

ULTRASONIC PROPAGATION FOR MEASURING THE ACTIVATION ENERGY AND VOLUME OF A HOLE IN LIQUIDS

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Mathematical expressions are introduced in this paper in order to measure the compressional relaxation time by the propagation of ultrasonic waves in associated and nonassociated liquids. The expressions are based on the concept of complex and frequency-dependent compressibility represented as a function of ultrasonic velocity and absorption in liquids. The available experimental data reported earlier in the literature are used in these mathematical expressions to calculate the molecular activation energy and the volume of a hole for some liquids. The introduced expressions concern the relations between the liquid compressional relaxation time and Frenkel's intermolecular relaxation time at different values of temperature and pressure. The effect of vibrational relaxation, bulk viscosity and structural rearrangement on ultrasonic absorption in liquids has been investigated.

1. Introduction

The propagation of ultrasonic waves in the medium can be used to explain most of the physical properties of solids, liquids and gases. The dispersion and absorption of ultrasonic waves are two important physical phenomena in liquids [1, 2]. They are important in calculating the intermolecular relaxation and intermolecular forces in the medium. The sources of ultrasonic wave energy dissipation in liquids are divided into two main categories: those due to losses in the medium (absorption) and those associated with losses at the boundaries of the medium (scattering).

Absorption and dispersion are closely related to the liquid compressibility. The liquid compressibility becomes a complex and frequency-dependent parameter under the action of a high frequency compressional ultrasonic wave. This is due to the phase shift between the applied wave and the medium response. Absorption is a result of this phase shift and the ultrasonic wave velocity in liquid becomes complex [3].

The present work is an attempt to increase the efficiency of the ultrasonic system modeling by submitting two expressions to evaluate two important parameters in viscoelastic liquid; those are the activation energy and the free volume of a hole. The two expressions can be solved by a computer program using the phase velocity and absorption of ultrasonic wave propagated in the medium at different temperature and pressures.

2. Mathematical analysis

The complex and frequency-dependent compressibility that is produced by the propagation of ultrasonic waves in liquids is given by, [4],

$$\beta^*(\omega) = \beta_1(\omega) - i\beta_2(\omega), \quad (1)$$

where $\beta^*(\omega)$ is the complex compressibility at angular frequency ω , $\beta_1(\omega)$ is the real part of compressibility at ω , and $\beta_2(\omega)$ is the imaginary part of compressibility at ω .

The complex compressibility $\beta^*(\omega)$ is related to the complex wave velocity $V^*(\omega)$ by the following relation, [5]:

$$\beta^*(\omega) = \frac{1}{\rho(V^*(\omega))^2}. \quad (2)$$

Also, the complex wave velocity $V^*(\omega)$ is related to the ultrasonic absorption coefficient α by [5]:

$$\frac{1}{V^*(\omega)} = \frac{1}{V(\omega)} - i\frac{\alpha}{\omega}, \quad (3)$$

where $V(\omega)$ is the real part of the wave velocity. Substituting equations (1) and (3) into equation (2), we obtain:

$$\beta_1(\omega) - i\beta_2(\omega) = \frac{1}{\rho} \left[\frac{1}{V(\omega)} - i\frac{\alpha}{\omega} \right]^2 = \left[-\frac{1}{\rho V(\omega)^2} - \frac{\alpha^2}{\rho\omega^2} \right] - i\frac{2\alpha}{\rho\omega V(\omega)}. \quad (4)$$

It is well known that $(\alpha/\omega)^2 \ll 1/V(\omega)^2$ at all ultrasonic frequencies, then equation (4) becomes:

$$\beta_1(\omega) - i\beta_2(\omega) = \frac{1}{\rho V^2(\omega)} - i\frac{2\alpha}{\rho\omega V(\omega)}. \quad (5)$$

Equating real and imaginary parts at both sides of equation (5), we obtain:

$$\beta_1 \cong \frac{1}{\rho V(\omega)^2}, \quad \beta_2 \cong \frac{2\alpha}{\rho\omega V(\omega)}. \quad (6)$$

Then:

$$\frac{\beta_2(\omega)}{\beta_1(\omega)} \cong \frac{2\alpha V(\omega)}{\omega}. \quad (7)$$

