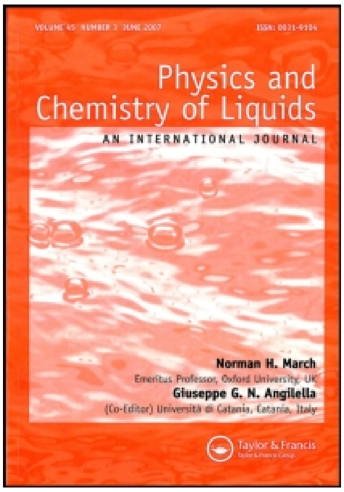

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Semi-empirical relation between freezing point and critical point properties of a wide variety of molecular liquids

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Semi-empirical relation between freezing point and critical point properties of a wide variety of molecular liquids

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Based on experimental data for some 28 freezing liquids, we define a semi-empirical relation connecting surface tension and molar volume with the molar critical volume. It is shown that the semi-empirical equation deduced by means of this relation allows one to calculate the given critical property for various molecular liquids with high accuracy.

Keywords: freezing liquids; energy balance; molar critical volume

1. Introduction

The main effect connected with the crystallisation of any liquid consists in the transition from a finite value of its fluidity to zero. At the same time its viscosity goes practically to infinity. The above transition is caused by the absence of one-particle translational jumping in the solid phase [1]. If we consider liquids at their normal freezing points, then their molecular thermal motion is being realised by means of three-dimensional vibrations and re-orientational motions of their molecules. The latter kind of molecular motion results in the fact that even the molecules of freezing liquids may be considered in some sense as spherical particles [1]. So, for instance, based on the experimental data connected with measurements of the Rayleigh scattering and the static dielectric constant of various liquid benzene derivatives, it has been shown in the monograph [2] that the symmetry of the force field of the molecules of the above mentioned liquid chemical substances is largely spherical, even at their freezing points.

However, if the value of the absolute temperature of a liquid is higher than T (where T is its freezing point), in this case its molecules can take part in their translational jumping motion which occurs between their different equilibrium positions [1,3]. Thus, the main condition required for the process of crystallisation of various liquids is cessation of this translational jumping motion of molecules therein. The presence of the above cessation of translational jumps within the liquid phase allows one to consider different freezing liquids as similar. Really, the absence of translational jumps of excited molecules in freezing liquids leads to the situation where the quantity of the volume of all the vacancies (holes)

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which are caused by jumps of the excited molecules situated therein on any straight-line segment of unit length (per unit time) goes to zero. As shown in the work by Gorbachev [4] in the case the viscosity of these liquids, which is inversely proportional to the above volume, will go to infinity. Thus, under these conditions, the process of crystallisation of these liquids becomes possible. Bearing in mind all the above mentioned points, one can suppose that an analytical expression describing the given process may be connected with some distribution of thermal energy between the molecules which belong to the above segment.

Thus, the aim of the present work consists of an attempt to define the mentioned expression, using the known experimental data for various freezing molecular liquids.

2. Theory

First of all we consider the molecules of the investigated liquid phase as spherical particles due to their fast mutual re-orientations caused by their rotational and librational motions. These re-orientations are being realised in the form of re-orientational jumpings which take place in the liquid phase even at its freezing point [1,2]. Further, let us consider all the molecules of the investigated liquid phase situated on the above mentioned segment of unit length which is oriented along the direction of flow of the given liquid phase (therefore, along the direction of some shearing force, acting on the liquid phase under consideration). Let, at first, its temperature T be higher than its freezing point. In this case it has been shown in [4] that the presence of some number of its excited molecules on this segment is the main condition of the process of flow of a given liquid phase. Really, the excited molecules situated on this segment take part in their translational jumping and, thus, can abandon this segment, forming some free volume within its length. Thus, the vibrating molecules, belonging to this segment, can displace along its length in the direction of the flow [4].

