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Some Empirical Correlations in Solvent Extraction

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Summary

Empirical equations with correlation coefficients greater than 0.9 for the solvent extraction of $GeCl_4$, $GeBr_4$, acetylacetone, trifluoroacetylacetone, thenoyltrifluoroacetone, 1-nitropropane, bis-thenoyltrifluoroacetone zinc(II), and several dicarboxylic acids in various solvents are presented.

INTRODUCTION

Although many attempts have been made to describe the solvent extraction of metal chelates, ion association systems, and molecular species in terms of the many factors which influence extraction, the role of the extracting solvent and its properties have received the most attention in the past decade (*2, 4, 6, 8–12, 15, 23, 27*).

The regular solution theory of Hildebrand and Scott (*12*) and the use of solubility parameters has been applied with some success to the extraction of many different solutes in a variety of solvent systems (*1, 3, 7, 14–22, 24, 25*).

The purpose of the present study was to determine whether any other correlations exist between the distribution constant and physical

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properties of the extracting solvent. Those equations found to have correlation coefficients greater than 0.9 are reported here.

RESULTS AND DISCUSSION

In an initial attempt to correlate physical properties of the extracting solvent with distribution constants, the extraction data of Mottola and Freiser (*15*) for the distribution of 8-quinolinol between water and 12 different organic solvents were used. However, no linear relationship could be found. It would appear that perhaps the effects of hydrogen bonding outweigh the effect of any of these properties. Classifying the solvents according to the method of Ewell (*6*) likewise produced no obvious correlation.

The same properties and combination of properties were compared

TABLE 1

Comparison of Experimental Values of D_0 for Germanium Tetrachloride and Those Calculated Using the Equation

$$\log D_0 = 0.8316[\log MR + 0.1(\delta_{GeCl_4} - \delta_0)^2 - 0.1d] + 1.847$$

Solvent	Exptl D_0	Calcd D_0	Per cent error
Isooctane	3.16	2.83	10.5
n-Hexane	4.44	4.18	5.9
n-Heptane	4.22	3.89	7.8
n-Octane	3.76	3.60	4.3
n-Decane	2.98	3.11	4.4
n-Hexadecane	2.48	2.22	10.5
Cyclohexane	5.14	5.14	0.0
Carbon tetrachloride	6.76	5.95	12.0
Toluene	4.35	4.23	3.0
o-Xylene	3.97	3.66	7.8
1,2-Dichloroethylene	5.63	6.24	10.8
Benzene	4.02	4.46	10.9
Chloroform	6.17	5.50	10.9
Trichloroethylene	5.50	4.76	13.4
Chlorobenzene	3.34	3.42	2.4
1,1,2,2-Tetrachloroethane	2.67	3.37	29.5
1,2-Dichloroethane	2.71	4.16	53.6
Bromoform	2.13	2.11	0.9

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TABLE 2

Comparison of Experimental Values of D_0 for Germanium Tetrabromide and Those Calculated Using the Equation
$\log D_0 = -0.544[\log MR + 0.25(\delta_{\text{GeBr}_4} - \delta_0)^2] + 1.270$

Solvent	Calcd D_0	Exptl D_0	Per cent error
Isooctane	0.98	0.94	4.1
n-Hexane	1.45	1.53	5.2
n-Heptane	1.53	1.55	1.3
n-Octane	1.54	1.40	10.0
n-Decane	1.53	1.38	10.9
n-Hexadecane	1.42	1.06	34.0
Cyclohexane	2.68	2.52	6.3
Carbon tetrachloride	3.01	3.27	8.0
Toluene	2.76	2.83	2.5
o-Xylene	2.52	3.15	20.0
1,2-Dichloroethylene	3.44	3.35	2.7
Benzene	2.90	2.99	3.0
Chlorobenzene	2.31	2.87	19.5
1,1,2,2-Tetrachloroethane	2.09	2.15	2.8
1,2-Dichloroethane	2.42	1.80	34.5

with many other sets of data found in the literature, including that of Siekierski and Olszer (*19*) for $GeCl_4$ and $GeBr_4$ between 18 different inert (nonoxygenated) solvents and water. Here it was found that an empirical relationship might exist between the logarithm of the distribution constant and the molecular refractive index, the solubility parameters of the solvent and solute, and the density of the solvent. Table 1 shows the results of log D_0 as a function of

$$\log MR + 0.1(\delta_{\text{GeCl}_4} - \delta_0)^2 - 0.1d$$

where D_0 is the distribution constant expressed in terms of volume fractions, MR is the molecular refractive index, δ_{GeCl_4} is the solubility parameter of $GeCl_4$, δ_0 is that of the solvent, and d is the density of the solvent. The molecular refractive index is defined as

$$MR = [n_D{}^2 - 1)/(n_D{}^2 + 2)](M/d)$$

where n_D is the refractive index, M is the molecular weight, and d is the density. Atomic refractions tabulated in various handbooks are additive properties of the molecule and can be used to calculate the molecular

