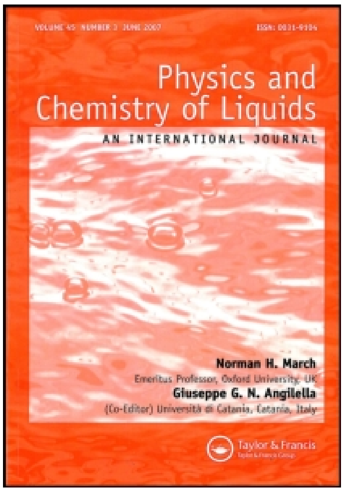

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Experimental Equations of State for Some Organic Liquids Between 273 and 333 K and Up to 280 MPa

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EXPERIMENTAL EQUATIONS OF STATE FOR SOME ORGANIC LIQUIDS BETWEEN 273 AND 333 K AND UP TO 280 MPa

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Five non-linear and three polynomial isothermal equations of state for liquids have been tested for their performance in describing the data of the density and the isothermal compressibility of benzene and cyclohexane from 288 to 323 K up to the melting pressures, and of methanol and ethanol between 273 and 333 K up to 280 MPa. It is found that the best representation is given by an expansion in temperature and density and the second best by the Usual Tait equation. The coefficients of these two equations for the four organic liquids are obtained by fitting the experimental data by a least squares analysis.

KEY WORDS: Equation of state, organic liquids, sound velocity, high pressure.

1 INTRODUCTION

A number of empirical and semi-empirical equations of state have been proposed to describe the volumetric behaviour of liquids as a function of pressure or temperature. These equations are very useful not only for the purpose of smoothing and interpolation, but also for determining derived thermodynamic functions which require differentiation and integration of an appropriate equation of state. It is, therefore, considered worthwhile to examine in how far these equations of state can describe liquid densities over a wider range of pressure and temperature and whether a certain type of equation should be preferred to others for obtaining the best performance for a particular substance.

The work described in this paper is stimulated by our recent ultrasonic measurements of the sound velocity in benzene, cyclohexane[1], methanol[2] and ethanol[3] at elevated pressures from which liquid densities, with accuracies comparable to those obtained from direct measurements, can be extracted following a method initiated by Davis and Gordon[3,4]. In view of the simplicity and rapidity of the experimental procedure, our ultrasonic measurements provide an extensive amount of data points covering a wider range of pressures and temperatures than those of previously direct measurements. All these factors are favourable for a critical examination of the existing equations of state for liquids.

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2 NONLINEAR AND POLYNOMIAL EQUATION

The present analysis is restricted to those isothermal equations of state which were frequently used in the past for describing liquid densities at elevated pressures. Following McDonald[5], these equations have been classified under separate groups, namely, nonlinear equations and polynomial equations. In this work, altogether five nonlinear and three polynomial equations have been critically examined for their performance in describing our density data for four organic liquids as a function of pressure, namely benzene, cyclohexane, methanol and ethanol. These are mostly two or three parameter equations in which the parameters are related to the isothermal bulk modules K_T, defined as

$$K_T = -V\left(\frac{\partial p}{\partial V}\right)_T ; \; K_{T0} = (K_T)_{p=0} \tag{1}$$

and its pressure derivatives

$$K'_T = \left(\frac{\partial K_T}{\partial p}\right)_T ; \; K'_{T0} = (K'_T)_{p=0} \tag{2}$$

$$K''_T = \left(\frac{\partial K'_T}{\partial p}\right)_T ; \; K''_{T0} = (K''_T)_{p=0} \tag{3}$$

The isothermal bulk modules is related to the isothermal compressibility β_T by the relation $K_T = \beta_T^{-1}$.

The five non-linear equations include the well-known Usual Tait equation, the quadratic secant modules equation, the Murnaghan equation and the two second order equations SOE_0 and SOE_1. These are presented in Table 1. The three polynomial equations, namely, the third degree Davis–Gordon equation in which the pressure p is expressed as a polynomial in reduced density, another density expansion and a pressure expansion of the density, are also presented in Table 1. The relation of parameters A, B and C with the quantities K_{T0}, K'_{T0} and K''_{T0} can easily be derived[5]. It should be pointed out here that, although the third order density expansion (3DEE) and the pressure expansion (3PEE) have four parameters A, B, C, and D as indicated in Table 1, they are essentially the same as those of the three parameter equations if the constant terms (A) in these equations are considered to be zero-pressure values.

