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Densities and Excess Volumes of Methyl 1,1-Dimethylpropyl Ether + Benzene, or Cyclohexane, or an Alkane (C_6−C_{16}) at 298.15 K

M. Witek, A. Gołdon,* T. Hofman, and U. Domańska

Division of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology,
ul. Noakowskiego 3, 00-664 Warszawa, Poland

Densities and excess volumes of {methyl 1,1-dimethylpropyl ether (TAME) + (benzene or cyclohexane or hexane or octane or decane or dodecane or tetradecane or hexadecane)} at 298.15 K are presented. The observed influence of the *n*-alkane length can be predicted qualitatively by the Flory equation of state.

1. Introduction

The use of methyl 1,1-dimethylpropyl ether (*tert*-amyl methyl ether or TAME) as gasoline-blending agent has led to an increased interest in the thermodynamic properties of mixtures of TAME with hydrocarbons. This paper reports densities and excess molar volumes V_m^E for the binary mixtures {TAME + (hexane or octane or decane or dodecane or tetradecane or hexadecane or cyclohexane or benzene)} at the temperature 298.15 K. Of all the eight systems presented in this work only V_m^E for {TAME + (benzene or cyclohexane)} has been previously reported by Linek (1987).

2. Experimental Section

TAME (purity 97 mass %), octane (99%), and benzene (99.9%) were obtained from Aldrich Chemical Co. The alkanes had stated purities of at least 99 mol % and were supplied by E. Merck (hexane), by International Enzymes Ltd. (hexadecane and cyclohexane), by Schuchardt (decane), by BDH Chemicals (dodecane), and by L. Light Co. Ltd. (tetradecane). Solvents were distilled, dried using 0.4 nm molecular sieves, and degassed before use. From gas chromatographic analysis we found the resulting purity 99.76 mass % for hexane and 99.92 mass % for cyclohexane. The densities of the components measured at 298.15 K agree reasonably with the literature values (Table 1).

Mixtures of the components were prepared by mass in vessels similar to those designed and recommended by Takenaka *et al.* (1980).

The maximum error in the mole fraction x of TAME is estimated to be less than 1×10^{-4}. All density measurements were made using an Anton-Paar DMA 02C vibrating-tube densimeter. Densities of components and mixtures were determined from the vibrational period of the densimeter using the relation

$$d = d_r + \kappa(\tau^2 - \tau_r^2) \qquad (1)$$

where d is the density and τ is the vibrational period of the densimeter. The subscript, r, refers to a reference standard, and κ is the calibration constant obtained from two reference standards. For our work we used dry air and distilled water.

The densimeter measuring cell was thermostated at the temperature (298.15 ± 0.01 K) with a Unipan 655 (Poland) ultrathermostat.

Table 1. Densities of Pure Substances at 298.15 K

component	density/g·cm^{-3} measd	density/g·cm^{-3} lit.	ref
TAME	0.765 67	0.765 91	*a*
benzene	0.873 84	0.873 62	*b*
cyclohexane	0.773 97	0.773 94	*a*
hexane	0.654 38	0.654 81	*c*
octane	0.698 18	0.698 49	*c*
decane	0.726 28	0.726 25	*c*
dodecane	0.745 07	0.745 16	*c*
tetradecane	0.759 71	0.759 29	*d*
hexadecane	0.769 89	0.770 06	*d*

[a] Zhu *et al.* (1994a). [b] Linek (1989). [c] Riddick and Bunger (1970). [d] Zhu *et al.* (1994b).

Values of V_m^E were derived from densities d using the relation

$$V_m^E = [xM_1 + (1 - x)M_2]/d - [xM_1/d_1 + (1 - x)M_2/d_2] \qquad (2)$$

where M_i and d_i are the molar mass and density of component i, respectively (1 for TAME and 2 for hydrocarbon). The maximum error of V_m^E is estimated to be less than 3×10^{-3} cm^3·mol^{-1} for medium compositions and should not exceed 1×10^{-3} cm^3·mol^{-1} for the limiting ones. It results mainly from the uncertainties of the density measurements which are stated to be $\pm 1 \times 10^{-5}$ g·cm^{-3}.

