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Reviews

Two Empirical Equations of State for Liquids To Improve p, V, T Data Representation and Physical Meaning

Siro Toscani*,† **and Henri Szwarc**‡

Laboratoire de Chimie du Solide et Inorganique Moléculaire—UMR 6511 CNRS, Bât. 10 B, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes, France, and Laboratoire de Chimie Physique, UMR 8000, Université de Paris Sud—CNRS, Bât. 490, 91405 Orsay, France

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A previously published four-parameter empirical equation of state of liquids is modified twice in order to improve the p, V, T data representation and its physical meaning, respectively. The first modification, a six-parameter relationship with two pressure square-root terms, was applied to 57 liquid compounds and to 6 mixtures and gives a very good representation (average percentage deviations of specific volume values less than 0.3%) of p, V, T data encompassing large pressure domains (0.1 to 1200 MPa). It could be useful for engineering applications. The second modified relationship exhibits the same fitting characteristics as the four-parameter one, but it has a better physical meaning. This equation contains an adjustable positive coefficient ξ which accounts for the intersections of the $(\partial\alpha/\partial p)_T$ isotherms at high pressure and also for the variations of the " pressure coefficient " $(\partial p/\partial T)_V$ as a function of both volume and temperature. Thermal expansion data may be represented with an average percentage deviation better than 5%.

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1. Introduction

In a paper published in 1993,[1] we presented the following four-parameter equation, which allows us to represent volumetric properties of liquids in the pressure and temperature domains varying within 0.1 and 300 MPa and within the melting and the normal boiling temperatures, respectively:

$$V = \frac{a + bp}{c - dT + p} \tag{1}$$

where V is the specific volume, p is the pressure, T is the temperature, and a, b, c, and d are positive constants.

In particular, the parameters d and $w = bc/a$ (w is the ratio of the volume b at infinite pressure to $V = a/c$, the volume at zero pressure and temperature) were found to exhibit only weak variations for each family of compounds. As a result, only two parameters are necessary to calculate the specific volume of a given compound as a function of temperature and pressure. However, despite its physical coherence (w turns out to be less than unity), eq 1 has some limitations. For large pressure domains (up to 800 MPa and more), as in the case of Bridgman's[2−5] and Brostow et al.'s[6] measurements, the fitting procedure leads to a poor representation of atmospheric-pressure results, in particular for hydrocarbons; for instance, the maximum percentage deviations for the specific volumes of 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane,[3] 3,3-diethylpentane, and n-heptadecane[6] vary between 2.3 and 3.3%. Two other limitations are more fundamental. According to eq 1, the pressure is

$$p = \frac{dVT}{V - b} - \frac{cV - a}{V - b} \tag{2}$$

and the so-called "pressure coefficient " $(\mathrm{d}p/\mathrm{d}T)_V$, namely, the ratio of thermal expansion α to compressibility β, is a function of volume only. As Bridgman[7] stated, "pressure should not be regarded as exerted by two mechanisms acting independently and additively, but there must be interaction between them" in a highly pressurized liquid, where molecules are very near one another. Consequently, along an isochore, such as $V = a/c$ for instance, where attractive and repulsive forces are initially balanced, "as temperature increases at constant volume (...), the part of pressure exerted by the attractive and repulsive forces changes. In this case, $(\mathrm{d}p/\mathrm{d}T)_V$ cannot be a mere function of volume only, but must involve the temperature also".

On the other hand, inasmuch as specific volume measurements showed the temperature derivative of thermal expansion $(\mathrm{d}\alpha/\mathrm{d}T)_p$ to become negative at high pressure, Bridgman argued that the isotherms representing the variation of thermal expansion versus pressure should intersect at high pressure. More recently, measurements of thermal expansion by Ter Minassian et al.[8−11] and of specific heat by Czarnota[12−15] proved that these curves intersect indeed in liquids. Obviously, eq 1 cannot take this feature of the liquid state into account.

In the following sections, we propose two unrelated modifications of this equation. The first one improves the representation of p, V, T data when measurements over large pressure ranges (up to 1200 MPa) are considered; the

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* To whom correspondence should be addressed. Telephone: (0033-2)-23235285. Fax: (0033-2)99383487. E-mail: siro.toscani@univ-rennes1.fr.

† Université de Rennes 1.

‡ Université de Paris Sud—CNRS.

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second one increases the physical worth of the primary equation because it accounts both for the volume and temperature dependencies of the "pressure coefficient" and for the intersections of thermal expansion versus pressure isotherms under high pressure.

These equations have been fitted to experimental results by means of linear least-squares regressions based upon the Gauss−Jordan matrix-inversion algorithm. On the average, the degree of freedom of the correlations is near 60. No smoothed p, V, T data have been taken into account, and all experimental points have been assigned the same statistical weight. Atmospheric pressure data were not considered to be more accurate than high-pressure ones, because the same apparatus and methods have been usually implemented in both measurements. Consequently, giving a greater statistical weight to atmospheric pressure data, thus forcing the fitting equations to include them, would not be legitimate.

2. Modified (p, V, T) Equations

2.1. Relation Improving the (p, V, T) Data Representation in a Wide Pressure Range. Whether eq 1 is applied to the data series on specific volume extending to very high pressure (1000 MPa and more), the representation of atmospheric pressure data of some liquid compounds, such as most hydrocarbons, is poor (errors may attain 2−3%). To improve the quality of the data representation over all the wide pressure domain considered (0−1177 MPa), extra terms depending on pressure are requested. Through a trial and error procedure, a form containing pressure square-root terms ($p^{1/2}$) was found, which gives good results:

$$V = \frac{a + bp + ep^{1/2}}{c - dT + p + fp^{1/2}} \tag{3}$$

Table 1 shows the values of the six parameters and the average deviations of the fittings of this equation restricted to Bridgman's,[2−5] Brostow et al.'s,[6] Dymond et al.'s[16−21] and Grindley et al.'s[22] results. These data were selected because they extend to pressures much higher than 300 MPa. The improvement with respect to eq 1 as to what concerns specific volume is good, in particular for saturated hydrocarbons. Except for the case of bromoethane, the maximum percentage deviations are less than 1.2% over all the pressure domain taken into account. Though specially conceived to improve data correlation for practical applications, eq 3 accounts for some general properties of the liquid state. As a matter of fact, except for the case of glycols, it predicts values for specific volumes b at infinite pressure which are smaller than those resulting from fittings by eq 1. It follows that the mean values of the parameter w for saturated hydrocarbons, alcohols, alkyl halides, and esters (the only exception is ethyldibenzyl malonate) are systematically lower than those reported in our previous paper. We have found 0.759, 0.728, 0.7016, and 0.756 instead of 0.987, 0.9752, 0.9712, and 0.969, respectively. Conversely, in the case of glycols, the value of w does not change very much (0.882 instead of 0.922). Furthermore, the calculated isothermal compressibility is predicted to be zero at infinite pressure and there will be no relative minimum or maximum of the function in eq 3, which of course is valid only for $p > 0$, if one of the following conditions is fulfilled. The first one, which is sufficient, is

$$(bc' - a)^2 - (bf - e)(c'e - af) < 0 \tag{4}$$

with $c' = c - dT$, where the first member of the inequality represents the discriminant of the quadratic equation obtained by putting $u = p^{1/2}$ and corresponding to $(\partial V/\partial p)_T = 0$. Anyway, if the first condition is not fulfilled, it is sufficient that the two inequalities

$$(a - bc')(bf - e) < 0 \tag{5a}$$

and

$$(e - bf)(c'e - af) < 0 \tag{5b}$$

be simultaneously fulfilled.

