Thermodynamics of Solvent Extraction of Metal Picrates with Crown Ethers: Enthalpy–Entropy Compensation. Part 2.[1] Sandwiching 1 : 2 Complexation

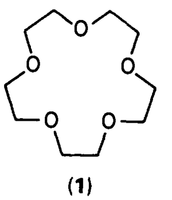
Yu Liu and Lin-Hui Tong
Lanzhou Institute of Chemical Physics, Academia Sinica, Lanzhou, Gansu, China
Yoshihisa Inoue* and Tadao Hakushi
Basic Research Laboratory and Department of Applied Chemistry, Himeji Institute of Technology, 2167 Shosha, Himeji, Hyogo 671-22, Japan

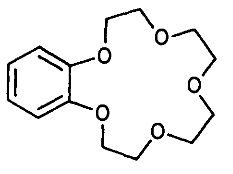
Thermodynamics of sandwich complexation in solvent extractions were investigated for the first time. Quantitative solvent extractions over a wide range of ligand concentration in the water–dichloromethane system at 10–25 °C gave the overall and stepwise extraction equilibrium constants and the thermodynamic quantities for both 1 : 1 and 1 : 2 complexations of some alkali, alkaline earth, and/or heavy metal picrates with 15-crown-5 (**1**), benzo-15-crown-5 (**2**), and *cis*-cyclohexano-15-crown-5 (**3**). The overall sandwich complexation process was deemed as being composed of the first stoicheiometric and the subsequent sandwiching complexation equilibrium. The feasibility of the second, sandwiching complexation in the solvent extraction and in the homogeneous solutions is discussed. Global treatments of the thermodynamic parameters obtained in the solvent extraction and of those reported in the homogeneous phase led to a comparable linear relationship between the enthalpy and entropy changes of complexation. The large slope (α) of the ΔH° *vs.* $T\Delta S^\circ$ plot indicates the substantial conformational change of not only the second but also of the originally ligating crown ether molecule upon the second, sandwiching complexation.

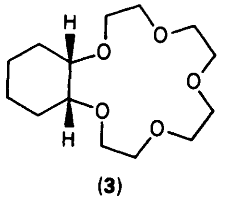
Cations larger in size than the crown ether's cavity have been known to form 1:2 cation:ligand 'sandwich'[2] complexes in the crystalline state[2–5] and in the solution phase as well.[6–11] Calorimetric titration studies have been performed with various combinations of cation and ligand to afford the thermodynamic parameters for the sandwich complexation in homogeneous solutions.[12–31] In contrast, no comparable effort has been devoted to solvent extraction at all, and the thermodynamics of sandwich complexation upon solvent extraction have been left unexplored. In the present paper we report the results of our quantitative solvent extraction study on the sandwich complexation in water–dichloromethane system at 10–25 °C, which affords the thermodynamic parameters for both 1:1 and 1:2 complexations of K^+, Rb^+, Cs^+, Tl^+, Sr^{2+}, and/or Ba^{2+} picrates with 15-crown-5 (**1**), benzo-15-crown-5 (**2**), and *cis*-cyclohexano-15-crown-5 (**3**). The thermodynamic parameters obtained are discussed in terms of the enthalpy–entropy compensation effect, which has been demonstrated to be useful for a more general and profound understanding of the complexation phenomena between cation and ligand in homogeneous phases.[32–34]

Experimental

The sources and syntheses of the materials used and the procedures and conditions of solvent extraction were fundamentally identical to those described in the preceding paper.[1] The only exception was the ligand concentrations in dichloromethane. With fixed concentrations of aqueous metal picrates (3 mmol dm^{-3}),[1] much wider ranges of ligand concentrations were employed in search of the possible 1:2 sandwich complexation; 0.3–66 mmol dm^{-3} for 15-crown-5 (**1**); 0.5–70 mmol dm^{-3} for benzo-15-crown-5 (**2**); 0.08–40 mmol dm^{-3} for *cis*-cyclohexano-15-crown-5 (**3**). Under these extraction conditions, the observed percentage extractability spanned the range 0.4–90% depending upon the properties of the ligand and the cation examined.


(**1**)


(**2**)


(**3**)

The standard continuous-variation method[35] was utilized in the solvent extraction of aqueous sodium and potassium picrates with benzo-15-crown-5 in dichloromethane to determine the cation:ligand stoicheiometry of complexation.[7,35] In a typical run, the initial concentration of a metal picrate (MA) in the aqueous phase, $[M^+]_i + [A^-]_i$, was varied continuously from 0 to 10 mmol dm^{-3}, while the total concentration of metal picrate in the aqueous phase (10 ml) and ligand (L) in the organic phase (10 ml), $[M^+]_i + [A^-]_i + [L]_i$ was kept constant at 10 mmol dm^{-3}; thus the mole fraction $([M^+]_i + [A^-]_i)/([M^+]_i + [A^-]_i + [L]_i)$ varies from zero to unity. After equilibration at 25 °C with each aqueous solution and the subsequent phase separation, an aliquot from each organic layer was diluted with a fixed amount of dichloromethane–acetonitrile (1:1) mixture to an appropriate concentration to fit into the measuring range of the spectrometer (absorbance <2.0).

