

N O T E

Saturated-liquid heat capacity of organic compounds: new empirical correlation model

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Abstract: A new saturated-liquid heat capacity model is recommended. This model is tested and compared with the known polynomial and quasi-polynomial models on 39 sets with 1453 experimental heat capacity data. The obtained results indicate that the new model is better than the existing models, especially near the critical point.

Keywords: heat capacity, saturated liquid, correlation.

INTRODUCTION

Calculation of the saturated-liquid heat capacities of organic compounds is an important step in the design of many unit operations. For heating or cooling liquids, the energy requirements are proportional to the heat capacity. Values of this property are, therefore, necessary in such areas as equipment sizing, energy requirements, equilibrium yields and separation ratios. Also, heat capacity of mixtures may be determined from the heat capacity of the individual components.

THE EXISTING HEAT CAPACITY CORRELATIONS MODELS

Experimental data for saturated liquid heat capacity of organic compounds are limited, and even when available, cover mostly restricted temperature ranges. Therefore, numerous correlation models have been developed. Most of these models are polynomial types, such as:

$$c_p = A + BT + CT^2 + DT^3 \quad (1)$$

In these type of the models, quality of the correlation depends on a number of parameters and slightly on the polynomial form.¹ Also, polynomials dependent only on temperature give yield incorrect functional behavior for heat capacities near the critical temperature.² Therefore, Watson,^{3,4} Lorensen and Tedder² and Roháč *et al.*⁵ proposed quasi-polynomial correlation model to cover a wide tem-

perature range from freezing to critical point.

Watson I³

$$c_p = A + B/(1 - T_r)^{1/3} + C/(1 - T_r)^{2/3} \quad (2)$$

Watson II⁴

$$c_p = A + B/(1 - T_r) + C(1 - T_r) + D(1 - T_r)^2 \quad (3)$$

Roháč *et al.*⁵

$$c_p/R = A + B/(1 - T_r) + C \ln(1 - T_r) + DT_r \quad (4)$$

Lorensen and Tedder²

$$c_p = c_{p,\text{ref}} \left(\frac{1 - T_{\text{ref}}/T_c}{1 - T/T_c} \right)^A \left(\frac{T}{T_{\text{ref}}} \right)^B \quad (5)$$

Critical temperature is required for quasi-polynomial models, whereas for Lorensen and Tedder² model the reference heat capacity must be employed, as well.

THE NEW HEAT CAPACITY MODEL

The aim of this article was to develop a new empirical logarithmic model, applicable to the wide temperature range, from freezing to critical point. On the basis of our study, next model is recommended:

$$\ln(c_p) = A + B \ln(1 - T_r) + C/(1 - T_r) + D(1 - T_r)^{1.2} \quad (6)$$

RESULTS AND DISCUSSION

The accuracy of the all presented models was tested on 35 sets of literature experimental data, with 1358 experimental points for 35 pure organic chemicals. A comparison of the previously recommended models and the new model is presented in Table I. The number of experimental points per set, temperature range, critical temperature and percentage average error for all six tested models are presented in this table.

TABLE I. The experimental data and quality of correlation

Compound*	<i>n</i>	$\Delta T/K$	T_c/K	$p_{\text{av}}/\%$					
				Eq. 1	Eq. 2	Eq. 3	Eq. 4	Eq. 5	Eq. 6
Methylcyclopentane	32	126.6–307.5	532.7	0.07	0.40	0.06	0.06	0.28	0.07
Dimethyl disulfide	25	192.0–352.3	605.0	0.07	0.20	0.07	0.08	0.14	0.08
Cyclobutane	19	184.4–284.6	460.0	0.23	0.28	0.23	0.23	0.29	0.23
Nitromethane	11	249.8–297.1	588.0	0.05	0.11	0.05	0.05	0.14	0.05
Trimethylamine	22	160.9–275.9	433.3	0.12	0.17	0.12	0.12	0.13	0.12
Methylethyl sulfide	21	147.2–297.6	532.8	0.03	0.23	0.03	0.03	0.08	0.03
Dipropyl ether	66	160.6–322.7	530.6	0.04	0.05	0.05	0.05	0.08	0.05

