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Effect of Temperature and Pressure on the Volumetric Properties of Branched and Cyclic Ethers

U. P. Govender[†] **and T. M. Letcher***[,‡]

Department of Chemistry, University of Natal, Private Bag X10, Dalbridge, 4014 Durban, South Africa

S. K. Garg and J. C. Ahluwalia

Department of Chemistry, Indian Institute of Technology, New Delhi 110-016, India

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The densities of liquid diisopropyl ether, 1,1-dimethylethyl methyl ether, 1,1-dimethylpropyl methyl ether, tetrahydrofuran, tetrahydropyran, and 1,4-dioxane have been determined from 288.15 to 328.15 K at pressures ranging from 0.1 to 8 MPa. The molar volumes (derived from densities) have been fitted to a polynomial as a function of temperature and pressure. Where available, the results have been compared to literature values.

Introduction

The second-order molar volume thermodynamic quantities of pure components such as the thermal expansion coefficient, α_P, and the isothermal compressibilities, κ_T, are necessary parameters used in the prediction of the excess thermodynamic quantities of liquid mixtures from theoretical models (Aicart et al., 1994; Heintz, 1985; Abe and Flory, 1965; Patterson et al., 1968, 1970). These models utilize an equation of state whose characteristic parameters for the pure liquids are obtained directly from α_P, κ_T, and V_m (molar volume). Reliable values of α_P and κ_T have been determined either experimentally or through derivation for only a few liquids and in some instances are not known to sufficient accuracy (Diaz Pena and Tardajos, 1979). In this paper we report the density ρ, molar volumes V_m, cubic expansion coefficients α_P, and isothermal compressibilities κ_T for diisopropyl ether (IPE), 1,1-dimethylethyl methyl ether (*tert*-butyl methyl ether, TBME), 1,1-dimethylpropyl methyl ether (*tert*-amyl methyl ether, TAME), tetrahydrofuran (THF), tetrahydropyran (THP), and 1,4-dioxane.

U.P.G. and T.M.L. have recently determined the excess properties of binary liquid mixtures containing a polar component + an ether (Letcher and Govender, 1995a,b; Letcher et al., 1994a,b). As a continuation of this work, we intend to use the data presented here to test the application of the extended real associated solution (ERAS) (Heintz, 1985) and Prigogine−Flory−Patterson (PFP) (Flory et al., 1964) theoretical models to our mixtures. These results will be detailed in a future paper.

Experimental Section

The preparation and purities of all the ethers used in this work have been described elsewhere (Letcher and Domanska, 1993). All the liquids were dried after purification and kept in a glovebox. They were degassed and analyzed for water content before use. All the liquids were analyzed by GLC and were found to be 99.8 mol % pure in the worst case (*tert*-amyl methyl ether). In all the cases the mole fraction of H_2O was determined by a Karl-Fischer titration to be <0.01 mol %.

Table 1. Densities ρ of Pure Compounds and Comparison of κ_T Results for Hexadecane with Literature Values

(a) Densities

compound	T/K	purity/%	ρ/(kg·m^{-3}) this work	lit.
cyclohexane	298.15	>99.8	773.80	773.74[a]
heptane	298.15	>99.9	679.26	679.53[b]
ethylbenzene	298.15	>99.5	862.25	862.46[c]
IPE	298.15	99.8	717.84	718.20[d]
TBME	298.15	>99.9	734.80	735.30[e]
TAME	298.15	>99.9	765.71	765.91[f]
THF	298.15	>99.9	881.42	881.90[g]
THP	298.15	>99.9	878.54	879.00[g]
1,4-dioxane	298.15	>99.9	1026.66	1027.90[h]

(b) κ_T Results

T/K	κ_T/TPa^{-1} exptl	lit.[i]
318.15	975	978
333.15	1080	1066

[a] Sun et al. (1988). [b] Banipal et al. (1991). [c] Garg et al. (1995). [d] Riddick et al. (1986). [e] *TRC Thermodynamic Tables* (1988). [f] Zhu et al. (1994). [g] Grolier et al. (1982). [h] Grolier et al. (1993). [i] Diaz Pena and Tardajos (1978).

