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Determination of Solvation Numbers of Rhodamine B in Various Solvents by Viscosity and Gas Chromatography Measurements

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Summary

Viscosity and gas chromatography measurements indicate that the solvation and hydration numbers for rhodamine B change when the compound is extracted into an organic phase. The results for several extraction systems are presented.

INTRODUCTION

A few of the fundamental questions that can be asked regarding the extraction of complexes and chelates are: (a) how many molecules of water and organic solvent are associated with the extractable species in the aqueous phase, and (b) does this number change during the extraction?

We used a viscosity method (*1*) and gas chromatography to study the aqueous system, and direct injection enthalpimetry (*2*), viscosity, and gas chromatography to examine the organic phase. The results for rhodamine B are presented in this paper and the results of other

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compounds plus the description of the differential direct injection enthalpimetry experiments will be reported in a later paper.

The requirements of a solute to be studied by the viscosity–gas chromatography methods are that it must be moderately soluble in water or organic solvent-saturated water, it must extract well into various organic solvents, and it should be a relatively large ion or molecule. The dye rhodamine B (a ligand), tris 1,10-phenanthroline iron(II) chloride (a complex), and iron(III) acetylacetonate (a chelate) were chosen for these studies. Rhodamine B is discussed here.

EXPERIMENTAL

Chemicals

All chemicals were reagent grade and were further redistilled or recrystallized before use (*3*).

Apparatus

Spectrophotometer: Beckman DB Viscometer: Cannon-Fenske type. Density: Weld bottles. Gas chromatograph: Micro-Tek 2500R, T.C. detector with Sargent SR recorder and a disk integrator.

Procedure

The procedure followed for the determination of the size and solvation number of rhodamine B was essentially that used by Kuruscev, Sargeson, and West (*1*). Solutions of the compounds were prepared from 0.01 to 0.05 *M*. 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.

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 bottle. In most cases the agreement between two measurements was better than 0.01%.

Viscosity. The viscosity of each of the solutions was determined at 25.0°C using Cannon-Fenske viscometers. In most cases the agreement between measurements was better than 0.2%.

Absorbance. The absorbance of each solution containing rhodamine B was measured at the wavelength of maximum absorbance, 550 nm. These measurements were used to determine the ligand concentration in each phase.

Extraction. Aqueous solutions of rhodamine B varying in concentration from 0.01 to 0.05 *M* were prepared in nitromethane-saturated water, 1-butanol-saturated water, and isoamyl alcohol-saturated water. Ten milliliters of each of these solutions was placed in a 50-ml polyethylene centrifuge tube, followed by 10 ml of the corresponding water-saturated solvent. The tube was shaken for 10 min in a mechanical wrist-action shaker. The tube was then placed in a centrifuge for 1 min and then in a constant temperature bath at 25.0°C for 30 min in order to achieve thermal equilibration of the two phases. The contents of the tube were then transferred to a separatory funnel and the two phases were separated. A blank containing no rhodamine B was treated in the same way. Solutions of rhodamine B were also prepared in 1-octanol-saturated nitromethane and extracted into nitromethane-saturated 1-octanol.

The concentration of each phase was determined spectrophotometrically after appropriate dilution. The distribution constant was calculated as the ratio of the concentration of solute in the organic phase to that in the aqueous phase.

Gas Chromatography. After extraction, the organic phase was analyzed for water content using the gas chromatography technique described by Gaede (*4*). Least squares analysis of the water concentration versus extracted solute concentration gave the solvation number after the method of Gere (*5*).

RESULTS AND DISCUSSION

Rhodamine B is known to exist in the free acid and lactone forms. Evidence for the conversion of one form to the other has been presented by Imai (*6*).

Since the degree of solvation may depend to some extent upon whether the dye is in the acid or lactone form, absorption spectra of rhodamine B in the UV region were obtained to determine which form was present in each of the solvents used. These spectra indicate that saturating water with 1-butanol, isoamyl alcohol, or 1-octanol does not produce a significant change in the structure of rhodamine B. There is very little difference in the absorbance at 258 and 355 nm, the absorption bands which Imai (*6*) has attributed to the acid form of the dye.

TABLE 1

Jones and Dole *B*-Coefficient and Apparent Molal Volume of Rhodamine B in Various Solvents

Solvent	Concentration range (mole/liter)	B	ϕ_v (cm^3/mole)
Aqueous ammonia buffer	0.01–0.09	1.52	379.56
Nitromethane-saturated water	0.01–0.09	1.49	397.50
Water-saturated nitromethane	0.01–0.07	1.51	392.63
Anhydrous nitromethane	0.01–0.09	1.33	396.30
Anhydrous 1-butanol	0.01–0.05	2.75	388.50
Water-saturated 1-butanol	0.01–0.05	1.81	387.88
1-Butanol-saturated water	0.01–0.05	1.83	402.96
Anhydrous nitrobenzene	0.01–0.05	1.81	383.40
Water-saturated nitrobenzene	0.01–0.05	2.07	379.18
Anhydrous 1-octanol	0.01–0.05	4.03	385.06
Water-saturated 1-octanol	0.01–0.05	4.00	382.21
Anhydrous isoamyl alcohol	0.01–0.05	3.51	385.81
Water-saturated isoamyl alcohol	0.01–0.05	2.64	390.90
Isoamyl alcohol-saturated water	0.01–0.05	2.00	403.27
Nitromethane-saturated 1-octanol	0.01–0.05	3.83	382.54
1-Octanol-saturated nitromethane	0.01–0.05	1.64	387.43