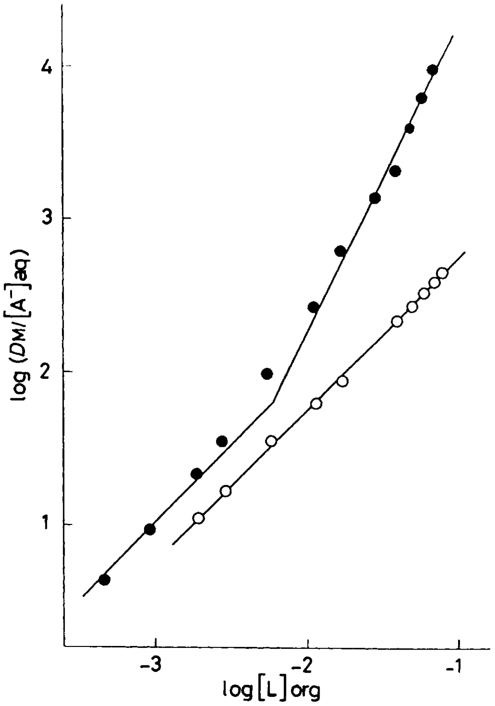


Figure 1. Typical plots of log $(D_M/[A^-]_{aq})$ *versus* log $[L]_{org}$ in solvent extration of aqueous sodium (○) and potassium (●) picrates (3 mmol dm^{-1}) with benzo-15-crown-5 (**2**) in dichloromethane at 25 °C, assuming stoicheiometric 1:1 complexation.

Results and Discussion

Extraction Equilibrium.—Assuming that only one species was extracted at any one time, the overall extraction equilibrium between an aqueous (aq) phase containing mono- or di-valent metal picrate (MA_m, $m = 1$ or 2) and an organic (org) phase containing ligand (L) is expressed by equation (1), where n denotes the ligand:cation ratio ($n = 1$ or 2).

$$M^{m+}{}_{aq} + mA^-{}_{aq} + nL_{org} \rightleftharpoons [ML_nA_m]_{org} \qquad (1)$$

The overall extraction equilibrium constants (β_1 and β_2) for the 1:1 and 1:2 cation:ligand complexation are given by equation (2).

$$\beta_n = \frac{D_M}{[A^-]_{aq}{}^m[L]_{org}{}^n} \qquad (2)$$

The distribution coefficient of metal ion (D_M) and the concentration of free ligand in the organic phase ($[L]_{org}$) after the equilibrium is established are calculated by equations (3) and (4) where $[L]_i$ represents the initial concentration of ligand

$$D_M = [ML_nA_m]_{org}/[M^{m+}]_{aq} \qquad (3)$$

$$[L]_{org} = ([L]_i - n[ML_nA_m]_{org})/(1 + K_d) \qquad (4)$$

dissolved in the organic phase, and K_d the distribution coefficient of ligand between the aqueous and organic phases ($K_d = [L]_{aq}/[L]_{org}$), which was determined in the preceding paper.[1] Modification of equation (2) led to equation (5).

$$\log (D_M/[A^-]_{aq}{}^m) = n\log [L]_{org} + \log K_{ex} \qquad (5)$$

Thus a plot of $\log(D_M/[A^-]_{aq}{}^m)$ as a function of log $[L]_{org}$ gives a straight line of slope n determined by the complex stoicheiometry, while the overall extraction equilibrium constant β_n is given from the intercept.

During our search for sandwich complexation, the quantitative solvent extraction experiments with aqueous alkali, alkaline earth, and heavy metal picrates were carried out up to very high ligand concentrations, which afforded 80–90% extraction in extreme cases. A set of extraction data obtained for each cation–ligand combination was analysed according to equation (5), first assuming the stoicheiometric 1:1 complex. As can be seen from the typical plots for benzo-15-crown-5 (**2**) in Figure 1, extraction of sodium picrate gives an excellent straight line of unit slope from low (2 mmol dm^{-3}) to very high (80 mmol dm^{-3}) ligand concentrations. On the other hand, the plot for potassium picrate is fitted to a bent line of two components, one of which is of unit slope at low concentrations and the other is of a slope of *ca.* 2 at high concentrations; a slope of exactly 2 was obtained when the horizontal axis, log $[L]_{org}$, was calibrated according to equation (4), assuming 1:2 stoicheiometry ($n = 2$). It was then deduced that the stoicheiometric 1:1 comples prevails at low ligand concentrations, *i.e.* log $[L]_{org} < -2.7$, and the 1:2 sandwich complex is predominantly formed at high concentrations, *i.e.* log $[L]_{org} > -2.2$, while there appears to be a mixed region in between. This sequence coincides with the stepwise sandwich complexation mechanism described below.

Similar examinations with the other cation–ligand combinations revealed that the following combinations afforded 1:2 sandwich complexes at high ligand concentrations under the conditions employed in the present study:[*]

15-Crown-5 (**1**): K^+, Rb^+, Cs^+, Tl^+, Sr^{2+}, Ba^{2+}
Benzo-15-crown-5 (**2**): K^+, Rb^+, Cs^+, Tl^+, Ba^{2+}
Cyclohexano-15-crown-5 (**3**):[*] K^+, Rb^+

The experiments were performed at 10, 15, 20, and 25 °C and the β_1- and β_2-values obtained at every temperature are listed in Table 1.

Continuous Variation.—In order to obtain definitive evidence for the sandwich complex formation at high ligand concentrations, the continuous-variation method, originally developed for the homogeneous-phase complexation,[36] was applied to the solvent extraction of sodium and potassium picrates with benzo-15-crown-5 (**2**). The total concentration was fixed at 10 mmol dm^{-1}, where the sandwich complex is the major extracted species as deduced from the quantitative extraction experiment shown in Figure 1. In Figure 2, the amount of the extracted picrate, as indicated by the absorbance, was plotted as a function of the initial mole fraction of aqueous picrate. Sodium picrate shows the peak intensity at *ca.* 0.67 as expected for the conventional 1:1 stoicheiometry, whereas potassium picrate gives the peak at 0.5. This result unequivocally confirms the 1:2 sandwich complex formation between potassium picrate and benzo-15-crown-5.

