54. Preferential Solvation of the Sodium Cation in Binary Mixtures of Tetrahydrofuran with Polyamines, in Relation with the Chelate Effect

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Summary

The problem of determining the chelate effect brushes against methodological snags: the choice of concentration units, and of the appropriate standard states. We avoid these pitfalls by defining the chelate effect from measurements on bidentate ligands alone, without recourse to comparison with the corresponding unidentate ligands. Quantitation of the parameters extracted from the data is effected by three independent and mutually consistent procedures. Solvation of the Na^+-cation by the polyamines follows the sequence: cadaverin $<$ 1,3-diaminopropane $\ll$ ethylene diamine $\ll$ diethylenetriamine. Entry of the first and of the second diamine molecule into the sodium coordination shell are independent and equiprobable steps: $K_1 = K_3$ and $K_2 = K_4$, within the accuracy of the measurements. For ethylene diamine, the values of K_1 and K_3 are in the range 1.0–1.5 and those for K_2 and K_4 are in the range 83–102: attachment of the second N-atom is considerably easier, by two orders of magnitude (chelate effect). The chelate effect is strongly reduced in cadaverin, with a longer hydrocarbon chain connecting the two amine functions.

Introduction. In this second article (for the first article *cf.* [1]), we examine solvation of the Na^+-cation by polyamines: ethylene diamine (*en*), diethylene triamine (*dien*), 1,3-diaminopropane (*dap*), and cadaverine (*cdv*). These bi- and polydentate ligands compete for preferential solvation of Na^+ against the unidentate solvent THF, chosen for reference, as in the preceding paper.

There are two goals: to obtain conclusive proof for the operation of a chelate effect, using multidentate ligands; and to measure the interaction between Na^+ and polyamines, which are involved jointly in important biological functions [3–5] and industrial processes [6].

Experimental Part

For purification of the compounds, and NMR. measurements, see [1]. Viscosity measurements and corrections are described in [2].

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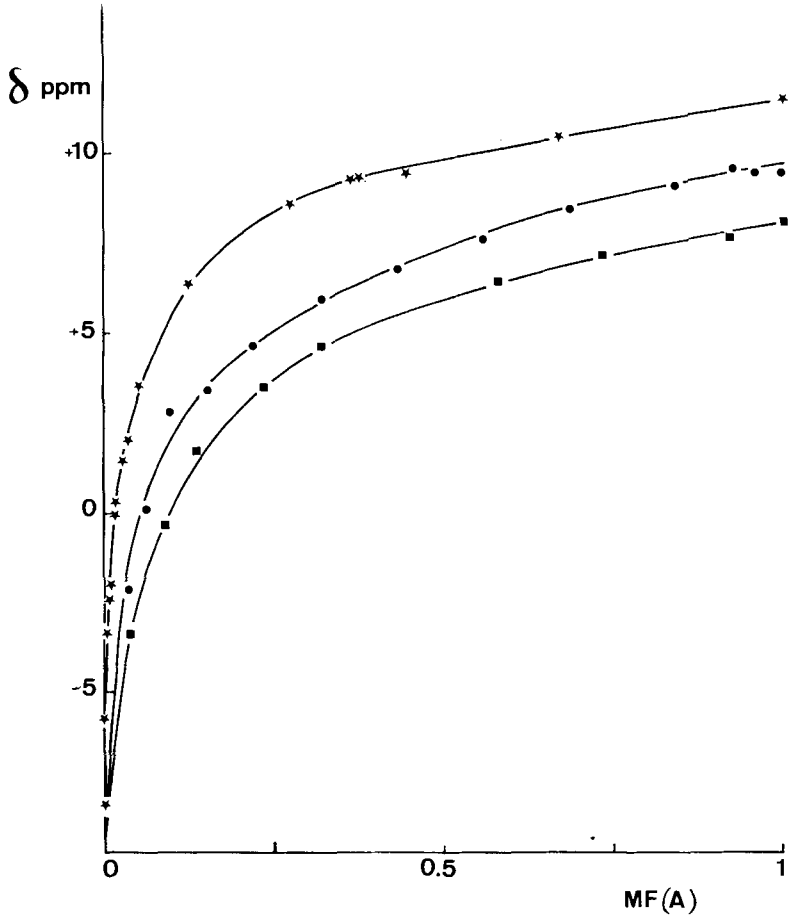


Fig. 1. *A plot of the variation of the ^{23}Na-chemical shift δ against mol-fraction of the polyamine A/(A + B) for* cdv (■), dap (●), *and* en (★)

Results and Procedures. – Plots of the ^{23}Na-chemical shift δ against the mol-fraction of polyamine *(Fig. 1)* deviate considerably from ideality: their curvature implies preferential solvation by the amine solvent, in the sequence $cdv < dap < en$. The limiting δ values in the pure amine follow the same sequence: (ppm) $cdv = 8.6$; $dap = 9.9$; $en = 11.9$.