Densities ρ were measured with an Anton Paar DMA 60/512 vibrating-tube densimeter as described elsewhere (Garg et al., 1993; Cullick and Matous, 1984). The bath temperature was measured with a Leeds and Northrup thermometer accurate to ±0.03 K on IPTS-68 and was maintained with a proportional temperature controller (YSI Model 72). Pressure was measured with a static high-pressure unit (Setaram) accurate to ±0.01 MPa. The unit was calibrated by the National Physical Laboratory, New Delhi, against its transfer standard gauges (Sharma et al., 1988). The reference pressure was taken as 1×10^5 Pa. Calibration of the densimeter was done with water and air, and all the measurements were made with reference to water. Water was distilled, deionized, and degassed by boiling. The accuracy of the density measurements is estimated at ±0.03 kg·m^{-3}. The densimeter was tested by measuring the densities of cyclohexane, *n*-heptane, and ethylbenzene at 298.15 K. The results are listed in Table 1a together with the density values of all the liquids used in this work at 298.15 K and atmospheric pressure. The results show good agreement with the literature values (Garg and Ahluwalia, 1995; Sun et al., 1988; Banipal et

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* To whom correspondence should be addressed.

[†] E-mail: govend2@che.und.ac.za.

[‡] E-mail: letcher@che.und.ac.za.

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al. 1991; Riddick et al., 1986; TRC Tables, 1988; Zhu et al., 1994; Grolier et al., 1993; Grolier et al., 1982). The difference between our values and the literature values is $<|0.0005\rho|$. The accuracy of the applied method of determining α_P and κ_T was checked by comparing our experimental κ_T results for hexadecane at 0.1 MPa along the 318.15 and 333.15 K isotherms to those of Diaz and Tardajos (1978). Our results are within 0.024 $\mathrm{GPa^{-1}}$ of those reported. These results are listed in Table 1b.

Results and Discussion

The measured densities for each of the six ethers at temperatures ranging from 288.15 to 328.15 K and pressures up to 8 MPa are summarized in Table 2. The density values of water, which was used as a reference, were taken from the NBS Steam Tables (NBS, 1988−1989). The molar volumes, V_m (M/ρ) were fitted to the following polynomial in T and P:

$$V_m(T,P)/(\mathrm{cm^3 \cdot mol^{-1}}) = v_0 + v_1(T/\mathrm{K}) + v_2(T/\mathrm{K})(P/\mathrm{MPa}) + v_3(P/\mathrm{MPa}) \quad (1)$$

The parameters v_0, v_1, v_2, and v_3, estimated by the method of unweighed least squares, are given in Table 3, together with the standard deviations. The cubic expansion coefficient α_P and isothermal compressibilities κ_T were derived from eq 1 using the following relations:

$$\alpha_P V = (\partial V/\partial T)_P \quad (2)$$

$$-\kappa_T V = (\partial V/\partial P)_T \quad (3)$$

α_P and κ_T were then fitted to the following polynomial power series in T and P:

$$\alpha_P(T,P)/\mathrm{kK^{-1}} = v_0' + v_1'(T/\mathrm{K}) + v_2'(T/\mathrm{K})(P/\mathrm{MPa}) + v_3'(P/\mathrm{MPa}) \quad (4)$$

$$\kappa_T(T,P)/\mathrm{GPa^{-1}} = v_0'' + v_1''(T/\mathrm{K}) + v_2''(T/\mathrm{K})(P/\mathrm{MPa}) + v_3''(P/\mathrm{MPa}) \quad (5)$$

The constants of eqs 4 and 5 are given in Tables 4 and 5 together with their standard deviations, respectively. For all the ethers studied in this work, plots of α_P and κ_T as a function of temperature (at 0.1 MPa) and pressure (at 298.15 K) are given in Figures 1 to 4.