In most cases for which the above conditions are not fulfilled (1,2-propandiol, 1,3-propandiol, 2,2′-oxydiethanol, water, 2,2′,2″-trihydroxytriethylamine, tri(ortho)cresyl phosphate, and ethyldibenzyl malonate in Bridgman's, oct-1-ene in Dymond et al.'s, and water in Grindley et al.'s results), eq 3 yields no significant improvement in the representation of experimental values with respect to that given by eq 1; it does not predict lower values for specific volumes at infinite pressure either. For 1,2-propanediol and 1,3-propanetriol, fitting Bridgman's results on specific volumes with eq 3 is even worse. It must be noticed that most compounds quoted above belong to the glycol family, for which application of eq 1 gives the best fits.[1]

In the cases where two or more series of data on the same compound are interpolated by means of eq 3, a difference in the values of the equation parameters may be noticed. This difference is generally to be ascribed to the different pressure ranges of the data series. Let us consider, for example, the two series on isooctane. Data by Dymond et al.[19] are comprised within 0.1 and 540 MPa while those by Bridgman[4] cover the domain within 0 and 981 MPa. As expected, Bridgman's data interpolation predicts a volume at infinite pressure (parameter b) lower than that given by Dymond et al.'s data. Conversely, the values of the parameters a, c, and d increase with increasing the pressure range of experimental data. This had to be expected, in particular for the parameter c (MPa), since it is related to the attractive forces in a liquid and, consequently, to its internal pressure. This dependence of the equation parameters on the pressure range was already pointed out in fitting eq 1 to experimental results.[1] For this reason, in that work, data were cut off at 300 MPa in order to study the scattering of each parameter inside a given family of compounds. Another aspect to be considered is the choice of the set of parameters for a given compound to be used to calculate p, V, T data under different conditions. For this to be done, some criteria have to be settled on. For instance, if one needs to predict p, V, T data for isooctane at pressures much higher than 540 MPa, the Bridgman's data interpolation should be used in order to avoid tricky extrapolations from the Dymond et al.'s data. Conversely, in the pressure range within 0 and 540 MPa, which is common to the two series of data, the use of Dymond et al.'s data is recommended, because their experimental uncertainty is smaller than that of Bridgman's data.

2.2. The Relation Taking α−p Curves' Intersections into Account. In this section, we present another modification of eq 1 that takes into account the intersection of the isothermal thermal expansion α versus pressure curves in liquids at high pressure together with the isothermal behavior of heat capacity C_p as a function of pressure. One can write

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p = -VT\left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p\right] \tag{6}$$

Table 1. Parameters *a* ($MPa \cdot cm^3 \cdot g^{-1}$), *b* ($cm^3 \cdot g^{-1}$), *c* (MPa), *d* ($MPa \cdot K^{-1}$), *e* ($MPa^{1/2} \cdot cm^3 \cdot g^{-1}$), and *f* ($MPa^{1/2}$) and Average and Maximum Percentage Deviations Δ_{ave} and Δ_{max} for Representation of Experimental Results of Specific Volume ($cm^3 \cdot g^{-1}$) by Eq 3[a]

compd or mixture	P/MPa	T/K	a	b	c	d	e	f	Δ_{ave}	Δ_{max}	ref
Hydrocarbons											
pentane	0−981	273−368	746.82	0.8512	634.36	0.5578	16.410	13.207	0.12	0.36	3
2-methylbutane	0−883	273−368	644.17	0.9693	540.55	0.4677	6.8748	6.2225	0.15	0.50	3
hexane	0−1079	273−368	651.68	0.8028	594.08	0.5619	24.175	17.824	0.10	0.26	3
	0−564	298−373	596.79	0.8939	544.12	0.5179	15.210	11.589	0.09	0.28	16
2-methylpentane	0−1177	273−368	667.27	0.7910	604.75	0.5771	26.239	19.665	0.14	0.47	3
3-methylpentane	0−1177	273−368	850.92	0.7760	763.36	0.6705	23.795	19.551	0.24	0.83	3
2,2-dimethylbutane	0−981	273−368	413.23	0.8339	390.07	0.4152	27.982	19.120	0.16	0.40	3
2,3-dimethylbutane	0−1079	273−368	631.81	0.7815	579.57	0.5499	25.166	18.844	0.18	0.57	3
heptane	0−1079	273−368	624.94	0.7290	589.39	0.5533	29.710	21.795	0.10	0.33	3
octane	0.1−460	298−348	573.45	0.8170	544.22	0.4826	19.619	14.556	0.07	0.24	17
2,2,4-trimethylpentane (isooctane)	0.1−540	298−373	506.93	0.8665	482.29	0.4506	17.361	13.140	0.11	0.34	19
	0−981	273−368	600.83	0.7527	562.07	0.4983	28.574	21.347	0.13	0.47	4
3,3-diethylpentane	0−800	303−423	448.91	0.7620	453.17	0.3686	24.090	18.130	0.07	0.48	6
dodecane	0.1−442	298−373	481.35	0.8856	463.98	0.3532	11.532	8.8075	0.07	0.23	17
heptadecane	0−800	303−453	492.59	0.7656	491.89	0.3633	22.322	16.748	0.07	0.91	6
0.5octane + 0.5dodecane	0.1−413	298−373	510.51	0.9452	483.79	0.3815	6.3141	5.2931	0.13	0.34	17
0.5isooctane + 0.5dodecane	0.1−605	298−373	416.69	0.9539	409.57	0.3572	5.5990	4.2013	0.23	0.57	19
0.5octane + 0.5isooctane	0.1−499	298−373	411.55	0.8552	391.61	0.3565	16.996	11.944	0.13	0.33	21
oct-1-ene	0.1−313	298−373	365.22	1.0508	349.62	0.3030	0.1445	0.6429	0.13	0.36	20
0.5oct-1-ene + 0.5octane	0.1−412	298−373	455.60	0.9704	433.33	0.3788	5.4384	4.5208	0.16	0.50	21
0.5oct-1-ene + 0.5isooctane	0.1−291	298−373	368.89	0.9550	353.90	0.3227	8.7452	6.5048	0.10	0.31	21
0.333oct-1-ene + 0.333octane + 0.333isooctane	0.1−415	298−373	421.77	0.8838	404.64	0.3689	15.044	10.774	0.11	0.34	21
benzene	0.1−391	298−373	422.34	0.7375	508.29	0.4676	10.691	9.4819	0.05	0.16	18
toluene	0.1−459	298−373	492.22	0.6911	570.01	0.4876	15.573	13.537	0.07	0.24	20
Alcohols											
methanol	0.1−1177	293−353	636.22	0.6978	688.40	0.6301	16.119	13.616	0.12	1.07	2
ethanol	0.1−1177	293−353	752.47	0.6283	791.30	0.6754	23.779	20.276	0.10	0.40	2
propan-1-ol	0.1−1177	293−353	619.76	0.6972	671.00	0.5859	25.834	21.706	0.12	0.58	2
propan-2-ol	0.1−1177	273−368	795.69	0.7127	816.26	0.6557	18.978	16.635	0.10	0.33	3
butan-1-ol	0.1−1177	273−368	816.16	0.7030	831.70	0.5841	19.354	16.969	0.07	0.25	3
2-methylpropan-1-ol	0.1−1177	293−353	700.03	0.7254	735.60	0.5940	15.804	14.124	0.12	0.84	2
2-methylbutan-2-ol	0.1−1177	293−353	635.87	0.6675	685.31	0.5660	24.845	20.949	0.12	0.47	2
octan-3-ol	0.1−1177	273−368	731.46	0.6885	773.61	0.5896	22.891	19.727	0.07	0.32	5
3-methylheptan-1-ol	0.1−1177	273−368	832.01	0.6567	871.42	0.6237	26.147	22.864	0.06	0.25	5
2-methylheptan-3-ol	0.1−1177	273−368	720.02	0.7484	754.46	0.5460	11.469	10.051	0.18	0.90	5
3-methylheptan-4-ol	0.1−1177	273−368	737.96	0.6775	793.07	0.6183	24.333	21.226	0.07	0.25	5
2-methylheptan-5-ol	0.1−1177	273−368	783.43	0.6791	823.15	0.6213	23.747	20.790	0.09	0.40	5
Alkyl Halides											
chloroethane	0.1−1177	293−353	394.79	0.4832	558.76	0.7410	29.510	28.677	0.15	0.76	2
bromoethane	0.1−1177	293−353	330.96	0.3671	667.89	0.6133	9.2989	14.215	0.16	1.93	2
iodoethane	0.1−1177	293−353	221.39	0.2545	597.83	0.5694	11.136	21.500	0.13	0.57	2
1-chloropropane	0−1177	273−368	681.67	0.6484	811.36	0.6861	7.5680	9.1465	0.20	0.55	5
1-bromopropane	0−1177	273−368	432.52	0.3792	789.92	0.7143	13.378	19.628	0.12	0.51	5
1-iodopropane	0−1177	273−368	401.83	0.3019	907.45	0.7072	9.5783	18.393	0.11	0.46	5
1-chlorobutane	0−1177	273−368	579.63	0.5698	705.16	0.6558	22.207	21.041	0.12	0.47	5
1-bromobutane	0−1177	273−368	465.35	0.4023	795.19	0.6897	15.268	21.075	0.11	0.44	5
1-iodobutane	0−1177	273−368	416.89	0.3375	861.82	0.6489	9.6200	16.824	0.13	0.44	5
1-chloropentane	0−1177	273−368	621.85	0.5804	745.14	0.6496	21.399	20.648	0.10	0.42	5
1-bromopentane	0−1177	273−368	484.82	0.4419	774.77	0.6224	14.202	18.658	0.08	0.32	5
1-iodopentane	0−1177	273−368	391.15	0.3417	779.66	0.6086	12.215	19.592	0.12	0.39	5
Glycols											
1,2-ethanediol	0−1177	273−368	881.69	0.6040	1166.5	0.6296	5.6342	6.4193	0.08	0.38	4
2,2-oxydiethanol	0−1177	273−368	836.18	0.6856	1071.8	0.4713	−8.3777	−8.9327	0.15	1.13	4
1,2-propanediol	0−1177	273−368	889.55	0.8074	1031.9	0.3566	−26.523	−27.217	0.27	0.72	4
1,3-propanediol	0−1177	273−368	899.19	0.7286	1089.4	0.4898	−9.1838	−8.8129	0.10	0.31	4
1,2,3-propanetriol	0−1177	273−368	1075.7	0.6736	1461.8	0.4892	−19.931	−23.736	0.14	0.46	4
Esters											
glycerol triacetate	0−1177	273−368	694.35	0.4936	1050.8	0.7526	15.909	19.452	0.09	0.35	4
glycerol trihexanoate	0−1177	273−368	772.95	0.6286	933.55	0.5991	12.304	13.230	0.06	0.31	4
butyl phthalate	0−1177	273−368	711.35	0.5900	918.07	0.5852	13.732	15.060	0.08	0.29	4
methyl oleate	0−981	273−368	654.55	0.6854	721.19	0.4893	17.939	15.774	0.14	0.45	4
ethyl dibenzylmalonate	0−490	273−368	359.41	0.7474	469.73	0.2541	−5.4315	−6.0553	0.17	0.42	4
Other Compounds											
carbon disulfide	0.1−1177	293−353	412.75	0.4065	719.92	0.6778	14.339	18.555	0.11	0.30	2
phosphorus trichloride	0.1−1177	293−353	349.09	0.3457	749.20	0.6814	11.451	19.003	0.10	0.43	2
diethyl ether	0.1−1177	293−353	402.06	0.5553	473.27	0.6265	38.631	27.738	0.19	0.93	2
propan-2-one	0.1−1177	293−353	520.57	0.5825	614.43	0.6896	28.885	22.787	0.10	0.29	2
water	0−800	298−363	1076.0	0.8430	1201.2	0.4393	−29.246	−26.802	0.09	0.72	6
	0−1079	273−368	1163.4	0.8997	1267.7	0.3825	−39.475	−36.375	0.17	0.47	3
2,2′,2″-trihydroxytriethylamine	0−981	273−368	883.87	0.6334	1158.1	0.4974	−0.9973	−0.3243	0.06	0.14	5
tri-*o*-cresyl phosphate	0−588	273−368	464.03	0.6414	647.70	0.3336	3.4773	3.9613	0.04	0.11	4

