International Journal of Thermophysics, Vol. 16, No. 1, 1995

Correlation of the Volumetric Properties of Fluorinated Ethers by the Group-Contribution Volume-Ratio Method[1]

R. Malhotra,[2,3] W. A. Van Hook,[2] and L. A. Woolf[4]

(p, V, T) data obtained with simple volumometers are usually restricted to a small range of temperatures below and above ambient temperature. The modified Tait equation has been very useful for extrapolating (p, V, T) data for individual liquids. The available volumetric data for fluorinated ethers is reviewed and is expressed as a correlation by using the Tait equation and the group-contribution volume-ratio method. Volume ratios obtained from this correlation used in combination with the densities of the liquid along the saturation boundary should provide the densities for a wide temperature and pressure range for the fluorinated ethers, including some which may be useful as long-term replacements for existing alternative refrigerants.

KEY WORDS: fluorinated ethers; group-contribution volume-ratio method; Tait equation of state.

1. INTRODUCTION

Some of the potential hydrochlorofluorocarbon (HCFC) replacements for banned chlorofluorocarbon (CFC) refrigerants are in production commercially. However, the prospect of phasing out HCFCs early in the next century presents a major challenge to the refrigerant industry. An additional class of compounds being considered for suitability as refrigerants is fluorinated ethers [1, 2]. Wang et al. [3] and Salvi-Narkhede et al. [4, 5] have reported vapor pressures and liquid molar volumes at moderate

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Chemistry Department, University of Tennessee, Knoxville, Tennessee 37996-1600, U.S.A.

[3] To whom correspondence should be addressed.

[4] Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia.

0195-928X/95/0100-0111$07.50/0 © 1995 Plenum Publishing Corporation

pressures for some fluorinated ethers with normal boiling points in the temperature range 235 to 279 K. Their purpose was to generate a description of various thermodynamic properties of the ethers by reference to the number of constituent fluorine atoms and the structure of the molecule [3].

Malhotra and Woolf [6] obtained p–V–T measurements and thermodynamic properties for a series of several related HCFCs including some currently accepted as alternative refrigerants [1]: 1,1-dichloro-2,2,2-trifluoroethane (R123) [7], 1,1-dichloro-1-fluoroethane (R141b) [8], and 1,2-dichloro trifluoroethane (R123a) [9]. The objective of that work was to obtain the contribution of individual chemical groups to the overall volume ratios of each related dense fluid. The authors employed the group-contribution volume-ratio method (GCVRM) devised by Malhotra and Woolf [10, 11] based on the Tait equation of state. The correlation was tested successfully by using volumetric data for some chlorofluorocompounds to predict the volumetric properties of other HCFCs recommended as alternative refrigerants [1].

Malhotra and Woolf [12] also obtained volume ratios for two commercially available fluorinated ethers, 2,2,2-trifluoroethyl-difluoromethylether (RE245) and 1,2,2,2-tetrafluoroethyl-difluoromethylether (RE236). The object of that work was, as earlier, to obtain a -F and -ether group contribution to the volumetric properties of the ethers using the GCVRM method and thus obtain a generalized correlation for volumetric properties of fluorinated ethers.

The present work reviews the available volumetric data for the fluorinated ethers [3–5, 12] and uses them to obtain a generalized correlation. The correlation, used in combination with liquid densities either at 0.1 MPa or at the saturation pressure (when the experimental temperature is above the normal boiling point), should enable prediction of densities in the liquid phase.

2. ASSESSMENT OF DATA

An on-line search for the volumetric properties of fluorinated ethers revealed only one reference [13] in addition to the data discussed above. Table I lists the fluorinated ethers for which volumetric property measurements have been made. Van Hook and co-workers determined liquid densities for a series of fluorinated ethers as a function of temperature and pressure in two ways: The first [14] employed a Mettler-Paar vibrating-tube DMA-05 densimeter for ($0.1 < p < 35$ MPa) and ($298 < T <$ the lesser of 373 K or $0.92\ T_c$), where T_c is the critical temperature; the second employed the (p, V_m, T) apparatus described by Kooner and Van Hook [15, 16] for ($0.1 < p < 6$ MPa) from room temperature to T_c. The accuracy of the densities of fluorinated ethers obtained using the first method is reported to be better than ±0.1%; the accuracy in the volume ratios V_p/V_{ref}, where V_p and V_{ref} are the volumes of fluids at experimental and reference pressures is estimated to be ±0.2%. The accuracy in the volume ratios V_p/V_{ref} from the second method is also estimated to be ±0.2%; however, in this method the errors accumulate and are expected to be greater at higher temperatures.

