Vapor pressures and lattice energies of oxalic acid, mesotartaric acid, phloroglucinol, myoinositol, and their hydrates

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Vapor pressures and lattice energies of oxalic acid, mesotartaric acid, phloroglucinol, myoinositol, and their hydrates

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In the present investigation, we report the enthalpy of dehydration and the enthalpy of sublimation of a number of organic hydrates and their anhydrous counterparts. These values are used to test the transferability of a set of atom–atom potential parameters, originally derived for carboxylic acids. The calculations showed that the parameter set was transferable to a fairly good degree.

I. INTRODUCTION

During the last few years, our group has been occupied with the study of the relations between structural and thermodynamic properties of molecular crystals containing hydrogen bonds. For this purpose, the method of atom–atom potentials is used. In order to test the transferability of a set of atom–atom potential parameters and especially those belonging to the description of the hydrogen bond derived by Derissen and Smit for carboxylic acids,[1] we undertook the present investigation. The systems chosen as the subject for this investigation were hydrates which form a group of physiologically and pharmacologically interesting compounds. Hydrates are in fact hydrogen-bonded, stoichiometric, complexes of water and the anhydrous molecules. In order to relate measured and calculated properties, we extracted structural information from the Cambridge crystallographic data file. Since the enthalpies of sublimation and enthalpies of dehydration are not known, (with a few exceptions) we determined them from the temperature dependence of the vapor pressures of the hydrates and their anhydrous counterparts.

II. EXPERIMENTAL

A. Samples

Oxalic acid. $2H_2O$, phloroglucinol. $2H_2O$, and meso-tartaric acid. $1H_2O$, were obtained from British Drug Houses (England). The anhydrates were prepared by prolonged evacuation of the hydrate and subsequent vacuum sublimation. Myoinositol was obtained from Sigma (USA) and purified by vacuum sublimation. A concentrated solution in water was made and the water was allowed to evaporate at temperatures below 20 °C. After filtration, the wet crystals were dried in a vacuum desiccator over the anhydrate which was kept at a slightly higher temperature than the hydrate.

B. Static vapor pressure measurements

Water vapor pressures over the solid hydrates were measured using a diaphragm capacitance manometer, MKS Baratron Inc. Model 94 AH (133 kPa full scale). The gauge was calibrated against a Consolidated Elec-trodynamics Corp. dead weight tester. The temperature was measured with a platinum thermometer calibrated against the 1968 International Practical Temperature scale (IPTS-68) to an accuracy of 0.01 K. A detailed description of the setup has been given previously.[2]

C. Dynamic vapor pressures

Vapor pressures of the anhydrates were measured with a simultaneous torsion and mass loss effusion technique. We used an effusion cell with two orifices, 1 mm in diam and 20 mm apart. Temperature was measured with thermistors calibrated on IPTS-68 and accurate within 0.05 K. A description of the setup is given elsewhere.[3,4]

III. EVALUATION OF THERMODYNAMIC PROPERTIES

A. Vapor pressure

The experimental vapor pressures as a function of temperature are fitted according to Clark and Glew[23] to

$$R \ln(p/p_0) = -\Delta G(\theta)/\theta + \Delta H^\circ(\theta)$$
$$\times (1/\theta - 1/T) + \Delta C_p^\circ(\theta)(\theta/T - 1 + \ln T/\theta) \quad (1)$$

in which p is vapor pressure, T is temperature, p_0 a reference pressure (1 Pa), θ is a reference temperature (usually chosen midrange), $\Delta G^\circ(\theta)$ is the Gibbs energy at temperature θ of vapor minus condensed phase, likewise $\Delta H^\circ(\theta)$ and $\Delta C_p^\circ(\theta)$. In a number of cases $\Delta C_p^\circ(\theta)$ is not significantly different from zero. In these cases, only the first two terms, $\Delta G^\circ(\theta)$ and $\Delta H^\circ(\theta)$, are evaluated. The error ranges in the coefficients are root mean square values. Accuracy limits are estimated not to exceed twice these values.

