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PURITY CONSIDERATIONS AND INTERFACIAL BEHAVIOR OF SOLVENT EXTRACTION SYSTEMS[1]

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ABSTRACT

The techniques to purify different components of a typical solvent extraction system, viz., n-hexane/di(2-ethylhexyl)phosphoric acid (HDEHP)/$CaCl_2$ solution, are described. Data showing how the purity of the different components affects the interfacial tension (γ) are given. The interfacial behavior of the n-hexane/HDEHP/0.01 mol dm^{-3} $CaCl_2$ solution system was studied as a function of HDEHP concentration and aqueous phase pH. γ-log [HDEHP] curves were also determined at pH 4 when the aqueous phase contained 0.05 mol dm^{-3} $MgCl_2$, $CaCl_2$, $SrCl_2$ or $BaCl_2$. γ-log [HDEHP] curves revealed interaction of the metal ions with the extractant and exhibited a behavior reminiscent of aggregate formation when the aqueous phase contained Ca^{2+}.

INTRODUCTION

Solvent extraction of metal ions from an aqueous solution to a non-polar organic phase has gained tremendous popularity in numerous separation operations, e.g., hydrometallurgical, nuclear waste processing, and spent fuel reprocessing technologies. Principally, three steps are involved in the transfer of metal ions from an

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aqueous solution to an organic phase: (i) adsorption of extractant molecules from the organic phase to the liquid/liquid interface, (ii) interfacial chemical reaction between such molecules and the metal ions to form an interfacial species capable of dissolving in the organic phase, and (iii) their desorption into the organic phase. Thus, the liquid/liquid interface plays an important role in the solvent extraction process.

It is worthwhile, therefore, to obtain information on the interfacial behavior of extractants. Due to their amphipathic nature, solvent extraction reagents tend to adsorb at the liquid/liquid interface and reduce the interfacial tension γ (2-9). The extent of the lowering of γ is related to the interfacial activity of the extractant. Several research groups have interpreted the interfacial activity of extractants to help explain the equilibrium and kinetic behavior observed in solvent extraction systems (10-16).

In surface chemical studies extreme care should be exercised with regards to the purity of the system because small amounts of surface-active impurities can affect the interfacial tension significantly. One of the purposes of this paper is to show how impurities in the typical solvent extraction system n-hexane/di (2-ethylhexyl)phosphoric acid (HDEHP)/aqueous solution affect the interfacial tension. In addition, the interfacial activity of the aforementioned system with 0.01 mol dm^{-3} $CaCl_2$ in the aqueous phase as a function of pH and concentration of HDEHP, i.e., [HDEHP], was studied. The interfacial activity in the presence of 0.05 mol dm^{-3} solutions of other alkaline earth metal chlorides such as $MgCl_2$, $SrCl_2$ and $BaCl_2$ also was investigated.

EXPERIMENTAL METHODS

An interfacial tensiometer based on the Wilhelmy plate technique (sandblasted glass plate) was constructed for the accurate measurement of γ of solvent extraction systems. The description of the experimental set up and general procedures have been described elsewhere (17). If we use the attachment method however, there seems to be some problem with the plate being wetted completely in the presence of metal ions and high concentrations (ca. > 10^{-3} mol dm^{-3}) of HDEHP. Hence, the procedure was slightly modified as follows: After just touching the bottom edge of the plate to the liquid/liquid interface and adjusting the plate to zero buoyancy, the position of the translator and, hence, that of the liquid/liquid interface was noted. The cell was then raised till the plate was immersed in the aqueous phase to effect what appears to be complete wetting of the plate. Finally, the cell was lowered to its original position (zero buoyancy), the pull was noted, and γ was calculated. γ was also determined by the maximum pull method. Both γ values agreed to within ±0.1 mN m^{-1}. The measurements were carried out at 20°C ±0.05°C.

RESULTS AND DISCUSSION

Purification Effects

Knowledge of the interfacial behavior of extractants and their specific chemical interactions with metal ions is important and will further our understanding of the mechanism by which transfer of metal ions occurs. Such studies, however, require well-defined systems free from interfering surface chemical impurities.

