Densities of Octamethylcyclotetrasiloxane + Methane and 2,2-Dimethylpropane + Methane from 10 to 200 MPa and from 294 to 433 K

Stefan J. Wappmann, Igor N. Tarassov, and Hans-Dietrich Lüdemann*

Institut für Biophysik und Physikalische Biochemie, Universität Regensburg, D-93040 Regensburg, Germany

Densities for octamethylcyclotetrasiloxane + methane and 2,2-dimethylpropane + methane have been determined in the one-phase region at temperatures between 294 and 433 K for a maximum pressure of 200 MPa in a piston cylinder apparatus. Polynomials capable of describing the density as a function of *P*, *T*, and composition have been derived.

Introduction

Our group has studied the pressure dependence of the self-diffusion coefficient *D* of binary mixtures consisting of nonpolar molecules of approximately spherical shape and very different masses and diameters, octamethylcyclotetrasiloxane + methane and 2,2-dimethylpropane + methane, by the pulsed field gradient technique. For the interpretation of these data by the usual modifications of the hard sphere models (Chandler, 1975; Speedy et al., 1989) and a comparison of the experimental diffusion coefficients *D* with the results obtained by molecular dynamics simulations for mixtures of hard spheres, reliable density data are necessary. Since the published density data for these two mixtures are very fragmentary, it was decided to measure all densities in the one-phase region of these mixtures in a simple cylinder piston type PVT cell (Francesconi et al., 1975; Wappmann et al., 1995). A preliminary account of part of the data has been given previously (Wappmann, 1993).

Experimental Section

Substances. Methane (99.75%) (Linde, Unterschleissheim, FRG) was taken directly from a steel bottle. It was dried by passing it through a steel column filled with silica gel and then condensed into a titanium autoclave described previously (Has and Lüdemann, 1990) and cooled to liquid nitrogen temperatures. Residual air was removed by several freeze−pump−thaw cycles. A final pressure of 10 Pa was reached in the pump cycles. Due to the high vapor pressure of methane at liquid nitrogen temperatures (78 K), a certain amount of the gas was lost in this process. Octamethylcyclotetrasiloxane (OMCTS) (≥99%) (Fluka, Buchs, Switzerland) and 2,2-dimethylpropane (DMP) (≥99%) (Linde, Unterschleissheim, FRG) were dried over molecular sieves (3 Å) and degassed by freeze−pump−thaw cycles to a final pressure of 10^{-3} Pa.

Apparatus. The densimeter, a modification of the piston cylinder design used by Francesconi et al. (1975), and its calibration have been described in detail recently (Wappmann et al., 1995).

Filling Procedures. The liquid component was filled into the evacuated densimeter with a syringe. The mass of the sample filled into the volume was determined by weighing the syringe before and after the filling with a precision of ±0.001 g. A defined amount of the methane was added to the liquid in the densimeter from a small stainless steel cylinder (volume 50 cm^3, maximum pressure 20 MPa). The mass of the methane and DMP was determined to ±0.001 g from the mass of the cylinder before and after the filling. The mass of a typical filling was around 30 g of the mixture.

Table 1. Density ρ of Octamethylcyclotetrasiloxane

	ρ/(kg·m^{-3})				
P/MPa	308.2 K	337.7 K	367.9 K	394.9 K	426.6 K
10	948	917	885	858	824
20	961	932	903	878	848
30	973	945	918	895	868
40		957	931	909	884
50		968	944		
60			954	934	912
80			973	955	934
100			991	973	953
120				989	970
140				1003	985
160					999
180					1011

Table 2. Density ρ of Octamethylcyclotetrasiloxane (1) + Methane (2) (x_1 = 0.772)

	ρ/(kg·m^{-3})						
P/MPa	313.2 K	333.2 K	353.2 K	373.2 K	393.2 K	413.2 K	433.2 K
30	935	915	896	878	859	841	824
40	946	928	910	892	875	859	842
50	956	939	922	905	889	874	858
60	966	950	933	917	902	887	872
80		968	952	938	924	910	896
100		984	970	956	943	929	917
120			985	972	959	947	935
140			998	986	974	962	951
160				999	987	976	965
180				1012	1000	989	978
200					1012	1001	991

