

Computer modelling of solid alkali metal carboxylates

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 9389

(<http://iopscience.iop.org/0953-8984/12/45/302>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 06:57

Please note that [terms and conditions apply](#).

Computer modelling of solid alkali metal carboxylates

L S Barreto†‡§, K A Mort†, R A Jackson†|| and O L Alves‡

† Lennard-Jones Laboratories, School of Chemistry and Physics, Keele University, Keele, Staffordshire ST5 5BG, UK

‡ Instituto de Química, Universidade Estadual de Campinas, Campinas-SP, Brazil

§ Departamento de Química, CCET, UFS, 49.100-000, São Cristóvão-SE, Brazil

E-mail: r.a.jackson@chem.keele.ac.uk

Received 19 July 2000, in final form 29 September 2000

Abstract. A computational study of solid lithium acetate dihydrate and anhydrous sodium acetate is presented. Interatomic potentials are obtained by empirical fitting to experimental structural data for both materials and the resulting potentials were found to be transferable to different phases of the same materials, giving good agreement with the experimental structure.

1. Introduction

Computer modelling methods based on the use of effective potentials are now capable of describing accurately the structure and properties of a wide range of materials. Much attention has been paid to ionic solids [1] and molecular solids [2]. Materials with a degree of covalency have also recently been extensively studied; for example, molecular anionic materials such as alkali phosphates and perchlorates [3–5], molecular cationic materials such as the ammonium halides, and materials such as ammonium nitrate which contain both molecular cations and molecular anions [6, 7].

Materials containing amphiphilic molecules such as surfactants with carboxylate or sulphate head groups, amides and carboxylic acids have also attracted considerable attention due the presence of hydrogen bonding. Such systems are of particular interest since the potentials derived for these materials give a good starting point for the modelling of materials of biological significance [8–10].

This paper is concerned with the alkali metal carboxylates, specifically lithium and sodium acetate. These compounds have been used to prepare glasses with optical transparency (240–1400 nm) and can also be useful as hosts for organic compounds with photochromic, electrochromic, non-linear optic, pharmaceutical, biocidal, fungicidal, or hormonal action properties [11].

Although the glassy phases of these materials are of primary interest in applications, these do not provide a good starting point for the derivation of potentials. Therefore the approach adopted is to use the crystalline phases of the materials to fit potentials, whose validity is tested by transfer to different crystalline phases of the same materials, with a view to using these potentials to model the glassy phases using molecular dynamics [19]. It is noted at this stage that given the complexity of the materials, modelling the crystalline phases is itself a

|| Author to whom any correspondence should be addressed.

considerable challenge, and also that materials such as these have not previously been studied extensively by computer modelling.

2. Computational method

The procedure employed was to obtain the potential using empirical fitting [12]. In this approach, the potential parameters are adjusted until the structure and lattice properties are reproduced to acceptable accuracy. For the alkali metal carboxylates, both bonded and non-bonded interactions are important. Thus the potential form employed must represent both interaction types, and is given below:

- (i) *Non-bonded interactions.* This part of the potential includes electrostatic interactions between ions, and short-range terms involving electron repulsion and van der Waals attraction. The form adopted has been widely used in studies of ionic and molecular ionic materials [1, 3], and is a Buckingham potential (a Born–Mayer potential [20] with an attractive r^{-6} -term added) supplemented by a term to account for ion–ion interactions:

$$V_{ij}(r_{ij}) = q_i q_j / r_{ij} + A_{ij} \exp(-r_{ij} / \rho_{ij}) - C_{ij} r_{ij}^{-6}.$$

In this potential, q_i and q_j are charges of ions i and j at distance r_{ij} , and A , ρ , and C are parameters whose values are obtained in the fitting process.

Formal values of charges can be used for the alkali metal ions, and the carboxylate molecular ion has a formal charge, with the charges of its constituent ions being varied during the potential-fitting process, with the constraint that the overall charge takes the formal value. Guidance on appropriate initial charge values for ions within the molecular ion has been taken from calculations on molecular solids [2].

