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To cite this Article Yurdakoç, M. , Karakaplan, M. and Hoşgören, H.(1999) 'Effect of Long-Chain Amines on the Extraction of Boron from $CaCl_2$ Brine with CTMP in Petroleum Benzine', Separation Science and Technology, 34: 13, 2615 — 2625
To link to this Article: DOI: 10.1081/SS-100100794
URL: http://dx.doi.org/10.1081/SS-100100794

SEPARATION SCIENCE AND TECHNOLOGY, **34**(13), pp. 2615–2625, 1999

Effect of Long-Chain Amines on the Extraction of Boron from $CaCl_2$ Brine with CTMP in Petroleum Benzine

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ABSTRACT

The effect of TOA (tri-*n*-octylamine), TOMA (tri-*n*-octylmethylammonium iodide), DEDA (*N*,*N*′-didodecylethylenediamine), DEDMA (*N*,*N*′-didodecyl-*N*,*N*′-tetramethylethylene-diammonium diiodide), and NDM (*N*-dodecylmorpholine) upon the solvent extraction of boron from $CaCl_2$ brine with CTMP [2-chloro-4(1,1,3,3,-tetramethylbutyl)-6-methylolphenol] in petroleum benzine has been studied. In order to extract boron effectively and reject other cations such as Ca^{2+}, the extraction of boron with CTMP was investigated in terms of extractant, the concentration of an amine, and solvent polarity. The results show that in the presence of long-chain amines, boron extraction with CTMP in all solvent systems was shifted to a more acidic pH range. Larger extraction, hence distribution, and an increase in selectivity are observed when CTMP is used together with long-chain amines and their ammonium salts in petroleum benzine.

INTRODUCTION

Boron concentration in aqueous medium may vary widely (for example, from 5 ppm to 1 M) depending on the source. In many natural and artificial waters and brines and in dilute solutions from many processes, boron is often present in relatively low concentrations. It is desirable to remove boron from such solutions for purification purposes; e.g., removal of boron contamination from irrigation waters because the boron content exceeds 2 or 3 ppm, which is the tolerable limit for citrus and some other agricultural crops (1). This problem is beginning to

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reach significant proportions in Turkey where there is danger at three large-scale operations of severe pollution in the not too distant future (2–4).

Boron contamination is commonly present in magnesium chloride brines. Boron interferes with the subsequent production of magnesium metal by electrowinning operations. It is desirable to remove boron contamination in many other situations as well. The quantity of boron that may be contained in some brines is economical as a source of relatively high purity boron compounds, preferably boric acid, which has relatively high market value compared (for example) with borax. Generally, borax and other boron-containing materials are recovered from dilute liquors by evaporation and/or by cooling the liquor so that the boron salt or boric acid crystallizes out of the solution. However, below a limiting boron concentration (and with the complication of other salts), this method is not economical. A more effective method is required such as a solvent extraction technique (5).

When solvent extraction has been employed to recover boron from aqueous solutions containing other metal ions, some of the other ions were likewise extracted resulting in a necessity for separating the boron from such ions. Such a coextraction process is undesirable since no important selective extraction process has been available which would remove boron and reject the other cations present. One or more of certain water-immiscible organic extraction agents specified in combination with certain alkylammonium salts were suggested to extract boron selectively from relatively concentrated brines or other aqueous solutions. Typical of such brines are the Monroe brines; magnesium chloride brines derived from seawater and other natural saline waters which contain minor amounts of boron. Other suitable aqueous solutions included mineral acid leaches of boron-containing metal alloy or ores (6).

A variety of dissolved ions will normally coexist with borates in natural or industrial leach solutions and all may have an effect upon extraction of boron from these solutions. Their effects have been considered in previous studies (2, 6). The extraction of borates, Na^+, Ca^{2+}, and Cl^-, singularly and in various mixtures, into EHD (2-ethyl-1,3-hexanediol), CTMP, and a 1:1 mixture of the two was investigated and reported as curves of extraction percent versus equilibrium pH (2).

