Derived properties of surface tension for hard sphere liquids from an equation of state

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Analytical expressions for the surface tension, derived by using the equation of state from the scaled particle theory and that from sound propagation through liquids, have been subjected to arrive at Eötvös constant and compressibility coefficient by forming the derivatives of surface energy and pressure coefficient of surface tension respectively. It is gratifying to note that value so obtained are in fair agreement with experiment, especially when it is noted that they are obtained as the second derivatives of Helmholtz free energy.

1. Introduction

Surface tension, which is one of the important equilibrium properties of liquids is related to other molecular and bulk properties of liquids. Theoretically, surface tension can be calculated from a knowledge of radial distribution function. In this publication it is proposed to derive certain associated properties of surface tension for which analytical expressions are available. In particular the compressibility and Eötvös constant, which are in the form of pressure and temperature derivatives, respectively, of surface tension, can be obtained easily if we have an analytical expression for the same.

2. Analytical Expressions for Surface Tension

Using Fowler's (1937) equation for surface tension expressed by the radial distribution function, it was possible to derive analytical expressions for hard sphere liquids for surface tension with the help of an equation of state. (Rao 1973).

There are two such equations of state that have been used extensively. One is acoustic equation of state derived by Rao *et al* (1969) and the other is an analytical expression given by Reiss *et al* (1959, 1965). The expressions obtained for the surface tension from Rao's equation of state is

$$\gamma = -\frac{\pi}{8} \ \frac{N^2}{V^2} \ kTg(d).d^4, \tag{1}$$

where

$$g(d) = \left[\frac{3V}{NG^2d^3} \left\{ \delta - \frac{1}{\delta} - 2 \ln \delta \right\} - 1 \right] \frac{3V}{2\pi N d^3}. \qquad \ldots \text{(2)}$$

Here γ is the surface tension of liquid, k is the Boltzmann constant, V is the molar volume, b is a structure factor and has a value of 1.78 for f.c.c. structure, N is Avogadro's number, T is absolute temperature, $g(d)$ is the radial distribution function $g(r)$ at $r = d$, the molecular diameter and δ is a dimensionless parameter derived from the concept of free volume and defined (Rao 1967) as

$$\delta = \frac{V^{1/3}}{V^{1/3} - N^{1/3}d}. \qquad \ldots \text{(3)}$$

Similarly, a simple treatment of the hard sphere liquid is provided by scaled particle theory. With this theory there is an altogether different approach to obtain the analytical expression for surface tension. The final equation, from this theory, for surface tension is

$$\gamma = -\frac{3}{4} \frac{\eta(\eta+1)}{(1-\eta)^3} \cdot \frac{NkT}{V} d, \qquad \ldots \text{(4)}$$

where η is a dimensionless parameter and is given by

$$\eta = \frac{1}{6} \frac{\pi N d^3}{V}. \qquad \ldots \text{(5)}$$

Thus eqs. (1) and (4) are analytical expressions for surface tension.

3. Evaluation of Compressibility

In eq. (1) only V and $g(d)$ depend on pressure at constant temperature and can be written as

$$\gamma = \frac{A \, g(d)}{V^2}, \qquad \ldots \text{(6)}$$

where

$$A = -\frac{\pi}{8} N^2 k T d^4, \qquad \ldots \text{(7)}$$

$$\left(\frac{d\gamma}{dP} \right)_T = 2\beta\gamma + \frac{\gamma}{g(d)} \cdot \frac{d}{dP} g(d), \qquad \ldots \text{(8)}$$

Remembering that

$$\beta \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \qquad \ldots \text{(9)}$$

where β is the compressibility, we immediately write

$$\left. \frac{d\gamma}{dP} \right)_T = 2\beta\gamma + \frac{3\beta\gamma V}{g(d).2\pi Nd^3} \left\{ 1 + \frac{V}{Nb^2 d^3} (\delta^2 - 9\delta + 5/\delta + 3 + 12 \ln \delta) \right\}$$

$$\ldots \ (10)$$

It was shown that Rao (1965)

$$\left(\frac{d\gamma}{dP} \right)_T = \frac{d}{4}. \qquad \ldots \ (11)$$

From eqs. (10) and (11) we get

$$\beta = \frac{d}{4} \left[2\gamma + \frac{3\gamma V}{2g(d)\pi Nd^3} \left\{ 1 + \frac{V}{Nb^2 d^3} (\delta^2 - 9\delta + 5/\delta + 3 + 12 \ln \delta) \right\} \right]^{-1}. \qquad \ldots \ (12)$$

Similarly way we can get β from eq. (4). The equation so obtained from the scaled particle theory for β is

$$\beta = \frac{d(1 - \eta^2)}{8\gamma(1 + 2\eta)}, \qquad \ldots \ (13)$$

where

$$\left(\frac{d\eta}{dP} \right) = \eta.\beta. \qquad \ldots \ (14)$$

The β values calculated from eqs. (12) and (13) are listed in table 1. The necessary data is taken from literature (Rao 1973).

4. Evaluation of Eötvös Constant

As is well known we have for the Eötvös constant

$$\frac{d}{dT} (\gamma V^{2/3}) = -K_E \qquad \ldots \ (15)$$

where $(\gamma V^{2/3})$ is the surface energy and K_E is Eötvös constant. The negative sign is there because surface energy decreases as temperature increases. The Eötvös constant is nearly 2 for all simple liquids.

