Studies of the Liquid-Liquid Partition Systems. I.
The Distribution of Radon(0) between Various Organic Solvents and Aqueous Solutions

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The partition of a chemical species between two equilibrated immiscible liquid phases has been studied for a long time, and the constants have been determined for various distribution, association, or dissociation equilibria. At the same time, the partition method has been applied in many different fields, and the "solvent extraction method" has been recognized as one of the most rapid and effective methods for the separation or the purification of various materials.

The present series will present the results of our study of the liquid-liquid partition systems. In them chemical species are distributed between two phases; usually one is an aqueous solution which contains non-electrolytes, complex-forming ligands, or electrolytes, while the other is an organic solvent with various extractants.

The first paper of this series will report on the distribution of radon(0) between aqueous solutions and pure organic solvents. Inert gases were chosen as one of the simplest molecules, and radon was chosen because it may be most easily polarized or most easily interacted with other molecules among the inert gas elements.

The Previous Work.—Even though the inert gases show a very poor interaction with other atoms or molecules, it has been established that they have some solubility in water. The distribution ratio of radon between the air and water was determined at different temperatures,[1-5] and it was reported to be affected by solutes in the water.[6] It was also found that radon is distributed from air to various solvents better than to water.[7] These findings were reviewed by Bonner and Kahn.[8]

Recently, some authors have studied the behavior of inert gases in solutions. Lawrence

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and his co-workers⁹⁾ described how xenon is twice as soluble in water and fat as nitrogen, while helium shows a lower solubility. They reviewed the solubilities of hydrogen, oxygen, carbon dioxide, nitrogen, helium, argon, krypton, xenon and radon in water and oil. Semenchenko¹⁰⁾ described a theory for the solubility of gases and discussed that of radon. Morrison and Billet¹¹,¹²⁾ described the salting-out of non-electrolytes and discussed the solubility of gases. Friedman¹³⁾ determined the solubility of rare gases, sulfur hexafluoride and osmium tetroxide in nitromethane and gave an equation which, in his opinion, correlated the solubility with two terms that depend on the solvents and gases. Diamond and Tuck¹⁴⁾ gave an indirect estimation of the distriribution of helium, neon, argon, krypton and xenon between water and nitromethane on the basis of Friedman's data. Clever and his co-workers¹⁵⁾ reported on the solubility of helium, neon, argon, krypton and xenon in methylcyclohexane and perfluorocyclohexane, and Nussbaum and Hursh¹⁶⁾ reported on the solubility of radon in fatty acids and triglycerides. Namiot¹⁷⁾ discussed the solubility of nonpolar gases in water.

The formation of inert gas hydrates or deuterates¹⁸⁻²¹⁾ has been observed and explained in terms of the dipole-induced dipole attraction. The hydration numbers of these compounds, $G \cdot xH_2O$ and $G \cdot yD_2O$, x and y, were reported to be approaching six, but becoming so only with the heaviest inert gases. The crystals of these compounds are obtained only when water and inert gases are cooled at a low temperature under pressure. Other examples of such solvates have been also reported, for instance, phenol derivatives, $Kr \cdot 2C_6H_5OH$, $Xe \cdot 2C_6H_5OH$, and $Rn \cdot 2C_6H_5OH$.²²⁾ Among other examples of the interaction between the inert gas atom and other atoms or molecules, the most remarkable are the xenon compounds with fluorine or oxygen, or krypton with fluorine.²³⁾

The Present Work.—The present work will first describe the distribution of radon between various organic solvents and water; next, it will describe the distribution of radon between carbon tetrachloride and calcium chloride solutions of various concentrations at 25°C. Finally, it will suggest the use of solvent extraction as a convenient separation or concentration technique for radon in various aqueous solutions where radium and its daughter nuclides coexist.