Sandwiching Complexation.—Only the overall extraction equilibrium constants β_1 and β_2 are experimentally measurable in the solvent extraction. Since the sandwich complex formation is obviously a stepwise process, equation (1) must be composed of two successive equilibria (1a) and (1b), where $K_1 = \beta_1$. Thus

$$M^{m+}{}_{aq} + mA^-{}_{aq} + L_{org} \overset{K_1}{\rightleftharpoons} [MLA_m]_{org} \qquad (1a)$$

$$[MLA_m]_{org} + L_{org} \overset{K_2}{\rightleftharpoons} [ML_2A_m]_{org} \qquad (1b)$$

---

[*] Owing to the limited sample availability of ligand (**3**), no survey for sandwich complexation was made with Na^+, Cs^+, Ag^+, Tl^+, Sr^{2+}, or Ba^{2+} picrate at high ligand concentrations. For the ligands (**1**) and (**2**), the survey was made with Na^+–Cs^+, Ag^+, Tl^+, and Ca^{2+}–Ba^{2+} at high ligand concentrations.

Table 1. Overall extraction equilibrium constants β_1 and β_2 for 1:1 and 1:2 cation:ligand complex stoicheiometries and the second-step equilibrium constants K_2, or β_2/β_1, for sandwiching complexation in solvent extraction of aqueous metal picrates with 15-crown-5, benzo-15-crown-5, and *cis*-cyclohexano-15-crown-5 in dichloromethane.

Ligand	Cation	Complex stoicheiometry (*n*)	log β 25 °C	 20 °C	 15 °C	 10 °C
15-Crown-5 (**1**)	K^+	1	4.33	4.45	4.59	4.73
		2	7.31	7.49	7.72	8.05
		K_2	2.98	3.04	3.13	3.32
	Rb^+	1	4.14	4.25	4.40	4.55
		2	6.86	7.10	7.39	7.63
		K_2	2.72	2.85	2.99	3.08
	Cs^+	1	3.67	3.83	3.93	4.06
		2	5.66	5.89	6.10	6.38
		K_2	1.99	2.06	2.17	2.32
	Tl^+	1	5.08	5.21	5.39	5.57
		2	7.59	7.83	8.16	8.34
		K_2	2.51	2.62	2.77	2.77
	Sr^{2+}	1	6.06	6.24	6.49	6.68
		2	8.04	8.35	8.62	9.02
		K_2	1.98	2.11	2.13	2.34
	Ba^{2+}	1	6.72	6.90	7.16	7.43
		2	9.49	9.94	10.60	10.84
		K_2	2.77	3.04	3.44	3.41
Benzo-15-crown-5 (**2**)	K^+	1	3.99	4.09	4.21	4.37
		2	6.34	6.84	7.13	7.41
		K_2	2.35	2.75	2.92	3.04
	Rb^+	1	3.70	3.77	3.89	4.03
		2	5.74	6.09	6.37	6.74
		K_2	2.04	2.32	2.48	2.71
	Cs^+	1	3.31	3.43	3.52	3.60
		2	4.79	5.03	5.17	5.38
		K_2	1.48	1.60	1.65	1.78
	Tl^+	1	4.30	4.39	4.56	4.72
		2	6.57	6.95	7.25	7.65
		K_2	2.27	2.56	2.69	2.93
	Ba^{2+}	1	5.62	5.70	5.83	5.99
		2	7.43	7.69	8.10	8.32
		K_2	1.81	1.99	2.27	2.33
Cyclohexano-15-crown-5 (**3**)	K^+	1	4.23	4.38	4.49	4.59
		2	6.67	6.88	7.04	7.29
		K_2	2.44	2.50	2.55	2.70
	Rb^+	1	4.16	4.30	4.40	4.50
		2	6.68	6.90	7.13	7.38
		K_2	2.52	2.60	2.73	2.88

the equilibrium constant K_2 for the second, sandwiching complexation process (1b) is given as a quotient, β_2/β_1; the K_2-values thus obtained are listed in Table 1. The equilibrium constants K_1 and K_2 for alkali metals are plotted against the ionic diameter in Figure 3. The relative cation selectivities observed in K_1 and K_2 apparently resemble with each other for these three crown ethers. However, close examination reveals that the selectivity in K_2 is greater than that in K_1, as indicated by the steeper plots for K_2 in Figure 3. We conclude, therefore, that the second, sandwiching complexation process discriminates the size of accommodating cation more rigorously than does the first step. This is somewhat unexpected, since, in the homogeneous-phase complexation with 15-crown-5 and benzo-15-crown-5, the alkali, and some alkaline earth, metals afford analogous log K_2-values of 2.5–2.7,[20] although fairly deviant K_2-values have also been reported for K^+–15-crown-5 by other groups.[21,22]

The feasibility of sandwiching complexation [equation (1b)] relative to stoicheiometric complexation [equation (1a)] may be evaluated by the relative equilibrium constant K_2/K_1. The K_2/K_1-values calculated from the data in Table 1 are listed in Table 2, along with the corresponding values reported for the

