M.F. Bolotnikov, Yu.A. Neruchev

ESTIMATION THERMOPHYSICAL PROPERTIES OF ORGANIC LIQUIDS ON THE DATA OF SOUND SPEED

Kursk State University
Russia, 305000 Kursk, Radishcheva st., 33
Ph. (0712) 56-80-61
e-mail: bolotnikov@mail.ru

The opportunity of estimation caloric properties of liquids in critical area is considered on the basis of experimental data about sound speed in them. Discussion of the received results is carried out in frameworks discretely - continuum models of a liquid.

Because of far more complexity of a structure and character of thermal movement of molecules the theory of the liquid state is advanced much less the theory of gas and crystal state. In these conditions use of simplifying models for the description of the certain range of properties of a liquid represents not only practical but also theoretical interest. Authors pay attention to an opportunity quantitatively to describe equilibrium properties of a liquid on the saturation line with the help simple discretely - continuum models. According to this model the liquid is considered as continuous isotropy medium. Discreteness of medium is shown only within the limits of the first coordination sphere - in limits of "lattice cell". Within the framework of this model it is possible to obtain [1] the relation.

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(|E_P| + \frac{N}{N_0}\frac{RT}{\mu}\right)\cdot\rho \ , \tag{1}$$

This relation is the differential form of the equation of state for the condensed system.

Let's check up validity of the equation (1) in the critical area on the basis of the data on sound speed received by different authors.

Let's show as within the framework of suggested model on the basis of the data on sound speed, density and pressure saturated vapor can estimate caloric properties of a liquid. For this purpose as an example calculation of heat capacities C_P, C_V, and C_S near to a critical point carried out. In this area direct measurements of heat capacities are complicated and have not high accuracy. Let's take advantage for this purpose of experimental data about thermodynamic properties of liquid methane, n-heptane and oxygen from fundamental publications [2 - 5] and the data of own measurements [8]

Calculation of values of heat capacities was carried out on the basis of well-known system of thermodynamic equations.

$$\beta_S = \frac{1}{\rho c^2}; \qquad \beta_T = \frac{\alpha_H}{\left(\frac{\partial P}{\partial T}\right)_V - \frac{dP}{dT}} \tag{2}$$

$$C_V = \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\rho\left(\frac{1}{\beta_S} - \frac{1}{\beta_T}\right)}; \qquad C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P; \qquad C_S = C_V + T\left(\frac{\partial P}{\partial T}\right)_V\frac{dV}{dT}. \tag{3}$$

Calculation of the thermal coefficient of pressure was carried out with the help of the equation (1) presented as

$$T\left(\frac{\partial P}{\partial T}\right)_V = B\rho^3 + \frac{N}{N_0}\cdot\frac{RT}{\mu}\rho \tag{4}$$

Here the dominating role of dispersive forces of interaction is taken into account. Energy of these forces is proportional to square of liquid density

$$\left|E_P\right| = B\rho^2 \tag{5}$$

As may be supposed in precritical area in liquid methane, oxygen and n-hexane the value N/N_0 is close to 1/2, /to be exact by 0.53. In critical area of width 2-3 K the above-mentioned equation (1) takes the new form that is taking into account phase transition a liquid – vapor.

$$T\left(\frac{\partial P}{\partial T}\right)_V = B\rho^3 + \left[1 - A'\left(T_K - T\right)^\beta\right]\cdot\frac{RT}{\mu}\rho \tag{6}$$

The empirical constant β in the equation (6) is the critical index of the scale theory [5, 6] is equal 0.33.
The constant *B* describing intensity of dispersive forces is determined too from the equation (1) written down for a critical point.

$$T_K\left.\frac{\partial P}{\partial T}\right|_K = B\rho_K^3 + \frac{RT_K}{\mu}\rho_K \tag{7}$$

Critical parameters ρ_K, T_K and $\left.\frac{\partial P}{\partial T}\right|_K$ of different substances included in the equation (7) are very well-known. Some difficulties are related to estimating of value of a derivative $\left.\frac{\partial P}{\partial T}\right|_K$ describing change of pressure saturated vapor from temperature in a critical point. On evidence derived from [2, 3, 9] critical parameters for methane, oxygen and n-heptane have the following values (Table 1).

Table 1. Critical parameters of the investigated substances

Substance	ρ_K, *kg/m³*	T_K, *K*	P_K, *bar*	$\left.\frac{\partial P}{\partial T}\right\|_K$, bar/*K*	B
Methane	162.65	190.551	45.995	1.4300	2.55
Oxygen	436.14	154.581	50.49	1.9608	0.1542
n-Heptane	234.0	540.2.	27.4	0.3756	0.765

In Table 2 values of heat capacities C_P, C_V, and C_S of methane designed are presented on the basis of the technique considered above and the data of direct measurements resulted in [2].