B. Lattice energies

We employed a Buckingham potential with an additional Coulombic potential and a Lippincott–Schroeder potential to describe the hydrogen bond. For the non-bonded parameters, we chose set III from the work of Derissen and Smit (1978).[1] To describe the Coulombic energy we used an atom-centered monopole point-charge
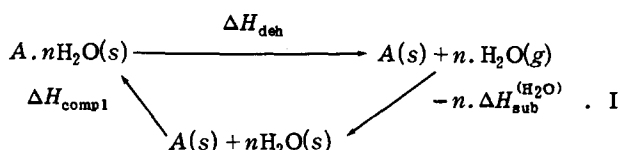
model, where the point charges were derived from Mulliken populations analyzed using CNDO/2 wave functions. This was done in order to be consistent with the work of Derissen and Smit, who used the same model in their derivation of the atom–atom and hydrogen-bond potential parameters. The convergence acceleration method of Williams (1971) was used with a convergence constant of 0.30 and limits of 6 Å and 0.6 Å^{-1} for summations in the direct and reciprocal space.[5] The crystal structures as reported in the literature[6-19] were used, except for the positions of the hydrogen atoms. We located the hydrogen atoms as follows:

(1) Aliphatic hydrogen atoms were placed at 1.09 Å with tetrahedral angles.

(2) Hydrogen atoms attached to a ring compound were placed at 1.09 Å, with the C–H bond in the plane formed by a C atom to which it is attached and the two neighboring C atoms, bisecting the C–C–C angle.

(3) Hydroxylic hydrogen atoms were all placed at a distance of 1.01 Å from the oxygen atoms to which it is attached on the line between the two oxygen atoms involved in the hydrogen bond.
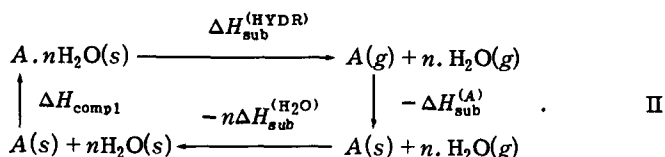
In the case of the oxalic acid hydrate, the atomic positions were taken from the neutron diffraction experiment of the deuterated compound. For the structure of ice, we took the proton ordered hexagonal structure according to Santry,[6] who used the neutron structure of Peterson and Levi as a basis.[7]

For mesotartaric acid monohydrate we follow the remark of Bootsma and Schoone, using the triclinic form as the stable one at room temperature.[15]

The only species evaporating from the hydrates is water. Similar things happen for instance, in quinhydrone complexes[22] and TTF-TCNQ complexes.[24] Therefore, it is necessary to have a closer look at the mechanism involved in the measurements and the ones used in our calculations. The sublimation process (I) is

$$
\begin{array}{ccc}
& \Delta H_{\text{deh}} & \\
A \cdot n\text{H}_2\text{O}(s) & \longrightarrow & A(s) + n \cdot \text{H}_2\text{O}(g) \\
\Delta H_{\text{compl}} \searrow & & \nearrow -n \cdot \Delta H_{\text{sub}}^{(\text{H}_2\text{O})} \quad . \quad \text{I} \\
& A(s) + n\text{H}_2\text{O}(s) &
\end{array}
$$

The process used in our calculations (II) is

$$
\begin{array}{ccc}
& \Delta H_{\text{sub}}^{(\text{HYDR})} & \\
A \cdot n\text{H}_2\text{O}(s) & \longrightarrow & A(g) + n \cdot \text{H}_2\text{O}(g) \\
\uparrow \Delta H_{\text{compl}} & -n\Delta H_{\text{sub}}^{(\text{H}_2\text{O})} & \downarrow -\Delta H_{\text{sub}}^{(A)} \quad . \quad \text{II} \\
A(s) + n\text{H}_2\text{O}(s) & \longleftarrow & A(s) + n \cdot \text{H}_2\text{O}(g)
\end{array}
$$

The equations which can be derived from these processes and which relate the observed and calculated quantities are