[a] $\Delta_{ave} = 10^2\langle \delta V/V \rangle$ and $\Delta_{max} = 10^2(\delta V/V)_{max}$, where δV is the absolute difference between the calculated and experimental specific volume V from eq 3.

The temperature derivative $(\partial\alpha/\partial T)_p$, which is positive at low pressure, experimentally proves to become negative at higher pressures. According to eq 6, this reversal involves the existence of a minimum of C_p as a function of pressure. However, this thermodynamic feature cannot be incorporated in eq 1 because the temperature derivative $(\partial\alpha/\partial T)_p$ it leads to

$$\left(\frac{\partial\alpha}{\partial T}\right)_p = \frac{d^2}{(c - dT + p)^2} = \alpha^2 \tag{7}$$

is always positive. Conversely, a relation such as

$$V = \frac{a + bp}{c - dT(1 - \xi T) + p} \tag{8}$$

where ξ is an adjustable positive coefficient, gives a temperature derivative $(\partial\alpha/\partial T)_p$ (α') which is equal to zero for the following value of pressure

$$p_{\text{inv}}^{\alpha'} = \frac{d(1 - 2\xi T)^2}{2\xi} - [c - dT(1 - \xi T)] \tag{9}$$

and becomes negative for $p > p_{\text{inv}}^{\alpha'}$. Similarly, the sign-inversion pressure $p_{\text{inv}}^{C_p'}$ for the pressure derivative $(\partial C_p/\partial p)_T$ (C_p') is

$$p_{\text{inv}}^{C_p'} = \frac{d(1 - 2\xi T)^2}{\xi} - [c - dT(1 - \xi T)] \tag{10}$$

at temperature T, with $p_{\text{inv}}^{C_p'}$ being related to and greater than $p_{\text{inv}}^{\alpha'}$, according to eqs 9 and 10. The $p_{\text{inv}}^{\alpha'}$ and $p_{\text{inv}}^{C_p'}$ values derived from these relations depend on temperature, so that the calculated intersections of the α curves occur within a pressure domain and not at a single point. This corresponds to what was experimentally observed by Ter Minassian et al. in the case of toluene.[10]

