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D. Noel[a,b]; C. E. Meloan[a]
[a] DEPARTMENT OF CHEMISTRY, KANSAS STATE UNIVERSITY MANHATTAN, KANSAS [b] Department of Chemistry, Kearney State College, Kearney, Nebraska

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The Determination of Solvation Numbers of Ligands, Chelates, and Complexes in Various Solvents by Differential Direct Injection Enthalpimetry, Viscosity, and Gas Chromatography Measurements

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D. NOEL* and C. E. MELOAN

DEPARTMENT OF CHEMISTRY
KANSAS STATE UNIVERSITY
MANHATTAN, KANSAS 66502

Abstract

The number of H_2O and organic solvent molecules associated with rhodomine B, tris-1,10-phenanthroline iron(II) chloride, and iron(III) acetylacetonate in seven extraction solvent systems was determined. The methods of measurement were viscosity, gas chromatography, and differential direct injection enthalpimetry.

INTRODUCTION

Previous work in this laboratory and elsewhere has been directed toward an understanding of the effect of water associated with solute in the extraction of metal chelates (*1–4*).

In a previous paper (*5*) the change in the hydration and solvation number of rhodamine B was determined when it was partitioned between various solvents. The work presented in this paper extends the rhodamine B work, examines a chelate and a complex, and demonstrates that

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* Present address: Department of Chemistry, Kearney State College, Kearney, Nebraska 68847.

a differential direct injection enthalpimetry measurement of water is applicable to compounds of this type.

The viscosity (*6*) and gas chromatographic techniques (*7*) for determining water and organic solvent molecules reported in the previous paper (*5*) were also used here.

Because of some difficulties with the previous methods on some systems and because a second independent method for making the measurements was desired, a differential direct injection enthalpimetry system was investigated (*8–11*).

The compounds chosen for these studies were rhodamine B (as a ligand), tris-1,10-phenanthroline iron(II) chloride (as a complex) and iron(III) acetylacetonate (as a metal chelate).

EXPERIMENTAL

Chemicals

All chemicals were reagent grade and with the exception of the Karl Fisher reagent were freshly distilled or recrystallized prior to use.

Equipment

Spectrophotometer: Beckman Model DB. Viscometer: Cannon-Fenske type. Pycnometer: Weld type. Gas chromatograph: Micro-Tek 2500 R. with thermal conductivity detector and disk integrator. Direct injection enthalpimeter.

The differential thermometric apparatus used in this work was similar to that used by Tyson et al. (*8*) for differential thermometric titrations. The design of the differential thermistor bridge circuit is essentially that of Tyson's with only a few modifications (*12*). The temperature-sensing elements consisted of two sets of four probe-type thermistors (General Electric 81G-154) connected in parallel. The specifications of these thermistors are as follows: resistance at 25°C, 150,000 Ω ± 20%; dissipation constant, 1.0 mW/°C; thermal time constant, about 1 sec in still water (0.3 sec in rapidly stirred water); and resistance ratio, $R_{25^\circ}/R_{125^\circ} = 39.7$. The two sets were matched, the resistance of each set was measured, and the agreement was better than 100 Ω.

Thermistors follow the resistance–temperature relationship $\tau = \tau_0 \exp B(1/\% - 1/T_0)$, where τ is the resistance of the thermistor, T is the absolute temperature, and B is a constant. The best value of B for the two sets was 3809.0.

The cells in which the thermometric measurements were made were constructed from 1-oz wide-mouth glass jars fitted with screw-on Bakelite lids. Holes were drilled in the lids to allow for insertion of the four thermistors which were mounted with paraffin in 6-mm glass tubing so that about 2 cm of each thermistor was exposed. A hole was also drilled for a piece of 4-mm o.d. glass tubing which served as a guide for the syringe needle when making injections.

The cells were insulated by a block of Styrofoam which had two hollowed out spaces to hold the jars, and the cell lids were cemented into a Styrofoam cover so that during the measurements the cells were surrounded completely by at least 1 in. of insulation. The solutions in the cells were stirred with magnetic stirrers which were partially imbedded in the lower Styrofoam jacket. The stirring rate was controlled with a transformer.

The bridge was connected to a Honeywell model 19 recorder and all deflections were measured on the 5 mV range. The measurements were made at an applied voltage of 12.0 V. A bucking circuit was used to adjust the output of the over-all circuit so that the baseline before injection of the samples was on the recorder scale.