Table 3. Density ρ of Octamethylcyclotetrasiloxane (1) + Methane (2) (x_1 = 0.531)

	ρ/(kg·m^{-3})						
P/MPa	313.2 K	333.2 K	353.2 K	373.2 K	393.2 K	413.2 K	433.2 K
30	880	859	838	819	799	780	760
40	893	874	855	837	818	800	783
50	905	886	869	851	834	818	802
60	916	898	881	865	849	833	818
80	935	918	903	888	873	858	845
100	951	936	921	907	893	880	867
120		951	937	924	910	898	886
140		965	952	939	926	915	903
160			965	953	941	929	918
180			978	966	954	943	932
200				977	966	955	945

0021-9568/96/1741-0084$12.00/0 © 1996 American Chemical Society

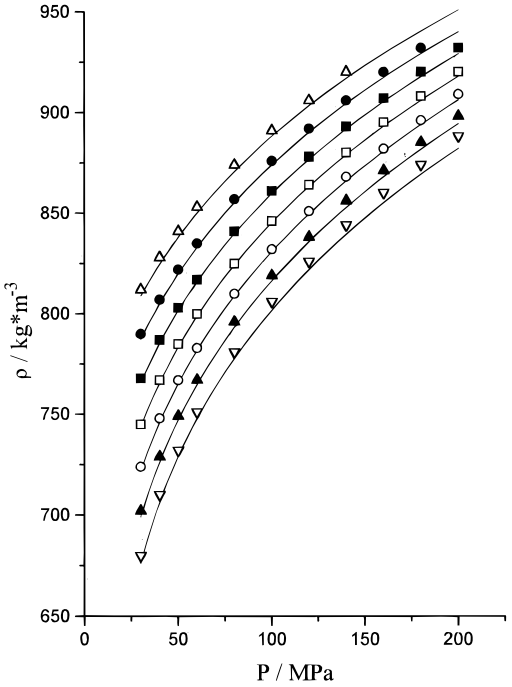

Figure 1. Experimental densities ρ of the OMCTS (1) + methane (2) mixture ($x_1 = 0.374$): (△) 313.2 K, (●) 333.2 K, (■) 353.2 K, (□) 373.2 K, (○) 393.2 K, (▲) 413.2 K, (tdo) 433.2 K. The lines drawn through the experimental points result from fitting the data to eqs 1−3.

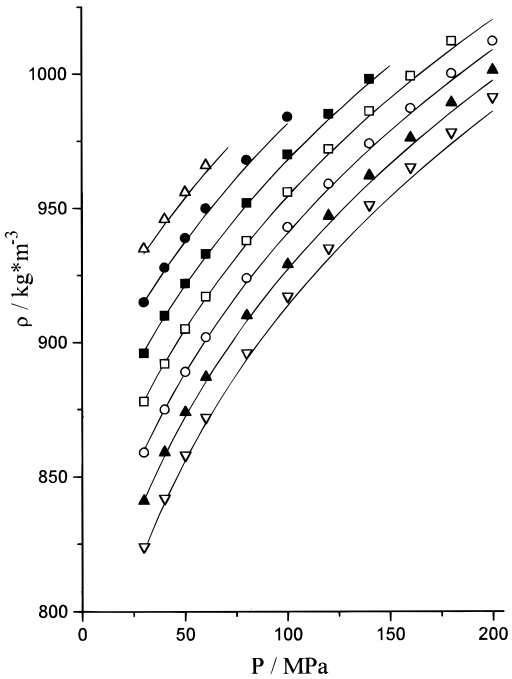

Figure 2. Experimental densities ρ of the OMCTS (1) + methane (2) mixture ($x_1 = 0.772$): (△) 313.2 K, (●) 333.2 K, (■) 353.2 K, (□) 373.2 K, (○) 393.2 K, (▲) 413.2 K, (▽) 433.2 K. The lines drawn through the experimental points result from fitting the data to eqs 1−3.

The temperature was determined in the densimeter with a calibrated metal-sheathed chromel−alumel thermocouple to ±0.2 K. The maximum uncertainty of T over the whole sample volume was ±0.3 K. Pressures are accurate to ±0.2 MPa in the range up to 100 MPa and to ±1 MPa above that range.

