TEMPERATURE EFFECTS ON THE SOLVENT EXTRACTION OF METAL CHELATES (I) 8-QUINOLINOL AND ITS COPPER CHELATE

By

Eiichiro NAKAYAMA

Instrumental Analysis Research Center, Faculty of Science, Kyoto University, Kyoto

ABSTRACT

The partition coefficients of 8-quinolinol and its copper chelate between water and three different types of organic solvents whose boiling points are relatively high have been determined over the temperature range of 20° to 90°C, and their thermodynamic properties in the distribution equilibrium have been compared. The results are discussed comparing with the data obtained by the technique of solid-liquid separation after liquid-liquid extraction developed by the author and the colaborators[6].

1. Introduction

In recent years much work has been carried out on the systematic examination of the various factors affecting the solvent extraction of metal chelates, but only a few studies have been reported concerning the effect of temperature.

In earlier work Scweitzer et al.[1],[2],[3] studied the effect of temperature on the extraction of several metal chelates of dithizone and 8-quinolinol. Mason et al.[4] determined the partition coefficients of the chelating reagent 8-quinolinol itself for three different solvents as a function of temperature. Lately Choppin et al.[5] tried to explain the mechanism of synergistic solvent extraction of metal β-diketonate by thermodynamic data. However these studies were carried out in the low temperature region below 50°C, since volatile organic solvents such as chloroform and benzene were used. Furthermore with the one exception very little was discussed about the relationship between the effect of temperature and the mechanism of extraction. Meanwhile the author and the colaborators[6],[7] have developed and have been studying a method of "Solid-liquid separation after liquid-liquid extraction" in which solid organic compounds are used as molten solvents in the high temperature at 80 to 90°C. The object of present work is to try to explain extraction behavior at high temperatures by comparing it with that of low temperatures.

In this study the partition coefficients of 8-quinolinol and its copper chelate between water and several organic solvents whose boiling points are relatively high were examined over the temperature range of 20 to 90°C. The organic solvents used were 1,1,2,2,-tetrachloroethane (b.p. 146°C), p-xylene(b.p. 138°C) and 1-octanol(b.p. 195°C) which were chosen as the homologue of chloroform, benzene and alcohols respectively.

The result was compared with the data obtained by the method of solid-liquid separation after liquid-liquid extraction in which biphenyl and naphtalene were used as molten solvents.

2. Experimental

Reagents: Commercially obtained 8-quinolinol was purified by recrystallization from ethanol after steam distillation.   Organic solvents were purified by distillation under reduced pressure. Sodium perchlorate was recrystallized from distilled water.   All other chemicals were analytical reagent grade.

Apparatus: Extraction was carried out with a magnetic stirrer in a cylindrical tube contained in large constant temperature bath.   Temperature was controlled by a thermoregulator $\pm 0.1°C$.   A Shimadzu UV-200 spectrophotometer was used for the determination of the concentration of 8-quinolinol.   Copper in both aqueous and organic phase was determined by a Jarrel Ash 780 atomic absorption spectrophotometer.   For pH measurements, a Hitachi-Horiba M-5 pH meter equipped with a glass-calomel electrode pair for high temperature work was used.

Procedure: 10 ml of 8-quinolinol solution in organic solvent was stirred with 30 ml of aqueous solution in a cylindrical tube standing in a constant temperature bath until equilibrium was attained (usually 30 min. required).   The initial aqueous solution was adjusted to the desired pH by a small quantity of buffer solution and to an ionic strength of 0.1 with sodium perchlorate (unless otherwise indicated).
    After stirring was stopped the pH value of aqueous phase was measured in situ (if necessary).   In the case of 8-quinolinol itself, the phases were immediately separated and cooled to room temperature.   An aliquot of the aqueous phase was extracted into chloroform, on the other hand an aliquot of the organic phase was dissolved into chloroform, then the concentrations of 8-quinolinol were determined spectrophotometrically measuring the absorbance at 312 nm.   In the case of the copper chelate, the aqueous phase was immediately analyzed with the atomic absorption spectrophotometer whereas the organic phase was analyzed after back extracting into aqueous hydrogen chloride solution.   Each value is the average of three or four measurements.   In each case, the volume of aqueous phase was corrected for temperature with the values of water density in the Smithsonian tables, and the volume of organic phases were corrected for temperature with experimentally determined density functions.   Thus the density at any desired temperature can be obtained by the following formulae,
$1.597 – 1.562 \times 10^{-3}$ (t–20) for 1,1,2,2-tetrachloroethane,
$0.8610 – 8.783 \times 10^{-4}$ (t–20) for p-xylene, and
$0.8256 – 7.415 \times 10^{-4}$ (t–20) for 1-octanol, where t is temperature in degrees centigrade.