Experimental

Reagents and Solutions.—All of the reagents used in this study were of reagent grade. The calcium content in the stock calcium chloride solution was determined by complexametry using a murexide indicator, while the chloride ion was titrated by argentometry using a fluorescein indicator. The calcium and chloride ion contents thus determined agreed with each other very well. Calcium chloride solutions of various concentrations were made by the addition of a weighed portion of water to a weighed portion of a calcium chloride stock solution.

The organic radon stock solution was prepared as follows: A pure radium nitrate solution in a bottle with a stopper had been left standing for a few days after the chemical separation from the daughter nuclides; then an organic solvent was added, and the whole was shaken for a few minutes. Then the organic phase was pipetted out and transferred into a stoppered centrifuging tube. Water was then added, and the tube was shaken again and centrifuged. The organic phase was pipetted off and used as the radon organic stock solution. In the earlier stage of the work, radon was emanated from a radium sulfate-barium sulfate precipitate into pure water. Radon was extracted from the supernatant solution with the various solvents to be studied.

Procedures.—All of the experiments were carried out in a thermostated room at 25°C. Ten milliliters of one of the organic radon solutions and 10 ml. of water were added to a glass stoppered centrifuging tube. The volume of the tube was about 21—22 ml. The two phases in the tube were equilibrated by mechanical agitation for about one hour and they separated by centrifugation. An 8 ml. portion was pipetted off from each phase and transferred into a small glass-stoppered 10 ml. test tube. Then 2 ml. of a non-radioactive organic solvent or water was added into the test tube to expel the air left at the top in order to avoid any changes in the geometrical efficiency of the radioactivity measurement which could be caused by the escape of radon into the gas phase.

The distribution ratio of radon between carbon tetrachloride and calcium chloride solutions of various concentrations was determined in just the

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same way as has been described above, except that the calcium chloride solutions were used as the aqueous phase instead of pure water.

The Measurement of Radioactivity.—After the samples in the small glass-stoppered test tubes for radioactivity measurements had been left stand more than six hours, the γ-radioactivity was measured with a well-type scintillation counter with a sodium iodide(Tl) scintillator.

Results

The Decay of the γ-Radioactivity.—Figure 1 gives an example of the decay curves of the γ-radioactivity. The half-life of the γ-radioactivity in all samples properly prepared agreed with the literature value (3.825 days for ^{222}Rn) after the radioactive equilibrium was reached. Six hours' standing after the phase separation was enough for both phases to reach the radioactive equilibrium.

The Distribution Constant for Radon between Water and Various Solvents.—The distribution constants, K_D, was defined as follows:

$$K_D=[\mathrm{Rn}]_{org}/[\mathrm{Rn}]_{aq}=\frac{\gamma\text{-count rate per ml. of org. soln.}}{\gamma\text{-count rate per ml. of aq. soln.}} \qquad (1)$$

Table I gives the distribution constants of radon between water and various organic solvents.

The Distribution of Radon between Carbon Tetrachloride and Calcium Chloride Solutions of Different Concentrations.—Table II gives the results of the distribution ratio of radon between carbon tetrachloride and aqueous solutions of calcium chloride at various concentrations. Figure 2 gives the plot of the distribution ratio against the calcium chloride concentration.

TABLE I. DISTRIBUTION CONSTANTS OF RADON BETWEEN WATER AND VARIOUS ORGANIC SOLVENTS AT 25°C

$K_D=[\mathrm{Rn}]_{org}/[\mathrm{Rn}]_{aq}$

	Solvent	K_D*
1	Carbon tetrachloride	59
2	Chloroform	56
3	Bromoform	39
4	Hexane	80
5	Methyl isobutyl ketone (Hexone)	37
6	Methyl isobutyl carbinol (Hexol)	33
7	Chlorobenzene	56
8	Bromobenzene	39
9	Nitrobenzene	21
10	*o*-Dichlorobenzene	50

* The values of K_D gives the average. The original data are follows: 1 (52, 53, 57, 61, 62, 62, 63); 2 (47, 51, 59, 60, 61); 3 (39, 39, 40); 4 (71,81, 89); 5 (32, 36, 44); 6 (27, 35, 36); 7 (53, 54, 61); 8 (39, 39, 40); 9 (20, 21, 22, 22); 10 (41, 47, 52, 53, 53, 55).
The results for benzene, toluene and xylene are not reproducible. The values are as follows: benzene (88, 88, 92, 113, 114, 119); toluene (72, 72, 82, 116, 118, 137); xylene (56, 65, 73, 84, 95, 107).

