Excess Volumes of Binary Mixtures of 1,4-Dioxane with Heptane, Tetradecane, and Cyclohexane at 323, 350, and 364 K and at Pressures around 7, 17, and 22 MPa

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Molar excess volumes V^E have been measured as a function of mole fraction at 323, 350, and 364 K and at three different pressures around 7.5, 16, and 22 MPa for three binary liquid systems, 1,4-dioxane + heptane, + tetradecane, and + cyclohexane, by using vibrating-tube densimetry. All excess volumes are positive and show similar temperature and pressure dependence; i.e., V^E increases when temperature increases and decreases when the pressure is increased.

Introduction

An unusual W-shape composition dependence of the excess molar heat capacity C_p^E was found for the first time (Grolier *et al.*, 1984; Inglese *et al.*, 1984) for binary liquid mixtures containing a cyclic ether as one component and an alkane as the other. Excess molar thermodynamic functions for such systems have been of particular interest although little attention has been paid to effects of temperature and pressure. As concerns excess volumes V^E, their values have been reported for binary mixtures of cyclic ethers with *n*-alkanes only at three temperatures up to 318 K (Inglese *et al.*, 1983). In the line of our systematic determinations of excess quantities for such mixtures we report here excess volumes of mixtures of 1,4-dioxane with heptane, tetradecane, and cyclohexane at much higher temperatures, namely, 323, 350, and 364 K, and at three pressures around 7.5, 16, and 22 MPa.

Experimental Section

Materials. 1,4-Dioxane (>99.5 mol %), heptane (>99.5 mol %), tetradecane (>99 mol %), and cyclohexane (>99.5 mol %) were from Fluka. They were used as received. Prior to measurements, all liquids were carefully dried with molecular sieves. Mixtures were prepared by mass with a possible error in the mole fraction estimated to be less than 10^{-4}.

Measurements. Densities ϱ were measured with a new high-temperature high-pressure vibrating-tube densimeter of the type described in detail by Albert and Wood (1984). The densimeter itself is essentially a vibrating-tube densimeter formed of a single piece of hastelloy C 276 tubing (1.5 mm o.d., with 0.2 mm wall thickness) anchored on a metal block which ensures thermal equilibrium and allows the entering liquid to be brought to the desired temperature. The liquid under study is circulated through the densimeter with a high pressure liquid-chromatography pump. Nitrogen and water were used as fluids for calibration (Albert and Wood, 1984), and water served as the reference liquid to obtain the reference "base line" value between two sample solutions. However, for measurements on organic solvents and in order to operate the densimeter in such a way to use water as the reference liquid, the original procedure used for aqueous salt solutions was modified (Albert *et al.*, 1985). For this a dual sample-loop assembly was inserted between the high-pressure pump and the densimeter; with this modified injection line an intermediate water miscible reference liquid (usually ethanol) could be inserted between water and the organic sample under study. The experimental procedure and associated precision were the same as those in previous investigations (Albert *et al.*, 1985; Gates *et al.*, 1986): temperature control was within about ±0.005 K, and pressure control was within ±0.05 MPa. Densities of the pure liquids and their mixtures were determined at the different selected temperatures and pressures: the maximum inaccuracy of the density measurements was estimated to be less than ±0.5 kg m^{-3}.

Table 1. Experimental Densities, ϱ, of Pure Liquid Components at Various Temperatures and Pressures

323.5 K		349.7 K		364.5 K	
P/MPa	ϱ/kg m^{-3}	P/MPa	ϱ/kg m^{-3}	P/MPa	ϱ/kg m^{-3}
		Heptane			
7.9	666.5	7.6	643.9	7.3	629.6
16.2	673.6	16.3	653.2	17.9	642.2
24.1	681.4			22.0	647.2
		Tetradecane			
7.9	747.7	7.6	728.9	7.3	718.6
16.2	753.7	16.3	735.2	17.9	726.2
24.1	758.7	21.7	739.6		
		Cyclohexane			
7.9	757.7	7.6	732.8	7.3	717.5
16.2	764.6	16.3	741.4	17.9	729.6
24.1	771.5	21.7	746.8	22.0	734.0
		1,4-Dioxane			
7.9	1007.8	7.6	978.3	7.3	959.1
16.2	1014.6	16.3	986.8	17.9	970.6
24.1	1020.6	21.7	991.7	22.0	974.8

