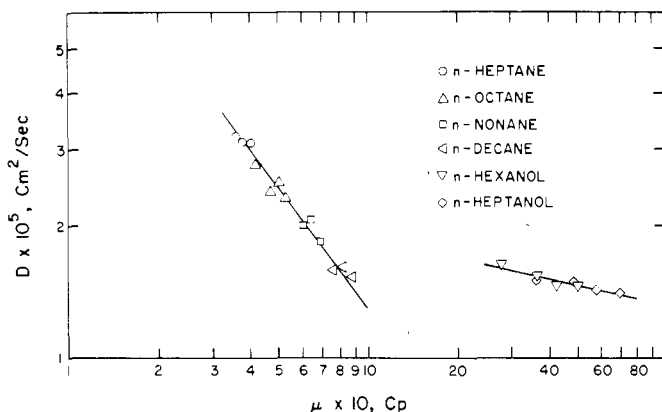


Figure 1. Dependency of diffusion coefficient of solute *n*-heptane on solvent viscosity

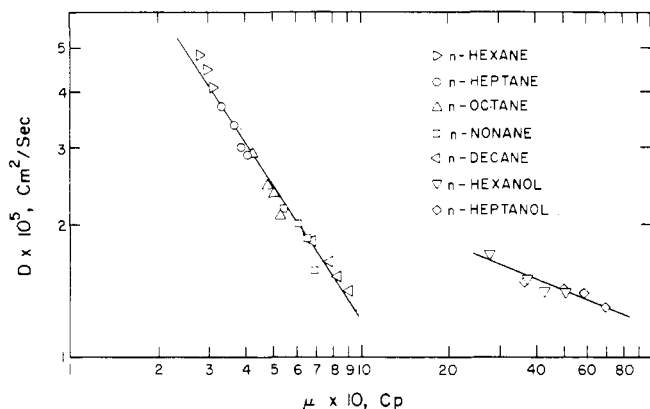


Figure 2. Dependency of diffusion coefficient of solute *n*-decane on solvent viscosity

racy to the recently developed and somewhat similar relation of Lusi and Ratchliff (10).

Othmer and Thaker (15) have proposed a diffusivity prediction relation which utilizes water as a reference material for correlation. As seen in Table IV, this method yielded the poorest overall results of any correlation considered.

It might be expected that the diffusivities of the *n*-alkane-*n*-alcohol systems would be more accurately predicted by a correlation that specifically attempts to account for molecular interaction. Sitaraman et al. (19) employed heat of vaporization data to characterize the relative degree of solute and solvent association. The diffusivity prediction relation developed by these authors, however, appears to offer no real advantage for the *n*-alkane-*n*-alcohol systems. King et al. (9) used a similar heat of vaporization ratio in their development of a diffusivity correlation. The King-Hsueh-Mao correlation is comparatively successful in predicting diffusion coefficients for the *n*-alcohol solvent systems studied in this investigation. Considering its simplicity, it appears to be the best diffusivity correlation for *n*-alkane systems.

Olander (14), Gainer and Metzner (5), and Mitchell et al. (12) have proposed modifications to the Eyring absolute rate theory equation for diffusion. All three approaches use a hold formation-jump step diffusion model as a means of predicting the activation energy requirements of the diffusion process. Except for the Mitchell et al. equation's prediction of *n*-decane-*n*-alkane diffusivities, all three methods predicted *n*-alkane diffusion coefficients with an average absolute deviation from the exper-

Table III. Curve-Fit Parameters for Equation 11

Solute	Solvent	$K_1 \times 10^5$	K_2	AAPD of $D_{Eq\ 11}$ from D_{exp}
<i>n</i> -Heptane	<i>n</i> -Alkane	1.36	-0.859	3.2
<i>n</i> -Decane	<i>n</i> -Alkane	1.22	-1.04	4.4
<i>n</i> -Heptane	<i>n</i> -Alcohol	0.969	-0.458	3.3
<i>n</i> -Decane	<i>n</i> -Alcohol	1.16	-0.634	3.3

Table IV. Prediction Accuracy of Diffusivity Correlations

Predictive Model	Binary systems, solute-solvent		
	<i>n</i> -Heptane- <i>n</i> -Alkanes, AAPD ^a	<i>n</i> -Decane- <i>n</i> -Alkanes, AAPD ^a	<i>n</i> -Alkane- <i>n</i> -alcohols, AAPD ^a
Wilke-Chang (22)	9	26	53
Scheibel (18)	20	10	42
Lusi-Ratchliff (10)	7	24	51
Othmer-Thakar (15)	43	53	71
Sitaraman-Ibrahim-Kuloor (19)	7	21	33
King-Hsueh-Mao (9)	13	8	25
Olander (14)	20	18	61
Gainer-Metzner (5)	12	9	166
Mitchell et al. (12)	7	34	15

^a Where the AAPD is calculated as:

$$AAPD = \frac{1}{n} \sum \left| \frac{D_{calcd} - D_{exp}}{D_{exp}} \right| \times 100$$

imental values of less than about 20%. The prediction relation of Mitchell et al. is the most accurate estimation technique of all those considered for the *n*-alkane-*n*-alcohol systems. The Gainer-Metzner equation was highly inaccurate for the alcohol systems because of a basic weakness in the prediction expression. For binary systems, such as the *n*-alkane-*n*-alcohol solutions considered in this work, hydrogen bonding is experienced only among the solute or solvent species. For systems such as these, the hydrogen-bonding component in Equation 25 of the Gainer-Metzner development (5) is unwarrantedly canceled out by the nature of the geometrically averaged energy terms.