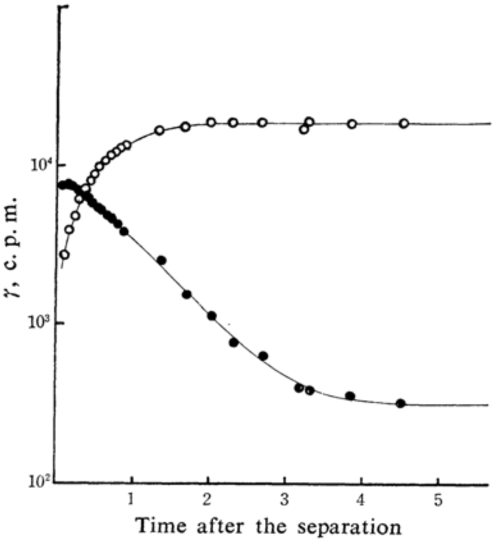

Fig. 1. Change of the γ-radioactivity in the organic and aqueous samples
Open circles; carbon tetrachloride
Closed circles; pure water

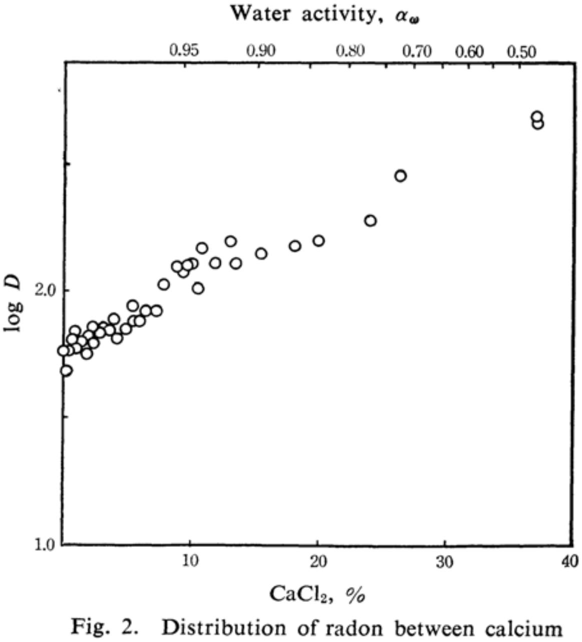

Fig. 2. Distribution of radon between calcium chloride solutions and carbon tetrachloride at 25°C.

TABLE II. DISTRIBUTION RATIO OF RADON BETWEEN CALCIUM CHLORIDE SOLUTIONS AND CARBON TETRACHLORIDE AT 25°C

$D=[\mathrm{Rn}]_{org}/[\mathrm{Rn}]_{aq}$

$CaCl_2$ %	log$D$	$CaCl_2$ %	log D	$CaCl_2$ %	log D
0.28	1.674	2.92	1.840	9.71	2.100
0.45	1.766	3.10	1.863	9.97	2.104
0.65	1.811	3.60	1.842	10.36	2.017
0.81	1.833	3.92	1.899	10.70	2.176
0.83	1.849	4.14	1.810	11.81	2.114
1.17	1.772	4.81	1.859	12.91	2.201
1.39	1.792	4.89	1.859	13.37	2.114
1.77	1.743	5.36	1.941	15.38	2.146
1.93	1.818	5.43	1.877	17.93	2.179
2.20	1.852	5.95	1.880	19.73	2.201
2.24	1.780	6.49	1.920	23.84	2.277
2.42	1.851	7.18	1.915	25.04	2.431
2.56	1.840	7.75	2.025	26.10	2.460
2.65	1.847	8.84	2.109	36.94	2.664
2.91	1.869	9.41	2.084	36.94	2.682

Discussion

The Measurement of γ-Radioactivity.—The decay chain of $(4n+2)$ series after ^{226}Ra has been well established. As the radium stock solution was purified from ^{210}Pb (half-life is 22 years.) before use, the radioactivity of the daughter nuclides after ^{210}Pb, ^{210}Bi, ^{210}Po and ^{206}Tl can be neglected in this experiment.