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Table 2. Comparison at Atmospheric Pressure and at Different Temperatures of the Present Extrapolated Densities with Literature Data

	ϱ/(kg m^{-3})								
	323.5 K			349.7 K			364.5 K		
liquid	extrap	lit.[a]	lit.[b]	extrap	lit.[a]	lit.[b]	extrap	lit.[a]	lit.[b]
heptane	659.1	657.7	657.6	635.8	630.0	634.0	620.9	620.0	620.5
tetradecane	742.5	742.5	742.3	723.1	725.0	724.3	713.4	715.0	713.9
cyclohexane	750.9	750.0	749.7	725.2	725.0	723.9	709.3		708.8
1,4-dioxane	1001.6		999.3	971.1		968.4	951.3		950.4

[a] TRC Thermodynamic Tables (1987). [b] CDATA (1990).

Table 3. Densities and Molar Excess Volumes for the Binary Mixtures 1,4-Dioxane + Heptane, + Tetradecane, and + Cyclohexane at Different Temperatures and Pressures

x_1	ϱ/(kg m^{-3})	V^E/(10^{-9} m^3 mol^{-1})	x_1	ϱ/(kg m^{-3})	V^E/(10^{-9} m^3 mol^{-1})	x_1	ϱ/(kg m^{-3})	V^E/(10^{-9} m^3 mol^{-1})
			1,4-Dioxane (1) + Heptane (2)					
			T = 323.5 K, P = 7.9 MPa					
0.1116	687.7	424	0.4217	763.2	799	0.7014	701.4	599
0.1803	702.2	595	0.4920	784.3	781	0.8247	824.7	360
0.2972	729.6	769	0.6213	827.9	703	0.8947	894.7	253
			T = 323.5 K, P = 16.2 MPa					
0.0913	691.1	288	0.4217	770.8	734	0.7040	871.7	496
0.1803	709.8	505	0.4920	792.1	696	0.8247	920.7	305
0.2789	732.5	702	0.6213	836.0	583	0.9156	966.4	162
			T = 323.5 K, P = 24.1 MPa					
0.0913	699.0	261	0.4217	778.6	698	0.7141	879.1	468
0.1803	717.7	472	0.4920	799.7	681	0.8227	926.8	284
0.2972	745.1	651	0.6213	843.3	585	0.9156	973.0	147
			T = 349.9 K, P = 7.6 MPa					
0.1116	664.6	438	0.4158	736.2	916	0.7027	831.9	682
0.2140	686.0	705	0.4991	760.5	922	0.7978	872.3	492
0.3137	709.3	867	0.6035	794.8	833	0.9068	966.2	267
			T = 349.7 K, P = 16.3 MPa					
0.1708	687.3	334	0.4021	742.3	816	0.6916	837.2	636
0.2399	701.5	683	0.4980	770.2	806	0.7927	879.3	476
0.3118	718.6	782	0.5868	798.9	762	0.8919	926.9	249
			T = 364.7 K, P = 7.3 MPa					
0.1038	653.7	513	0.4055	717.5	951	0.6810	806.3	729
0.1892	665.4	729	0.4876	740.8	958	0.8969	901.9	270
0.3031	691.2	907	0.6094	780.2	837			
			T = 364.3 K, P = 17.9 MPa					
0.1028	660.7	457	0.3915	726.6	905	0.7108	830.4	667
0.2042	681.6	682	0.4729	749.4	906	0.8969	914.0	258
0.3008	703.5	861	0.5988	789.3	819			
			T = 364.5 K, P = 22.0 MPa					
0.1078	666.8	440	0.3998	734.1	848	0.7038	832.6	652
0.2068	687.4	612	0.5063	764.6	844	0.7945	869.4	574
0.3023	709.1	808	0.6160	800.0	810	0.8984	918.8	245
			1,4-Dioxane (1) + Tetradecane (2)					
			T = 323.5 K, P = 7.9 MPa					
0.0986	747.7	573	0.4169	776.5	1422	0.7015	852.9	1368
0.2252	775.0	978	0.4979	791.4	1505	0.8036	888.9	1119
0.3102	767.1	1290	0.6040	804.9	1468	0.8977	934.6	696
			T = 323.5 K, P = 16.2 MPa					
0.0986	761.2	512	0.4169	797.7	1378	0.7033	860.1	1309
0.2252	773.4	904	0.5090	816.5	1425	0.8036	896.0	1026
0.3102	783.1	1146	0.6040	833.3	1454	0.8972	941.4	662
			T = 323.5 K, P = 24.1 MPa					
0.0986	766.5	423	0.4169	803.5	1222	0.7033	866.1	1209
0.2252	778.6	864	0.5090	819.0	1363	0.8036	901.9	976
0.3102	788.6	1039	0.6040	839.2	1338	0.8972	947.6	608
			T = 349.9 K, P = 7.6 MPa					
0.1086	763.5	707	0.4201	771.0	1554	0.7031	703.1	1523
0.1928	743.9	1041	0.5109	785.5	1701	0.8010	801.0	1266
0.3107	756.6	1330	0.6048	804.5	1659	0.8939	893.9	816
			T = 349.7 K, P = 16.3 MPa					
0.1192	744.4	528	0.4543	783.4	1471	0.7079	839.0	1383
0.2244	754.1	937	0.4992	791.0	1499	0.7893	866.3	1198
0.3326	766.1	1291	0.6115	813.7	1501	0.8907	912.3	768

