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Excess Molar Volumes of 2,4,6,8-Tetramethylcyclotetrasiloxane with Benzene, Toluene, and Xylene at T = (288.15, 298.15, and 308.15) K

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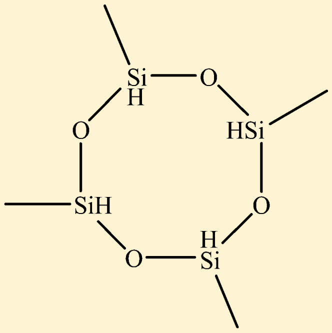
ABSTRACT: Densities of binary mixtures of 2,4,6,8-tetramethylcyclotetrasiloxane with benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene have been determined at temperatures of (288.15, 298.15, and 308.15) K using an Anton Paar DMA 4500 oscillating u-tube densitometer. Excess molar volumes have been derived from the density data. The experimental data were satisfactorily fitted to the Redlich–Kister equation and the Legendre polynomials.



■ INTRODUCTION

As one of the most important chemicals, 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H, CAS RN: 2370-88-9) is widely used in the silicone industry, and its structure is shown in Figure 1. It is a kind of active siloxane containing silicon–hydrogen bond and thus plays an important role in synthesizing hydrogen-containing silicone oil, the cross-linking agents which are essential for addition-type liquid silicone rubbers or silicone resins.

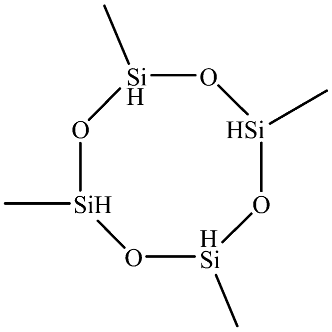


Figure 1. Structure of 2,4,6,8-tetramethylcyclotetrasiloxane.

The excess properties are used in the design and calculation of the chemical engineering process involving substance separations, heat transfers, mass transfers, and fluid flows.[1] Information about the excess properties of liquid mixtures containing D_4^H and aromatic compounds and their dependence on compositions and temperature is very important fundamental data for their applications in the separation fields. Moreover, excess thermodynamic properties of mixtures are also used to express the deviations of the mixing process from ideality and thus are useful in the study of molecular interactions and arrangements.[2] The excess molar volume (V^E) is one of the important excess properties which can be used in the understanding of molecular interactions between different components of mixtures and also in engineering applications.[3]

However, the excess properties involving D_4^H have not been investigated before. Here we report the values of densities and excess molar volumes (V^E) for the binary systems of D_4^H with aromatic hydrocarbon (benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene) at T = (288.15, 298.15, and 308.15) K at atmospheric pressure. The V^E data were further correlated with the Redlich–Kister equation and the Legendre polynomials.

■ EXPERIMENTAL SECTION

All chemicals were used without further purification, and their purities were detected by gas–liquid chromatography (Table 1).

Table 1. Sample Table

chemical name	source	final mole fraction purity	analysis method
benzene	Sigma-Aldrich	0.999	GC[b]
toluene	Tedia	0.999	GC[b]
o-xylene	Alfa Aesar	0.999	GC[b]
m-xylene	Alfa Aesar	0.999	GC[b]
p-xylene	Alfa Aesar	0.999	GC[b]
D_4^H[a]	Guangdong Xibo	0.999	GC[b]

[a] D_4^H = 2,4,6,8-tetramethylcyclotetrasiloxane. [b] Gas–liquid chromatography.

