



Gibbs Transfer Energies of Macrocyclic Ligands in Methanol+*N*-methyl-2-pyrrolidinone Mixtures by Solubility and Partition Measurements

C. KALIDAS and S. BALAJI

Department of Chemistry, Indian Institute of Technology, Chennai – 600 036, India

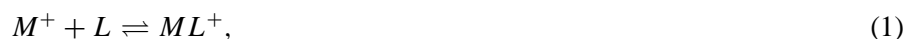
(Received: 11 January 1999; in final form: 22 April 1999)

Abstract. The standard Gibbs transfer energies of 18-crown-6, dibenzo-18-crown-6, cryptands 21, 22 and 222 from methanol to methanol + *N*-methyl-2-pyrrolidinone (NMP) mixtures were determined from solubility and partition measurements at 30 °C. While the Gibbs energy of transfer of 18-C-6 is positive, increases up to $X_{\text{NMP}} = 0.7$ and thereafter decreases, the transfer energy of dibenzo-18-C-6 is negative and decreases with the addition of NMP. However, the transfer energy of cryptand 21 becomes increasingly negative with the addition of NMP while that of cryptand 22 is positive and increases under the same conditions. For cryptand 222, the transfer energy is slightly negative up to $X_{\text{NMP}} = 0.5$ but decreases markedly at higher compositions of NMP. These results have been explained in terms of the various types of interaction between the ligand molecules, solvent components and the effect of solvent–solvent interactions on them.

Key words: Solvation, 18-crown-6, dibenzo-18-crown-6, cryptands 21, 22 and 222, methanol + *N*-methyl-2-pyrrolidinone mixtures, Gibbs transfer energies.

1. Introduction

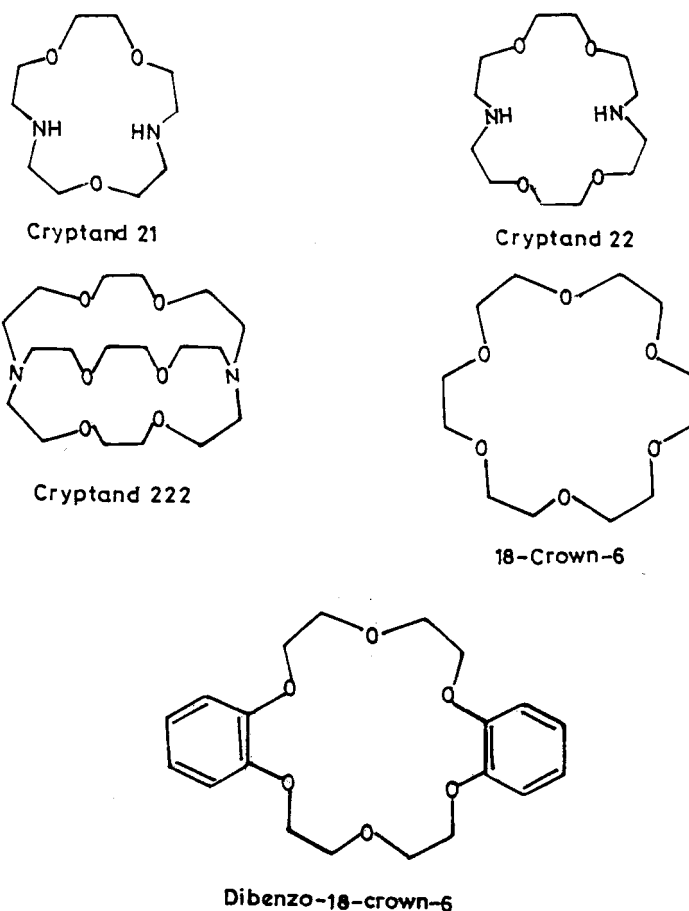
The difference in the Gibbs energies of complexation ($\Delta_C G^\circ$) for the reaction



where M^+ is a univalent metal cation and L is a macrocyclic ligand between the solvents S and R (reference solvent) is given by

$$\begin{aligned} \Delta_C G^\circ(s) - \Delta_C G^\circ_{(R)} &= 2.303RT \log \frac{K_s(R)}{K_s(S)} \\ &= \Delta_t G^\circ_{(\text{MLClO}_4)} - \Delta_t G^\circ_{(L)} - \Delta_t G^\circ_{(\text{MClO}_4)} \end{aligned} \quad (2)$$

where $\Delta_t G^\circ$ and K_s in Equation (2) refer to the standard Gibbs energy of transfer and the stability constant of reaction (1). Knowledge of the Gibbs energy of transfer data of the ligand $\Delta_t G^\circ(L)$ is necessary to understand the contribution of ligand solvation to the thermodynamics of the complexation reaction (1) and it is not subject to an extrathermodynamic assumption. Although it is possible in principle



