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EQUATION OF STATE AND RELATED PROPERTIES OF LIGHT AND HEAVY WATERS AND THEIR MIXTURES

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ABSTRACT

In this paper we have shown that the p–V–T measurements for light and heavy water systems can be represented with sufficient accuracy by the logarithmic form of the two parameter Tait equation. One of the parameters, which is dimensionless, turns out to be the same for both types of water. We make the plausible assumption that even for their mixtures this parameter has the same value. The other parameter can then be determined from the limiting isothermal compressibility which is obtainable with great precision from the speed of sound measurements at normal pressure. The p–V–T data for the water mixtures can thus be generated by using the Tait equation. This simple equation is very useful in the determination of the values of those thermodynamic functions which are not easily accessible to direct experimental measurements at elevated pressures. Lastly the principle of corresponding states is shown to be applicable for the two water systems.

INTRODUCTION

The thermodynamic properties of light water (H_2O) have been investigated experimentally in great detail[1]. Similar though less extensive work with heavy water (D_2O) has been carried out in the last few decades. However, the study of mixtures of the two waters, which are ideally suited from the point of view of theory of mixtures, has strangely attracted little attention so far. It is hoped that this work will generate some activity which would help in filling this gap.

Equation of state measurements for the two waters in the liquid phase have been carried out by a number of workers. From these we have selected Bridgman's data[2] and discussed the problem of their analytical representation by a simple two-parameter equation. Such a representation is very useful in determining the values of some of the thermodynamic functions which are not easily measured directly at elevated pressures. Next, in the absence of direct experimental p–V–T measurements on the mixtures of two waters, we have given a procedure by which these data may be generated. The only mixture property which is needed is the isothermal compressibility under ordinary conditions as a function of temperature and concentration. It is well known that the most reliable values of the limiting compressibility can be obtained from the speed of sound measurements provided the values of the ratio $\gamma = C_p/C_v$ are known. Recently, we have reported the speed of sound measurements[3] in the mixtures of two waters. Unfortunately no corresponding specific heat results are available at present, so that one can generate p–V–T data for water mixtures by making a tentative assumption that the specific heat of mixing is zero.

EQUATION OF STATE

The need to represent the p–V–T data by a suitable equation can hardly be over-emphasized. Tait[4] sought an equation to represent the compressibility of sea water and proposed the equation

$$(V_0 - V)/V_C = ap/(b+p) \tag{1}$$

where V_0 is the zero pressure volume, while a and b are parameters to be suitably chosen. This was later modified to the form

$$(V_0 - V)/V_0 = C \ln(1+p/B) \tag{2}$$

which is again a two parameter equation. This equation has been employed with considerable success for the analysis of the experimental p–V–T data for the normal paraffins and some high polymers[5]. The utility of this representation stems from the fact that for these systems the dimensionless parameter C could be assigned the same value 0.08936. In the case of light and heavy waters, the fitting of Bridgman's data with eqn (2) gives $C = 0.1240$ for both water systems. This result constitutes a great step forward in the determination of thermodynamic properties of water mixtures. No such simplification is, however, found possible with the representation corresponding to eqn (1). The values of parameters in eqns (1) and (2) for the two waters are given in Table 1. The volume values calculated from eqn (1) show a deviation from the experiment which exceeds 1.5% on the high pressure side. On the other hand,

TABLE 1

PARAMETERS OF EQNS (1) AND (2) FOR LIGHT AND HEAVY WATERS

T (K)	*Eqn (1)*				*Eqn (2)*[a]	
	H_2O		*D_2O*		*H_2O*	*D_2O*
	a	*b (kbar)*	*a*	*b (kbar)*	*B (kbar)*	*B (kbar)*
273.15	0.2867	5.607	0.2931	5.565	2.418	2.330
293.15	0.3220	7.232	0.3164	6.831	2.648	2.589
313.15	0.3246	7.587	0.3204	7.363	2.763	2.735
333.15	0.2885	6.357	0.2982	6.613	2.730	2.720
353.15	0.2900	6.189	0.2950	6.344	2.656	2.652

[a] The second parameter C has the same value equal to 0.1240.

using eqn (2) the maximum deviation does not exceed 0.1%. In view of this we have only used the logarithmic form of the Tait equation. It may be noted from Table 1 that the B values for the two waters seem to converge on the high temperature side. This could be due to the diminishing effect of hydrogen bonding with increase in temperature.