The purpose of this study is to consider selective boron removal from aqueous $CaCl_2$ solutions using CTMP and a combination of certain new long-chain amines such as DEDA, DEDMA, NDM, and other conventional amines such as TOA and TOMA.

EXPERIMENTAL

Apparatus

The equilibrium pH was measured by a RCN AL-ON, MP 8100 precision model pH meter. A Heildolph Type RZR 50 model mechanical stirrer equipped with a multiple purpose helical impeller and Grant Type W 14 model water circulator thermostatic bath were used in the boron extraction experiments. Boron concentrations were determined spectrophotometrically by a Schimadzu 160 model UV-Visible spectrophotometer.

Reagents and Solutions

Standard Boron Solution. A stock solution containing 3.7×10^{-2} M boron and 1.71 M $CaCl_2$ was obtained by dissolving boric acid in deionized water. Working solutions were prepared by accurate dilutions of the stock solution.

Azomethine-H Solution. One gram of azomethine-H sodium salt ($C_{17}H_{12}NNaO_8S_2$) and 3 g of L(+)-ascorbic acid ($C_6H_8O_6$) were dissolved and made up to 100 mL with water. The solution was stored in a plastic bottle and was stable for approximately 1 week if kept in a refrigerator.

Buffer Solution (pH 5.9). Citric acid (28.88 mL, 0.002 M) and sodium citrate (19.41 mL, 0.001 M) were mixed and made up to 100 mL with water.

Reagent Solution. Equal volumes of azomethine-H solution and buffer solution pH 5.9 were mixed before the analysis. The solution must be kept in a refrigerator. The four solutions mentioned above were used to determine boron from the aqueous phase. The procedure is described below in the next section. The following three solutions were employed to determine Ca^{2+} titrimetically from the aqueous phase.

EDTA Solution (0.01 M). Ethylenediaminetetraacetic acid disodium salt ($C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$, 3.725 g) was made up to 1 L with water.

Indicator Solution. Eriochrome black T (0.5 g) was dissolved in 100 mL triethanolamine.

Buffer Solution (pH 10). Ammonium chloride (6.75 g) and EDTA disodium-magnesium salt ($C_{10}H_{12}N_2O_8Na_2Mg$, 0.05 g) were dissolved in 57 mL ammonia (25%) and made up to 100 mL with water.

Reagents used in this study, such as NDM, DEDA, and DEDMA, were synthesized in analytical purity, as described previously (7–9). The spectroscopic and microanalysis data are consistent with previous ones. The synthesis of CTMP was carried out from literature methods (10). TOMA (Fluka Catalog No. 69487) and TOA (Fluka Catalog No. 92828) were purchased from Fluka. Petroleum benzine (Merck Catalog No. 1777, boiling range 80–100°C) and other reagents were obtained from Fluka or Merck and used without further purification.

Extraction of Boron with CTMP and the Mixture of CTMP and Long-Chain Amine

The extraction experiments were carried out in a specially designed jacketed glass tube. The jacket was connected to a thermostated water supply at

