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A Transferable Interatomic Potential for Alkali Chlorates and Bromates

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Abstract

Interatomic potential parameters obtained *via* empirical fitting techniques provide good agreement between predicted and experimentally derived structural parameters for a range of alkali chlorate and bromate salts, as well as a double chlorate/bromate salt. Examination of the transfer of these parameters to modelling the structural properties of the divalent salt strontium chlorate provided a reasonable, albeit poorer, reproduction of the experimental data. Calculated elastic constants for all materials are provided.

1. Introduction

The increasing use of molecular, surface, interface and solid-state modelling techniques in defining the processing properties of particulate solids is currently restricted to materials that have well defined interatomic potential parameters. Whilst well established interatomic potential data has been available for simple organic solids, those for molecular ionic systems, where long-range forces are much more important, have only been developed more recently. In recent work, however, potential parameters for carbonates (Jackson & Price, 1992), sulfates (Allan, Rohl, Gay, Catlow, Davey & Mackrodt, 1993), phosphates (Telfer, Wilde, Jackson, Meenan & Roberts, 1996) and perchlorates (Roberts, Telfer, Jackson, Wilde & Meenan, 1995; see also Jackson *et al.*, 1995) have been developed, thus providing, for the first time, an improvement in our capabilities to model this range of industrially important materials. In this paper, we extend this work to examine the modelling of some alkali chlorate and bromate salts. This group of materials is important in the pulp and paper industry, as defoliants and herbicides in the agricultural industry, and in the manufacture of pyrotechnic devices. In addition, the extension of the potentials developed for the alkali salts to divalent chlorate salts is also considered.

2. List of symbols

$E_{\rm cr}$	lattice energy
$q_{i,j}$	charge on atom i,j
r_{ij}	separation distance
Φ_{ij}	two-body interaction, *e.g.* Buckingham, Morse *etc.*
A, ρ, C	potential parameters for Buckingham form
D_e	depth of potential-energy minimum
β	$(\mu/2D_e)^{1/2}\omega$
μ	reduced mass of molecule
ω	frequency
r_o	equilibrium bond length
k_b	bond-bending force constant
Θ	coordinate angle
Θ_o	equilibrium coordinate angle

3. Computational methodology

The overall approach to the empirical derivation of interatomic potential parameters (where the interatomic interactions are deduced from the macroscopic properties of the substance) is embodied by the *GULP* program (Gale, 1992–97). The crystal structure of the compound together with structural information (*e.g.* elastic constants) are taken as observables. Therefore, any attempt at producing a model of the interatomic potential should, as well as possible, reproduce these. The form and exact value of the potential, at a given ion–ion distance, depend on the values of these parameters appropriate to the correct reproduction of the observables. This is known as fitting since the variable parameters are fitted to the observables and is summarized in Fig. 1. During the procedure, weights are involved and so there is no unique parameter set. The weighting factors used were 1000.0 for cell strains, 10 000.0 for fractional

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coordinates and 1.0 for elastic constants. The values chosen reflect a number of points. Firstly, the relative magnitudes of the quantities involved. Secondly, the crystallographic data are more reliable than the elastic constants and therefore are higher in weight. Finally, unless the crystallographic data are well reproduced, there is no point in getting the elastic data to high accuracy as this is not particularly meaningful. Hence, there is further argument for increasing the weight on the crystal structure.

It is important to choose realistic and physically sensible starting values for parameters to be fitted as there is the possibility of local minima in parameter space. Initial values can be taken from potentials that have already been fitted to, say, binary oxides with intramolecular parameters obtainable from quantum-mechanical calculations.

It is necessary to obtain the equilibrium configuration if crystal properties are to be calculated. In order to achieve this, the total energy of a system (comprising the short-range and Coulombic interactions) must be minimized with respect to the lattice ion positions. The theory behind the energy minimization and the calculation of lattice properties may be found elsewhere (Jackson & Catlow, 1988; Catlow & Mackrodt, 1982).