The parameters appear nonlinearly in most of the equations of state presented in Table 1. In order to evaluate the parameters of these equations, an iteration procedure, such as the Newton–Raphson's method for sets of non-linear equations, is generally used. Normally, this method gives a rapid convergence only if the choice of the initial values A_0, B_0 and C_0 are very close to the true values A, B and C. However, it is difficult to obtain good initial values, in particular for a three parameter nonlinear equation. Therefore, we have followed a method, which turns out to be better than the Newton–Raphson method and which is described in the appendix. Extensive computations have shown that this method is capable of giving rapid convergence compared to the previous method and the initial values should only be within an order of magnitude of the true values.

Table 1 Nonlinear and polynomials equations of state for liquids. In the following, A, B, C and D are coefficients and ρ_0 is the density at zero pressure.

Equation name	*Acronym*	*Form*
Usual Tait	UTE	$\rho = \rho_0/[1 - A \ln(1 + Bp)]$
Quadratic Secant Modulus	QSME	$\rho = \rho_0 (A + Bp - Cp^2)/(A + Bp - Cp^2 - p)$
Murnaghan	ME	$\rho = \rho_0(1 + Ap)^B$
Second-order 0	SOE_0	$\rho = \rho_0 \exp[p/(A + Bp)]$
Second-order 1	SOE_1	$\rho = \rho_0[(1 + Ap)/(1 + Bp)]^C$
Third-degree Davis–Gordon	3DGE	$p = Ax + Bx^2 + Cx^3$ where $x = (\rho - \rho_0)/\rho_0$
Third-degree density expansion	3DEE	$p = A + B\rho + C\rho^2 + D\rho^3$
Third-degree pressure expansion	3PEE	$\rho = A + Bp + Cp^2 + Dp^3$

3 ANALYSIS AND RESULTS

In order to make a comparison between the various equations of state for liquids, a least-squares analysis has been carried out to fit both the linear and nonlinear equations to the experimental data of the four liquids. The fits are carried out along 6 isotherms from 298 to 323 K up to melting line for benzene and cyclohexane, along 7 isotherms from 213 to 333 K up to 280 MPa for methanol, and 8 isotherms from 193 to 333 K up to 280 MPa for ethanol. The parameters have been determined for each temperature separately. It should be mentioned here that for each equation applied to a particular liquid, we only present a single value of the deviation which is obtained by averaging the absolute standard deviations of all isotherms considered for each liquid, the so-called averaged absolute standard deviation, which is useful for inter-comparisons between different equations of state. The inter-comparison between the various equations is based on the following distinct criteria:

1) The relative magnitude of the averaged absolute standard deviations of the densities as given in Table 2. As shown, except for the equations SOE_0 and 3PEE,

Table 2 Averaged absolute standard deviations $\sigma \times 10^4$ of the least squares fits for the density. The numbers in the brackets denotes those of coefficients.

	Benzene	*Cyclohexane*	*Methanol*	*Ethanol*
UTE (2)	0.42	0.47	1.4	1.6
QSME(3)	0.42	0.44	1.6	1.3
ME (2)	0.65	0.51	3.0	2.8
SOE_0 (2)	2.0	0.80	9.1	7.8
SOE_1 (3)	0.36	0.45	0.51	0.45
3DGE (3)	0.12	0.11	0.20	0.21
3DEE (4)	0.07	0.04	0.14	0.10
3PEE (4)	0.96	0.26	5.3	4.5

the deviations are mostly rather small, namely, about 1×10^{-4} which is comparable to the error in the experimental density[3]. Therefore, this criterion is not sufficient to select the best equation of state for the four liquids.