25°C whose temperature constancy was controlled to within ±0.1°C. A 10-mL portion of an aqueous solution having a 1.71 molar concentration of $CaCl_2$ and 0.4 $g{\cdot}L^{-1}$ (400 ppm) of boron (initial pH 5.81) was extracted with 10 mL of a 0.4 molar solution of CTMP in petroleum benzine. A second 10-mL portion of $CaCl_2$ solution having 400 ppm of boron was extracted in the same manner except that the CTMP solution contained a 0.05 molar concentration of various amines and their quaternary amine salts. Petroleum benzine was chosen as a solvent due to the low price and better solubility of long-chain amines in this solvent. The parameters used throughout the experiment were as follows: phase ratio 1.0, temperature 25°C, contact time 15 minutes, and stirring rate 1300 rpm. After the extraction was completed, the phases were separated. Initial pHs of aqueous phase were adjusted before the extraction took place by the addition of NaOH and HCl solutions so that the equilibrium pH required can be approximately obtained. Aqueous phase boron concentrations at a certain equilibrium value were determined spectrophotometrically by azomethine-H sodium salt (11). The following procedure was used for each sample and standard, 4–10 standards and samples being treated simultaneously. An aliquot of standard boron solution containing up to 0.4 ppm boron is placed in a 10-mL test tube equipped with a stopper and 2 mL reagent solution is added to each of the solutions and the absorbance measured at 414 nm, using a 10 mm quartz cell, with reagent solution as a reference. Since the initial concentration of boron is known, the percentage of boron extracted into the organic phase was calculated according to the following equation:

$$R\% = \frac{[\mathrm{B}]_0 - [\mathrm{B}]}{[\mathrm{B}]_0} \times 100$$

where $R\%$ = percent extraction
$[\mathrm{B}]_0$ = initial concentration of boron in aqueous phase
$[\mathrm{B}]$ = concentration of boron remaining in aqueous phase at equilibrium

The Ca^{2+} concentration remaining in the aqueous phase at a certain equilibrium pH was determined titrimetrically by EDTA (11). The percentage of Ca^{2+} extracted into the organic phase was calculated in the same way used to calculate that for boron.

RESULTS AND DISCUSSION

Liquid–liquid extraction of boron with CTMP in various solvents such as petroleum benzine, chlorobenzene, and nitrobenzene was studied at different equilibrium pHs. A larger extraction of boron is possible with solvents of low polarity such as petroleum benzine. The order of the percent extraction is:

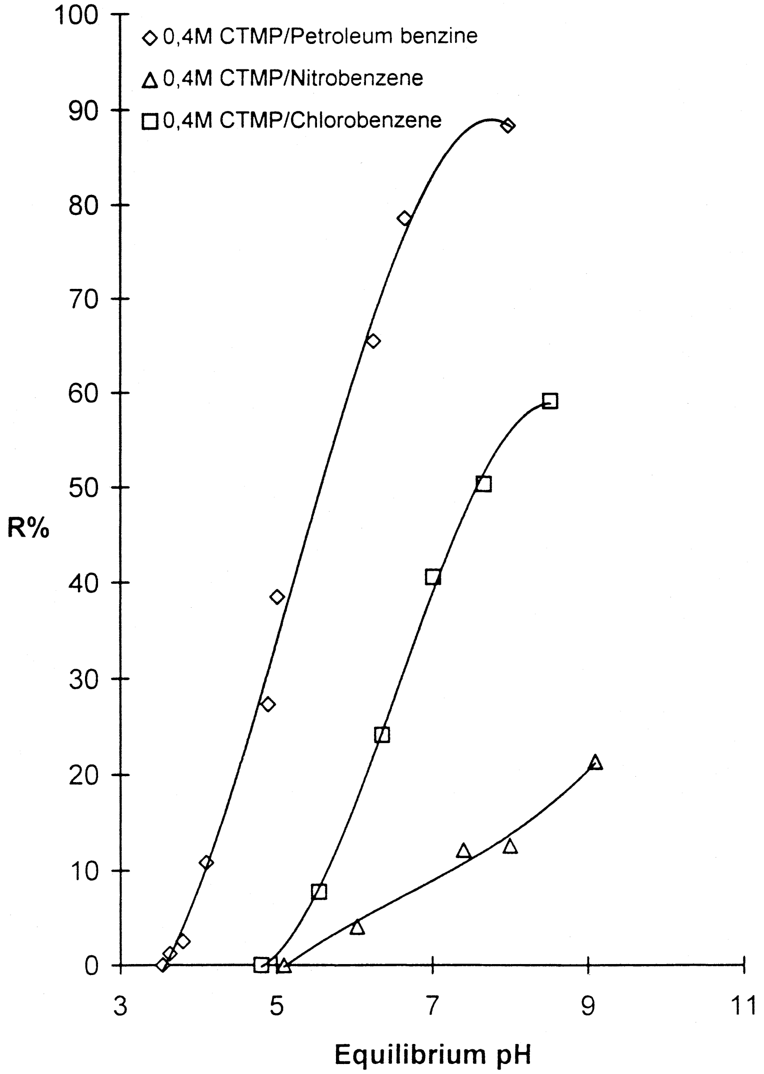

FIG. 1 The influence of various solvents on the percent extraction of boron in $CaCl_2$ brine.

petroleum benzine (PB) > chlorobenzene (CB) > nitrobenzene (NB) (see Fig. 1).

To optimize the extraction of boron with the mixture of CTMP and TOMA, the effect of each extractant component on the extraction was studied while the concentration of other components was kept constant at the same initial pH (see Tables 1 and 2).

In order to extract boron effectively, it was necessary to employ a molar ratio of 0.4:0.05, diol to long-chain amine. Boron is extracted by employing CTMP together with TOMA in this molar ratio at pH 3.36 (83.15%), while boron was not extracted at all when CTMP is employed alone at the same pH

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TABLE 1
Effect of TOMA Concentration on the Extraction of Boron in $CaCl_2$ Brine with 0.4 M CTMP in Petroleum Benzine

Equilibrium pH	TOMA (M)	*R*%[a]	*R*%[b]
6.20	0.0125	77.03	66.93
5.90	0.0250	82.62	59.23
3.36	0.0500	83.15	0
3.51	0.0750	87.76	0

[a] B% extraction with CTMP containing TOMA.
[b] B% extraction with CTMP.

TABLE 2
Effect of CTMP Concentration on the Extraction of Boron in $CaCl_2$ Brine with 0.05 M TOMA in Petroleum Benzine

Equilibrium pH	CTMP (M)	*R*%
6.61	0.1	27.36
5.95	0.2	60.43
4.93	0.3	82.64
3.36	0.4	83.15
3.51	0.5	84.01

TABLE 3
Extraction of Ca^{2+} and B (all at 400 ppm) with 0.4 M CTMP in Petroleum Benzine[a]

		Extraction %	
Extractant	Equilibrium pH	B	Ca^{2+}
CTMP	3.90	0.74	3
CTMP + NDM	4.22	85.60	0
CTMP	6.29	14.73	36.66
CTMP + NDM	6.93	90.88	0
CTMP	9.43	68.52	100
CTMP + NDM	10.10	77.00	100

[a] For comparison, extractions were conducted in the same manner except that CTMP solution also contained 0.05 M NDM. Initial pH 6.20.

(see Table 1). The 0.3–0.4 M concentration range of CTMP was found to be sufficient for the recovery of boron from a working solution which contained 400 ppm of boron (see Table 2).

In our experiments the calcium and boron concentrations were 1.71 M and 400 ppm, respectively. The calcium concentration was very high. For this reason, no selectivity was observed with this high calcium concentration. In order to see the selective extraction of boron, a 400-ppm B and 400-ppm Ca^{2+} solution was extracted with CTMP in petroleum benzine. As seen from Table 3, 68.52% of the boron and 100% of the calcium was extracted with CTMP at