From eqn (2), it is readily seen that the isothermal compressibility

$$K_T(p) = -(\partial V/\partial p)_T/V = C/\{\xi(p+B)\} \tag{3}$$

where,

$$\xi = 1 - C\ln(1+p/B)$$

This gives,

$$K_T(0) = C/B \tag{4}$$

Equation (4) provides the limiting value of isothermal compressibility which is extremely difficult to measure directly from p–V measurements. Alternatively, accurate values of this quantity can be obtained from the speed of sound measurements and the knowledge of γ values. In Table 2 we have shown a comparison of $K_T(O)$ values for the two waters as obtained from eqn (4) and the speed of sound. It is noted that the differences in the two sets of compressibility values are generally less than 2%. This shows the reliability of eqn (2) for the representation of p–V–T data for both waters even in the low pressure region.

TABLE 2

$K_T(O) \times (10^6$ bar) FOR LIGHT AND HEAVY WATERS

T (K)	*H_2O*		*D_2O*	
	Speed of sound	*Eqn (4)*	*Speed of sound*	*Eqn (4)*
293.15	45.84	46.83	47.05	47.89
313.15	44.10	44.88	44.80	45.34
333.15	44.56	45.42	44.82	45.55
353.15	46.06	46.69	46.45	46.76

Equation of state studies of water mixtures have not been carried out so far. However, our foregoing analysis of the data of pure water systems permits us to generate p–V–T data for mixtures. Since the parameter C is identical for the two water systems, it seems reasonable to assume the same value for their mixtures. Making use of eqn (4) the values of parameter B as a function of temperature may be determined provided the corresponding isothermal compressibility values are known. The speed of sound measurement in the mixtures of heavy and light waters yields the adiabatic compressibility. Unfortunately, no specific heat measurements in water mixtures have been reported so far. We have tentatively assumed that the

TABLE 3

$K_T(0)\times(10^6$ bar) FOR MIXTURES OF HEAVY AND LIGHT WATERS FOR VARIOUS VOLUME CONCENTRATIONS R OF HEAVY WATER EXPRESSED IN PERCENTAGE

T (K)	R		
	25	50	75
293.15	46.12	46.25	46.59
313.15	44.24	44.24	44.46
333.15	44.64	44.49	44.68
353.15	46.11	46.05	46.30

specific heat of mixing for the water mixtures is zero and used the computed γ values to determine the isothermal compressibility. The results are shown in Table 3. This procedure for generating p–V–T data may be adopted for other systems (pure or mixtures) where the validity of the Tait representation may be assumed and provided the value of C can be inferred.

CALCULATION OF THERMODYNAMIC FUNCTIONS

Equation (3) gives the isothermal compressibility in terms of the Tait representation. Similarly using eqn (2) and the well-known thermodynamic relations the following expressions representing the pressure variation of other thermodynamic functions are obtained. Isobaric coefficient of volume increase,

$$\alpha_p(p) = (\partial V/\partial T)_p/V = \alpha_p(0) + (C/B)B'[p/\{\xi(p+B)\}] \tag{5}$$

Internal pressure,

$$p_i(p) = T(\partial p\, \partial T)_V - p = \xi(T\alpha_p(0)/C)(p+B) + p[(T/B)B' - 1] \tag{6}$$

where the primed quantities stand for their derivatives with respect to temperature.