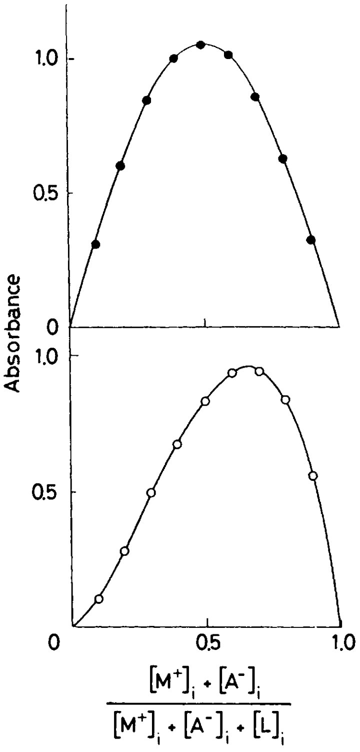


Figure 2. Continuous-variation method applied to solvent extraction of aqueous sodium (○) and potassium (●) picrates with benzo-15-crown-5 (**2**) in dichloromethane at 25 °C; absorbance in arbitrary units of picrate extracted into organic phase is plotted as a function of ($[M]_i$ + $[A^-]_i$)/($[M^+]_i$ + $[A^-]_i$ + $[L]_i$).

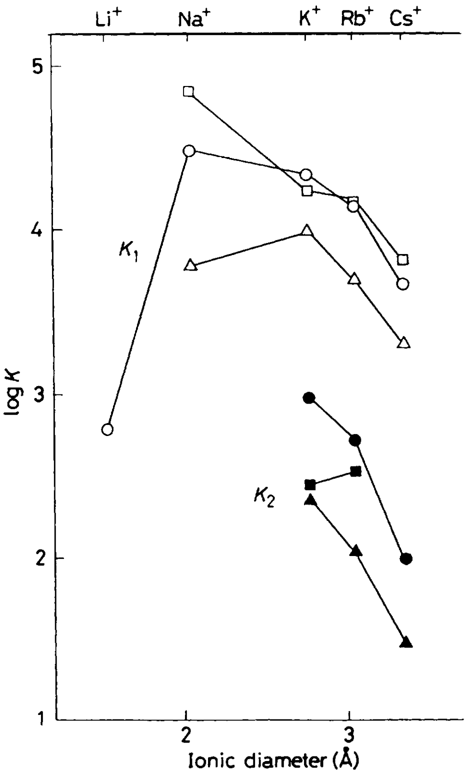


Figure 3. Stepwise extraction equilibrium constants K_1 (open symbols) and K_2 (closed symbols) for solvent extraction of aqueous alkali picrates with 15-crown-5 (circle), benzo-15-crown-5 (triangle), and cyclohexano-15-crown-5 (square) in dichloromethane.

Table 2. Feasibility of sandwiching complexation as measured by K_2/K_1 in solvent extraction [a] and by K_2'/K_1' in homogeneous solution [b] at 25 °C.

Ligand	Cation	K_2/K_1 (water–CH_2Cl_2 [a])	K_2'/K_1' (MeOH [b])
15-Crown-5 (**1**)	K^+	0.045	0.042
	Rb^+	0.038	0.028
	Cs^+	0.021	0.089
	Tl^+	0.0027	*c*
	Sr^{2+}	0.000 08	0.27
	Ba^{2+}	0.000 11	0.033
Benzo-15-crown-5 (**2**)	K^+	0.023	0.044
	Rb^+	0.022	0.039
	Cs^+	0.015	0.15
	Tl^+	0.0093	*c*
	Sr^{2+}	*d*	0.41
	Ba^{2+}	0.000 15	0.098
Cyclohexano-15-crown-5 (**3**)	K^+	0.016	0.020
	Rb^+	0.023	*c*
	Cs^+	*e*	0.13

[a] This work. [b] Ref. 20 [for ligands (**1**) and (**2**)] and ref. 6 [for ligand (**3**)]. [c] Not reported. [d] Sandwich complex not formed under the conditions employed. [e] Not determined.

Table 3. Thermodynamic parameters at 25 °C (in kcal mol^{-1} [a]) for sandwiching 1:2 complexation in solvent extraction of aqueous metal picrates with 15-crown-5, benzo-15-crown-5, and *cis*-cyclohexano-15-crown-5 ethers in dichloromethane.

Ligand	Cation	$-\Delta G°$	$-\Delta H°$	$-T\Delta S°$
15-Crown-5 (**1**)	K^+	4.0	8.6	4.6
	Rb^+	3.71	9.96	6.25
	Cs^+	2.72	7.65	4.93
	Tl^+	3.4	7.1	3.7
	Sr^{2+}	2.7	8.5	5.8
	Ba^{2+}	3.8	17.8	14.0
Benzo-15-crown-5 (**2**)	K^+	3.3	17.2	13.9
	Rb^+	2.82	16.75	13.93
	Cs^+	2.0	7.3	5.3
	Tl^+	3.2	16.3	13.1
	Ba^{2+}	2.5	14.2	11.7
Cyclohexano-15-crown-5 (**3**)	K^+	3.31	6.44	3.13
	Rb^+	3.42	9.36	5.94

[a] 1 cal = 4.184 J.

homogeneous-phase sandwich complexation.[6,20] We note that the K_2/K_1-values possess distinctly different dimensions in the solvent extraction equilibrium and in the homogeneous-phase equilibrium, and should not be compared directly. The sandwich complexation equilibria in the homogeneous solution are written as equations (1a′) and (1b′). Then K_2'/K_1' =

$$M^{m+} + L \xrightleftharpoons{K_1'} ML^{m+} \qquad (1a')$$

$$ML^{m+} + L \xrightleftharpoons{K_2'} ML_2{}^{m+} \qquad (1b')$$

$([M^{m+}][ML_2{}^{m+}])/[ML^{m+}]^2$ in the homogeneous solution, whereas $K_2/K_1 = ([M^{m+}]_{aq}[A^-]_{aq}{}^m[ML_2A_m]_{org})/[MLA_m]_{org}{}^2$ in the solvent extraction.

