BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2836—2839 (1967)

Some Applications of the Regular Solution Theory to Solvent Extraction. IV. Oxine-Inert Solvent System

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(Received June 27, 1967)

The distribution coefficients of oxine between aqueous solutions with the ionic strength of 0.1 and 12 inert solvents were determined photometrically at 25°C. By a previously-proposed equation, the distribution coefficients were then correlated quantitatively with the solubility parameters of the solvents. The solubility parameter for oxine was evaluated as 10.9, and that for an aqueous solution, as 16.9_5, while the molar volume of oxine was estimated to be 124 cc/mol. The distribution of the two methyl derivatives of oxine was also discussed.

In this series of papers,[1-3] the partition equilibria of β-diketones and their scandium chelates have been studied as a test of the validity of an equation[1] previously derived from the regular solution theory.

The distribution coefficient of compound A, P_A, defined as the ratio of the mole fractions in the two phases, is given by:

$$\log P_A = \frac{V_A}{2.30\,RT}(\delta_{aq}+\delta_{org}-2\delta_A)(\delta_{aq}-\delta_{org}) \tag{1}$$

where V_A stands for a molar volume of A, δ_i, for a solubility parameter of the component, i, and the subscripts org and aq, for the organic and aqueous phases respectively. This equation is based on the assumption that a given species constitutes a regular solution in both phases. In a previous work,[1] it was shown that an aqueous solution could apparently be treated as a regular one as long as an empirical value was used for the solubility parameter in an aqueous solution. The empirical value for an aqueous solution was 16.3_5 in the case of β-diketone.

In the present study, the author will determine the distribution coefficients of oxine between inert solvents and an aqueous solution, and test the applicability of Eq. (1) to this system.

Experimental

Reagents. The solvents used are listed in Table 1; they were all of a guaranteed reagent grade, and no further purification was carried out except in the case of chloroform. The chloroform was washed twice by shaking it with redistilled water. The oxine (Kanto Chemical Co.) was purified by recrystallization from ethanol and dried over phosphorus pentoxide.

Procedures. A volume of 5 m*l* of an organic solvent containing a known amount of oxine was shaken for 3 hr at 25°C with an equal volume of a phosphate buffer solution with an ionic strength of 0.1, adjusted by sodium chloride. After equilibration, a constant volume of diluted perchloric acid was added to an aliquot of the aqueous phase in order to obtain a constant pH value of 1.0. The absorbance of this solution was then measured at the wavelength of 251 mμ against a blank saturated with the solvent. In the case of volatile solvents with an absorption near the wavelength of 250 mμ, such as benzene or xylene, the solution was allowed to stand in a beaker until the blank showed a transmittance of above 99 per cent against 0.1 M $HClO_4$. A volume reduction by the volatilization of the water for this period was cancelled out by employing a standard aqueous solution of oxine treated under the same conditions.

Calculation of Distribution Coefficient. From the absorbance and the initial concentration of oxine in the organic phase, the distribution ratio of the reagent was calculated. The intial concentration of oxine was below 3×10^{-3} M in all cases. The distribution ratio of oxine in terms of molarity, D, is given by:

$$D=\frac{[H^+]K_1D_0}{[H^+]^2+[H^+]K_1+K_1K_2}$$

where K_1, K_2, and D_0 are, respectively, the first and the second dissociation constants and the distribution coefficient defined as the ratio of the molarities of the undissociated oxine in the two phases. The values of pK_1 and pK_2[4] are so different that the maximum distribution ratio can be equated to the distribution coefficient with an error of less than one per cent. The maximum appears in the pH range between 7 and 8. The values of pH adopted were about 7.1, 7.4, and 7.7 at equilibrium in each run. The tabulated values were obtained as the average of three independent runs.

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[1] T. Wakabayashi, S. Oki, T. Omori and N. Suzuki, *J. Inorg. Nucl. Chem.*, **26**, 2255 (1964).

[2] T. Omori, T. Wakabayashi, S. Oki and N. Suzuki, *ibid.*, **26**, 2265 (1964).

[3] S. Oki, T. Omori, T. Wakabayashi and N. Suzuki, *ibid.*, **27**, 1141 (1965).

[4] $pK_1=5.02$ (20°) $pK_2=9.81$ (25°). R. Näsänen, P. Lumme and A. L. Mukula, *Acta Chim. Scand.*, **5**, 1199 (1951).

Results and Discussion

The distribution coefficients, D_0, are summarized in Table 1. Taking account of the low concentrations of oxine, the distribution coefficients, P, in terms of the mole fraction can easily be obtained from D_0 by multiplying the ratio of V_{org} to $V_{\mathrm{H_2O}}$ at 25°C.

In the present study, Eq. (1) involves three unknown values, that is, the molar volume of oxine, V_{ox}, at 25°C, and the solubility parameters of oxine, δ_{ox}, and of an aqueous solution, δ_{aq}. If the equation is valid in the present system, it should express the observed data quantitatively when a reasonable set of numerical values is given for the three unknown quantities. The numerical values can be obtained as three coefficients of the quadratic equation for the solubility parameter of an organic solvent:

$$2.3\boldsymbol{RT}\log P = A\delta^2{}_{\mathrm{org}} + B\delta_{\mathrm{org}} + C$$

where $A = -V_{\mathrm{ox}}$, $B = 2\delta_{\mathrm{ox}}V_{\mathrm{OX}}$

and $C = \delta_{\mathrm{aq}}(\delta_{\mathrm{aq}} - 2\delta_{\mathrm{ox}})V_{\mathrm{ox}}$.