The coefficient ξ can be adjusted by trial and error through a standard procedure of fitting p, V, T data by means of eq 8 until eq 9 is fulfilled for a ($p_{\text{inv}}^{\alpha'}$, T) couple of values for which the sign-reversal of $(\partial\alpha/\partial T)_p$ has been experimentally observed. If $p_{\text{inv}}^{\alpha'}$ turns out to be experimentally temperature-independent, as in the cases of hexane[23] and of carbon disulfide,[11] the average temperature of the experimental (p, V, T) range is usually used as the $(\partial\alpha/\partial T)_p$ sign-reversal temperature in calculations. The α values can then be computed by means of the thermal expansion equation derived from eq 8

$$\alpha = \frac{d(1 - 2\xi T)}{c - dT(1 - \xi T) + p} \tag{11}$$

and compared with experimental values. The same iterative procedure can obviously be applied to eq 10 if the pressure at the minimum of C_p is known. For instance, we have incorporated couples of ($p_{\text{inv}}^{\alpha'}$, T) values for hexane by Pruzan,[23] for carbon disulfide by Tomaszkiewicz and Ter Minassian,[11] and for toluene by Ter Minassian et al.[10] in fitting accurate correspondent p, V, T results by Mopsik[24,25] and by Muringer et al.[26] For the three compounds, the average percentage deviations for specific volume data are almost the same as those obtained by fitting p, V, T results by eq 1, which proves that eqs 1 and 8 have the same ability to restitute p, V, T data. As to what concerns α values, the average deviation between experimental and calculated values was less than 5% within the whole p, T range of the p, V, T data in the case of hexane and carbon disulfide, whereas for toluene it was less accurate (around 7%), as reported in Table 2. In Figure 1, calculated α values for hexane, carbon disulfide, and toluene are plotted to show how eq 8 describes the α versus p isotherms. To make evident the pressure range within which the isotherms cross, for each compound we have considered only the isotherms situated at the lowest and at the highest temperature, respectively. As to what concerns toluene, the isotherm at 219 K was taken into account instead of that at 202 K, since the last one does not extend until the highest pressure (240 MPa). It may be noticed that for hexane, carbon disulfide, and toluene the isotherms' intersection pressures are near 80, 200, and 55 MPa, respectively. On the other hand, eq 11 was also fitted to the experimental α values on hexane and on carbon disulfide as a function of temperature and pressure. The parameter ξ was again forced to incorporate the couples of ($p_{\text{inv}}^{\alpha'}$, T) values for the two compounds. The calculated

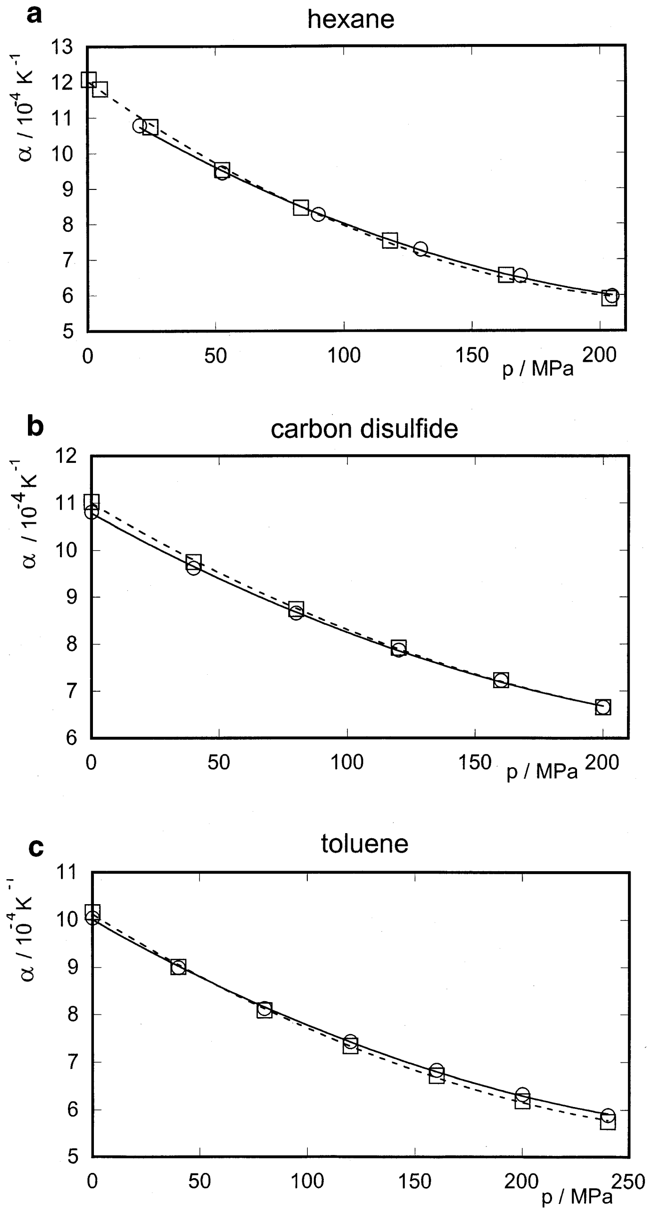

Figure 1. Calculated α Values for Hexane, Carbon Disulfide, and Toluene by Interpolation of Data from refs 23, 11, and 10 by means of eq 8. Isotherms: (a) (hexane) circles, 238.6 K; squares, 301.6 K; (b) (carbon disulfide) circles, 246.3 K; squares, 293.4 K; (c) (toluene) circles, 218.9 K; squares, 304.5 K.

Table 2. Parameters *a* (MPa·cm^3·g^{-1}), *b* (cm^3·g^{-1}), *c* (MPa), *d* (MPa·K^{-1}), and ξ (K^{-1}), Average and Maximum Percentage Deviations Δ_{ave} and Δ_{max} for Representation, by Eq 8, of Experimental Results on the Specific Volume (cm^3·g^{-1}) for Hexane, Carbon Disulfide, and Toluene from Refs 24, 25, and 26, Respectively, Average Temperature $\langle T\rangle$ (K) of the *p*, *V*, *T* Experimental Range, Experimental Sign-Inversion Pressures $p_{inv}^{\alpha'}$ and $p_{inv}^{C_p'}$ (MPa) of the $(\partial\alpha/\partial T)_p$ and $(\partial C_p/\partial p)_T$ Curves, Respectively, for Each Aforementioned Compound (Refs 23, 11, and 10), Given by Eqs 9 and 10 in Fitting *p*, *V*, *T* Data by Eq 8, and Pressure (MPa), Experimental (α_{exp}) and Calculated (α_{calc}) Thermal Expansion (K^{-1}), and Percentage Deviation Δ in Order to Compare α Values from Refs 23, 11, and 10 with Those Calculated by Means of Eq 11 Using the *c*, *d*, and ξ Parameters Obtained by Fitting *p*, *V*, *T* Results by Eq 8[a]

compd	*a*	*b*	*c*	*d*	ξ	Δ_{ave}	Δ_{max}	$\langle T\rangle$/K	$p_{inv}^{\alpha'}$/MPa	$p_{inv}^{C_p'}$/MPa
hexane	295.03	1.1119	272.55	0.2942	3.4×10^{-4}	0.08	0.32	260	90.4	383.6

p/MPa	$10^4\alpha_{exp}$/K^{-1}	$10^4\alpha_{calc}$/K^{-1}	Δ	*p*/MPa	$10^4\alpha_{exp}$/K^{-1}	$10^4\alpha_{calc}$/K^{-1}	Δ
Isotherm: 238.6 K							
20.4	10.22	10.79	5.58	129.8	7.03	7.29	3.70
52.6	8.82	9.45	7.14	168.8	6.18	6.54	5.83
89.8	7.80	8.27	6.03	204.7	6.10	5.97	−2.13
Isotherm: 251.8 K							
8.2	11.21	11.44	2.05	155.5	6.70	6.76	0.90
40.3	9.39	9.94	5.86	193.9	6.20	6.11	−1.45
84.9	7.90	8.41	6.46				
Isotherm: 264.7 K							
2.6	11.98	11.81	−1.42	105.8	7.47	7.84	4.42
10.1	11.08	11.39	2.80	144.9	6.77	6.96	2.81
17.8	10.47	10.99	4.97	190.6	6.18	6.15	−0.49
38.3	9.54	10.05	5.35	211.4	5.94	5.84	−1.68
70.9	8.29	8.85	6.76				
Isotherm: 301.6 K							
0.6	13.65	12.08	−11.5	117.9	7.13	7.52	5.47
5.0	13.04	11.81	−9.43	163.2	6.33	6.56	3.63
24.6	10.94	10.75	−1.74	203.6	5.79	5.90	1.90
52.5	9.10	9.53	4.73				
83.2	7.94	8.47	6.68				