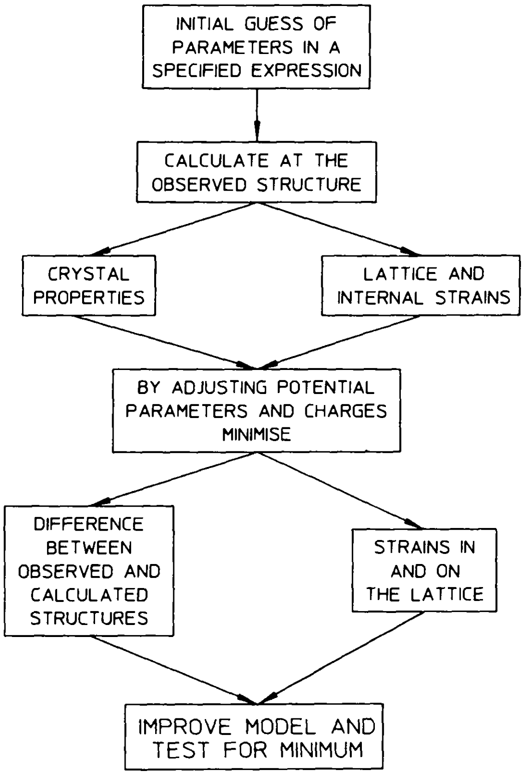

Fig. 1. Flow chart illustrating the fitting procedure used to obtain empirical atom–atom potentials, after Roberts, Telfer, Jackson, Wilde & Meenan (1995).

A classical approach based on the Born model was applied. In this model, it is postulated that the total energy of a system can be separated into two components, *e.g.* the lattice energy ($E_{\rm cr}$) of a two-bodied system may be described as follows:

$$E_{\rm cr} = \sum_{i>j} [q_i q_j / r_{ij} + \Phi_{ij}(r_{ij})]. \qquad (1)$$

The first term represents the standard electrostatic interaction based on Coulomb's law, where q_i, q_j are the charges on the ions i, j, and r_{ij} is the separation distance. The second term represents two-body central force atomic interactions, for example, as given by the Buckingham form:

$$\Phi_{ij} = A\exp(-r/\rho) - Cr^{-6} \qquad (2)$$

or Morse potential form:

$$\Phi_{ij} = D_e(\{1 - \exp[-\beta(r - r_o)]\}^2 - 1), \qquad (3)$$

where A, ρ, C, D_e, β and r_o are the potential parameters for the forms used, which are derived in this work. The Born model may be further enhanced by the inclusion of three-bodied interaction potentials, such as bond bending, which are important in modelling systems with a significant covalent component:

$$E_B = \tfrac{1}{2}k_b(\Theta - \Theta_o)^2. \qquad (4)$$

In this equation, which is used in this work to represent the O—Cl—O bond within the anion, k_b is the bond-bending constant and the expression in parentheses describes the deviation from the equilibrium coordinate angle Θ_o. Including this potential form is a major contributor in enhancing the degree of accuracy of the simulation of any system containing a significant amount of covalency and angle-dependent forces (Catlow, Freeman, Islam, Jackson, Leslie & Tomlinson, 1988; Parker Kelsey, Oliver & Titiloye, 1993). A more detailed account of the potential fitting procedure can be found in an article by Gale (1996).

4. Results and discussion

4.1. *An interatomic potential for sodium chlorate and its transferability to other chlorate salts*

For the chlorate potentials, the initial structure considered was that of sodium chlorate. It crystallizes in a cubic structure ($P2_13$), where $a = 6.575$ Å and there are four formula units within the unit cell (Burke-Laing & Trueblood, 1977). A quantum-mechanical optimization of the gas-phase anion was performed at the MP2/6-31G** level using the program *CADPAC* (Amos *et al.*, 1994). Although many ionic and partially ionic materials have been successfully modelled with formal charges, thus removing the ambiguity in assigning charges, molecular systems are more readily treated using partial charges within the anion. Hence, we initially assigned the monopoles within the chlorate species according to the Mulliken analysis from the quantum-mechanical calculation. Subsequently during fitting, the charge distribution was allowed to optimize subject to the constraint that the total charge on the anion remained -1. Fixing the charges once and for all from the gas-phase calculation, according to any definition of charge, is unrealistic as the ionicity will change significantly in the crystalline potential. The results of the quantum-mechanical calculation also provided information about the molecular geometry for the isolated anion. If these data are used to determine the equilibrium bond lengths and angles for any bond-stretching and bond-bending potentials then any distortions can be attributed to the crystal packing forces.