Accuracy. In the elaborate calibration described previously (Wappmann et al., 1995) the published densities of methanol (Goodwin 1987) could be reproduced to ±0.2%.

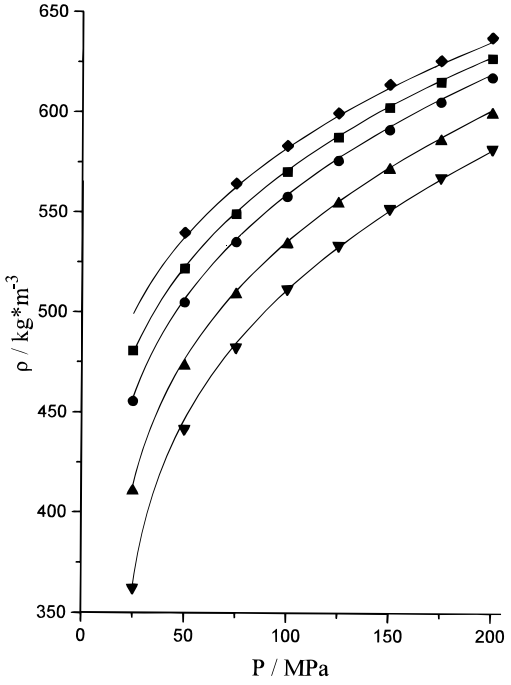

Figure 3. Experimental densities ρ of the DMP (1) + methane (2) mixture ($x_1 = 0.485$): (◆) 295 K, (■) 313.6 K, (●) 334 K, (▲) 373.6 K, (▼) 414.2 K. The lines drawn through the experimental points result from fitting the data to eqs 1−3.

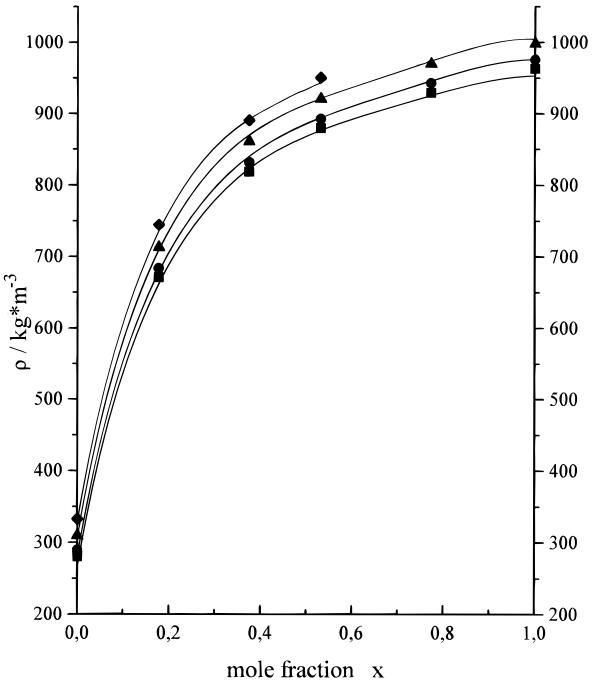

Figure 4. Experimental densities ρ plotted against the mole fraction x for the mixture x OMCTS + $(1 - x)$ CH_4 at 100 MPa: (◆) 313.2 K, (▲) 353.2 K, (●) 393.2 K, (■) 413.2 K. The lines drawn through the experimental points result from fitting the data to eqs 1−3.

The mole fractions x of the mixtures are accurate to ±0.003. The overall error of the results given here, which includes the uncertainty of pressure, temperature, volume, and mass determination, is estimated to ±0.4% for the pure OMCTS and DMP and to ±0.6% for all mixtures studied.

