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CALORIMETRIC STUDY OF COMPLEX FORMATION DIBENZO-24-CROWN-8 WITH SALTS OF ALKALI AND ALKALINE-EARTH METALS.

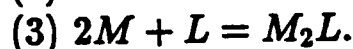
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Stoichiometry of complex, values of the enthalpy and the entropy changes for the interaction of 2,3,14,15-dibenzo-24-crown-8 with alkali and alkaline-earth metal thiocyanates in acetonitrile were determined by a calorimetric titration technique at 298K. The stability constants, the enthalpies ΔH , the entropies ΔS for detected 1:1, 2:1, and 1:2 (M:L) complexes were determined from the calorimetric data by using a nonlinear least squares curve fitting procedure. The binding sequence, based on the value of $\log K$ 1:1 at 298 K, is found to be $Ba^{2+} > Sr^{2+} > Ca^{2+} > NH_4^+ \approx Na^+ \approx K^+ > Li^+ > Mg^{2+}$. Influence of cationic parameters upon complexation properties is discussed.

Salt	Reaction	$lg\beta$	ΔH kJ/mol	ΔS J/mol K	$-\Delta H$ RTln10	ΔS Rln10
$LiClO_4$	1	1.72	-20.8	-37.0	3.65	-1.93
	3	2.83	35.2	172.4	-6.18	9.01
$NaNCS$	1	3.71	-22.0	-2.7	3.85	-0.14
	3	5.00	-14.6	46.5	2.57	2.43
$KNCS$	1	3.68	-20.7	0.9	3.63	0.05
NH_4NCS	1	3.73	-20.5	2.6	3.59	0.14
	2	5.89	-18.2	51.9	3.18	2.71
$Mg(NCS)_2^*)$	-	-	-	-	-	-
$Ca(NCS)_2$	1	4.15	-22.5	4.2	3.93	0.22
$Sr(NCS)_2$	1	4.21	-32.6	-28.6	5.71	-1.49
$Ba(NCS)_2$	1	5.35	-42.2	-39.1	7.39	-2.04

Reactions:



*) Complexation was not detected.