The numerical values obtained by the method of least squares are 124 cc/mol, 10.8_8, and 16.9_5 for the molar volume of oxine at 25°C (hypothetical supercooled liquid), for the solubility parameter of oxine, and for that of an aqueous solution respectively. The distribution coefficients of oxine then calculated from the equation with the three parameters thus obtained are listed in the last column of Table 1. The reproducibility is fairly good.

TABLE 1. DISTRIBUTION COEFFICIENTS OF OXINE, 25°C

No.	Solvent	δ6)	log D_0	
			Obs	Calcd
1	*n*-Hexane	7.3	1.34	1.31
2	*n*-Heptane	7.45	1.35	1.35
3	*n*-Octane	7.55	1.34	1.36
4	Carbon tetrachloride	8.6	2.05	2.13
5	Isopropylbenzene	8.65	2.03	2.00
6	*m*-Xylene	8.8	2.12	2.10
7	Toluene	8.9	2.21	2.21
8	Benezene	9.15	2.35	2.37
9	Chloroform	9.3	2.58	2.46
10	Chlorobenzene	9.5	2.39	2.41
11	Methylene chloride	9.7	2.58	2.65
12	*o*-Dichlorobenzene	10.0	2.48	2.47

The molar volumes of oxine were measured over a temperature range between 75°C and 100°C. As Fig. 1 shows, the molar volume of liquid oxine at 25°C can be estimated to be about 120 cc/mol by considerably long extrapolation. The value compares favorably with the calculated value.

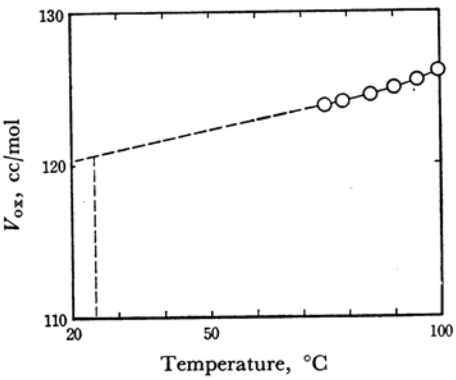

Fig. 1. Molar volume of oxine.

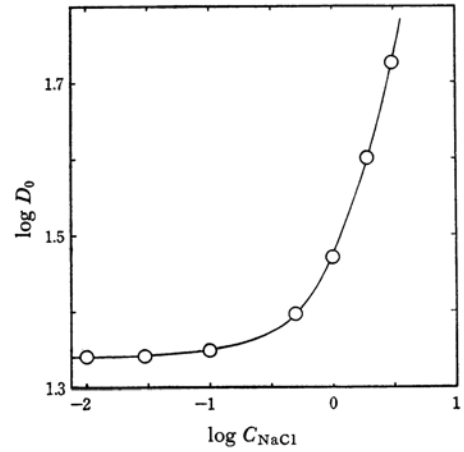

Fig. 2. Distribution coefficient of oxine between *n*-hexane and aqueous solution as a fuction of the concentration of salt (NaCl).

As the solubility parameter for an aqueous solution with an ionic strength of 0.1, two values were obtained; 16.3_5 for a β-diketone-inert solvent system in the previous work, and 16.9_5 for an oxine-inert solvent system in the present work. The ionic strength of an aqueous solution has no essential influence upon the distribution of oxine at a low ionic strength, as is shown in Fig. 2. Therefore, it is expected that the empirical value as the solubility parameter for an aqueous solution with an ionic strength of zero is nearly the same with the value obtained for an aqueous solution with an ionic strength of 0.1. In the regular solution theory the heat of mixing is expressed in terms of the square of the difference between the solubility parameters of the two species; *i. e.,* it is always positive, and if there is any specific interaction between the two species, the value estimated from the solubility parameters becomes larger than the real value. The solubility parameter for water, as calculated from the heat of vaporization, is 23.8; this value gives a satisfactory explanation of the solubility of water in many hydrocarbons5)

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5) C. Black, G. G. Joris and H. S. Taylor, *J. Chem. Phys.*, **16**, 537 (1948).

which are normal liquids, while the present reagents have functional groups which interact strongly with water. From these considerations it may be understood why the low values have been obtained as the solubility parameters for water and why different values may be obtained for different systems.