2) The relative magnitude of the averaged absolute standard deviations of the isothermal compressibility β_T ($\equiv 1/\rho(\partial\rho/\partial p)_T$) which are obtained by differentiating each fitted equation with respect to pressure. It is clear that a differentiation procedure enlarges the errors considerably so that this criterion is a serious test of the validity of the equation of state. However, an inter-comparison between the equation of state needs a large number of β_T data. These data are very difficult to obtain from direct experiment or from conventional pVT measurements. In contrast, in the present study, the values for β_T were obtained from previous ultrasonic work[1-3] using the thermodynamic relation:

$$\beta_T = u^{-2} + \alpha_p^2 T/C_p, \tag{4}$$

where u is the sound velocity, α_p is the thermal expansion coefficient at constant pressure and C_p the specific heat at constant pressure. It can easily be shown (cf. Sun *et al.*[1-3]) that the largest contribution for the values of β_T for these four organic compounds comes from the term u^{-2} which was directly determined so that the values of β_T are very accurate. In Table 3, the magnitude of the averaged absolute standard deviation of the isothermal compressibility β_T is computed for the four liquids. It is shown that the deviations for the β_T values are about two orders of magnitude larger than those for the densities (cf. Table 2 and Table 3). Furthermore, from the comparison of these tables, one may conclude that the two density expansion equations (3DEE and 3DGE) are the best.

3) An important criterion for selecting the best equation of state is to examine whether the extrapolated equation predicts the experimental values at high pressure. We have chosen some equations to evaluate the parameters by fitting the experimental density data for each liquid up to half of the maximum experimental pressure and subsequently calculated the density in the remaining pressure range. The average absolute standard deviation between the experimental and extrapolated values for each liquid are recorded in Table 4. Again it turns out that the two density expansion

Table 3 Averaged absolute standard deviations $\sigma \times 10^2$ of the least square fits for the isothermal compressibility. The numbers in the brackets denotes those of coefficients.

	Benzene	*Cyclohexane*	*Methanol*	*Ethanol*
UTE (2)	0.62	0.71	1.3	1.5
QSME(3)	0.81	0.89	1.8	1.7
ME (2)	0.94	0.82	2.2	2.2
SOE_0 (2)	2.4	1.5	6.4	5.2
SOE_1 (3)	0.58	0.65	0.77	0.77
3DGE (3)	0.26	0.52	0.18	0.15
3DEE (4)	0.13	0.06	0.29	0.22
3PEE (4)	1.7	0.66	5.5	4.6

Table 4 Averaged absolute standard deviations $\sigma \times 10^4$ of the least squares fits obtained from the extrapolation procedure.

	Benzene	*Cyclohexane*	*Methanol*	*Ethanol*
UTE (2)	0.81	1.4	6.4	7.4
ME (2)	2.4	1.0	14	14
3DGE(3)	2.1	2.5	1.7	1.4
3DEE (4)	0.70	0.12	0.92	0.52
3PEE (4)	33	7.8	230	190

equations (3DEE and 3DGE) are the best and these are capable of predicting the experimental density data better than 0.02 percent.

It is interesting to examine whether the temperature dependence of the density can be reproduced by introducing temperature dependent parameters in the equation of state. This has been done only for the density expansion which is found to reproduce the isothermal data the best and for the Tait equation because of its simplicity. In order to introduce the temperature dependent parameters, the two equations are written in the forms:

$$p - p_0 = \sum_{i=1}^{3} \sum_{j=0}^{2} C_{ij}(\rho - \rho_0)^i T^j, \tag{5}$$

$$\rho = \rho_0 \Big/ \left[1 - \left(\sum_{i=0}^{2} A_i T^i \right) \ln\left(1 + p \sum_{j=0}^{2} B_j T^j \right) \right] \tag{6}$$

In both cases, the coefficients C_{ij}, A_i and B_j for the four liquids have been evaluated from the experimental data using a least squares analysis. The ρ_0 is the density at $p_0 = 0.1$ MPa and reported previously[1-3]. In the case of benzene and cyclohexane, the experimental data cover a temperature range between 288 to 323 K and in the case of methanol and ethanol a temperature range from 273 to 333 K. It turns out that the standard deviation of the fit with Eq. (5) is less than 0.002% and with Eq. (6) is less than 0.01%. The maximum deviations in the two cases do not exceed 0.005% and 0.05%, respectively. The values of the coefficients C_{ij}, A_i and B_j are tabulated in Tables 5 and 6.