Calibration Curve

The solvents were dried over 4A molecular sieve for a minimum of 24 hr. Five standard solutions were prepared by injecting various quantities of water from a 10-μl syringe into the dry solvents. Karl Fischer reagent (25 ml, stabilized, single solution) was placed in each of the cells and 25 μl of anhydrous solvent (blank) was injected into one and simultaneously 25 μl of standard water solution was injected into the other. The recorder deflection was plotted vs. the water concentration and the slope calculated by the method of least squares.

PROCEDURE

The procedure followed for the determination of the size and solvation number of rhodamine B, tris-1,10-phenanthroline iron(II) chloride, and iron(III) acetylacetonate was essentially that used by Kuruscev, Sargeson, and West (*6*). Rhodamine B solutions were prepared in anhydrous and water-saturated nitromethane, nitrobenzene, 1-butanol, 1-octanol, and isoamyl alcohol. Solutions of rhodamine B were also prepared in 1-octanol-saturated nitromethane and nitromethane-saturated 1-octanol for extraction studies between these two phases. Solutions of tris-1,10-phenanthroline iron(II) chloride were prepared in anhydrous and water-saturated nitromethane, water, and nitromethane–saturated water. Iron(III) acetylacetonate was dissolved in anhydrous methanol and chloroform, 80% methanol–20% water by volume, and 80% methanol–10% water–10% chloroform by volume.

Density

The density of each solution as well as that of the solvents was determined at 25.0°C using the Weld-type specific gravity bottles.

Viscosity

The viscosity of each of the solutions was determined at 25.0°C using the Cannon-Fenske viscometer.

Absorbance

The absorbance of each solution was measured at the wavelength of maximum absorbance, 550 nm for rhodamine B and 509 nm for $Fe(phen)_3Cl_2$. The molar absorptivity was calculated for each using the least squares slope of the straight line obtained by plotting the concentration vs. the absorbance.

Extraction

Solutions of tris-1,10-phenanthroline were prepared in water-saturated nitromethane and extracted into nitromethane-saturated water as described previously (*5*) for rhodamine B.

Gas Chromatography

After extraction, the organic phase was analyzed for water content using the gas chromatography technique described by Gaede (*7*). Least squares analysis of the water concentration vs. extracted solute concentration gave the solvation number after the method of Gere (*1*).

Nitromethane in the nitromethane-saturated aqueous phase containing extracted tris-1,10-phenanthroline iron(II) chloride was analyzed in a similar manner. Five microliter samples were injected and least squares analysis of the CH_3NO_2 concentration vs. the chelate concentration data gave the number of CH_3NO_2 molecules associated with the chelate.

1-Octanol associated with rhodamine B extracted from 1-octanol into nitromethane was determined also. An attempt was made to determine the nitromethane associated with rhodamine B in the 1-octanol phase using the same column and the same operating conditions, but the solubility of nitromethane in 1-octanol was so great that no increase above the blank could be detected.

Direct Injection Enthalpimetry

Calibration curves were prepared using the same standard water solutions used for the gas chromatography studies. Karl Fischer reagent (25 ml) was placed in each of the thermistor cells and the potentiometers adjusted so that the baseline was on the recorder scale. Anhydrous solvent (25 μl, blank) was injected into one cell and 25 μl of the standard water solution was simultaneously injected into the other. The recorder deflection was plotted vs. the water concentration and the slope calculated by the method of least squares.

Samples of the water-saturated organic phase after extraction were injected in a similar manner using water-saturated solvent as the blank. The water concentration was calculated from the recorder deflection using the least squares slope of the calibration curve. Water analyses were performed on the same solutions which had been analyzed by the gas chromatography method in order to compare the two methods.

RESULTS AND DISCUSSION

Before any extractions were performed, the density and viscosity of rhodamine B, tris-1,10-phenanthroline iron(II) chloride, and iron(III)

TABLE 1

Jones and Dole *B* Coefficient and Apparent Molal Volume of Iron Acetylacetonate in Various Solvents

Solvent	Concentration range (mole/1)	*B*	ϕ_v (cm^3/mole)
Absolute methanol	0.01–0.10	0.83	261.19
80% Methanol–20% water	0.01–0.08	0.69	261.90
Anhydrous chloroform	0.01–0.09	0.79	261.90
80% Methanol–10% water–10% $CHCl_3$	0.01–0.10	0.62	276.12

TABLE 2

Jones and Dole *B* Coefficient and Apparent Molal Volume of Tris-1,10-phenanthroline Iron(II) Chloride in Various Solvents