3. Results and Discussion

The densities and excess molar volumes (V_m^E) at 298.15 K for [$xC_2H_5C(CH_3)_2OCH_3 + (1 - x)${an alkane}] are shown in Table 2 and drawn in Figures 1 and 2. They are consistent with the data of Linek (1987) for {TAME + (benzene or cyclohexane)} reported at the same temperature and displayed in the same figures.

The Redlich−Kister expansion of the form

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = x(1 - x)\sum_{i=0}^{m} a_i(2x - 1)^i \qquad (3)$$

was fitted to the data by the least-squares method. The coefficients and standard deviations of the adjustment are collected in Table 3.

The observed molar excess volumes exhibit interesting dependence with respect to the *n*-alkane carbon number. Excess volumes increase with increasing *n*-alkane length up to octane, for which the highest positive V_m^E is observed. For higher *n*-alkanes this tendency is reversed and

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Table 2. Densities and Excess Molar Volumes V_m^E for [$x\mathrm{C_2H_5C(CH_3)_2OCH_3}$ + (1 − x){a Hydrocarbon}] at 298.15 K

x	d/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x	d/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x	d/g·cm^{-3}	V_m^E/cm^3·mol^{-1}
$x\mathrm{C_2H_5C(CH_3)_2OCH_3} + (1 - x)\mathrm{C_6H_6}$								
0.0140	0.871 49	0.0114	0.2756	0.834 05	0.0729	0.6499	0.794 06	0.0443
0.0739	0.861 91	0.0454	0.3422	0.825 99	0.0716	0.7509	0.785 22	0.1287
0.1232	0.854 62	0.0513	0.4156	0.817 60	0.0696	0.8480	0.777 20	0.0878
0.2283	0.840 15	0.0663	0.5180	0.806 77	0.0601	0.9543	0.769 04	0.0295
$x\mathrm{C_2H_5C(CH_3)_2OCH_3} + (1 - x)\mathrm{C_6H_{12}}$								
0.0215	0.773 48	0.0391	0.4524	0.767 09	0.4221	0.6267	0.766 02	0.3832
0.1239	0.771 37	0.1995	0.4743	0.766 90	0.4248	0.6739	0.765 86	0.3531
0.2229	0.769 71	0.3116	0.5091	0.766 66	0.4219	0.7697	0.765 62	0.2795
0.3152	0.768 45	0.3835	0.5476	0.766 42	0.4131	0.8594	0.765 55	0.1857
0.4155	0.767 40	0.4185	0.5755	0.766 27	0.4039	0.9575	0.765 61	0.0606
$x\mathrm{C_2H_5C(CH_3)_2OCH_3} + (1 - x)\mathrm{CH_3(CH_2)_4CH_3}$								
0.0458	0.659 30	0.0482	0.4583	0.704 59	0.2170	0.6662	0.727 89	0.1752
0.1139	0.666 77	0.0867	0.4967	0.708 86	0.2167	0.6757	0.728 96	0.1722
0.2111	0.677 33	0.1532	0.5222	0.711 69	0.2183	0.7749	0.740 11	0.1373
0.3106	0.688 28	0.1896	0.5672	0.716 74	0.2088	0.8627	0.750 10	0.0829
0.3772	0.695 62	0.2057	0.5798	0.718 15	0.2048	0.8714	0.751 09	0.0764
0.4182	0.700 16	0.2122	0.6309	0.723 88	0.1941	0.9634	0.761 54	0.0179
$x\mathrm{C_2H_5C(CH_3)_2OCH_3} + (1 - x)\mathrm{CH_3(CH_2)_6CH_3}$								