Unfortunately, some investigators studying solvent extraction use extractants, diluents, and modifiers without any further purification. The liquid/liquid interface is very sensitive to trace contaminants relative to the liquid/air interface. The presence of impurities in the liquid/liquid system will lead to a lowering of γ as a result of their accumulation at the interface. For example, presumed high purity 99 mole % n-dodecane (diluent) has been used in the "as received" condition, and a value of 44 mN m^{-1} has been reported for the interfacial tension of the n-dodecane/0.1 N HCl interface (12). This value is about 8.8 mN m^{-1} less than that obtained recently in this laboratory (17), presumably due to the presence of impurities in the earlier study. Hence, it is necessary to ensure that the system under investigation is free from interferring surface chemical impurities by following stringent precautions and purification procedures.

Impurities may come from two possible sources: (i) glassware and parts of the apparatus coming into contact with the system and (ii) different chemical components of the system. In order to avoid contamination from the first source, sufficient care should be taken in cleaning the glassware. Soap and detergent solutions should be avoided. Use of chromic acid for cleaning the glassware is not advisable from an environmental pollution point of view. Also, chromium ions have been found to be present on glass surfaces even after ten rinses with distilled water (18,19). In this study we used a mixture of Nochromix (Godax Laboratories) and concentrated sulfuric acid as the cleaning solution. Nochromix is an inorganic oxidizer containing no metallic ions, its solution with concentrated sulfuric acid is a stronger oxidizing agent than chromic acid, and yet it rinses more completely from glass surfaces. The jacketed Pyrex cell and its cover, the Wilhelmy glass plate, and all the glassware used for making solutions are soaked overnight in Nochromix-sulfuric acid cleaning solution and then rinsed many times with reverse-osmosis deionized water, distilled water, and finally with our best quality water distilled in an all-quartz distilling apparatus.

A typical solvent extraction system consists of different components such as water, organic diluent, extractant, acid or base, and metal ions. One of the objectives of this paper is to demonstrate how the impurities in the different components affect γ assuming that the glassware are free from impurities as evidenced later. The purification methods for the different components in the n-hexane/HDEHP/aqueous solution system are described below.

Water used in this investigation was purified as follows: St. Paul city water was passed through a carbon filter, Culligan Aqua-Clear reverse-osmosis unit and Culligan Uni-Bed exchanger. The reverse-osmosis deionized water was then distilled in an all-

Pyrex bi-distillation apparatus, the first distillation being from alkaline potassium permanganate to oxidize any organic impurities. The distillate from each stage was passed through double traps and a column packed with cut Pyrex tubing. The Pyrex receiver was fitted with three traps in series containing double-distilled water, sulfuric acid, and sodium hydroxide solution in order to avoid contacting the final distillate with laboratory air. The double-distilled water was further distilled in a quartz bidistillation apparatus (Heraeus-Amersil, Model Bi-4), and the final distillate was stored in clear fused quartz flasks. The surface tension of the purified water was 72.94 and 72.13 mN m^{-1} at 20 and 25°C, respectively. These values are in excellent agreement with literature values (20-23), thus confirming its high purity.

Although 99 mole % pure grade n-hexane (diluent) was obtained from Phillips Chemical Company, it was not suitable to use in the "as received" condition because a 9-11 mN m^{-1} lowering in γ, depending on the batch, was observed for the n-hexane/water interface. Hence, the n-hexane was first distilled, and the middle fraction was passed slowly through two 4-ft long columns packed with adsorbents, viz., silica gel, Florisil, and activated alumina, to adsorb surface-active contaminants, if any, in n-hexane. The percolation rate was maintained to about 6 drops per minute. The columns were equipped with traps of purified n-hexane so that the percolated diluent did not come into contact with the laboratory air. The n-hexane, thus obtained, was finally distilled in an all-Pyrex distillation apparatus. Additional distillation did not increase the value of γ. Table I depicts how the contaminants in n-hexane lower the value of γ. The interfacial tension of the purified n-hexane/water interface at 20°C was found to be 50.60 mN m^{-1}. This value is in good agreement with the values reported in the literature (24,25) and thus provides an ultimate check on the high purity of the bulk phases and the cleanliness of the associated glassware.