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refractive index. The least squares slope and intercept of the line was calculated for $GeCl_4$, giving the equation

$$\log D_0 = -0.8316[\log MR + 0.1(\delta_{GeCl_4} - \delta_0)^2 - 0.1d] + 1.847$$

The correlation coefficient for the data was 0.914.

The same equation without the density term was used for $GeBr_4$. Log D_0 was plotted as a function of

$$\log MR + 0.25(\delta_{GeBr_4} - \delta_0)^2$$

Least squares treatment of the data gave the equation

$$\log D_0 = -0.544[\log MR + 0.25(\delta_{GeBr_4} - \delta_0)^2] + 1.270$$

with a correlation coefficient of 0.935. The calculated and experimental values of D_0 are given in Table 2.

The distribution constants determined by Omori et al. (*17*) for three β-diketones were compared with those calculated using the equation

$$\log D_0 = A[\log MR + 0.1(\delta_c - \delta_0)^2 - 0.1d] + B$$

where δ_c is the solubility parameter of the diketone, and A and B are the slope and intercept of the line obtained when D_0 is plotted versus the function on the right. Values of the slope and intercept and correla-

TABLE 3

Comparison of Experimental Values of D_0 for Acetylacetone and Those Calculated Using the Equation

$$\log D_0 = -1.77[\log MR + 0.1(\delta_{AA} - \delta_{AA} - \delta_0)^2 - 0.1d] + 3.376$$

Solvent	Exptl D_0	Calcd D_0	Per cent error
n-Hexane	0.92	0.97	5.0
Carbon tetrachloride	3.19	2.93	8.1
Methylene chloride	20.65	20.75	0.5
Ethyl bromide	7.10	7.59	6.9
Benzene	5.45	4.73	13.2
Chlorobenzene	5.99	5.41	9.7
o-Dichlorobenzene	5.21	6.29	20.7
Nitrobenzene	7.26	7.23	0.4
Chloroform	23.3	10.3	55.8
Toluene	4.18	5.48	31.1
m-Xylene	3.35	4.80	43.3

TABLE 4

Comparison of Experiment Values of D_0 for Trifluoroacetylacetone and Those Calculated Using the Equation

$$\log D_0 = -1.104[\log MR + 0.1(\delta_{TFA} - \delta_0)^2 - 0.1d] + 1.586$$

Solvent	Exptl D_0	Calcd D_0	Per cent error
n-Hexane	0.317	0.313	1.3
Carbon tetrachloride	1.39	1.27	8.6
Chloroform	1.94	1.87	3.6
Methylene chloride	2.51	2.38	5.2
Ethyl bromide	1.72	1.95	13.4
Benzene	1.28	1.27	0.8
o-Dichlorobenzene	0.883	0.964	9.2

tion coefficient as calculated by the method of least squares were −1.77, 3.38, 0.932; −1.104, 1.586, 0.994; and −0.494, 2.344, 0.943 for acetylacetone (AA), trifluoroacetone (TFA), and thenoyltrifluoroacetone (TTA), respectively. Tables 3, 4, and 5 give the calculated and experimental values of D_0 for each solute.

The dependence of the distribution constant for 1-nitropropane on

TABLE 5

Comparison of Experimental Values of D_0 for Thenoyltrifluoroacetone and Those Calculated Using the Equation

$$\log D_0 = -0.494[\log MR + 0.1(\delta_{TTA} - \delta_0)^2 - 0.1d] + 2.344$$

Solvent	Exptl D_0	Calcd D_0	Per cent error
Chloroform	53.8	53.8	0.0
Methylene chloride	69.2	63.1	8.8
Ethyl bromide	49.0	52.5	7.1
Benzene	41.7	44.7	7.2
Chlorobenzene	44.7	44.7	0.0
o-Dichlorobenzene	38.9	43.7	12.3
Toluene	39.9	39.0	2.2
m-Xylene	37.2	35.5	4.6
p-Xylene	38.1	34.7	8.9
Mesitylene	31.7	33.2	4.7