Table 2. Heat capacity of methane *(J/mole·K)*

T, K	C_S calculat.	C_S [2]	%	C_P calculat.	C_P [2]	%	C_V calculat.	C_V [2]	%
172	75.5	75.5	-0.1	85.4	85.4	-0.0	29.3	29.3	-0.0
173	76.4	76.3	0.2	87.2	87.1	0.1	29.3	29.3	0.1
174	77.3	77.4	-0.0	89.2	89.2	-0.0	29.4	29.4	-0.1
175	78.8	78.8	-0.0	92.0	92.0	-0.0	29.3	29.3	-0.0
176	80.5	80.6	-0.0	95.4	95.4	-0.0	29.1	29.1	-0.1
177	82.1	82.1	-0.0	98.7	98.7	-0.0	29.0	29.0	-0.0
178	83.7	83.8	-0.0	102.4	102.5	-0.0	29.0	29.0	-0.0
179	85.9	85.9	-0.0	107.1	107.2	-0.0	28.9	29.0	-0.1
180	88.6	88.6	-0.0	113.0	113.0	-0.0	28.9	28.9	-0.0
181	91.5	91.6	-0.1	119.8	119.9	-0.0	28.8	28.8	-0.1

182	95.1	95.8	-0.7	128.6	129.1	-0.4	28.7	29.0	-1.1
183	99.2	99.2	-0.0	139.1	139.1	-0.0	28.6	28.6	-0.0
184	104.8	104.8	-0.0	153.9	153.9	-0.0	28.6	28.6	-0.0
185	110.8	110.8	-0.0	172.2	172.2	-0.0	28.6	28.6	0.0
186	122.3	122.3	0.0	205.7	205.7	0.0	28.5	28.5	0.0
187	141.2	141.2	0.0	264.6	264.6	0.0	28.4	28.4	0.0
188	175.5	172.3	1.9	378.8	380.1	-0.3	29.6	28.6	3.5
189	226.4	224.8	0.7	590.0	592.7	-0.4	32.9	32.5	1.9
190	385.4	379.4	1.7	1413.8	1455.0	-2.7	38.9	37.7	3.2

The fine consent between the theory and experiment is observed for all investigated interval of temperatures. Some inconsistent with the experiment takes place in immediate proximity to a critical point. However it does not surpass accuracy of experimental data C_P, C_V, and C_S resulted in [2]. Similar results are obtained for liquid oxygen and n-heptane. For these liquids by quoted above procedure calculating heat capacities C_P, C_V, and C_S have been determined in the immediate region of critical point (Tables 3 and 4). The data resulted in Tables 2 - 4 are lending support to the validity of the method.

Table 3. Heat capacity of oxygen *(J/mole·K)*

T, K	C_P calculat.	C_P calculat. on C_V	%	C_V calculat.	C_V [3]	%
140	87.3	86.1	-1.4	27.4	26.6	2.7
141	90.3	89.3	-1.1	27.3	26.7	2.2
142	93.3	92.5	-0.9	27.3	26.8	1.8
143	97.6	96.9	-0.7	27.3	26.9	1.5
144	102.6	102.1	-0.5	27.3	27.0	1.0
145	108.1	107.9	-0.1	27.3	27.2	0.3
146	115.2	115.3	0.1	27.4	27.4	-0.1
147	124.1	124.2	0.1	27.6	27.7	-0.2
148	135.8	136.2	0.3	27.8	28.0	-0.8
149	151.7	152.5	0.5	28.0	28.4	-1.5
150	174.7	175.9	0.7	28.3	29.0	-2.4
151	211.3	213.0	0.8	28.6	29.8	-3.9
152	280.9	281.6	0.3	29.9	30.9	-3.1
153	461.7	462.1	0.1	32.8	32.6	0.6
154	1136.7	1185.4	4.1	38.3	36.1	6.0

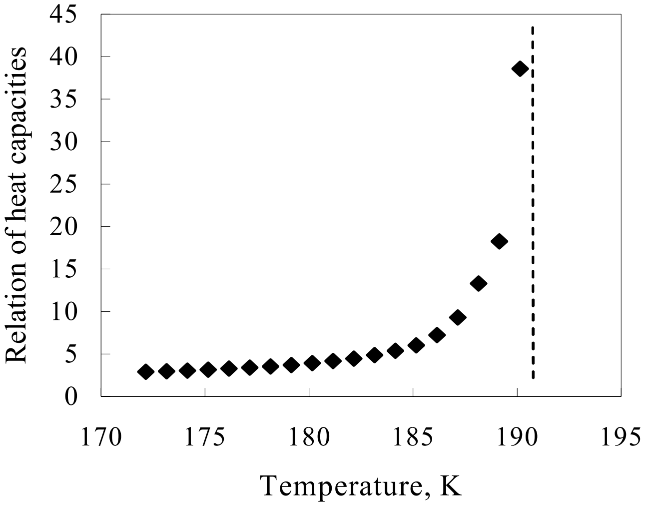

Figure. 1

Table 4. Heat capacity of n-hexane, *(J/mole·K)*

t, °C	C_V	C_V [4]	%
246	259.8	268.7	-3.3
247	261.9	269.3	-2.8
248	263.6	270.0	-2.3
249	265.8	270.6	-1.8
250	268.6	271.3	-1.0
251	271.2	271.9	-0.3
252	274.0	272.6	0.5
253	276.8	273.2	1.3
254	279.3	273.9	2.0
255	283.1	274.6	3.1
256	282.5	275.3	2.6
257	284.8	276.0	3.2
258	286.0	276.7	3.4
259	286.6	277.4	3.3
260	287.4	278.1	3.3
261	287.2	278.8	3.0
262	287.1	279.5	2.7
263	286.0	280.3	2.0
264	286.9	281.0	2.1
265	293.7	281.7	4.2

Observable distinction between calculated and experimental values of heat capacities C_V and C_P does not more than the mistake of measurements. As an example in Figure 1 temperature dependence of the ratio of heat capacities for liquid methane is resulted. Similar curves $\gamma = \gamma(T)$ are observed for other liquids. As is seen from the Figure 1 the ratio of heat capacities rise steeply and to tend to infinity in the critical point. The received results specify realness discretely - continuum models of the liquid.

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