The results are shown in the *Hill* representation [1] in *Figure 2*. Notice that these four *Hill* plots, for *en, dap, cdv* and *dien, deviate strongly from linearity with a unit slope.* The deviations follow the same sequence as that shown by the arching plots of *Figure 1:* the *Hill* plot is furthest from a linear unit slope relation when the number n of methylene groups between the two amine groups is the smallest: *cdv* (5); *dap* (3); *en* (2). Notice also that the tridentate ligand *deta* deviates even more than the bidentate *en.*

These facts mean apparently, according to the classical interpretation of *Hill* plots [7], that pronounced *anti*-cooperativity occurs in the binding of each of these

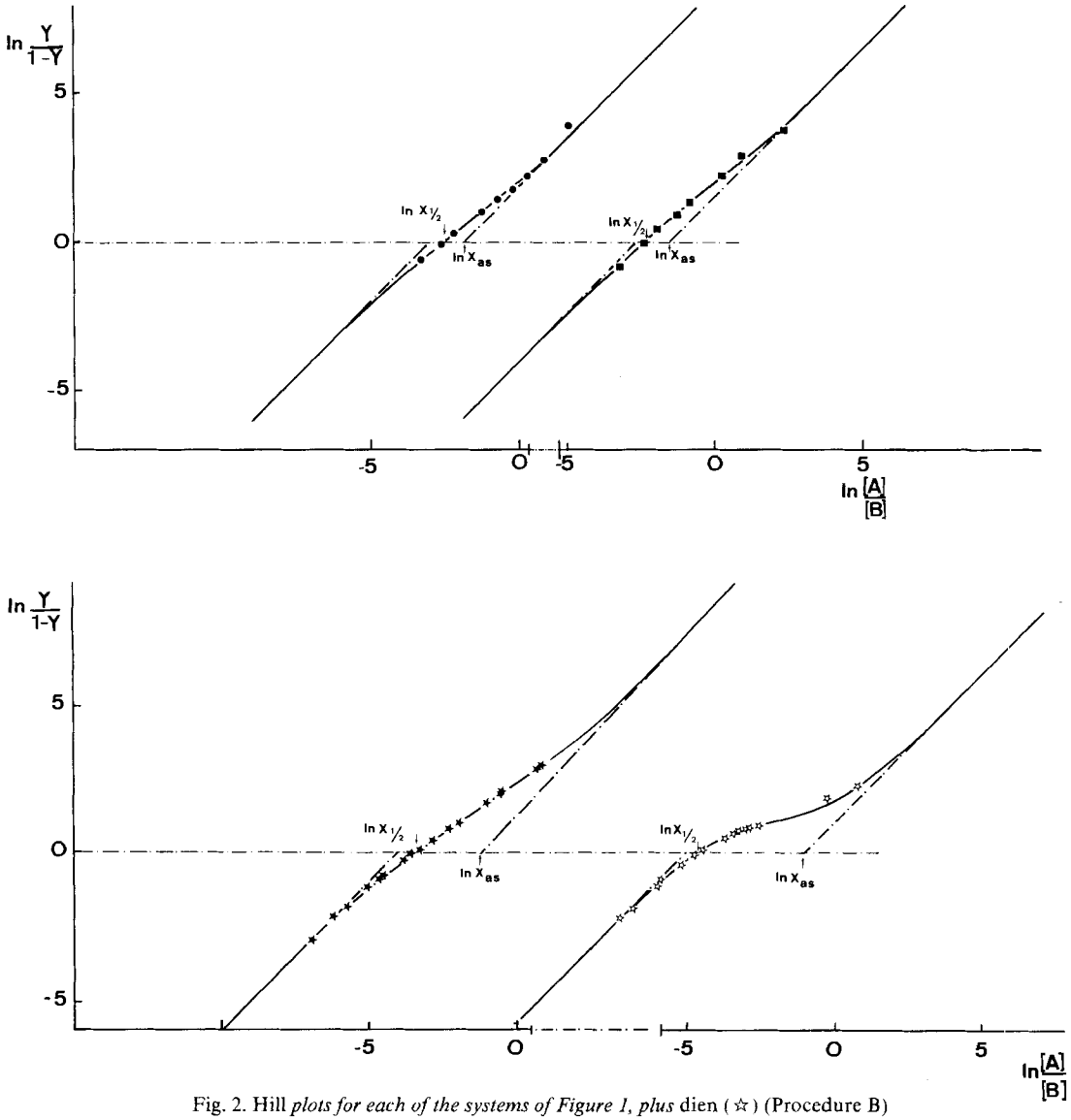


Fig. 2. Hill *plots for each of the systems of Figure 1, plus* dien (☆) (Procedure B)