compd	*a*	*b*	*c*	*d*	ξ	Δ_{ave}	Δ_{max}	$\langle T\rangle$/K	$p_{inv}^{\alpha'}$/MPa	$p_{inv}^{C_p'}$/MPa
carbon disulfide	241.18	0.5858	413.28	0.4034	2.84×10^{-4}	0.06	0.14	260.0	199.8	715.7

p/MPa	$10^4\alpha_{exp}$/K^{-1}	$10^4\alpha_{calc}$/K^{-1}	Δ	*p*/MPa	$10^4\alpha_{exp}$/K^{-1}	$10^4\alpha_{calc}$/K^{-1}	Δ
Isotherm: 246.3 K							
0.1	10.81	10.81	0.00	120.0	7.54	7.87	4.38
40.0	9.30	9.62	3.44	160.0	6.97	7.22	3.59
80.0	8.28	8.66	4.59	200.0	6.51	6.66	2.30
Isotherm: 273.2 K							
0.1	11.37	10.94	−3.78	120.0	7.61	7.90	3.81
40.0	9.58	9.69	1.15	160.0	7.00	7.23	3.29
80.0	8.43	8.70	3.20	200.0	6.51	6.66	2.30
Isotherm: 293.4 K							
0.1	11.91	11.03	−7.39	120.0	7.68	7.92	3.13
40.0	9.83	9.75	−0.81	160.0	7.02	7.23	2.99
80.0	8.56	8.74	2.10	200.0	6.51	6.66	2.30

compd	*a*	*b*	*c*	*d*	ξ	Δ_{ave}	Δ_{max}	$\langle T\rangle$/K	$p_{inv}^{\alpha'}$/MPa	$p_{inv}^{C_p'}$/MPa
toluene	363.89	0.8608	421.86	0.4046	3.55×10^{-4}	0.06	0.26	251.0	55.5	440.3

p/MPa	$10^4\alpha_{exp}$/K^{-1}	$10^4\alpha_{calc}$/K^{-1}	Δ	*p*/MPa	$10^4\alpha_{exp}$/K^{-1}	$10^4\alpha_{calc}$/K^{-1}	Δ
Isotherm: 202.0 K							
0.1	9.00	10.01	11.22	120.0	7.35	7.44	1.22
40.0	8.33	8.98	7.80	160.0	6.97	6.85	−1.72
80.0	7.79	8.14	4.49				
Isotherm: 218.9 K							
0.1	8.98	10.04	11.80	160.0	6.66	6.83	2.55
40.0	8.18	8.99	9.90	200.0	6.31	6.33	0.32
80.0	7.57	8.13	7.40	240.0	6.01	5.89	−2.00
120.0	7.07	7.43	5.09				
Isotherm: 241.4 K							
0.1	9.15	10.08	10.16	160.0	6.39	6.81	6.57
40.0	8.14	9.00	10.57	200.0	6.01	6.30	4.83
80.0	7.41	8.13	9.72	240.0	5.70	5.86	2.81
120.0	6.84	7.41	8.33				
Isotherm: 263.0 K							
0.1	9.44	10.11	7.10	160.0	6.22	6.78	9.00
40.0	8.20	9.01	9.88	200.0	5.82	6.26	7.56
80.0	7.35	8.12	10.48	240.0	5.49	5.82	6.01
120.0	6.71	7.39	10.13				
Isotherm: 304.5 K							
0.1	10.28	10.16	−1.17	160.0	6.03	6.72	11.44
40.0	8.46	9.01	6.50	200.0	5.59	6.19	10.73
80.0	7.36	8.09	9.92	240.0	5.23	5.75	9.94
120.0	6.59	7.34	11.38				

[a] $\Delta_{ave} = 10^2\langle\delta V/V\rangle$, $\Delta_{max} = 10^2(\delta V/V)_{max}$, and $\Delta = 10^2(\delta\alpha/\alpha)$, where δV and $\delta\alpha$ are the absolute differences between calculated and experimental values of specific volume, *V*, and of thermal expansion, α, respectively.

Table 3. Parameters *a* (MPa·cm^3·g^{-1}), *b* (cm^3·g^{-1}), *c* (MPa), *d* (MPa·K^{-1}), and *e* (MPa·K^{-2}), Average and Maximum Percentage Deviations Δ_{ave} and Δ_{max} for Representation of Experimental Results on the Specific Volume (cm^3·g^{-1}) for Hexane, Carbon Disulfide, and Toluene from Refs 24, 25, and 26, Respectively, by Eq 12, Average Temperature $\langle T\rangle$ (K) of the *p*, *V*, *T* Experimental Range, and Sign-Inversion Pressures $p_{\mathrm{inv}}^{\alpha'}$ and $p_{\mathrm{inv}}^{C_p'}$ (MPa) Calculated by Means of Eqs 9 and 10, Respectively

compd	*a*	*b*	*c*	*d*	*e*	Δ_{ave}[a]	Δ_{max}[a]	$\langle T\rangle$/K	$p_{\mathrm{inv}}^{\alpha'}$/MPa	$p_{\mathrm{inv}}^{C_p'}$/MPa
hexane	291.79	1.1116	266.27	0.2656	5.08×10^{-5}	0.08	0.31	260.0	362.4	925.5
carbon disulfide	246.08	0.5832	418.93	0.3906	7.76×10^{-5}	0.06	0.14	260.0	467.8	1258
toluene	365.21	0.8500	426.84	0.4341	1.99×10^{-4}	0.06	0.30	251.0	−49.8	230.8

[a] $\Delta_{\mathrm{ave}} = 10^2\langle\delta V/V\rangle$ and $\Delta_{\mathrm{max}} = 10^2(\delta V/V)_{\mathrm{max}}$, where δV is the absolute difference between calculated and experimental specific volume V from eq 12.

values of the parameters *c*, *d*, and ξ are rather well correlated to the corresponding ones derived from interpolation of *p*, *V*, *T* results by Mopsik by means of eq 8, which are reported in Table 2. We obtained $c = 255.47$ MPa, $d = 0.2760$ MPa·K^{-1}, and $\xi = 3.44 \times 10^{-4}$ K^{-1} for hexane and $c = 369.52$ MPa, $d = 0.3602$ MPa·K^{-1}, and $\xi = 2.74 \times 10^{-4}$ K^{-1} for carbon disulfide. The average percentage deviation of the calculated α values was satisfactory only for carbon disulfide data (1.3%) while for hexane ones it was worse (3.7%). Further temperature-dependent terms are likely necessary to improve the interpolating power of eq 11, in particular to take account of the increase of α approaching to the normal boiling temperature. Conversely, the divergent behavior of the α curves in the critical region cannot be accounted for by such an equation.

At this stage, for each compound, the remaining *a* and *b* parameters could have been obtained by least-squares regressions taking all the *p*, *V*, *T* data into account. However, as the parameters *c*, *d*, and ξ were frozen by interpolation of the α data, the representation of the *p*, *V*, *T* data turned out to be slightly less accurate than that in the case when eq 8 is directly fitted to *p*, *V*, *T* data. However, this two-step interpolation method may offer some interest in the case where the α versus pressure behavior of a liquid compound has been fully investigated and, concurrently, one disposes of few *p*, *V*, *T* data on it.