Let the number of the above mentioned excited molecules be N. As shown in Gorbachev's works [4,5], the following semi-empirical equation holds for N:

$$N = \left[\left(\frac{N_A}{V}\right)Z\right]^{1/3}. \tag{1}$$

In Equation (1), V is molar volume of a liquid, N_A is Avogadro number and Z is defined as:

$$Z = \exp\left(-\frac{gsV^{2/3}}{T}\right), \tag{2}$$

where s is surface tension of a liquid and g is the constant, whose numerical value is equal to 9.35×10^6 ($\mathrm{J^{-1}\,K\,mol^{2/3}}$). It does not depend on T or on the nature of the liquid phase [4,5].

As the total number of all the molecules situated on the segment equals to $(N_A/V)^{1/3}$, so the number of the vibrating molecules situated on it will be:

$$N_\mathrm{o} = \left(\frac{N_A}{V}\right)^{1/3}\left(1 - Z^{1/3}\right). \tag{3}$$

Now, we must take into account that the investigated liquid is at its freezing point. The given circumstance means that all its excited (active) molecules, including the excited ones situated on the above mentioned segment, cannot abandon their equilibrium positions [1–3]. At the same time, some average one-particle amplitude of their vibrations is essentially higher than that of the non-active molecules situated on the given segment. In other words, the above average thermal energy of these active molecules is less than some of its value which is required for the beginning of their jumping translational motion. However, if all the molecules (active and non-active) of the segment cannot abandon it, so for the investigated liquid the process of its flow become impossible [4]. Therefore, the above mentioned absence of one-particle translational jumping and the flow of the investigated liquid phase can be considered as some basic conditions, causing the process of its crystallisation.

Further, as we consider all the molecules of the investigated liquid as hard spheres, in this case their three-dimensional vibrations (but not their rotations or librational motions) will be responsible for any destruction of their linear order on the segment considered. Thus, if the process of crystallisation takes place, we shall suppose hereafter that the given fact indicated that for any normal freezing liquid phase, some constant balance in the distribution of the molecular vibrational kinetic energy between all the above mentioned active (excited) and non-active molecules situated on the unit segment is reached.

Bearing in mind the given supposition, we shall consider that the relation, x, of the total vibrational kinetic energy of all the active 'hot' molecules of the segment to that of all its non-active ones remains constant for different liquids at their normal freezing points. Further, let us assume that the one-particle vibrations of all the molecules, belonging to the segment, are three-dimensional and harmonic. As in the freezing liquid phase, the number of its excited molecules is essentially less than that of its non-active ones, so one can write the following equation for the average one-particle vibrational kinetic energy, E_o, of the non-active molecules of the unit segment under consideration:

$$E_o = 3kT. \tag{4}$$

At the same time, it has been shown in previous work [5] that the average one-particle vibrational kinetic energy, E, of the excited molecules which are almost ready to abandon their equilibrium positions can be described by means of the following equation:

$$E = cs(V_c^{1/3} - V^{1/3})^2, \tag{5}$$

where V_c is the molar critical volume of a liquid and c is some coefficient of proportionality which does not depend on T and is constant for different liquids.

Now, using Equations (1)–(5), we can write the following expression for the above mentioned quantity x:

$$x = \frac{EN}{E_o N_o} = \frac{s\left(V_c^{1/3} - V^{1/3}\right)^2 Z^{1/3}}{T(1 - Z^{1/3})}, \tag{6}$$

where all constant coefficients of Equations (4) and (5) are included into constant x, and Z is defined by means of Equation (2). It is to be noted that as the Boltzmann's constant k is included into x, and V_c and V given in ($\mathrm{m^3\,mol^{-1}}$), so, hereafter, the dimension of x is defined in ($\mathrm{J\,K^{-1}\,mol^{-2/3}}$).

Here it is to be especially noted that Equations (1), (2) and (6) are semi-empirical. It follows from the fact that the numerical value of the constant g (see Equation (2)) was defined on the basis of the corresponding experimental data [5]. The numerical value of x is being defined in the same way (see below).