Results and Discussion

All experimental densities are given in the Tables 1−7. These experimental densities were fitted to the modified

Table 4. Density ρ of Octamethylcyclotetrasiloxane (1) + Methane (2) ($x_1 = 0.374$)

	ρ/(kg·m^{-3})						
P/MPa	313.2 K	333.2 K	353.2 K	373.2 K	393.2 K	413.2 K	433.2 K
30	812	790	768	745	724	702	680
40	828	807	787	767	748	729	710
50	841	822	803	785	767	749	732
60	853	835	817	800	783	767	751
80	874	857	841	825	810	796	781
100	891	876	861	846	832	819	806
120	906	892	878	864	851	838	826
140	920	906	893	880	868	856	844
160		920	907	895	882	871	860
180		932	920	908	896	885	874
200			932	920	909	898	888

Table 5. Density ρ of Octamethylcyclotetrasiloxane (1) + Methane (2) ($x_1 = 0.177$)

	ρ/(kg·m^{-3})						
P/MPa	313.2 K	333.2 K	353.2 K	373.2 K	393.2 K	413.2 K	433.2 K
30	635	608	581	554	527	501	476
40	662	638	614	592	570	548	527
50	681	660	639	618	599	580	561
60	697	678	658	642	622	605	588
80	723	706	689	673	657	642	627
100	745	728	713	699	684	671	657
120	763	748	733	720	706	694	682
140	779	764	751	738	725	714	702
160	793	779	766	754	742	731	720
180	806	793	780	769	757	747	736
200	818	805	793	782	771	761	751

Tait equation (1). The pressure, temperature, and concentration dependence of the parameters *A* and *B* of eq 1 was derived from a fit of all density data to the polynomials given by eq 2. For each experimental isotherm (Tables 1−7) a density, $\rho_0(P_0)$, was chosen as the reference point for the modified Tait equation [ρ_0(50 Mpa) for neat OMCTS and for all OMCTS + CH_4 mixtures and ρ_0(100 Mpa) for neat DMP, CH_4, and all DMP + CH_4 mixtures]. In order to be able to interpolate these data for mixtures of all composi-

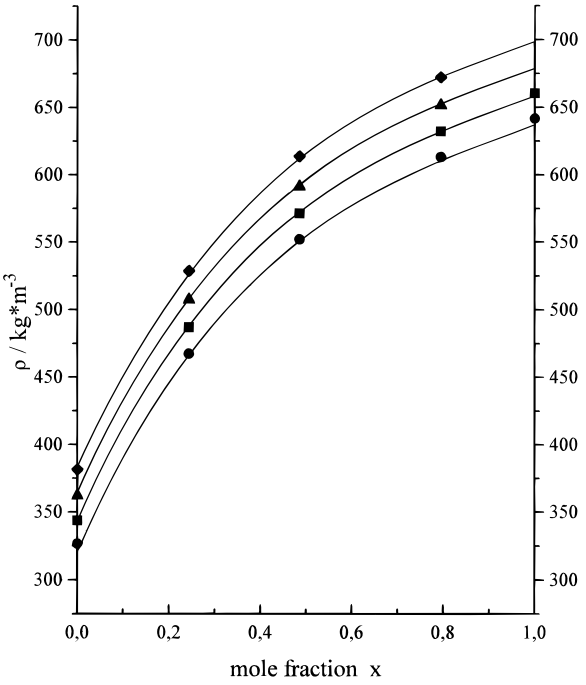

Figure 5. Experimental densities ρ plotted against the mole fraction *x* for the mixture *x* DMP + (1 − *x*) CH_4 at 150 MPa: (◆) 295 K, (▲) 334 K, (■) 373.6 K, (●) 414.2 K. The lines drawn through the experimental points result from fitting the data to eqs 1−3.

Table 6. Density ρ of 2,2-Dimethylpropane (1) + Methane (2)

	ρ/(kg·m^{-3})									
	$x_1 = 0.485$					$x_1 = 0.243$				
P/MPa	294.0 K	313.6 K	334.0 K	373.6 K	414.2 K	295.0 K	313.6 K	334.0 K	373.6 K	414.2 K
25		480.6	455.4	410.6	362.4	386.2	362.0	336.0	288.0	250.3
50	539.8	521.7	504.8	473.0	441.8	440.9	423.7	406.0	372.8	341.3
75	564.4	549.0	535.1	508.8	482.5	472.7	458.5	443.8	416.5	390.5
100	583.3	570.2	557.8	534.1	511.8	495.0	482.6	469.6	445.7	423.1
125	599.5	587.4	575.8	554.5	533.6	513.2	502.0	490.1	468.5	447.8
150	613.8	602.1	591.3	571.4	552.1	528.9	518.2	507.3	487.1	467.6
175	625.8	614.9	604.9	585.8	567.6	542.2	532.5	521.9	503.0	485.1
200	637.2	626.6	617.2	598.9	581.8	554.2	544.8	535.0	516.8	499.7