polyamines. This result comes as a surprise: cooperativity was being expected. In fact, these curves should not resemble those obtained with unidentate ligands, and they can*not* be analyzed in like manner: with multidentate ligands, the characteristic equations in the *Hill* procedure are essentially different. They are described below.

The model. – We shall outline now the precise mathematical treatment for extracting binding constants from the data. Let us consider the following equi-

libria [1], in which A denotes a diamine, and B is the THF reference solvent (using a simpler notation than in the preceding article [1]):

$$Na^+(B)_4 + 2\,A \overset{K_1}{\rightleftharpoons} Na^+(A)(B)_3 + A + B \tag{1}$$

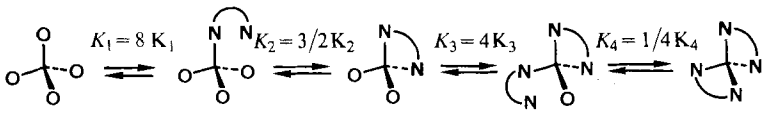
$$Na^+(A)(B)_3 + A + B \overset{K_2}{\rightleftharpoons} Na^+(A)(B)_2 + A + 2\,B \tag{2}$$

$$Na^+(A)(B)_2 + A + 2\,B \overset{K_3}{\rightleftharpoons} Na^+(A)_2(B) + 3\,B \tag{3}$$

$$Na^+(A)_2(B) + 3\,B \overset{K_4}{\rightleftharpoons} Na^+(A)_2 + 4\,B \tag{4}$$

The apparent equilibrium constants K_i are related to the *intrinsic* equilibrium constants K_i (i= 1–4) through the statistical factors appearing in the *Scheme:*

Scheme



With the same notation as in the preceding article [1]:

$$X = [A]/[B];\ a_0 D = 1;\ a_1 D = K_1 X;\ a_2 D[B] = K_1 K_2 X;\ a_3 D[B] = K_1 K_2 K_3 X^2;$$
$$a_4 D[B]^2 = K_1 K_2 K_3 K_4 X^2 \tag{5}$$

where

$$D = 1 + K_1 X + K_1 K_2 X[B]^{-1} + K_1 K_2 K_3 X^2 [B]^{-1} + K_1 K_2 K_3 K_4 X^2 [B]^{-2}.$$

The relations 5 are more complex for bidentate than for monodentate amines [1], mainly because the THF-concentration [B] enters the equations. The major difficulty thus introduced is removed by a simple and easy to accept assumption: ligands A and B have additive volumes, to first approximation (deviation from this ideal behavior is very small and leads to insignificant changes of the NMR. measurements). Writing this additivity as $V_T = V_A + V_B$, and expressing $V_{A,B}$ in terms of the molar volume R of the constituents A or B:

$$V_A = [A] V_T R_A \tag{6a}$$

$$V_B = [B] V_T R_B. \tag{6b}$$

R is the ratio of the density ρ to the molecular weight M, so that:

$$[A] V_T \frac{M_A}{\rho_A} + [B] V_T \frac{M_B}{\rho_B} = V_T \quad \text{or} \quad [A] R_A + [B] R_B = 1. \tag{7}$$

Thus, dividing by [B], one can write:

$$R_A X + R_B = [B]^{-1}. \tag{8}$$

It thus becomes possible to express the mol-fractions a_i in terms only of the β_i values and of the concentration ratio $X = [A]/[B]$:

$$\begin{aligned} a_0 &= D^{-1}; & a_3 &= \beta_3 X^2 (R_A X + R_B) D^{-1}; \\ a_1 &= \beta_1 X D^{-1}; & a_4 &= \beta_4 X^2 (R_A X + R_B)^2 D^{-1}; \\ a_2 &= \beta_2 X (R_A X + R_B) D^{-1}; \end{aligned} \tag{9}$$

where $\beta_i = K_1 K_2 \ldots K_i$.