A regular linear variation of density with either pressure or temperature is a feature common to all the ethers. For all the ethers, the cubic expansion coefficients decrease with an increase in temperature or pressure while the isothermal compressibilities increase with an increase in temperature or pressure over the temperature and pressure ranges used in this work. Like the density isotherms, those of α_P and κ_T exhibit complete linearity at the pressures used in this work. This linear behavior is expected within the pressure ranges used in this work and is in agreement with the characteristic behavior previously observed for most liquids in the similar range of pressures (Baonza et al., 1994; Minassian et al., 1988; Garg et al., 1993). At higher pressures (20−100 MPa), it has been observed that curvilinear forms of α_P and κ_T are characteristic, with the temperature dependence of α_P changing sign at some intermediate pressure (Baonza et al., 1994). In general, an increase in density implies a decrease in the molar volume, V_m, with a corresponding decrease in the free intermolecular space. As a result, the ability of the liquid to expand or compress decreases as well. This trend of compressibility/expansivity opposite that of density as a function of temperature or pressure has been shown to be true for the n-alkanes (Diaz Pena and Tardajos, 1978) and the methyl-substituted benzenes (Minassian et al.,

Table 2. Experimental Densities ρ for Branched and Cyclic Ethers at Different Temperatures and Pressures

	ρ/(kg·m^{-3})				
P/MPa	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 328.15
			Diisopropyl Ether		
0.1	726.44	717.84	708.28	701.56	693.66
0.5	726.91	718.27	710.57	702.29	694.66
1.0	727.50	719.18	711.41	703.15	695.63
2.0	728.64	720.28	712.92	704.83	697.50
3.0	729.77	721.57	714.36	706.41	699.22
4.0	730.93	722.76	715.71	707.81	700.78
5.0	732.03	724.00	716.93	709.25	702.45
6.0	733.10	725.12	718.21	710.58	703.98
7.0	734.17	726.45	719.39	711.87	705.75
8.0	735.21	727.59	720.56	713.19	707.29
			tert-Butyl Methyl Ether		
0.1	743.39	734.80	727.20	718.75	715.18
0.5	743.86	735.33	727.81	719.49	715.92
1.0	744.55	735.95	728.54	720.31	716.75
2.0	745.57	737.15	729.75	721.90	718.24
3.0	746.70	738.35	731.03	723.35	719.63
4.0	747.69	739.47	732.32	724.78	721.11
5.0	748.68	740.59	733.53	726.11	722.52
6.0	749.65	741.64	734.76	727.34	723.96
7.0	750.63	742.90	735.92	728.58	725.36
8.0	751.49	743.94	737.00	729.71	726.69
			tert-Amyl Methyl Ether		
0.1	773.29	765.71	758.83	752.10	746.63
0.5	773.72	766.13	759.28	752.61	747.19
1.0	774.20	766.68	759.86	753.22	747.90
2.0	775.17	767.70	761.00	754.45	749.28
3.0	776.04	768.69	762.12	755.64	750.55
4.0	776.96	769.84	763.16	756.81	751.72
5.0	777.79	770.63	764.17	757.93	752.95
6.0	778.59	771.54	765.15	759.07	754.11
7.0	779.45	772.64	766.16	760.13	755.21
8.0	780.23	773.56	767.14	761.13	756.34
			Tetrahydrofuran		
0.1	889.44	881.42	873.78	865.89	859.04
0.5	889.81	881.78	874.20	866.35	859.51
1.0	890.26	882.26	874.71	866.95	860.10
2.0	891.05	883.15	875.70	868.08	861.35
3.0	891.76	884.01	876.66	869.14	862.49
4.0	892.57	884.84	877.61	870.17	863.50
5.0	893.31	885.68	878.47	871.16	864.52
6.0	894.02	886.47	879.33	872.10	865.51
7.0	894.80	887.46	880.19	873.04	866.47
8.0	895.51	888.26	881.07	873.83	867.42
			Tetrahydropyran		
0.1	885.39	878.54	871.20	864.04	858.70
0.5	885.61	878.85	871.54	864.42	859.20
1.0	885.73	879.46	872.04	864.92	859.77
2.0	886.65	880.15	873.02	865.95	860.89
3.0	887.43	881.00	873.95	866.92	861.97
4.0	888.26	881.78	874.85	867.90	862.94
5.0	889.01	882.72	875.73	868.85	863.95
6.0	889.81	883.33	876.57	869.75	864.92
7.0	890.61	884.29	877.44	870.71	865.85
8.0	891.41	885.05	878.23	871.64	866.79
			1,4-Dioxane		
0.1	1034.65	1026.66	1019.71	1011.68	1005.57
0.5	1034.95	1027.25	1020.11	1012.04	1005.95
1.0	1035.29	1027.73	1020.55	1012.51	1006.49
2.0	1035.93	1028.06	1021.41	1013.43	1007.52
3.0	1036.62	1028.82	1022.28	1014.32	1008.43
4.0	1037.40	1029.55	1023.07	1015.19	1009.26
5.0	1038.14	1030.30	1023.86	1016.06	1010.19
6.0	1038.87	1031.39	1024.66	1016.85	1011.11
7.0	1039.62	1031.90	1025.40	1017.70	1011.96
8.0	1040.31	1032.66	1026.11	1018.51	1012.85