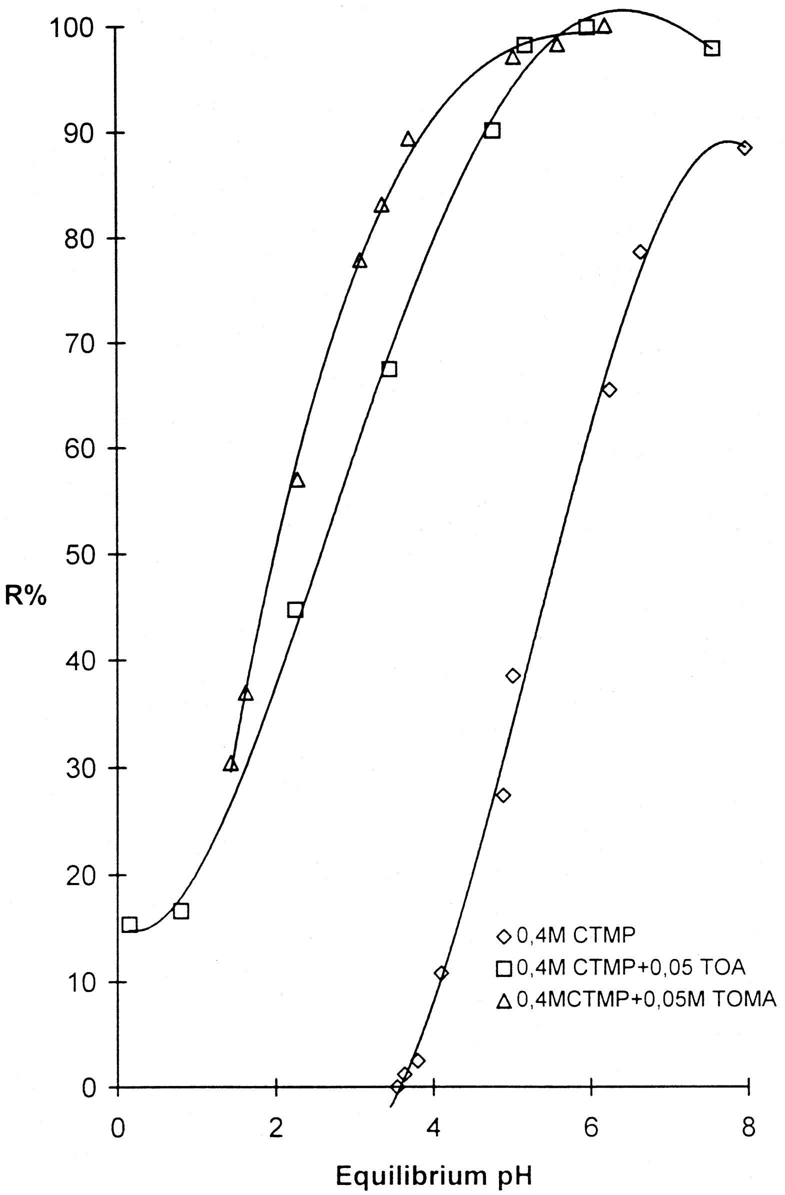

FIG. 2 The influence of TOA and TOMA on the percent extraction of boron in $CaCl_2$ brine.