Table 7. Density ρ of 2,2-Dimethylpropane (1) + Methane (2)

	ρ/(kg·m^{-3}) ($x_1 = 1.00$)					ρ/(kg·m^{-3}) ($x_1 = 0.794$)				
P/MPa	313.6 K	334.0 K	373.6 K	414.2 K	*P*/MPa	295.0 K	313.6 K	334.0 K	373.6 K	414.2 K
10	581.4									
25	601.5	585.0	551.0	517.5	25		566.0	547.4	511.4	472.0
40	617.9				50	609.8	595.6	580.3	551.2	522.6
50	627.5	612.8	858.8	558.6	75	629.6	617.6	603.6	578.5	554.5
75		634.5	610.8	587.1	100	646.1	635.0	622.5	600.2	578.4
100		652.0	630.6	609.1	125	660.1	649.6	638.1	617.6	597.3
125			646.6	627.1	150	672.4	662.5	651.6	632.3	613.3
150			660.5	641.8	175	685.2	674.2	663.8	645.4	627.4
175				655.3	200	697.3	684.4	674.9	657.2	640.1
200				667.3						

Table 8. Fit Parameters and Indices for Eqs 2 and 3 in the Composition Range $0.176 \le x_1 \le 1$ for Octamethylcyclotetrasiloxane (1) + Methane (2) Mixtures

	$i = 0$	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$	$i = 6$	$i = 7$	$i = 8$
				$\xi = 4$, $\xi = 8$ $\nu = 3$, $\vartheta = 7$					
a_i	0.42287	−1.71779	3.7384	−3.64405	1.3073	−0.07296	0.2719	−0.34833	0.14976
b_i	−25.5999	−186.96	107.76	17.617	0.4693	79.891	14.38	−49.106	
				$P_0 = 50$ MPa, $\alpha = 3$, $\beta = 7$					
κ_i	794.432	1392.57	−1635.04	682.38	−1.1237	0.8207	−0.7427	0.2559	

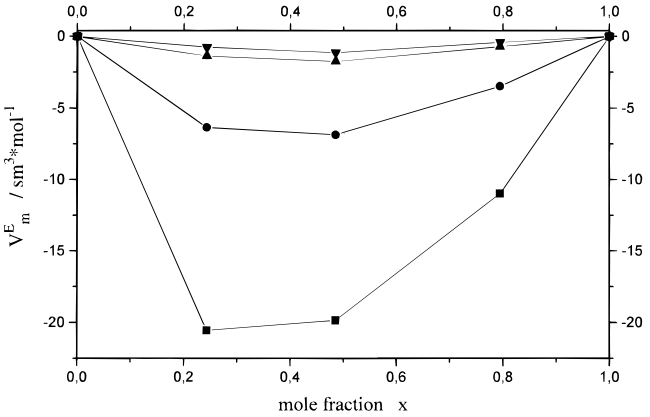

Figure 6. Experimental excess molar volumes V_m^E at 414.2 K plotted against the mole fraction x for x DMP + (1 − x) CH_4: (■) 25 MPa, (●) 50 MPa, (▲) 125 MPa, (▼) 200 MPa.

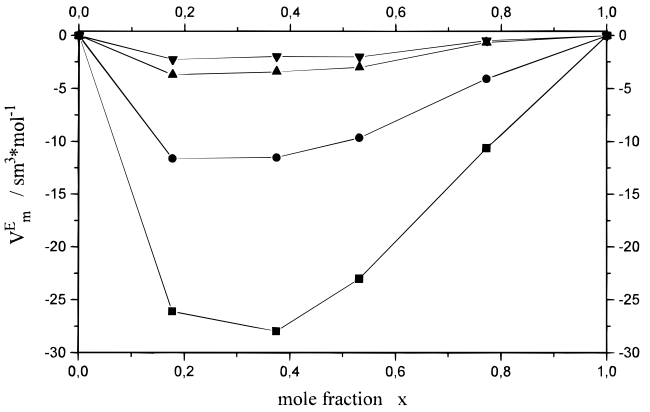

Figure 7. Experimental excess molar volumes V_m^E at 413.2 K plotted against the mole fraction x for x OMCTS + (1 − x) CH_4: (■) 30 MPa, (●) 50 MPa, (▲) 100 MPa, (▼) 140 MPa.