Table 3. Parameters v_i and Standard Deviations σ Calculated by Using Eq 1

compound	$v_0 \times 10^{-1}$	$v_1 \times 10$	$v_2 \times 10^3$	$v_3 \times 10$	$\sigma \times 10$
diisopropyl ether	9.3332	1.6434	−3.4028	7.6991	0.73
tert-butyl methyl ether	8.0136	1.3342	−2.4150	5.3549	0.38
tert-amyl methyl ether	9.4729	1.2971	−3.8330	9.7449	2.7
tetrahydrofuran	6.0397	0.71809	−0.83637	1.7080	0.19
tetrahydropyran	7.5381	7.6166	−0.83465	1.5608	0.56
1,4-dioxane	6.7441	0.61589	−0.48950	0.82509	0.36

Table 4. Parameters v_i' and Standard Deviations σ Calculated by Using Eq 4 for α_P

compound	$v_0' \times 10^3$	$v_1' \times 10^6$	$v_2' \times 10^8$	$v_3' \times 10^5$	$\sigma \times 10^6$
diisopropyl ether	1.54	−1.31	4.69	−3.62	0.794
tert-butyl methyl ether	1.33	−1.10	3.46	−2.70	0.453
tert-amyl methyl ether	1.25	−0.927	4.78	−4.21	1.920
tetrahydrofuran	1.10	−0.759	1.59	−1.42	0.298
tetrahydropyran	0.954	−0.596	1.18	−1.14	0.468
1,4-dioxane	0.870	−0.511	0.775	−0.752	0.323

Table 5. Parameters v_i'' and Standard Deviations σ Calculated by Using Eq 5 for κ_T

compound	$v_0'' \times 10^3$	$v_i'' \times 10^5$	$v_2'' \times 10^8$	$v_3'' \times 10^5$	$\sigma \times 10^6$
diisopropyl ether	−4.68	2.15	8.26	−2.16	3.84
tert-butyl methyl ether	−3.87	1.81	5.85	−1.50	2.40
tert-amyl methyl ether	−6.79	2.70	8.35	−2.32	5.52
tetrahydrofuran	−1.79	0.923	1.86	−0.460	1.20
tetrahydropyran	−1.34	0.766	1.51	−0.360	0.793
1,4-dioxane	−0.782	0.510	0.813	−0.187	0.520