Specific heat at constant pressure,

$$\begin{aligned} C_p(p) &= C_p(0) - T\int_0^p (\partial^2 V/\partial T^2)_p \mathrm{d}p \\ &= C_p(0) + T[F_1 p + \{F_2 + V_0''(p+B)\}(1-\xi) - F_3 p/(p+B)] \end{aligned} \tag{7}$$

where,

$$F_1 = (CV_0/B^2)B'^2 - (1+C)V_0'' - (2C(B)V_0'B' - (CV_0/B)B'',$$

$$F_2 = 2B'V_0' + V_0B'',$$

and

$$F_3 = (CV_0/B)B'^2$$

Entropy,

$$S(p, T) = S(0, T) + \int_0^p (\partial V/\partial T)_p \mathrm{d}p$$
$$= S(0, T)+p[V_0'(1+C)+(CV_0/B)B']-(1-\xi)[V_0'(p+B)+V_0B')] \quad (8)$$

The values of V_0 as a function of temperature for the two waters can be determined using Kell's relation[6]. For calculating the temperature derivatives of B, the polynomial

$$B = \sum_{r=0}^{4} C_r t^r \quad (9)$$

may be employed; here t is the temperature in °C. The values of coefficients of eqn (9) for the two waters are given in Table 4. The values of B calculated using eqn (9) do not differ by more than 0.1% from the direct determinations from eqn (2) for representing the p–V–T data.

TABLE 4

COEFFICIENTS OF EQN (9) WITH BAR AS THE UNIT OF PRESSURE

Coefficients	*H_2O*	*D_2O*
C_0	2418.0	2330.0
C_1	12.149	12.669
$C_2\times10^{-3}$	52.896	122.18
$C_3\times10^{-5}$	−496.43	−631.54
$C_4\times10^{-7}$	358.71	429.64

From eqns (3) and (5)–(8), various thermodynamic functions can be easily calculated and the effect of pressure on their behaviour investigated. As an illustration, the variations of α_p and C_p for heavy water are shown in Fig. 1 and Fig. 2, respectively. These two functions were chosen because of some interesting features.

In Fig. 1 the variation of α_p with pressure is shown for three different temperatures. It is observed that on the low temperature side α_p increases with pressure. However, at higher temperatures the effect of pressure weakens and ultimately shows an opposite trend. Calculations show a similar behaviour in the case of light water. Here our results are in agreement with those of Fine and Millero[7] who have reported values of α_p upto 1 kbar.

In Fig. 2 the variation of C_p with pressure is shown at five different temperatures. In all cases the change is non-monotonic. It may be further observed that the minimum in C_p as a function of pressure with increasing temperature first shifts to the low pressure side, but around 323 K this trend is reversed. Another interesting feature is that the effect of pressure on C_p increases first with rising temperature. However,

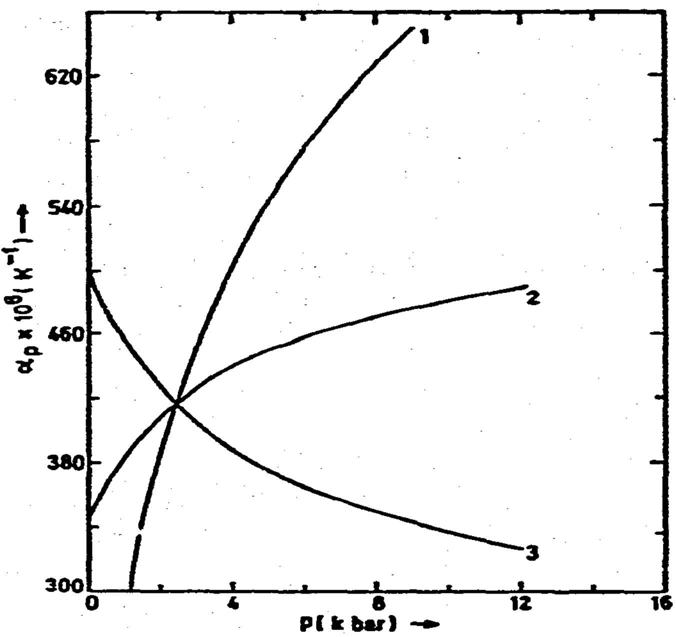

Fig. 1. Variation of isobaric coefficient of volume increase with pressure for heavy water. Curve 1: 293.15 K; curve 2: 313.15 K; curve 3: 333.15 K.