0.0179	0.699 03	0.0323	0.4785	0.725 43	0.3380	0.6687	0.738 62	0.2993
0.1502	0.705 95	0.1660	0.5122	0.727 65	0.3383	0.7397	0.743 91	0.2690
0.2538	0.711 74	0.2399	0.5311	0.728 93	0.3349	0.7792	0.746 99	0.2391
0.3284	0.716 08	0.2871	0.5634	0.731 14	0.3308	0.8555	0.753 08	0.1843
0.3840	0.719 45	0.3123	0.5923	0.733 15	0.3252	0.8976	0.756 70	0.1243
0.4284	0.722 23	0.3236	0.6172	0.734 91	0.3168	0.9316	0.762 28	0.0426
0.4477	0.723 44	0.3319						
$x\mathrm{C_2H_5C(CH_3)_2OCH_3} + (1 - x)\mathrm{CH_3(CH_2)_8CH_3}$								
0.0299	0.726 94	0.0396	0.4229	0.738 02	0.3151	0.6052	0.744 86	0.3266
0.1190	0.729 12	0.1234	0.4433	0.738 73	0.3186	0.6691	0.747 61	0.3069
0.2267	0.731 98	0.2129	0.4667	0.739 53	0.3293	0.7020	0.749 14	0.2865
0.3205	0.734 71	0.2754	0.5043	0.740 91	0.3321	0.7681	0.752 32	0.2463
0.3683	0.736 23	0.2941	0.5404	0.742 27	0.3343	0.8331	0.755 65	0.2037
0.4193	0.737 93	0.3081	0.5744	0.743 61	0.3310	0.9839	0.764 65	0.0174
$x\mathrm{C_2H_5C(CH_3)_2OCH_3} + (1 - x)\mathrm{CH_3(CH_2)_{10}CH_3}$								
0.0124	0.745 17	0.0162	0.4835	0.751 11	0.3086	0.7143	0.756 03	0.2783
0.0308	0.745 35	0.0304	0.4893	0.751 22	0.3080	0.7593	0.757 24	0.2542
0.0610	0.745 62	0.0629	0.5114	0.751 61	0.3122	0.8145	0.758 86	0.2150
0.1352	0.746 34	0.1336	0.5429	0.752 20	0.3130	0.8621	0.760 43	0.1686
0.2229	0.747 32	0.1976	0.5881	0.753 11	0.3106	0.9379	0.763 15	0.0905
0.3082	0.748 38	0.2553	0.6171	0.753 74	0.3050	0.9789	0.764 83	0.0316
0.3897	0.749 57	0.2849	0.6492	0.754 46	0.2974	0.9895	0.765 22	0.0275
0.4517	0.750 56	0.3026	0.6750	0.755 08	0.2866	0.9963	0.765 56	0.0089
$x\mathrm{C_2H_5C(CH_3)_2OCH_3} + (1 - x)\mathrm{CH_3(CH_2)_{12}CH_3}$								
0.0457	0.759 75	0.0330	0.4786	0.760 70	0.2410	0.6839	0.761 82	0.2323
0.1419	0.759 87	0.0979	0.5070	0.760 81	0.2461	0.7392	0.762 25	0.2149
0.2628	0.760 08	0.1654	0.5430	0.760 97	0.2497	0.8086	0.762 90	0.1823
0.3633	0.760 31	0.2114	0.5736	0.761 14	0.2472	0.8842	0.763 81	0.1256
0.4135	0.760 47	0.2255	0.5851	0.761 19	0.2478	0.9712	0.765 18	0.0297
0.4494	0.760 58	0.2367	0.6242	0.761 42	0.2449			
$x\mathrm{C_2H_5C(CH_3)_2OCH_3} + (1 - x)\mathrm{CH_3(CH_2)_{14}CH_3}$								
0.0193	0.769 81	0.0170	0.4834	0.767 77	0.2434	0.7066	0.766 76	0.2193
0.1389	0.769 32	0.1032	0.5068	0.767 70	0.2422	0.7754	0.766 52	0.1864
0.2530	0.768 82	0.1697	0.5380	0.767 57	0.2415	0.8603	0.766 17	0.1365
0.3524	0.768 39	0.2105	0.5879	0.767 31	0.2407	0.9087	0.766 00	0.0963
0.4200	0.768 08	0.2325	0.6068	0.767 26	0.2376	0.9806	0.765 80	0.0207
0.4574	0.767 89	0.2397	0.6669	0.766 98	0.2285			