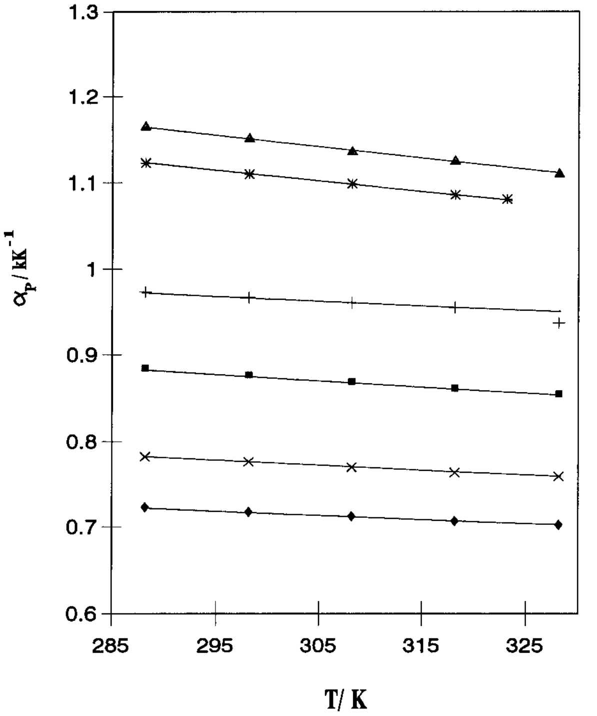

Figure 1. Cubic expansion coefficient versus temperature at 0.1 MPa for (▲) IPE, (*) TBME, (+) TAME, (■) THF, (×) THP, and (◆) 1,4-dioxane.

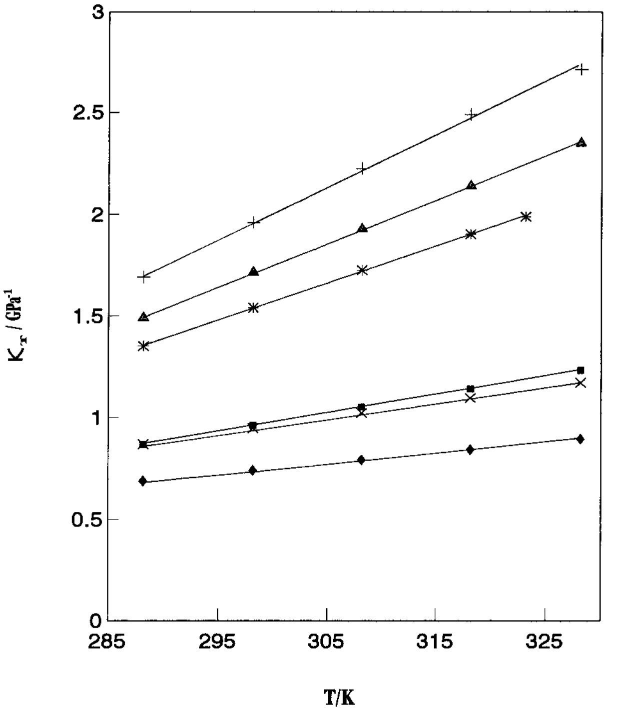

Figure 2. Isothermal compressibilities versus temperature at 0.1 MPa for (▲) IPE, (*) TBME, (+) TAME, (■) THF, (×) THP, and (◆) 1,4-dioxane.

1988; Baonza et al., 1994). In this work, however, as the density decreases the corresponding increase in the molar volume is observed, but this is accompanied by a slight decrease in the cubic expansion coefficient, α_P (Figure 1). This deviation from the expected behavior is unusual and could be attributed to the presence of different functional groups present in the molecule.

For IPE and TBME, Obama et al. (1985) have reported α_P results at 298.15 K and atmospheric pressure of 1.45 and 1.42 kK^{-1}, respectively while those reported here are 1.15 and 1.11 kK^{-1}, respectively. For the cyclic ethers, our α results at 298.15 K and 0.1 MPa for THF, THP, and 1,4-dioxane are 0.8767, 0.7760, and 0.7171 kK^{-1}, respectively, while those reported by Spanedda et al. (1991) are 1.24, 1.14, and 1.09 kK^{-1}, respectively.