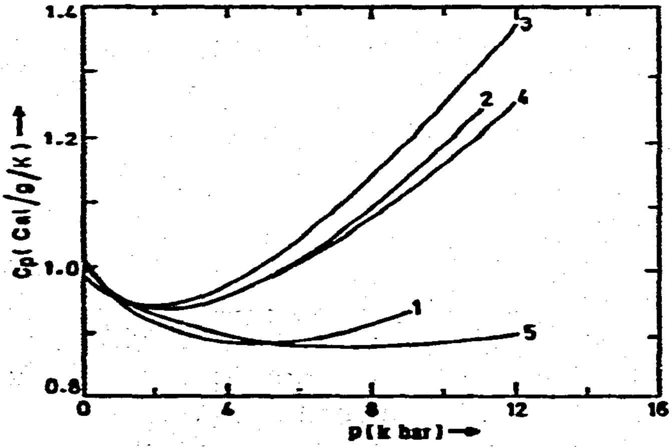

Fig. 2. Variation of specific heat at constant pressure with pressure. Curve 1: 293.15 K; curve 2: 303.15 K; curve 3: 313.15 K; curve 4: 323.15 K; curve 5: 333.15 K.

beyond 313 K this effect becomes progressively weaker. Similar behaviour is also observed in the case of light water.

PRINCIPLE OF CORRESPONDING STATES

If for a class of materials the parameter C of Tait's equation has the same value and provided the principle of corresponding states is obeyed, eqn (2) assumes the following form in terms of the reduced variables

$$1-\tilde{V}_p(\tilde{T})/\tilde{V}_0(\tilde{T}) = C\ln\left(1+\tilde{p}/\tilde{B}(\tilde{T})\right) \qquad (10)$$

Here the reduced volumes at zero and finite pressure are defined as $\tilde{V}_0 = V_0/V^*$ and $\tilde{V}_p = V_p/V^*$ in terms of a characteristic volume V^*. Similarly the reduced pressure $\tilde{p} = p/(E^*/V^*)$ and hence $\tilde{B} = B/(E^*/V^*)$ and also the reduced temperature $\tilde{T} = T/(E^*/(\eta k))$ where E^* represents a characteristic energy, η is the number of volume dependent degrees of freedom and k is the Boltzmann constant. If it can be demonstrated that for a class of materials $\tilde{B}$ and $\tilde{V}_0$ are both universal functions of the reduced temperature $\tilde{T}$, then it follows that a reduced equation of state

$$\tilde{p} = \tilde{p}(\tilde{V}, \tilde{T}) \qquad (11)$$

exists. We have considered such a possibility for the two waters. Since the absolute value of the scale parameters is not important here, we arbitrarily take V^*, $p^*(=E^*/V^*)$ and T^* to be unity for light water. In these units if we take for heavy water $V^* = 1.007$, $p^* = 0.991$ and $T^* = 1.012$, the superposition of $\tilde{V}_0$ versus $\tilde{T}$ and $\tilde{B}$ versus $\tilde{T}$ values for the two water systems, as shown in Figs. 3 and 4, is quite satisfactory. This shows that for the two waters the principle of corresponding states is valid in the temperature and pressure ranges considered here. We also find that $p^*V^*/T^* = 1.014$