From eq. (1) we obtain the following expression for Eötvös constant.

$$-K_E = \frac{d(\gamma V^{2/3})}{dT} = -\frac{4}{3} B.T.g(d) V^{-7/3}. \frac{dV}{dT} + B.V.^{-4/3}.g(d) + B.V^{-4/3}. \frac{d\,g(d)}{dT},$$

$$\ldots \ (16)$$

where

$$B = -\frac{\pi}{8} N^2 k.d^4, \qquad \ldots \ (17)$$

Table 1

S.No.	Liquid	γ (dyne/ cm)	V (c.c.)	d (Å)	T (°K)	δ	Compressibility $\beta \times 10^6$ atm^{-1}		
							From eq.(12)	From eq.(13)	Experi- mental
1.	Pentane	13.72	112	5.1^c	293	9.6	183	313	176
2.	n-Hexane	18.18	131	4.58^a	296	11.1	118	204	159
3.	n-Octane	21.8	163	4.78^a	296	12.3	96	180	121
4.	Benzene	28.86	89	4.06^a	293	11.5	64	112	95
5.	Toluene	28.4	106	4.16^a	293	11.5	69	121	91
6.	Methyl acetate	24.6	79	4.4^a	293	11.5	82	117	101
7.	Ethyl acetate	24.3	98	4.18^a	293	11.5	80	138	105
8.	Methyl alcohol	22.6	40	3.06^a	273	12.7	58	111	90
9.	Ethyl alcohol	22.3	57	4.06^a	273	10.0	88	113	100
10.	n-Propyl alcohol	23.78	75	4.32^a	293	12.85	755	120	—
11.	Carbon tetrachloride	26.66	97	4.79^b	293	12.4	76	114	105
12.	Carbon disulphide	31.4	59	3.94^a	319	10.8	60	85	87
13.	Chloroform	27.13	80	4.34^a	293	11.8	102	109	101
14.	Ether	17.01	106	4.74^a	303	10.8	130	192	167
15.	Ethylene bromide	38.37	86	3.94^a	293	11.6	57	84	59
15.	Acetone	26.21	73	3.54^a	297	9.3	73	118	93

a. Gopala Rao R. V. & Venkataseshiah V. 1969 *Zeit. Phys. Chem.* (Leipzig) **242**, 193.
b. Gopala Rao R. V. & Venkataseshiah V. 1972 *Zeit. Phys. Chem. Neue Folge.* **7**, 26.
c. Gopala Rao R. V. & Venkataseshiah V. 1969 *Indian J. Phys.* **43**, 424.

Substituting dV/dT by αV, where α is the thermal expansivity we get from eq. (16)

$$-K_E = -\frac{4}{3}\gamma V^{2/3}.\alpha + \frac{\gamma V^{2/3}}{T} + \frac{\gamma V^{2/3}}{g(d)}\cdot\frac{d\ g(d)}{dT} \quad \quad \dots \text{(18)}$$

From the above equation we immediately write

$$K_E = -\gamma V^{2/3}\left[\frac{1}{T} + \frac{2}{3}\alpha + \frac{0.7925 V\alpha}{g(d).d^3}\left\{1 + \frac{V}{Nb^2 d^3}(3\delta + 1/\delta - \delta^2 - 3)\right\}\right]. \dots \text{(19)}$$

Assuming a f.c.c. type lattice packing, eq. (19) becomes

$$K_E = -\gamma V^{2/3}\left[\frac{1}{T} + \frac{2}{3}\alpha + \frac{0.7925 V\alpha}{g(d)d^3}\left\{1 + \frac{0.5238 V}{d^3}(3\delta + 1/\delta - \delta^2 - 3)\right\}\right]. \dots \text{(20)}$$

In a similar way we can calculate K_E from the temperature derivative of eq. (4). The final equation for K_E obtainable from eq. (4) is

$$K_E = \gamma V^{2/3} \left[\frac{2\alpha(\eta^2 + 6\eta + 2)}{3(1 - \eta^2)} - \frac{1}{T} \right]. \qquad \ldots (21)$$

The values thus calculated from eqs. (20) and (21) for a set of typical liquids are tabulated in table 2, along with the experimental values.

Table 2

S.No.	Liquid	$\alpha \times 10^3$ deg^{-1}	Eotvos constant K_E. erg/degree		
			From eq.(20)	From eq.(21)	Experimental[a]
1.	Carbon tetrachloride	1.208	1.677	0.2988	2.21
2.	Chloroform	1.248	1.416	0.1698	2.1
3.	Benzene	1.209	1.37	−0.264	2.2
4.	n-Octane	1.147	1.563	−0.474	2.3
5.	Ethyl acetate	1.352	1.585	−0.059	2.3
6.	Methyl alcohol	1.148	0.6285	−0.06131	1.0
7.	n-Propyl alcohol	1.004	0.8535	−0.1165	1.3

a. From Lange's *Hand Book of Chemistry*, Revised Tenth Edition (1967), McGraw Hill Book Company, N.Y. The other necessary data are taken from table 1.

5. Discussion

The values of β obtained from eq. (12) are generally lower than the experimental ones while those calculated from eq. (13) are higher.

The values for Eötvös constant calculated from eq. (20) are low but those obtained from eq. (21) are very low and in some cases negative.

References

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