Our κ_T results at 298.15 K and 0.1 MPa for THF, THP, and 1,4-dioxane are 0.9603, 0.9462, and 0.7392 GPa^{-1}, respectively, while those reported by Spanedda et al. (1991) and Berti et al. (1989) are 1.00, 0.99, and 0.72 GPa^{-1}, respectively. This discrepancy between our results and those reported previously could possibly be due to the method of estimation. The data reported here involve density measurements made as a function of temperature and pressure. Spanneda and co-workers (1991) have obtained their data from previously reported density values from many laboratories with possible differences in purity, technique, and precision. No other results detailing the change in α_P or κ_T with temperature and pressure could

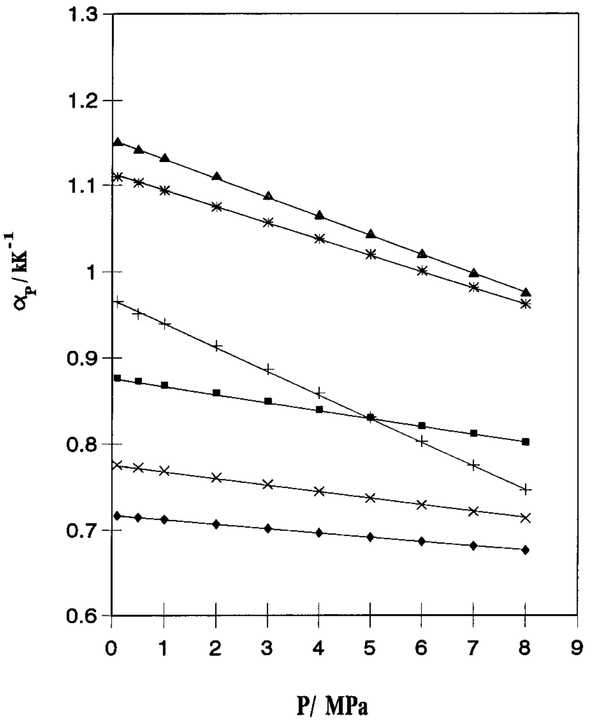

Figure 3. Cubic expansion coefficient versus pressure at 298.15 K for (▲) IPE, (*) TBME, (+) TAME, (■) THF, (×) THP, and (◆) 1,4-dioxane.

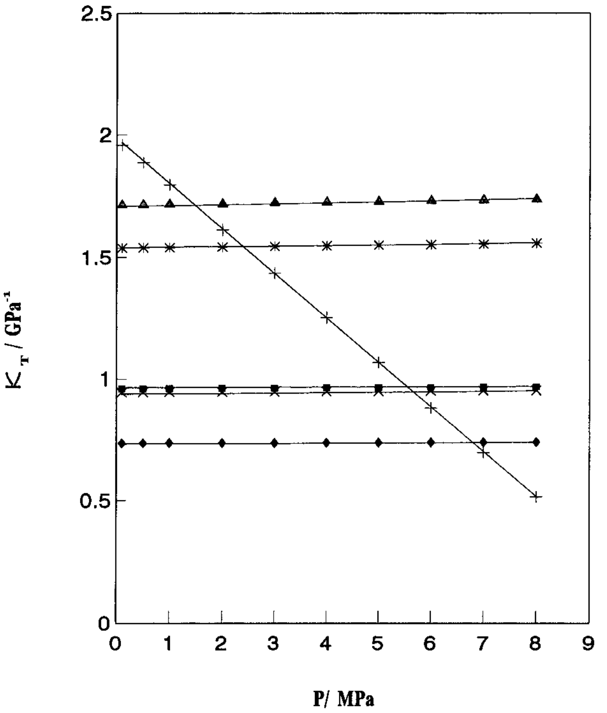

Figure 4. Isothermal compressibilities versus pressure at 298.15 K for (▲) IPE, (*) TBME, (+) TAME, (■) THF, (×) THP, and (◆) 1,4-dioxane.

be found in the literature for the liquids involved in this work.

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