The density measurements for all solvents conducted at T = 298.15 K were listed in Table 2 and compared with those in literature.[4−10]

All of the binary solutions were prepared in airtight stopped glass bottles to prevent evaporation. Masses of these samples

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Table 2. Experimental Densities (ρ) of the Pure Liquid Components and Literature Values at T = 298.15 K

	$\rho/\mathrm{g\cdot cm^{-3}}$			$\rho/\mathrm{g\cdot cm^{-3}}$	
solvent	exptl	lit.	solvent	exptl	lit.
water	0.99708	0.99705[4]	*o*-xylene	0.87572	0.8757[8]
benzene	0.87357	0.87357[5]	*m*-xylene	0.85986	0.85985[9]
toluene	0.86223	0.86223[6]	*p*-xylene	0.85667	0.86668[10]
D_4^H	0.98614	0.986[7]			

were determined by weighing on an analytical balance (Sartorius, model BS 224S, ± 0.1 mg). The uncertainty in the determination of the molar fraction basis is about 0.0001. The densities of pure components and their mixtures at different temperatures were measured with an Anton Paar DMA 4500 oscillating u-tube densitometer. The uncertainty of the density is ± 0.00005 $\mathrm{g\cdot cm^{-3}}$. The densitometer was calibrated periodically with ultrapure water and dry air. Two integrated Pt 100 platinum thermometers ($u_r(T) = 0.01$) together with Peltier elements provide an extremely precise thermostatting of the sample. The estimated uncertainty of V^E is about 0.001 $\mathrm{cm^3\cdot mol^{-1}}$.

■ RESULTS AND DISCUSSION

Densities of the pure components and their binary mixtures with D_4^H were used to determine the excess molar volumes V^E given in Table 3 by

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \quad (1)$$

where x_i, ρ_i, and M_i represent the molar fraction, the density, and the molecular weight of the pure component, respectively, while ρ represents the density of the mixture.

The composition dependence of V_m^E could be represented by the following two equations:

(a) Redlich–Kister[11] type smoothing equation:

$$V_m^E = x_1x_2 \sum_{i=0}^{n} A_i(x_1 - x_2)^i \quad (2)$$

where x_1 was the molar fraction of D_4^H, A_i was the adjustable parameter, and n was the number of the fitted parameters.

(b) Legendre polynomials $L_k(x_1)$:[12]

$$\begin{aligned} V_m^E &= x_1x_2 \sum_{i=0}^{n} a_kL_k(x_1) \\ &= x_1x_2[a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1) \\ &\quad + a_3(20x_1^3 - 30x_1^2 + 12x_1 - 1) \\ &\quad + a_4(70x_1^4 - 140x_1^3 + 90x_1^2 - 20x_1 + 1)] \end{aligned} \quad (3)$$

where x_1 is the molar fraction of D_4^H, a_i is the adjustable parameter.

The Redlich–Kister equation is very powerful and frequently used to correlate the excess Gibbs function, excess volumes, and excess enthalpies of mixing. But it is difficult to explain that the values of its adjustable parameters change as the number of terms in the series increased. Legendre polynomials have the valuable characteristic that for a continuous series of observations (infinite) the values of the coefficients do not change as the number of terms in the series increased.[2]

The parameters for the Redlich–Kister equation and Legendre polynomials were obtained by the least-squares fit method, and the results were listed in Tables 4 and 5. The following equation was used to calculate the root-mean-square deviation (rmsd) values:

$$\mathrm{rmsd} = \sqrt{\frac{1}{N}\sum_{i}^{N}(V_{\mathrm{cal}(i)}^E - V_{\exp(i)}^E)^2} \quad (4)$$

where $V_{\mathrm{cal}(i)}^E$ and $V_{\exp(i)}^E$ are the calculated and experimental values of the excess molar volume, respectively, and N is the number of data points for each data set.

The values of the partial excess volume of solute and solvents at infinite dilution $\bar{V}_i^{E,\infty}$ can be calculated either from the adjustable parameters of Redlich–Kister smoothing equation or the Legendre polynomials when $x_1 \to 0$ and $x_2 \to 1$. Under such circumstance, the presentations for partial excess volumes were deduced as shown in eqs 5 to 8, and their values were calculated and shown in Tables 6 and 7, respectively:

