The lattice energies of complexes of poly(ethylene oxide) with sodium halides

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The lattice energy of the poly(ethylene oxide)–sodium iodide (PEO–NaI) complex has been computed using the Chatani–Okamura crystallographic analysis of this system. Comparison of the computed results with literature data for the lattice energies of the pure salt and pure polymer predicts that complex formation will occur if a partial electronic charge of (+)0.2 to 0.23 on the carbon atom (−0.4 to −0.46 on oxygen) is assumed. Estimates of corresponding energetic parameters for PEO–NaBr and PEO–NaCl also afford plausible interpretations of the observed complex formation in the former case but phase separation of polyether and salt in the latter.

(Keywords: poly(ethylene oxide)–alkali salt complexes; lattice energy; computations)

INTRODUCTION

Poly(ethylene oxide)–alkali salt complexes are known for their significant ionic conductivity[1], which has aroused interest for their application as electrolytes in the fabrication of lightweight batteries employing alkali-metal electrodes[2,3]. Although ionic conduction occurs most readily through the amorphous phases of these materials, the most conductive systems are those with salts of low lattice energy which are usually able to crystallize in the presence of unmodified poly(ethylene oxide) (PEO). Furthermore, the crystalline complexes with both inorganic and organic alkali salts represent a novel class of materials forming structures which undergo thermotropic reorganizations[4–6] or which are deposited in macrodomains following lyotropic organization in solution[5,6]. Electronically conducting films have also been prepared by charge-transfer reactions of films and fibres of PEO–NaI with tetracyanoquinodimethan (TCNQ)[7].

The report of the first detailed structural analysis of a PEO–alkali ion complex, that of PEO–NaI by Chatani and Okamura[8], prompts an investigation of the lattice energy of this material as a basis for establishing the 'ground rules' for the formation of complexes between alkali salts and polyethers. In this paper, an attempt is made to account for the formation of PEO–NaI by computations of the lattice energy of the complex using the crystallographic data of Chatani and Okamura. The observed formation of a PEO–NaBr complex and the failure of NaCl to form a complex with PEO is also considered using plausible estimates of the energies of polymer–salt interactions in these cases.

COMPUTATIONAL PROCEDURES

In the formation of the PEO–NaX complex, 1 mol of a segment of three ethylene oxide units (3EO) associates with 1 mol of NaX:

$$3\text{EO(crystalline PEO)} + \text{NaX} = 3\text{EO–NaX} \qquad (1)$$

The reference 3EO segment is shown by the filled and hatched carbon and oxygen atoms in *Figure 1*. Neglecting entropy changes we assume that complex formation will occur provided that:

$$E(\text{complex}) < E(3\text{EO}) + E(\text{NaX}) \qquad (2)$$

where E(complex), E(3EO) and E(NaX) are the lattice energies of the complex, of the appropriate segmental length of the pure crystalline polymer and of the pure salt, respectively. E(complex) may be conveniently subdivided into several contributions thus:

$$E(\text{complex}) = \varepsilon(\text{NaX}) + \varepsilon(3\text{EO–NaX–intra}) + \varepsilon(3\text{EO–NaX–inter}) + \varepsilon(3\text{EO}) \qquad (3)$$

In equation (3), ε(NaX) is the lattice energy of the salt within the complex, ε(3EO–NaI–intra) is the energy of interaction of the 3EO reference segment with the ion pairs (labelled 1–5 in *Figure 1*) within the same