The ethers selected from the data of Van Hook and co-workers for correlation of the volumetric properties were those for which liquid volumes had been measured with a Mettler-Paar vibrating-tube densimeter in the pressure range saturation vapor pressure (svp) to 35 MPa. The volumetric data for these ethers were generated for (svp $< p <$ 35 MPa) from the coefficients in Table V of Ref. 3. They were used with the measured volume ratios for RE245 and RE236. For temperatures (278.15 to 298.15 K) for RE245 and for temperatures (278.15 to 288.15 K) for RE236 [12], these data are estimated to have an accuracy of ±0.002–0.04% for pressures above 50 MPa, varying to ±0.1% at pressures approaching 0.1 MPa. For higher temperatures, above the normal boiling points (313. 15 to 338.15 K for RE245 and 298.15 to 338.15 K for RE236), the accuracy is estimated to be ±0.1% for pressures above 50 MPa, varying to ±0.15–0.20% at pressures approaching 0.1 MPa.

Table I. Literature Data on the Volumetric Properties of Fluorinated Ethers

Fluid	T_r range	p range (MPa)	Method	Ref. No.
CF_3OCH_3	0.80–0.93	svp[a]-35	DMA-05	3
CHF_2OCHF_2	0.65–0.87	svp-5.5	Densimeter	13
CF_3OCHF_2	0.86–0.94	svp-35	DMA-05	3
	0.67–0.99	svp-6	pvt app.	4
$CF_2OCH_2CF_3$	0.61–0.74	svp-400	Bellows	12
$CF_2OCHFCF_3$	0.62–0.76	svp-400	Bellows	12
$CF_3OCF_2CHF_2$	0.78–0.94	svp-35	DMA-05	3
	0.63–0.78	svp-6	pvt app.	5
$CF_3OCF_2CF_2CF_3$	0.62–0.99	svp-6	pvt app.	5
c-$CF_2CF_2CF_2O$	0.84–0.92	svp-35	DMA-05	3
	0.67–0.76	svp-6	pvt app.	4
c-$CF_2CF_2CF_2CF_2O$	0.60–0.97	svp-6	pvt app.	5
$CF_3OCF_2OCF_3$	0.81–0.92	svp-35	DMA-05	3
	0.66–0.81	svp-6	pvt app.	5
c-$CF_2OCF_2OCF_2$	0.65–0.99_6	svp-6	pvt app.	4

[a] Saturation vapor pressure.

3. RESULTS

The volumetric properties data in the liquid region for five ethers [3]; *F*-methyl methyl ether (CF_3OCH_3), pentafluorodimethyl ethyl (CF_3OCF_2H), 2-hydryl-*F*-ethyl-*F*-methyl ether ($CF_3OCF_2CF_2H$), *F*-oxtane (c-$CF_2CF_2CF_2O$), and perfluorodimethoxymethane ($CF_3OCF_2OCF_3$) at a reference pressure 2.5 MPa expressed as volume ratios, $V_p/V_{2.5\,MPa}$, were fitted to the modified Tait equation [17]

$$1 - k = C \log[(B + p)/(B + p_{ref})] \tag{1}$$

Here k is the volume ratio ($= V_p/V_{ref}$) of volumes at pressure p and reference pressure p_{ref}, and B and C are adjustable parameters. The optimized coefficients obtained using Eq. (1) fit the volume-ratio data for each individual isotherm for all five ethers within the estimated experimental accuracy of $\pm 0.2\,\%$ with the exception of isotherms for temperatures greater than $0.92T_c$, where the difference between experimental volume ratios and those calculated using Eq. (1) is of the order of ± 0.3–$0.4\,\%$. To enable interpolation or extrapolation of volume ratios for each individual ether [18], the parameter C in Eq. (1) was assigned a temperature-independent common value chosen to give the best fit for all the experimental temperatures. The temperature dependence of the corresponding B values for the fixed value of C has been represented as inversely proportional to the reduced temperature $T_r (= T/T_c)$,

$$B = A_1 + A_2/T_r \tag{2}$$

The value of C and parameters of Eq. (2) are given in Table II. The root mean square deviation (rmsd) in representing the set of volume ratios for each ether using Eq. (1) with the parameters C from Table II and B from Eq. (2) is within the estimated accuracy of the data, with the exception of the highest temperature corresponding to a reduced temperature greater than 0.9. The coefficients in Table II enable extrapolation of volume ratios of the ethers by as much as ±70 K outside the experimental temperature