(a) Redlich–Kister:

$$\bar{V}_1^{E,\infty} = A_0 - A_1 + A_2 - A_3 + A_4 \quad (5)$$

$$\bar{V}_2^{E,\infty} = A_0 + A_1 + A_2 + A_3 + A_4 \quad (6)$$

(b) Legendre polynomials:

$$\bar{V}_1^{E,\infty} = a_0 - a_1 + a_2 - a_3 + a_4 \quad (7)$$

$$\bar{V}_2^{E,\infty} = a_0 + a_1 + a_2 + a_3 + a_4 \quad (8)$$

The expansibility, $\alpha = -(1/\rho)(\partial\rho/\partial T)_p$,[13] is calculated from the temperature dependence of density given as

$$\rho = A + BT + CT^2 \quad (9)$$

The parameters for A, B, and C were obtained by the least-squares fit method. The results of α for five binary mixtures at T = 298.15 K were illustratively shown in Figure 2, and they increased in the following sequence: benzene < toluene < *p*-xylene < *m*-xylene < *o*-xylene. To further indicate the influence of temperature on the expansibility, the trend of α as a function of composition for D_4^H (1) + *o*-xylene (2) at T = (288.15, 298.15, and 318.15) K are shown in Figure 3 as an example. The results indicate that the expansibility increases with temperature.

The influence of the molar fraction of D_4^H in the binary solution on the V^E values at different temperatures could be drawn in figures. To exhibit the changing tendency of the V^E with the molar fraction of D_4^H, the excess molar volumes of these five binary systems at T = 298.15 K are presented in Figure 4 for illustration. Similarly, the trend of V^E as a function of composition of the binary system (D_4^H (1) + *o*-xylene (2)) at T = (288.15, 298.15, and 318.15) K are shown in Figure 5 for illustration. Obviously, all of the excess molar volumes are negative over the whole composition range and they increase in absolute value in the following sequence: benzene < toluene < *m*-xylene < *p*-xylene < *o*-xylene. The absolute values of excess volume increased with temperature.

The negative contributions which arise from changes of free volume in the real mixtures are from physical, chemical, and structural characteristics of liquids.[14] The negative V^E values of these binary systems indicate the preponderance of the weak intermolecular interactions which exist between the siloxane

Table 3. Densities ρ and Excess Molar Volumes (V^E) for 2,4,6,8-Tetramethylcyclotetrasiloxane (1) + Aromatic Hydrocarbon (2) at T = (288.15, 298.15, and 318.15) K[a]

