

Investigation of the Use of Group Contribution Methods to Estimate Physical Properties of Organophosphates

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The lack of known physical property data for numerous organophosphate compounds has been a recurring issue for the process simulation community. Performing experiments to measure physical properties for these compounds is both expensive and hazardous. The most cost efficient method is to estimate unknown physical properties, but established estimation methods lack information for phosphorus. Adaptation of existing group contribution methods to estimate the normal boiling point for organophosphates is presented. A review of the existing group contribution methods available reveals the derivation and limitations of each method. The boiling point of every compound was calculated using each method, and compared against an experimental value. Despite the accuracy of these methods being similar, the range of estimated values indicate the lack of a general trend. Accurate and reliable experimental physical property data for a larger set of chemical compounds could substantially improve results.

Keywords: organophosphates, group contribution method, boiling point estimation, physical properties, experimental boiling point, Joback, Joback & Reid, Marrero & Pardillo, Modified Joback.

Introduction

The importance of physical property data, such as, normal boiling point (T_b°), vapor pressure curve (P_v), critical temperature (T_c), critical pressure (P_c), critical volume (V_c), etc., is demonstrated by the use of such popular thermodynamic modeling software as ChemCAD and Aspen Plus. Without the appropriate physical property data, these modeling programs cannot be used properly.

Objectives

The objective of this study is to evaluate the adaptation of existing group contribution methods to estimate the normal boiling point of organophosphate compounds. This includes a review and evaluation of existing estimation methods, with respect to organophosphorous compounds, and derivation of the appropriate group contributions using known physical properties for a set of organophosphates. The ultimate goal is to be able to use the derived phosphorous group contributions, with established group contribution methods, to estimate select physical properties of organophosphate compounds of which physical property values are unknown or questionable.

Organophosphate Compounds Studied

The compound name, CAS registry number, chemical formula, and molecular weight are shown in Table I for the organophosphates used in this study.

Table I. Organophosphate Compounds Used in this Study

Compound Name	CAS Registry Number	Chemical Formula	Molecular Weight
Malathion	121-75-5	C ₁₀ H ₁₉ O ₆ PS ₂	330.38
Diazinon	333-41-5	C ₁₂ H ₂₁ N ₂ O ₃ PS	493.03
Dursban	2921-88-2	C ₉ H ₁₁ Cl ₃ NO ₃ PS	350.59
Methyl Parathion	298-00-0	C ₈ H ₁₀ NO ₅ PS	263.22
Parathion	56-38-2	C ₁₀ H ₁₄ NO ₃ PS	291.28
Fenitrothion	122-14-5	C ₉ H ₁₂ NO ₅ PS	277.25
diethyl methylphosphonate	683-08-9	C ₅ H ₁₃ O ₃ P	152.15
diethyl ethylphosphonate	78-38-6	C ₆ H ₁₅ O ₃ P	166.00
diisobutylphosphite	1189-24-8	C ₈ H ₁₉ O ₃ P	194.00
diisopropyl methylphosphonate	1445-75-6	C ₇ H ₁₇ O ₃ P	180.21
Dimethyl methylphosphonate	756-79-6	C ₃ H ₉ O ₃ P	124.09
Isopropyl methylphosphonofluoridate	107-44-8	C ₄ H ₁₀ FO ₂ P	140.11
pinacolyl methylphosphonofluoridate	96-64-0	C ₇ H ₁₆ FO ₂ P	182.20
methylphosphonic dichloride	676-97-1	CH ₃ Cl ₂ OP	148.91
methylphosphonic difluoride	676-99-3	CH ₃ F ₂ OP	100.01

Results and Discussion

The scarcity of known physical property data for numerous organophosphate compounds is the primary obstacle in the development of a valid estimation method. The few physical property resources containing experimental data were not only expensive but also lacked information about the origin and validity of the data.

The phosphorous group contributions developed in this study were derived using experimental T_b° data with each of the group contribution methods discussed.

The P=S contribution was derived using experimental data for the following three compounds: Malathion, Methyl Parathion, and Parathion. The large deviations discussed below come from the low experimental boiling point for Methyl Parathion. This experimental value appears significantly lower, with respect to the estimated values, than the experimental values for both Malathion and Parathion, and is possibly an erroneous value.

The estimated T_b° s for all three chemicals are higher than the determined experimental values, for the Joback & Reid¹⁰, Modified Joback¹⁷, and Marrero & Pardillo⁹ methods, as can be seen in Table II.

The estimated T_b° s for two of the three chemicals are lower than the determined experimental values, for the Marrero & Pardillo Method⁹, as can be seen in Table II. However, all of the estimated values for Methyl Parathion are significantly larger than the estimates for other chemicals in this study. Therefore, the estimate for this chemical is ignored here.