It is often beneficial to fit to multiple structures at the same time, as a single-structure fit can lead to unphysical parameters for some terms because of the heavy bias towards one structure. *I.e.* if a single structure only is fitted, the potentials may not always have sensible values from an empirical fit due to any errors in the data being fitted. With a fit to multiple structures, any errors in the observables, if they are random rather than systematic, will be smoothed out. This was the route adopted for the chlorate example.

The sodium chlorate system was fitted simultaneously with potassium chlorate, which crystallizes in a monoclinic ($P2_1/m$) structure, with $a = 4.657$, $b = 5.591$, $c = 7.099$ Å and $\beta = 109.648°$ and two formula units in the unit cell (Danielson, Hazell & Larsen, 1981). From examination of the structure, it was decided to treat any interaction between Na and Cl as being purely Coulombic. The repulsive intermolecular potential between O atoms was taken to be that of Catlow, Freeman, Islam, Jackson, Leslie & Tomlinson (1988), determined using *ab initio* Hartree–Fock methods for the $O^- \cdots O^-$ interaction, though again the Coulomb term dominates the repulsion. The main short-range force between the O atoms comes from the attractive term mimicking dispersion, the coefficient for which was fitted.

The short-range potential parameters for sodium chlorate are shown in Table 1 along with the metal–oxygen parameters for the transferred potentials. (The metal–oxygen parameters are re-fitted for the additional systems as the transferability refers to the anion potential only.) Table 2 shows the Morse potential interactions for the chlorate and bromate systems. Rows 1 and 2 of Table 3 show the comparison of the calculated and observed (in parentheses) lattice parameters for sodium and potassium chlorate. From these it can be seen that the fit of the chlorate potential is very good and the results show excellent agreement. This agreement can be backed up further by looking at the bond lengths, distances, fractional coordinates and elastic constants, where available (Srinivasan & Gopal, 1975), which are detailed in Tables 1 to 7. These confirm that the potential fit is good for the two systems, with the change in bond lengths (Table 4) and distances (Table 5) being minimal and the greatest change in any one fractional coordinate (Table 6) being 0.015. These results also show the sodium to be in an octahedral arrangement. As detailed above, experimental elastic constants are available for the sodium system. These also compare well with calculated values. Experimental data were not available for $KClO_3$. However, a study of the phonon frequencies reveals that the phonons are all real and so it can be assumed that the crystal is in the correct space group (for the local minimum that is being considered) and is symmetry stable.

Table 1. *Short-range potential parameters*

C (eV Å^6) = 0 for cation–oxygen interaction and 30.273 for O–O interaction. Charges ($|e|$): $q(\mathrm{Na}) = 1.0$; $q(\mathrm{K}) = 1.0$; $q(\mathrm{Rb}) = 1.0$; $q(\mathrm{Sr}) = 2.0$; $q(\mathrm{Cl}) = 0.927$, $q(\mathrm{O}) = -0.642$ for chlorates; $q(\mathrm{Br}) = 2.313$, $q(\mathrm{O}) = -1.104$ for bromates.

	Interaction	A (eV)	ρ (Å)
$NaClO_3$	Na–O	645.733	0.2973
	Cl–O	893.286	0.3088
	O–O	22764.300	0.1490
$KClO_3$	K–O	1161.395	0.3056
$RbClO_3$	Rb–O	12542.298	0.2589
$NaBrO_3$	Br–O	4501.636	0.3030
$KBrO_3$	K–O	58741.223	0.2199
$SrClO_3$	Sr–O	1101.450	0.3276

Table 2. *Morse and bond-bending potential parameters for the chlorate and bromate systems*

	Interaction	D_e (eV)	β (Å^{-1})	r_o (Å)	k_b (eV rad^{-2})	Θ (°)
Chlorate	Cl–O	5.000	1.8029	1.498	8.751	112.6
Bromate	Br–O	5.249	0.7678	1.504	7.698	120.9

Table 3. *Calculated lattice parameters for chlorate and bromate systems*

Experimental data are given in parentheses.