Table 3 (Continued)

x_1	ϱ/(kg m^{-3})	V^E/(10^{-9} m^3 mol^{-1})	x_1	ϱ/(kg m^{-3})	V^E/(10^{-9} m^3 mol^{-1})	x_1	ϱ/(kg m^{-3})	V^E/(10^{-9} m^3 mol^{-1})
			1,4-Dioxane (1) + Tetradecane (2)					
			T = 349.7 K, P = 21.7 MPa					
0.1206	749.0	511	0.4003	779.6	1422	0.8015	875.6	556
0.2117	759.5	893	0.5007	785.8	1492	0.8953	919.4	304
0.3368	771.2	1266	0.6027	816.4	1472			
			T = 364.7 K, P = 7.3 MPa					
0.1206	726.3	977	0.3989	755.7	1715	0.8048	849.0	1310
0.1968	733.1	1187	0.6550	802.6	1764	0.8906	887.8	814
0.3250	746.4	1566	0.7034	815.4	1666			
			T = 364.3 K, P = 17.9 MPa					
0.1245	735.5	588	0.4086	766.2	1460	0.7140	828.5	1469
0.2234	744.4	975	0.4960	779.9	1528	0.7918	854.3	1256
0.3308	756.2	1261	0.6087	801.6	1594	0.8888	902.4	768
			1,4-Dioxane (1) + Cyclohexane (2)					
			T = 323.5 K, P = 7.9 MPa					
0.1007	774.6	471	0.4131	838.5	1010	0.7095	915.1	733
0.2045	794.2	745	0.5005	859.4	990	0.8065	944.0	523
0.3019	814.0	921	0.6097	887.5	885	0.8996	973.6	290
			T = 323.5 K, P = 16.2 MPa					
0.1000	781.6	434	0.4088	844.8	957	0.7095	922.1	719
0.1953	799.4	710	0.5149	870.0	963	0.8065	950.9	519
0.3019	821.0	903	0.6097	894.5	870	0.8996	980.5	283
			T = 323.5 K, P = 24.1 MPa					
0.1000	788.9	370	0.4088	852.0	890	0.7095	928.6	707
0.1953	806.5	666	0.5149	877.3	879	0.8065	957.4	497
0.3019	828.4	816	0.6097	901.4	824	0.8996	986.9	261
			T = 349.9 K, P = 7.6 MPa					
0.1216	725.8	600	0.4059	810.2	1066	0.6856	880.1	846
0.2071	768.7	832	0.4963	831.4	1037	0.7879	909.6	624
0.3047	788.3	991	0.5974	856.5	973	0.9056	946.4	282
			T = 349.7 K, P = 16.3 MPa					
0.1587	768.5	657	0.3909	816.9	1014	0.6959	891.8	797
0.2109	778.5	769	0.4987	840.8	1004	0.7819	916.5	625
0.2991	700.9	930	0.5922	863.9	958	0.8889	949.6	344
			T = 349.7 K, P = 21.7 MPa					
0.1026	763.8	469	0.3932	821.7	994	0.7005	898.5	757
0.2111	781.8	766	0.5010	846.6	1000	0.7999	927.2	556
0.3039	802.6	907	0.6234	877.1	931	0.8916	9558	304
			T = 364.7 K, P = 7.3 MPa					
0.1218	736.9	662	0.3986	791.3	1186	0.6930	864.2	878
0.2254	755.9	950	0.5174	818.7	1153	0.7857	891.0	621
0.3103	772.8	1083	0.5993	839.2	1050	0.8747	918.1	377
			T = 364.3 K, P = 17.9 MPa					
0.1050	746.4	539	0.3896	801.7	1118	0.6957	877.1	829
0.2012	763.2	906	0.4740	820.8	1111	0.7975	906.2	592
0.3006	782.9	1049	0.6231	858.0	917	0.8890	934.1	350
			T = 364.5 K, P = 22.0 MPa					
0.1057	751.1	511	0.4002	808.7	1077	0.6995	882.9	770
0.2067	768.1	813	0.4909	829.4	1064	0.7932	909.6	501
0.3091	789.2	1029	0.5889	853.7	941	0.9038	943.0	310