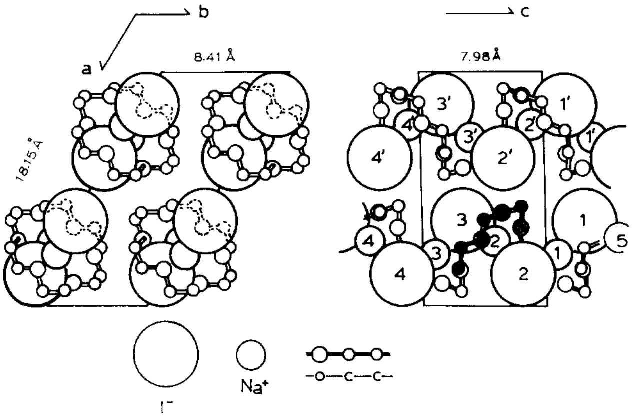

Figure 1 The crystal structure of PEO–NaI after Chatani and Okamura[8]. The filled carbon atoms and hatched oxygen atoms indicate the 'reference' 3EO segment. The interactions of ion pairs labelled 1–5 and 1'–4' with the segment give the components ε(3EO–NaI–intra) and ε(3EO–NaI–inter) of the lattice energy of the complex (see text)

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Table 1 Van der Waals parameters

	Polarizabilities (Å^3)	Effective atomic number	Radius (Å)
Na^+ 'high'	0.24	10.0	0.95
Na^+ 'low'	0.24	10.0	1.60
I^- 'high'	10.0	30.0	1.60
I^- 'low'	6.0	30.0	2.20
C	1.8	7.0	1.90
O	0.64	7.0	1.60

polymer–salt molecular adduct, and ε(3EO–NaX–inter) is the energy of interaction of the 3EO reference segment with the ion pairs (1′–4′) of neighbouring molecular adducts. Finally, ε(3EO) consists of the energy of interaction of the 3EO segment with neighbouring PEO helices and changes in the internal energy of the reference EO segment consequent upon its transfer from the environment of the lattice of pure PEO to that of the complex. Thus:

$$\varepsilon(3\text{EO})=\varepsilon(3\text{EO–inter})+\varepsilon(3\text{EO–intra})+\varepsilon(\text{tors})+\varepsilon(\text{str}) \tag{4}$$

In equation (4), ε(3EO–inter) is the energy of interaction of the segment with neighbouring PEO helices, ε(3EO–intra) is the difference between the non-bonded interaction energies of the atoms of the 3EO segment in the pure, crystalline polymer and in the complex, and ε(tors) and ε(str) represent the corresponding differences in the torsional energies of the bond rotational states and the strain energies of the skeletal bonds. The torsional potentials, V, about skeletal bonds were given by:

$$V=V_0(1-\cos\varphi)/2 \tag{5}$$

where V_0 is the barrier height for a given bond type and φ is the rotation angle which was measured from the *trans* (*t*) state = 0°. The bond angle strain energies, S, were given by:

$$S=F(\Delta\theta)^2/2 \tag{6}$$

where F is the force constant and $\Delta\theta$ is the deformation in radians.

In calculating the lattice energy of the PEO–NaI complex according to equations (3)–(6), the contributions of the hydrogen atoms, which should be small, were ignored. According to established procedures, interatomic Coulombic energies between atoms i and j were given by $N_A e^2 q_i q_j/r_{ij}$ per mol where N_A is Avogadro's constant, e is the electronic charge, q_i and q_j are the signs and magnitudes in units of the electronic charge on atoms i and j, and r_{ij} is their distance apart. It was assumed that the partial charge on the oxygen atom, $q_O=-2q_C$ throughout (where q_C is the partial charge on carbon). Since all atoms in the vicinity of the reference atoms (apart from the hydrogens) were considered in the calculations, a dielectric constant of unity was assumed, as is the normal practice in calculating the lattice energies of pure ionic crystals. The van der Waals energies for interactions involving at least one non-ionic atom were calculated according to:

$$E_{ij}=A_{ij}r_{ij}^{-12}-C_{ij}r_{ij}^{-6}$$

where the C_{ij} were obtained from the Slater–Kirkwood equation[9] using the van der Waals parameters given in *Table 1*. The A_{ij} repulsive parameters were then obtained by minimization of the energies at the internuclear distances corresponding to the sums of the van der Waals radii. However, in computing the energy of the ionic lattice within the complex, ε(NaI), a Born repulsive term[10] was allowed to operate only for the contacting ions along each zigzag; non-Coulombic repulsions between ions in neighbouring zigzags were neglected. Therefore ε(NaI) was given by:

$$\begin{aligned}\varepsilon(\text{NaI})=\tfrac{1}{2}N_A\sum\big[(e^2q_iq_j/r_{ij})(1-1/n) &\qquad k,l=0\\ +e^2q_iq_j/r_{ij} &\qquad k,l\neq 0\\ -C_{ij}/r_{ij}^6\big] &\end{aligned} \tag{7}$$

where the parameter n assumes a value of 10 for NaI according to Pauling's scheme[10], k, l and m (see also *Table 2*) index the PEO–salt molecular adducts (helices and ion zigzags) with respect to the reference 3EO segment ($k, l, m=0$). Thus, k indexes the ranks of adducts in the direction of a, l indexes the ranks along b, and m indexes the unit cells on either side of the cell containing the reference 3EO segment along the direction of c.

The factor of '$\frac{1}{2}$' in equation (7) takes account of the duplication of specific interionic interactions when the interactions of a reference ion with all other ions in the lattice are summed throughout all $2N_A$ ions. This factor was similarly applied in summing the intersegmental interactions in ε(3EO–inter) and ε(3EO–intra).

Following Flory and coworkers[11,12], the torsional barriers V_0 were assigned values of 12.5 kJ mol^{-1} and 11.4 kJ mol^{-1} for C–C bonds and C–O bonds respectively[11] and the force constant for bond angle deformation was taken to be 670 kJ mol^{-1} rad^{-2} for bond angles centred on both C and O atoms to sufficient approximation[12].

DISCUSSION

From equations (2) and (3) complex formation will occur provided that:

$$\varepsilon(3\text{EO–NaX–intra})+\varepsilon(3\text{EO–NaX–inter})+\varepsilon(3\text{EO}) < E(\text{NaX})+E(3\text{EO})-\varepsilon(\text{NaX}) \tag{8}$$

The crystallographic data given by Chatani and Okamura for PEO–NaI (*Figure 1*) has been used to compute the terms on the left-hand side of equation (8) and the lattice energy of the ions within the complex, ε(NaI), which appears on the right-hand side. The computed result for ε(NaI) (−540.2 kJ mol^{-1}) is given in *Table 2*, which also shows that the calculations (equation (7)) effectively converged for three unit cells

Table 2 Computed values of the ionic lattice contribution, ε(NaI), the lattice energy of the 3EO–NaI complex (kJ mol^{-1}), from equation (7)

Indices of helix rank (k, l) and unit cell (m) (see text)	Coulombic energy	Born energy	Van der Waals energy	Total, ε(NaI)
$k, l, m=0$	−498.7			
$k, l=0, m=-1$ to 1	−567.6			
$k, l=0, m=-2$ to 2	−573.9			
$k, l=0, m=-3$ to 3	−575.6	57.6	−12.1	−530.1
$k, l, m=-1$ to 1	−585.8			
$k, l=-1$ to 1, $m=-3$ to 3	−585.3			
$k, l=-2$ to 2, $m=-3$ to 3	−577.3			
$k, l, m=-3$ to 3	−584.8	57.6	−13.0	−540.2