Figure 1 seems to show the following; (i) the distribution of radon into the organic phase is very high, but that of its γ-radioactive daughter nuclides is low. (ii) The γ-radioactive daughter nuclides in the decay products of ^{222}Rn, ^{214}Pb (RaB, 26.8 min.) and ^{214}Bi (RaC, 19.7 min.) grow in the organic phase during the radon decays to ^{218}Po (RaA, 3.05 min.). On the other hand, these nuclides in the aqueous phase decrease, until finally the radioactive equilibrium is reached between the ^{222}Rn and these nuclides. (iii) The radioactive equilibrium between ^{222}Rn and these γ-radioactive daughter nuclides is first reached in the organic phase, but it takes longer in the aqueous phase because a large amount of ^{214}Pb and ^{214}Bi are back-extracted from the organic phase, which contains a much larger amount of ^{222}Rn than does the aqueous phase.

From these results, it may be concluded that the distribution ratio of ^{222}Rn in a liquid sample in an air-tight container can be determined by the direct measurement of the γ-radioactivity with a welltype scintillation counter if the samples are left standing until the radioactive equilibrium between the ^{222}Rn and its γ-radioactive daughter nuclides, ^{214}Pb and ^{214}Bi, is reached.

The Distribution of Radon between Water and Varous Organic Solvents.—In a liquid-liquid partition system, the K_D value generally gives the ratio of the relative solubility of radon in the two phases when they are mutually saturated; that is,

$$K_D=\frac{\text{the solubility of Rn in the organic solvent satd. with water}}{\text{the solubility of Rn in the water satd. with the organic solvent}} \tag{2}$$

and when the distribution constant of radon between air and a liquid, K, is defind as follows:

$$K=\frac{\text{the concn. of Rn in the liquid}}{\text{the concn. of Rn in air } (\sim 1\text{ atm.})} \tag{3}$$

Therefore, one may calculate K_D' as follows:

$$K_D'=\frac{\text{the solubility of Rn in a pure organic solvent}}{\text{the solubility of Rn in pure water}}=\frac{K_{org}}{K_{aq}} \tag{4}$$

The difference between K_D in Eq. 2 and K_D' in Eq. 4 depends on whether or not the two phases are mutually saturated. Table III gives K_D' values calculated from previous data by Eq. 4.

TABLE III. CALCULATED DISTRIBUTION CONSTANTS OF RADON BETWEEN WATER AND VARIOUS ORGANIC SOLVENTS AT 18°C FROM PREVIOUS WORK

$K_{D'}=K_{org}/K_{aq}$

$$K=\frac{(\text{concn. of Rn in liq. phase})}{(\text{concn. of Rn in air (ca. 1 atm.)})}$$

Solvent	K_{org}	K_D'	Ref.
Chloroform	15.1	53.0	7
Chloroform	15.08	52.9	1
Carbon disulfide	23.1	81.1	7
Hexane	16.56	58.1	7
Benzene	12.82	45.0	7
Toluene	13.24	46.5	1
Toluene	13.2	46.3	7
Xylene	12.75	44.7	1
Xylene	15.4	54.0	7
Cyclohexane	18.04	65.3	7
Ethyl acetate	7.35	25.8	7
Ethyl acetate	7.35	25.8	1
Ethyl ether	15.1	53.0	7

The K_D values in Table I (present work) and the K_D' values in Table III do not agree well, except for chloroform. Until now it has not been possible to ascertain whether these differences were caused by the mutual saturation or by some other reasons.