	288.15 K		298.15 K		308.15 K	
	ρ	V^E	ρ	V^E	ρ	V^E
x_1	g·cm^{-3}	cm^3·mol^{-1}	g·cm^{-3}	cm^3·mol^{-1}	g·cm^{-3}	cm^3·mol^{-1}
			D_4^H (1) + Benzene (2)			
0.0000	0.88417	0.000	0.87357	0.000	0.86286	0.000
0.0497	0.89888	−0.044	0.88824	−0.066	0.87755	−0.097
0.0999	0.91174	−0.109	0.90099	−0.145	0.89029	−0.204
0.1499	0.92278	−0.174	0.91191	−0.220	0.90126	−0.312
0.1997	0.93230	−0.225	0.92132	−0.282	0.91069	−0.405
0.2501	0.94072	−0.273	0.92965	−0.339	0.91893	−0.478
0.3000	0.94804	−0.308	0.93687	−0.381	0.92610	−0.537
0.3500	0.95456	−0.339	0.94315	−0.396	0.93228	−0.563
0.3999	0.96028	−0.353	0.94881	−0.418	0.93773	−0.576
0.4498	0.96546	−0.366	0.95389	−0.433	0.94265	−0.585
0.4999	0.97005	−0.360	0.95840	−0.429	0.94702	−0.577
0.5498	0.97422	−0.354	0.96244	−0.416	0.95092	−0.557
0.5999	0.97803	−0.342	0.96616	−0.402	0.95453	−0.541
0.6486	0.98136	−0.319	0.96941	−0.376	0.95765	−0.506
0.7001	0.98461	−0.295	0.97254	−0.341	0.96064	−0.458
0.7495	0.98743	−0.259	0.97528	−0.301	0.96327	−0.409
0.8001	0.99004	−0.207	0.97780	−0.241	0.96571	−0.343
0.8499	0.99242	−0.156	0.98012	−0.186	0.96791	−0.275
0.8986	0.99456	−0.099	0.98219	−0.121	0.96990	−0.201
1.0000	0.99867	0.000	0.98614	0.000	0.97344	0.000
			D_4^H (1) + Toluene (2)			
0.0000	0.87145	0.000	0.86223	0.000	0.85289	0.000
0.0499	0.88660	−0.198	0.87708	−0.207	0.86753	−0.228
0.0999	0.89994	−0.374	0.89019	−0.396	0.88040	−0.430
0.1500	0.91167	−0.518	0.90166	−0.546	0.89168	−0.597
0.2000	0.92198	−0.629	0.91175	−0.663	0.90157	−0.727
0.2500	0.93115	−0.718	0.92071	−0.758	0.91033	−0.830
0.3000	0.93931	−0.781	0.92870	−0.829	0.91815	−0.911
0.3502	0.94671	−0.832	0.93591	−0.882	0.92511	−0.959
0.4000	0.95326	−0.856	0.94225	−0.902	0.93131	−0.988
0.4501	0.95923	−0.864	0.94805	−0.910	0.93694	−0.997
0.5004	0.96463	−0.856	0.95332	−0.901	0.94201	−0.982
0.5504	0.96956	−0.831	0.95811	−0.882	0.94661	−0.955
0.5998	0.97398	−0.792	0.96238	−0.839	0.95074	−0.911
0.6497	0.97802	−0.732	0.96626	−0.770	0.95447	−0.837
0.6994	0.98174	−0.666	0.96983	−0.695	0.95790	−0.756
0.7497	0.98515	−0.576	0.97312	−0.601	0.96105	−0.655
0.8000	0.98834	−0.487	0.97619	−0.506	0.96399	−0.552
0.8494	0.99118	−0.378	0.97890	−0.387	0.96661	−0.432
0.8995	0.99385	−0.258	0.98145	−0.256	0.96904	−0.292
1.0000	0.99867	0.000	0.98614	0.000	0.97344	0.000
			D_4^H (1) + *o*-Xylene (2)			
0.0000	0.88405	0.000	0.87572	0.000	0.86728	0.000
0.0499	0.89679	−0.256	0.88817	−0.273	0.87945	−0.293
0.1000	0.90822	−0.477	0.89930	−0.505	0.89028	−0.538
0.1500	0.91840	−0.662	0.90922	−0.703	0.89995	−0.752
0.2000	0.92756	−0.814	0.91811	−0.864	0.90859	−0.926
0.2500	0.93582	−0.938	0.92611	−0.995	0.91633	−1.064
0.2998	0.94320	−1.027	0.93325	−1.090	0.92321	−1.163
0.3501	0.94998	−1.094	0.93980	−1.162	0.92953	−1.242
0.3998	0.95606	−1.137	0.94566	−1.207	0.93516	−1.289
0.4496	0.96156	−1.149	0.95095	−1.222	0.94025	−1.308
0.4998	0.96665	−1.144	0.95584	−1.218	0.94492	−1.303
0.5497	0.97124	−1.116	0.96022	−1.185	0.94910	−1.269
0.5997	0.97545	−1.065	0.96425	−1.135	0.95296	−1.221
0.6496	0.97925	−0.989	0.96788	−1.056	0.95636	−1.129

