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THERMODYNAMIC INVESTIGATION OF THE SYSTEM PERRHENATE–TETRAZOLIUM SALT–WATER–CHLOROFORM

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ABSTRACT

Thermodynamic investigations of the system ReO_4^-–tetrazolium salt–water–chloroform have provided numerous experimental data about the distribution coefficient and the equilibrium extraction constant. The entire data were processed in a logical mathematical consecutive order, using known relationships. The final result has led to the evaluation of the enthalpy (ΔH), isobaric–isothermic potential (ΔG) and entropy (ΔS), which characterize the thermodynamic state of the system.

INTRODUCTION

A set of extraction studies with the system ReO_4^-–tetrazolium salt–water–chloroform [1–3] has led to results which characterize the tetrazole ion-association complexes of ReO_4^- as stable crystal compounds, slightly soluble in water and very easily extracted by polar organic solvents. If to the already determined magnitudes (solubility product, association, distribution and extraction constants) we add thermodynamic constants such as ΔH, ΔG and ΔS, the extraction system will be defined much more completely, rendering deductions related to the extraction of rhenium more reliable.

EXPERIMENTAL

Reagents and equipment

Ammonium perrhenate, Fluka, 3.22×10^{-2} mol l^{-1} aq. soln. Triphenyltetrazolium chloride (TTC), Reanal, 1×10^{-2} mol l^{-1} aq. soln. Iodinenitro-tetrazolium chloride (INT), Fluka, 2×10^{-3} mol l^{-1} aq. soln. Thiazolyl

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blau (MTT), Fluka, 4×10^{-3} mol l^{-1} aq. soln. Neotetrazolium chloride (NTC), Fluka, 5×10^{-3} mol l^{-1} aq. soln. *p*-Nitro-tetrazolium chloride (*p*-NTC), Reanal, 5×10^{-3} mol l^{-1} aq. soln. Nitroblau-tetrazolium chloride (NBT), Merck, 5×10^{-3} mol l^{-1} aq. soln. Chloroform, p.a. Spectrophotometer, SF-16 (U.S.S.R.). Shaking machine, THYS 2 (G.D.R.). Ultrathermostate type U2C (G.D.R.).

Experimental technique

The reagents tetrazolium salt (0.1 ml TTC, 0.2 ml *p*-NTC, 0.5 ml MTT, 0.5 ml INT, 0.2 ml NTC, 0.1 ml NBT) and 60–180 μg perrhenate were placed in a separation funnel with a water jacket for constant temperature maintenance and distilled water added to 10 ml. Extraction was carried out with 10 ml chloroform for 10 min under continuous temperature control conditions. After stratification, the organic layer was photometrically checked at wavelength 260 nm. The distribution coefficient was determined by the standard curves traced at identical temperature.

RESULTS AND DISCUSSION

The equilibrium extraction constant (K_{ex}) was determined according to the chemical model [1] or by the method of Likussar and Boltz [4], using the values of the distribution coefficient.

Having experimental data for the distribution coefficient (D) and K_{ex}, further on we used the following method for evaluation [5].

The relationship between D and temperature is given by the equation:

$$D = A\ \mathrm{e}^{-\Delta H/RT} \tag{1}$$

Using the isochore equation

$$\frac{\ln D}{\mathrm{d}T} = -\frac{\Delta H}{RT^2} \tag{2}$$

and a subsequent conversion and integration, we can present it as a linear relationship between D and T (eqn. 2):

$$2.3 \log D = -\frac{\Delta H}{R}\frac{1}{T} + K \tag{3}$$

This linear relationship can be expressed graphically in coordinates log D vs. $1/T$ (Figs. 1 and 2).

Equation (3) can be written in a more convenient form for calculations:

$$\log D = -\frac{\Delta H}{4.576}\frac{1}{T} + K \tag{4}$$

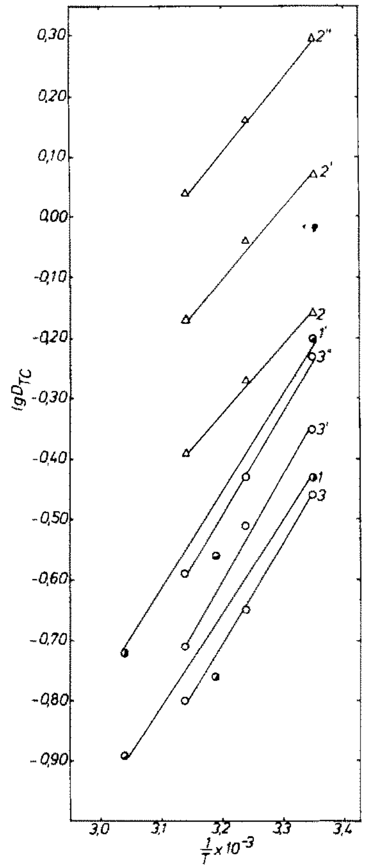

Fig. 1. Graphical presentation of the linear relationship log D vs. T: (●) TTC–ReO_4^-–$CHCl_3$–H_2O, C_{TTC} (mol l^{-1}) = 1×10^{-4}, $C_{ReO_4^-}$ (mol l^{-1}) = 3.22×10^{-5} (1), 5.37×10^{-5} (1′); 4 (△) INT–ReO_4^-–$CHCl_3$–H_2O, C_{INT} (mol l^{-1}) = 2×10^{-4}, $C_{ReO_4^-}$ (mol l^{-1}) = 2.14×10^{-5} (2), 3.00×10^{-5} (2′), 3.86×10^{-5} (2″), (○) p-NTC–ReO_4^-–$CHCl_3$–H_2O, $C_{p\text{-NTC}}$ (mol l^{-1}) = 2×10^{-4}, $C_{ReO_4^-}$ (mol l^{-1}) = 2.14×10^{-5} (3), 3.00×10^{-5} (3′), 3.86×10^{-5} (3″).

In this straight-line equation, the term $-\Delta H/4.576$ represents the slope of the straight line and can be presented as:

$$\tan\alpha = -\frac{\Delta H}{4.576} \qquad (5)$$

The graphical relationship (Figs. 1 and 2) is used for the determination of $\tan\alpha$ and by applying eqn. (5) the enthalpy (ΔH) of the system ReO_4^-–tetrazolium salt–$CHCl_3$–water can be easily calculated.

The enthalpy can be evaluated much more accurately by using the least-squares method for calculation of the coefficient $-\Delta H/4.576$.

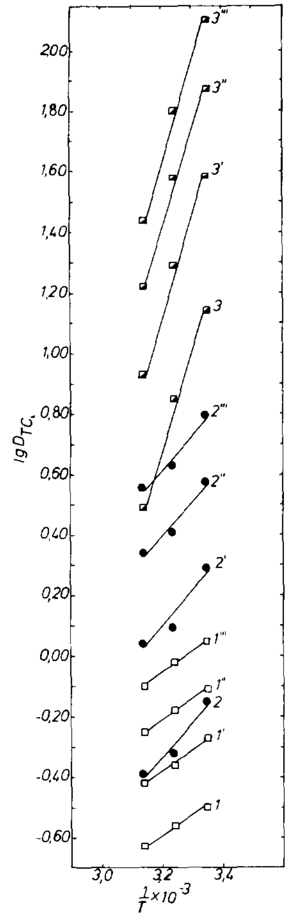

Fig. 2. Graphical presentation of the linear relationship log D vs. T: (□) MTT-ReO_4^--$CHCl_3$-H_2O, C_{MTT} (mol l^{-1}) = 4×10^{-4}, $C_{ReO_4^-}$ (mol l^{-1}) = 0.40×10^{-5} (1), 1.28×10^{-5} (1′), 2.14×10^{-5} (1″), 3.00×10^{-5} (1‴); (●) NTC-ReO_4^--$CHCl_3$-H_2O, C_{NTC} (mol l^{-1}) = 2×10^{-4}, $C_{ReO_4^-}$ (mol l^{-1}) = 1.28×10^{-5} (2), 2.14×10^{-5} (2′), 3.00×10^{-5} (2″), 3.86×10^{-5} (2‴); (◩) NBT-ReO_4^--$CHCl_3$-H_2O, C_{NBT} (mol l^{-1}) = 1×10^{-4}, $C_{ReO_4^-}$ (mol l^{-1}) = 1.28×10^{-5} (3), 2.14×10^{-5} (3′), 3.00×10^{-5} (3″), 3.86×10^{-5} (3‴).

Equation (6) provides the relationship between the isobaric–isothermic potential (ΔG) of the extraction system and the equilibrium constant (K_{ex}):

$$\Delta G = -RT \ln K_{ex} \tag{6}$$

The K_{ex} values determined at each temperature, obtained from the experimental data for D, were used for the evaluation of ΔG according to eqn. (6).

In a way similar to the linear relationship log $D = f(1/T)$, we can present the equation log $K_{ex} = f(1/T)$ (Fig. 3).