Hence the saturation fraction $Y/(1-Y)$ is given by:

$$\frac{Y}{1-Y} = \frac{\beta_1 X + 2\beta_2 X (R_A X + R_B) + 3\beta_3 X^2 (R_A X + R_B) + 4\beta_4 X^2 (R_A X + R_B)^2}{4 + 3\beta_1 X + 2\beta_2 X (R_A X + R_B) + \beta_3 X^2 (R_A X + R_B)} \tag{10}$$

Procedures for obtaining equilibrium constants. – A) *Graphical determination.* – *A-1.* It follows that:

$$\lim_{X \to \infty} \left(\frac{Y}{1-Y} \right) = \frac{4\beta_4 X^4 R_A^2}{\beta_3 R_A X^3} = 4 K_4 R_A X \tag{11}$$

Hence, the intersection of the asymptote at high saturation with the horizontal axis *(Fig. 2)* provides K_4:

$$\ln \left(\frac{Y}{1-Y} \right)_{as.} = \ln (4 K_4 R_A) + \ln X \tag{12}$$

$$\rightarrow \ln X_{as.} = -\ln (4 K_4 R_A) \tag{13}$$

A-2. If K_1 can be neglected with respect to the product $\beta_2 = K_1 \cdot K_2$, by taking the limit of equation 10:

$$\left(\frac{Y}{1-Y} \right)_{X \to 0} = \frac{1}{2} \beta_2 X R_B \tag{14}$$

the intersection of this asymptote at low saturation with the horizontal axis gives the product $\beta_2 = K_1 \cdot K_2$:

$$\ln X_{as'} = -\ln (\beta_2 R B/2) \tag{15}$$

A-3. Define now $X_{1/2}$ as the value of the abscissa corresponding to $Y/(1-Y)=1$. If $X=X_{1/2}$, then:

$$\beta_3\{(R_AX+R_B)X^2[2K_4(R_AX+R_B)+1]\}-\beta_1X-2=0 \qquad (16)$$

which is simplified (β_1X being negligible) into:

$$\beta_3=2[(R_AX+R_B)X^2(2K_4(R_AX+R_B)+1]^{-1} \qquad (17)$$

Indeed, we find that $K_1 \ll \beta_2$ is a condition fulfilled quite generally by the polyamines studied (see the following sections). Hence, by simple inspection of the *Hill* plot, it is possible to determine reliably the values of the three constants $K_1 \cdot K_2$, K_3 and K_4.

B) *Multi-parameter fitting on the* Hill *plot.* This procedure starts, as in the first article [1] with a *Hill* plot, but with a multi-parameter fitting in order to account for the observed *anti*-cooperativity, *i.e.* with no prior assumption on the K_i's. It is performed with a non-linear least squares multiple regression on equation 10. The results are shown in *Table 2*, together with the uncertainties on each of the parameters thus derived.

C) *Simultaneous adjustment on the δ and ν* curves.* This procedure is described elsewhere [2], with the hypothesis of additive chemical shifts. The weight of the α_1 species *(Scheme)* is neglected, since it remains too small at all compositions X for a reliable determination to be made. This procedure is performed using Simplex optimization, which suffers from not providing error limits on the derived parameters *(Table 2)*. We could not resort to a multiple regression as in procedure B, unfortunately, because with the six additional parameters (chemical shifts and linewidths) of *Table 3*, it becomes unwieldy.

The two following *Tables* summarize the results obtained with these different approaches. Results obtained with the graphical approach (Procedure A) compose *Table 2.*

Table 1. *Slopes at half-height* ($S_{1/2}$), *composition at half-height* ($X_{1/2}$), *intersections with the horizontal axis of the high* (X_{as}) *and of the low* ($X_{as'}$) *saturation asymptotes, and the difference* $\Delta = lnX_{1/2} - lnX_{as}$

Amine solvent	$S_{1/2}$	$lnX_{1/2}$	lnX_{as}	$lnX_{as'}$	Δ
cdv	0.87	−2.28	−1.4	−2.5	0.96
dap	0.75	−2.50	−1.7	−3	0.80
en	0.66	−3.50	−1.8	−4	1.70
dien	0.67	−4.75	−1.0	−5.1	3.75

Table 2. *Values of the intrinsic equilibrium constants* K_3, K_4 *and of the products* $K_1 \cdot K_2$ *and* $K_3 \cdot K_4$ *according to the different procedures detailed in the text*

Amine solvent	$K_1 \cdot K_2$ by procedure			K_3 by procedure			$K_3 \cdot K_4$ by procedure			K_4 by procedure		
	A	B	C	A	B	C	A	B	C	A	B	C
cdv	25	20±5	17	0.6	2.1 ±0.6	0.6	24	33±12	34	40	41±5	57
dap	41	45±6	38	0.4	0.33±0.04	0.6	28	27± 5	32	65	81±6	53
en	110	114±3	112	1	0.87±0.07	1.0	94	79± 7	91	97	91±5	91