Table 3. Coefficients a_i and Standard Deviations σ of a Least-Squares Fit of V_m^E for [$x\mathrm{C_2H_5C(CH_3)_2OCH_3}$ + (1 − x){a Hydrocarbon}] at 298.15 K by Eq 3

hydrocarbon	a_0	a_1	a_2	a_3	a_4	σ
benzene	0.2570 ± 0.0088	−0.2076 ± 0.0255	−0.1451 ± 0.0822	−0.1690 ± 0.0652	0.3379 ± 0.1332	0.0024
cyclohexane	1.6883 ± 0.0014	−0.2122 ± 0.0042				0.0010
hexane	0.8634 ± 0.0059	−0.1334 ± 0.0157	−0.1167 ± 0.0336			0.0038
octane	1.3393 ± 0.0061	0.0878 ± 0.0202				0.0051
decane	1.3191 ± 0.0044	0.1765 ± 0.0150				0.0036
dodecane	1.2407 ± 0.0048	0.2121 ± 0.0126	0.1033 ± 0.0268			0.0033
tetradecane	0.9777 ± 0.0030	0.2695 ± 0.0086	0.0410 ± 0.0186			0.0019
hexadecane	0.9693 ± 0.0030	0.1675 ± 0.0085	0.0559 ± 0.0183			0.0019

excess volumes decrease with increasing *n*-alkane size. A similar phenomenon was reported for (dipropyl ether + *n*-alkane) systems by Wang *et al.* (1989) who also noticed a maximum extent of V_m^E for octane.

An ability of the Flory equation of state (Flory, 1965) to predict the excess volumes was checked. Parameters used in calculations are summarized in Table 4. The ratio s_1/s_2 of the surface contact sites per segment were estimated

Table 4. Parameters Used in the Flory Equation-of-State Calculations

					results of the H^E_m correlation		
component	p^*/J·cm^{-3}	V^*_m/cm^3·mol^{-1}	V_m/cm^3·mol^{-1}	ref	X_{12}/J·cm^{-3}	(σ/H^E_{max})/%	source of data
TAME	456.1	103.32	133.44	*a*			
benzene	628.0	69.22	89.41	*b*	8.64	8.5	*f*
cyclohexane	538.4	84.29	108.75	*c*	15.7	2.7	*f*
hexane	421.4	99.5	131.57	*d*	10.1	2.1	*f*
octane	441.2	127.8	163.51	*c*	11.1	1.4	*a*
decane	449.7	155.9	195.95	*d*	12.7	1.1	*a*
dodecane	438.8	184.1	228.57	*e*	14.4	1.1	*a*
tetradecane	461	212.21	261.29	*b*	16.0	1.0	*a*
hexadecane	461	240.39	294.09	*b*	17.7	1.1	*a*

[a] Zhu *et al.* (1994b). [b] Diaz Peña *et al.* (1976). [c] Cabañas *et al.* (1994). [d] Funke *et al.* (1989). [e] Kaur *et al.* (1991). [f] Zhu *et al.* (1994a).

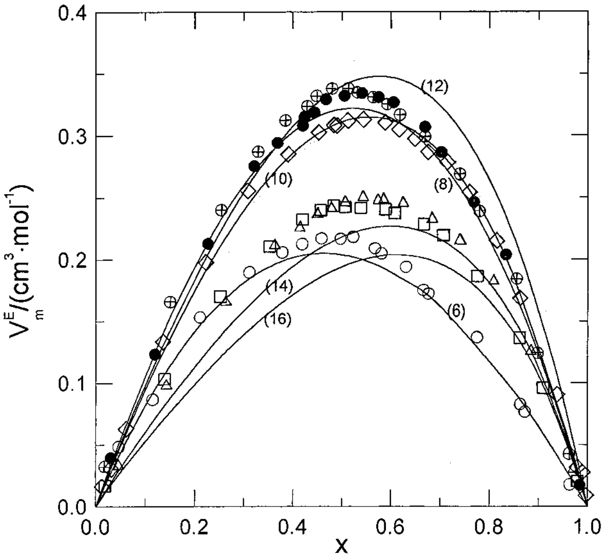

Figure 1. Excess molar volumes for $\{xC_2H_5C(CH_3)_2OCH_3 + (1 - x)C_nH_{2n+2}\}$ at 298.15 K. Experimental results: (○) $n = 6$; (⊕) $n = 8$; (●) $n = 10$; (◇) $n = 12$; (△) $n = 14$; (□) $n = 16$. (—) Predicted by the Flory theory. Labels (n) show numbers of carbon atoms in the alkane molecule.