3. Results and Discussion

The partition coefficients P_r for 8-quinolinol can be obtained by measuring the distribution ratio in a pH-independent range of the extraction curve.   So although the extraction curves transfer toward the acidic range with rise in temperature on account of the corresponding decrease in pK_1 and pK_2 as shown in table (I) where

K_1 and K_2 are the acidic dissociation constants of protonated 8-quinolinol and neutral 8-quinolinol respectively, a suitable range for the extraction exists between pH 6.5 and pH 7.5 for all temperatures. The partition coefficients P_c for copper chelate of 8-quinolinol can be determined in the same manner as 8-quinolinol by measuring the distribution ratio in the pH range of the extraction curves above pH 4.5 at all temperatures when the concentration of 8-quinolinol in organic solvents is 0.01M.   This fact was experimentally confirmed.

Values of $\log P_c$ and $\log P_r$ for tetrachloroethane are plotted against the reciprocal of absolute temperatures in Fig. (1). Both plots indicate that the distribution into the organic phase decreases while the distribution into the aqueous phase increases with an increase in temperature though a rapid change in slope occured

Table 1.   Acidic dissociation constants of 8-quinolinol, ionic strength 0.1, determined
as a function of temperature by potentiometric titration

temp. °C	pK_1	pK_2
16	5.21	—
20	—	9.89
25	5.05	9.81
35	4.91	9.60
45	4.80	—
55	4.72	—
65	4.60	—
70	4.53	9.07
80	4.45* (4.38)	8.95* (9.09)
90	4.40* (4.25)	8.82* (8.96)

* extrapolated value, (   ) obtained by solvent extraction for which biphenyl was used
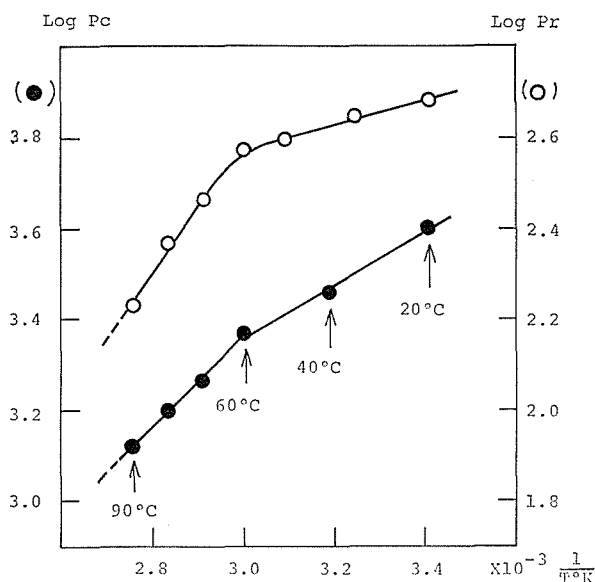as a molten solvent.

Fig. 1.   Temperature Effects on the Partition Coefficients of 8-Quinolinol and its Copper
Chelate between TCE and Water.

at about 60°C in both curves. In other words the rate of change of partition coef-
ficients with respect to temperature is discontinuous at around 60°C. Both plots
however, are approximately parallel to each other over the whole temperature
range. Similarly in Fig. (2) and Fig. (3), the values of log P_r and log P_c are plotted
for p-xylene and 1-octanol against the reciprocal of temperature. These plots show
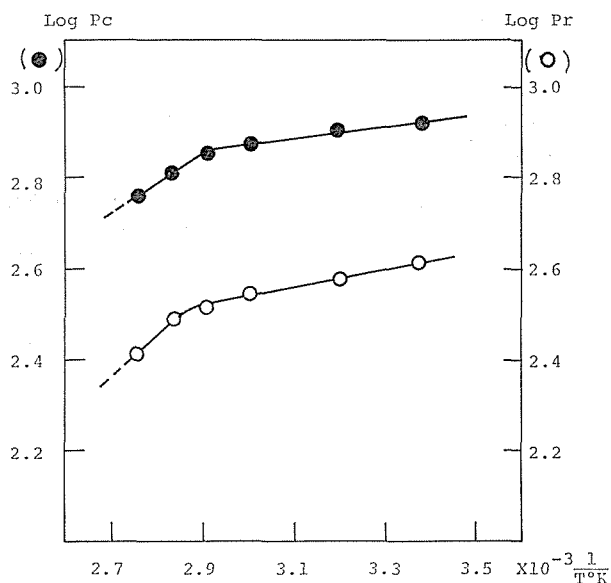