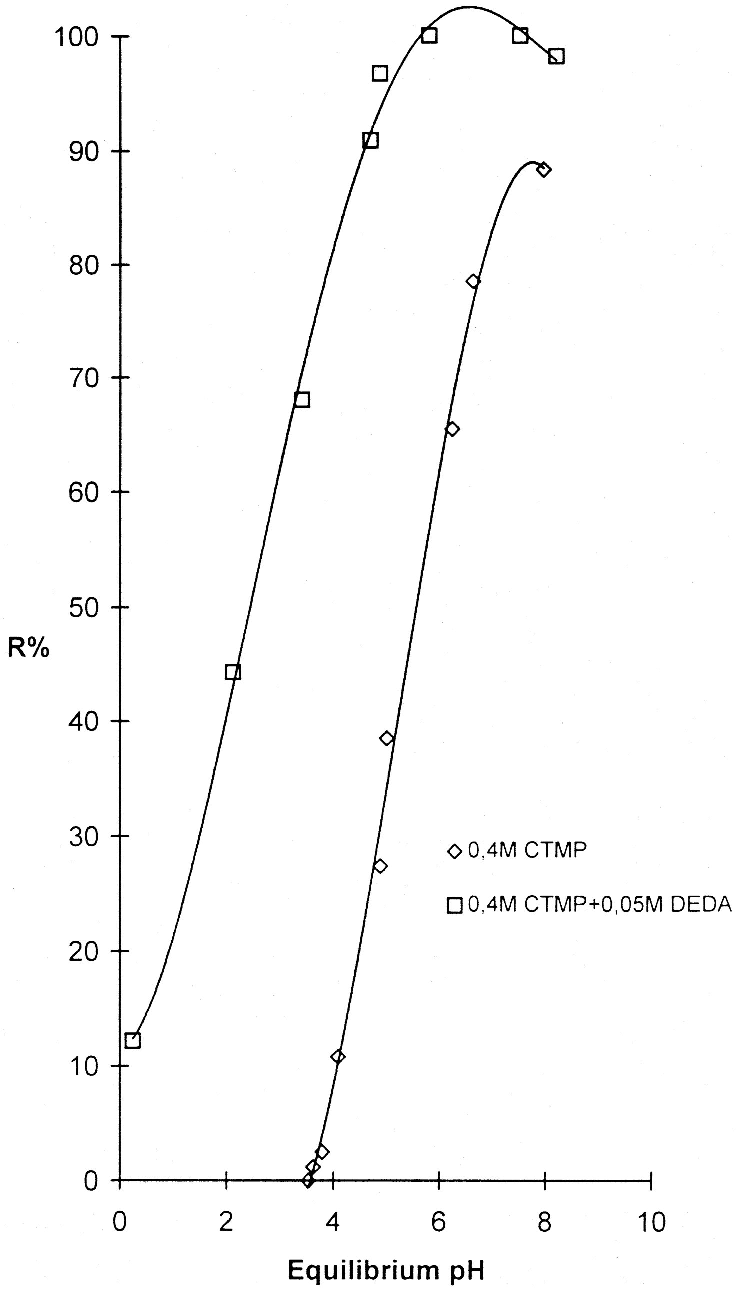

FIG. 3 The influence of DEDA on the percent extraction of boron in $CaCl_2$ brine.

pH 9.43. On the other hand, 90.88% of the boron was extracted to the organic phase and Ca^{2+} remained in the aqueous phase when the mixture of NDM and CTMP was employed at pH 6.93. But at higher pHs, NDM has no effect on the selective extraction of boron. This means that the extraction of boron is shifted to the acidic region due to the effect of the amine, thus resulting in the selective extraction of boron.

The influence of long-chain amines and their salts such as TOA and TOMA, DEDA and DEDMA, and NDM on the percent extraction of boron were investigated in relation to pH changes. In the case of all amines and their salts with a combination of CTMP, the percent extraction of boron increases with the decrease in equilibrium pHs (see Figs. 2–4). According to the shapes of the plots of *R*% against pH, the extraction of boron is shifted to a more acidic pH range when CTMP is used with a combination of long-chain amines and their salts. $pH_{0.5}$ values for mixtures of TOA, TOMA, NDM, and DEDA with CTMP in petroleum benzine were found to be 2.65, 1.90, 1.90, and 2.40, respectively, while in the case of CTMP alone the $pH_{0.5}$ was 5.60.