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TABLE 6

Comparison of Experimental Values of ${}^{x}k^{\infty}$ for 1-Nitropropane and Those Calculated Using the Equation
$\log {}^{x}k^{\infty} = 6.93S^{0.1} = 3.37$

Solvent	Exptl ${}^{x}k^{\infty}$	Calcd ${}^{x}k^{\infty}$	Per cent error
Isooctane	2.8	2.37	14.2
Cyclohexane	3.38	4.49	28.5
Carbon disulfide	7.0	7.13	1.8
Toluene	25.0	22.8	12.8
Chloroform	82.0	85.9	4.7
Carbon tetrachloride	9.7	8.91	8.2

the molar solubility of water in the extracting solvent was found to be linear. Values of ${}^{x}k^{\infty}$, the distribution constant at infinite dilution expressed in terms of mole fractions, have been determined by Kemula (*13*). Least-squares treatment of the data gives the equation

$$\log {}^{x}k^{\infty} = 6.93S^{0.1} - 3.37$$

where S is the molar solubility of water in the organic solvent. The correlation coefficient for the data is 0.995. The calculated and experimental values of ${}^{x}k^{\infty}$ are given in Table 6.

Another empirical correlation was observed for the distribution of bis-thenoyltrifluoroacetone zinc(II) trioctylphosphine oxide and the

TABLE 7

Comparison of the Experimental Values of K for Bis-thenoyltrifluoroacetone Zinc(II) Trioctylphosphine Oxide and Those Calculated Using the Equation
$\log K = 5.10(\log P - \log \Sigma) - 11.56$

Solvent	Exptl K	Calcd K	Per cent error
Chloroform	0.0003	0.0003	0.0
Benzene	0.028	0.026	7.2
Carbon tetrachloride	0.051	0.042	17.6
Cyclohexane	0.132	0.104	21.2
Hexane	0.175	0.260	48.5

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TABLE 8

Comparison of Experimental Values of K for the Distribution of Various Dicarboxylic Acids between Isobutanol and Water and Those Calculated Using the Equation $\log K = 0.0399(N_c)^{1.8} - 0.453$

Acid	Exptl K	Calcd K	Per cent error
Oxalic	0.50	0.49	3.0
Malonic	0.70	0.68	2.3
Succinic	0.96	1.01	5.3
Glutaric	2.00	1.85	7.5
Adipic	3.50	3.56	1.7
Pimelic	7.30	7.41	1.5
Azelaic	42.9	42.5	0.9

Sugden parachor and dielectric constant of the extracting solvent. Table 7 shows the results of $\log K$ as a function of $\log P - \log \Sigma$ where P is the parachor and Σ is the dielectric constant. The slope and intercept were calculated to be 5.10 and −11.50, respectively. The correlation coefficient is 0.996. The calculated values for K are compared with those determined experimentally by Walker and Farrell (*26*) in Table 7.

If the logarithm of the distribution constants for various dicarboxylic acids determined by Collander (*5*) for the ether/water system and

TABLE 9

Comparison of Experimental Values of K for the Distribution of Various Dicarboxylic Acids between Ether and Water and Those Calculated Using the Equation $\log K = 0.0200N_c^{2.2} - 1.269$

Acid	Exptl K	Calcd K	Per cent error
Oxalic	0.12	0.066	45.0
Malonic	0.10	0.090	10.0
Succinic	0.15	0.141	6.0
Glutaric	0.269	0.266	1.1
Adipic	0.54	0.572	5.9
Pimelic	1.50	1.52	1.3
Azelaic	1.60	1.78	11.2

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Apparatus and Materials

UV-Visible Spectrophotometer. All spectrophotometric data were obtained with a Beckman Model DB recording spectrophotometer equipped with matched 1 cm silica cells.

Atomic Absorption Spectrophotometer. A Jarrell-Ash model 82-360 Ebert-mounted 0.5 m grating monochrometer equipped with Jarrell-Ash electronics, including a 90 H2 mechanical chopper, ac amplifier, Sargent Model S-72150 recorder, and a 1P28 photomultiplier detector were used. The sampling system was a Beckman large bore turbulent flow burner. The spectral source was a Westinghouse Model WL 22811 zinc hollow-cathode.

Gas Chromatograph. A Micro Tek 2500R chromatograph equipped with a thermal conductivity detector was used for chromatographic measurements. A Sargent SR (1 mV) recorder and Disc Instruments, Inc., integrator were used to record the chromatograms and measure peak areas. Injections were made with a 10 μl Hamilton syringe equipped with a Chaney adapter.