Fig. 2. Temperature Effects on the Partition Coefficients of 8-Quinolinol and its
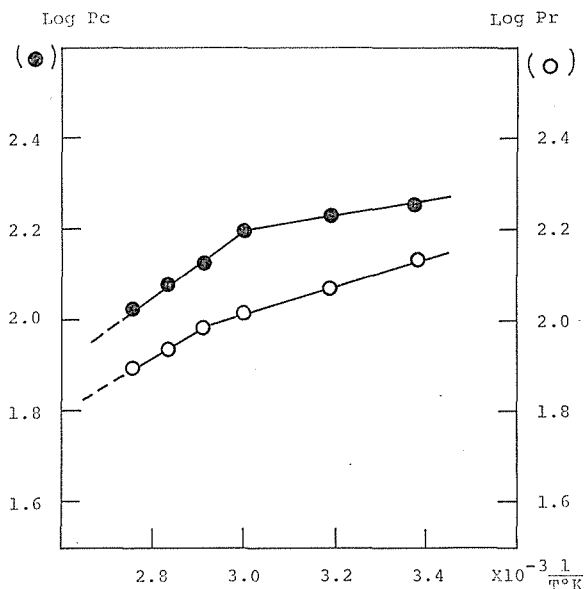Copper Chelate between 1-Octanol and Water.

Fig. 3. Temperature Effects on the partition Coefficients of 8-Quinolinol and its
Copper Chelate between p-Xylene and Water.

the same tendencies as that for tetrachlorethane: for the values of the partition coefficients decrease with rising temperature, a rapid change occured in the slope of the plots appears at 60 to 70°C, and the slopes are approximately parallel to each other.

No appreciable difference was observed in the extraction behavior, when sodium chloride was used instead of sodium perchlorate to adjust the aqueous solution to an ionic strength of 0.1. From these results it is clear that the temperature effect on the distribution equilibrium of copper chelate of 8-quinolinol, which readily isolates coodinated water molecules, is very similar to that of 8-quinolinol. The fact that the change in slopes in the curves at ca. 60°C occures as the result of an extreme change in the properties of water as a solvent since the solubility of organic solvents in the aqueous phase increases at the temperature. The thermodynamic data calculated from the slopes in Fig. (1), (2) and (3) in the low temperature region are summerised in Table (II). These data show the resemblance of thermodynamic properties of both copper chelate and its ·chelating ·reagent. ΔH values for tetracloroethane, especially in the case of P_c, appear to be a little higher than the values for the other two solvents. This fact can be attributed to the extraordinary behavior of a halogenated hydrocarbon in the solvent extraction of a metal chelate. It seems that all the values of ΔH are small negative values rather lower than the value of energy in hydrogen bonding and all the values of ΔS are sufficiently similar to each other. Data obtained perviously by the method of solid-liquid separation after liquid-liquid extraction is summerised in Table (III). Although naphthalene and biphenyl are homologues of p-xylene, the log P_r values for both molten solvents are slightly higher than expected from the results for p-xylene, being 1.94 at 80°C and 1.89 at 90°C. Moreover the values of log Pc both molten solvents are much higher than expected, cf. p-xylene, 2.08 at 80°C and 2.02 at 90°C. This fact can be attributed to the coprecipitation of the metal chelate and the reagent on the solidified solvent surface during the cooling period. Because the phases are separated in this method, the remaining naphthalene (or biphenyl) in the dissolved state at high temperatures would deposit out in the aqueous phase coprecipitating with the residual chelate and reagent. Thus the values of the partition coefficient turn

Table 2.   Summary of Thermodynamic data

solvent	P_r		P_c	
	ΔH kcal/mole	ΔS cal/mole °K	ΔH kcal/mol	ΔS cal/mole °K
TCE*	−1.2	8.0	−2.6	7.7
1-Octanol	−0.8	6.2	−1.0	8.6
p-xylene	−1.0	6.1	−0.8	7.7

* 1,1,2,2,-tetrachloroethane

Table 3.   Partition coefficients obtained from solid-liquid separation after liquid-liquid extraction

Solvent	log P_r (temp.)	log P_c (temp.)
Biphenyl	2.05 (80°C)	2.80 (80°C)
Biphenyl	2.02 (90°C)	———
Naphthalene	2.08 (90°C)	*2.87 (90°C)

out to be higher than expected in the molten solvent extraction.

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REFERENCES

1) F. F. Dyer, G. K. Scweitzer, Anal. Chim. Acta, **23**, 1 (1960)
2) H. E. Hellwege, G. K. Scweitzer Anal. Chim. Acta, **28**, 236 (1963)
3) G. K. Schweitzer, G. R. Coe, Anal. Chim. Acta, **24**, 311 (1961)
4) J. G. Mason, I. Lipshitz, Talanta, **18**, 1111 (1971)
5) G. R. Choppin, A. T. Kandil, H. F. Aly, M. Raieh, J. Inorg. Nucl. Chem., **37**, 229 (1975)
6) T. Fujinaga, T. Kuwamoto, E. Nakayama, Talanta, **16**, 225 (1969)
7) T. Fujinaga, T. Kuwamoto, E. Nakayama, M. Satake, Japan Analyst, **18**, 397 (1969)