

temperature ranges studied. The system obeys Henry's law and the gas appears to be more soluble in low-polarity solvents.

### Acknowledgment

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### Glossary

$P_{CO}$  carbon monoxide pressure (kPa)  
 $K$  Henry's law constant (kPa)  
 $X_{CO}$  mole fraction of carbon monoxide in the liquid phase

**Registry No.** CO, 630-08-0; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 2-methyl-1-propanol, 78-83-1; 2-butanol, 78-92-2; 2-methyl-2-propanol, 75-65-0; 2-propanol, 67-63-0.

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## Excess Volumes of Binary Mixtures of *m*-Xylene + *n*-Alkanes

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**Excess volume of the binary mixtures *m*-xylene + *n*-hexane, + *n*-octane, + *n*-decane, + *n*-dodecane, + *n*-tetradecane, and + *n*-hexadecane have been measured at 298.15 K as a function of composition by a dilatometric method.**

### Introduction

The experimental excess volumes of binary mixtures of *n*-alkanes with *p*-xylene (1) and *o*-xylene (2) at 298.15 K have been published previously. In this paper the results for the same *n*-alkanes with *m*-xylene at the same temperature are reported. No excess volume data have been found for these systems in the consulted literature.

### Experimental Section

The alkanes were the same as those used in earlier works (3). The *m*-xylene (Carlo-Erba RPE) was dried with sodium with no further purification. Gas-chromatography analysis and refractive index and density determinations were used as a criterion of purity.

The experimental density at 298.15 K was found to be 0.85999 g cm<sup>-3</sup> and the literature value (4) is 0.86000 g cm<sup>-3</sup>. The experimental refractive index,  $n_D(303.15\text{ K})$ , was found to be 1.49215 and the literature value (4) is 1.49200.

**Excess Volume Measurements.** Excess volumes have been measured as a function of the mole fraction by a semicontinuous dilatometric procedure. The dilatometer is the same used

in previous works (2) and has been described in detail elsewhere (1).

### Results

Experimental excess volumes are given in Table I and are plotted in Figure 1.

As in previous works the experimental results were fitted to an equation of the type

$$V^E/[x(1-x)] = \sum A_i(2x-1)^i \quad (1)$$

where  $x$  is the *m*-xylene mole fraction. The coefficients of eq 1 and the standard deviations are given in Table II.

As is shown in Figure 1, the excess volume for *n*-hexane + *m*-xylene is negative. The rest of the *n*-alkanes with *m*-xylene show a positive  $V^E$ . This behavior was also observed for the binary mixtures of *n*-alkanes with *p*-xylene (1) and *o*-xylene (2).

Comparing the behavior of the three xylenes with the different *n*-alkanes, we found that the magnitude of the excess volume increases in the order ortho < para < meta when the alkane is *n*-decane. For *n*-dodecane, *n*-tetradecane, and *n*-hexadecane the order is para < ortho < meta. The systems with a negative excess volume show the order meta < para < ortho for the absolute value of  $V^E$ . The behavior shown by *n*-hexane with the three xylenes ( $V^E < 0$ ) is also found for binary mixtures of *n*-pentane with the three xylenes (5). Octane with *m*- or *p*-xylene always shows a positive excess volume along the whole mole fraction range being meta > para. However the system *n*-octane + *o*-xylene has a positive  $V^E$  for mole fractions smaller than 0.3 becoming negative when the mole fraction of *o*-xylene increases from 0.3 to 1. The magnitude of  $V^E$  for this system is always smaller in absolute value