98% pure HDEHP was obtained from Alfa Products. The major impurity in this material is the mono-homologue. HDEHP was further

TABLE I

Effect of Purity of n-Hexane on the Interfacial Tension (mN m^{-1}) of the n-Hexane/Water Interface at 20°C

99 Mole %	Distilled Once	Distilled and passed through packed columns	Distilled, passed through packed columns, and redistilled
40-42	50.35	50.40	50.60

purified by forming its copper salt and then reforming HDEHP upon contact with 0.5 N HCl as described elsewhere (26). Water and traces of solvents (ether and acetone) were removed by using a rotary evaporator at 50°C and high vacuum for 3 hours. All solvents used in the purification process were high purity glass distilled solvents (Burdick and Jackson) and were again distilled twice prior to use. An attempt to distill HDEHP even under reduced pressure resulted in decomposition of HDEHP, and hence it was not subjected to distillation. The results showing the effect of the purity of HDEHP on the organic/0.1 N HCl interfacial tension is illustrated in Table II. Note that γ increased by about 4 mN m^{-1} after purification. Subsequent purification had no significant effect.

Even the Ultrex Grade inorganic acids (J.T. Baker) such as HCl, HNO_3, or H_2SO_4, if used to adjust the pH of the aqueous solution in extraction systems, were found to yield lower γ values, presumably due to the presence of trace impurities. Therefore, these acids were vacuum distilled twice in an all-Pyrex distillation apparatus with proper traps. The effect of the purity of HCl on the γ values in the absence and presence of HDEHP is shown in Table III. In the presence of HDEHP it was difficult to detect impurities in the acid because of the relatively low interfacial energy of the system.

The salts may sometimes be another source of contamination if used without purification. We found that even ultra-high purity

TABLE II

Effect of Purity of HDEHP on the Interfacial Tension (mN m^{-1}) of the Organic/0.1 N HCl Interface at 20°C

Organic = 7.6×10^{-4} mol dm^{-3} HDEHP in purified n-hexane

98 mol % HDEHP	Once purified HDEHP	Twice purified HDEHP
32.04	36.10	36.25

TABLE III

Effect of Purity of HCl on the Interfacial Tension (mN m^{-1}) of the Organic/0.1 N HCl Interface at 20°C

Ultrex Grade HCl	Once vacuum distilled HCl	Twice vacuum distilled HCl
Organic = Purified n-hexane		
50.07	50.67	50.72
Organic = 7.6×10^{-4} mol dm^{-3} HDEHP in purified n-hexane		
36.07	36.24	36.25

salts obtained from commercial suppliers are not suitable for use in high quality surface chemical research in the "as received" condition. Salts used in this work were obtained from Spex Industries. A certificate of analysis, which was helpful in making solutions of known concentrations, was provided for each salt. Salt solutions of desired concentrations were prepared with purified water and extracted two times with purified n-hexane in a clean separatory funnel to remove surface-active impurities, if any, present in the salt. Some salts having high melting points such as NaCl, KCl, etc. can be roasted at temperatures below their melting points for 24 hours before making solutions. Table IV illustrates how γ between purified n-hexane and 0.01 mol dm^{-3} $CaCl_2$ in 0.1 N HCl increases as the purification processes are carried out. Atomic absorption spectroscopy revealed that the concentration of the salt solution ($CaCl_2$) remains unchanged to within 1×10^{-5} mol dm^{-3} after extraction with n-hexane.

Interfacial Behavior

Since knowledge of the interfacial activity is important from the mechanistic point of view of the extraction process, γ was measured as a function of [HDEHP] at various equilibrium pH of the aqueous phase for the system n-hexane/HDEHP/0.01 mol dm^{-3} $CaCl_2$ solution at 20°C. γ-log [HDEHP] curves for this system at different pH are shown in Fig. 1 along with a curve obtained in the absence of Ca^{2+} at pH 2. In the presence of Ca^{2+} a slight lowering in γ is observed at pH 2. However, γ is lowered significantly at pH 3, 4 and 5. At these pH values the slope of the γ-log [HDEHP] curves changes suddenly. The HDEHP concentration at which this break occurs depends on the pH for a given concentration of metal ions and decreases with increasing pH. The abrupt change in the slope of the γ-log [HDEHP] curve may be ascribed to a change in the packing, orientation, or nature of the adsorbed species. It is worth noting that at pH 4 and 5 curves characteristic of the aggregation of surfactant molecules in solution are obtained, possibly due to the formation of reversed micelles.