Before and after each series of measurements at a given temperature the instrument was calibrated.

From the densities, the molar excess volumes V^E were obtained according to

$$V^E = V_m - (x_1V_1 + x_2V_2)$$
$$= x_1M_1(\varrho_m^{-1} - \varrho_1^{-1}) + x_2M_2(\varrho_m^{-1} - \varrho_2^{-1}) \quad (1)$$

where V_i, M_i, ϱ_i, and x_i denote, respectively, the molar volume, the molar mass, the density, and the mole fraction of either cycloether (i = 1) or alkane (i = 2); quantities with subscript m refer to the mixture. The molar excess volumes V^E were known with an estimated accuracy of better than $\pm 5 \times 10^{-9}$ m^3 mol^{-1}.

Results and Discussion

Densities of the pure liquids are listed in Table 1 for the different temperatures and pressures investigated. For each of the average temperatures 323.2, 349.7, and 364.5 K, we observe a linear dependence of ϱ on pressure. The extrapolated values of ϱ to atmospheric pressure at each temperature and for each pure component compare well with literature values as shown in Table 2. Densities and molar excess volumes as determined via eq 1 are presented in Table 3. At each temperature and each pressure, the excess volumes were fitted with a smoothing polynomial

$$V^E/(10^{-9}\ \mathrm{m^3\ mol^{-1}}) = x_1(1 - x_1)\sum_{j=0}^{k-1} A_j\,(1 - 2x_1)^j \quad (2)$$

by the method of unweighted least squares. For each system the set of coefficients A_j was selected according to the corresponding standard deviation and the uncertainty associated with individual coefficients. The coefficients A_j selected and the corresponding standard deviations are given in Table 4. Graphical representation of the results

Table 4. Coefficients A_i and Standard Deviations $\sigma(V^E)$ for Representation of Molar Excess Volumes at Different Temperatures and Pressures (Eq 2)

T/K	P/MPa	$A_0/(10^{-9}$ $m^3\ mol^{-1})$	$A_1/(10^{-9}$ $m^3\ mol^{-1})$	$A_2/(10^{-9}$ $m^3\ mol^{-1})$	$A_3/(10^{-9}$ $m^3\ mol^{-1})$	$A_4/(10^{-9}$ $m^3\ mol^{-1})$	$s/(10^{-9}$ $m^3\ mol^{-1})$
			1,4-Dioxane (1)+ Heptane (2)				
323.5	7.9	3147	−938.6	467.9	−340.1		13
	16.2	2781	−1381	785.3	846.9	−1366	14
	24.1	2731.5	−1034	−307.1	310.5		7
349.9	7.6	3675	−919.0	−405.2		980.3	9
	16.3	3201	−1146.1	2179	3935	−7533	33
364.7	7.3	3746	−1183	737.9		−1077	16
	17.9	3588	−857.4	326.2	−653.8		13
	22.0	3430	−377.4	563.1	−928.0		29
			1,4−Dioxane (1) + Tetradecane (2)				
323.5	7.9	5304	1142	545.8			18
	16.2	5801	1225	−587.3	−472.8	2450	17
	24.1	5303	1231	552.1	−273.5		19
349.9	7.6	6581	1506	1960	−1165		26
	16.3	6022	978.7	1015.4	1572	−688.0	11
	21.7	5982	985.5	551.8	2250		27
364.7	7.3	7424	1655		−3483	3948	22
	17.9	6223	1798	1106			15
			1,4−Dioxane (1) + Cyclohexane (2)				
323.5	7.9	3974	−957.9	−268.2	−356.5	957.3	7
	16.2	3846	−874.0	215.4	−297.3		7
	24.1	3535	−563.5	1126	−464.9	−1826	9
349.9	7.6	4182	−839.4	798.4	−1009	−400.9	7
	16.3	4052	−726.4	346.8	−487.7		8
	21.7	4014	−614.9	173.2	−1093		16
364.7	7.3	4676	−1178	−809.5	−1129	1801	9
	17.9	4335	−1522	665.5			16
	22.0	4199	−1605		671.8	644.0	8