I: $\Delta H_{\text{deh}} = n * \Delta H_{\text{sub}}^{(\text{H}_2\text{O})} - \Delta H_{\text{compl}}$,   (2)

II: $\Delta H_{\text{compl}} = \Delta H_{\text{sub}}^{(A)} + n * \Delta H_{\text{sub}}^{(\text{H}_2\text{O})} - \Delta H_{\text{sub}}^{(\text{HYDR})}$.   (3)

The specific quantities in Eqs. (2) and (3) have the following meaning:

ΔH_{deh}:   The enthalpy of dehydration (per mole of H_2O)

$\Delta H_{\text{sub}}^{(\text{H}_2\text{O})}$:   The enthalpy of sublimation of ice

$\Delta H_{\text{sub}}^{(A)}$:   The enthalpy of sublimation of the anhydrous form

$\Delta H_{\text{sub}}^{(\text{HYDR})}$:   The enthalpy of sublimation of the hydrate

ΔH_{compl}:   The enthalpy of complexation (per mole of substance).[22]

The calculated values for $\Delta H_{\text{sub}}^{(A)}$, $\Delta H_{\text{sub}}^{(\text{H}_2\text{O})}$, and $\Delta H_{\text{sub}}^{(\text{HYDR})}$ were derived via the relation

$$\Delta H_s = -(|\Delta U_{\text{latt}}| + 2RT) , \qquad (4)$$

where ΔU_{latt} is the lattice energy and the $2RT$ is the correction due to the lattice vibrations.[20]

IV. RESULTS AND DISCUSSION

A. Vapor pressure measurements

In Table I, we give experimental results expressed as coefficients of Eq. (1). For the anhydrates, the value of p_m/p_t,[3] being a measure for association or decomposition, is near unity and so we conclude that no decomposition occurs. A remark must be made on mesotartaric acid. The values reported in Table I are found by extrapolation to the start of the measurements, as a steady increase in vapor pressure was observed during the measurements. This is probably due to a slight decomposition which was also observed, but more pronounced, when we tried to measure D, L, and DL-tartaric acid. For these latter substances we could not obtain reliable and reproducible results and they were skipped. Due to decomposition, we were not able to measure a reliable heat of sublimation for citric acid. Therefore, it was left out of Table I. In Table II, we give the values of the enthalpies of dehydration of the hydrates. No values for the enthalpy of dehydration of chloranilic acid and phenol are given, because we did not succeed in preparing the stable stoichiometric complexes as described in the crystallographic reports.[26,27] They were also left out of the computations.

The difference between the values of the enthalpy of dehydration for myoinositol, measured in the solid state and measured from a saturated solution (21.15 kJ/mol) is due to the heat of solution of this compound. This value is of the same order of magnitude as the value of the heat of solution measured for the citric acid monohydrate system, 17.5 kJ/mol.[21] In all cases where doubt arose about the structure caused by possible phase transitions or decomposition, x-ray powder diagrams were recorded to ensure consistency between experimental and calculated results. In Tables III and IV we give the vapor pressures of the anhydrates and the hydrates as a function of temperature.

We also tabulate the residuals of the least-squares fit of the data to Eq. (1).

B. Calculations

The results of the lattice energy calculations according to Eqs. (2), (3), and (4) are presented in Table V. The overall agreement between calculated and measured quantities is good with a few exceptions. The enthalpy

TABLE I. Experimental results of simultaneous torsion and mass loss effusion expressed as coefficients of Eq. (1).

	Torsion effusion					Mass loss effusion			
	$\dfrac{T1}{K}$	$\dfrac{T2}{K}$	$\dfrac{\theta}{K}$	$\dfrac{\Delta G°(\theta)}{J\ mol}$	$\dfrac{\Delta H°_{sub}(\theta)}{kJ\ mol}$	$\dfrac{\theta}{K}$	$\dfrac{\Delta G°(\theta)}{J\ mol}$	$\dfrac{\Delta H°_{sub}(\theta)}{kJ\ mol}$	$p_m/p_t(\theta)$
α oxalic acid	310	335	323.69	2466	98.5	323.43	2464	95.6	1.03
phloroglucinol	383	406	394.94	3009	127.9	395.04	3010	126.0	0.99
meso tartaric acid	411	440	428.18	3262	158.0	427.89	3260	153.3	1.03
myoinositol	454	472	462.14	3521	165.4	462.12	3521	168.0	1.00
chloranilic acid	375	398	388.15	2957	118.6	388.50	2960	119.1	0.97
phenol	253	265	256.28	1952	69.0	256.25	1952	67.1	1.00