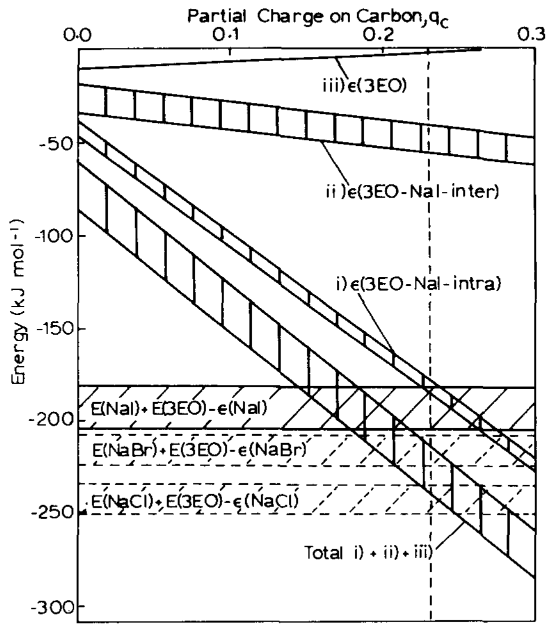

Figure 2 Computed values for components of the lattice energy of PEO–NaI as a function of q_C, the partial charge on carbon ($q_O = -2q_C$). The vertical hatching denotes the range of results for 'high' and 'low' van der Waals parameters (see text and *Table 1*). The 'Total' corresponds to the left-hand side of equation (8). The diagonal hatching denotes the range of results for the total of the terms on the right-hand side of equation (8) between the 'calculated' and 'thermochemical cycle' values for E(NaI), the lattice energy of NaI. Corresponding estimates for PEO–NaBr and PEO–NaCl are given by the broken hatched areas (see text)

on either side of the reference along the direction of c ($m = -3$ to 3) and for the first-neighbour ranks of ion-pair zigzags along a and b directions ($k, l = -1$ to 1). The van der Waals energies in *Table 2* derive from the 'high' set of parameters in *Table 1* (see below); the corresponding energy using the 'low' set was 8 kJ mol^{-1}.

The computed results for the terms on the left-hand side of equation (8) for PEO–NaI are plotted as functions of the partial electronic charge on the carbon atom, q_C ($= -0.5q_O$), in *Figure 2*. The ranges of uncertainty in the plots, denoted by the vertical hatching, represent the differences in the results computed by use of the plausibly 'high' and 'low' van der Waals parameters for the sodium and iodide ions in *Table 1* which afford maximum and minimum van der Waals attractions respectively in interactions involving these ions. Thus, the Pauling radius for I$^-$ (2.2 Å) has been coupled with a 'low' literature value[13] for the polarizability (6.0 Å^3). Noting the internuclear distance between each ion in pure NaI crystals (~3.2 Å), the smaller radius for I$^-$ (1.6 Å) is inferred from the larger radius for sodium (1.6 Å) which is a plausible value for a high coordination number[14] and which was assumed by Wipff *et al.*[15] in their molecular mechanics analysis of the alkali ion complexes of 18-crown-6. The generous 'high' value for the polarizability of I$^-$ (10 Å^3) is greater than the value given by Mott and Gurney[16] (8 Å^3) and is approximately equal to the cube of the ionic radius[17]. However, the ionic radius is the most sensitive of the van der Waals parameters and in order to maintain consistency with the internuclear distance in the pure NaI lattice, the 'high' set of parameters for Na$^+$ was used in conjunction with the 'low' parameters for I$^-$ and *vice versa*. In ε(3EO–NaI–intra), where the ions are in contact, this procedure afforded a narrower range of uncertainty in the computed results than in ε(3EO–NaI–inter) where the range in the results is almost entirely accounted for by the uncertainty in the van der Waals attraction of the iodide ion.

It was found that for ε(3EO–NaI–intra) the computations converged for interactions of the 3EO segment with ion pairs beyond those labelled 4 and 5 in *Figure 1*. The strongest interaction is with Na$^+$ '2' but there are significant interactions with the other ions. For example, with the 'high' set of van der Waals parameters and a partial electronic charge of -0.4 on oxygen the 3EO$\cdots\cdots$Na$^+$ energies for ions 5, 1, 2, 3 and 4 are -19.0, -77.0, -187.6, $+15.5$ and $+12.7$ kJ mol^{-1} respectively. The corresponding 'low' interactions with I$^-$ ions are $+9.9$, $+34.9$, $+38.8$, $+54.8$ and -40.5 kJ mol^{-1} respectively. In view of the convergence of the results for ε(NaI) with the first-neighbour ion-pair zigzags, the computations of ε(3EO–NaI–inter) were also assumed to converge for interactions with first-neighbour zigzags ($k, l = -1$ to 1).