Solvent	Concentration range (mole/1)	*B*	ϕ_v (cm^3/mole)
Water	0.01–0.03	1.72	0.648
Nitromethane-saturated water	0.006–0.028	1.58	0.705
Water-saturated nitromethane	0.006–0.027	2.39	0.618
Anhydrous nitromethane	0.006–0.017	3.50	0.595

acetylacetonate were measured in various anhydrous and water-saturated organic solvents, aqueous and solvent-saturated aqueous solutions, and the data used to calculate the size and solvation numbers of the solutes. Kuruscev et al. (*6*) have used this method for the determination of the size and hydration number of various complexes, including tris-1,10-phenanthroline iron(II) chloride, in aqueous solution. Noel and Meloan (*5*) have presented results for rhodamine B in several solvents.

When the specific viscosity was plotted vs. molar concentration of the three solutes investigated, a straight line was obtained in each case, indicating a value of zero for the *A* coefficient in the Jones and Dole equation (*13*). The slope of the line in each case was calculated by the method of least squares and gave the best value of *B*. Values of the *B* coefficient for iron(III) acetylacetonate are given in Table 1. Table 2 shows the value of *B* for tris-1,10-phenanthroline iron(II) chloride.

According to Gurney (*14*), the *B* coefficient represents the contribution to the viscosity from the solvation spheres of the ions and hence is a measure of the volume of the solvated ion. The contributions from each individual ion are considered to be additive so that $B = \Sigma n_i B_i$.

In 1906 Einstein derived the viscosity equation $\eta_{sp} = 2.5\gamma$, where γ is the volume fraction occupied by the solute. Use of this equation with the Jones and Dole equation leads to the relationship $v = 400B_i/N$, where N is Avogadro's number. v is the hydrodynamic volume and represents the volume, in cubic centimeters, occupied by the ion and its solvation sphere. Values of v for iron(III) acetylacetonate and tris-1,10-phenanthroline iron(II) chloride are given in Tables 3 and 4, respectively.

In order to determine the volume occupied by the solvation sphere alone and hence the number of solvent molecules in the sphere, the ionic volume of the solute must be subtracted from v. The apparent molal volumes of the three solutes studied were calculated from density measurements using the equation $v_2 = 1000(d_0 - d)/mdd_0 + M/d$ (*15*), where d_0 is the density of the pure solvent and d is the density of the solution of molality m of a solute having a molecular weight M. The apparent molal volumes were constant over the concentration range used and the average values for iron(III) acetylacetonate and tris-1,10-phenanthroline iron(II) chloride are given in Tables 1 and 2.

In the case of rhodamine B and tris-1,10-phenanthroline iron(II) chloride the ionic volume of Cl^- had to be subtracted from the molecular volume in order to give the volume of the cation. A value of 39 Å^3 was used for the ionic volume of Cl^- which is the average of the values reported by Eucken (*16*) and Darmois (*17*). The molecular volume of iron(III) acetylacetonate and tris-1,10-phenanthroline iron(II) chloride are shown in Tables 3 and 4, respectively. The volumes occupied by the solvation spheres alone, v_{solv}, are also given in these tables.

The number of solvent molecules which are contained in the solvation sphere can be calculated from the volume of the sphere if the solvent is pure water or an anhydrous organic solvent. The number of solvent molecules in the sphere is calculated using the equation $n = v_{solv}d_0N/M$, where d_0 is the density of the solvent, N is Avogadro's number, and M is the molecular weight of the solvent.

The values of 112 ± 99 and 91 ± 205 Å^3 for v_{solv} of iron(III) acetylacetonate in anhydrous methanol and chloroform, respectively, correspond to 1.66 ± 1.46 molecules methanol and 0.68 ± 1.53 molecules chloroform per molecule of chelate. The poor precision results from the

TABLE 3

Calculated Values of Solvated Chelate, Chelate, and Solvent Sheath Volumes for Iron(III) Acetylacetonate in Various Solvents

Solvent	v (Å^3)	v_c (Å^3)	v_{solv} (Å^3)
Absolute methanol	546 ± 78	434 ± 21	112 ± 99
80% Methanol–20% water	459 ± 78	435 ± 18	24 ± 97
Anhydrous chloroform	526 ± 193	435 ± 12	91 ± 205
80% Methanol–10% water–10% $CHCl_3$	415 ± 68	460 ± 17	−45 ± 85

TABLE 4

Calculated Values of Solvated Ion, Ionic, and Solvent Sheath Volumes for the Tris-1,10-phenanthroline Iron(II) Cation