By definition, the relative equilibrium constants K_2/K_1 and K_2'/K_1' are related formally to the following equilibria in the solvent extraction [equation (6)] and in the homogeneous solution [equation (6′)], respectively.

$$2[MLA_m]_{org} \rightleftharpoons M^{m+}{}_{aq} + mA^-{}_{aq} + [ML_2A_m]_{org} \qquad (6)$$

$$2ML^{m+} \rightleftharpoons M^{m+} + ML_2{}^{m+} \qquad (6')$$

As can be seen from Table 2, both K_2/K_1- and K_2'/K_1'-values are critical functions of the diameter and charge of the cation sandwiched; again, the different dimension applied is responsible for the much smaller K_2/K_1-values in the solvent extraction of divalent alkaline earths. The profiles of the change in K_2/K_1 and K_2'/K_1' differ considerably. For the sandwich complexation of alkali metals by the ligands (**1**) and (**2**), the K_2/K_1-value decreases with increasing cation diameter, while the K_2'/K_1'-value, though it fluctuates, appears to increase with the cation diameter. The tendency for the alkaline earths, in spite of the limited data available, also seems reversed.

The primary difference between solvent extraction and homogeneous-phase complexation is the constituent of the complexed species, *i.e.* contact ion-pair complexes, MLA_m and ML_2A_m, *versus* dissociated ion complex, ML^{m+} and $ML_2{}^{m+}$. It is inferred that the presence of a contacting counteranion in the primary complex MLA_m interferes with their further association [equation (6)] to form sandwich complex ML_2A_m, the influence of which may be greater for the larger cations, which originally interact more weakly, as compared with smaller cations. In the same context, the above mentioned higher cation selectivity in K_2 than in K_2', and probably K_1, may also be rationalized in terms of the difference in the complexed species involved. Since the sandwiching complexation [equation (1b)] in solvent extraction inevitably involves transformation of the tight contact ion-pair complex MLA_m to the loosely bound ligand-separated ion-pair complex ML_2A_m against the electrostatic interaction between M^+ and A^-, the originally less favoured larger cations must be still less efficient in forming the separated ion-pair complex ML_2A_m, while the dissociated ion complex ML^{m+}, free from the electrostatic interaction with A^-, will form the sandwich complex $ML_2{}^{m+}$ with lower cation selectivity.

Thermodynamics.—The free-energy change ($\Delta G°$) for the sandwiching process [equation (1b)] is calculated from the equilibrium constant K_2 by equation (7) and is related to the

$$\Delta G° = -RT \ln K_2 \qquad (7)$$

enthalpy and entropy changes ($\Delta H°$ and $\Delta S°$) through the Gibbs–Helmholtz equation (8).

$$\Delta G° = \Delta H° - T\Delta S° \qquad (8)$$

Combining equations (7) and (8), we obtain equation (9) which describes the temperature dependence of K_2.

$$\log K_2 = (1/2.303R)(\Delta S° - \Delta H°/T) \qquad (9)$$

Plots of the log K_2-value, shown in Table 1, as a function of the inverse temperature gave good straight lines. The thermodynamic parameters obtained for each crown ether are listed in Table 3, and the corresponding data in the homogeneous solutions in Table 4. In spite of the apparently different species involved in equations (1b) and (1b′), the enthalpy and entropy changes of sandwich complexation are in fair agreement and show similar trends for the solvent extraction and the homogeneous-phase complexation of the alkali metals in particular. This may be taken as being natural in the sense that the equilibria (1b) and (1b′) are both attained in the homogeneous phase of dichloromethane or methanol.

Enthalpy–Entropy Compensation.—Before discussing enthalpy–entropy relationships in the solvent-extraction thermodynamics, we should first examine the data treatment in our previous paper.[33] We formerly gathered the reported thermodynamic parameters associated with the overall stability

Table 4. Reported thermodynamic parameters at 25 °C (kcal mol^{-1}) for sandwiching 1:2 complexation of various cations with crown ethers in homogeneous solutions.