On the other hand, if the product ξd is treated as a fifth independent parameter *e* in eq 8, that is to say

$$V = \frac{a + bp}{c - dT + eT^2 + p} \qquad (12)$$

even very accurate (*p*, *V*, *T*) data sets do not allow us to predict fair $p_{\mathrm{inv}}^{\alpha'}$ and $p_{\mathrm{inv}}^{C_p'}$ values. As can be observed in Table 3, the $p_{\mathrm{inv}}^{\alpha'}$ and $p_{\mathrm{inv}}^{C_p'}$ values calculated for *n*-hexane and carbon disulfide are much greater than those measured by Ter Minassian and co-workers and accounted for by eq 8. In the case of toluene, the sign-inversion of $(\partial\alpha/\partial T)_p$ is calculated to occur at a negative pressure. However, a relevant feature of eq 12, when applied to many series of experimental data, is its ability to predict the trend of the slopes of the isochores $(\partial p/\partial T)_V$. Hence, the reiteration of the sign of the parameter *e* has been investigated without imposing any constraint on it. A straightforward conclusion may be drawn by using this equation to interpolate (*p*, *V*, *T*) data sets only. Table 4 shows the values of the five parameters and the average deviations of the fits of this equation to Boelhouwer's,[27] Baonza et al.'s,[28] Kuss and Tasmili's,[29] Lowitz et al.'s,[30] and Figuière and Szwarc's[31] results, too. We have taken into account families of organic compounds, as already done previously.[1] It turns out that the parameter *e* is positive in most cases (around 81%) and its value is around 5×10^{-4} MPa·K^{-2}. As eq 12 yields the following expression for pressure

$$p = \frac{dVT - eVT^2}{V - b} - \frac{cV - a}{V - b} \qquad (13)$$

from eq 13 it becomes

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{d - 2eT}{1 - \dfrac{b}{V}} \qquad (14)$$

and

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = -\frac{2e}{1 - \dfrac{b}{V}} \qquad (15)$$

Hence, as parameter *e* is positive in most cases, it can be inferred that $(\partial p/\partial T)_V$ should decrease as temperature increases; moreover, the resulting decrease should be proportional to *e*, as indicated by the expression of the second derivative.

Moreover, if we consider the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad (16)$$

where *U* is the internal energy of the liquid, from eq 13 we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{cV - a - eVT^2}{V - b} \qquad (17)$$

where $(\partial U/\partial V)_T$ is the internal pressure of the liquid. This pressure may be considered as the resultant of the forces of attraction and the forces of repulsion between the molecules in a liquid. From eq 17, it follows that, along a given isotherm, the specific volume V_0 at which internal pressure cancels out

$$V_0 = \frac{a}{c - eT^2}, \qquad (18)$$

increases as the isotherm temperature increases, proportional to parameter *e*.

3. Discussion

In Table 5, it is shown that average deviations on specific volume are systematically less than the experimental uncertainties of the results from refs 2−5, for fittings by eq 3, and of the results from refs 2−5, 26, 28, 29, and 31, for fittings by eq 12. In the case of eq 12, deviations may become noteworthy (2−3%) near atmospheric pressure only in the case of series stretching over a pressure range much

Table 4. Parameters *a* (MPa·cm^3·g^{-1}), *b* (cm^3·g^{-1}), *c* (MPa), *d* (MPa·K^{-1}), and *e* (MPa·K^{-2}) and Average and Maximum Percentage Deviations Δ_{ave} and Δ_{max} for Representation of Experimental Results of Specific Volume (cm^3·g^{-1}) by Eq 12[a]