When rhodamine B is extracted from one of the alcohol-saturated aqueous solutions into the corresponding water-saturated alcohol, there is no significant amount of conversion from one form of the dye to the other.

In order to determine the effect of the extraction pH on the absorbance of rhodamine B, 2×10^{-6} M solutions of the dye were prepared in McIlvaine buffers over the pH range of 1.68 to 9.90. The absorbance was measured at 550 nm. Changes in pH over the range from 4.5 to 9.9 had little or no effect on the absorbance, so extractions were performed in unbuffered solutions. Concentrations were corrected for changes in E in each solvent combination.

Before any extractions were performed, the density and viscosity of rhodamine B 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.

Jones and Dole (*7*) found that the viscosity of dilute solutions of strong electrolytes is related to the concentration of the solute by the equation $\eta = \eta_0(1 + A\sqrt{c} + Bc)$, where η_0 is the viscosity of the pure solvent, η is the viscosity of the solution of concentration c moles per liter, and A and B are constants characteristic of the solute. Rearrangement of the equation gives $\eta_r - 1 = A\sqrt{c} + Bc$, where η_r, the relative viscosity, is η/η_0. The quantity $\eta_r - 1$ is known as the specific viscosity, η_{sp}. Substitution of this term into the equation gives $\eta_{sp} = A\sqrt{c} + Bc$. Jones and Dole suggest that the $A\sqrt{c}$ term, which becomes predominant at low concentrations, might be due to interionic electrostatic forces.

When the specific viscosity was plotted versus molar concentration, of the solutes investigated, a straight line was obtained in each case indicating a value of zero for the A-coefficient. Kurucsev (1) also found A to be zero for all but one complex ion. Plots of specific viscosity versus concentration of solute were made. The slope of the line in each case was calculated by the method of least squares and gave the best value of B. Table 1 shows the values of B for rhodamine B.

According to Gurney (*8*), 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 $B = \Sigma n_i B_i$.

TABLE 2

Calculated Values of Solvated Ion Volumes, Ionic Volumes, and Solvent Sheath Volumes for the Rhodamine B Cation in Various Solvents

Solvent	v (A^3)	v_i (A^3)	v_{solv} (A^3)
Aqueous ammonia buffer	1010 ± 146	591 ± 2	419 ± 148
Nitromethane-saturated water	990 ± 95	621 ± 5	369 ± 100
Water-saturated nitromethane	1003 ± 36	614 ± 6	389 ± 42
Anhydrous nitromethane	886 ± 114	619 ± 5	267 ± 119
Anhydrous 1-butanol	1827 ± 141	606 ± 12	1221 ± 153
Water-saturated 1-butanol	1209 ± 73	605 ± 15	604 ± 88
1-Butanol-saturated water	1214 ± 74	630 ± 17	584 ± 91
Anhydrous nitrobenzene	1203 ± 62	595 ± 12	608 ± 74
Water-saturated nitrobenzene	1375 ± 68	591 ± 13	784 ± 81
Anhydrous 1-octanol	2678 ± 68	601 ± 13	2077 ± 81
Water-saturated 1-octanol	2658 ± 240	596 ± 5	2062 ± 245
Anhydrous isoamyl alcohol	2332 ± 92	602 ± 18	1730 ± 110
Water-saturated isoamyl alcohol	1754 ± 59	610 ± 10	1144 ± 69
Isoamyl alcohol-saturated water	1329 ± 77	631 ± 14	698 ± 91
Nitromethane-saturated 1-octanol	2445 ± 208	596 ± 19	1949 ± 227
1-Octanol-saturated nitromethane	1090 ± 69	604 ± 5	486 ± 73

TABLE 3

Values of Solvation Numbers of Rhodamine B in Various Solvents Calculated From Viscosity Data

Solvent	Solvation number
Water	14.0 ± 4.9
Nitromethane	3.0 ± 1.3
Nitrobenzene	3.6 ± 0.4
1-Butanol	8.0 ± 1.0
Isoamyl alcohol	9.5 ± 0.4
1-Octanol	7.9 ± 0.2

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 has been referred to by Ogston (*9*) as the hydrodynamic volume and represents the volume, in cubic centimeters, occupied by the ion and its solvation sphere. Values of v for rhodamine B are given in Table 2.