The X_{as} value cannot be determined with much accuracy because it results from extrapolation of δ-values to high saturation. The slope at half-height $S_{1/2}$ would be unity in the absence of cooperativity. Hence, cooperativity increases in the sequence: *cdv* < *dap* < *en* < *dien*, which is the very same sequence as appeared from qualitative examination of *Figures 1* and *2*. Likewise, the Δ-values measure cooperativity, and they vary according to the sequence: *cdv* ~ *dap* < *en* < *dien*. The parameter $X_{1/2}$ is the isosolvation point [8]. It is directly related to the equilibrium constant for preferential solvation in the absence of cooperativity. In the presence of cooperativity, as here, $X_{1/2}$ still corresponds qualitatively to this equilibrium constant: the solvating power is seen from *Table 1* to follow the sequence *dien* ≫ *en* ≫ *dap* > *cdv*. Procedure A has the merits of being simple and expeditious.

Procedure A is further justified by the comparison with procedures B and C in *Table 2:* the parameters differ little when obtained by any of the three procedures. Procedure B is the most reliable, because it provides one with a statistical criterion of accuracy on the values obtained. Procedure C provides both additional confirmation and additional information, since it yields the parameters listed in *Table 3*. For each of the bidentate amines, it is apparent that the product $K_1 \cdot K_2 \sim K_3 \cdot K_4$: this indicates equivalent binding to the sodium ion of the first and of the second amine molecule.

Determination of the chelate effect. – We define the chelate effect as the ratio of complexes having bidentate attachment of the ligand to the metal, to the complexes in which only unidentate binding occurs: hence the chelate effect is measured by the quantities a_2/a_1 or a_4/a_3. The former is out of reach, since the concentration of species 1 remains too small – precisely because of the chelate effect – to be determined reliably. Taking $a_4/a_3 = K_4(R_A X + R_B)$, its limiting value at low saturation ($X \to 0$) is $K_4 R_B$. Hence, with the above definition, it will be sufficient to compare this value of $K_4 \cdot R_B$ to unity in order to evaluate the chelate effect. Relying upon the results from procedure B, it is calculated as: 1.9 ± 0.1 (*en*), 1.7 ± 0.1 (*dap*), a, d 0.8 ± 0.1 (*cdv*). Due to the definition used, these values are *lower limits* of the chelate effect. It is seen to decrease in the sequence: *en* > *dap* > *cdv*. This last value, for cadaverin, does not differ significantly from unity. These results conform to chemical intuition: as the second N-atom is removed from the first by five intervening methylene groups (*cdv*), ring formation becomes prohibitive in terms of loss of degrees of freedom for internal rotations, and the two N-atoms bind independently to the cation, as they would in a unidentate ligand.

A useful visualization of the operation of the chelate effect is provided in *Figure 3*, showing the changes in the relative amounts of the five coexisting entities. $a_0 - a_4$ with composition of the binary mixture.

Table 3. *Characteristic linewidths normalized to unit viscosity* (v_i^*) *and the limiting chemical shifts* δ_0 *and* δ_4, *by application of procedure C* (see text)

Amine solvent	v_0^*	v_2^*	v_3^*	v_4^*	δ_0	δ_4	δ_4 (obs.)
cdv	3.4	16	12	2.7	−7.48	8.54	8.59
dap	3.0	14	20	5.8	−7.87	10.11	9.90
en	3.0	15	52	5.5	−7.81	11.90	11.93

