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Gas Chromatographic Determination of Solvation Number by an Investigation of the Extraction Processes

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Synopsis. A simple gas chromatographic method for the determination of the solvation number by an investigation of the extraction processes using MIBK as the solvent has been proposed. Gas chromatography was applied for the determination of the solvation number by extraction of the halometallic acids $HFeCl_4$, $HMoO_2Cl_3$ in MIBK as well as by extraction of $BiCl_4^-$ and $SbCl_4^-$ as ion-associate complexes with long-chain quaternary ammonium salts in MIBK.

The donor active solvents, e.g. 4-methylpentan-2-one (MIBK), can bring about the extraction of metal ions by direct solvation of their coordinatively unsaturated chelate and ion-associate complexes or of the proton.[1-3] The most convenient way to determine the solvation number is to vary the concentration of the solvent by diluting it with an inert solvent at constant concentration of the extracting reagent, and of the metal ion. The $\log D/\log C_s$ slop (C_s=total MIBK concentration) shows the solvation number (s), provided that the concentration ratio of unbound extractant/total extractant is constant.[4-6] For some extraction systems the solvation number might be estimated on the basis of infrared spectrometry data.[7] The peak area for the associated C=O band corresponds to the concentration of the solvated MIBK.

In the present paper a new method for evaluating the solvation number is developed. The method is based on a determination of the concentration of MIBK, included in the extracted species by means of gas chromatography (GC).

Experimental

Apparatus. The GC studies were carried out on a Hewlett-Packard 5890A gas chromatograph with a singleflame ionization detector (FID), and an HP-3396 A computing integrator. The working conditions were as follows: Temperature of the injection system, 200 °C; temperature of the FID, 250 °C; temperature of the oven linearly programmed from 90 to 150 °C by 20 °C min^{-1}; carrier gas (N_2) flow rate of 16 ml min^{-1}; the GC-column (L=20 cm, ID=0.2 cm) was filled with 20% silicone OV-225 on 70—80 mesh silicagel AW/DMCS/HMDS.

GC Determination of the Solvation Number. The metal-ion solution (1 ml, 5×10^{-3} mol dm^{-3} Bi(III), 2×10^{-3} mol dm^{-3} Sb(III) was placed into a separating funnel and diluted with 20 ml of 0.5 mol dm^{-3} HCl for Bi(III) and of 2 mol dm^{-3} HCl for Sb(III). Then 2.0 ml of 0.01 mol dm^{-3} benzyldimethyltetradecylammonium chloride (BDTA) or cetyltrimethylammonium bromide (CTAB) were added to the aqueous phase. For a determination of the solvation number by extraction of halometallic acids, one ml, 2×10^{-3} mol dm^{-3} Fe(III), Sb(III) and 5×10^{-3} mol dm^{-3} Mo(VI) was diluted with 20 ml of 6 mol dm^{-3} HCl. The extraction was carried out with 5.0 ml MIBK for 5 min. After separation of the phases, 3.0 ml of the organic layer was transferred to a test tube and dryed under vacuum. The drying procedure was held for 30 min after building of the solid residue. In this way complexes of the type MCl_x^{n-} $(H_3O^+)_n\cdot m H_2O\cdot s$MIBK and $MCl_x^{n-}\cdot s$MIBK$(BDTA)_n^+$ or $MCl_x^{n-}\cdot$sMIBK$(CTA)_n^+$ were obtained. The blanks were prepared in the same manner. The extracted complex, obtained as a dry residue, was dissolved in 1 ml $CHCl_3$, and 1 µl of this solution was injected into the gas chromatograph. A calibration curve was prepared from a series of standard solutions containing 5×10^{-4}—8×10^{-3} mol dm^{-3} MIBK in $CHCl_3$.