Table 3. continued

	288.15 K		298.15 K		308.15 K	
	ρ	V^E	ρ	V^E	ρ	V^E
x_1	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$
D_4^H (1) + *o*-Xylene (2)						
0.7001	0.98282	−0.900	0.97127	−0.963	0.95958	−1.034
0.7502	0.98605	−0.791	0.97432	−0.846	0.96244	−0.906
0.7998	0.98896	−0.659	0.97709	−0.711	0.96504	−0.762
0.8480	0.99161	−0.525	0.97954	−0.559	0.96733	−0.601
0.9002	0.99423	−0.360	0.98202	−0.389	0.96965	−0.421
1.0000	0.99867	0.000	0.98614	0.000	0.97344	0.000
D_4^H (1) + *m*-Xylene (2)						
0.0000	0.86836	0.000	0.85986	0.000	0.85124	0.000
0.0500	0.88200	−0.203	0.87313	−0.204	0.86429	−0.229
0.1001	0.89434	−0.385	0.88516	−0.392	0.87606	−0.432
0.1500	0.90542	−0.533	0.89600	−0.552	0.88660	−0.598
0.1999	0.91545	−0.656	0.90580	−0.687	0.89612	−0.737
0.2498	0.92455	−0.751	0.91465	−0.786	0.90473	−0.844
0.2999	0.93294	−0.835	0.92280	−0.874	0.91266	−0.941
0.3500	0.94055	−0.892	0.93019	−0.935	0.91983	−1.006
0.3995	0.94741	−0.921	0.93684	−0.967	0.92634	−1.054
0.4504	0.95392	−0.938	0.94311	−0.978	0.93241	−1.070
0.5000	0.95971	−0.931	0.94869	−0.967	0.93779	−1.054
0.5500	0.96511	−0.909	0.95390	−0.943	0.94281	−1.035
0.5996	0.97004	−0.869	0.95865	−0.900	0.94734	−0.984
0.6500	0.97469	−0.817	0.96310	−0.840	0.95162	−0.923
0.6995	0.97887	−0.741	0.96714	−0.764	0.95547	−0.838
0.7495	0.98281	−0.655	0.97092	−0.673	0.95907	−0.739
0.7996	0.98648	−0.554	0.97442	−0.563	0.96242	−0.625
0.8498	0.98984	−0.428	0.97765	−0.434	0.96547	−0.483
0.8994	0.99298	−0.303	0.98064	−0.300	0.96832	−0.343
1.0000	0.99867	0.000	0.98614	0.000	0.97344	0.000
D_4^H (1) + *p*-Xylene (2)						
0.0000	0.86528	0.000	0.85667	0.000	0.84796	0.000
0.0499	0.87933	−0.231	0.87042	−0.241	0.86148	−0.264
0.0999	0.89203	−0.435	0.88282	−0.452	0.87361	−0.487
0.1501	0.90351	−0.607	0.89396	−0.620	0.88448	−0.665
0.1999	0.91385	−0.748	0.90411	−0.778	0.89433	−0.824
0.2500	0.92325	−0.860	0.91334	−0.907	0.90335	−0.965
0.2999	0.93183	−0.955	0.92170	−1.009	0.91140	−1.058
0.3501	0.93962	−1.011	0.92923	−1.061	0.91880	−1.131
0.4000	0.94673	−1.050	0.93618	−1.110	0.92553	−1.181
0.4502	0.95329	−1.068	0.94254	−1.121	0.93167	−1.199
0.4997	0.95921	−1.062	0.94826	−1.121	0.93719	−1.190
0.5493	0.96463	−1.026	0.95354	−1.093	0.94224	−1.152
0.6001	0.96979	−0.983	0.95845	−1.034	0.94703	−1.102
0.6501	0.97440	−0.909	0.96293	−0.964	0.95137	−1.036
0.7002	0.97867	−0.816	0.96702	−0.864	0.95531	−0.935
0.7472	0.98239	−0.717	0.97062	−0.765	0.95876	−0.832
0.7998	0.98627	−0.592	0.97432	−0.630	0.96230	−0.691
0.8492	0.98969	−0.470	0.97756	−0.493	0.96538	−0.545
0.9002	0.99292	−0.319	0.98061	−0.326	0.96828	−0.368
1.0000	0.99867	0.000	0.98614	0.000	0.97344	0.000

[a] x_1 is the mole fraction of D_4^H in the different solvents. Standard uncertainties u are $u(T) = 0.01$ K, $u(x_1) = 0.0001$ and the combined expanded uncertainties U_c are $U_c(\rho) = 0.00005\ g \cdot cm^{-3}$, and $U_c(V^E) = 0.001\ cm^3 \cdot mol^{-1}$.

and π-electrons of aromatic hydrocarbon mixtures along with disruption in the orientational order of the pure components.