Table 9. Standard deviation σ for Octamethylcyclotetrasiloxane (1) + Methane (2) Mixtures

x_1	0.177	0.374	0.531	0.772	1.0
$\sigma[\rho_0(50\ \text{MPa})]/(\text{kg·m}^{-3})$	1.2	2.0	2.5	1.4	0.4
$\sigma(\rho)/(\text{kg·m}^{-3})$	3.7	2.5	5.6	2.2	2.0

$$\frac{\rho_0(P_0)}{\rho} = 1 - A \ln\left[\frac{B+P}{B+P_0}\right] \tag{1}$$

$$A = \sum_{i=0}^{\zeta} a_i x^i + \frac{10^3 K}{T\,(\text{K})} \sum_{i=\xi+1}^{\zeta} a_i x^{i-(\zeta+1)}$$
$$B = \sum_{i=0}^{\nu} b_i x^i + \frac{10^3 K}{T\,(\text{K})} \sum_{i=\nu+1}^{\vartheta} b_i x^{i-(\nu+1)} \tag{2}$$

tions, the reference densities $\rho_0(P_0)$ were fitted with the polynomial given in eq 3.x is the mole fraction of the heavier component of the two binary mixtures. In Table 8 the parameters for eqs 2 and 3 for the system OMCTS (1) + CH_4 (2) are compiled. These equations describe the experimental densities in the mole fraction range 0.176 ≤ x_1 ≤ 1 under inclusion of the published data for neat OMCTS (Easteal and Woolf, 1984). At the methane rich side of the mixtures the influence of the composition upon the density is very strong, and it proved impossible to devise a set of equations valid over the whole range of composition with sufficient accuracy. Table 9 shows the standard deviation σ for the reference points and the complete experimental isotherms defined by

Table 11. Standard Deviation σ for 2,2-Dimethylpropane (1) + Methane (2) Mixtures

x_1	0	0.243	0.485	0.794	1.0
$\sigma[\rho_0(100\ \text{MPa})]/(\text{kg·m}^{-3})$	2.7	1.0	1.1	1.4	1.9
$\sigma[\rho]/(\text{kg·m}^{-3})$	6.4	3.0	1.7	1.4	4.5

Table 12. Comparison with Literature Values for Neat DMP and OMCTS

			$\rho/(\text{kg·m}^{-3})$			
neat component	P/MPa	T/K	this paper	lit.	deviation/ %	ref
DMP	40	450	517	523[a]	+1.1	Das et al. (1977)
DMP	25	450	487	489[a]	+0.4	Das et al. (1977)
DMP	20.6	310.9	598	604	+1.0	Gonzalez and Lee (1968)
OMCTS	40	323.2	968	968.7	+0.06	Easteal and Woolf (1984)
OMCTS	20	323.2	947	947.6	+0.06	Easteal and Woolf (1984)
OMCTS	SVP	337.7	906	905	−0.1	Marsh (1968)
OMCTS	SVP	308.2	936	938	−0.2	Marsh (1968)

[a] Data from the compressibility factor.

$$\rho_0(P_0) = \sum_{i=0}^{\alpha} \kappa_i x^i + [T\,(\text{K})] \sum_{i=\alpha+1}^{\beta} \kappa_i x^{i-(\alpha+1)} \tag{3}$$

$$\sigma = \left[\frac{1}{n}\sum_{i=1}^{n}[\rho_i - \rho(P,T,x)]^2\right]^{1/2} \tag{4}$$

The corresponding data for DMP (1) + CH_4 (2) are compiled in the Tables 10 and 11. For this system it proved possible to fit the experimental densities over the whole mole fraction range 0 ≤ x_1 ≤ 1.0 under inclusion of the published data for neat methane (Setzmann and Wagner, 1991) and DMP (Das et al., 1977; Gonzalez and Lee, 1968). Representative examples for the quality of the fits and the experimental densities are compiled in Figures 1−5. Our data for neat OMCTS and DMP agree well with literature data and do not show systematic deviations (see Table 12). When extrapolated to vapor pressure, our results for OMCTS are in agreement with the values given by Marsh (1968).