- (ii) *Bonded interactions.* This part of the potential describes covalent interactions through harmonic bond-stretching and bond-bending terms:

$$V_b(r_{ij}, \theta) = 0.5k_s(r_{ij} - r_0)^2 + 0.5k_b(\theta - \theta_0)^2.$$

Here k_s and k_b are bond-stretching and bond-bending constants; r_0 and θ_0 are the equilibrium bond length and angle respectively. Values of the force constants are obtained by empirical fitting, although guidance on starting values may be available from spectroscopic measurements.

All calculations were carried out using the general utility lattice program (GULP) [13], which is a general-purpose code for empirical potential fitting and lattice energy minimization. This code has now been widely used in modelling of ionic and molecular ionic materials; examples of its use in obtaining potentials for molecular ionic materials are given in [6].

3. Potential fitting to lithium and sodium acetate

3.1. Lithium acetate dihydrate

The crystal structure of lithium acetate dihydrate has been determined at 293 and 1.5 K using neutron powder diffraction [14–16]. The structure at 293 K belongs to the $Cmmm$ space group. The CH_3 groups are dynamically disordered, and there are short hydrogen bonds between the water molecules and the acetate oxygen atoms. There is a phase transition to the low-temperature form, with space group $Pman$. The CH_3 groups are ordered in this phase, but have large thermal ellipsoids even at 1.5 K. The structure consist of layers of water molecules and acetate ions in the xy -plane which are separated by layers of Li ions. There are

two crystallographically distinct water molecules, which are hydrogen bonded to each other (1.85 Å). In addition, one of the water molecules also forms hydrogen bonds (1.79 Å) that link the acetate and water plane.

The potential parameters for lithium acetate dihydrate were obtained by fitting to the orthorhombic structure, space group *Pman* (form I). They are given in table 1. Table 2 shows the comparison of calculated and experimental lattice parameters obtained using this potential. It is seen that the lattice parameters are reproduced to within approximately $\pm 2\%$. Table 3 gives calculated values for the elastic constants. While experimental values of these are not currently available, the values obtained are comparable to those obtained for related materials. The potential parameters were subsequently transferred to form II, space group *Cmmm*. Table 4 gives a comparison of calculated and experimental lattice parameters, with agreement of better than $\pm 3\%$, showing that the potential can be successfully transferred. It is noted that the low-temperature phase transition involves an ordering of the methyl group orientations, along with a small reduction of intermolecular interactions. Potentials for the hydrogen bonds were obtained from literature values [2].

Table 1. Short-range potential parameters for lithium acetate dihydrate. Here w denotes that the atom is part of a water molecule.

Interaction	A (eV)	ρ (Å)	C (eV Å ⁶)
H-H	0.2922	0.2580	0.00
Hw-Hw	377.000	0.263	0.00
Hw-Ow (hydrogen bond)	156522.33	0.1285	14.566
Hw-O (hydrogen bond)	156522.33	0.1285	14.566
H-O	3310.00	0.1976	0.000
Li-Ow	809.8176	0.2352	0.000
Li-O	809.8176	0.2498	0.000
Ow-Ow	5297.2549	0.2410	25.065
O-O	2082.8795	0.3099	14.636
Ow-O	2118.7515	0.3110	22.00

Partial charges on atoms (|e|)

$$q_{\text{Li}} = 1.0, q_{\text{C1}} = 0.12, q_{\text{C2}} = -0.10,$$

$$q_{\text{O}} = -0.60, q_{\text{H}} = 0.06,$$

$$q_{\text{Hw}} = 0.417, q_{\text{Ow}} = -0.834$$

Bond stretching force constants and equilibrium bond lengths

$$k_s(\text{C-H}) = 28.987 \text{ eV \AA}^{-2} \quad r_0 = 1.074 \text{ \AA}$$

$$k_s(\text{C-C}) = 10.000 \text{ eV \AA}^{-2} \quad r_0 = 1.522 \text{ \AA}$$

$$k_s(\text{C-O}) = 34.229 \text{ eV \AA}^{-2} \quad r_0 = 1.242 \text{ \AA} \quad (\text{average value})$$

$$k_s(\text{Hw-Ow}) = 32.904 \text{ eV \AA}^{-2} \quad r_0 = 0.984 \text{ \AA} \quad (\text{average value})$$