Table II. Coefficients of Eqs. (1) and (2) for Fluorinated Ethers

Fluid	C	$-A_1$	A_2	SD
CF_3OCH_3	0.2099	75.873	72.462	0.49
CF_3OCHF_2	0.2057	70.166	67.103	0.12
$CF_3OCF_2CHF_2$	0.1896	77.212	72.019	0.44
c-$CF_2CF_2CF_2O$	0.1939	70.774	66.926	0.43
$CF_3OCF_2OCF_3$	0.1924	62.535	58.951	0.58

range; the comparison of these extrapolated volume ratios with the measured volume-ratio data for ethers [4, 5] is within the estimated experimental accuracy.

It is interesting to note the volumetric properties data for the three normal fluorinated ethers CF_3OCH_3, CF_3OCHF_2, and $CF_3OCF_2CHF_2$ can be represented by Eq. (1) with a fixed value of $C = 0.205$ and B values in the range $(0.78 < T_r < 0.93)$ expressed as

$$B = -75.257 + 71.672/T_r \tag{3}$$

Although the molecular composition of each of these ethers is different, the representation of the temperature dependence of B does not require inclusion of a contribution δB_{fg} by a specified functional group. In the case of n-alkanes [19], ketones [10], and hydrochlorofluorocarbons [11], the temperature dependence of B values in the range $(0.4 < T_r < 0.7)$ involves a term giving the contribution δB_{fg} of a specified functional group

$$B = f(T, T_c) + \sum N_{fg}\, \delta B_{fg} \tag{4}$$

where N_{fg} is the number of occurrences of each functional group in the compound.

The analysis of volumetric data for RE245 and RE236 using the Tait equation of state [Eq. (1)] is described elsewhere [12]. Here volumetric data for these ethers restricted to a maximum pressure of 150 MPa are examined using the group-contribution volume-ratio method (GCVRM) [11] to enable prediction of the volumetric properties of fluorinated ethers including those of interest as long-term replacements for currently suggested alternative refrigerants. (Although volumetric data for these ethers are available for pressures up to 400 MPa, the chosen pressure limit of 150 MPa is arbitrary and has been selected for several reasons: (1) Dymond and Malhotra [19] examined (p, V, T) data for n-alkanes $(C_6$–$C_{17})$ and found that 150 MPa was a cutoff limit which enabled them to reproduce the data by using one value of C and a temperature-dependent B as a $f(T/T_c, C_n)$ in terms of the critical temperature T_c, and carbon number C_n; (2) this spurious Tait equation is actually the linear secant-modulus equation, expressed in the reciprocal form [17], and a recent statistical-mechanical analysis [20] indicates nonlinearity of the secant bulk modulus when the density range is large. Thus the conservative pressure limit chosen should ensure that the correlation obtained using the Tait equation of state and the GCVRM method is accurate when used for the prediction of volume ratios for fluids for which no volumetric properties data are available.)

