Indian Journal of Chemistry
Vol. 22A, February 1983, pp. 179-180

# Effect of Diluents on the Extraction of Mercury(II) by *n*-Butyl Acetate

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*Received* 9 *June* 1982; *revised and accepted* 4 *October* 1982

The influence of isooctane, *n*-hexane, *n*-heptane, cyclohexane, $CCl_4$ and $CHCl_3$ as diluents on the extraction of mercuric chloride by *n*-butyl acetate has been studied. It has been found that the theory of regular solutions is applicable to these systems. The solubility parameter of the extracted species computed from the extraction studies is higher than that calculated from the latent heat of vaporization data. This is attributed to the solvation of the extracted species.

As a part of our programme[1] on the extraction of mercury(II) using organic esters as extractants, we report here the results of studies on the effect of some diluents on the extraction of Hg(II) by *n*-butyl acetate.

A stock solution (0.05*M*) of mercuric chloride (E. Merck), was prepared and diluted appropriately. The tracer $^{203}$mercury in the form of mercuric nitrate in nitric acid solution (specific activity 30 m Ci/g, mercury) was supplied by the Isotope Division, BARC, Bombay. *n*-Butyl acetate (BDH, India) was used after purification. AR grade samples of the organic solvents were fractionated immediately before use.

A single channel analyser (SC 604 ECIL, India) coupled with a 3 inch well-type scintillation detector (Nuclear, Chicago) was used for $\gamma$ -activity measurements of $^{203}$Hg.

*Procedure*—An aqueous phase (15 ml) containing $1.0 \times 10^{-4}M$ of mercuric chloride and tracer was equilibrated with an equal volume of *n*-butyl acetate solution in the organic solvent (5 ml in 15 ml) for about 5 min and the two phases were separated, after allowing the mixture to stand for 5 min. Equal aliquots (10 ml) of each phase were used to measure the activity, and the distribution coefficient ($Q$) was calculated using the equation,

$$Q = \frac{\text{counts/min in the organic phase}}{\text{counts/min in the aqueous phase}}$$

The extractions were repeated for checking reproducibility.

Due to the limitation on the availability of diluents into which there is no extraction of mercury, the studies were carried out only with isooctane, *n*-hexane, *n*-heptane, cyclohexane, carbon tetrachloride and chloroform as diluents. In each case, the extracted species was found to be $HgCl_2.2S$ as revealed by the procedure of Hesford *et al.*[2]. The extraction efficiencies were in the order (dielectric constants are given in the parentheses) : *n*-hexane ($\epsilon = 1.9$) > *n* heptane ($\epsilon = 4.3$) > cyclohexane ($\epsilon = 2.02$) > carbon tetrachloride ($\epsilon = 2.24$) > isooctane ($\epsilon = 1.94$) > chloroform ($\epsilon = 4.80$).

Table 1—Influence of the Organic Solvents on the Extraction of the Species $HgCl_2$ by *n*-Butyl Acetate
$[HgCl_2] = 1.0 \times 10^{-4}M$

| Solvent | $Q$ | $\epsilon_{org}$ | log $K_x$ † | $\delta_{org}$ | $\delta_c$ |
|---|---|---|---|---|---|
| Isooctane | 0.2220 | 1.94 | 0.3112 | 6.85 | 15.1 |
| *n*-Hexane | 0.4255 | 1.90 | 0.4942 | 7.30 | 15.3 |
| *n*-Heptane | 0.3557 | 4.30 | 0.4632 | 7.45 | 15.3 |
| Cyclohexane | 0.3370 | 2.02 | 0.3103 | 8.20 | 15.7 |
| Carbon tetrachloride | 0.2430 | 2 24 | 0.1177 | 8.60 | 15.9 |
| Chloroform | 0.2140 | 4.80 | 0.0172 | 9.30 | — |
| | | | | Average $\delta_c$ = | 15.5 |

†Values of $K_x$ were obtained from the expression $K_x = Q\,(V_o/V_{aq})$ where the molar volumes are calculated from densities valid at 25°C.

The results show a poor correlation between the extraction efficiency of the solvent and its dielectric constant ($\epsilon$). The solvents, however, can be correlated better by the application of the theory of regular solutions[3-5].