	Lattice parameter			
	a (Å)	b (Å)	c (Å)	β (°)
$NaClO_3$	6.563			
	(6.575)			
$KClO_3$	4.663	5.581	7.106	109.643
	(4.657)	(5.591)	(7.099)	(109.648)
$RbClO_3$	6.320		8.011	
	(6.092)		(8.173)	
$NaBrO_3$	6.701			
	(6.705)			
$KBrO_3$	6.174		8.192	
	(6.011)		(8.152)	
$Na(ClO_3)_{0.7}(BrO_3)_{0.3}$	6.598			
	(6.630)			
$Sr(ClO_3)_2$	13.051	11.032	7.430	
	(12.535)	(11.457)	(7.482)	

Table 4. *Comparison of halogen–oxygen bond lengths in the chlorate and bromate systems before (in parentheses) and after minimization*

	Halogen–oxygen bond length (Å)
$NaClO_3$	1.50 (1.49)
$KClO_3$	1.49 (1.48)
$RbClO_3$	1.49 (1.48)
$NaBrO_3$	1.63 (1.65)
$KBrO_3$	1.61 (1.65)
$Na(ClO_3)_{0.7}(BrO_3)_{0.3}$	1.54 (1.57)
$Sr(ClO_3)_2$	1.47 (1.45)
	1.50 (1.47)
	1.50 (1.51)

Table 5. *Comparison of metal–oxygen distances in the chlorate and bromate systems before (in parentheses) and after minimization*

	Metal–oxygen distance (Å)
$NaClO_3$	3 × 2.4089 (2.4165)
	3 × 2.4778 (2.4967)
$KClO_3$	2 × 2.8096 (2.8077)
	1 × 2.8200 (2.8223)
	2 × 2.8206 (2.8614)
	2 × 2.9100 (2.9489)
	2 × 3.1868 (3.1223)
$RbClO_3$	3 × 3.2011 (3.1723)
	6 × 3.2117 (3.1163)
$NaBrO_3$	3 × 2.3335 (2.4080)
	3 × 2.5874 (2.5170)
$KBrO_3$	3 × 3.0000 (2.9291)
	6 × 3.1517 (3.0632)
$Na(ClO_3)_{0.7}(BrO_3)_{0.3}$	3 × 2.3859 (2.4181)
	3 × 2.5153 (2.5057)
$Sr(ClO_3)_2$	2 × 2.5741 (2.5862)
	2 × 2.6255 (2.6099)
	2 × 2.6178 (2.6380)
	2 × 2.6773 (2.6746)

A test of the transferability of the chlorate potential was carried out by taking the parameters for the chlorate anion and using them in an energy minimization of rubidium chlorate (the Rb—O Buckingham parameter being re-fitted as described earlier). This material crystallizes in a trigonal structure (*R*3*m*) with $a = 6.092$, $c = 8.173$ Å, $\beta = 120°$ and three formula units in the unit cell (Brunton, 1973). The potential parameters are again given in Tables 1 and 2, with the agreement between observed and calculated lattice parameters shown in Table 3. The transference, although reasonable, is not ideal. One reason for this may be because of significant metal polarizability, which is neglected in this work so far. Also, oxygen polarizability is ignored. This limitation reflects the difficulties associated with combining partial charges with the shell model (Dick & Overhauser, 1958). The bond lengths and fractional coordinates are in better agreement than the lattice parameters initially indicate, with the exception of the z values.