	Mean values		
	$\dfrac{\theta}{K}$	$\dfrac{\Delta G°(\theta)}{J\ mol}$	$\dfrac{\Delta H°_{sub}(\theta)}{kJ\ mol}$
α oxalic acid	323.56	2465	97.1
phloroglucinol	394.99	3009	127.0
meso tartaric acid	428.04	3261	155.7
myoinositol	462.13	3521	166.7
chloranilic acid	388.32	2958	118.9
phenol	256.26	1952	68.1

TABLE II. Coefficients of vapor pressure equation [Eq. (1)] and least squares error at mean experimental temperature θ and at 298.15 K.

	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	n	$\dfrac{\theta}{K}$	$\dfrac{\Delta G°(\theta)}{J\ mol^{-1}}$	$\dfrac{\Delta H°_{deh}(\theta)}{kJ\ mol^{-1}}$	$\dfrac{\Delta C°_p(\theta)}{J\ K^{-1}\ mol^{-1}}$	$\dfrac{\rho(\theta)}{Pa}$
α oxalic acid · $2H_2O$	250	326	13	287	$-11\,890 \pm 11$	56.53 ± 0.13	···	145.9 ± 0.7
				298.15	$-14\,548 \pm 12$	56.53 ± 0.13	···	353.9 ± 1.7
phloroglucinol · $2H_2O$	252	329	15	285	$-12\,936 \pm 35$	56.74 ± 0.28	-43 ± 28	235 ± 4
				298.15	$-16\,138 \pm 34$	56.18 ± 0.48	-43 ± 28	672 ± 9
mesotartaric acid · $1H_2O$	274	332	15	304	$-18\,156 \pm 37$	59.08 ± 0.42	-92 ± 43	1317 ± 19
				298.15	$-16\,664 \pm 37$	59.62 ± 0.40	-92 ± 43	830.9 ± 12
myoinositol · $2H_2O$	262	292	10	284	$-16\,075 \pm 43$	60.94 ± 1.16	···	904.9 ± 16
				298.15	$-19\,913 \pm 75$	60.94 ± 1.16	···	3080 ± 94
				296.3	$-19\,411 \pm 69$	60.94 ± 1.16	···	2642 ± 75
myoinositol (sat. sol.)	296	328	16	312	$-22\,547 \pm 37$	39.79 ± 1.31	···	5954 ± 84
				298.15	$-19\,780 \pm 69$	39.79 ± 1.31	···	2920 ± 81
				296.3	$-19\,410 \pm 76$	39.79 ± 1.31	···	2642 ± 81
citric acid · $1H_2O$	(Ref. 21)			298.15	-9980 ± 30	56.8 ± 0.80	-93 ± 130	1770 ± 5

TABLE III. Vapor pressure temperature table; calculated with the results of Table I.

P/Pa	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
					T/K					
α oxalic acid	311.59	317.46	321.00	323.56	325.57	327.24	328.66	329.90	331.00	331.99
phloroglucinol	381.31	388.03	392.07	394.99	397.28	399.18	400.79	402.20	403.45	404.58
mesotartaric acid	414.89	421.36	425.24	428.04	430.24	432.05	433.59	434.93	436.13	437.20
myoinositol	447.82	454.86	459.09	462.13	464.52	466.49	468.17	469.63	470.93	472.10
chloranilic acid	374.23	381.14	385.31	388.32	390.69	392.64	394.31	395.77	397.07	398.23
phenol	245.60	250.82	253.97	256.26	258.06	259.55	260.83	261.94	262.93	263.83

TABLE IV. Experimental vapor pressures and residuals of least squares fit to Eq. (1) coefficients are given in Table II.