Equation (6) shows that $\beta_1(\omega)$ depends upon $V(\omega)$ only, while $\beta_2(\omega)$ depends upon both $V(\omega)$ and α . The adiabatic compressibility of liquids can be expressed as a function of the compressional relaxation time τ [4, 5, 6], therefore:

$$\beta^*(\omega) - \beta_1(\infty) = \frac{\beta_1(0) - \beta_1(\infty)}{1 + i\omega\tau}, \quad (8)$$

where $\beta_1(0)$ is the compressibility at zero frequency, i.e. the static or total compressibility, and $\beta_1(\infty)$ is the compressibility at very high frequency due to the reduction in the molecular volume. It is the instantaneous value of compressibility and it is in phase with applied pressure. Substituting equation (1) into equation (8), we obtain:

$$\beta_1(\omega) - \beta_1(\infty) - i\beta_2(\omega) = [\beta_1(0) - \beta_1(\infty)] \frac{1 - i\omega\tau}{1 + i\omega\tau}. \quad (9)$$

Separating equation (9) into real and imaginary parts, we obtain:

$$\beta_1(\omega) - \beta_1(\infty) = \frac{\beta_1(0) - \beta_1(\infty)}{1 + \omega^2 \tau^2} \quad (10)$$

and

$$\beta_2(\omega) = [\beta_1(0) - \beta_1(\infty)] \frac{\omega \tau}{1 + \omega^2 \tau^2}. \quad (11)$$

The difference $[\beta_1(0) - \beta_1(\infty)]$ is the relaxation part of the compressibility β_{rc} . Thus the total or static compressibility $\beta_1(0)$ is given by:

$$\beta_1(0) = \beta_{rc} + \beta_1(\infty). \quad (12)$$

The relaxation part β_{rc} is due to structural rearrangement and it lags behind the applied pressure wave. $\beta_1(0)$ and $\beta_1(\infty)$ may be rewritten as a function of the wave velocity using equation (6), then:

$$\beta_1(0) \cong \frac{1}{\rho V_0^2}, \quad \beta_1(\infty) \cong \frac{1}{\rho V_\infty^2}, \quad (13)$$

where V_0 and V_∞ are the velocity of the ultrasonic wave in liquids at zero and high frequencies, respectively. Two conditions may appear depending on the values of V_0 and V_∞ :

- a) When $V_0 \approx V_\infty$, then $\beta_1(0) \cong \beta_1(\infty)$.
- b) When $V_0 < V_\infty$, then $\beta_1(0) > \beta_1(\infty)$ and $\beta_{rc} \ll \beta_1(0)$ or $\beta_1(\infty)$.

Dividing equation (11) by equation (10), we obtain:

$$\frac{\beta_2(\omega)}{\beta_1(\omega) - \beta_1(\infty)} = \omega \tau. \quad (14)$$

Then

$$\beta_2(\omega) = \omega \tau [\beta_1(\omega) - \beta_1(\infty)] = \beta_1(\omega) \omega \tau \left[1 - \frac{\beta_1(\infty)}{\beta_1(\omega)} \right] \quad (15)$$

or

$$\frac{\beta_2(\omega)}{\beta_1(\omega)} = \omega \tau \left[1 - \frac{\beta_1(\infty)}{\beta_1(\omega)} \right]. \quad (16)$$

Using equations (6), (7) and (13) we obtain:

$$\frac{2\alpha V(\omega)}{\omega^2} = \tau \left[1 - \left[\frac{V(\omega)}{V(\infty)} \right]^2 \right]. \quad (17)$$

The compressional relaxation time τ is then given by

$$\tau = \frac{2\alpha V(\omega)/\omega^2}{1 - \left[\frac{V(\omega)}{V(\infty)} \right]^2}. \quad (18)$$

The velocity $V(\omega)$ and absorption α/ω^2 of ultrasonic waves at angular frequency ω propagated in liquid, are measurable quantities that can be measured by means of various kinds of spectrometers, like those used by RICHARD CHALLIS [6]. These quantities are available in the published literature for most liquids at various values of pressure P

