

TABLE 7*
(PRESSURE RANGE 0-1200 KG/CM²)

Compound	Temp. °C	ln A	B	Degree of Fit
N-Heptane	0	10.155	15.6458	0.9293
	30	9.929	15.2842	0.9997
	60	9.659	15.2984	0.9996
	90	9.351	15.6791	0.9994
	120	9.029	15.7234	0.9996
N-Octane	30	10.056	14.0174	0.9992
	60	9.809	14.8342	0.9986
	90	9.530	15.3992	0.9994
	120	9.224	15.4811	0.9985
N-Nonane	30	10.135	15.6135	0.9988
	60	9.901	15.6825	0.9992
	90	9.650	15.7623	0.9999
	120	9.357	16.3178	0.9997
N-Hexadecane	30	10.452	18.5744	0.9952
	60	10.274	16.1487	0.9989
	90	10.083	16.2620	0.9991
	120	9.881	16.3547	0.9989
N-Dodecane	30	10.324	15.7838	0.9999
	60	10.104	16.4597	0.9997
	90	9.898	16.1850	0.9999
	120	9.654	16.3964	0.9999

*Data taken from Reference (16).

The parameters K and q are both functions of temperature. For the substances investigated, K and q are correlated graphically in Figures 3 and 4. It is apparent that while it may be possible to deduce a single expression for K in the case of alkanes, no simple functional relationship would suffice for q .

Finally, a comparison of the Hudleston equation to the proposed equation of state was effected. The Hudleston equation was rewritten as

$$Y = A + BX \dots \dots \dots (15)$$

where

$$Y = \log [P v_R^{2/3} / (1 - v_R^{1/3})]$$

and

$$X = [1 - v_R^{1/3}]$$

Results of the regression analysis on the Hudleston equation are shown in Tables 5, 6, 7 and 8. For the most part, both the Hudleston equation and the proposed equation of state are seen to yield a comparable fit. For the aldehyde data, however, the proposed equation is superior. The average coefficient of correlation for the Hudleston equation is 0.9827, as opposed to 0.9993 for Equation (14). In addition, the water data correlate more satisfactorily on the basis of the proposed equation of state.

Conclusions

A semi-empirical equation of state has been developed and tested for aldehydes, alkanes, alcohols, and water. The equation is seen to correlate the data for these substances in an excellent manner.

Acknowledgment

The authors are grateful to the National Research Council for their financial support of this investigation.

Nomenclature

- a, b = constants, Equation (3)
- A, B = constants, Equation (2)
- A', B' = constants, Equation (4)
- C, D = constants, Equation (1)
- f = intermolecular force

TABLE 8*
(PRESSURE RANGE 0-10,000 KG/CM²)

Compound	Temp. °C	ln A	B	Degree of Fit
N-Propyl Alcohol	20	10.2829	17.1125	0.9993
	80	9.8529	16.7923	0.9991
Iso-Butyl Alcohol	20	10.2536	14.8991	0.9996
	80	9.8546	15.0509	0.9985
Iso-Amyl Alcohol	20	10.3404	15.7352	0.9996
	80	9.9780	15.3847	0.9991
Iso-Propyl Alcohol	0	10.4551	14.3213	0.9991
	50	10.0768	15.1932	0.9993
	95	9.8830	13.8416	0.9988
Iso-Butyl Alcohol	0	10.5891	14.8044	0.9989
	50	10.3608	14.0840	0.9995
	95	10.0890	14.3915	0.9998
Water	0	10.9426	10.4926	0.9990
	50	11.1267	9.2038	0.9989
	95	11.0600	9.3018	0.9994

*Data obtained from Reference (6).

- h = constant, Equation (7)
- K = constant, Equation (11)
- l = distance between molecules measured with reference to centre of gravity
- l_0 = distance between molecules corresponding to zero intermolecular force
- P = pressure, psi
- P_0 = atmospheric pressure
- q = constant, Equation (7)
- r = intermolecular distance
- R = gas law constant
- s = constant, Equation (8)
- T = absolute temperature
- v = specific volume
- v_0 = specific volume under atmospheric conditions
- v_R = relative volume, v/v_0

Greek

- ϵ = minimum energy of interaction
- μ = viscosity
- μ_0 = viscosity under atmospheric conditions
- Φ = potential function
- σ = collision diameter

References

- (1) van der Waals, J. D., Die Kontinuität des Gasförmigen und Flüssigen Zustandes (Barth, Leipzig), 1873.
- (2) Mie, G., Ann. Physik, 11, 657 (1903).
- (3) Kirkwood, J. G., J. Chem. Phys., 11, 657 (1935).
- (4) Kirkwood, J. G., ibid., 18, 380 (1950).
- (5) Munster, A., Statistische Thermodynamik (Berlin), 1956.
- (6) Bridgman, P. W., The Physics of High Pressure, G. Bell and Sons, London (1958).
- (7) Lennard-Jones, J. E. and Devonshire, A. F., Proc. Roy. Soc., London, (A)163, 53 (1937).
- (8) Lennard-Jones, J. E. and Devonshire, A. F., ibid., (A)165, 1 (1938).
- (9) Tait, P. G., Physics and Chemistry of the Voyage of H.M.S. Challenger, H.M. Stationary Office, London, Vol. 2, Part IV (1888).
- (10) Hudleston, L. J., Trans. Faraday Soc., 33, 97 (1937).
- (11) Wohl, A., Z. Physik Chem., 99, 234 (1921).
- (12) Carl, H., ibid., 101, 238 (1922).
- (13) Gibson, R. E. and Kincaid, J. F., J. Am. Chem. Soc., 60, 511 (1938).
- (14) Eduljee, H. E., Newitt, D. M. and Weale, K. E., J. Chem. Soc. (London), IV, 3086 (1951).
- (15) Cutler, W. G., McMickle, R. H., Wabb, H. and Schiessler, R. W., J. Chem. Phys., 29, 727 (1958).
- (16) Boelhower, J. W. M., Physica, 26, 1021 (1960).
- (17) Doolittle, A. K. and Doolittle, D. B., A.I.Ch.E. Journal, 6, 153 (1960).
- (18) Doolittle, A. K. and Doolittle, D. B., ibid., 6, 157 (1960).
- (19) Bond, A., J. Chem. Phys., 14, 591 (1946).
- (20) Hirschfelder, O. J., Curtiss, C. F. and Bird, R. B., Molecular Theory of Gases and Liquids, John Wiley, N.Y., 1954.
- (21) Hamann, S. D., Physico-Chemical Effects of Pressure, Butterworth, London (1957).
- (22) Chaudhuri, P. M., M.A.Sc. Thesis, Univ. of Windsor, Windsor, Ontario (1967).

Manuscript received August 17; accepted September 12, 1967.

★ ★ ★