The methyl group is the potential electron donating group to the aromatic ring. When methyl group is introduced in benzene ring, it can increase the density of the π-electron cloud and strengthen the interactions between the solute and the solvent molecules. Therefore, a higher negative contribution is derived from these stronger interactions, and the excess molar volume of the D_4^H (1) + toluene (2) system is more negative than that of the D_4^H + benzene mixture. When more methyl groups are bonded to the aromatic ring, the density of the π-electron cloud is higher than that of the toluene, and the interactions between

Table 4. Regressed Parameters A_i in the Redlich−Kister Equation and the Root-Mean-Square Deviation (σ)

T	A_0	A_1	A_2	A_3	A_4	
K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	σ
D_4^H (1) + Benzene (2)						
288.15	−1.44649	0.11747	−0.08378	−0.07146	0.86931	0.002
298.15	−1.70885	0.21280	−0.13386	−0.03829	0.80795	0.003
308.15	−2.30856	0.52852	−0.46104	−0.67272	0.93468	0.004
D_4^H (1) + Toluene (2)						
288.15	−3.42207	0.69182	−0.17710	0.17735	0.07096	0.002
298.15	−3.61340	0.73660	−0.17717	0.32865	0.27808	0.004
308.15	−3.93866	0.88852	−0.18038	0.10369	0.09983	0.003
D_4^H (1) + *o*-Xylene (2)						
288.15	−4.57680	0.75489	−0.08543	0.10281	−0.03474	0.002
298.15	−4.86703	0.75556	−0.14191	0.12079	−0.01323	0.002
308.15	−5.21062	0.79008	−0.13281	0.12657	−0.07447	0.003
D_4^H (1) + *m*-Xylene (2)						
288.15	−3.72871	0.54147	−0.14657	0.04602	0.08484	0.003
298.15	−3.87763	0.66597	−0.21810	−0.04159	0.46942	0.002
308.15	−4.24841	0.62214	0.13260	−0.02337	−0.27017	0.003
D_4^H (1) + *p*-Xylene (2)						
288.15	−4.23796	0.78352	0.20187	0.02124	−0.21095	0.003
298.15	−4.48305	0.76927	0.20381	0.06307	0.05363	0.004
308.15	−4.75688	0.71918	0.03876	0.05310	−0.06206	0.005

Table 5. Regressed Parameters a_i in Legendre Polynomials and the Root-Mean-Square Deviation (σ)

	a_0	a_1	a_2	a_3	a_4	
T/K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	σ
D_4^H (1) + Benzene (2)						
288.15	−1.29994	0.07416	0.44354	−0.03025	0.19952	0.002
298.15	−1.59120	0.18865	0.37431	−0.01661	0.18829	0.003
308.15	−2.27481	0.12623	0.22837	−0.26975	0.21352	0.004
D_4^H (1) + Toluene (2)						
288.15	−3.46660	0.79729	−0.07580	0.07160	0.01733	0.002
298.15	−3.61749	0.93257	0.03926	0.13045	0.06087	0.004
308.15	−3.97838	0.94893	−0.06283	0.0409	0.02275	0.003
D_4^H (1) + *o*-Xylene (2)						
288.15	−4.61270	0.81385	−0.07918	0.03934	−0.00793	0.002
298.15	−4.91535	0.82765	−0.09851	0.04623	−0.00072	0.002
308.15	−5.26933	0.86588	−0.13234	0.05161	−0.01763	0.003
D_4^H (1) + *m*-Xylene (2)						
288.15	−3.76101	0.56834	−0.04954	0.02066	0.01875	0.002
298.15	−3.85637	0.64007	0.12177	−0.02002	0.10341	0.002
308.15	−4.25684	0.60932	−0.06563	−0.00732	−0.05172	0.004
D_4^H (1) + *p*-Xylene (2)						
288.15	−4.21321	0.79868	0.01445	0.00966	−0.04797	0.003
298.15	−4.39972	0.81017	0.17427	0.03260	0.03054	0.005
308.15	−4.75687	0.74918	−0.01176	0.01855	−0.01771	0.005