3. Results and discussion

In order to verify the constancy of x, the 28 liquids presented in Table 1 were investigated. The values of their quantities V and s at their normal freezing points, T, side-by-side with their critical volumes, V_c, were taken from previous studies [3,7–21]. Here it is to be noted that the substances presented in Table 1 were chosen because of following reasons: first, they are well studied experimentally; second, they have various chemical structures which

Table 1. The constancy of the quantity x defined by means of Equation (6) for various freezing liquids.

No.	Compound	T (K)	$V \times 10^6$ ($\mathrm{m^3\,mol^{-1}}$)	$V_c \times 10^6$ ($\mathrm{m^3\,mol^{-1}}$)	$s \times 10^3$ ($\mathrm{N\,m^{-1}}$)	$x \times 10^7$ ($\mathrm{JK^{-1}\,mol^{-2/3}}$)
1	Hydrogen	13.96	23.44	65.00	2.911	0.3984
2	Deuterium	18.73	23.14	64.69	3.844	0.4088
3	Neon	24.55	16.17	44.30	5.68	0.4026
4	Oxygen	54.36	24.60	78.05	22.31	0.3922
5	Nitrogen	63.15	32.20	90.03	11.15	0.4006
6	Carbon monoxide	68.13	32.72	92.17	12.40	0.4030
7	Argon	83.78	27.97	75.26	12.93	0.3896
8	Carbon tetrafluoride	89.45	46.5	146.7	22.9	0.3992
9	Methane	90.67	35.0	99.5	17.2	0.3992
10	Diborane	108.30	53.6	173.1	26.3	0.4083
11	Krypton	115.78	34.13	92.3	16.1	0.3916
12	Chloroethane	134.45	57.7	199	38.42	0.4005
13	Bromoethane	147.65	62.0	215	41.07	0.3979
14	Xenon	161.3	44.16	119.5	19.3	0.3901
15	Chlorine	172.17	41.25	123.40	38.0	0.4023
16	Nitrous oxide	182.15	35.7	96.92	23.58	0.3991
17	Hydrogen sulfide	187.61	34.8	97.4	32.4	0.3979
18	Chlorobenzene	227.55	95.4	308.4	41.1	0.3858
19	Fluorobenzene	231.25	87.3	269.2	34.71	0.4057
20	Iodobenzene	241.75	106.6	351.2	41.60	0.3938
21	Bromobenzene	242.33	100.2	324.0	41.72	0.3901
22	2,2,3-Trimethylbutane	248.25	136.00	398	23.12	0.3951
23	Carbon tetrachloride	250.27	92.3	276.0	32.1	0.4030
24	Tungsten (VI) fluoride	275.15	85.4	233	19.8	0.4043
25	Benzene	278.68	88.28	254.5	30.79	0.4007
26	Cyclohexane	279.70	107.5	308	25.88	0.4020
27	Bromoform	281.05	89.9	283	47.11	0.3935
28	Phosphorus trichloride	334	110.6	374.6	57.54	0.4086

differ significantly. A part of them belongs to inorganic compounds; another is presented by organic substances. Nevertheless, the above mentioned physico-chemical parameters of these compounds obey Equation (6).

The comparison of the data of the last column of Table 1 shows that the numerical value of x remains practically constant for all the substances under investigation. The average numerical value of x, defined on the basis of the dataset of Table 1, is equal to 0.3987×10^{-7} ($\mathrm{J\,K^{-1}\,mol^{-2/3}}$).

Here it is to be noted that Equation (6) can be used, for instance, for definition of critical volumes – V_c – of liquids. So, using Equation (6), the following semi-empirical equation can be deduced for the quantity V_c:

$$Vc = \left\{ V^{1/3} + \left\{ \frac{xT(z^{-1/3} - 1)}{s} \right\}^{1/2} \right\}^{3}. \tag{7}$$

The values of V_c calculated by means of Equation (7) for some liquids are presented in Table 2. All the calculations of V_c were performed on the basis of the above mentioned numerical value of the constant x. The values of s, V and T needed for this aim were taken from the previous studies [7,8,11,14,15,22,23]. The comparison of the values of V_c calculated by means of Equation (7) and the corresponding experimental ones taken from some of the papers [7,11,14,22] shows that Equation (7) describes the quantity V_c adequately. For the liquids presented in Table 2, the average absolute value (module) of its calculation error is equal to 0.9%.