In the computations of ε(3EO) (equation (4)), the bond rotational angles and skeletal bond angles in the sequence of the 3EO segment in the complex (nominally *ttgttgttḡ*) was compared to that of the 7_2 helix in pure PEO crystals (nominally $(ttg)_7$) as reported by Takahashi and Tadokoro[18]. Here t, g and $\bar{g}$ denote nominal bond rotational states having energy minima at 0°, 120° and $-120°$ respectively. The torsional angles in the pure polymer deviate from the angles of the potential minima to a greater extent than those of the complex. On the other hand, the skeletal bond angles in the complex are strained from their tetrahedral values. Thus, the computed results for the corresponding energy differences between the 3EO segment in the complex and an averaged 3EO segment in the pure polymer, ε(tors) = -7.8 kJ mol^{-1} and ε(str) = $+7.3$ kJ mol^{-1}, are mutually compensating. The major contributions to ε(3EO) are therefore those of ε(3EO–inter), which are mainly van der Waals interactions, and the largely Coulombic interactions of ε(3EO–intra). In the latter case, the repulsions between the oxygens coordinating Na$^+$ '2' (relative to their interactions in the more extended conformation in the pure polymer) are principally responsible for the positive slope of ε(3EO) *versus* q_C.

The remaining terms on the right-hand side of equation (8), E(NaI) and E(3EO), were obtained from the literature. The 'thermochemical cycle' value for the lattice energy of pure NaI is -704 kJ mol^{-1} and the calculated value is -682 kJ mol^{-1} (ref. 19). The lattice energy of the pure 3EO segment was taken to be the negative of its energy of vaporization, E_{vap}. This may be deduced from the solubility, or 'Hildebrand', parameter for PEO which is defined by $(E_{\text{vap}}/V)^{1/2}$ and is reported[20] to have a value of 20 (J cm^{-3})$^{1/2}$. Taking the density of crystalline PEO to be 1.33 g cm^{-3}, a value for $-E_{\text{vap}}$ of -300 J g^{-1} or -39.7 kJ (mol of 3EO segment)$^{-1}$ is obtained.

The total energy of the three terms on the right-hand side of equation (8) for PEO–NaI is drawn as a horizontal band with diagonal hatching in *Figure 2*. The width of the band corresponds to the difference between thermochemical cycle and calculated values for E(NaI).

The vertical broken line in *Figure 2* at $q_C = 0.23$ ($q_O = -0.46$) indicates the partial charge distribution in the C–O bond (bond moment 0.99 Debye[21]) employed by Mark and Flory[22] in their treatment of the dipole

Table 3 Lattice energies (kJ mol^{-1}) of sodium halides in pure salts and complexes

	E(NaX), calc.[a]	Coulombic part of ε(NaX)	n	Van der Waals energy	ε(NaX)	E(NaX) + E(3EO) − ε(NaX)	E(NaX), cycle[a]
NaI	−682	−585[b]	10	−13[b]	−540[b]	−182	−704
NaBr	−731	−625[c]	9	−6[c]	−562[c]	−208	−747
NaCl	−769	−647[c]	8	−3[c]	−570[c]	−238	−786

[a] See Ref. 19

[b] See *Table 2*

[c] Estimated results, see text

moments of PEO oligomers. This charge distribution clearly renders the criterion for complex formation in PEO–NaI according to equation (8) consistent with observation in that the total of the left-hand side terms has a greater negative value than the total of the right-hand side terms regardless of uncertainties in the van der Waals energies or in the lattice energies. In their analysis of cation·····18-crown-6 complexes, Wipff and coworkers[15] considered that the oxygen atom adopts a partial charge of −0.3 in the uncomplexed crown ether but that a charge of −0.6 ($q_C = 0.3$) should be assigned in the complex. The adoption of the latter charge distribution would afford an even greater margin of stability for PEO–NaI.