and temperature T , as for instance in: *Landolt-Bornnstein Numerical Data and Functional Relationships in Science and Technology; Group II Atomic and Molecular Physics*, volume 5; Molecular Acoustics, Springer Verlag, Berlin. Equation (18) can be used to calculate the compressional relaxation time τ fore these liquids at different P and T . The data listed in Appendix I show that $V(\omega)$ and α/ω^2 decrease with increasing temperature. The exception is water in which $V(\omega)$ increases and α/ω^2 decreases as T increases [4, 8, 9, 10, 11, 12]. In benzene, nitrobenzene and some other nonassociated liquids, $V(\omega)$ decreases and α/ω^2 increases as T increases. In most liquids $V(\omega)$ increases and α/ω^2 decreases as P increases. In general, at normal P and T , the ultrasonic dispersion in nonassociated liquids and liquids of low shear viscosity is small and $V(\omega)/V(\infty)$ is around 0.85, while in associated liquids and liquids of high shear viscosity, $V(\omega)/V(\infty)$ is in the range of 0.74 to 0.85 at the same P and T . Therefore, $V(\omega)/V(\infty)$ can be treated as being approximately independent of P and T and the term $[1 - (V(\omega)/V(\infty))^2]$ can be treated as a constant value even during the change of P and T . This approximation is useful in solving Equation (18) with the shortage in data and inaccuracy in measuring $V(\omega)$ at high ultrasonic frequencies [5, 13]. Frenkel, Mason and some others proved that the intermolecular time τ due to the change in structure and packing is given by:

$$\tau = \tau_0 \exp \left[\frac{W - Pv}{KT} \right], \quad (19)$$

where τ_0 is constant (the maximum relaxation time), W is the activation energy (energy required to take one molecule out of its bonding), v is the volume of a hole that is approximately 10% to 20% of the molecular volume, and K is the Boltzmann constant. To evaluate the activation energy and the volume of a hole, we shall compare Eq. (18) with equation (19) as follows:

$$\tau_0 \exp \left[\frac{W - Pv}{KT} \right] = \frac{2\alpha V(\omega)/\omega^2}{1 - \left[\frac{V(\omega)}{V(\infty)} \right]^2}, \quad (20)$$

or

$$\tau_0 \left[1 - \left[\frac{V(\omega)}{V(\infty)} \right]^2 \right] \exp \left[\frac{W - Pv}{KT} \right] = \frac{2\alpha V(\omega)}{\omega^2}. \quad (21)$$

Equation (21) can be written in the logarithmic form as follows:

$$\ln \left[\tau_0 \left[1 - \frac{V(\omega)^2}{V(\infty)^2} \right] \right] + \left[\frac{W - Pv}{KT} \right] = \ln \left[\frac{2\alpha V(\omega)}{\omega^2} \right]. \quad (22)$$

The value of $\ln[2\alpha V(\omega)/\omega^2]$ has been calculated for eleven liquids from the experimental data listed in Appendix I. Values of $\ln[2\alpha V(\omega)/\omega^2]$ have been presented in Figs. 1 and 2 as a function of $1/T$ (small circles) for each considered liquid. The simulation program was used to find an equation to fit the data of each liquid in figures. Most data of each liquid lied on or very close to the first order polynomial or straight line equation plotted in Figs. 1 and 2 as a solid line for all liquids. This indicates that Eq. (22) is a straight

line equation and the first log term is independent of T . Equation (22) corresponding to the general linear equation:

$$Y = mX + c. \quad (23)$$

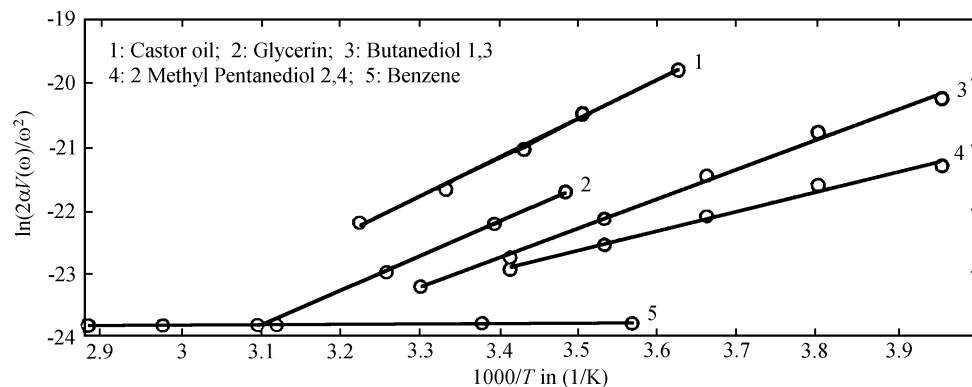


Fig. 1. Change of $\ln(2\alpha V(\omega)/\omega^2)$ with $(1/T)$ for some liquigs at atmospheric P .