Table 6. Calculated Partial Excess Molar Volumes at Infinite Dilution at T = (288.15, 298.15, and 318.15) K from Redlich−Kister Parameters A_i

	288.15		298.15		308.15	
	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$
	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
D_4^H (1) + benzene (2)	−0.7070	−0.6150	−1.2093	−0.8603	−1.6907	−1.9791
D_4^H (1) + toluene (2)	−4.3974	−2.6590	−4.5777	−2.4472	−5.0114	−3.0270
D_4^H (1) + *o*-xylene (2)	−5.5547	−3.8393	−5.8985	−4.1458	−6.3346	−4.5013
D_4^H (1) + *m*-xylene (2)	−4.3779	−3.2030	−4.2507	−3.0019	−4.9848	−3.7872
D_4^H (1) + *p*-xylene (2)	−5.0518	−3.4423	−5.0580	−3.3933	−5.5525	−4.0079

Table 7. Calculated Partial Excess Molar Volumes at Infinite Dilution at T = (288.15, 298.15, and 318.15) K from Legendre Parameters a_i

	288.15		298.15		308.15	
	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$
	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
D_4^H (1) + benzene (2)	−0.7008	−0.6130	−1.2006	−0.8566	−1.6894	−1.9764
D_4^H (1) + toluene (2)	−4.3940	−2.6562	−4.5804	−2.4543	−5.0083	−3.0286
D_4^H (1) + *o*-xylene (2)	−5.5530	−3.8466	−5.8885	−4.1407	−6.3368	−4.5018
D_4^H (1) + *m*-xylene (2)	−4.3808	−3.2028	−4.2512	−3.0111	−4.9762	−3.7722
D_4^H (1) + *p*-xylene (2)	−5.0551	−3.4384	−5.0377	−3.3521	−5.5541	−4.0186

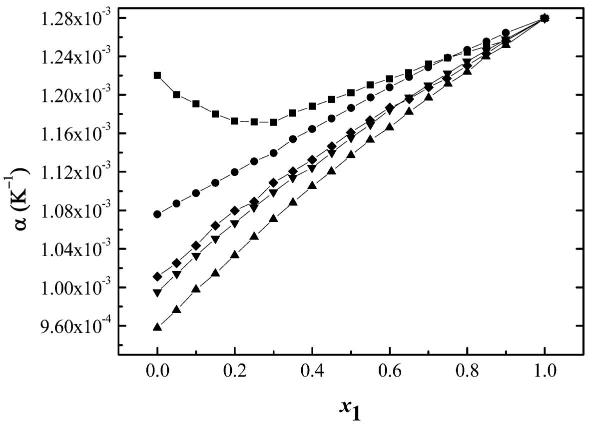

Figure 2. Expansibility α for five binary mixtures at T = 298.15 K as a function of molar fraction: ■, D_4^H (1) + benzene (2); ●, D_4^H (1) + toluene (2); ▼, D_4^H (1) + *m*-xylene (2); ♦, D_4^H (1) + *p*-xylene (2); ▲, D_4^H (1) + *o*-xylene (2).