Scheme 1.

to obtain these data via Equation (2) it is desirable [1] to determine $\Delta_r G^\circ(L)$ independently by experiment. Such data may also be used to consider the effect of the ligand [2] on the solubility of the salt in *R* and in *S* by the application of Equation (2). However, only a few reports [3] on the direct determination of transfer energies of free ligand between different solvents are available and practically no data have been reported hitherto in mixed solvents over the complete range of solvent compositions.

The present investigation therefore deals with the determination of Gibbs transfer energies of some macrocyclic ligands, viz. 18-C-6, dibenzo-18-C-6, cryptands 21, 22 and 222 (Scheme 1) in methanol + *N*-methyl-2 pyrrolidinone mixtures over the complete range of solvent compositions by solubility and partition measurements.

These protic + dipolar aprotic solvent mixtures (which are isodielectric and have a fairly high dielectric constant) [4] have recently been found [5] to be of

considerable value as media for the determination of single ion transfer energies by employing the simple complexation reaction (1) using some of the above ligands in contrast to the other involved methods used [6] for this purpose hitherto.

2. Experimental

Materials. The crown ethers 18-crown-6 (18-C-6) and dibenzo-18-crown-6 (dibenzo-18-C-6) supplied by either Fluka or Merck-Schuchardt (stated purity >99%) were used as received. Cryptands 21 (1,4,10-trioxa-7,13-diazacyclopentadecan), 22 (1,7,10,16-tetraoxa-4,13-diazacyclooctadecan) and 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo(8,8,8)hexacosan) (Merck-Schuchardt, purity >99%) were used without further purification. Methanol and *N*-methyl-2-pyrrolidinone (NMP) were purified by standard procedures described previously [7]. *n*-Hexadecane (Merck-Schuchardt, purity >99%), employed as the partitioning solvent in these studies, was used as such.

2.1. PROCEDURE AND RESULTS

(a) *Dibenzo-18-C-6*

The Gibbs transfer energy data (reference solvent : methanol) of dibenzo-18-crown-6 were derived from solubility measurements of the compound in various compositions of methanol +NMP mixtures. The general procedure adopted in solubility measurements has been described previously [8]. The saturated solution in the given solvent composition was suitably diluted and its absorbance was measured spectrophotometrically at the λ_{\max} of the solution. The concentration in the saturated solution was computed from a calibration graph prepared earlier. The standard Gibbs energy of transfer of the ligand was calculated from the solubility data (*S*) using the relation,

$$\Delta_t G_{(DB18-C-6)}^\circ = 2.303RT \log \frac{S_{MeOH}}{S_{MeOH+NMP}}. \quad (3)$$

The activity coefficient of the ligand in the saturated solutions was assumed to be equal to unity in view of its observed low solubility in the mixtures.

(b) *18-C-6*

The Gibbs energy of transfer (reference solvent : methanol) in this case was determined from partition measurements between *n*-hexadecane and methanol or its mixtures with NMP according to the procedure of Chantooni and Kolthoff [9]. A known concentration of 18-C-6 was partitioned between *n*-hexadecane and methanol or methanol +NMP mixtures of definite composition by shaking vigorously for 3 to 4 hours and then allowing the layers to settle. The extracted 18-C-6 in the hexadecane layer was treated with aqueous potassium picrate to convert it into the

K 18-C-6 picrate complex. This complex was then re-extracted into dichloromethane and its absorbance was measured at its $\lambda_{\max} = 370$ nm. The concentration in dichloromethane was computed from a previously constructed calibration graph. The partition coefficient, P , was calculated from these data according to

$$P = \frac{[18 - C - 6]_{\text{hexadecane}}}{[18 - C - 6]_{\text{MeOH or MeOH+NMP}}}. \quad (4)$$

