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Abstract

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EXTRACTION RECOVERY OF PERRHENATES BY KETONES

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Earlier, one of the authors [1] showed that certain compounds of Re VII and Tc VII are extracted by ketones from acidic, neutral, and alkaline solutions, and a number of methods were developed for separating these elements using methyl ethyl ketone and acetone [2]. These methods were also used for isolating technetium [3] and for the quantitative separation of rhenium from molybdenum [4]. The results obtained in the study found good confirmation in later works [5]. In the present communication, some data are given on the influence on the distribution coefficient (α) of the nature of the ketone, and an attempt is made to consider the mechanism of extraction recovery using certain thermodynamic parameters and investigations in the infrared region of the spectrum.

Table 1

Some extraction parameters

Ketone	α'	$-\Delta H$, kcal	$\Delta\nu_{C=O}$ in the presence of $NaReO_4$ and H_2O, cm^{-1}	$\Delta\nu_{C=O}$ in the presence of H_2O, cm^{-1}
Methyl ethyl ketone	120	7.1 ± 0.2	20	10
Cyclohexanone	68	6.6 ± 0.2	17–20	15
Diethyl ketone	3.2	2.2 ± 0.2	12	10–12

It is known that, in a series of extractants of one class, the highest distribution coefficients are possessed by solvents with large values of dipole moments, i.e., with a shorter carbon chain [6]. For oxygen-containing solvents the ratio O : C is used as a characteristic. In our investigations, as a characteristic factor for ketones, the ratio 28 : MW was chosen (28 is the molecular weight of the CO group, MW is the molecular weight of the ketone). The influence of this parameter on the distribution coefficient α is presented in Fig. 1, from which it is evident that in the series of methyl ketones a linear dependence is observed. However, in the case of ketones having the same molecular weight as methyl ketones but differing in structure, a deviation from this regularity occurs (for aliphatic ketones a decrease in α, for cyclic ketones or those containing a cyclic radical—an increase).

The data we obtained in studying the influence of reciprocal temperature $\left(\frac{1}{T}\right)$ on the "thermodynamic" * distribution coefficient (α'), under conditions of low mutual solubility of the ketone and aqueous phase, showed that in the coordinates $\lg \alpha' - \frac{1}{T}$ a linear dependence is observed (Fig. 2); consequently, from the angle of inclination it is possible to determine the total heat of extraction recovery. It turns out that, in the series of methyl ketones, the value of ΔH is the same and equal to 7.2 ± 0.3 kcal, whereas for other types of ketones this parameter has somewhat different values. As can be seen from Table 1, for different types of ketones there is a general tendency toward a decrease in the value—

* The values of the "thermodynamic" distribution coefficients were found experimentally under conditions imposed by the phase rule.

···of both α' and ΔH and the shifts of the frequency of the stretching vibrations of the C=O group in ketones in the presence of sodium perrhenate.

Since, apparently, one cannot expect a fundamental difference in the mechanism of extraction of sodium perrhenate within a single class of solvents, the data presented probably indicate a difference in the composition of the solvates formed.

Fig. 1. Effect of ketone composition on the distribution coefficient of $NaReO_4$ and $NaTcO_4$.
I –$NaReO_4$ from $1.2\,M$ Na_2SO_4;
II –$NaReO_4$ from $2\,M$ NaOH;
III –$NaTcO_4$ from $2\,M$ NaOH (2);
IV –$NaTcO_4$ from $0.5\,M$ Na_2SO_4 (5);
a –cyclohexanone; b –diethyl ketone; v –acetophenone.
$C_{\mathrm{ReVII}} = 10^{-6}\,M$, $T = 298^{\circ}K$.

As the studies have shown, ketones extract both the perrhenates of ammonium and alkali metals and the perrhenates of divalent and trivalent metals; moreover, in the organic-solvent phase the extracted compound is partially dissociated (10), which is confirmed by conductivity data in a high-frequency field*. The dissociation constant of sodium perrhenate in methylethyl ketone, determined by the extraction method, is 0.7 ± 0.2. A graphical analysis of the dependence of α on magnesium perrhenate concentration shows that in the methylethyl ketone phase a first-order reaction with respect to the perrhenate ion proceeds. It may be assumed that this is connected with the formation of the complex cation $MgReO_4^+$, analogous to the described $CaCl^+$ (7).