Bond bending force constants and equilibrium bond angles

$$k_b(\text{O-C-O}) = 18.113 \text{ eV rad}^{-2} \quad \theta_0 = 124.40^\circ$$

$$k_b(\text{H-C-H}) = 1.574 \text{ eV rad}^{-2} \quad \theta_0 = 108.70^\circ \quad (\text{average value})$$

$$k_b(\text{C-C-H}) = 1.468 \text{ eV rad}^{-2} \quad \theta_0 = 109.64^\circ \quad (\text{average value})$$

$$k_b(\text{C-C-O}) = 1.631 \text{ eV rad}^{-2} \quad \theta_0 = 117.80^\circ \quad (\text{average value})$$

$$k_b(\text{Hw-Ow-Hw}) = 6.913 \text{ eV rad}^{-2} \quad \theta_0 = 107.30^\circ \quad (\text{average value})$$

Table 2. Comparison of observed and calculated lithium acetate structures (form I).

Structural parameter	Observed value [16]	Calculated value	% difference
a (Å)	6.70246	6.65578	−0.70
b (Å)	10.87932	11.05496	1.61
c (Å)	6.56998	6.436571	−2.03
Volume (Å ³)	479.071162	473.5992	−1.14
α, β, γ (deg)	90.0	90	0.00

Table 3. Elastic constants for lithium acetate—form I (units: 10^{11} dyn cm^{−2} = 10 GPa).

	1	2	3	4	5	6
1	3.9823	2.4094	2.4195	0.0000	0.0000	0.0000
2	2.4094	6.1429	4.2584	0.0000	0.0000	0.0000
3	2.4195	4.2584	7.7249	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000	0.2457	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.1170	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.3942

Table 4. Comparison of observed and calculated lithium acetate structures (form II).

Structural parameter	Observed value [16]	Calculated value	% difference
a (Å)	6.82082	6.62712	−2.90
b (Å)	10.88842	11.15063	1.48
c (Å)	6.59911	6.41573	−1.81
α, β, γ (deg)	90.0	90	0.00
Volume (Å ³)	490.10239	474.204189	−3.24

3.2. Anhydrous sodium acetate

Anhydrous sodium acetate exhibits phase transitions that occur over a wide range of temperatures, and there is disagreement as to the number of these transitions. X-ray diffraction has allowed identification of at least three forms of anhydrous sodium acetate. The structures of two different modifications of the anhydrate (forms I and II) have been solved by the use of single-crystal methods and they belong to the *Pcca* space group [17], and a third modification of sodium acetate (β -sodium acetate) belongs to space group *Pmn*2₁ [18].

For form II, crystallographic data have been averaged so as to obey the constraints implied by two contributing structures, *Pcca* and *Icab*. The two structures are related to one another by an $(a + c)/2$ translation of the central layer of acetate and sodium ions, relative to the top and bottom layers, and this translation leaves the interlayer methyl–methyl contacts unaffected. Thus, the packing energies of the two structures are nearly the same, and the structure composed of alternating domains of the two is energetically favourable.

Table 5 gives the potential parameters as fitted to form I of anhydrous sodium acetate and table 6 compares experimental and calculated lattice parameters. Agreement of better than $\pm 3\%$ is obtained. In table 7, the potential is used to calculate the lattice parameters of form II, which are then compared with experimental values. Here, agreement of better than $\pm 1\%$ is achieved, which is significant given that the potential was fitted to a different phase of the material.

Table 5. Short-range potential parameters for anhydrous sodium acetate. (The bond-stretching and bond-bending force constants are the same as for lithium acetate.)

Interaction	A (eV)	ρ (Å)	C (eV Å ⁶)
H–O	3310.00	0.1976	0.0000
H–H	0.2922	0.258	0.0000
H–C	427.6882	0.2382	0.0000
Na–O	2683.7358	0.2406	0.0000
O–O	2082.5177	0.2504	14.636

Equilibrium bond lengths

$$r_0(\text{C–H}) = 1.090 \text{ \AA}$$

$$r_0(\text{C–C}) = 1.518 \text{ \AA}$$

$$r_0(\text{C–O}) = 1.255 \text{ \AA}$$

Equilibrium bond angles

$$\theta_0(\text{O–C–O}) = 123.60^\circ$$

$$\theta_0(\text{H–C–H}) = 109.47^\circ$$

$$\theta_0(\text{C–C–H}) = 109.50^\circ$$

$$\theta_0(\text{C–C–O}) = 118.70^\circ$$

Table 6. Comparison of observed and calculated sodium acetate structures (form I).