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 $v_2 = 1000(d_0 - d)/mdd_0 + M/d$ (*5*), 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 rhodamine B are given in Table 2.

In the case of rhodamine B 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 A^3 was used for the ionic volume of Cl^- which is the average of the values reported by Eucken (*10*) and Darmois (*11*). The molecular volume of rhodamine B is shown in Table 2. The volumes occupied by the solvation spheres alone, v_{solv}, are also given.

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 solvation numbers of rhodamine B in various solvents are given in Table 3.

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 as suggested by Das (*12*).

The amount of water associated with the ions as they were extracted from water into the organic solvent was determined by the gas chromatography method described by Gaede (*4*). This technique has since been modified and improved by using methanol as an internal standard in the determination of water in various solvents (*13*). The results of the least squares analysis of the data are given in Table 4.

Since rhodamine B did not extract from nitromethane into water to a sufficient extent for gas chromatographic analysis of nitromethane, the extraction was simulated by dissolving various amounts of the dye in water which had been preequilibrated with nitromethane and then 5–10 drops of excess nitromethane added to resaturate the solution. It was assumed that the few drops of excess nitromethane did not extract enough rhodamine B to significantly alter the concentration of the aqueous phase. A blank was treated in the same manner.

The amount of organic solvent contained in the solvation sphere of rhodamine B dissolved in 1-octanol-saturated water and nitrobenzene-saturated water could not be determined by the gas chromatography method because of the low solubility of the dye in these solvents. An

TABLE 4

Moles Water/Mole Rhodamine B When Extracted into Various Solvents

Solvent	Moles water/mole rhodamine B
1-Butanol	17.8 ± 3.3
Isoamyl alcohol	17.8 ± 3.4
1-Octanol	7.3 ± 1.9
Nitromethane	5.6 ± 0.5
Nitrobenzene	10.8 ± 3.1

TABLE 5

Values of Solvation Numbers of Rhodamine B 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
Nitromethane saturated water	1.11 ± 0.2 Nitromethane	9.0 ± 3.4 Water
Water-saturated nitromethane	5.6 ± 0.5 Water	2.5 ± 0.7 Nitromethane
Water-saturated nitrobenzene	10.8 ± 3.1 Water	2.7 ± 1.0 Nitrobenzene
Water-saturated 1-butanol	17.8 ± 3.3 Water	0.5 ± 1.2 1-Butanol
Water-saturated isoamyl alcohol	17.8 ± 3.4 Water	3.3 ± 0.9 Isoamyl alcohol
Water-saturated 1-octanol	7.3 ± 1.9 Water	7.0 ± 1.2 1-Octanol
1-Octanol-saturated nitromethane	0.8 ± 0.6 1-Octanol	3.0 ± 2.5 Nitromethane

attempt to determine 1-butanol and isoamyl alcohol in the solvation sphere of rhodamine B dissolved in the corresponding alcohol-saturated aqueous solutions by this method was also unsuccessful because of the high solubility of the alcohols in water. No difference could be observed between the chromatographic peak areas of the samples and the blank.

The method was useful, however, in determining the amount of nitromethane in the solvation sphere of rhodamine B in nitromethane-saturated aqueous solutions. The results of the least squares analysis of the data indicate 1.1 ± 0.2 moles of organic solvent per mole of rhodamine B.

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 are given in Table 5 for rhodamine B.

Rhodamine B solutions were also prepared in nitromethane-saturated 1-octanol and the dye extracted into 1-octanol-saturated nitromethane. Viscosity and density measurements were made on both phases and the solvation sphere volumes calculated, the results of which are shown in Tables 1 and 2. Gas chromatographic analysis of the nitromethane phase showed 0.84 ± 0.56 1-octanol molecules per molecule of rhodamine B. The amount of nitromethane associated with rhodamine B in the octanol phase could not be determined by gas chromatography because of the high solubility of nitromethane in 1-octanol.

Comparison of the solvation numbers of rhodamine B 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 values are given in Table 6. When the same calculations are performed on the data in nitromethane-saturated water, it is found that 5.0 molecules of water are displaced from rhodamine B when the water is saturated with nitromethane. Since 1.1 molecules of nitromethane are associated with

TABLE 6

Comparison of Solvation Numbers of Rhodamine B in Anhydrous and Water-Saturated Solvents

Solvent	Number of organic solvent molecules displaced from rhodamine B by saturating solvent with water	Number of water molecules associated with rhodamine B in water-saturated solvent	Number of water molecules required to displace one organic solvent molecule from the solvation sheath of rhodamine B
1-Butanol	7.5	17.8	2.4
Isoamyl alcohol	6.2	17.8	2.9
1-Octanol	0.9	7.3	8.1
Nitromethane	0.5	5.6	11.2
Nitrobenzene	0.9	10.8	12.0

rhodamine B in nitromethane-saturated water, it appears that 0.22 molecules of nitromethane are required to displace each molecule of water from the solvation sphere.

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