$\dfrac{T}{K}$	$\dfrac{P}{Pa}$	$100 * \Delta \ln p$	$\dfrac{T}{K}$	$\dfrac{P}{Pa}$	$100 * \Delta \ln p$
α Oxalic adid $\cdot$ 2H$_2$O			Mesotartaric acid $\cdot$ 1H$_2$O		
250.91	4.80	-0.62	301.14	1084	2.81
254.16	6.80	-0.50	304.43	1370	0.64
262.59	16.31	1.11	309.28	1953	-0.36
269.64	32.45	2.20	309.66	2011	-0.18
269.69	32.51	1.93	314.97	2842	-3.82
282.00	95.42	-0.48	324.50	5575	-1.07
282.46	98.34	-1.35	324.69	5565	-2.51
298.73	361.0	-2.45	332.43	8952	-4.01
298.75	366.8	-0.95	332.64	10 214	7.94
303.35	515.5	-1.50	Myoinositol $\cdot$ 2H$_2$O		
303.40	519.0	-1.14	286.23	1014	-8.75
326.51	2613	1.86	275.72	378.0	-9.78
326.69	2645	1.93	281.30	746.0	-5.50
Phloroglucinol $\cdot$ 2H$_2$O			272.43	311.2	2.87
			262.81	116.9	3.43
252.26	10.26	1.73	285.22	1035	2.36
252.28	10.41	2.89	288.40	1343	0.15
263.29	31.58	-1.53	291.59	1725	-2.70
263.37	31.75	-1.80	296.03	2678	3.66
266.06	39.97	-5.44	296.06	2677	3.30
272.87	82.08	1.78			
272.93	82.40	1.65	Myoinositol $\cdot$ (Satd. sol.)		
273.35	81.38	-3.48	310.89	5685	0.87
295.14	266.7	6.10	308.12	4654	-5.34
298.73	687.6	-2.11	298.33	2750	-6.97
300.35	848.3	6.67	303.71	3781	-3.53
305.28	1120	-1.70	300.38	3467	5.26
308.94	1424	-3.78	302.97	3823	1.41
314.68	2182	-0.56	308.24	5133	3.90
329.07	3493	-0.40	310.79	6114	8.63
			312.60	5771	-6.04
			312.67	5772	-6.37
Mesotartaric acid $\cdot$ 1H$_2$O			314.62	7213	6.42
274.32	99.44	0.57	314.81	7311	6.84
274.52	100.9	0.03	320.09	8981	2.33
274.77	101.5	-1.78	325.40	10 490	-6.50
285.94	289.8	-1.61	327.28	11 692	-4.13
293.74	620.3	7.01	327.95	12 972	3.27
298.01	791.8	-3.65			

of sublimation of myoinositol shows a large difference between calculated and observed value. The calculated value of 266.6 kJ/mol for this enthalpy of sublimation is relatively high, which is mainly due to the large contribution of the six hydrogen bonds in which each myoinositol molecule is involved. The contribution of the hydrogen bond energy to the total attractive energy is about 65% for this substance.

For the other compounds having, at the most, four hydrogen bonds per molecule, this contribution is about 50%. Thus, an imperfect description of this hydrogen bond energy will have a strong negative influence, especially on myoinositol. Another discrepancy is shown in the value for the enthalpy of dehydration for the system mesotartaric acid and its monohydrate. We have two error sources here. The first one is the fact that because of decomposition during the pressure measurements, the value for the enthalpy of sublimation may be too high and unreliable. The second problem arises

from the fact that the sample we used for the vapor pressure measurements turned out to have the orthorhombic structure by x-ray analysis instead of the triclinic form we had assumed for our calculations.