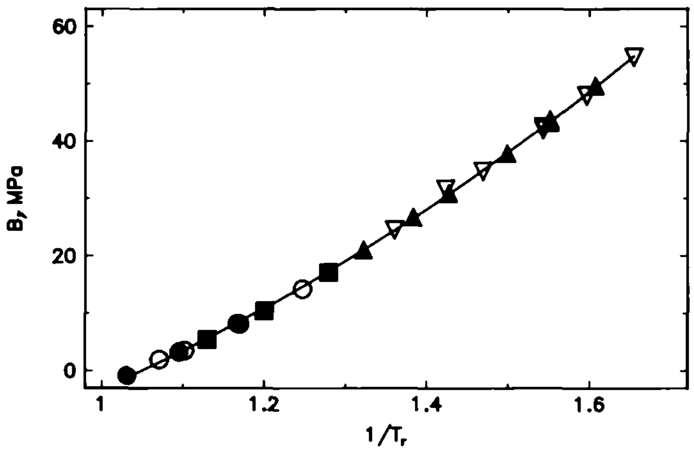

Fig. 1. Variation of optimized *B* value ($C = 0.205$) against the reciprocal of the reduced temperature for (○) CF_3OCH_3, (●) CF_3OCHF_2, (■) $CF_3OCF_2CHF_2$, (▽) $CF_2OCH_2CF_3$, and (▲) $CF_2OCHFCF_3$.

Malhotra and Woolf [12] fitted the volumetric data of RE245 and RE236 using Eq. (1) and a fixed value of C and found that the temperature dependence of B for each compound was a linear function of $1/T_r$, differing at the same T_r only by a value corresponding to the contribution to B from the additional F atom of RE236. The volumetric data of RE245 and RE236 in the range $(0.61 < T_r < 0.76)$ could be represented for a fixed value of $C = 0.205$ by a version of Eq. (3) in which the δB contribution was given only for the additional F in RE236

$$B = -111.715 + 100.104/T_r - (N_F - 5)\,\delta B_F \qquad (0.61 < T_r < 0.76) \qquad (5)$$

where

$$\delta B_F = 1.346 + 0.8115/T_r \qquad (6)$$

and N_F corresponds to the number of functional F atoms. Using a constant value of $C = 0.205$ in Eq. (1), the optimized B values for RE245 and RE236 [with the latter corrected for the additional F value using Eq. (6)] can be combined with those of CF_3OCH_3, CF_3OCF_2H, and $CF_3OCF_2CHF_2$. This extends the B value $(0.78 < T_r < 0.93)$ range to $(0.61 < T_r < 0.93)$ as shown in Fig. 1, which can be represented by

$$B/\text{MPa} = -24.034 - 20.1443/T_r + 40.9994/T_r^2 + (N_C - 3)\,\delta B_C - (N_F - 5)\,\delta B_F \qquad (7)$$

where

$$\delta B_C = 1, \quad \delta B_F \text{ is given by Eq. (6) and } \quad (\delta B_C = \delta B_F = 0 \text{ for } T_r \geqslant 0.8) \quad (8)$$

N_F and N_C correspond to the number of functional fluorine and carbon atoms, respectively.

For all normal ethers in Table II the correlated or predicted volume ratios for the temperature range $(0.8 < T_r < 0.92)$ are within the expected accuracy of the experimental data. The maximum deviation from the raw data of the volume ratio calculated using $C = 0.205$ and B from Eq. (7) with Eq. (1) is ±0.3–0.4% at the highest temperature. With the exception of $CF_3OCF_2CHF_2$ at 303.25 K $(T_r = 0.782)$, the predicted volume ratios using $C = 0.205$ and B from Eq. (7) in Eq. (1) agreed within the accuracy of the volumetric data for all normal ethers [4, 5] in Table I. The correlated volume ratios for RE245 and RE236 for all temperatures and pressures up to 150 MPa, with the exception for RE245 at 323.15 K, were within the experimental uncertainty of the data; the differences between correlated and experimental volume ratios for RE245 at 323.15 K for the $(40 < p < 150$ MPa) range were ±0.22–0.30%.

Measured liquid densities for bis(difluoromethyl) ether CHF_2OCHF [13], which has been suggested as a possible replacement for refrigerant CF_2ClCF_2Cl (R114), are for $(0.65 < T_r < 0.87)$ and pressures up to 5.3 MPa with a reported accuracy of ±0.05%. These data, with the exception of 1% of data points, expressed in terms of volume ratios are within ±0.1% of the volume ratios predicted using Eq. (1) in combination with Eq. (7) and $C = 0.205$; the maximum percentage deviation between the predicted and the experimental values is ±0.2% for only two data points.

The existing recommended method [21] for estimating liquid densities for polar, nonpolar, and quantum fluids under pressure is the COSTALD (COrresponding STates And Liquid Density) correlation [22]; this is also based on the Tait equation. The errors in volume ratios estimated for CHF_2OCHF_2 using the COSTALD method compared to experimental measurements are of the order of ±0.1–0.7% and are generally three times greater than GCVRM errors.