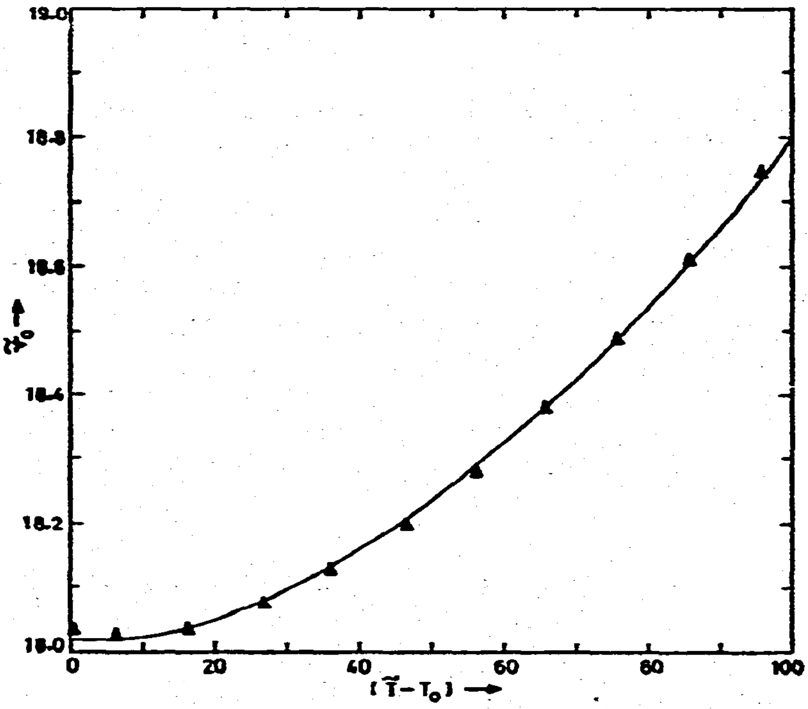

Fig. 3. Variation of reduced volume $\tilde{V}_0$ of light and heavy waters with $(\tilde{T}-T_0)$ where $T_0 = 273.15$. Full line: light water; ▲: heavy water.

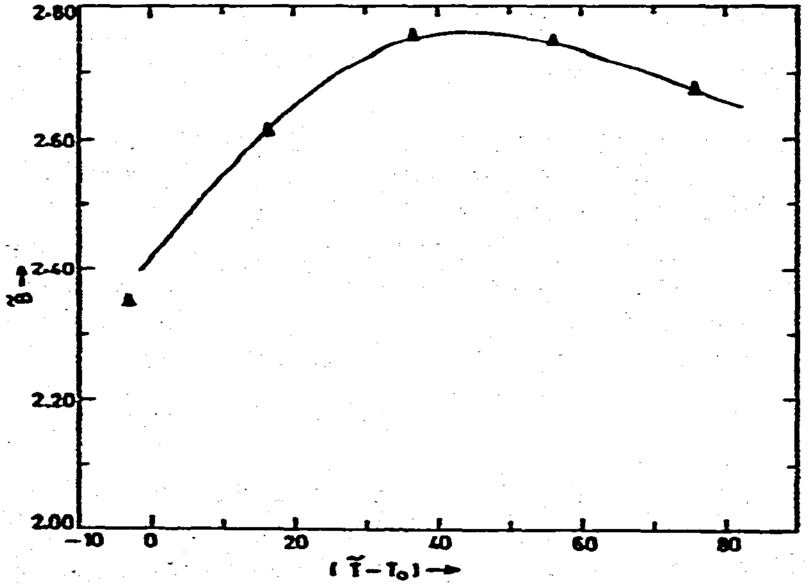

Fig. 4. Plot of reduced Tait parameter $\tilde{B}$ of light and heavy waters against $(\tilde{T}-T_0)$. Full line: light water; ▲: heavy water.

which shows that the number of volume-dependent degrees of freedom for heavy water is somewhat larger as compared to light water.

CONCLUSIONS

In the present paper we have taken an important step towards the study of light and heavy water mixtures. Extensive work in this direction is expected to pave the way for the development of a satisfactory theory of water. It has been shown in this paper that the p–V–T measurements of both waters can be represented by the logarithmic form of Tait's equation with a sufficiently high accuracy upto 12 kbar which is the limit of Bridgman's data. A simple procedure for generating p–V–T data for the water mixtures has also been given. By using the procedure described in this paper it is possible to evaluate readily the thermodynamic functions at elevated pressures from the knowledge of their corresponding values under ordinary conditions. Lastly the validity of the principle of corresponding states for the two water systems has been established over the temperature and pressure ranges considered in this work.

REFERENCES

1 D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Clavendon Press, Oxford, 1969.
2 P. W. Bridgman, *J. Chem. Phys.*, 3 (1935) 597.
3 R. N. Gupta, P. C. Jain and V. S. Nanda, *J. Chem. Thermodyn.*, in press.
4 J. S. Rowlinson, *Liquid and Liquid Mixtures*, Butterworth, London, 1969, p. 29.
5 V. S. Nanda and R. Simha, *J, Chem. Phys.*, 41 (1964) 3870.
6 G. S. Kell, *J. Chem. Eng. Data*, 12 (1967) 66.
7 R. A. Fine and F. J. Millero, *J. Chem. Phys.*, 59 (1973) 5529.