In order to check whether the interesting behavior observed in Fig. 1 at higher pH is common to alkaline earth metal ions or is only characteristic of Ca^{2+}, we determined γ-log [HDEHP] curves also in the presence of Mg^{2+}, Sr^{2+} and Ba^{2+}. Figure 2 shows γ-log [HDEHP] curves at pH 4 in the absence and presence of 0.05 mol dm^{-3} $MgCl_2$, $CaCl_2$, $SrCl_2$ or $BaCl_2$ in the aqueous phase.

TABLE IV

Effect of Purity of $CaCl_2$ on the Interfacial Tension (mN m^{-1}) of the n-Hexane/Aqueous Interface at 20°C

Aqueous = 0.01 mol dm^{-3} $CaCl_2$ in 0.1 N HCl

Unextracted $CaCl_2$ solution	Once extracted $CaCl_2$ Solution	Twice extracted $CaCl_2$ Solution
50.36	50.61	50.70

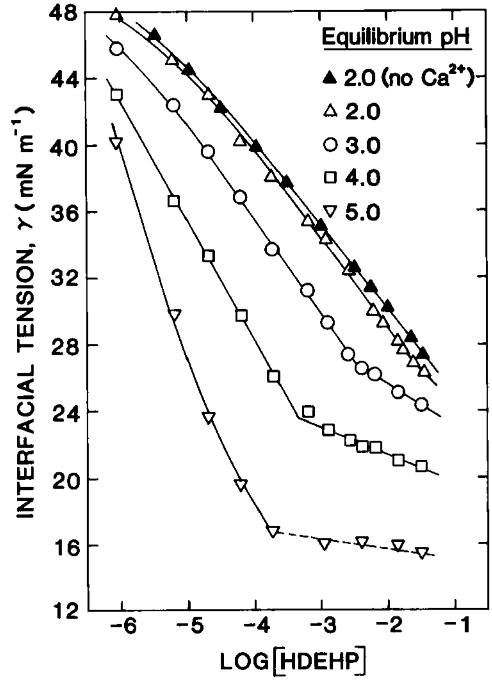

FIGURE 1

γ-log [HDEHP] curves for the n-hexane/HDEHP/0.01 mol dm^{-3} $CaCl_2$ solution system at various pH and 20°C.

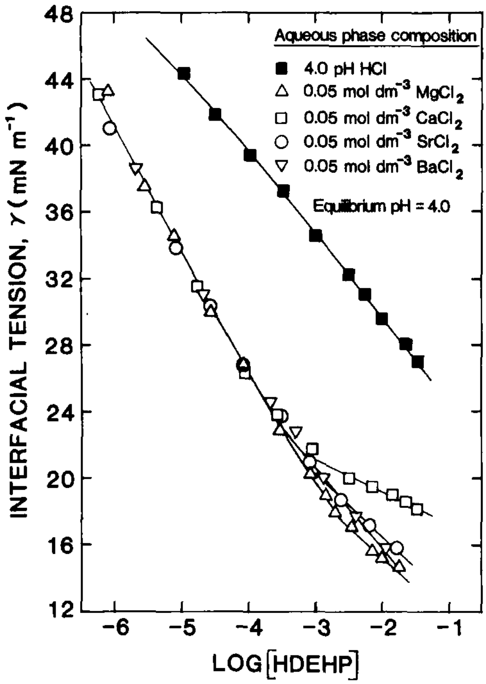

FIGURE 2

γ-log [HDEHP] curves for the n-hexane/HDEHP/0.05 mol dm^{-3} alkaline earth metal chloride ($MgCl_2$, $CaCl_2$, $SrCl_2$ or $BaCl_2$) solution system at pH 4 and 20°C.