Here it is to be noted that Equations (6) and (7) do not hold for liquids, whose molecules are strongly associated at their freezing points (for instance, by means of intermolecular hydrogen bonds).

Table 2. The values of V_c calculated by means of Equation (7).

No.	Compound	T (K)	$V \times 10^6$ ($\mathrm{m^3\,mol^{-1}}$)	$s \times 10^3$ ($\mathrm{N\,m^{-1}}$)	$V_c \times 10^6$ ($\mathrm{m^3\,mol^{-1}}$) Calculated	$V_c \times 10^6$ ($\mathrm{m^3\,mol^{-1}}$) Experimental
1	Ethanethiol	125.75	59.4	36.74	208.2	207.1
2	Propadiene	137.90	51.0	35.20	164	162
3	Trimethylamine	149.15	77.0	30.60	252	254
4	Sulfur (IV) fluoride	151.0	51.6	33.9	160	162
5	*trans*-2-Butene	167.60	75.7	29.72	236.0	235.7
6	*n*-Hexane	177.83	112.6	30.18	377	370
7	*n*-Heptane	182.55	127.0	30.98	438	432
8	Ethyl acetate	189.55	86.0	38.43	287	286
9	Ethyl formate	192.65	71.0	38.51	226	229
10	Acetic anhydride	200.05	84.6	44.37	292	290
11	Dipropylamine	210.0	124.3	31.31	406.5	407.0
12	*n*-Octane	216.36	149.1	28.92	490	490
13	Cyclopentanone	220.35	82.5	41.36	266	268
14	Boron tribromide	227.31	89.0	38.1	282	280
15	2,2-Dimethylpropane	256.60	112.4	15.96	306	303
16	1,3-Dimethylbenzene	286.41	123.2	29.27	364	366
17	Mercury (II) chloride	550.0	62.2	53.2	170	174

Let us consider an example. Ethanol has its freezing point at 159.1 K [8]. Its values of s and V at this temperature are equal to 49.7×10^{-6} ($\mathrm{m^3\,mol^{-1}}$), respectively [7,12]. The value of V_c calculated by means of Equation (7) is equal to 150×10^{-6} ($\mathrm{m^3\,mol^{-1}}$). The corresponding experimental one is equal to 167×10^{-6} ($\mathrm{m^3\,mol^{-1}}$) [7]. However, when inter-molecular association is not so strong as in the above case, Equation (6) holds, and Equation (7) describes the quantity V_c adequately (cf. with the case of ethanethiol in Table 2).

It is to be noted that for some liquids possessing very low freezing points, the effective form of their molecules, which is caused by their thermal motion, cannot be considered as spherical. So, for instance, the value of V_c of freezing *n*-pentane (at $T = 143.4$ K [12]) calculated by means of Equation (7) (s and V are equal to 32.79×10^{-3} ($\mathrm{N\,m^{-1}}$) and $93.6 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$), respectively [7,8], is equal to $337 \times 10^{-6}(\mathrm{m^3\,mol^{-1}})$. The corresponding experimental value of V_c is $304 \times 10^{-6}(\mathrm{m^3\,mol^{-1}})$ [7]. At the same time Equations (6) and (7) hold for *n*-hexane, *n*-heptane, *n*-octane and 2,3-dimethylpropane, whose freezing points are essentially higher than that of *n*-pentane (see Table 2).

4. Conclusions

The following conclusions may be drawn. For various liquids considered at their normal freezing points the relation-x of the thermal kinetic energy of their active (excited) molecules to that of their non-active ones remains constant for any segment of unit length situated therein and containing within its boundaries all the above molecules (see Equation (6) and Table 1). In turn Equation (7), following from Equation (6), allows one to calculate the quantity V_c of critical volumes of these liquids.

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