Solvent	v (Å^3)	v_c (Å^3)	v_{solv} (Å^3)
Water	1143 ± 115	641 ± 17	502 ± 132
Nitromethane-saturated water	1048 ± 113	705 ± 8	343 ± 121
Water-saturated nitromethane	1588 ± 138	607 ± 17	981 ± 155
Anhydrous nitromethane	2326 ± 392	582 ± 15	1744 ± 407

fact that the difference between the volumes of the solvated and unsolvated chelate is relatively small and the small relative errors in calculating these volumes are cumulative and give a large relative error in v_{solv}. Considering the error involved, this method does not confirm the existence of a solvate in either methanol or chloroform. However, a dichloroformate of iron(III) acetylacetonate has been observed by other methods (*18*, *19*).

The values of 502 ± 132 and 1744 ± 407 Å^3 for v_{solv} of tris-1,10-phenanthroline iron(II) chloride in water and nitromethane, respectively, correspond to 16.7 ± 4.4 molecules of water and 19.4 ± 4.5 molecules of nitromethane per ion of complex. This is in good agreement with Kuruscev (*6*) who found a hydration number of 17 for this complex in aqueous solution.

When the size of the solvated ions was determined in water-saturated organic solvents and solvent-saturated water, the volume of the solvation sphere was determined in the same manner as for the pure solvents. In this case, however, the solvation number obviously could not be determined by this method alone as both water and organic solvent could be present.

The amount of water associated with the ions as they were extracted from water into the organic solvent was determined by gas chromatography.

The method was useful in determining the amount of nitromethane in the solvation spheres of rhodamine B and tris-1,10-phenanthroline iron(II) chloride in nitromethane-saturated aqueous solutions. The results of the least squares analysis of the data show 1.11 ± 0.1 molecules nitromethane/molecule rhodomine B and 2.35 molecules nitromethane/molecules of tris-1,10-phenanthroline iron(III) chloride, both extracted into water.

After the water had been determined by gas chromatography, the results were combined with the viscosity data to give the number of organic solvent molecules occupying the remaining volume of the solvation sphere. This was done by calculating the volume occupied by the water molecules and subtracting this volume from the total volume of the solvation sphere as determined from viscosity measurements. The number of organic solvent molecules which could occupy the remaining volume was calculated in the same manner as described for anhydrous solvents and pure water. The results of these calculations for tris-1,10-phenanthroline iron(II) chloride are given in Table 5.

As a means of confirming the results obtained by gas chromatography, direct injection enthalpimetry measurements were performed on the same solutions. The results of the gas chromatography and enthalpimetry methods are compared in Table 6. The results appear to be somewhat less precise for the enthalpimetry method, especially for rhodamine B in 1-butanol and isoamyl alcohol. This is no doubt due to the high solubility of water in these solvents. Otherwise, the agreement is good.

For tris-1,10-phenanthroline iron(II) chloride extracted into nitromethane, the number of water molecules associated with the complex was found to be 14.4 ± 2.0 by enthalpimetry and 15.7 ± 0.1 by gas chromatography. These results are in good agreement with the value of 14 found by Gere (*1*) for the number of water molecules associated with

TABLE 5

Values of Solvation Numbers of Tris-1,10-phenanthroline Iron(II) Chloride in Various Solvents Calculated From Gas Chromatography and Viscosity Data

Solvent	Number of associated solvent molecules determined by gas chromatography	Number of solvent molecules occupying remaining volume in solvation sheath
Water		16.7 ± 4.4[a]
Nitromethane		19.4 ± 4.5[a]
Water-saturated nitromethane	15.7 ± 0.1 Water	5.7 ± 2.0 Nitromethane
Nitromethane-saturated	2.4 ± 0.2 Nitromethane	4.3 ± 4.1 Water

[a] Calculated from viscosity data only.

TABLE 6

Comparison of Results Obtained by Gas Chromatography and Direct Injection Enthalpimetry for the Determination of the Number of Water Molecules Associated with Rhodamine B Extracted into Various Solvents

Solvent	Molecules water per molecule rhodamine B by gas chromatography	Molecules water per molecule rhodamine B by enthalpimetry
1-Butanol	17.8 ± 3.3	15.1 ± 4.4
Isoamyl alcohol	17.8 ± 3.4	16.1 ± 2.8
1-Octanol	7.3 ± 1.9	8.2 ± 1.7
Nitromethane	5.6 ± 0.5	4.4 ± 0.8
Nitrobenzene	10.8 ± 3.1	10.1 ± 3.3

tris-1,10-phenanthroline iron(II) perchlorate extracted into nitromethane using the Karl Fischer method.