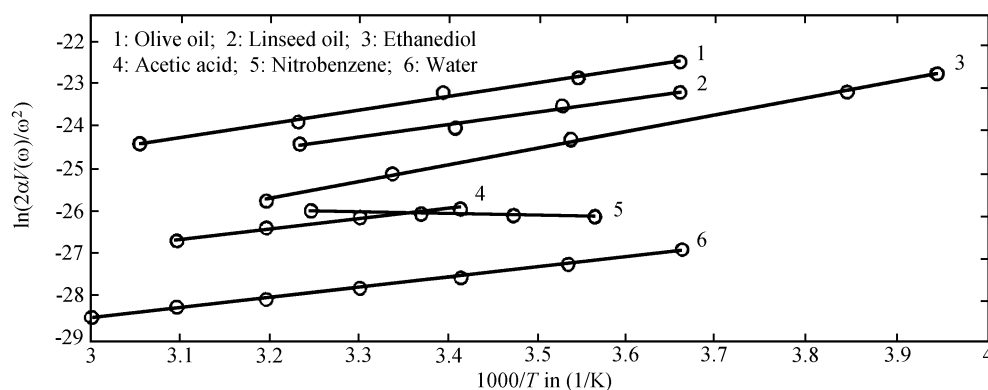


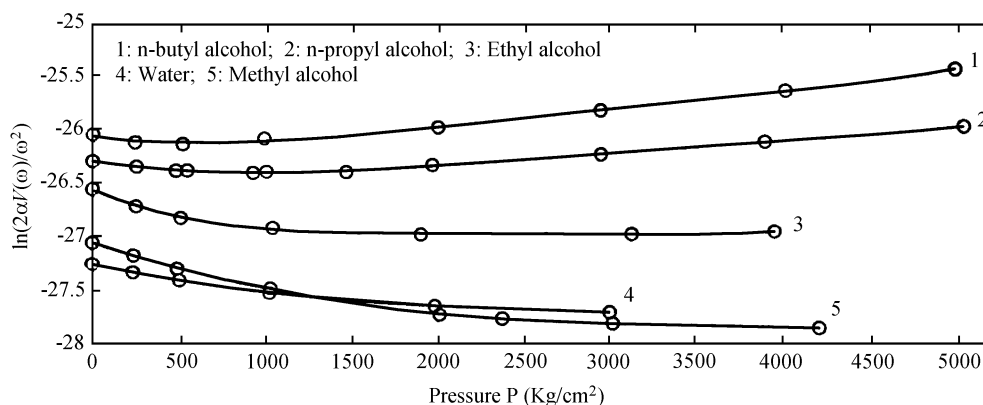
Fig. 2. Change of $\ln(2\alpha V(\omega)/\omega^2)$ with $(1/T)$ for some liquigs at atmospheric P .

The slope m in Eq. (23) corresponds to the value $(W - Pv)/K$, and c equals to $\ln[\tau_0(1 - (V(\omega)/V(\infty))^2)]$. The activation energy W for most liquids at normal P and T is nearly equal to 0.1 eV but its corresponding P value is equal 10^{-4} eV. Thus, we shall neglect the term Pv/KT in Eq. (22) without missing the figure of accuracy. The first derivative of the equation gives the slope (W/K) that is used to evaluate the activation energies for the liquids with sufficient accuracy. The calculated values of the activation energy for the eleven liquids are given in Table 1.

Table 1. The activation energy of eleven different liquids using Eq. (23) and Appendix 1.

Liquid	Butanediol	Castor oil	glycerin	water	ethanediol	Olive oil
W(ev)	0.398	0.508	0.463	0.217	0.342	0.282
Liquid	Linseedoil	Acetic acid	Benzene*	Nitrobenzene*	Methylpenanediol 2,4	
W(ev)	0.257	0.209	0.001	0.0307	0.268	

• subject of data correction, see discussion and conclusion

Fig. 3. Change of $\ln(2\alpha V(\omega)/\omega^2)$ with P for some liquids at 303 K.