If $K_x$ is the distribution coefficient expressed in mole fraction ratio,

$$-\triangle F_{part} = 2.303\, RT \log K_x = V_c\,(\delta_c - \delta_{aq})^2 - (\delta_c - \delta_{org})^2 \quad \ldots(1)$$

where $\triangle F_{part}$ is the free energy of partition of the solute ($HgCl_2.2S$); $\delta_c$, $\delta_{org}$ and $\delta_{aq}$ are the solubility parameters of the extracted species, the organic solvent and the aqueous phase respectively. $V_c$ is the molar volume of the extracted species. Since $V_c$, $\delta_c$ and $\delta_{aq}$ are constants, a plot of log $K_x$ against $\delta_{org}$ should take the form of a parabola[6], and the results now obtained (Table 1) are in agreement with this expectation.

The extraction of mercury by *n*-butyl acetate dissolved in the mixture of a good solvent (cyclohexane) and the poor solvent (chloroform) has been also studied. The theoretical treatment of the data has been carried out according to Irving and Rossotti's procedure[7] for the purpose of calculation of the distribution coefficient ($Q_{cal}$) and the solubility parameter ($\delta_M$) of the mixtures [the terms good and poor are considered with respect to the extraction efficiency of Hg(II) by *n*-butyl acetate-organic solvent system]. The results are dipicted in Fig. 1. Progressive dilution of cyclohexane by chloroform produces the expected decrease in the distribution coefficient $Q$ leading to a minimal extraction when its mole fraction ratio is 0.33, and thereafter a gradual increase in the distribution coefficient is noticed due to the increase in the mole fraction of chloroform (Fig. 1, curve a).

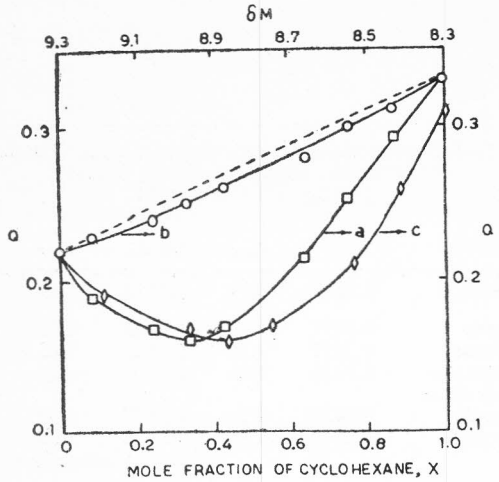


Fig. 1.—The extraction of $HgCl_2$ {$[HgCl_2]=1.0\times10^{-4}M$} by solutions of *n*-butyl acetate in mixtures of chloroform and cyclohexane. The variation of $Q$ with the mole fraction of cyclohexane is shown in (curve a) (lower abscissa). Values calculated by Irving and Rossotti's theory[7] are given as circles (curve b). The plot of $Q_{cal}$ against $\delta_M$ (upper abscissa) is shown in curve c.

The calculated curve (Fig. 1, curve b) deviates markedly from the experimental curve confirming the importace of solvent-solvent and solute-solvent interactions in this system. On the other hand, a plot of $Q_{cal}$ against $\delta_M$ of the mixture (Fig. 1, curve c) gives a better agreement with the experimental curve.

*Calculation of the solubility parameter of the extracted mercury species* ($HgCl_2.2S$)—An attempt was made to determine the solubility parameter of the extracted species ($HgCl_2.2S$) as described below. In Eq. (1), the term $V_c(\delta_c-\delta_{aq})^2$ on the right hand side represents the free energy of solution of the solute in the aqueous phase, while the second term is the free energy of solution of the solute in the organic phase.

Substituting the values of log $K_x$, $\delta_{org}$, $\delta_{aq}$ and $V_c$ in Eq. (1), $\delta_c$ can be calculated (Table 1). A value of 23.4 was assigned to $\delta_{aq}$ for the purpose of the calculation of $\delta_c$. In view of the fact that the concentration of extracted mercury ($10^{-4}M$) was very much less than that of the extractant, *n*-butyl acetate ($2.5M$), $V_c$ was calculated to be 571.7, assuming the density of the extracted species as the density of the extractant (0.88 g/ml at 25°C). $\delta_c$ thus computed from the experimental data is greater than solubility parameter of the mercuric chloride ($\delta_{HgCl_2}=11.4$) calculated from the latent heat of vaporization ($\triangle H_v$) and molar volume data[3]. The difference may probably be due to the solvation of extracted mercury species.

Thanks are due to the UGC, New Delhi for financial assistance under the project entitled Desalination and Economic Recovery of Chemical Products.

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