At this stage it is not possible to use the GCVRM equations developed above for linear ethers to predict volumetric data for cyclic ethers and other compounds with two ether groups. However, the experimental volumetric data for two cylic ethers, c-$CF_2CF_2CF_2O$ and c-$CF_2CF_2CF_2CF_2O$ [3–5], indicate that the δB_{fg} contribution to B suggested above can be used. Using $C = 0.1939$, with B for c-$CF_2CF_2CF_2O$ from Table II, and taking into account the δB_{fg} contribution to B from the additional -C and -F in c-$CF_2CF_2CF_2CF_2O$ the predicted volume ratios in the $(0.59 < T_r < 0.68)$

range are within the estimated accuracy of the experimental measurements. However, the predicted values and experimental measurements diverge as the temperature increases above 0.68 T_c.

4. CONCLUSION

The present work has added to the growing body of evidence that the semiempirical equation method, GCVRM [11], is suitable for correlation and prediction of the volumetric properties of any family of related compounds. Although the COSTALD method [22] covers the same range of compounds, it requires four characteristic parameters for each individual compound and is limited in its use to pressures up to 70 MPa; its accuracy in prediction generally is not as good as the GCVRM. The GCVRM method tested here is expected to cover a greater pressure range than COSTALD and should be able to predict volumetric properties with an accuracy close to that obtainable for experimental measurements of the properties. The GCVRM requires only one characteristic parameter, the critical temperature, for an individual compound.

REFERENCES

1. M. O. McLinden, W. M. Haynes, J. T. R. Watson, and K. Watanabe, A Survey of Current Worldwide Research on the Thermophysical Properties of Alternative Refrigerants, NIST IR 3969 (U.S. Department of Commerce, Washington, DC, 1991).
2. W. L. Kopko, *Rev. Int. Froid.* **13**:79 (1990).
3. B. H. Wang, J. L. Adcock, S. B. Mathur, and W. A. Van Hook, *J. Chem. Thermodyn.* **23**:699 (1991).
4. M. Salvi-Narkhede, B. H. Wang, J. L. Adcock, and W. A. Van Hook, *J. Chem. Thermodyn.* **24**:1065 (1992).
5. M. Salvi-Narkhede, J. L. Adcock, A. Gakh, and W. A. Van Hook, *J. Chem. Thermodyn.* **25**:643 (1993).
6. R. Malhotra and L. A. Woolf (unpublished data).
7. R. Malhotra and L. A. Woolf, *Int. J. Thermophys.* **14**:1021 (1993).
8. R. Malhotra and L. A. Woolf, *Fluid Phase Equil.* **92**:195 (1994).
9. R. Malhotra and L. A. Woolf, *J. Chem. Eng. Data* (in preparation).
10. R. Malhotra and L. A. Woolf, *12th IUPAC Themodynamics Conferences*, Snowbird, Utah (1992).
11. R. Malhotra and L. A. Woolf, *High Temp. High Press.* **25**:179 (1993).
12. R. Malhotra and L. A. Woolf, *Int. J. Themophys.* (in preparation) (1994).
13. D. B. Defibaugh, K. A. Gillis, M. R. Moldover, G. Morrison, and J. W. Schmidt, *Fluid Phase Equil.* **81**:285 (1992).
14. S. Matsuo and W. A. Van Hook, *J. Phys. Chem.* **88**:1032 (1984).
15. Z. S. Kooner and W. A. Van Hook, *J. Phys. Chem.* **90**:4860 (1986).
16. Z. S. Kooner and W. A. Van Hook, *J. Phys. Chem.* **92**:6414 (1986).
17. A. T. J. Hayward, *Br. J. Appl. Chem.* **18**:965 (1967).

18. R. Malhotra and L. A. Woolf, *High Temp. High Press.* **23**:107 (1991).
19. J. H. Dymond and R. Malhotra, *Int. J. Themophys.* **8**:541 (1987).
20. T. Song, B. Caswell, and E. A. Mason, *Int. J. Themophys.* **12**:107 (1991).
21. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1987).
22. G. H. Thomson, K. R. Brobst, and R. W. Hankinson, *AIChE J.* **28**:671 (1982).