compd	*P*/MPa	*T*/K	*a*	*b*	*c*	*d*	*e*	Δ_{ave}	Δ_{max}	ref
Hydrocarbons										
hexane	0.1−203	223−298	295.48	1.1117	269.90	0.2710	5.52×10^{-5}	0.08	0.31	24
	0.1−196	298−353	270.15	1.1213	275.83	0.4252	3.09×10^{-4}	0.08	0.27	29
	0−1079	273−368	532.37	0.9778	503.69	0.6365	4.19×10^{-4}	0.36	1.57	3
heptane	0−118	273−393	211.99	1.1660	193.06	0.1510	-4.63×10^{-5}	0.08	0.42	27
	0.1−263	198−311	357.90	1.0534	333.77	0.3324	1.07×10^{-4}	0.08	0.66	26
	0.1−196	298−353	252.77	1.1188	246.17	0.2934	1.41×10^{-4}	0.11	0.36	29
	0−1079	273−368	495.21	0.9606	453.27	0.4217	1.08×10^{-6}	0.52	2.29	3
octane	0−118	303−393	199.89	1.1598	188.64	0.1654	1.69×10^{-6}	0.10	0.54	27
nonane	0−118	303−393	201.97	1.1507	192.58	0.1666	1.26×10^{-5}	0.07	0.39	27
dodecane	0−118	303−393	225.94	1.1113	220.95	0.1858	3.13×10^{-5}	0.06	0.22	27
hexadecane	0−118	303−393	252.71	1.0789	248.31	0.1850	1.60×10^{-5}	0.04	0.15	27
isopentane	0.1−203	223−298	249.92	1.1645	221.55	0.2259	7.55×10^{-7}	0.10	0.42	25
	0−883	273−368	483.75	1.0193	387.46	0.2087	-2.12×10^{-4}	0.30	1.52	3
2-methylpentane	0−1177	273−368	525.02	0.9781	478.28	0.5219	2.67×10^{-4}	0.49	2.69	3
3-methylpentane	0−1177	273−368	571.28	0.9426	616.99	1.1147	1.13×10^{-3}	0.60	2.96	3
3-ethylpentane	0.1−196	298−353	253.89	1.1029	228.02	0.1471	-9.76×10^{-5}	0.10	0.29	29
2,2-dimethylbutane	0−981	273−368	500.56	1.0218	504.59	0.8385	8.51×10^{-4}	0.27	1.20	3
2,3-dimethylbutane	0−1079	273−368	502.13	0.9704	466.82	0.5328	3.05×10^{-4}	0.49	2.42	3
isooctane	0−981	273−368	502.74	0.9644	489.56	0.6160	4.92×10^{-4}	0.39	1.79	4
cyclopentane	0.1−196	298−353	280.26	1.0057	298.38	0.3777	2.41×10^{-4}	0.05	0.14	29
cyclohexane	0.1−85	288−323	217.76	1.0459	196.18	0.0075	-3.37×10^{-4}	0.03	0.10	26
benzene	0.1−170	288−323	266.46	0.8915	298.09	0.1696	-1.67×10^{-4}	0.03	0.10	26
toluene	0.1−263	182−320	365.21	0.8600	426.84	0.4341	1.99×10^{-4}	0.05	0.30	26
toluene	0.1−203	223−298	336.03	0.8751	389.04	0.3853	1.11×10^{-4}	0.05	0.12	25
squalane	0.1−200	298−353	363.22	0.9769	373.02	0.3146	1.45×10^{-4}	0.04	0.11	29
squalene	0.1−196	298−353	394.32	0.9206	462.71	0.5658	4.72×10^{-4}	0.03	0.11	29
bixylyltoluene	0.1−196	298−353	384.68	0.8797	390.67	0.0778	-2.45×10^{-4}	0.02	0.05	29
trans-decaline	0.1−196	298−353	335.36	0.9083	399.03	0.4795	3.80×10^{-4}	0.04	0.17	29
7-hexyltridecane	0.1−340	311−408	331.92	0.9954	356.78	0.4088	2.83×10^{-4}	0.13	0.67	30
11-decylheneicosane	0.1−340	311−408	312.90	0.9988	301.01	0.1361	-9.05×10^{-5}	0.18	0.77	30
13-dodecylhexacosane	0.1−340	311−408	366.52	0.9699	374.16	0.2788	8.55×10^{-5}	0.09	0.34	30
1,1-diphenylethane	0.1−340	311−372	378.40	0.7941	481.32	0.4065	1.82×10^{-4}	0.09	0.39	30
1,1-diphenylheptane	0.1−340	311−408	362.03	0.8388	464.07	0.5224	3.90×10^{-4}	0.09	0.52	30
1,1-diphenyltetradecane	0.1−340	311−408	342.75	0.8809	439.38	0.5491	4.44×10^{-4}	0.08	0.26	30
1,2,3,4,5,6,7,8,13,14,15,16-dodecahydrochrysene	0.1−340	311−408	379.96	0.7898	459.07	0.1861	-7.54×10^{-5}	0.04	0.1	30
perhydrochrysene	0.1−340	311−408	385.46	0.8314	463.53	0.3420	1.66×10^{-4}	0.05	0.25	30
1,1-di(α-decalyl)hendecane	0.1−300	311−408	359.45	0.8829	389.91	0.1710	-6.24×10^{-5}	0.07	0.20	30
Alcohols										
methanol	0.1−1177	293−353	594.92	0.8105	752.43	1.3402	1.34×10^{-3}	0.27	1.29	2
ethanol	0.1−1177	293−353	627.53	0.8035	686.49	0.8017	5.52×10^{-4}	0.32	1.78	2
propan-1-ol	0.1−1177	293−353	553.91	0.8597	573.16	0.4569	9.83×10^{-5}	0.34	1.77	2
butan-1-ol	0.1−1177	273−368	610.58	0.8418	648.06	0.6281	3.64×10^{-4}	0.29	1.08	3
propan-2-ol	0.1−1177	273−368	587.15	0.8494	562.11	0.2591	-2.66×10^{-4}	0.35	1.57	3
2-methylpropan-1-ol	0.1−1177	293−353	567.06	0.8301	662.71	0.9186	7.65×10^{-4}	0.31	1.79	2
pentan-1-ol	0.1−1177	293−353	587.20	0.8307	615.32	0.5131	1.86×10^{-4}	0.32	1.59	2
octan-3-ol	0.1−1177	273−368	638.03	0.8354	713.70	0.8319	6.67×10^{-4}	0.22	0.97	5
2-methylheptan-3-ol	0.1−1177	273−368	653.79	0.8238	726.56	0.7949	5.60×10^{-4}	0.29	1.13	5
2-methylheptan-5-ol	0.1−1177	273−368	644.33	0.8318	700.25	0.7193	4.88×10^{-4}	0.26	1.17	5
3-methylheptan-1-ol	0.1−1177	273−368	689.60	0.8241	717.42	0.5625	2.58×10^{-4}	0.22	1.14	5
3-methylheptan-4-ol	0.1−1177	273−368	640.13	0.8296	696.82	0.6760	4.14×10^{-4}	0.24	1.25	5
Alkyl Halides										
chloroethane	0.1−1177	293−353	450.50	0.6846	557.31	0.5274	7.83×10^{-5}	0.35	1.78	2
bromoethane	0.1−1177	293−353	353.12	0.4284	632.35	0.2614	-3.44×10^{-4}	0.23	2.03	2
iodoethane	0.1−1177	293−353	247.67	0.3335	755.92	1.3621	1.46×10^{-3}	0.31	1.64	2
1-chloropropane	0−1177	273−368	534.87	0.6951	518.37	0.2443	-1.18×10^{-3}	0.30	1.50	5
1-bromopropane	0−1177	273−368	370.20	0.4729	764.67	1.2479	1.20×10^{-3}	0.32	1.64	5
1-iodopropane	0−1177	273−368	327.76	0.3682	789.94	0.9397	7.22×10^{-4}	0.27	1.28	5
1-chlorobutane	0−1177	273−368	523.17	0.7253	648.67	0.7720	5.25×10^{-4}	0.34	1.62	5
1-bromobutane	0−1177	273−368	397.73	0.5065	724.53	0.9528	7.76×10^{-4}	0.30	1.65	5
1-iodobutane	0−1177	273−368	354.17	0.4028	774.08	0.8661	6.37×10^{-4}	0.26	1.19	5
1-chloropentane	0−1177	273−368	540.24	0.7264	670.32	0.7929	5.70×10^{-4}	0.30	1.81	5
1-bromopentane	0−1177	273−368	418.42	0.5379	656.77	0.5331	1.76×10^{-4}	0.24	1.62	5
Glycols										
1,2-ethanediol	0−1177	273−368	827.42	0.6364	1076.3	0.4990	-8.86×10^{-5}	0.10	0.36	4
1,3-propanediol	0−1177	273−368	774.79	0.6848	1022.3	0.8723	5.88×10^{-4}	0.12	0.52	4
1,2-propanediol	0−1177	273−368	917.30	0.6572	1272.6	1.4994	1.41×10^{-3}	0.19	0.64	4
2,2′-oxydiethanol	0−1177	273−368	794.54	0.6439	1039.1	0.5169	8.83×10^{-6}	0.13	1.13	4
1,2,3-propanetriol	0−1177	273−368	1187.2	0.5689	1772.6	1.3778	1.03×10^{-3}	0.13	0.32	4
Esters										
glycerol triacetate	0−1177	273−368	605.64	0.5883	970.55	1.0841	8.50×10^{-4}	0.17	0.54	4
glycerol trihexanoate	0−1177	273−368	621.62	0.7071	748.51	0.4925	1.05×10^{-4}	0.17	0.85	4
butyl phthalate	0−1177	273−368	630.86	0.6695	826.51	0.6507	3.37×10^{-4}	0.16	0.62	4

Table 4 (Continued)

compd	P/MPa	T/K	a	b	c	d	e	Δ_{ave}	Δ_{max}	ref
					Ethers					
diethyl ether	0.1−1177	293−353	601.34	0.8439	505.30	0.0661	-5.67×10^{-4}	0.38	2.65	2
furan	11−897	209−257	547.66	0.6953	713.61	0.8863	8.83×10^{-4}	0.14	1.34	31
anisole (methoxybenzene)	0.1−196	298−353	321.23	0.7948	399.81	0.2615	-5.04×10^{-5}	0.04	0.14	29
1-(methoxyphenyl)-1-phenylethane	0.1−196	298−353	358.57	0.7791	460.19	0.3264	1.08×10^{-4}	0.03	0.09	29
1-(methoxycyclohexyl)-1-cyclohexylethane	0.1−196	298−353	371.67	0.8564	454.07	0.4644	3.33×10^{-4}	0.03	0.08	29
2,4-bis(α-phenylethyl)phenyl ethyl ether	0.1−196	298−353	367.77	0.7688	481.74	0.3740	1.94×10^{-4}	0.03	0.10	29
2,4-bis(α-cyclohexylethyl)cyclohexyl methyl ether	0.1−196	298−353	355.27	0.8334	430.61	0.3722	2.30×10^{-4}	0.04	0.12	29
					Other Compounds					
carbon disulfide	0.1−203	223−298	246.08	0.5832	418.93	0.3906	7.76×10^{-5}	0.05	0.14	25
	0.1−102	198−298	208.03	0.6062	345.01	0.2510	-9.94×10^{-5}	0.03	0.14	28
carbon tetrachloride	0.1−198	273−323	145.21	0.4808	331.39	0.4064	2.23×10^{-4}	0.06	0.15	25
phosphorus trichloride	0.1−1177	293−353	309.16	0.4228	667.87	0.7259	3.97×10^{-4}	0.30	1.76	2
tetramethylsilane	0.1−102	198−298	185.92	1.1541	174.95	0.1986	2.76×10^{-5}	0.07	0.32	28
water	0−800	298−363	875.45	0.6509	1018.0	0.3757	-2.92×10^{-4}	0.13	0.82	22
propan-2-one	0.1−1177	1177	611.96	0.7930	738.75	1.1726	1.06×10^{-3}	0.27	1.88	2

[a] $\Delta_{ave} = 10^2\langle \delta V/V \rangle$ and $\Delta_{max} = 10^2(\delta V/V)_{max}$, where δV is the absolute difference between calculated and experimental specific volume V from eq 12.