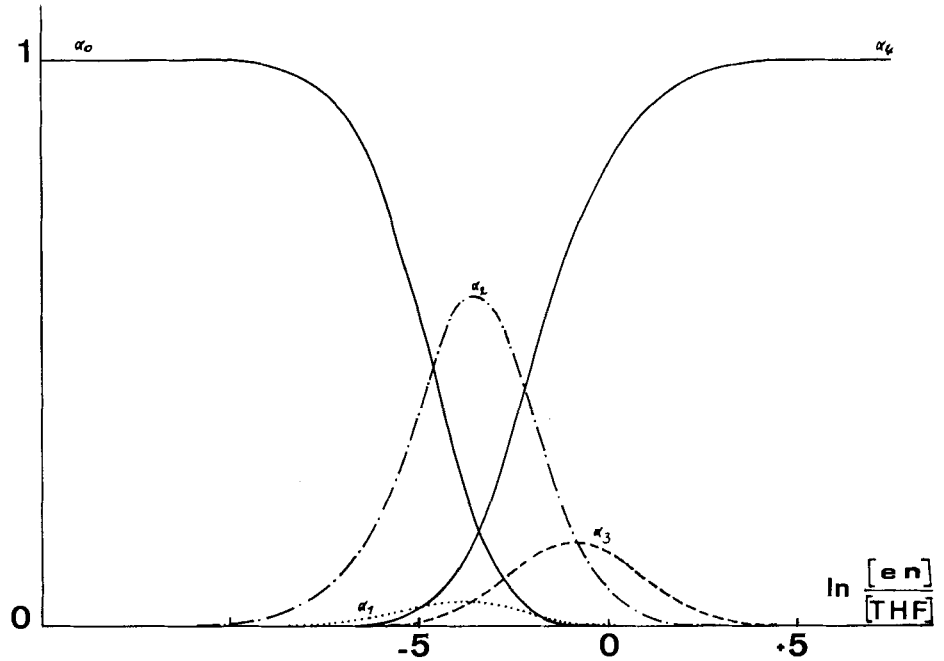


Fig. 3. *A plot of the relative fractions* a_i *(i = 0–4) for each of the intermediate solvates, in the* en-*THF system.* Note that the (very small) values of a_1, which are calculated, are presented only for the sake of logical consistency. Had they been ignored, this would have led to negligible changes in the values of a_2–a_4 and of a_0.

Going from the thermodynamic to the NMR. results, these are shown for the bidentate ligands in *Table 3*, and for the tridentate *dien* in *Table 4.*

The values of $v_0^* = 3.0$ in *Table 3* are nicely in agreement with the results published elsewhere [2]. As for the v_4^* values of 5.5, 5.8 and 2.7, they are low, as expected for a symmetrical species *(Scheme)* with a vanishing asymmetry parameter, and devoid of a substantial electrostatic field gradient, but having lost the full T_d symmetry [2]. They are also low when compared to the corresponding v_4^* values for propylamine and *i*-propylamine [2], of 13–14: *cdv, dap* and *en* appear to pack

Table 4. *Results for the* dien-*system*

	Procedure		
	B	C	exp.
β_3	3.1×10^4	3.1×10^4	–
K_4	0.78	1.04	–
δ_0	–	– 7.86	– 7.84
δ_3	–	– 7.27	–
δ_4	–	12.32	12.33
v_0^*	–	3.25	3.24
v_3^*	–	26.6	–
v_4^*	–	10.6	10.6

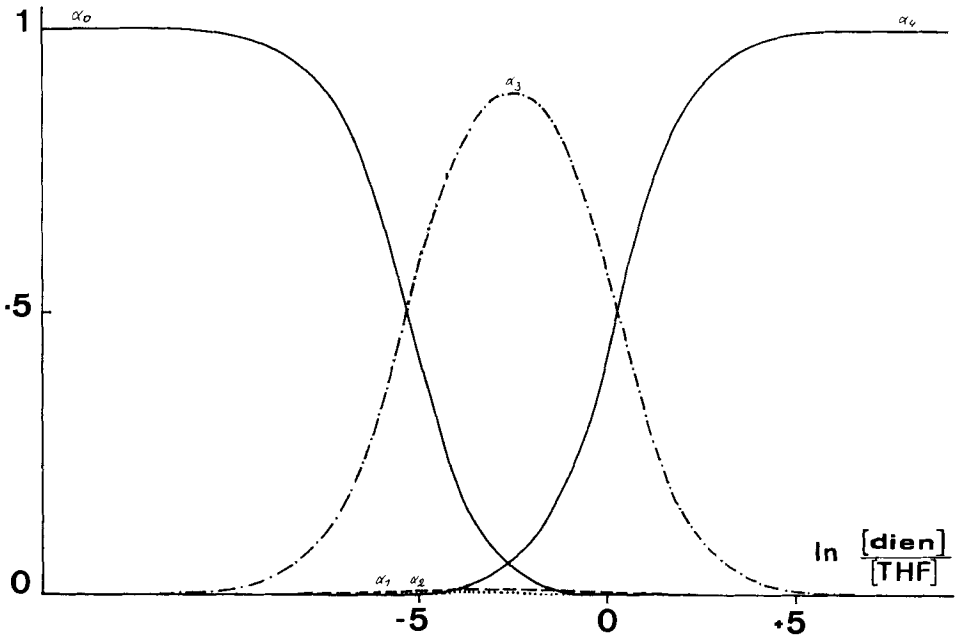


Fig. 4. *Same as* Figure 3, *for the* dien-*THF system*

into a more symmetrical arrangement around the Na^+-ion. These low v_0^* and v_4^* values, below 6, contrast with the much greater v_2^* and v_3^* values, in the range of 12–52, which characterize *unsymmetric* solvates having significant permanent electrostatic field gradients.