TABLE I. Continued

Compound*	<i>n</i>	$\Delta T/K$	T_c/K	$P_{av}/\%$					
				Eq. 1	Eq. 2	Eq. 3	Eq. 4	Eq. 5	Eq. 6
Cyclopentane	19	184.1–291.4	511.7	0.21	0.20	0.19	0.19	0.23	0.19
Benzaldehyde	69	218.0–425.3	694.8	0.14	0.18	0.14	0.15	0.29	0.15
1,1-Dichloroethene	37	157.5–290.9	489.0	0.17	0.19	0.18	0.18	0.20	0.18
Perfluoropropane	36	125.8–233.0	420.6	0.26	0.28	0.26	0.26	0.32	0.26
1-Butyne	22	149.9–275.1	463.7	0.21	0.22	0.22	0.22	0.22	0.21
Propylenoxid	62	166.4–301.4	482.2	0.10	0.29	0.09	0.10	0.18	0.10
Methylpropyl ether	116	137.7–308.9	476.3	0.04	0.09	0.04	0.04	0.06	0.04
Ethylpropyl ether	62	151.3–316.3	500.2	0.65	0.67	0.56	0.51	0.72	0.50
Acetic acid	48	293.2–400.2	592.7	0.05	0.04	0.05	0.05	0.05	0.04
Propionic acid	74	254.8–447.2	604.0	0.12	0.30	0.15	0.18	0.50	0.19
Butyric acid	32	272.8–373.1	624.0	0.06	0.06	0.06	0.06	0.06	0.06
Heptane	96	185.0–301.0	540.2	0.06	0.28	0.08	0.10	0.31	0.10
1-Propanol	66	181.8–303.1	536.7	0.08	0.08	0.08	0.08	0.56	0.08
Diphenyl	24	350.0–480.0	789.0	0.55	0.55	0.55	0.55	0.58	0.55
2,3-Dimethyl-2-butene	18	204.3–318.1	501.0	0.01	0.10	0.01	0.02	0.13	0.02
2-Butanethiol	28	135.5–306.9	551.0	0.04	0.25	0.04	0.03	0.10	0.03
Ethanol	20	163.5–294.3	514.1	0.32	0.32	0.32	0.31	0.38	0.31
1-Brombutane	35	176.9–292.3	569.5	1.27	1.35	1.28	1.28	1.32	1.28
Acetone	14	180.3–297.0	508.1	0.34	0.38	0.34	0.34	0.38	0.34
1-Butene	24	81.3–253.4	419.6	0.13	0.70	0.16	0.20	0.27	0.19
Ethylpropyl sulfide	25	165.6–366.0	584.0	0.03	0.42	0.03	0.06	0.38	0.07
1-Heptene	21	151.1–295.1	537.3	0.13	0.20	0.13	0.14	0.15	0.14
1,4-Pentadiene	23	125.4–292.5	478.0	0.12	0.50	0.13	0.14	0.36	0.14
Benzene	25	281.0–353.0	562.1	0.10	0.13	0.10	0.10	0.17	0.10
Toluene	35	281.0–383.0	591.8	0.08	0.21	0.08	0.21	0.08	0.08
2-Butyne	10	249.5–284.3	488.7	0.58	0.56	0.58	0.58	0.54	0.58
2-Methylbutane	83	115.7–297.8	460.4	0.27	0.29	0.27	0.27	0.25	0.26
2,3-Dimethylbutane	38	149.4–306.5	500.0	0.08	0.08	0.08	0.08	0.11	0.08
<i>The experimental data and quality of correlation near the critical temperature</i>									
Methane	9	114.5–187.5	190.6	14.55	2.99	1.09	0.76	6.68	0.40
Ethane	50	96.8–294.9	305.3	2.05	0.72	0.99	0.72	0.67	0.73
Diborane	14	170.1–282.3	289.8	4.08	0.61	0.50	0.39	1.51	0.39
Methane ⁶	20	97.7–188.2	190.6	14.42	3.47	1.88	1.92	8.27	1.02
Overall percent error				1.07	0.47	0.29	0.27	0.70	0.24

* Literature references for all sets of experimental data (except for the last set) are given in the previous paper¹

The applicability of all investigated models was also tested on 4 sets of data near the critical point, with 93 experimental points for 3 pure organic chemicals. A comparison of the previously recommended models and the new model is presented in Table I.

Overall percent errors are calculated as follow

$$P_{av} = \frac{\sum_{i=1}^N n_i P_{av,i}}{\sum_{i=1}^N n_i}, \quad p_{av} = 100 \sum_{i=1}^n |(c_{p,exp,i} - c_{p,cal,i}) / c_{p,exp,i}| \quad (7)$$

The obtained overall percent error (0.24 %) in Table I indicate that the accuracy of the new recommended model is slightly better than the existing models. The percent errors for the experimental data, near the critical point, indicate that the applicability of the new recommended model is better than the existing ones.

According to this study, we recommend the new model for accurate correlation and prediction of saturated liquid heat capacity over entire temperature range, especially near the critical point.

NOTATION

c_p	Saturated-liquid heat capacity, J/mol K
$c_{p,ref}$	Saturated-liquid heat capacity of the reference temperature T_{ref} , J/mol K
T_{ref}	Reference temperature, K
T_c	Critical temperature, K
T	Temperature, K
T_r	Reduced temperature
A, B, C, D	Adjustable parameters of the models
p_{av}	Percentage average error, %
P_{av}	Percentage overall error, %
n	Number of experimental data points
N	Number of compounds
ΔT	Temperature range, K
R	Gas constant, 8.3146 J/mol K

Subscripts

exp	Experimental value
cal	Calculated value

ИЗВОД

ТОПЛОТНИ КАПАЦИТЕТ ЗАСИЋЕНЕ ТЕЧНОСТИ ОРГАНСКИХ ЈЕДИЊЕЊА: НОВ ЕМПИРИЈСКИ КОРЕЛАЦИОНИ МОДЕЛ

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У овом раду је препоручен нов емпиријски модел за корелисање топлотног капацитета засићене течности органских једињења. Модел је тестиран и упоређен са

познатим полиномским и квази-полиномским моделима коришћењем 39 сетова са 1453 експериментална податка. Добијени резултати указују да је нов модел бољи од постојећих, нарочито у околини критичне тачке.

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REFERENCES

1. J. D. Jovanović, D. K. Grozdanić, *J. Serb. Chem. Soc.* **68** (2003) 479
2. S. S. Lorensen, D. W. Tedder, *Chem. Eng.* June (1994) 106
3. J. T. R. Watson, *Engineering Science Data Item Number 76010*. Engineering Science Data Unit (ESDU), London 1976
4. J. T. R. Watson, *Engineering Science Data Item Number 86023*. Engineering Science Data Unit (ESDU), London 1986
5. V. Roháč, J. E. Musgrove, K. Růžička, V. Růžička, M. Záborský, *J. Chem. Thermodynamics*, **31** (1999) 971
6. R. Wiebe, M. J. Brevoort, *J. Am. Chem. Soc.* **52** (1930) 622.