Chromatographic Columns. For the determination of the distribution of water between nitromethane and decanol a 6 ft by $\frac{1}{4}$ in. stainless steel tube packed with 60/80 mesh Poropak Q, Waters Assoc., Inc. Framingham, Massachusetts was used.

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PROCEDURE

Extraction and Analysis of Complexes

Bis(8-quinolinolo)dioxouranium(IV)-8-quinolinol and Bis(8-quinolinolo)dioxouranium(IV). The procedure for the extraction and determination of the uranium complexes was more rigorous than those for the zinc and iron complexes because of the influence of water on the absorptivities of the uranium compounds. With the exception of a few slight modifications, the procedures for the self-adduct and "normal" uranium chelates were the same. The following procedure was used for the extraction of $UO_2(Ox)_2HOx$ into nitromethane. The appropriate amount of water was weighed in a capped polyethylene centrifuge tube and 10 ml of nitromethane added by means of a pipet. Dissolution of the water was aided by a vortex mixer. Ten milliliters of decanol containing $2.00 \times 10^{-4} UO_2(Ox)_2HOx$ were pipetted into the tube and the extraction carried out on a Burrell Wrist-Action shaker for 1 min (300 inversions).

REFERENCES

1. A. Abrahamson, *Zh. Prikl. Khim.*, *38*, 2597 (1965).
2. C. P. Brown and A. R. Mathieson, *J. Phys. Chem.*, *58*, 1057 (1954).
3. H. Buchowski, *Nature*, *194*, 674 (1962).
4. J. Chechniki, *Thiszcze, Srodki Piorace, Kosmet.*, *1967*, 282; *Chem. Abstr.*, *69*, 100058t (1968).
5. R. Collander, *Acta Chem. Scand.*, *4*, 1085 (1950).
6. R. Ewell, *Ind. Eng. Chem.*, *36*, 872 (1944).
7. H. Freiser, *Anal. Chem.*, *41*, 1354 (1969).
8. L. M. Gindin, B. I. Peshchevitskii, and V. L. Kheifets, *Dokl. Akad. Nauk SSSR*, *172*, 633 (1967).
9. Z. Golynko, *Zh. Prikl. Khim.*, *38*, 271 (1965).
10. C. Hansch, J. E. Quinlan, and G. L. Lawrence, *J. Org. Chem.*, *33*, 347 (1968).
11. T. Higuchi, H. Michaelis, T. Tan, and H. Hurwitz, *Anal. Chem.*, *39*, 974 (1967).
12. J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes*, 3rd ed., Reinhold, New York, 1950.
13. W. Kemula, H. Buchowski, R. Lewandowski, W. Powlowski, and J. Terpek, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, *12*, 343 (1964).
14. *Idem, Ibid.*, *14*, 395 (1966).
15. H. Mottola and H. Freiser, *Talanta*, *13*, 55 (1966).
16. *Idem, Ibid.*, *14*, 864 (1967).
17. T. Omori, T. Wakahayashi, S. Oki, and N. Suzuki, *J. Inorg. Nucl. Chem.*, *26*, 2265 (1964).
18. S. Siekierski, *Nucleonika*, *9*, 601 (1964).
19. S. Siekierski and R. Olszer, *J. Inorg. Nucl. Chem.*, *25*, 1351 (1963).
20. B. Skytte-Jensen, *Solvent Extr. Chem., Int. Conf. Gotinborg, 1966*, 517.
21. N. Suzuki, K. Akiba, T. Kanno, and T. Wakahayashi, *J. Inorg. Nucl. Chem.*, *30*, 2521 (1968).
22. V. M. Vdovenki, T. V. Kovaleva, and M. A. Ryazamov, *Radiokhimiya*, *7*, 133 (1965).
23. A. Vignes, *J. Chim. Phys. Physico-chim. Biol.*, *57*, 966 (1960).
24. T. Wakabayashi, *Bull. Chem. Soc. Jap.*, *40*, 2836 (1967).
25. T. Wakahayashi, S. Oki, T. Omori, and N. Suzuki, *J. Inorg. Nucl. Chem.*, *26*, 225 (1964).
26. R. Walker and W. Farrell, *Ibid.*, *28*, 1483 (1966).
27. V. I. Yashkichev and E. E. Vinogradov, *Radiokhimiya*, *5*, 136 (1963).

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