Table 5 Coefficients A_i and B_j of Eq. (6).

	Benzene	*Cyclohexane*	*Methanol*	*Ethanol*
A_0	0.1422063	0.9981933	0.5671756×10^{-1}	0.6665581×10^{-1}
A_1	$-0.4056105 \times 10^{-3}$	$-0.5851701 \times 10^{-2}$	0.2529665×10^{-3}	0.1811811×10^{-3}
A_2	0.7894467×10^{-6}	0.9386494×10^{-5}	$-0.3676869 \times 10^{-6}$	$-0.2819286 \times 10^{-6}$
B_0	0.7859517×10^{-2}	-0.1071213	0.2161233×10^{-1}	0.1829842×10^{-1}
B_1	$-0.5935508 \times 10^{-4}$	0.6496628×10^{-3}	$-0.1430840 \times 10^{-3}$	$-0.1177928 \times 10^{-3}$
B_2	0.2281236×10^{-6}	$-0.8325112 \times 10^{-6}$	0.3753929×10^{-6}	0.3207107×10^{-6}

Table 6 Coefficients C_{ij} of Eq. (5).

	Benzene	*Cyclohexane*	*Methanol*	*Ethanol*
C_{10}	0.5680264×10^{1}	0.6515981×10^{1}	0.3804965×10^{1}	0.3914969×10^{1}
C_{11}	$-0.2192048 \times 10^{-1}$	$-0.2718745 \times 10^{-1}$	$-0.1280360 \times 10^{-1}$	$-0.1272398 \times 10^{-1}$
C_{12}	0.2299094×10^{-4}	0.3084505×10^{-4}	0.1156877×10^{-4}	0.1109424×10^{-4}
C_{20}	0.2550693×10^{-1}	0.6172169×10^{-1}	0.2439591×10^{-1}	0.2478901×10^{-1}
C_{21}	$-0.8657760 \times 10^{-4}$	$-0.2849253 \times 10^{-3}$	$-0.9973436 \times 10^{-4}$	$-0.9363383 \times 10^{-4}$
C_{22}	0.7542323×10^{-7}	0.3508908×10^{-6}	0.1239069×10^{-6}	0.1116134×10^{-6}
C_{30}	0.1334041×10^{-3}	$-0.1066154 \times 10^{-2}$	0.3062450×10^{-4}	0.2507466×10^{-4}
C_{31}	$-0.7192519 \times 10^{-6}$	0.6708949×10^{-5}	$-0.6541676 \times 10^{-7}$	$-0.2239760 \times 10^{-7}$
C_{32}	0.1075835×10^{-8}	$-0.1035795 \times 10^{-7}$	$0.1976063 \times 10^{-10}$	$-0.4012650 \times 10^{-10}$

4 CONCLUSIONS

By using several criteria, namely the relative magnitudes of the standard deviations of the density and isothermal compressibility and the deviations of the extrapolated densities from the experimental values, one may draw the following conclusions:

1) Of all the equations of state for the organic liquids, the density expansion equation is the best for describing the pVT and thermodynamic properties of these liquids.

2) The well-known and widely used two parameter Tait equation is also good for liquid benzene and cyclohexane, but only fair for liquid methanol and ethanol.

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References

1. T. F. Sun, P. J. Kortbeek, N. J. Trappeniers and S. N. Biswas, *Phys. Chem. Liq.*, **16**, 163 (1987).
2. T. F. Sun, C. A. ten Seldam, P. J. Kortbeek, N. J. Trappeniers and S. N. Biswas, *Phys. Chem. Liq.*, **18**, 107 (1988).
3. T. F. Sun, S. N. Biswas, N. J. Trappeniers and C. A. ten Seldam, *J. Chem. Eng. data*, **33**, 395 (1988).
4. L. A. Davis and R. B. Gordon, *J. Chem. Phys.*, **46**, 2650 (1967).
5. J. R. MacDonald, *Rev. Mod. Phys.*, **41**, 316 (1969).
6. W. Brostow and P. Maynadier, *High temp. Sci.* **11**, 11 (1979).