Ligand	Solvent	Cation	$-\Delta G°$	$-\Delta H°$	$T\Delta S°$	Ref.
12-Crown-4	MeOH	Na^{+}	3.11	6.70	−3.60	*a*
		Na^{+}	2.73	7.52	−4.93	*b*
		K^{+}	1.84	1.84	0.26	*b*
		Ag^{+}	2.59	6.66	−4.08	*b*
		Ba^{2+}	3.25	1.36	1.86	*c*
		Pb^{2+}	2.88	2.29	0.57	*d*
	Propylene carbonate	K^{+}	3.62	2.08	1.53	*e*
	MeNO$_2$	Li^{+}	2.16	4.60	−2.44	*f*
	MeCN	H^{+}	2.87	5.26	−2.41	*g*
	MeCN	K^{+}	3.12	3.47	−0.36	*e*
Thia-12-crown-4	MeOH–water (7:3)	Ag^{+}	5.02	10.54	−5.52	*h*
1,7-Dithia-12-crown-4	MeOH	Ba^{2+}	2.43	1.20	1.22	*c*
15-Crown-5 (**1**)	MeOH	Na^{+}	3.78	2.32	1.43	*i*
		K^{+}	3.62	8.80	−5.20	*j, k*
		K^{+}	4.04	8.40	−5.00	*j, l*
		K^{+}	3.38	10.83	−7.48	*i*
		K^{+}	3.70	8.10	−4.40	*m*
		Rb^{+}	3.37	10.52	−7.13	*i*
		Cs^{+}	3.45	5.11	−1.71	*i*
		Ag^{+}	4.19	1.72	2.42	*n*
		Ca^{2+}	2.90	−4.80	7.00	*j, k*
		Ca^{2+}	2.30	−0.90	3.00	*j, l*
		St^{2+}	3.59	5.40	−1.50	*i*
		Ba^{2+}	3.56	9.27	−5.70	*i*
		Pb^{2+}	2.73	5.04	−2.31	*o*
	Propylene carbonate	K^{+}	5.16	7.29	−2.15	*e*
	MeCN	H^{+}	4.87	4.51	0.33	*g*
		K^{+}	3.75	7.19	−3.47	*e*
Benzo-15-crown-5 (**2**)	MeOH–water (8:2)	K^{+}	4.42	12.66	−8.24	*p*
	MeOH	Na^{+}	3.30	0.00	3.28	*i*
		K^{+}	3.51	10.40	−6.91	*i*
		Rb^{+}	3.49	9.85	−6.41	*i*
		Cs^{+}	3.66	3.63	0.00	*i*
		Sr^{2+}	3.45	4.49	−1.07	*i*
		Ba^{2+}	3.57	4.23	−0.71	*i*
	MeCN	H^{+}	4.45	3.46	0.96	*g*
4′-Methylbenzo-15-crown-5	MeOH–water (8:2)	K^{+}	4.77	14.33	−8.83	*p*
4′-t-Butylbenzo-15-crown-5	MeOH–water (8:2)	K^{+}	4.64	4.26	1.26	*p*
4′-Nitrobenzo-15-crown-5	MeOH–water (8:2)	K^{+}	3.68	11.86	−8.16	*p*
4′-Bromobenzo-15-crown-5	MeOH–water (8:2)	K^{+}	4.25	18.99	−14.73	*p*
6-Methylbenzo-15-crown-5	MeOH	K^{+}	3.01	6.09	−3.08	*q*
Cyclohexano-15-crown-5 (**3**)	MeCN	H^{+}	5.28	3.65	1.60	*g*
	MeOH	Na^{+}	3.96	3.94	0.00	*i*
		K^{+}	3.51	8.22	−4.70	*i*
		Rb^{+}	3.49	10.97	−7.48	*i*
		Cs^{+}	3.71	4.45	−0.71	*i*
		Sr^{2+}	3.41	4.95	−1.57	*i*
		Ba^{2+}	3.55	8.25	−4.70	*i*
	Propylene carbonate	K^{+}	4.37	4.80	−0.45	*e*
	MeCN	K^{+}	3.41	3.11	0.29	*e*
Thia-15-crown-5	Water	Ag^{+}	3.34	3.47	−0.13	*h*
1,7-Diaza-15-crown-5	MeOH	Sr^{2+}	3.42	2.96	0.43	*r*
		Ba^{2+}	3.30	2.70	0.57	*r*
2-(2-Methoxybenzyl)-15-crown-5	MeOH	K^{+}	3.45	8.80	−5.40	*j, k*
		K^{+}	3.36	9.44	−6.09	j, *l*
2-(4-Methoxybenzyl)-15-crown-5	MeOH	K^{+}	3.78	7.40	−3.70	*j, k*
		Cs^{+}	3.23	−3.20	6.00	*j, k*
N-Propyl-monoaza-15-crown-5	MeOH	Na^{+}	3.80	−3.50	7.00	*j, k*
N-(3-Oxabutyl)-monoaza-15-crown-5	MeOH	Na^{+}	3.14	0.50	2.60	*j, k*
		K^{+}	2.99	0.60	2.40	*j, k*
		Ca^{2+}	3.70	−1.80	5.50	*j, k*
N-Phenyl-monoaza-15-crown-5	MeOH	Na^{+}	2.50	4.40	−1.92	*i*
		K^{+}	2.32	7.67	−5.34	*i*
		Rb^{+}	1.86	7.31	−5.49	*i*
		Sr^{2+}	3.45	4.30	−0.86	*i*
		Ba^{2+}	3.44	3.27	0.14	*i*
18-Crown-6	MeOH	Cs^{+}	5.65	1.51	4.13	*i*
		Cs^{+}	2.81	3.32	−0.51	*m*
	Pyridine	Cs^{+}	2.58	5.80	−3.19	*s*
Benzo-18-crown-6	MeOH	Cs^{+}	3.18	10.30	−7.20	*o*
Dicyclohexano-18-crown-6	MeOH	Cs^{+}	3.87	6.72	−2.85	*i*

Table 4 (*continued*)

Ligand	Solvent	Cation	$-\Delta G^\circ$	$-\Delta H^\circ$	$T\Delta S^\circ$	Ref.
Pyridino-18-crown-6	MeOH	Ag^+	3.52	2.58	−0.94	*t*, *m*
N-(3-Oxabutyl)-monoaza-18-crown-6	MeOH	Na^+	3.70	1.40	2.30	*j*, *k*
		Cs^+	2.87	0.90	1.90	*j*, k
		Ca^{2+}	4.71	−0.73	5.00	j, *k*
N-(3,6-Dioxaheptyl)-monoaza-18-crown-6	MeOH	Na^+	5.10	0.44	4.70	*j*, *k*
		Ca^{2+}	4.20	−1.10	5.30	*j*, *k*

[a] Ref. 12. [b] Ref. 13. [c] Ref. 14. [d] Ref. 15. [e] Ref. 16. [f] Ref. 17. [g] Ref. 18. [h] Ref. 19. [i] Ref. 20. [j] Ref. 21. [k] Salt solution used as titrant. [l] Ligand solution used as titrant. [m] Ref. 22. [n] Ref. 23. [o] Ref. 24. [p] Ref. 25. [q] Ref. 26. [r] Ref. 27. [s] Ref. 28. [t] Ref. 29.