The Constantinou & Gani method⁸ provides the necessary group contributions for only one of the chemicals in this study. The estimated T_b° for this chemical is lower than the determined experimental value, as can be seen in Table II. The deviation for Malathion is 138.

The Marrero & Gani Method¹⁸ does not provide the necessary group contributions for the Oxygen and Sulfur components of the chemicals in this study, as can be seen in Table II.

The P contribution was derived using experimental data for the following seven compounds: diethyl methylphosphonate, diethyl ethylphosphonate, dimethyl methylphosphonate, methylphosphonic dichloride, methylphosphonic difluoride, isopropyl methylphosphonofluoridate, and pinacolyl methylphosphonofluoridate.

The estimated T_b 's for all seven chemicals are lower than the determined experimental values, for both the Joback & Reid¹⁰ and Modified Joback¹⁷ methods, as can be seen in Table III.

The Constantinou & Gani⁸ and Marrero & Gani¹⁸ methods do not provide the necessary group contributions for any of the chemicals in this study, as can be seen in Table III. Therefore, calculations could not be performed to estimate T_b 's.

Phosphorous Group Contribution Verification

In order to assess the value of the derived phosphorous group contributions, the normal boiling points for the organophosphates used in the development were recalculated using the derived contributions for each method evaluated in this study.

The results for the organophosphates with the P=S group are shown in Tables II. The normal boiling point estimate with the P=S group contribution is more accurate than the method without the derived P=S contribution for 55% of the chemicals and methods. The improved accuracy ranges from 15-75% reduction in the difference from

experimental. For the remaining 45% of the chemicals and methods used in the derivation, the estimate is less accurate with the derived P=S group contribution, with an accuracy decrease of 15-75%. These results vary widely due to the fact that only three chemicals were used for this derivation because of limited property data availability.

The results for the organophosphates with the P group are shown in Table III. For each compound and each method, the normal boiling point estimate with the P group contribution is more accurate than the method without the derived P contribution. The improved accuracy ranges from 15-98% reduction in the difference from experimental. The Joback & Reid and Modified Joback methods both averaged roughly an 80% accuracy improvement, while the Marrero & Pardillo method averaged only a 20% improvement.

Table II. Estimated Boiling Point Using Derived Contribution for Organophosphates with P=S Group

Physical Property Data Resource	Boiling Point (K)			
	Malathion 121-75-5 C ₁₀ H ₁₉ O ₆ PS ₂	Methyl Parathion 298-00-0 C ₈ H ₁₀ NO ₅ PS	Parathion 56-38-2 C ₁₀ H ₁₄ NO ₅ PS	Fenitrothion 122-14-5 C ₉ H ₁₂ NO ₅ PS
<i>Experimental</i>	640	416	648	--
Joback & Reid ¹⁰	659	634	680	662
<i>Difference from Exp.</i>	-19	-218	-32	--
Joback & Reid with derived P=S contribution	569	545	590	573
<i>Difference from Exp.</i>	71	-129	58	--
Modified Joback ¹⁷	695	633	680	661
<i>Difference from Exp.</i>	-55	-217	-32	--
Modified Joback with derived P=S contribution	594	532	579	560
<i>Difference from Exp.</i>	47	-116	70	--
Marrero & Pardillo ⁹	529	543	578	562
<i>Difference from Exp.</i>	111	-126	70	--
Marrero & Pardillo with derived P=S contribution	547	561	596	580
<i>Difference from Exp.</i>	93	-145	52	--

Comparison of the normal boiling point from each estimation method with and without the P=S group contribution derived in this study, as well as against the experimental reference value for the organophosphates with P=S group. A ‘—’ indicates data is unavailable.

Table III. Estimated Boiling Point Using Derived Contribution for Organophosphates with P Group

Physical Property Data Resource	Boiling Point (K)						
	diethyl methylphosphonate 683-08-9 C ₅ H ₁₃ O ₃ P	diethyl ethylphosphonate 78-38-6 C ₆ H ₁₅ O ₃ P	dimethyl methylphosphonate 756-79-6 C ₃ H ₉ O ₃ P	methylphosphonic dichloride 676-97-1 CH ₂ Cl ₂ OP	methylphosphonic difluoride 676-99-3 CH ₂ F ₂ OP	isopropyl methylphosphonofluoridate 107-44-8 C ₄ H ₁₀ FO ₂ P	pinacolyl methylphosphonofluoridate 96-64-0 C ₇ H ₁₆ FO ₂ P
Experimental	465	478	454	438	373	431	440
Joback & Reid ¹⁰	315	338	269	298	222	291	356
Difference from Exp.	150	141	185	140	151	141	84
Joback & Reid with derived P contribution	490	534	444	440	340	425	490
Difference from Exp.	-25	-56	10	-2	33	6	-50
Modified Joback ¹⁷	349	393	303	299	199	284	349
Difference from Exp.	116	85	151	140	174	147	91
Modified Joback with derived P contribution	478	522	432	428	328	413	478
Difference from Exp.	-13	-44	22	10	45	18	-38
Marrero & Pardillo ⁹	329	354	276	277	157	289	309
Difference from Exp.	136	124	179	161	216	143	131
Marrero & Pardillo with derived P contribution	354	378	302	303	185	314	332
Difference from Exp.	111	100	152	135	188	117	108