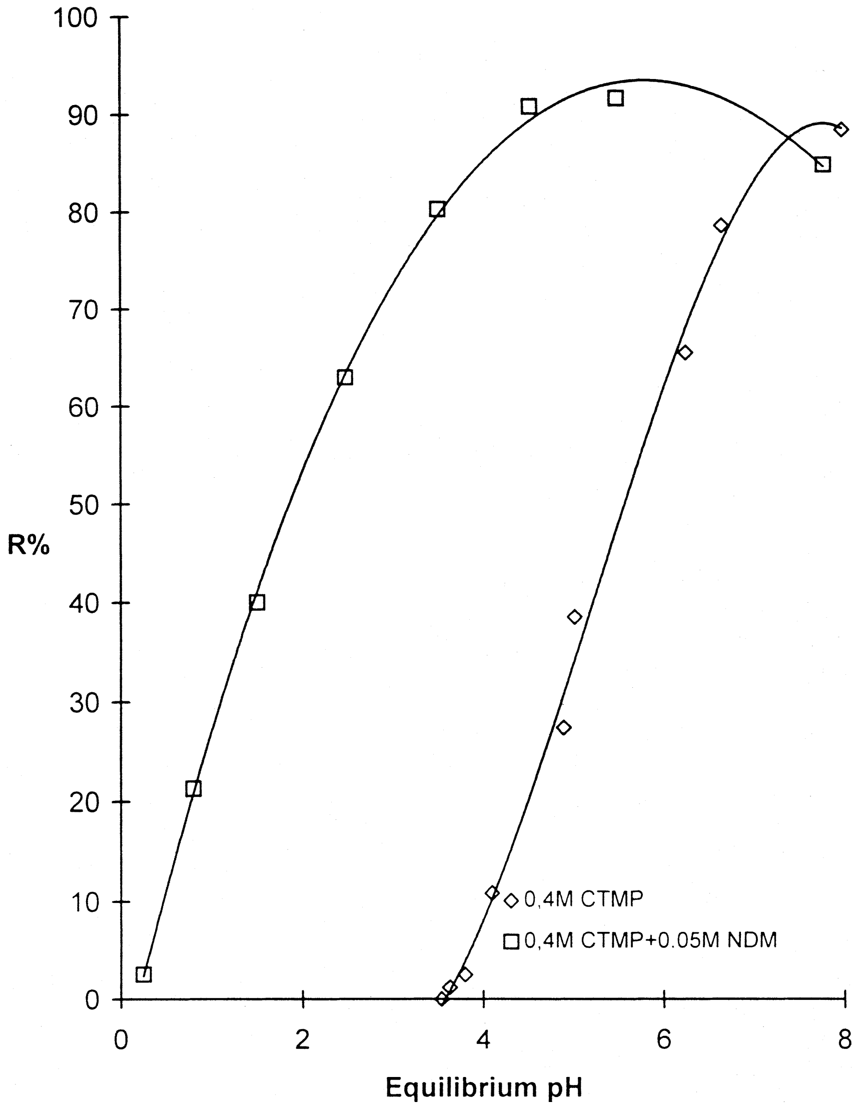

FIG. 4 The influence of NDM on the percent extraction of boron in $CaCl_2$ brine.