Structural parameter	Observed value [17]	Calculated value	% difference
a (Å)	17.850	18.1254	1.54
b (Å)	9.982	9.7925	–1.90
c (Å)	6.068	6.2491	2.98
α, β, γ (deg)	90.0	90.0	0
Volume (Å ³)	1081.188	1109.1605	2.59

Table 7. Comparison of observed and calculated sodium acetate structures (form II).

Structural parameter	Observed value [17]	Calculated value	% difference
a (Å)	5.951	5.9412	–0.16
b (Å)	20.213	20.4145	1.00
c (Å)	5.902	5.9205	0.31
α, β, γ (deg)	90.0	90.0	0.00
Volume (Å ³)	709.9372	718.078	1.15

4. Conclusions

This paper has shown that it is possible to obtain potentials that reproduce the structural properties of alkali metal carboxylates. Reproduction of lattice parameters within a few per cent is obtained, showing the applicability of the potential model to these materials. As has already been noted, the interest in these materials in terms of applications is in their glassy phases, and these will be studied by molecular dynamics, with the results reported in a subsequent paper. However, the availability of an accurate potential is an essential prerequisite to this future work [19].

Acknowledgments

The authors are grateful to CAPES/PICDT (Brazil) for financial support and to Dr J D Gale for the use of the GULP program.

References

- [1] Catlow C R A (ed) 1997 *Computer Modelling in Inorganic Crystallography* (New York: Academic)
- [2] Gavezzotti A 1997 *Theoretical Aspects and Computer Modelling of the Molecular Solid State* (New York: Wiley)
- [3] Jackson R A, Price G D, Meenan P, Roberts K J, Telfer G B and Wilde P J 1995 *Mineral. Mag.* **59** 617
- [4] Jackson R A, Meenan P, Roberts K J, Telfer G B and Wilde P J 1995 *J. Chem. Soc. Faraday Trans.* **91** 4133
- [5] Telfer G B, Wilde P J, Jackson R A, Meenan P and Roberts K J 1996 *Phil. Mag.* **B 73** 147
- [6] Mort K A, Wilde P J and Jackson R A 1999 *J. Phys.: Condens. Matter* **11** 3967
- [7] Jackson R A and Mort K A 2000 *Comput. Mater. Sci.* **17** 230
- [8] Watanabe K and Klein M L 1991 *J. Phys. Chem.* **95** 4158
- [9] Ploeg P V and Berendsen H J C 1982 *J. Chem. Phys.* **76** 3271
- [10] Lifson S, Hagler A T and Dauber P 1979 *J. Am. Chem. Soc.* **101** 5111
- [11] Blair J A, Duffy J A and Wardell J L 1992 *J. Non-Cryst. Solids* **146** 159
- [12] Gale J D 1996 *Phil. Mag.* **B 73** 3
- [13] Gale J D 1997 *J. Chem. Soc. Faraday Trans.* **93** 629
- [14] Galigne J C, Mouvet M and Falgueirettes J 1970 *Acta Crystallogr. B* **26** 368
- [15] Cadene M and Vergnoux A M 1972 *Spectrochim. Acta A* **28** 1663
- [16] Kearley G J, Nicolai B, Radaelli P G and Fillaux F 1996 *J. Solid State Chem.* **126** 184
- [17] Hsu L and Norman C E 1983 *Acta Crystallogr. C* **39** 690
- [18] Helmholdt R B, Sonneveld E J and Schenk H 1998 *Z. Kristallogr.* **213** 596
- [19] Barreto L S, Mort K A, Jackson R A and Alves O L 2000 unpublished
- [20] Born M and Mayer J E 1932 *Z. Phys.* **75** 1