The partition experiments were repeated twice in each composition and the results are accurate to within $\pm 1\%$. The $\Delta_t G^\circ$ of 18-C-6 was calculated from the partition data using the expression

$$\Delta_t G^\circ_{18-C-6} = 2.303RT \log \frac{P_{(\text{MeOH+NMP or NMP})}}{P_{\text{MeOH}}}. \quad (5)$$

(c) *Cryptands 21, 22 and 222*

The Gibbs transfer energy data (reference solvent: methanol) for these ligands were obtained from partition measurements between *n*-hexadecane and methanol or its mixtures with NMP. A known concentration of the ligand was partitioned between *n*-hexadecane and the solvent mixture of the given composition by vigorous shaking for 3 to 4 hours and then allowing the layers to settle. The extracted ligand in the hexadecane layer was titrated against standard aqueous nitric acid solution using methyl orange as indicator until the colour changed from yellow to orange. In the case of cryptand 222, standard methanolic HCl solution was used as the titrant acid and bromocresolgreen as the indicator [10] with the color change being from blue to yellow. The partition measurements on each ligand were carried out twice and the results agreed to within $\pm 1\%$. The partition coefficient P and the $\Delta_t G^\circ$ of the ligand were calculated using relations (4) and (5). In all partition measurements, mutually saturated solvents were used to minimize volume changes. All the measurements were carried out at 30 ± 0.1 °C. The solubility, partition coefficient and Gibbs transfer energy data for all the ligands are given in Tables I and II.

3. Discussion and Conclusions

3.1. 18-C-6 AND DIBENZO 18-C-6

The $\Delta_t G^\circ$ of 18-C-6 is positive and attains a maximum at $X_{\text{NMP}} = 0.7$. Thus its transfer from methanol to methanol + NMP mixtures is thermodynamically unfavourable. Considering that 18-C-6 is primarily solvated by H-bonding to the hydroxylic hydrogen in methanol, addition of NMP, a good H-bond acceptor, leads to a decrease in the availability of H-bonding sites in the mixtures. This results in an increasingly positive value of $\Delta_t G^\circ$. Also, NMP forms a hydrogen bonded

Table I. Gibbs transfer energy data $\Delta_t G^\circ$ (reference solvent : methanol)^a from partition coefficient (P) and solubility (S) measurements for 18-C-6 and dibenzo-18-C-6 in methanol-NMP mixtures at 30 °C.

X_{NMP}	18-C-6		Dibenzo-18-C-6	
	P	$\Delta_t G^\circ/\text{kJ mol}^{-1}$	$S \times 10^3/\text{mol kg}^{-1}$	$\Delta_t G^\circ/\text{kJ mol}^{-1}$
0.0	0.0226	0.0	2.6	0.0
0.3	0.0307	0.77	19.1	-5.0
0.5	0.0358	1.2	38.0	-6.8
0.7	0.0585	2.4	40.5	-6.9
0.9	0.0404	1.5	-	-
1.0	0.0361	1.2	54.6	-7.7

^a Accurate to $\pm 0.1 \text{ kJ mol}^{-1}$.

Table II. Gibbs transfer energy data $\Delta_t G^\circ$ (reference solvent : methanol)^a from partition coefficient measurements for cryptands 21, 22 and 222 in methanol-NMP mixtures at 30 °C.

X_{NMP}	Cryptand 21		Cryptand 22		Cryptand 222	
	P	$\Delta_t G^\circ/\text{kJ mol}^{-1}$	P	$\Delta_t G^\circ/\text{kJ mol}^{-1}$	P	$\Delta_t G^\circ/\text{kJ mol}^{-1}$
0.0	0.2710	0.0	0.0561	0.0	0.1120	0.0
0.3	0.2240	-0.48	0.0703	0.57	0.1014	-0.25
0.5	0.2033	-0.72	0.0730	0.66	0.0955	-0.40
0.7	0.1805	-1.0	0.0742	0.69	0.0763	-0.97
0.9	0.1140	-2.2	0.0773	0.81	0.0736	-1.1
1.0	0.0884	-2.8	0.0800	0.90	0.0479	-2.1

^a Accurate to $\pm 0.1 \text{ kJ mol}^{-1}$.

complex between the two solvents [11]. Both these factors lead to an increase of $\Delta_t G^\circ$ as observed.