Table 5. Experimental Uncertainties Δ_{exp} (%) of Specific Volume Measurements Affecting the Results Used for Our Correlation by Means of Eqs 3 and 12, Respectively, and Mean Δ_{ave} and Maximum Δ_{max} Deviations Calculated for the Compound of Each Series Whose Results Turn out to Be the Most Poorly Interpolated[a]

author(s)	Δ_{exp}	ref	Δ_{ave}	Δ_{max}	compd	ref
			Correlation by Eq 3			
Bridgman	1	2−5	0.27	0.72	1,2-propanediol	4
Brostow and Grindley	0.01	6	0.07	0.91	heptadecane	6
Dymond et al.	0.20	16−21	0.23	0.57	0.5isooctane + 0.5dodecane	19
Grindley and Lind	0.01	22	0.09	0.72	water	22
			Correlation by Eq 12			
Bridgman	1	2−5	0.60	2.96	3-methylpentane	3
Grindley and Lind	0.01	22	0.13	0.82	water	22
Mopsik	0.03	24−25	0.10	0.42	isopentane	25
Muringer et al.	0.20	26	0.08	0.66	heptane	26
Boelhouwer	0.04	27	0.10	0.54	octane	27
Garcia Baonza et al.	0.20	28	0.07	0.32	tetramethylsilane	28
Kuss and Tasmili	0.20	29	0.11	0.36	heptane	29
Lowitz et al.	0.14	30	0.18	0.77	11-decylheneicosane	30
Figuière and Szwarc	1	31	0.14	1.34	furan	31

[a] $\Delta_{exp} = 10^2\langle \delta V^*/V \rangle$, $\Delta_{ave} = 10^2\langle \delta V/V \rangle$, and $\Delta_{max} = 10^2(\delta V/V)_{max}$, where δV^* and δV are the absolute differences between the measured and actual specific volume V and, by applying eq 12, between the calculated and measured one, respectively.

larger than 300 MPa, such as those investigated by Bridgman that extend beyond 1000 MPa. The two proposed modifications of eq 1 are in fact unrelated. Anyway, some conclusions may be drawn in comparing their interpolation features. To this purpose, let us deal with accurate specific volume data on hexane at 298 K, as conclusions drawn for this compound may be extended to other ones, in particular most hydrocarbons. Along this isotherm, in the pressure range within 0 and 500 MPa, according to the analysis of the data accuracy made by Pruzan,[23] we considered as reference values those by Ha'an.[32] In ref 23, these data are included in a Tait equation, with their greatest deviation from measured specific volumes being 0.08%. In Table 6, the comparisons between the reference data and the values calculated by means of eqs 3 and 12 using parameters obtained from the Mopsik's and Bridgman's data are presented. The values calculated by means of eq 3 when parameters were derived from Bridgman's data are very well correlated to the reference data all along the pressure domain ranging from 0 to 500 MPa and more. Conversely, those calculated by means of eq 12 deviate from the reference ones for pressures less than 200 MPa, whereas correlation is very good for higher pressures. As for values calculated using parameters from the Mopsik's data, it is shown that making extrapolations outside the experimental range of the data (0−200 MPa) is tricky whatever the uncertainty of the data is. At 500 MPa, the value predicted from Mopsik's data, whose uncertainty is much less than that on Bridgman's data, is 1.75% higher than the experimental reference value. Furthermore, deviation unceasingly increases as pressure increases.

It is worth noticing that in eq 12, as well as in primary eq 1, the parameter c turns out to be proportional to the attractive forces which contribute to the internal pressure of a liquid. Hence, a comparison about this parameter may be made between eqs 3 and 12. For this to be done, we have retained the values of c computed from Bridgman's data for several compounds belonging to five different families.

From Tables 1 and 4 it may be concluded that the mean value of parameter c increases going from hydrocarbons to glycols. In particular, by using eq 12, the mean c values for hydrocarbons, alcohols, alkyl halides, esters, and glycols are 488, 671, 681, 848, and 1102 MPa, respectively. The mean scatters of the parameter are 13.2, 9.0, 13.0, 13.3, and 10.5%, respectively. By using eq 3, the same value rank is roughly respected, provided that the families of compounds be taken into account in the aforementioned order.

Table 6. Experimental Reference Data on the Specific Volume V ($cm^3 \cdot g^{-1}$) of Hexane at 298 K as a Function of Pressure from Ref 32, Calculated Values from Ref 3 Data Interpolated by Means of Eq 3 and from Refs 3 and 24 Data by Means of Eq 12, and Respective Average Percentage Deviations Δ_{ave} from Reference Data (the Values Extrapolated outside Their Own Experimental Pressure Range Are Reported in Italic Characters)

	V ($cm^3 \cdot g^{-1}$)			V ($cm^3 \cdot g^{-1}$)		V ($cm^3 \cdot g^{-1}$)	
P/MPa	ref data (ref 32)	eq 3 (data from ref 3)	Δ_{ave}	eq 12 (data from ref 3)	Δ_{ave}	eq 12 (data from ref 24)	Δ_{ave}
0.1	1.5270	1.5250	−0.13	1.5156	−0.75	1.5225	−0.29
50	1.4400	1.4316	−0.58	1.4487	0.60	1.4385	−0.10
100	1.3860	1.3814	−0.33	1.3965	0.76	1.3830	−0.22
150	1.3468	1.3437	−0.23	1.3548	0.59	1.3435	−0.25
200	1.3160	1.3134	−0.20	1.3206	0.35	1.3141	−0.14
300	1.2692	1.2665	−0.21	1.2679	−0.10	*1.2731*	0.31
400	1.2338	1.2309	−0.24	1.2293	−0.36	*1.2460*	0.99
500	1.2055	1.2026	−0.24	1.1998	−0.47	*1.2266*	1.75
600	*1.1818*	1.1792	−0.22	1.1764	−0.46	*1.2121*	2.56
700	*1.1615*	1.1596	−0.16	1.1575	−0.34	*1.2009*	3.39

Except for the case of glycols, for which the mean c value slightly diminishes, c values are only around 12% higher than those calculated by means of eq 12, that is, 584, 770, 750, 967, and 1090 MPa, respectively. The mean scatters of the parameter c are 16.6, 8.3, 13.6, 7.5, and 5.2%, respectively. As does eq 12, eq 3 seems to account for the increase of the attractive forces in liquids as their dipolar moments increase. Besides, these forces are shown to increase very much with the increase of the number of the functional groups forming hydrogen bonds, such as the alcoholic groups. In fact, the mean c value for glycols is much greater than that for alcohols, whichever equation is used.

4. Conclusion

In this paper, two modifications, eqs 3 and 8 (or 12), of an empirical four-parameter equation (eq 1) previously proposed[1] are presented.

Equation 3 gives a better representation of volumetric properties up to very high pressures for a great number of liquids and for some liquid mixtures, but it requires two more parameters. Even if it cannot be considered *stricto sensu* an improvement of eq 1 because it does not take account of the α versus p curves' intersection, this equation enhances p, V, T data correlation over large pressure domains and should suit application purposes.

On the other hand, eq 8 (and 12) proves to have a better physical coherence than eq 1 has because it incorporates the possible intersections of the thermal expansion curves at high pressure, which are thought of as a fundamental property of the liquid state. Furthermore, it predicts a pressure coefficient, $(\partial p/\partial T)_V$, which depends both on volume and on temperature. Equation 12, in which the product $e = \xi d$ is considered as a fifth independent parameter, makes the same prediction. This result appears to be in agreement with Bridgman's predictions about the previously discussed temperature dependency of the pressure coefficient. Both equations account for the decrease and the sign-reversal of the internal pressure of a liquid when pressure is isothermally increased. Furthermore, they show that the volume at which sign-reversal occurs depends on the temperature of the isotherm proportional to the parameters ξ and e, respectively. In the case of eq 8, this feature turns out to be related to its ability to account for the intersections of the α versus p isotherms. So, despite their reduced number of parameters, eqs 8 and 12 have been proved to incorporate the thermodynamic behavior of the liquid state at high pressure.

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