TABLE 1

Results from the evaluation of the thermodynamic constants ΔH, ΔG and ΔS of the extraction system ReO_4^- –tetrazolium salt–$CHCl_3$–H_2O, processed at a statistical certainty of 95%

	$C_{ReO_4^-}$ $\times 10^{-5}$	ΔH (kJ mol^{-1} l^{-1})		t (°C)	K_{ex}	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
		tan α	Least-squares method				
TTC	3.22	-24.85 ± 5.75	-24.85 ± 5.75	25	$(1.15 \pm 0.68) \times 10^4$	-23.13 ± 1.59	-6.37 ± 2.53
	5.37			40	$(0.52 \pm 0.06) \times 10^4$	-21.92 ± 0.31	-9.17 ± 1.33
				55	$(0.38 \pm 0.03) \times 10^4$	-21.84 ± 0.72	-7.49 ± 1.62
p-NTC	2.14	-33.22 ± 0.22	-32.51 ± 2.91	25	$(3.13 \pm 0.24) \times 10^3$	-19.95 ± 0.19	-42.13 ± 2.11
	3.00			35	$(2.11 \pm 0.34) \times 10^3$	-19.60 ± 0.40	-41.89 ± 2.10
	3.86			45	$(1.36 \pm 0.14) \times 10^3$	-19.08 ± 0.27	-42.20 ± 1.99
MTT	0.40	-13.02 ± 1.39	-13.75 ± 1.26	25	$(9.47 \pm 0.31) \times 10^3$	-22.17 ± 1.73	30.71 ± 1.94
	1.28			35	$(9.06 \pm 0.15) \times 10^3$	-22.45 ± 0.16	30.60 ± 1.57
	2.14			45	$(8.64 \pm 0.25) \times 10^3$	-22.73 ± 0.29	30.39 ± 1.61
	3.00						
INT	2.14	-21.76 ± 1.64	-21.12 ± 2.69	25	$(7.22 \pm 1.56) \times 10^3$	-21.95 ± 1.09	3.26 ± 1.92
	3.00			35	$(5.68 \pm 2.26) \times 10^3$	-22.09 ± 1.02	3.15 ± 2.14
	3.86			45	$(4.43 \pm 1.44) \times 10^3$	-22.17 ± 0.82	3.31 ± 2.53
NTC	1.28	-24.73 ± 7.17	-24.63 ± 6.38	25	$(1.70 \pm 0.37) \times 10^8$	-46.97 ± 0.68	74.93 ± 8.81
	2.14			35	$(1.16 \pm 0.72) \times 10^8$	-47.97 ± 1.37	74.32 ± 8.57
	3.00			45	$(0.98 \pm 0.07) \times 10^8$	-48.62 ± 0.36	75.46 ± 8.23
	3.86						
NBT	1.28	-61.12 ± 3.71	-59.12 ± 0.08	25	$(3.34 \pm 0.80) \times 10^9$	-54.35 ± 0.60	-15.95 ± 0.43
	2.14			35	$(1.72 \pm 0.40) \times 10^9$	-54.45 ± 0.68	-15.43 ± 0.51
	3.00			45	$(0.77 \pm 0.49) \times 10^9$	-54.04 ± 1.85	-15.93 ± 1.25
	3.86						

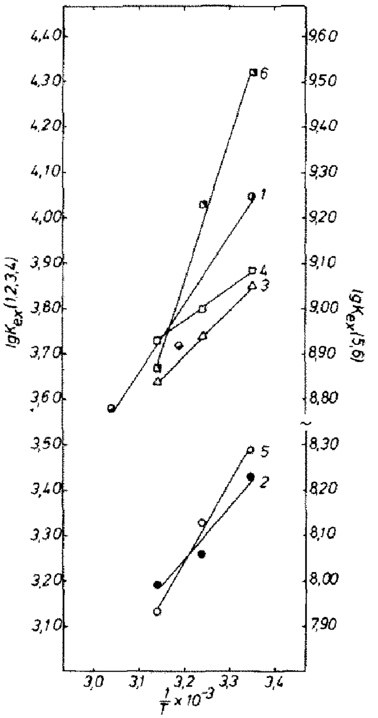

Fig. 3. Graphical expression of the linear relationship log K_{ex} vs. T: (1) TTC-ReO_4^--$CHCl_3$-H_2O; (2) p-NTC-ReO_4^--$CHCl_3$-H_2O; (3) INT-ReO_4^--$CHCl_3$-H_2O; (4) MTT-ReO_4^--$CHCl_3$-H_2O; (5) NTC-ReO_4^--$CHCl_3$-H_2O; (6) NBT-ReO_4^--$CHCl_3$-H_2O.

From the ΔH values for each extraction system and the ΔG figures of these systems at each temperature, ΔS is calculated using the equation [6]:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7}$$

The results of the calculations for the system ReO_4^--tetrazolium salt-$CHCl_3$-H_2O using six tetrazolium salts are presented in Table 1.

CONCLUSION

By the above-described sequence of investigations, representing a logical combination of well-known relationships, the thermodynamic magnitudes ΔH, ΔG and ΔS are determined. These parameters characterize the extraction systems ReO_4^--tetrazolium salt-$CHCl_3$-H_2O as reliable media both for analytical and other applications related to the extraction of ReO_4^- with tetrazolium salts.

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