Excess molar volumes were computed from the experimental densities and composition using the relation

$$V_m^E = \frac{[x_1 M_1 + (1-x_1)M_2]}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{(1-x_1)M_2}{\rho_2} \tag{5}$$

where x_1 is the mole fraction of the first component in the mixture, M_1 and M_2 represent molecular masses, ρ, ρ_1, and

Table 10. Fit Parameters and Indices for Eqs 2 and 3 in the Composition Range 0 ≤ x_1 ≤ 1.0 for 2,2-Dimethylpropane (1) + Methane (2) Mixtures

	$i=0$	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$
			$\zeta=3, \xi=6; \nu=2, \vartheta=4$				
a_i	0.48196	−0.89692	0.8498	−0.262897	−0.085094	0.165944	−0.101553
b_i	−25.6212	−108.508	36.5576	0.51631	41.3774		
			$P_0 = 100$ MPa, $\alpha=3, \beta=4$				
κ_i	522.115	751.4	−663.73	243.707	−0.596		

ρ_2 are the respective densities of the mixture and pure components 1 and 2. Figure 6 shows the experimental excess volumes as a function of the mole fraction of DMP for the DMP + CH_4 mixtures at 414.2 K. The temperature dependence of V_m^E is weak for this system, the data analysis being limited by the steep melting pressure curve of the neat DMP. Figure 7 gives V_m^E in the OMCTS + CH_4 system at 413.2 K. The pressure dependence is similar in both systems. The OMCTS system shows the larger negative excess volumes, indicating that in these mixtures attractive interactions are more pronounced.

Acknowledgment

We thank Mr. Knott, Mr. Niesner, and Mrs. Löw for their expert technical help.

Literature Cited

Chandler, D. Rough hard sphere theory of the self-diffusion constant for molecular liquids. *J. Chem. Phys.* **1975**, *62*, 1358−1363.

Das, T. R.; Reed, C. O.; Eubank, P. T. PVT Surface and Thermodynamic Properties of Neopentane. *J. Chem. Eng. Data* **1977**, *22*, 16−21.

Easteal, J. A.; Woolf, L. A. Self-diffusion and Volumetric Measurements for Octamethylcyclotetrasiloxane under Pressure at 323 K. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 549−551.

Francesconi, A.; Lentz, H.; Franck, E. U. Die PVT-Daten des Acetonitrils bis 450 C und 2500 bar. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 897−901.

Gonzalez, M. H.; Lee, A. L. Viscosity of 2,2-Dimethylpropane *J. Chem. Eng. Data* **1968**, *13*, 66−69.

Goodwin, R. *J. Phys. Chem. Ref. Data* **1987**, *16*, 799.

Has, M.; Lüdemann, H.-D. Self Diffusion in Compressed Tetrafluoromethane. *J. Mol. Liq.* **1990**, *46*, 7−16.

Marsh, K. N. Thermodynamics of Octamethylcyclotetrasiloxane Mixtures. *Trans. Faraday Soc.* **1968**, *64*, 883−893.

Setzmann, U.; Wagner, W. A New Equation of State and Tables of Thermodynamic Properties for Methane Covering the Range from the Melting Line to 625 K at Pressures up to 1000 MPa. *J. Phys. Chem. Ref. Data* **1991**, *20*, 1061−1155.

Speedy, R. J.; Prielmeier, F. X.; Vardag, T.; Lang, E. W.; Lüdemann, H.-D. Diffusion in Simple Fluids. *Mol. Phys.* **1989**, *66*, 577−590.

Wappmann, S. Ph.D. Dissertation, Universität Regensburg, 1993.

Wappmann, S.; Karger, N.; Lüdemann, H.-D. pVT Data of Liquid 1-, 2-, and 3-Pentanol from 10 to 200 MPa and from 233 to 433 K. *J. Chem. Eng. Data* **1995**, *40*, 233−236.

Received for review July 3, 1995. Accepted October 17, 1995.[⊗] Financial support by the Fonds der Chemie is gratefully acknowledged.

JE950158C

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1995.