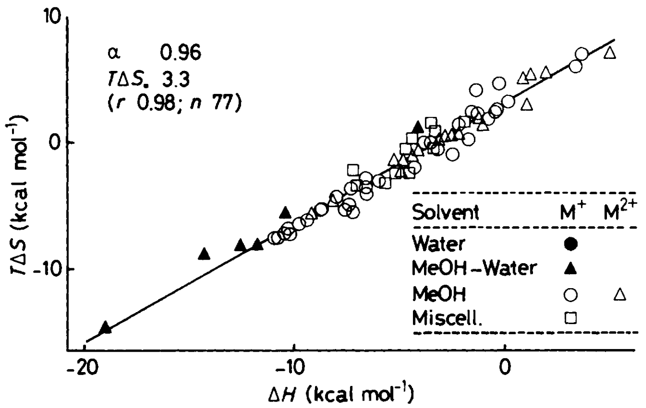


Figure 4. Enthalpy–entropy compensation plot for sandwiching 1:2 complexation of mono- and di-valent cations with various crown ethers in homogeneous solutions; see Table 4 for original data.

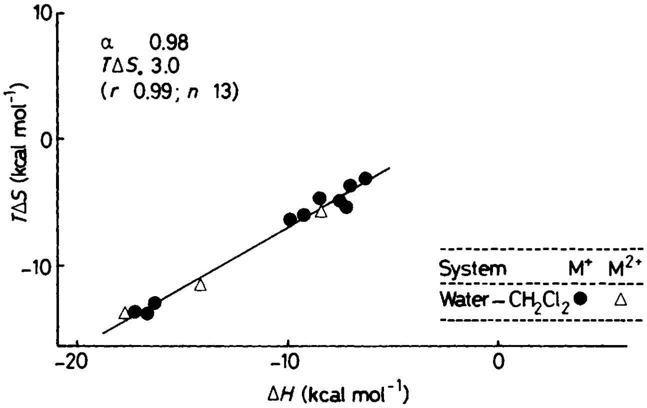


Figure 5. Enthalpy–entropy compensation plot for sandwiching 1:2 complexation in solvent extraction of aqueous metal picrates with some 15-crown-5 derivatives; see Table 5 for original data.

constant β_2 in the homogeneous solution, with which the analysis was made in terms of the enthalpy–entropy compensation effect. The analysis gave the slope and intercept not for the second, sandwiching process [equation (1b′)] but for the overall sandwich complexation; these values which, incidentally, very close to those obtained for the first stoicheiometric 1:1 complexation [equation (1a′)]. In order to discuss the very sandwiching process (1b′), we tabulated all the reported thermodynamic parameters in the homogeneous phase in Table 4, and the entropy changes are plotted against the enthalpy change to give an excellent straight line (correlation coefficient *r* 0.98), as shown in Figure 4.

Table 5. Slope (α) and intercept ($T\Delta S_0$) of $\Delta H^\circ - T\Delta S^\circ$ plots for stoicheiometric 1:1 and sandwiching 1:2 complexation with various ligands in homogeneous-phase complexation and solvent extraction.

Ligand	Complex stoicheiometry	Homogeneous phase α	Homogeneous phase $T\Delta S_0$	Solvent extraction α	Solvent extraction $T\Delta S_0$
Glyme/podand	1:1	0.86[a]	2.3[a]		
Crown ether	1:1	0.76[a]	2.4[a]	0.72[b]	2.6[b]
	1:2	0.96[c]	3.3[c]	0.98[c]	3.0[c]
Cryptand	1:1	0.51[a]	4.0[a]		
Antibiotic	1:1	0.95[a]	5.6[a]		
Bis(crown ether)s	1:1	1.03[d]	4.6[d]		

[a] Ref. 33. [b] Ref. 1. [c] This work. [d] Ref. 34.

A similar plot (Figure 5) for the thermodynamic parameters obtained in the present study (Table 3) also afforded an excellent straight line (*r* 0.99) for the sandwiching complexation in the solvent extraction, although the available size is much smaller. The slope and the intercept obtained in the homogeneous solution and in the solvent extraction are summarized in Table 5, together with those for the other ligand types and stoicheiometries.[33]

First of all, we emphasize that the solvent extraction and the homogeneous-phase complexation afford practically the same slope (α) and intercept ($T\Delta S_0$), indicating that the essential nature of the complexation equilibria (1b) and (1b′) is common in both systems, regardless of the presence/absence of the contact counteranion and of the phase difference. The individual slope and intercept values obtained also shed light on the detailed mechanism of the hitherto less understood sandwiching complexation process. According to our previous studies,[32–34] the slope (α) and the intercept ($T\Delta S_0$) function well as quantitative measures of the conformational change and the extent of desolvation of the components upon complexation, respectively. Thus the large slope near unity and the positive intrinsic entropic gain ($T\Delta S_0$) clearly indicate that the enthalpic gain from the ion–dipole interaction between the cation and the ligand's donor atoms is almost totally cancelled by the entropic loss arising from the accompanying large conformation change, but the moderate intrinsic entropic gain $T\Delta S_0$ arising from desolvation makes sandwich complexation possible even in the absence of enthalpic gain.[32] These slopes (α 0.98 or 0.96) are much larger than those for the 1:1 complexation (0.72 or 0.76) and rather comparable to those for macrocyclic antibiotics (0.95) and bis(crown ether)s (1.03). These results strongly indicate that, upon sandwiching complexation, not only does the second crown ether form a sandwich but also the originally ligating crown ether must suffer substantial conformational changes in the second complexation process (1b) or (1b′).