Table 6. *Comparison of calculated and observed (in parentheses) fractional coordinates for the chlorate and bromate systems*

	Atom	x	y	z
$NaClO_3$	Na	0.070	0.070	0.070
		(0.068)	(0.068)	(0.068)
	Cl	0.422	0.422	0.422
		(0.418)	(0.418)	(0.418)
	O	0.298	0.592	0.508
		(0.303)	(0.593)	(0.505)
$KClO_3$	K	0.344	0.250	0.694
		(0.354)		(0.709)
	Cl	0.135	0.250	0.174
		(0.122)		(0.176)
	O	0.400	0.250	0.101
		(0.396)		(0.115)
	O	0.151	0.468	0.299
		(0.146)	(0.461)	(0.305)
$RbClO_3$	Rb	0.000	0.000	0.979
				(0.000)
	Cl	0.000	0.000	0.544
				(0.466)
	O	0.128	0.872	0.479
		(0.129)	(0.871)	(0.398)
$Sr(ClO_3)_2$	Sr	0.000	0.000	0.000
	Cl	0.982	0.302	0.067
		(0.980)	(0.304)	(0.065)
	O	0.064	0.215	0.123
		(0.058)	(0.211)	(0.119)
	O	0.146	0.022	0.242
		(0.131)	(0.010)	(0.271)
	O	0.947	0.869	0.729
		(0.958)	(0.870)	(0.726)
$NaBrO_3$	Na	0.092	0.092	0.092
		(0.078)	(0.078)	(0.078)
	Br	0.412	0.412	0.412
		(0.406)	(0.406)	(0.406)
	O	0.282	0.595	0.507
		(0.287)	(0.597)	(0.508)
$KBrO_3$	K	0.000	0.000	0.000
	Br	0.000	0.000	0.443
				(0.483)
	O	0.139	0.861	0.369
		(0.145)	(0.855)	(0.400)
$Na(ClO_3)_{0.7}(BrO_3)_{0.3}$	Na	0.078	0.078	0.078
		(0.072)	(0.072)	(0.072)
	Br	0.419	0.419	0.419
		(0.410)	(0.410)	(0.410)
	Cl	0.419	0.419	0.419
		(0.410)	(0.410)	(0.410)
	O	0.295	0.593	0.500
		(0.296)	(0.594)	(0.506)

4.2. *Extension of the potential to the modelling of alkali bromate salts*

Sodium bromate is isomorphous with the sodium chlorate system, having $a = 6.705$ Å (Templeton & Templeton, 1985). As the bromate system is very similar to the chlorate, the values of the chlorate potential were taken as the starting point for the bromate fit. This was carried out in a similar manner to the previous transfer, but in this case the metal–oxygen parameter was left

Table 7. *Calculated elastic constants (10^{10} Pa) with experimental values, where available, given in parentheses*

Elastic constant	$NaClO_3$	$KClO_3$	$RbClO_3$	$NaBrO_3$	$KBrO_3$	$Na(ClO_3)_{0.7}$-$(BrO_3)_{0.3}$	$Sr(ClO_3)_2$
C_{11}	3.47 (4.89)	2.51	3.73	5.34 (5.57)	5.78	4.63	6.61
C_{12}	1.52 (1.38)	1.72	1.24	2.04 (1.70)	1.73	1.42	1.28
C_{13}		1.02	1.00		1.84		2.28
C_{14}			−0.23		−0.52		
C_{15}		−0.18					
C_{22}		2.42	3.73		5.78		2.48
C_{23}		0.19	1.00		1.84		1.95
C_{24}			0.23		0.52		
C_{25}		−0.08					
C_{33}		2.22	2.38		4.19		2.84
C_{35}		−0.42					
C_{44}	0.67 (1.17)	0.46	0.84	1.81 (1.57)	1.93	1.01	1.17
C_{46}		−0.33					
C_{55}		0.73	0.84		1.93		2.20
C_{56}			−0.23		−0.52		
C_{66}		1.37	1.25		2.03		0.62

untouched and the interactions involving bromine were re-fitted.