However, because of the relatively low solubility of perrhenates in ketones, it is impossible to establish the exact composition of the solvate by any simple method (8). Therefore, in order to obtain at least qualitative data on the nature of the bond between the ketone and the extracted compound, the results of studies by IR spectroscopy were used for extracts of perrhenic acid and its salts with organic cations, and of solutions of the acid and certain salts in ketones.

It should be noted that the shifts in the frequencies of the absorption bands of the CO and OH groups in extracts and solutions of $HReO_4$ and its salts with organic cations in ketones are identical, which indicates the closeness of the structures of the solvates obtained by different methods. From Table 1 and Fig. 3 it is seen that, in the ketone–water system, the latter is bound to the ketone by a relatively weak hydrogen bond (9). Upon introduction of a perrhenate-ion salt, on the one hand, the frequency of the band of the C=O group shifts somewhat more strongly, and, on the other hand, the spectrum of water changes: the OH frequencies caused by a weak bond with the ketone disappear, and new OH-group frequencies appear, characterizing stronger bonds either with the salt cation or directly with the rhenium ion. From Fig. 3 it is seen that the spectrum of water in a series of solvated associates of the perrhenate ion with hydrogen, sodium, calcium, and aluminum ions practically does not change. Replacement of the solvating cations by deliberately hydrophobic ones ($(C_6H_5)_4As^+$, $(C_6H_5NH)_3C^+$) leads to some redistribution of intensities in the water spectrum; however, the major part of the water remains more firmly bound than in the ketone–water system. On this basis it may be supposed that the perrhenate ion is hydrated, which agrees with data on the hydration of a series of anions (12). From Table 1 it is seen that the frequency shift of the OH-group absorption band in the presence of salts is somewhat greater than in the presence of water. From a comparison of all the data one may suggest that in the solvate the ketone is bound directly to the rhenium ion.

* Conductivity measurements were carried out on a VU-2A apparatus (11).

Since the coordination number for Re(VII) is unknown, but the possibility that it is greater than 4 is not excluded, one may, although very cautiously, assume that the water molecules entering into the solvate are also bound to the rhenium ion. A change in the ratio between the number of ketone molecules and the number of water molecules entering into the solvates leads, as a result of energetic and steric factors, to differences in the values of α on going from one type of ketone to another. However, this assumption requires further verification.

Fig. 2. Effect of temperature on the distribution coefficient of $NaReO_4$.
I –methyl ethyl ketone, $1\,M$ Na_2SO_4;
I' –methyl ethyl ketone, $2\,M$ NaOH;
II –cyclohexanone, $1\,M$ Na_2SO_4;
III –diethyl ketone, $1\,M$ Na_2SO_4;
IV –methyl-*n*-propyl ketone, $1\,M$ Na_2SO_4;
V –acetylacetone, $1\,M$ Na_2SO_4;
VI –methyl isobutyl ketone, $1\,M$ Na_2SO_4.

Fig. 3. IR spectra of vibrations of the OH group.
I –methyl ethyl ketone + H_2O + $NaReO_4$;
II –the same without $NaReO_4$;
III –diethyl ketone + H_2O + $NaReO_4$;
IV –the same without $NaReO_4$;
V –cyclohexanone + H_2O;
VI –the same + $HReO_4$;
VII –the same as *V* + $NaReO_4$;
VIII –*V* + $Mg(ReO_4)_2$;
IX –*V* + $Al(ReO_4)_3$;
X –extract of $HReO_4 + H_2O$ in cyclohexanone;
XI –extract of $TPhPReO_4 + H_2O$ in cyclohexanone;
XII –extract of $TPhAReO_4 + H_2O$ in cyclohexanone.

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