If the above discussion is adequate, it should be possible to estimate the solubility of the reagents in water reasonably by using the numerical values obtained by Eq. (1) from the data of the partition equilibria. The activity of a certain species, A, is given by:⁶⁾

$$\ln a_{\mathrm{A}} = \ln X_{\mathrm{A}} + \frac{V_{\mathrm{A}}\phi^2{}_{\mathrm{B}}(\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^2}{\boldsymbol{R}T} \tag{2}$$

where a_{A}, X_{A}, and ϕ_{B} are the activity of A, the mole fraction of A, and the volume fraction of the solvent, B, in the solution respectively. In the equation the pure liquid at the same temperature is chosen as the standard state, while the supercooled liquid is chosen when dealing with solids. From Eq. (2) the solubility of reagents can be calculated. Since the activity of acetylacetone is equal in both phases when the acetylacetone phase and the aqueous phase are saturated with each other, the solubility of acetylacetone in water can be obtained by replacing the left-hand side of Eq. (2) with $\ln X'_{\mathrm{AA}}$, which is the mole fraction of acetylacetone in its phase and which is calculated from Eq. (2) by regarding water as the solute. When V_{AA}, δ_{AA}, and $\delta_{\mathrm{H_2O}}$ are taken as 102 cc, 10.6, and 16.3_5,¹⁾ the solubility of acetylacetone in water is calculated to be 0.117 M, a value which is comparable to the observed value of 0.122 M.⁷⁾

To calculate the solubility of oxine, the activity of solid oxine referred to the hypothetical liquid supercooled below the melting point is required; it is estimated from the equation on the assumption that the heat of fusion is constant:

$$\ln a^{\mathrm{s}} = \frac{\Delta H^{\mathrm{F}}}{\boldsymbol{R}} \frac{T - T_{\mathrm{m}}}{T_{\mathrm{m}}T} \tag{3}$$

where ΔH^{F} is the heat of fusion of oxine, and T_{m}, the melting point. There is no available data about the heat of fusion of oxine; however, it may be assumed to be approximately 5—6 kcal/mol from the heat of fusion of 5.6 kcal/mol for α-naphthol, which is similar to oxine in many respects; the structure, the melting point (372°K for oxine and 368°K for α-naphthol), and the boiling point (540°K and 556°K). From Eqs. (2) and (3), the solubility of oxine is calculated to be 7.6×10^{-3} M for the heat of fusion of 5 kcal and 6.0×10^{-3} M for 6 kcal. The intrinsic solubility of oxine in an aqueous solution with an ionic strength of 0.1 at 25°C has been calculated to be 4.75×10^{-3} M by Irving *et at.*⁸⁾; this value is of the same order as the calculated value.

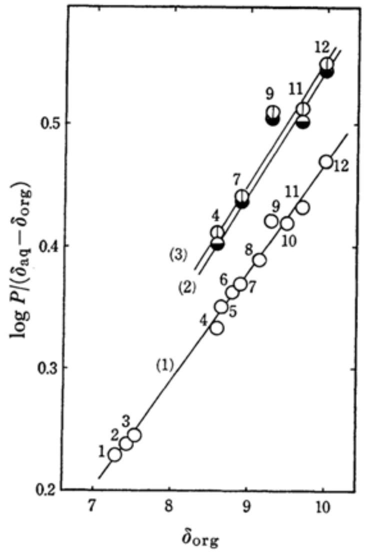

Fig. 3. Correlation between distribution coefficients of oxine and its methyl derivatives and solubility parameters of solvents.
(1) Oxine ○
(2) 2-Methyl-oxine ◒
(3) 4-Methyl-oxine ⦶

TABLE 2. SOLUBILITY PARAMETERS AND MOLAR VOLUMES OF OXINE AND ITS METHYL DERIVATIVES

	δ	V, cc/mol
Oxine	10.8_8	124 (120)*
2-Methyloxine	10.7_2	139
4-Methyloxine	10.6_7	139

* From Fig. 1

Figure 3 shows the plots of the data on the two methyl derivatives of oxine by Mottola and Freiser,⁹⁾ together with the data of oxine. The solubility parameter for an aqueous solution is taken as 16.9_5 for both the methyl derivatives on the assumption that the interaction between the reagents and water molecule is much the same as in the case of oxine. The applicability of Eq. (1) is confirmed by the linearity of the plots.

In the case of chloroform, considerable deviations are observed, and the same is true in β-diketone-inert solvent systems. These facts suggest the presence of some specific interactions between the solvent and solutes.

From the slopes of these lines and from the intersections with ordinates, molar volumes and the

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6) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, New Jersey (1962).

7) "Handbook of Chemistry and Physics," 41st Edition, Chemical Rubber Publishing Co. (1960).

8) H. Irving, A. D. Ewart and J. T. Wilson, *J. Chem. Soc.*, **1949**, 2672.

9) H. A. Mottola and H. Freiser, *Talanta*, **13**, 55 (1966).

solubility parameters for the reagents can be estimated. The values are listed in Table 2.

It is evident from the study that, for inert solvent-water system, the regular solution theory gives a good interpretation and enables us to estimate the solvent extraction of chelating agents provided that a suitable parameter is chosen for the aqueous solution. It has also been shown that the empirical solubility parameter for an aqueous solution determined from the partition equilibria of a reagent by Eq. (1) not only fits the data, but also constitutes a measure of the interaction between the reagent and water.

The author wishes to take this opportunity to express his thanks to Professor K. Seto and N. Suzuki for their continuing interest and discussion, and to Mrs. R. Suzuki for her assistance.