Acknowledgements
See corresponding section of preceding paper.

References

1 Part 1: Y. Inoue, F. Amano, N. Okada, H. Inada, M. Ouchi, A. Tai, T. Hakushi, Y. Liu, and L.-H. Tong, preceding paper.
2 C. J. Pedersen, *J. Am. Chem. Soc.*, 1970, **92**, 386.
3 P. R. Mallinson and M. R. Truter, *J. Chem. Soc., Perkin Trans., 2*, 1972, 1818.
4 N. K. Dalley, 'Synthetic Multidentate Macrocyclic Compounds,' eds. R. M. Izatt and J. J. Christensen, Academic, New York, 1978, p. 207.
5 R. Hilgenfeld and S. Saenger, 'Host Guest Complex Chemistry,' ed. F. Vögtle, Springer, Berlin, 1982, vol. 2, p. 1.
6 H. K. Frensdorff, *J. Am. Chem. Soc.*, 1971, **93**, 600.
7 K. H. Wong, M. Bourgoin, and J. Smid, *J. Chem. Soc., Chem. Commun.*, 1974, 715.
8 A. Sadakane, T. Iwachido, and K. Toei, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 60.
9 R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, and J. J. Christensen, *J. Am. Chem. Soc.*, 1976, **98**, 7626.
10 F. de Jong and D. N. Reinhoudt, 'Stability and Reactivity of Crown Ether Complexes,' Academic, London, 1981, p. 3.
11 Y. Takeda, 'Host Guest Complex Chemistry,' eds. F. Vögtle and E. Weber, Springer, Berlin, 1982, vol. 3, p. 1.
12 G. Michaux and J. Reisse, *J. Am. Chem. Soc.*, 1982, **104**, 6895.
13 H.-J. Buschmann, *J. Solution Chem.*, 1987, **16**, 181.
14 H.-J. Buschmann, *Inorg. Chim. Acta*, 1986, **125**, 31.
15 H.-J. Buschmann, *Thermochim. Acta*, 1986, **107**, 219.
16 H.-J. Buschmann, *Polyhedron*, 1988, **7**, 721.
17 A. J. Smetana and A. I. Popov, *J. Solution Chem.*, 1980, **9**, 183.
18 H.-J. Buschmann, *Inorg. Chim. Acta*, 1986, **118**, 77.
19 R. M. Izatt, R. E. Terry, L. D. Hansen, A. G. Avondet, J. S. Bradshaw, N. K. Dalley, T. E. Jensen, and J. J. Christensen, *Inorg. Chim. Acta*, 1978, **30**, 1.
20 H.-J. Buschmann, *Chem. Ber.*, 1985, **118**, 2746.
21 R. B. Davidson, R. M. Izatt, J. J. Christensen, R. A. Shultz, D. M. Dishong, and G. W. Gokel, *J. Org. Chem.*, 1984, **49**, 5080.
22 J. D. Lamb, R. M. Izatt, C. S. Swain, and J. J. Christensen, *J. Am. Chem. Soc.*, 1980, **102**, 475.
23 H.-J. Buschmann, *Chem. Ber.*, 1985, **118**, 4297.
24 R. M. Izatt, G. A. Clark, J. D. Lamb, J. E. King, and J. J. Christensen, *Thermochim. Acta*, 1986, **97**, 115.
25 Y. Liu, H. Liu, and Z. Guo, *Huawu Tangbao*, 1983, **3**, 82.
26 M.-C. Shen, Q.-H. Luo, X.-D. Feng, Q.-Y. Tu, G.-Y. Lu, and A.-B. Dai, *Chem. J. Chin. Univ.*, 1986, **7**, 1055.
27 H.-J. Buschmann, *J. Solution Chem.*, 1986, **15**, 453.
28 E. Mei, J. L. Dye, and A. I. Popov, *J. Am. Chem. Soc.*, 1977, **99**, 5308.
29 R. M. Izatt, N. E. Izatt, B. E. Rossiter, J. J. Christensen, and B. L. Haymore, *Science*, 1978, **199**, 994.
30 M. Kodama and E. Kimura, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2465.
31 R. M. Izatt, J. D. Lamb, N. E. Izatt, J. J. Christensen, Jr., B. E. Rossiter, J. J. Christensen, and B. L. Haymore, *J. Am. Chem. Soc.*, 1979, **101**, 6273.
32 Y. Inoue and T. Hakushi, *J. Chem. Soc., Perkin Trans. 2*, 1985, 935.
33 Y. Inoue, T. Hakushi, Y. Liu, L.-H. Tong, J. Hu, G.-D. Zhao, S. Huang, and B.-Z. Tian, *J. Phys. Chem.*, 1988, **92**, 2371.
34 Y. Liu, L.-H. Tong, S. Huang, B.-Z. Tian, Y. Inoue, and T. Hakushi, *J. Phys. Chem.*, 1990, **94**, 2666.
35 Y. Inoue, Y. Liu, F. Amano, M. Ouchi, A. Tai, and T. Hakushi, *J. Chem. Soc., Dalton Trans.*, 1988, 2735.
36 W. B. Guenther, 'Quantitative Chemistry—Measurement and Equilibrium,' Addison-Wesley, Reading, MA, 1968, Ch. 20.

Paper 9/05076K
Received 28*th November* 1989
Accepted 1*st February* 1990