Although not shown in Table IV, the self-diffusivity correlation proposed by Nagarajan, Ryan, and Shemilt, as described by Reid and Sherwood (16), predicted *n*-heptane self-diffusivities with an AAPD of about 15% and *n*-decane self-diffusivities with an AAPD of about 6%. The King-Hsueh-Mao equation predicted self-diffusivities with AAPD's of 7 and 3% for these same respective liquids.

Summary

The unsteady-state porous frit technique has been used to measure the diffusivity of *n*-heptane and *n*-decane in several *n*-alkanes and two *n*-alcohols. The diffusivity of the solute *n*-decane in *n*-hexane (25°C) and in *n*-heptane (20°C) as measured in this work differed from values reported in the literature. The Hayduk-Cheng empirical relationship correlates this work's data well. The predictions of all major diffusivity correlations were compared to the experimental values. The King-Hsueh-Mao

equation is recommended for diffusivity prediction in *n*-alkane-*n*-alkane systems, and the Mitchell et al. equation is recommended for diffusivity prediction in *n*-alkane-*n*-alcohol systems.

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Nomenclature

A_T = effective mass transfer per side of frit, cm^2
 B = an experimental constant defined in Equation 8
 C = solute concentration (activity) within the frit, g-mol/l . (cpm/ml)
 C_f = solute concentration (activity) in the solvent bath, g-mol/l . (cpm/ml)
 D = molecular diffusivity, cm^2/sec
 k = Boltzmann constant, 1.380×10^{-16} erg/K
 K_1, K_2 = solute-solvent parameters of Equation 11
 L_{eff} = effective length of the diffusion path from the surface to the center of the frit, cm
 M = molecular weight, g/g-mol
 N = number of samples taken during the experimental run
 N_A = Avogadro's number, 6.0248×10^{23} mol $^{-1}$
 t = time, sec
 V_f = volume of solvent in the solvent bath, cm^3
 x = distance, cm

Greek Letters

μ = viscosity, cp

Subscripts

calcd = calculated from a prediction expression

exp = experimental quantity

i = sample index number

Superscripts

$^{\circ}$ = initial value

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Solubility of Zinc Iodate in Aqueous Solution at 20.2°, 28.4°, and 40.6°C

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The solubility of zinc iodate in aqueous solutions of varying ionic strengths adjusted by potassium nitrate was determined as a function of temperature by radiotracer techniques. The solubility product constants were 3.57×10^{-6} , 5.40×10^{-6} , and 7.39×10^{-6} at 20.2°, 28.4°, and 40.6°C, respectively. Mean ionic activity coefficients were also determined.

Few determinations of the solubility of $\text{Zn}(\text{IO}_3)_2$ are reported in the literature. Ricci and Nesse (3) gave the solubility of $\text{Zn}(\text{IO}_3)_2$ in aqueous solution at 25°C as 0.01548M. Saegusa (4) determined the solubility as a function of ionic strength at 25°C and found the solubility product constant to be 3.905×10^{-6} . Seidell and Linke (5) listed the solubility of $\text{Zn}(\text{IO}_3)_2$ in hot and cold water.

Radiotracer techniques employing a Zn^{65} -labeled precipitate of $\text{Zn}(\text{IO}_3)_2$ have been used to determine the sol-

ubility of $\text{Zn}(\text{IO}_3)_2$ as a function of ionic strength at 20.2°, 28.4°, and 40.6°C. The activity coefficients were determined through the Debye-Hückel relations, and the solubility product constants were found at each temperature.

Experimental

Zinc iodate was prepared by the method of Ricci and Nesse (3). Solutions of J. T. Baker AR potassium iodate and zinc nitrate were heated to boiling. The iodate solution was added slowly to the zinc nitrate solution with continuous stirring. The precipitate was allowed to digest and after filtration was dried over phosphorus pentoxide. The precipitate was dissolved, and the dilute solution titrated with a solution of arsenous oxide following the procedure of Vogel (7) and was 98.6% pure. The radioactive precipitate was prepared in the same fashion with tracer amounts of Zn^{65} , a gamma emitter of 1.11 MeV with a half-life of 245 days.

A standard solution of $\text{Zn}^{65}(\text{IO}_3)_2$ was prepared by quantitatively transferring weighed amounts of the tagged

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