The total recovery of radon was found to be nearly quantitative; that is, the escape of radon from the two phases was small. However, if some part of the aqueous phases escapes into the air during the operation, it causes a large error in K_D even though it causes only a small loss in the total recovery because the aqueous phase contains an only small part of the total radon.

The results for benzene, toluene, and xylene were scattered, and so no values are given for these solvents in Table I, but the data obtained are shown at the foot of the table.

The results in Table I can be summarized as follows: (i) The distribution constant of radon is generally smaller when the solvent is more soluble in the water (methyl isobutyl carbinol $\sim$ methyl isobutyl ketone $<$ hexane). (ii) Bromine-containing solvents give smaller distribution constants than their chlorine homologues (bromoform $<$ chloroform, bromobenzene $<$ chlorobenzene). (iii) The distribution constants are much larger than unity; that is, the relative solubility of radon in the organic solvents is much higher than that in water.

The interaction between radon and water has been explained by the dipole-induced dipole interaction.[21] However, radon interacts with the organic solvents better than with water, although the solvents show smaller dipole moments than the water. Further information seems to be necessary in order to explain these results.

The Distribution of Radon between Calcium Chloride Solutions and Carbon Tetrachloride.—It was observed in the present work that the addition of calcium chloride to the water increases the extraction of radon even when the concentration is less than 10%. This agrees with the observation of Kofler.[24] He described how the solubility of radon in water is decreased by the addition of even a very small amount of salts. For example, he reported that the addition of 1% sodium chloride decreases the relative solubility of radon, K in Eq. 3, to 88.5% of that in pure water (0.270 at 18°C).

Radon in the aqueous phase may be hydrated (cf. Refs. 18—21), whereupon some or all of the water molecules combined with radon will be dissociated when the radon is distributed from the aqueous phase to the organic phase. It may also happen that the hydration number of radon changes with the change in the water activity. Thus the change in the water activity may be one of the reasons for this strong salting-out. Figure 2 also shows the water activity in the solution described in the literature.[25]

A Solvent Extraction Method for the Separation and the Concentration of Radon from Aqueous Radium Solution.—From the results of the present work, the following solvent extraction procedure can be suggested for the separation and the concentration of radon in aqueous solutions of radium(II).

Solvents.—Any of the organic solvents in Table I can be used. However, those which are not very soluble in water are more useful, and the use of carbon tetrachloride or hexane, for example, is recommended.

Aqueous Solution.—Any radium(II) aqueous solution can be used. The addition of a small amount of acid or a complexing agent (such as disodium ethylenediaminetetraacetate) will prevent the radiocolloid formation which sometimes causes the loss of radium or the contamination of the organic phase. The addition of electrolytes may improve the recovery of radon into the organic phase.

Recommended Procedure.—The aqueous radium solution and the organic solvent are placed in a small, stoppered tube. The space occupied by air should be minimized for a good recovery. The tube is then rotated mechanically to agitate the phases, and centrifuged. The organic phase is taken as a radon solution and, if necessary, the organic solution is washed with an aqueous solution containing acid or some complexing reagent in order to make further purification from radium and the daughter nuclides. When no quantitative recovery of radon is necessary, radon can be extracted only by shaking an aqueous solution of radium with an organic solvent in a glass-stoppered bottle or a separatory funnel.

Summary

(1) The distribution of radon between various organic solvents and water has been determined at 25°C. Radon is always distributed better into the organic phase. The distribution constants of radon in these liquid-liquid partition systems are in the range from 25 to 80.

(2) The distribution of radon between aqueous calcium chloride solution of various concentrations and carbon tetrachloride has been determined at 25°C. A remarkable salting-out effect for radon has been observed.

(3) A solvent extraction method for the separation of radon from radium(II) and the decay products in aqueous solutions has been suggested.

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