The addition of two phenyl groups in dibenzo-18-C-6 leads to an enhanced solubility of dibenzo-18-C-6 in the mixed solvents and $\Delta_t G^\circ$ thus decreases and becomes increasingly negative with the addition of NMP. This suggests that its transfer from methanol to methanol + NMP mixtures is thermodynamically favoured. The phenyl groups seem to disfavour interaction with methanol (similar to the hydrophobic nature of these groups to water) and thus this ligand is better solvated in the mixed solvents than in methanol.

3.2. CRYPTANDS 21, 22 AND 222

The $\Delta_t G^\circ$ of cryptand 21 is seen to have small negative values up $X_{\text{NMP}} = 0.7$ and thereafter it decreases markedly up to pure NMP. This implies that it is better solvated in the mixed solvents than in methanol. The presence of a secondary

NH group in this ligand and the possibility of NMP also participating in H-bond formation with the amino nitrogen is favourable for its lowered free energy in the mixed solvents than in methanol

Cryptand 22 contains one more O—CH₂—CH₂ group as compared to cryptand 21 which shows the presence of an additional site for H-bonding with the methanolic oxygen of methanol. Thus the presence of more H-bonding centres in this molecule seems to favour H-bonding interactions with methanol even in the mixed solvents which implies better solvation by methanol than the mixtures. Thus $\Delta_r G^\circ$ is perceptibly positive and further increases slightly with addition of NMP.

The presence of two more O—CH₂—CH₂ groups (compared to cryptand 22) and two tertiary nitrogen atoms in cryptand 222 may be expected to result in even stronger solvation of cryptand 222 by methanol than in the case of cryptand 22. This is contrary to the observed experimental results and it is seen that $\Delta_r G^\circ$ of cryptand 222 is negative and quite small up to $X_{\text{NMP}} = 0.5$ but shows a marked decrease (becomes more negative) at higher compositions of NMP.

The observed variation of $\Delta_r G^\circ$ of cryptand 222 may be due to the presence of exo—exo, endo—exo and endo—endo conformational isomers in the molecule and the associated complex entropy effects in the ligand on transfer from methanol to methanol + NMP mixtures. Apart from the above, the opposing effects of favourable solvation of ether groups and the specific H-bonded interactions between the nitrogen atoms of the cryptand and the hydroxylic hydrogen of methanol may also be a contributing factor.

Acknowledgement

The authors thank the CSIR, New Delhi for the award of an Emeritus Scientist Scheme to one of us (C.K).

References

1. B. G. Cox, P. Firman, H. Horst, and H. Schneider: *Polyhedron* **2**, 343 (1983).
2. B. G. Cox and H. Schneider: *Pure Appl. Chem.* **61**, 171 (1989).
3. B. G. Cox, J. Stroka, P. Firman, I. Schneider, and H. Schneider: *Aust. J. Chem.* **36**, 2133 (1983).
4. T. K. Varadarajan, T. V. Ramakrishna, and C. Kalidas: *Ber. Bunsenges. Phys. Chem.* **101**, 676 (1997).
5. C. Kalidas and S. Balaji: *Ind. J. Chem. (Sec. A)* (in press).
6. K. K. Kundu and A. J. Parker: *J. Sol. Chem.* **9**, 683 (1980).
7. T. K. Varadarajan, T. V. Ramakrishna, and C. Kalidas: *J. Chem. Eng. Data* **43**, 527 (1998).
8. C. Kalidas and H. Schneider: *Z. Phys. Chem. Neue Folge* **120**, 145 (1980).
9. M. K. Chantooni Jr. and I. M. Kolthoff: *Proc. Natl. Acad. Sci. USA* **78**, 7245 (1981).
10. M. H. Abraham and H. S. Ling: *J. Chem. Soc., Faraday Trans. I* **80**, 3445 (1984).
11. M. M. Dupin: *J. Electroanal. Chem.* **52**, 75 (1974).