These parameters were then transferred to a different bromate system, in this case the potassium salt, which crystallizes in a trigonal structure (*R*3*m*) with a = 6.011, c = 8.152 Å and three formula units in the unit cell (Templeton & Templeton, 1985). The potential parameters (including the metal–oxygen parameter for its transfer to potassium bromate) are given in Tables 1 and 2. Again, the comparison of the lattice parameters, elastic constants (where available), fractional coordinates and bond lengths show a consistent fit of the potential. These results are given in Tables 3 to 7. From the results arising from both of these calculations, the main discrepancy in the fractional coordinate results is in that of the Na atom, however the lattice parameters are still in reasonable agreement, as are bond lengths. Calculated elastic constants can be compared very favourably for the sodium bromate and again, although no experimental data are available for the potassium case, the indices are reported.

4.3. *Simulation of the double salt $Na(ClO_3)_{0.7}(BrO_3)_{0.3}$*

The mixed chlorate/bromate compound $Na(ClO_3)_{0.7}(BrO_3)_{0.3}$ is isomorphous with the parent salts having a lattice parameter a = 6.630 Å and four formula units per unit cell (Raja, Mohanlal & Chandrasekaran, 1984). Within *GULP*, a 'partial-occupancy' calculation can be carried out. Here, a mean-field approximation is used in which the parameters for a single molecule are the weighted averages (according to the occupancies) of the chlorate and bromate potentials. From a physical viewpoint, the Br—O and Cl—O bond lengths would be different owing to the difference in the ionic radii of bromine and chlorine. However, only the averaged bond length is obtained in this approach. In the case of this mixed system, the potential parameters were not re-fitted. Therefore, the potential parameters from the individual chlorate and bromate fits were input to the mixed system and minimized using the partial occupancy mode, which allowed both sets of charges and both sets of parameters to be employed in the minimization at a ratio of 70:30. From the figures detailed in Tables 3 to 7, it can be seen that the potential parameters for the singular sodium chlorate and bromate can be successfully applied to the mixed compound. Despite the absence of experimental elastic constants, it is clear that the values are consistent with those of the mother chlorate and bromate sodium salts.

4.4. *Transfer of the potential to a divalent salt: strontium chlorate*

The transferability of the potential to a chlorate salt containing a divalent cation was carried out using the same method as that for the rubidium chlorate but using crystal data for strontium chlorate. This crystallizes in an orthorhombic structure (*Fdd*2) with a = 12.353, b = 11.457, c = 7.482 Å and eight formula units in the unit cell (Lutz, Buchmeier, Alici & Eckers, 1985). The agreement between the observed and calculated lattice parameters in Table 3 is not ideal with the unit cell being slightly distorted in the a and b directions. However, bond lengths (Table 4) compare well as do the fractional coordinates, in general (Table 6). The discrepancy in the lattice parameters could be because we are examining a different part of the energy surface, as the anion density will differ with a doubly charged cation. *I.e.* the average distance between anions will be different in mono- and divalent metal compounds as the ratio of metal to anion is different, therefore different anion–anion distances are being sampled.

5. Conclusions

The results indicate a good empirical fit and subsequent transfer of an interatomic potential for chlorate and bromate systems. Agreement between experimental and calculated lattice parameters is very good showing that the potentials transfer well to the other compounds considered, which include different systems and structure types, not to mention a mixed chlorate/bromate system. For the elastic constant data, experimental values are not always available but where this information does exist the agreement with calculated values is generally acceptable.

The shape of crystals prepared in industrial crystallization processes is important, as an inadequately defined crystal morphology may have a detrimental impact on particulate properties such as ease of separation, caking, packing density, dissolution rate, handling, packaging and storage. The interatomic potentials derived herein could be of significant use within the sphere of process engineering and particulate technology to predict crystal properties such as morphology and elastic properties. The former applicability has been demonstrated in the case of perchlorates (Roberts, Telfer, Jackson, Wilde & Meenan, 1995). In turn, this will also lead to an ability to predict the effect of additives and solvents on particle shape. In the latter case, effects associated with mechanical action in bulk industrial crystallization, such as secondary nucleation and attrition, can also be predicted using the derived potential data.

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