However, a requirement for some constraint on the fall in energy with complex formation is suggested by experimental observation. Thus, while complex formation in PEO–NaBr is observed (unit-cell data have been reported by Hibma[23]), NaCl invariably phase separates from mixtures with PEO; a complex of the latter system is apparently thermodynamically unstable. A computational analysis of the energy of the PEO–NaBr system must await detailed crystallographic data for this system. However, Hibma[23] has concluded that the stoichiometry of PEO–NaBr is the same as in PEO–NaI and that the unit cell is also monoclinic with $a = 16.1$ Å, $b = 16.2$ Å, $c = 7.6$ Å and the non-orthogonal angle (assigned to 'β' by Hibma) is 96°. Taking Hibma's unit cell to correspond to twice the dimension along b of Chatani and Okamura's for the PEO–NaI system it seems likely that PEO–NaBr is essentially isomorphous with PEO–NaI with the PEO helix contracting somewhat along c to accommodate the smaller anion.

An estimate of ε(NaBr) can be made by assuming that, like PEO–NaI, by far the major contribution to the Coulombic energy in ε(NaBr) is from the intramolecular cation–anion contacts along the zigzag (see *Table 2*). To good approximation these interactions should therefore be inversely proportional to the cation–anion internuclear separation. In PEO–NaI, consecutive cation–anion separations are 3.20 and 2.91 Å (ref. 8). For the purpose of estimating ε(NaBr), mean interionic distances of 3.10 and 2.90 Å are assumed for $Na^+ \cdots\cdots I^-$ and $Na^+ \cdots\cdots Br^-$ contacts respectively. The Coulombic part of ε(NaBr) is then estimated to be $-585 \times 3.10/2.90$ or -625 kJ mol^{-1}. The Born n value for NaBr is 9 (ref. 10). Since the anion·····anion interactions make the largest contribution to the van der Waals energy in ε(NaX), these may be assumed to vary approximately as the square of their polarizabilities. Taking the polarizabilities of I^- and Br^- to be $\simeq 6$ $Å^3$ and $\simeq 4$ $Å^3$ respectively[13], the van der Waals contribution to ε(NaBr) is estimated to be approximately -6 kJ mol^{-1}, giving -562 kJ mol^{-1} in total. Thus, the total terms on the right-hand side of equation (8) amount to -208 kJ mol^{-1} (*Table 3*).

An estimate of the hypothetical quantity, ε(NaCl), may be made by similar reasoning to that for ε(NaBr). Taking the cation–anion internuclear distance to be 2.80 Å and the polarizability of Cl^- to be $\simeq 3$ $Å^3$ in this case, the results given in *Table 3* are obtained. The estimated totals for the right-hand side of equation (8) for both PEO–NaBr and PEO–NaCl are drawn in *Figure 2*. The range of the results in each case which correspond to the differences in calculated and thermal cycle values for E(NaX) are shown by the broken hatching.

Estimates of the left-hand side totals of equation (8) for the PEO–NaBr and PEO–NaCl systems are rather more speculative in the absence of crystallographic data and no attempt has been made to quantify these terms in this work. However, the small difference in the fibre repeat distances of the PEO–NaI and PEO–NaBr systems suggests minor differences in the helical conformations so that the major contribution, which is the ε(3EO–NaX–intra) interactions, should be very similar in each case. The increase in oxygen–oxygen repulsions in ε(3EO) with reduction in the fibre repeat should be offset to some degree by simultaneous increases in intermolecular Coulombic attractions in ε(3EO–NaI–inter) with reduction in the volume of the unit cell. However, a small reduction in the van der Waals total for the left-hand side terms of the PEO–NaBr relative to PEO–NaI and a larger reduction for the PEO–NaCl system are to be anticipated in view of the progressively smaller polarizabilities of the smaller anions.

The results in *Figure 2* afford a plausible interpretation of observations bearing in mind the limitations of the analyses. The observations are consistent with the partial charge distribution employed by Mark and Flory or with slightly lower partial charges on the skeletal atoms of the polyether. However, the distribution advocated by Wipff *et al.* for 18-crown-6 complexes ($q_C = 0.3$) may perhaps allow too great a stability of the complexed system so as incorrectly to predict complex formation in PEO–NaCl. Further crystallographic analyses and energy computations of PEO–alkali salt systems should assist in establishing ground rules for complex formation in this class of materials.

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