Results and Discussion

A typical gas-chromatogram obtained from the injected 1 µl solution containing $(BiCl_4\cdot s\text{MIBK})^-(BDTA)^+$ in chloroform is shown in Fig. 1. It is evident that two different peaks corresponding to solvents $CHCl_3$ and MIBK exist. The third peak belongs to CH_3OH dissolved in $CHCl_3$. Under these conditions, the other part of the extracted complex, $BiCl_4^-(BDTA)^+$, does not evaporate. The amount of MIBK solvated to the extracted species was calculated from the corresponding peak area in the chromatogram using the calibration curve method. Due to a quantitative extraction of Bi (as well as of all investigated elements)

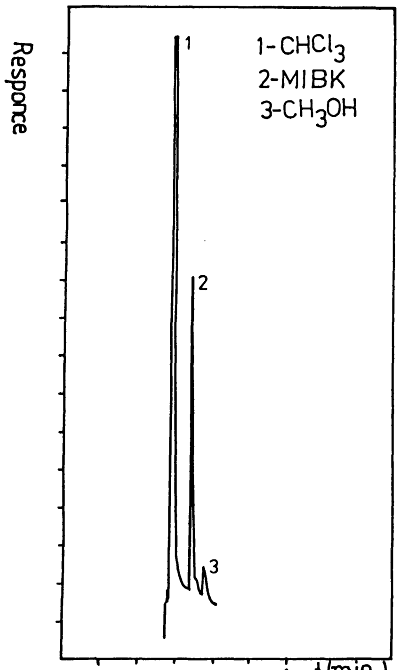

Fig. 1. Typical chromatogram for gas chromatographic determination of the solvation number. The extracted complex is $(BiCl_4\cdot s\text{MIBK})^-(BDTA)^+$.

Table 1. Solvation Number (s) for MIBK, Determined by Means of Gas Chromatography (GC), IR-Spectroscopy (IR), and Equilibrirum Shift Method (ES)

No.	Extracted species with s MIBK	GC	IR	ES
		$s \pm 0.07$	$s \pm 1$	$s \pm 0.05$
1	$(BiCl_4)^-(CTA)^+$	1.06	1.1	1.04
2	$(BiCl_4)^-(BDTA)^+$	1.09	1.1	1.02
3	$(SbCl_4)^-(BDTA)^+$	1.14	1.2	1.08
4	$(SbCl_4)^-(CTA)^+$	1.08	1.1	1.09
5	$HFeCl_4$	2.14	2.1	2.08
6	$HMoO_2Cl_3$	2.08	2.0	2.11
7	$HSbCl_4$	2.14	2.1	2.02

the amount of $BiCl_4^-$ $(BDTA)^+$ can be determined from the concentration of Bi(III) in the initial solution. Hence, the solvation number (s) can be calculated according to the equation

$$s = S_{MIBK} \cdot C_{st} \cdot V_{ex} / S_{st} \cdot C_M \cdot V_g,$$

where:

S_{MIBK} is the peak area of MIBK in the chromatogram of the extracted species; C_{st} the concentration of MIBK in chloroform solution used as the calibration standard; S_{st} the peak area of MIBK in the chromatogram of the standard solution; C_M the concentration of the investigated element in the initial solution; V_{ex} the volume of the organic phase after extraction; and V_g the volume of the organic phase used for a GC-determination of s.

The results obtained for the solvation number by means of the described gas chromatographic method are presented in Table 1. As can be seen from Table 1, the GC-data for the solvation number are in good agreement with the data from IR-measurement and from the equilibrium shift method. The insignificant difference in the solvation numbers obtained by means of three independent methods justify the accuracy of the proposed gas chromatographic method.

In conclusion, it might be stated that gas chromatography is applicable for the determination of the solvation number by an investigation of the extraction processes using MIBK as an organic solvent. The essential difference in the volatility of the solvent and the other part of the extracted complex allows a simple, reliable, and accurate determination of the solvation number for most extraction systems applicable to analytical chemistry. It might be applied for investigations of solvation processes for extraction systems with complicated IR spectra (overlapped absorption bands) as well as for cases when the equilibrium shift method does not provide correct results. The main advantage of the proposed gas chromatographic method is its wide range of applicability.

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