Finally, the results from application to the *dien* system of procedures B and C are listed in *Table 4.*

The conclusions earlier obtained by an approximate phenomenological treatment and published in a preliminary communication [9] are fully vindicated by the present more exact treatments. A single intermediate solvate has a measurable weight, as depicted in *Figure 4:* that consisting of one *dien* and one THF molecule.

Discussion. – As in the preceding article [1], only *loose* ion pairs of $Na^+ClO_4^-$ are present in these dilute solutions, and their concentration remains invariant with the composition of the solvent mixture and negligible. Hence, the analysis can be restricted to the Na^+-polyamine interactions.

Clearly, whatever the procedure of analysis, the results on the *en*-THF mixture *(Table 2)* are: $K_3 = 0.9$–1; and $K_4 = 90$–100. Two orders of magnitude differentiate between attachment of the first N-atom of the ligand and attachment of the second N-atom: this is nothing but the chelate effect in operation.

The preceding sentence could be construed as a fairly strong and provocative statement, given articles in the literature claiming that the so-called chelate effect is a bogus effect: 'the chelate effect' is a heatedly agitated topic in analytic and inorganic chemistry. Let us summarize briefly the evidence in the following paragraphs.

Long ago, it was realized that bi- and polydentate ligands form stronger complexes in solution than monodentate ligands. The chelate effect is defined usually, and in quite normal manner, by comparison of two equilibrium constants:

$$M^+ + L{-}L \overset{K_1}{\rightleftharpoons} M^+\!\!<^{L}_{L} \tag{18}$$

$$M^+ + 2\,L' \overset{K_2}{\rightleftharpoons} M^+(L'_2) \tag{19}$$

where L–L, and L′ are ligands sharing very similar chemical features. It is found routinely that $K_1 > K_2$, which is attributed to the greater loss in translational entropy in eq. 19 as compared to eq. 18 [10]. This approach raises problems of two types [11]:

1) Equilibrium constants K_1 and K_2 are formulated necessarily with different units; so that a change of units modifies the numerical value of the chelate effect, to the extent that it can disappear altogether (with, admittedly, unrealistic choices of concentration units) [12–14]. However, the chelate effect remains a reality when standard states close to experiment are being chosen [11].

2) In many cases, arbitrarily unsymmetrical standard states are affixed to the solute and to the solvent [15–16]: typically, solute concentration are expressed in mol · l^{-1} while the solvent concentration is a mol-fraction (then taken as equal to unity, so that one really works with *apparent* equilibrium constants).

Our approach bypasses both these problems completely. Since all the results are obtained relative to one and the same reference solvent (THF), we isolate the chelate effect with no ambiguity. And the present work is convincing proof for the existence of the chelate effect, from data obtained solely on the bidentate ligands. Instead of an *inter*molecular comparison between bidentate and unidentate ligands, we make the more appropriate *intra*molecular comparison between unity and the second *intrinsic* binding constants for a bidentate ligand, corrected for the presence of the reference solvent (K_4R_B).

The abundant literature of the chelate effect is somewhat reminiscent of theological discussions, in that the problem of existence is compounded by the problem of explanation: granted that the chelate effect exists, what causes it?

The question of the origin of the chelate effect is easier to answer now that we know that the phenomenon all but vanishes in the gas phase [17]. Witness the *Gibbs* standard free energies (kcal · mol^{-1}) for the reactions:

$K^+ + 2\,NH_3$	$\rightleftarrows$ $K^+(NH_3)_2$	$\Delta G° = -20.8$
$K^+ + 2\,CH_3NH_2$	$\rightleftarrows$ $K^+(CH_3NH_2)_2$	$\Delta G° = -21.7$
$K^+ + H_2NCH_2CH_2NH_2$	$\rightleftarrows$ $K^+(H_2NCH_2CH_2NH_2)$	$\Delta G° = -19.0$

This disappearance of the chelate effect has been explained cogently and convincingly by compensation between the corresponding enthalpy and entropy terms [17]. In the gas phase, the enthalpy for binding two unidentate CH_3NH_2 ligands is

much more favorable than that for the bidentate eda ligand: *ca.* -36 kcal · mol^{-1} as compared to *ca.* -26 kcal · mol^{-1}. This is because the unconstrained unidentate ligands are able to solvate the cation at maximum distance from one another, thus minimizing their dipolar repulsion; and because of a polarization or a field effect in the bidentate ligand upon attachment of the first N-atom to the cation, making the second N-atom a weaker electron donor. Conversely, the loss in translational entropy is approximately twice as much for 2 L′ than for L–L. And there is approximate cancellation of the favorable entropy by the unfavorable enthalpy term [17].