Equation (2) is also used to evaluate the volume of a hole v for liquids from the variation of $\ln[2\alpha V(\omega)/\omega^2]$ with P at constant T . $\ln[2\alpha V(\omega)/\omega^2]$ evaluated from the data listed in Appendix (II) for five different liquids and shown in Fig. 3 as a function of P (small circles), [4, 5, 11, 14, 15, 16]. The same simulation program is used to find an equation of second order that fits the experimental data for each liquid in Fig. 3. Most data for any liquid in Fig. 3 lies on or very close to a second order polynomial equation plotted in the figure by a solid line. The first order derivative value of each equation at pressure equal to 1 atmosphere gives the slope of the tangent ($-V/KT$) that was used to evaluate the volume of a hole v for the liquids under study. In Figure 3, $\ln[2\alpha V(\omega)/\omega^2]$ decreases slowly at low pressures, and increases very slowly at higher pressures with a broad minimum at low pressures. The slopes has been evaluated at 1 atmosphere because at this pressure, v may be expected to be independent of P . At higher pressures, v becomes a very complex function of P . The evaluated value v for all liquids studied in this paper are given in Table 2.

Table 2. Volume of a hole for five different liquids using Eq. (23) and Appendix 2.

Liquid	Water	ethylalcohol	n-butylalcohol	n-propylalcohol	methyl	alcohol
$V \times 10^{-24} \text{ cm}^3$	1.322	2.833	0.758	0.926	0.342	0.282

3. Discussion and conclusion

The data listed in Appendix I and the straight lines shown in Figs. 1 and 2 indicated that $\ln[2\alpha V(\omega)/\omega^2]$ decreases as the temperature increases through the range of temperatures between 153 K and 333 K for all liquids except for benzene and nitrobenzene. Interpolation technique was used to find a first order polynomial equation that fitted most of the experimental data points for liquid in Figs. 1 and 2. The linearity in these figures does agree with the approximation introduced to Equation (18) and confirms that W is independent of T . The change in KT values lies between $(5 \text{ to } 8) \times 10^{-3}$ eV, while W is about $(209 \text{ to } 507) \times 10^{-3}$ eV. Hence, a small change in the thermal energy KT can not affect the binding energy W of the molecule in liquids. The calculated values of W listed in Table 1 using the deduced mathematical expressions for all associated liquids in study are reasonable and lie between 0.2091 eV and 0.5073 eV.

The behaviour of benzene and nitrobenzene was studied by QUINN and PELLAM [7, 12]. They found that α/ω^2 increases and $V(\omega)$ decreases with the increase of T ; this means that $\ln[2\alpha V(\omega)/\omega^2]$ or τ remains nearly constant with the change of T as in benzene, while τ increases slightly with the increase of T as in nitrobenzene. These two liquids and some other liquids are nonassociated liquids. The absorption of these liquids is mainly due the intermolecular vibrational relaxation where a large amount of ultrasonic wave energy is used to excite the liquid internal mode. The absorption value α/ω^2 given in Appendix I is the total absorption that consists of three kinds of absorption; those are: 1) absorption due to shear viscosity μ_s , 2) absorption due to compressional viscosity η_c , 3) absorption due to vibrational relaxation. The total absorption due to η_c and vibrational relaxation is known as the absorption due to bulk viscosity. In nonassociated liquids, absorption due to vibrational relaxation is effective and increases with T , while absorption due to μ_s and η_c is due to structural changes and considered mainly in the evaluation of compressional relaxation time τ . The value $\ln[2\alpha V(\omega)/\omega^2]$ discussed here is the relaxation time associated with the compressions and rarefactions in the medium that is an intermolecular phenomenon. If α/ω^2 is due to intermolecular vibrational relaxation subtracted from the total value of α/ω^2 in Appendix I, then it could be possible to evaluate α/ω^2 for nonassociated liquids due to compressional relaxation.

The nonlinear curves in Fig. 3 indicate that the variation of $\ln[2\alpha V(\omega)/\omega^2]$ with P is nonlinear. The ultrasonic wave velocity increases in liquids as the pressure increases; this is because the increase of P increases the medium density and its elasticity, and the liquid property approach the solid properties. Frenkel equation (19), could be used to explain the behaviour of the curve in Fig. 3. Both τ_0 and W are two variables independent of P and T if v does not change with P , then as P increases the value Pv will reduce the term $(W - Pv)$ and decrease $\ln[2\alpha V(\omega)/\omega^2]$. At slightly higher pressure, v decreases due to the applied pressure, so that Pv remains constant as well as τ . Increasing the pressure P will decrease Pv and τ will increase again very slowly.

Appendix 1.

The following table represents experimentally measured values of velocity and absorption of ultrasonic waves for various values of temperature.