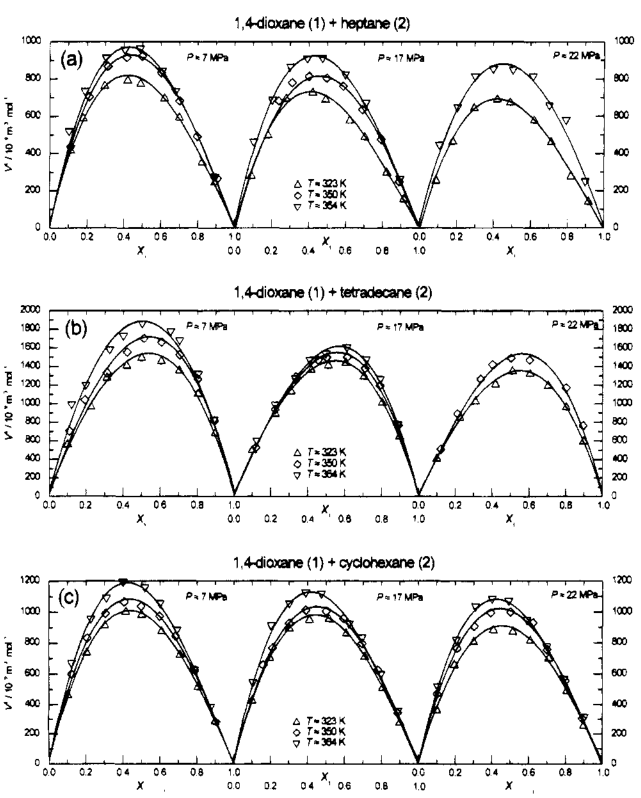

Figure 1. Molar excess volumes, V^E, of binary liquid mixtures of 1,4-dioxane + heptane, + tetradecane, and + cyclohexane at different temperatures and pressures (see Table 3) plotted against the molar fraction, x_1, of 1,4-dioxane. Experimental results: (△) at 323 K, (◇) at 350 K, (▽) at 464 K; curves are calculated from eq 2 using the coefficients given in Table 4; (a) mixtures with heptane; (b) mixtures with tetradecane; (c) mixtures with cyclohexane.

is shown in Figure 1. The different V^E curves exhibit the same behavior: all curves are positive with a parabolic shape. However, for mixtures with similar size alkanes (heptane and cyclohexane) all curves have a maximum around $x_1 \simeq 0.40-0.45$ as a consequence of the self-association effect of 1,4-dioxane whereas with the longer chain n-alkane (tetradecane) the entropy effect overswamps the association effect and shifts the maximum toward the n-alkane side ($x_1 \simeq 0.55-0.60$). As expected, for all mixtures, at a given pressure, V^E increases with increasing temperature, while an increase of pressure results in a decrease of V^E. No literature values could be found for comparison at such high temperatures and pressures, but the present results agree with the general trend observed at atmospheric pressure when temperature increases (Inglese *et al.*, 1983).

Our results can be used to estimate the excess isobaric thermal expansivities or the isothermal compressibilities of such systems, however, and most interestingly they can also be used to estimate the change of the molar Gibbs energy with pressure. The present data will serve to obtain the molar excess heat capacities at constant pressure from the volumetric heat capacities at constant pressure when they are available.

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