The situation becomes much more complex in solution, and many factors are then involved [18]. For instance, since electrostatic interactions are proportional to the inverse of the dielectric constant, the dipolar repulsions in the solvation sphere are considerably diminished for the unidentate ligands. The field effect for bidentate ligands is also suppressed. *Myers* [18] has studied in great detail the thermodynamics of chelation. He has come to the conclusion that the solution enthalpies and entropies of the ligands are very important factors. True, some reactions have $\Delta H° \simeq 0$ and $\Delta S°$ near the calculated value of *ca.* 16 e.u., in conformity with the traditional view of the chelate effect as entropy-determined [10] [19]. This is due, in fact, to the confluence of several large and opposing enthalpy and entropy changes.

These general considerations apply to our measurements. It is then rather remarkable that they lead to such simple results, when the solution enthalpy of the ligands and the solution entropy of the coordinated cation *e.g.* could both vary with the composition of binary mixture. Despite this note of caution, the results show interesting trends. Besides the decrease of the chelate effect as the number n of methylene units in the chain increases from 2 to 5, we note also the smaller values of $K_3 = 0.3$–2.1 for *en*, *dap* and *cdv* as compared to the intrinsic binding constant $K = 4.4$ for propylamine [1], an observation consonant with decrease of *Lewis* basicity of the second N-atom from introduction of the first N-atom, in these diamines.

Conclusion. – The present work provides indisputable proof for the presence of a chelate effect in the complexation of the sodium cation by diamines. The *Hill* plot procedure is extremely well adapted to the problem, it yields the relative amounts of the successive solvates. It has helped us very greatly in evolving an original method for characterization of the chelate effect. More detailed interpretation will have to await for determination of the corresponding ΔH and ΔS variations.

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REFERENCES

[1] *A. Delville, C. Detellier, A. Gerstmans & P. Laszlo,* Helv. Chim. Acta *64*, 547 (1981).
[2] *A. Delville, C. Detellier, A. Gerstmans & P. Laszlo,* J. Magn. Reson., in press.
[3] *J. Janne, H. Poso & A. Raina,* Biochim. Biophys. Acta *473*, 241 (1978).
[4] *T.P. Karpetsky, P.A. Hieter, J.J. Frank & C.C. Levy,* Mol. Cell. Biochem. *17*, 89 (1977).
[5] *S.S. Cohen,* Adv. Polyamine Res. *1*, 1 (1978).
[6] See 'Polyamine-Chelated Alkali Metal Compounds', A.W. Langer, Ed., Adv. Chem. Series *130*, ACS, 1974.
[7] *A. Cornish-Bowden & D.E. Koshland jr.*, J. Mol. Biol. *95*, 201 (1975).
[8] *L.S. Frankle, C.H. Langford & T.R. Stengle,* J. Phys. Chem. *74*, 1376 (1970).
[9] *C. Detellier, A. Gerstmans & P. Laszlo,* Inorg. Nucl. Chem. Lett. *15*, 93 (1979).
[10] *G. Schwarzenbach*, Helv. Chim. Acta *35*, 2344 (1952).
[11] *D. Munro*, Chem. Brit. *13*, 100 (1977).
[12] *R.F. Jameson*, in MTP Int. Rev. Sci. (Physical Chemistry), Skinner, H.A., ed., Butterworths, London 1972, vol. 10, ch. 2.
[13] *J. Agterdenbas*, J. Chem. Ed. *45*, 230 (1968).
[14] *J.E. Prue*, J. Chem. Ed. *46*, 12 (1969).
[15] *G. Beech*, Quart. Rev. Chem. Soc. *23*, 410 (1969).
[16] *C.F. Bell*, 'Metal Chelation, Principles and Applications', Oxford Chemistry Series, Oxford University Press 1977.
[17] *W.R. Davidson & P. Kebarle*, Can. J. Chem. *54*, 2594 (1976).
[18] *R.T. Myers*, Inorg. Chem. *17*, 952 (1978).
[19] *E.L. Simmons*, J. Chem. Ed. *56*, 578 (1979).