Comparison of the normal boiling point from each estimation method with and without the P group contribution derived in this study, as well as against the experimental reference value for the organophosphates with P group.

In addition to the verification against the compounds used in the derivation, Tables IV and V show how the derived P=S group contributions estimate T_b° for two compounds not used in this study. For the Joback & Reid method, using the derived P=S group contributions resulted in an 85% improved accuracy for both Diazinon and Dursban. For the Marrero & Pardillo method, a 25% improvement is shown for Dursban and a 50% decrease in accuracy for Diazinon.

Table IV. Normal Boiling Point Estimation Using the P=S Contribution Derived with the Joback & Reid Method

	Normal Boiling Point (K)	
	Diazinon 333-41-5 $C_{12}H_{21}N_2O_3PS$	Dursban 2921-88-2 $C_9H_{11}C_{13}NO_3PS$
<i>Experimental T_b from ChemFinder</i>	579	573
Without P=S Contribution	684	679
Difference from Experimental	-105	-106
With P=S Contribution	594	590
Difference from Experimental	-15	-17

Comparison of the estimated boiling point with and without the P=S contribution derived in this study, as well as against the experimental reference value.

Table V. Normal Boiling Point Estimation Using the P=S Contribution Derived with the Marrero & Pardillo Method

	Normal Boiling Point (K)	
	Diazinon 333-41-5 C ₁₂ H ₂₁ N ₂ O ₃ PS	Dursban 2921-88-2 C ₉ H ₁₁ C ₁₃ NO ₃ PS
<i>Experimental T_b from ChemFinder</i>	579	573
Without P=S Contribution	592	536
Difference from Experimental	-13	37
With P=S Contribution	603	546
Difference from Experimental	-24	27

Comparison of the estimated boiling point with and without the P contribution derived in this study, as well as against the experimental reference value.

Conclusions and Recommendations

For organophosphate compounds, the methods that include all the necessary group contributions, except for phosphorous, are: Joback & Reid¹⁰, Modified Joback¹⁷, and Marrero & Pardillo⁹. All three of these methods yield estimates of similar accuracy for these compounds. The other methods discussed in this study cannot be used for these compounds without additional modifications. For the P=S group, the Joback & Reid¹⁰ and Modified Joback¹⁷ methods overestimate the T_b, while the Marrero & Pardillo⁹ method underestimates this property. For the P group, all three methods underestimate. Table VI includes the derived contributions for the P=S group, and Table VII includes the derived contributions for the P group.

Table VI. Group Contributions Developed in this Study for P=S

Estimation Method	Group Contribution
Joback & Reid ¹⁰	-89
Modified Joback ¹⁷	-101
Constantinou & Gani ⁸	Group contributions unavailable
Marrero & Pardillo ⁹	91
Marrero & Gani ¹⁸	Group contributions unavailable

Table VII. Group Contributions Developed in this Study for P

Estimation Method	Group Contribution
Joback & Reid ¹⁰	142
Modified Joback ¹⁷	129
Constantinou & Gani ⁸	Group contributions unavailable
Marrero & Pardillo ⁹	156
Marrero & Gani ¹⁸	Group contributions unavailable

Recommendations for Future Work

The comparison of available experimental data for T_b° with estimated values from existing group contribution methods demonstrates the need for further research for an estimation method for organophosphates. The primary obstacle to improving the application of these phosphorous group contributions is the lack of accurate and reliable experimental physical property data (T_b , vapor pressure, T_c , etc.) for a large set of organophosphates.