Once again γ decreased significantly in the presence of the metal ions. A change in the slope of the γ-log [HDEHP] curves was exhibited at [HDEHP] $\simeq$ 5 x 10^{-4} mol dm^{-3} in the presence of Ca^{2+}, Sr^{2+} or Ba^{2+} and [HDEHP] $\simeq$ 2 x 10^{-3} mol dm^{-3} in the presence of Mg^{2+} with the change being very abrupt when Ca^{2+} was present.

It is surprising that the system behaves peculiarly when the aqueous phase contains Ca^{2+} in that γ-log [HDEHP] curves characteristic of aggregate formation are obtained at pH 4 and 5. As indicated earlier, these aggregates may be reversed micelles. Aggregate formation might be expected to lead to an enhancement of the extraction process due to the solubilization of metal ions in the polar core of the reversed micelles (27). Measurements of mass transfer coefficients using a Lewis-type cell are in progress with the view to correlate interfacial tension with the results of mass transfer studies on calcium extraction systems. The mass transfer results will be discussed in a forthcoming paper.

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REFERENCES

1. Published as Scientific Journal Series Paper No. 14,112 of the University of Minnesota Agricultural Experiment Station.

2. E.C. Hunt, J. Colloid Interface Sci., 29, 105 (1969).

3. D.S. Flett, Acc. Chem. Res., 10, 99 (1977).

4. G. Scibona, P.R. Danesi, A. Conte and B. Scuppa, J. Colloid Interface Sci., 35, 631 (1971).

5. S.J. Lyle and D.B. Smith, J. Colloid Interface Sci., 61, 405 (1977).

6. T.A.B. Al-Diwan, M.A. Hughes and R.J. Whewell, J. Inorg. Nucl. Chem., 39, 1419 (1977).

7. G.F. Vandegrift and E.P. Horwitz, J. Inorg. Nucl. Chem., 42, 119 (1980).

8. K. Osseo-Asare and M.E. Keeney, Metall. Trans. B., 11, 63 (1980).

9. K. Osseo-Asare and M.E. Keeney, Sep. Sci. Technol., 15, 999 (1980).

10. P.R. Danesi, R. Chiarizia and Saltelli., J. Inorg. Nucl. Chem., 38, 1687 (1976).

11. S.J. Lyle and D.B. Smith, J. Chem. Soc. Faraday I, 72, 1241 (1976).

12. R. Chiarizia, P.R. Danesi, G. D'Alessandro and B. Scuppa, J. Inorg. Nucl. Chem., 38, 1367 (1976).

13. G.F. Vandegrift and E.P. Horwitz, J. Inorg. Nucl. Chem., 39, 1425 (1977).

14. M. Cox and D.S. Flett, in "Proceedings of the International Solvent Extraction Conference ISEC 77," Toronto, The Canadian Institute of Mining and Metallurgy, 1979, Vol. 1, p. 63.

15. P.R. Danesi, R. Chiarizia and G.F. Vandegrift, J. Phys. Chem., 84, 3455 (1980).

16. M. Cox and M. Gray, in "Proceedings of the International Solvent Extraction Conference ISEC 83," Denver, American Institute of Chemical Engineers, 1983, p. 321.

17. A.G. Gaonkar and R.D. Neuman, J. Colloid Interface Sci., 98, 112, (1984).

18. E.P. Laug, Ind. Eng. Chem. Anal. Ed., 6, 111 (1934).

19. R.V. Henry and E.C. Smith, Science, 104, 2705 (1946).

20. G.J. Gittens, J. Colloid Interface Sci., 30, 406 (1969).

21. J.J. Jasper, J. Phys. Chem. Ref. Data, 1, 841 (1972).

22. J.A.G. Taylor and J. Mingins, J. Chem. Soc. Faraday Trans. I, 71, 1161 (1975).

23. S. Ross and R.E. Patterson, J. Chem. Eng. Data, 24, 111 (1979).

24. R. Aveyard and D.A. Haydon, Trans. Faraday Soc., 61, 2255 (1965).

25. R.E. Johnson and R.H. Dettre, J. Colloid Interface Sci., 21, 610 (1966).

26. J.A. Partridge and R.C. Jensen, J. Inorg. Nucl. Chem., 31, 2587 (1969).

27. J.H. Fendler and E.J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York, 1975.