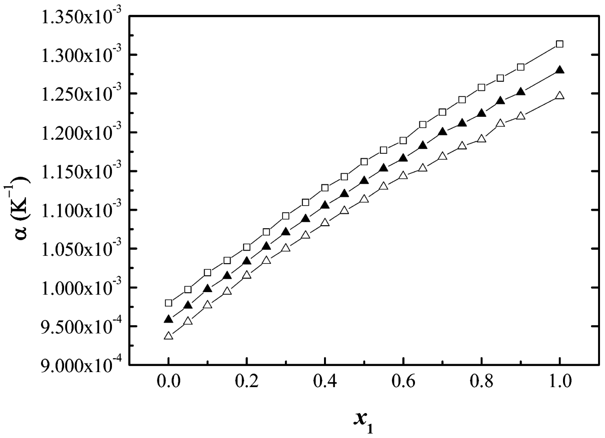

Figure 3. Expansibility α for the system D_4^H (1) + *o*-xylene (2) as a function of molar fraction: △, 288.15 K; ▲, 298.15 K; □, 308.15 K.

the solute and the solvent molecules are more significant, which leads to the more negative values of V^E than the D_4^H + benzene mixture.[15] Therefore, the excess molar volumes of binary solution of D_4^H with xylene are more negative than that of the D_4^H (1) + toluene (2) mixture.

The differences in the excess molar volumes among these five mixtures are resulted from the influence of the diversity of the structure on the steric hindrance. The position of the substituted groups also plays an important role on the electron density in the aromatic ring. Among the three isomers of xylene, *o*-xylene seems to offer minimum steric hindrance, thus increasing electron donor−acceptor interaction to the maximum and hence making the V^E minimal.[15]

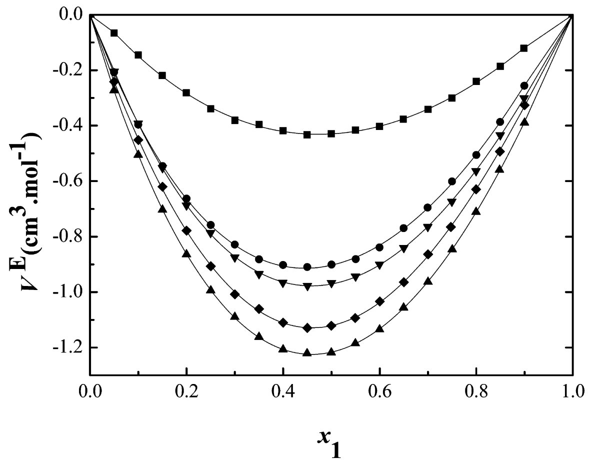

Figure 4. Excess molar volumes for the system D_4^H (1) + aromatic hydrocarbon (2) as a function of molar fraction at T = 298.15 K: ■, D_4^H (1) + benzene (2); ●, D_4^H (1) + toluene (2); ▼, D_4^H (1) + *m*-xylene (2); ♦, D_4^H (1) + *p*-xylene (2); ▲, D_4^H (1) + *o*-xylene (2); lines calculated by eq 2 using parameters in Table 4.

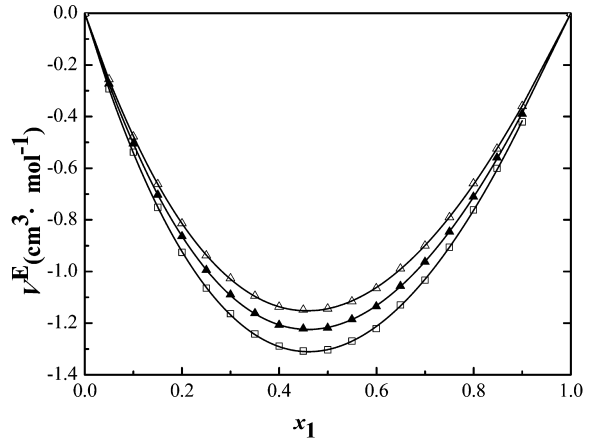

Figure 5. Excess molar volumes of the system D_4^H (1) + *o*-xylene (2) as a function of molar fraction: △, 288.15 K; ▲, 298.15 K; □, 308.15 K; lines calculated by eq 2 using parameters in Table 4.

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Notes

The authors declare no competing financial interest.

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