List of Abbreviations

ACD	Advanced Chemistry Development
AIChE	American Institute of Chemical Engineers
CBDCE	US Army Chemical Biological Defense Command Edgewood
MSDS	Material Safety Data Sheet

List of Symbols

T_b	Boiling Point
T_b°	Normal boiling point (Boiling point at 1 atmosphere)
T_c	Critical temperature
P_c	Critical pressure
V_c	Critical volume
Σ	Summation
P	Phosphorous atom
S	Sulfur atom
P=S	Phosphorous double-bonded to a Sulfur
K	Kelvin
MW	Molecular weight
kPa	Units of pressure (1 atm = 101.325 kPa)
Torr	Units of pressure (1 torr = 1 mm Hg)
$\text{cm}^3/\text{g-mole}$	Units of volume

Literature Cited

1. Beilstein's Handbuch der Organischen Chemie, Beilstein Institut zur Foerderung der Chemischen Wissenschaften. 1988-2001.
2. Boublik, Tomas. *The Vapour Pressures of Pure Substances*. Volume 17 of Elsevier's Physical Science Data Series.
3. DECHEMA. DETERM Chemical Database. Online. www.dechema.de Dykyi, J. and M. Repas. "Saturation Vapor Pressure of Organic Compounds." *Veda Vydavatelstvo Slovenskej Akademie Vied*, Bratislava, 1979.
4. MSDS Solutions. Online. <http://www.msds.com/>.
5. Cambridge Software. ChemFinder Chemical Database. Online. www.chemfinder.com CambridgeSoft Corporation. Cambridge, MA USA. Cambridge CB5 8LA UK. 2004.
6. Yan, Xinjian, Qian Dong, and Xiangrong Hong. "Reliability Analysis of Group-Contribution Methods in Predicting Critical Temperatures of Organic Compounds." *J. Chem. Eng. Data*, 48 (2003): 374-380.
7. Carlson, Eric C. "Don't Gamble With Physical Properties for Simulations." *Chemical Engineering Progress*. (October 1996): 35-46.
8. Constantinou, L. and R. Gani. "New Group Contribution Method for Estimating Properties of Pure Compounds." *AIChE Journal*, Vol. 40, No. 10 (October 1994): 1697.
9. Marrero-Marejon, Jorge and Eladio Pardillo-Fontdevila. "Estimation of Pure Compound Properties Using Group-Interaction Contributions." *AIChE Journal*, Vol. 45, No. 3 (March 1999): 615-621.
10. Joback, K.G. and R.C. Reid. "Estimation of Pure-Component Properties from Group-Contributions." *Chem. Eng. Commun.* 57 (1987): 233.
11. ChemSW. Molecular Modeling Pro Estimation Software. Online. <http://www.chemsw.com/13052.htm>
12. Joback, Kevin G. Cranium Estimation Software. Molecular Knowledge Systems, Inc. Online. <http://www.molknow.com/Products/Cranium/cranium.htm>
13. ACDLabs. ChemSketch Estimation Software. Online. <http://www.acdlabs.com/download/chemsk.html>

14. Perry, Robert H., Don Green, and James O. Maloney. *Perry's Chemical Engineers' Handbook*. Sixth Edition. New York: McGraw Hill, 1984.
15. Joback, Kevin G. "Cranium: Component Software for Physical Property Estimation." Molecular Knowledge Systems, Inc. (March 1998) Online.
<http://www.molknow.com/Papers/Cranium/paper1.htm>
16. Klincewicz, K.M. and R.C. Reid. "Estimation of Critical Properties with Group Contribution Methods." *AIChE Journal*, Vol. 30, No. 1 (1984): 137.
17. Devotta, Sukumar and V. Rao Pendyala. "Modified Joback Group Contribution Method for Normal Boiling Point of Aliphatic Halogenated Compounds." *Industrial & Engineering Chemistry Research*, Vol. 31, No. 8 (August 1992): 2042-2046.
18. Marrero, Jorge and Rafiqul Gani. "Group-Contribution Based Estimation of Pure Component Properties." *Fluid Phase Equilibria*, 183-184 (2001): 183-208.
19. Breau, L. *Journal of Labelled Compounds and Radiopharmaceuticals*. Vol. 25,3(1988): 301-12.
20. Kukhar, V. P. *Zhurnal Obshchei Khimii*. Vol. 49,7 (1979): 1470-4.
21. Chakraborty, Subir K. *Synthetic Communications*. Vol. 21,8-9 (1991): 1039-46.
22. Al'fonsov, V. A. *Zhurnal Obshchei Khimii*. Vol. 51,12 (1981): 2657-61.
23. Filippov, L. P. "Description of the Properties of Liquids in Terms of Similarity Theory." *Zhurn. Fiz. Khim.* 37, 201 (1963).
24. Dykyj, Jaroslav. *Vapor Pressure Of Organic Compounds*. First Edition. Bratislava: Veda, 1979-1984.
25. Merck. USDA ARS Database. Online. www.arsusda.gov/ppdb2.html
26. Meister, Edward L., et al. *Farm Chemical Handbook*. Meister Publishing Co., Willoughby, Ohio (1977).