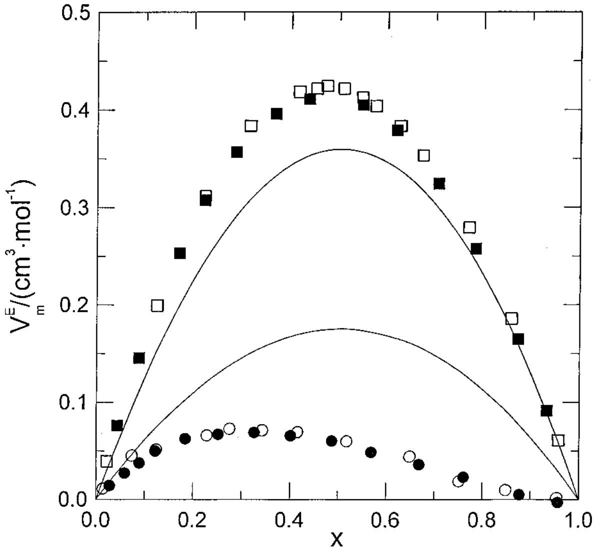

Figure 2. Excess molar volumes for $\{xC_2H_5C(CH_3)_2OCH_3 + (1 - x)$(benzene or cyclohexane$)\}$ at 298.15 K. Experimental results: (○) benzene; (□) cyclohexane. Filled symbols represent data of Linek (1987). (—) Predicted by the Flory theory.

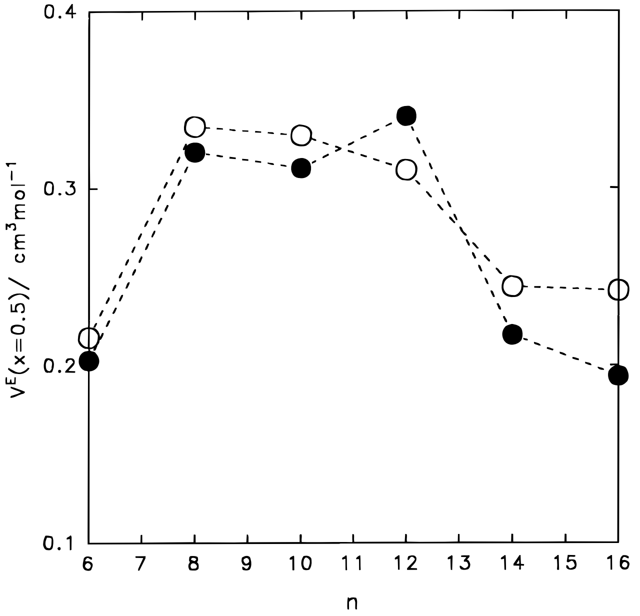

Figure 3. Excess molar volumes for $\{0.5C_2H_5C(CH_3)_2OCH_3 + 0.5C_nH_{2n+2}\}$ at 298.15 K: (○) experimental; (●) predicted by the Flory equation of state.

by $(V^*_{m2}/V^*_{m1})^{1/3}$ according to Abe and Flory (1965). The same estimates were used by Zhu *et al.* (1994b) to describe excess enthalpies for (TAME + alkane) systems. The energy interchange coefficients X_{12} were determined through fitting to the excess enthalpy data of (TAME + corresponding alkane) mixtures. The quality of fit is presented as the ratio of the standard deviation to the maximum value of excess enthalpy (σ/H^E_{max}) for each experimental data set. The best description of experimental dependencies is observed for short hydrocarbons. Larger deviations for higher alkanes result mainly from less accurate reproduction of the maximum on the H^E_m *vs* x curve. It may be explained by difficulties in accurate determination of the ratio of hard core volumes of both components if they differ greatly in size.

The X_{12} parameters were used to predict molar excess volumes for the measured systems. Results of prediction are plotted in Figure 1 (TAME + n-alkanes) and Figure 2 (TAME + benzene or cyclohexane). The calculated and measured equimolar excess volume *vs* carbon number of an alkane are compared in Figure 3. For the first group of the systems the prediction accuracy should be estimated as fairly good. The influence of the n-alkane size is correctly predicted although maximum molar excess volume corresponds to dodecane rather than to octane, which is actually observed.

It is evident that the Flory theory fails to predict excess volumes for the (TAME + benzene) system.

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