Liquid	Temp. T(°K)	Velocity $V \times 10^{-5}$ cm/s	Absorption $\alpha/f^2 \times 10^{17}$ s ² /cm	$\ln[2\alpha V(\omega)/\omega^2]$ evaluated value
Butanediol 1,3	253.0	1.509	1100	-23.199
	263.0	1.574	1660	-22.745
	273.0	1.584	3060	-22.140
	283.0	1.600	5840	-21.471
	293.0	1.638	11100	-20.805
	303.0	1.875	16410	-20.279
2 Methyl pentanediol 2,4	253.0	1.356	1580	-22.973
	263.0	1.445	2180	-22.558
	273.0	1.500	3320	-22.100
	283.0	1.526	5310	-21.614
	293.0	1.697	6495	-21.306
Castor oil	275.7	1.57	29500	-22.185
	285.2	1.530	15800	-21.672
	291.6	1.500	9500	-21.049
	300.0	1.470	4500	-20.521
	310.0	1.430	3200	-19.870
Glycerin	287.0	1.930	3800	-23.789
	294.0	1.910	2350	-22.977
	307.0	1.885	700	-22.204
	323.0	1.840	500	-21.713
Benzene	280.0	1.389	660	-23.793
	296.0	1.298	720	-23.793
	320.5	1.192	770	-23.792
	336.0	1.118	820	-23.794
	346.5	1.078	850	-23.793
Water	273	1.400	34.0	-28.514
	283	1.450	21.25	-28.25
	293	1.480	14.9	-28.048
	303	1.510	11.26	-27.777
	313	1.530	8.50	-27.520
	323	1.540	6.94	-27.188
	333	1.550	5.9	-26.824
Ethanediol	253.6	1.771	1560	-25.723
	260.0	1.756	1010	-25.072
	282.9	1.710	331	-24.275
	297.0	1.668	153	-23.133
	313.0	1.623	82	-22.689
Linseed oil	273.1	1.520	1130	-24.398
	283.5	1.490	830	-24.014
	293.5	1.470	500	-23.493
	309.2	1.430	350	-23.165
Acetic acid	293.0	1.155	90000	-26.659
	303.0	1.121	82500	-26.337
	313.0	1.089	66200	-26.087
	323.0	1.054	46500	-25.885
Nitrobenzene	280.5	1.518	63.0	-25.94
	288.0	1.491	65.3	-25.999
	296.8	1.462	69	-26.035
	308.0	1.439	74.4	-26.053

Appendix 2.

The following table represents experimental measurement values for the variation of ultrasonic wave velocity and absorption with the change of pressure at 303 K for five different liquids. The last column contains the values obtained from Equation (23).

Liquid	Pressure P (Kg/cm ²)	Velocity V × 10 ⁻⁵ cm/s	Absorption $\alpha/f^2 \times 10^{17}$ s ² /cm	ln[2 $\alpha V(\omega)/\omega^2$] evaluated value
Water	1.0	1.510	18.8	-27.268
	228	1.556	17.0	-27.339
	494	1.600	15.4	-27.409
	1017	1.687	13.0	-27.526
	1978	1.834	10.7	-27.637
	3001	1.982	9.4	-27.689
Ethylalcohol	1	1.115	51.5	-26.563
	246	1.256	39.2	-26.717
	501	1.386	32.0	-26.822
	1036	1.578	25.7	-26.911
	1896	1.816	21.2	-26.963
	3130	2.074	18.8	-26.951
	3958	2.261	17.8	-26.919
n-butylalcohol	1	1.234	77.4	-26.054
	238	1.348	66.2	-26.122
	512	1.469	60.2	-26.131
	986	1.634	57.2	-26.076
	1998	1.905	55.0	-25.962
	2948	2.087	59.3	-25.795
	4023	2.283	65.7	-25.603
	4983	2.428	76.1	-25.395
n-propylalcohol	1	1.190	62.7	-26.301
	247	1.325	53.6	-26.351
	474	1.437	48.4	-26.372
	923	1.605	42.4	-26.393
	1000	1.624	42.4	-26.382
	1464	1.749	39.4	-26.381
	2951	2.086	39.4	-26.205
	3903	2.264	41.2	-26.078
	5031	2.431	44.8	-25.923
Methylalcohol	1	1.094	31.7	-27.078
	232	1.216	24.0	-27.179
	482	1.331	19.8	-27.298
	1023	1.518	14.8	-27.482
	2007	1.761	10.3	-27.716
	2369	1.843	10.0	-27.751
	3019	1.979	8.10	-27.791
	4211	2.178	7.50	-27.820

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