Comparison of the solvation numbers in the various anhydrous solvents with the combined results of the gas chromatography–viscosity studies of the extracted solute in the water-saturated solvents allows one to calculate the number of organic solvent molecules displaced from the solvation sphere by saturating the solvent with water. From these calculations the number of water molecules required to displace one solvent molecule can be determined.

These calculations for tris-1,10-phenanthroline iron(II) chloride show that 15.7 molecules of water displaced 13.7 molecules of nitromethane from the solvation sphere by saturating nitromethane with water, giving a value of 1.2 for the number of water molecules required to displace 1 nitromethane molecule.

When an aqueous solution of the iron complex was saturated with nitromethane, 2.4 molecules of nitromethane displaced 12.4 molecules of water giving a value of 0.2 molecules nitromethane required to displace each molecule of water. This is almost identical to that found for rhodamine B (*5*).

An attempt was made to correlate these values with the distribution constant *K* which was determined spectrophotometrically as described previously. Values of *K* for rhodamine B are given in Table 7. The initial concentration of rhodamine B in each solvent-saturated aqueous phase was 1×10^{-3} *M* before extraction.

No direct relationship between the distribution constant of rhodamine

B and the solvation number or the number of water molecules required to displace a solvent molecule from the solvation sphere is apparent.

When physical properties of the solvent such as density, refractive index, molecular refractive index, dielectric constant, dipole moment, parachor, solubility of the solvent in water, solubility of water in the solvent, and solubility parameters are compared to the solvation data and distribution constants, again no definite relationship appears to exist. The best correlation that can be made is between the number of water molecules required to displace a molecule of solvent from the solvation sphere and either the density, dielectric constant, or dipole moment of the solvent. The relationship is not linear, but the trend is in the same direction.

The distribution constant for rhodamine B between anhydrous 1-octanol and nitromethane was also determined. Extractions were made into 1-octanol-saturated nitromethane. *K*, defined as concentration in nitromethane/concentration in octanol, was found to be 1.87. This was somewhat unexpected since *K* for rhodamine B between 1-octanol and water is greater than K for the dye between nitromethane and water. An attempt was made, therefore, to determine if water might affect the distribution of rhodamine B between nitromethane and octanol as Motley (*20*) found for uranyl 8-hydroxyquinoline between nitromethane and decanol. Before this could be determined, the effect of water on the absorbance of rhodamine B in both solvents had to be measured.

Table 8 shows the absorbance values in the octanol solutions.

When the absorbance is plotted vs. $-[\log]$ water concentration, a linear curve is obtained.

In order to determine the effect of water on the distribution constant of rhodamine B between nitromethane and 1-octanol, solutions were prepared in nitromethane-saturated 1-octanol. These solutions were extracted with an equal volume of 1-octanol-saturated nitromethane and the absorbance of the nitromethane phase measured. The absorbance was constant within experimental error over the entire range of water concentrations, indicating that, at least for these concentrations, water has no effect on the distribution.

The effect of changing the initial concentration of rhodamine B in the octanol phase before extraction was determined. The distribution constant *K* was calculated as concentration in nitromethane/concentration in octanol. The results are given in Table 9.

A plot of *K* vs. $1/c$, where c is the initial concentration of rhodamine

TABLE 7

Distribution Constants for Rhodamine B Between Various Solvents and Water

Solvent	K
1-Butanol	60.2
Isoamyl alcohol	98.9
1-Octanol	150.0
Nitromethane	68.7
Nitrobenzene	144.4

TABLE 8

Effect of Water Concentration on the Absorbance of a 4×10^{-6} M Rhodamine B Solution in Nitromethane-Saturated 1-Octanol at 550 nm

Water concentration (M)	Absorbance
0.00	0.190
0.25	0.227
0.50	0.263
0.75	0.286
1.00	0.301

TABLE 9

Effect of Initial Concentration of Rhodamine B in 1-Octanol on the Distribution Constant Between Nitromethane and 1-Octanol

Initial concentration (M)	K
0.977×10^{-2}	1.30
2.03×10^{-2}	1.11
2.94×10^{-2}	1.05
4.00×10^{-2}	1.01
4.99×10^{-2}	0.99

B in octanol, is linear. Least squares treatment of the data gives the equation

$$K = 3.82 \times 10^{-3} (1/c) + 0.92$$

Values of K calculated using this equation are within 1% of the experimental values.

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