APPENDIX Procedure for fitting nonlinear equations by least-squares analysis

We assume to have a known non-linear function with two parameters A and B:

$$y = f(A, B, x). \tag{1}$$

where A and B will be determined from fitting the experimental data by a least-squares analysis. The deviations are defined by

$$R_i = Y_i - y_i = Y_i - f(A, B, x_i) \tag{2}$$

in which i is an integer from 1 to N (N is a number of experimental data points), Y_i denotes the experimental value, y_i is the value from Eq. (1) corresponding to x_i, with x_i assumed to be exact. We minimize the sum of squares,

$$S = \sum_{i=1}^{N} R_i^2 = \sum_{i=1}^{N} [Y_i - f(A, B, x_i)]^2. \tag{3}$$

At the minimum, all the partial derivatives $\partial S/\partial A$ and $\partial S/\partial B$ vanish, from which the following equations are obtained:

$$\sum R_i \frac{\partial R_i}{\partial A} = 0 \tag{4}$$

$$\sum R_i \frac{\partial R_i}{\partial B} = 0 \tag{5}$$

where $\sum$ denotes $\sum_{i=1}^{N}$.

Now, we expand the variables A and B of Eqs (4) and (5) around A_0 and B_0, the initial values for A and B, and use $\Delta A = A - A_0$ and $\Delta B = B - B_0$. Therefore, we have

$$\sum R_i \frac{\partial R_i}{\partial A} + \sum\left(\frac{\partial R_i}{\partial A}\frac{\partial R_i}{\partial A} + R_i \frac{\partial^2 R_i}{\partial A^2}\right)\Delta A + \sum\left(\frac{\partial R_i}{\partial B}\frac{\partial R_i}{\partial A} + R_i \frac{\partial^2 R_i}{\partial A \partial B}\right)\Delta B = 0 \tag{6}$$

$$\sum R_i \frac{\partial R_i}{\partial B} + \sum\left(\frac{\partial R_i}{\partial A}\frac{\partial R_i}{\partial B} + R_i \frac{\partial^2 R_i}{\partial A \partial B}\right)\Delta A + \sum\left(\frac{\partial R_i}{\partial B}\frac{\partial R_i}{\partial B} + R_i \frac{\partial^2 R_i}{\partial B^2}\right)\Delta B = 0. \tag{7}$$

This is the well known Newton–Raphson's method for sets of non-linear equations. For given initial values A_0 and B_0, the final results A and B can be found via ΔA and ΔB by means of Eqs (6) and (7). However, the determination of the solutions of A and B needs good initial values A_0 and B_0, otherwise the solutions diverge. In fact, it is very difficult to choose good initial values for a non-linear equation.

However, it is our experience that in practice the solution can easily be found, if the second derivative terms are omitted from Eqs (6) and (7) and then these become

$$\sum R_i \frac{\partial R_i}{\partial A} + \sum\left(\frac{\partial R_i}{\partial A}\frac{\partial R_i}{\partial A}\right)\Delta A + \sum\left(\frac{\partial R_i}{\partial B}\frac{\partial R_i}{\partial A}\right)\Delta B = 0 \tag{8}$$

$$\sum R_i \frac{\partial R_i}{\partial B} + \sum\left(\frac{\partial R_i}{\partial A}\frac{\partial R_i}{\partial B}\right)\Delta A + \sum\left(\frac{\partial R_i}{\partial B}\frac{\partial R_i}{\partial B}\right)\Delta B = 0. \tag{9}$$

It turns out that the solutions of Eqs (8) and (9) are equal to those of Eqs (6) and (7), but the initial values for solving Eqs (8) and (9) are more easily chosen.

The principle can also be applied to non-linear equations with 3 parameters.