Unfortunately, the orthorhombic structure is not yet solved, so recalculations could not be made. For β oxalic acid dihydrate, no stable hydrate could be obtained with the published crystal structure,[14] thus making it impossible to determine an enthalpy of dehydration for this compound. The calculated value, however, seems plausible if one compares it with the values determined for α oxalic acid dihydrate. Finally, a large deviation, of the order of 15%, is found for the enthalpy of sublimation of ice. This deviation may be caused partly by the fact that the "ordered" structure of ice, with linear hydrogen bonds, is physically not quite justified, as it gives a value for the enthalpy of sublimation which is too high. As in the case of myoinositol, part of this deviation may be caused by the obviously

TABLE V. Observed and calculated values of the enthalpies of sublimation and dehydration according to Eqs. (2) and (3).

	ΔH_s^A (calc) kJ mol^{-1}	ΔH_s^A (obs) kJ mol^{-1}	ΔH_{deh} (calc) kJ mol^{-1}	ΔH_{deh} (obs) kJ mol^{-1}
Ice 1h	61.6	51.5[a]	...	...
phloroglucinol	122.1	127.9	...	...
phloroglucinol $\cdot$ 2H$_2$O	...	...	59.0	56.2
myoinositol	266.6	168.0	...	...
myoinositol $\cdot$ 2H$_2$O	...	...	60.9	60.9
α oxalic acid	93.3	98.5 (97.9[g])	...	...
α oxalic acid $\cdot$ 2H$_2$O[c]	...	...	57.9	56.5
β oxalic acid	91.3	92.5[b] (93.3)[g]	...	...
β oxalic acid $\cdot$ 2H$_2$O	...	...	58.1	...
mesotartaric acid[d]	151.9	156.9	...	...
mesotartaric acid $\cdot$ 1H$_2$O[e]	...	...	83.8	59.6
citric acid	217.1	...	...	...
cirtic acid $\cdot$ 1H$_2$O	...	...	61.1	56.8[f]

[a]Reference 18.
[b]Reference 1.
[c]57.3 kJ mol^{-1} Ref. 19.
[d]Triclinic form.

[e]Triclinic form.
[f]51.5 kJ mol^{-1} Ref. 19.
[g]Reference 25.

poor description of the hydrogen bond potential and its parametrization. We will return to this subject in the next section. The deviation in the enthalpy of sublimation of ice and the poor hydrogen bond description do, however, have a less important effect on the values given in Table V. Since these values of the enthalpy of dehydration are calculated as a difference according to Eq. (2), errors may cancel. Thus, difference values may still be quite good even when absolute values are in error.

Because of the slow convergence properties of the Coulombic energy, we have repeated our calculations with an Ewald constant of 0.4 instead of 0.3. This resulted in a mean deviation of only 0.4% (all contributions had the same sign) in the lattice energies, which is very small, compared to the errors already mentioned above. Since the enthalpy of dehydration is calculated as a difference, the influence of the aforementioned changes will be even less important for this quantity, due to cancellation of errors. Therefore, we did not consider it necessary to add these results to the ones in Table V.

V. CONCLUSIONS

A comparison of the calculated and observed values presented in Table V leads to the following conclusions: the good agreement obtained for the anhydrous compounds indicates that the parameter set is readily transferable. The results for the hydrates and especially those of ice lead to the conclusion that the description of the hydrogen bond is rather poor. The Lippincott–Schroeder potential we used has, as its main disadvantage, the existence of a discontinuity which depends

on the arbitrary choice of a constant. Another disadvantage is the relatively large number of parameters it needs. As mentioned before elsewhere,[22] the description of the electrostatic energy by means of CNDO/2 wave functions underestimates this contribution significantly. Since the method of derivation of the nonbonded parameters introduces strong correlations among these parameters and the components (Coulombic, hydrogen bond, etc.) of the energy, any shortcoming of these components will be introduced into the parameters during the fitting procedure. This makes transferability to other chemically different kinds of compounds doubtful. To overcome these problems, we will have to improve the descriptions of the electrostatic-, and hydrogen-bond energy which may be done by introducing *ab initio* derived charges and analyzing the typical hydrogen bond interaction by means of well-defined quantum-chemical interaction schemes. We are working on these subjects presently and hope to report on them in the near future.

ACKNOWLEDGMENTS

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