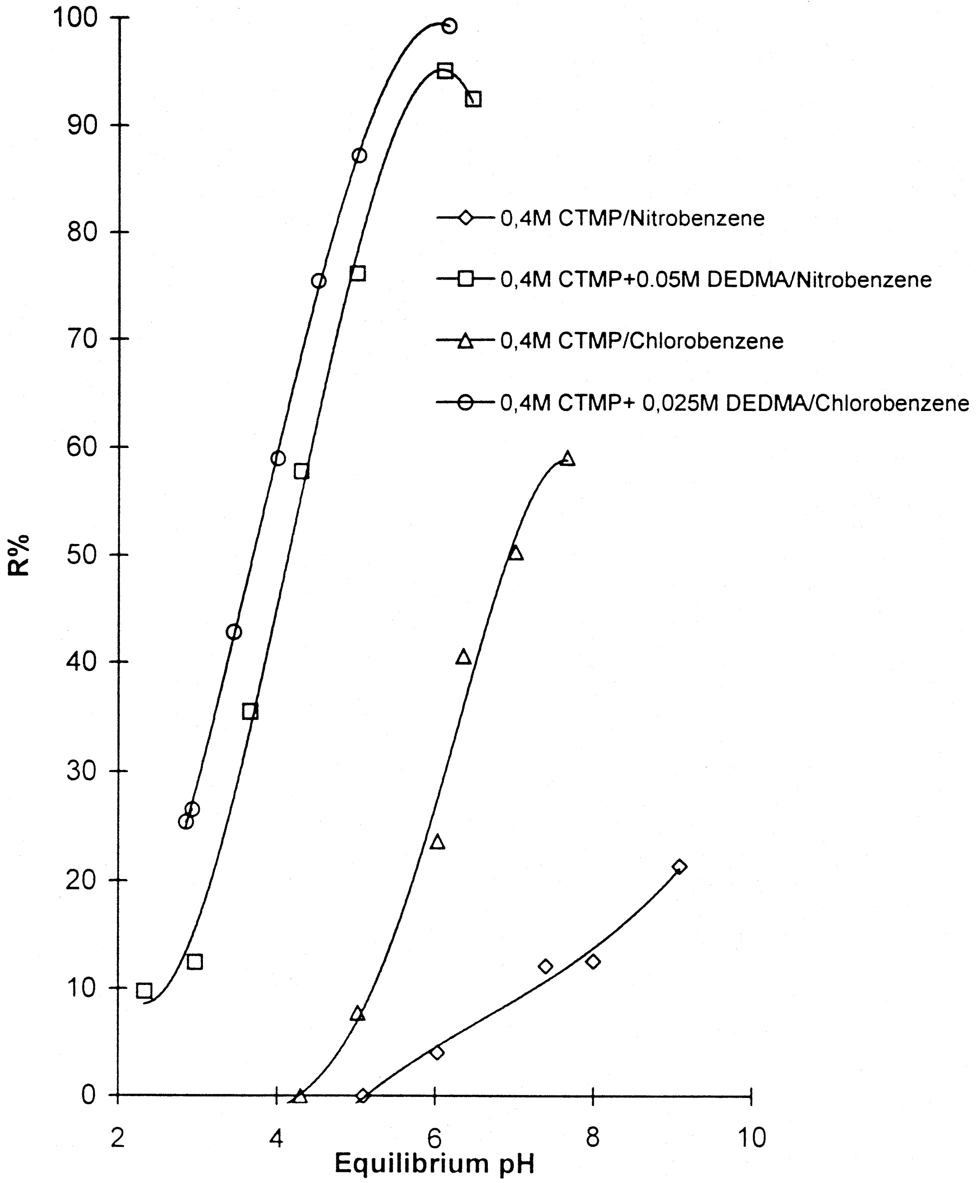

FIG. 5 The influence of DEDMA on the percent extraction of boron in $CaCl_2$ brine.

Due to the low solubility of DEDMA in petroleum benzine, extraction of boron with this amine salt was studied in more polar solvents such as chlorobenzene and nitrobenzene. The effect of this amine combination with CTMP on the percent extraction of boron was also studied with CTMP alone in the same solvents, namely chlorobenzene and nitrobenzene, for the sake of comparison. These results are shown in Fig. 5.

CONCLUSIONS

Boron is not extracted at all when CTMP is used alone as an extractant in petroleum benzine at pH 3.54, but when it is used with amines such as TOA, TOMA, DEDA, and NDM, boron is extracted up to 85% in the same solvent and pH. Similar results are also observed when CTMP is used together with DEDMA in CB and NB at pHs 4.80 and 5.09, respectively.

Coextracting reagents such as NDM and DEDA, which were used first in this study, are the best coextracting reagents for boron extraction with CTMP as much as are conventional amine TOA and its ammonium salt TOMA.

Boron can be selectively extracted with NDM when the calcium concentration is decreased to 400 ppm. The change in the amount of Ca^{2+} can not be accurately determined at higher calcium concentration (1.71 M).

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Received by editor April 6, 1998
First revision received September 1998
Second revision received October 23, 1998

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