Table I. Experimental Excess Volumes  $V^E$  at 298.15 K

$x$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$x$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$x$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$
<i>m</i> -Xylene + <i>n</i> -Hexane					
0.0412	-0.0260	0.3901	-0.1859	0.6716	-0.1851
0.0542	-0.0364	0.4058	-0.1901	0.6917	-0.1793
0.1051	-0.0665	0.4617	-0.1979	0.7146	-0.1721
0.1922	-0.1109	0.4838	-0.2019	0.7336	-0.1655
0.2209	-0.1255	0.5578	-0.2037	0.7990	-0.1315
0.2419	-0.1340	0.5668	-0.2025	0.8944	-0.0799
0.3221	-0.1672	0.5976	-0.2011	0.9059	-0.0683
0.3366	-0.1734	0.6380	-0.1931	0.9635	-0.0273
<i>m</i> -Xylene + <i>n</i> -Octane					
0.0819	0.0297	0.4883	0.0832	0.6642	0.0683
0.2252	0.0645	0.5032	0.0833	0.7332	0.0590
0.3419	0.0804	0.5153	0.0827	0.7448	0.0574
0.3500	0.0795	0.5307	0.0812	0.8221	0.0420
0.3636	0.0812	0.5455	0.0803	0.8293	0.0423
0.3875	0.0817	0.5718	0.0800	0.9175	0.0209
0.4017	0.0838	0.5845	0.0766	0.9218	0.0226
0.4413	0.0838	0.5991	0.0757	0.9683	0.0081
0.4457	0.0842	0.6507	0.0700	0.9703	0.0087
<i>m</i> -Xylene + <i>n</i> -Decane					
0.0748	0.0516	0.5176	0.2088	0.7250	0.1752
0.2085	0.1233	0.5475	0.2053	0.7955	0.1476
0.3200	0.1710	0.5747	0.2082	0.8666	0.1078
0.4326	0.1999	0.5905	0.2045	0.9402	0.0537
0.4725	0.2058	0.6151	0.2027	0.9779	0.0204
0.4907	0.2030	0.6660	0.1920		
<i>m</i> -Xylene + <i>n</i> -Dodecane					
0.1707	0.1294	0.5455	0.2761	0.7265	0.2392
0.2886	0.1974	0.5766	0.2766	0.7563	0.2289
0.3332	0.2195	0.6175	0.2706	0.7968	0.2054
0.4346	0.2604	0.6480	0.2656	0.8673	0.1512
0.4745	0.2687	0.6676	0.2594	0.9406	0.0745
0.5197	0.2751	0.7103	0.2485		
<i>m</i> -Xylene + <i>n</i> -Tetradecane					
0.2042	0.1631	0.5840	0.3141	0.7272	0.2816
0.3533	0.2538	0.6133	0.3112	0.7818	0.2502
0.4975	0.3036	0.6402	0.3091	0.8450	0.2033
0.5386	0.3120	0.6568	0.3087	0.9066	0.1362
0.5534	0.3115	0.6798	0.2999		
<i>m</i> -Xylene + <i>n</i> -Hexadecane					
0.1328	0.1190	0.6961	0.3285	0.8026	0.2714
0.3330	0.2566	0.7022	0.3274	0.8262	0.2516
0.4715	0.3201	0.7117	0.3224	0.8569	0.2213
0.6073	0.3435	0.7321	0.3180	0.8784	0.2024
0.6458	0.3374	0.7377	0.3122	0.9089	0.1578
0.6504	0.3402	0.7545	0.3012		
0.6754	0.3363	0.7793	0.2891		

Table II. Parameters in Smoothing Eq 1 and Standard Deviations for Excess Volumes,  $\sigma(V^E)$ 

systems	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma(V^E)/(\text{cm}^3 \text{ mol}^{-1})$
<i>m</i> -xylene + <i>n</i> -hexane	-0.813	-0.120	0.092	0.075	0.0012
<i>m</i> -xylene + <i>n</i> -octane	0.330	-0.065	0.018		0.0008
<i>m</i> -xylene + <i>n</i> -decane	0.825	0.120	0.019		0.0014
<i>m</i> -xylene + <i>n</i> -dodecane	1.083	0.281	0.023		0.0017
<i>m</i> -xylene + <i>n</i> -tetradecane	1.219	0.411	0.083		0.0012
<i>m</i> -xylene + <i>n</i> -hexadecane	1.306	0.542	0.241		0.0019

than the  $V^E$  found for any of the other two systems.

From the comparison of the experimental results of the xylenes with those of *n*-alkanes with benzene ( $\delta$ ) it is shown that the methyl groups on the aromatic ring have a decreasing effect on the value of  $V^E$ .

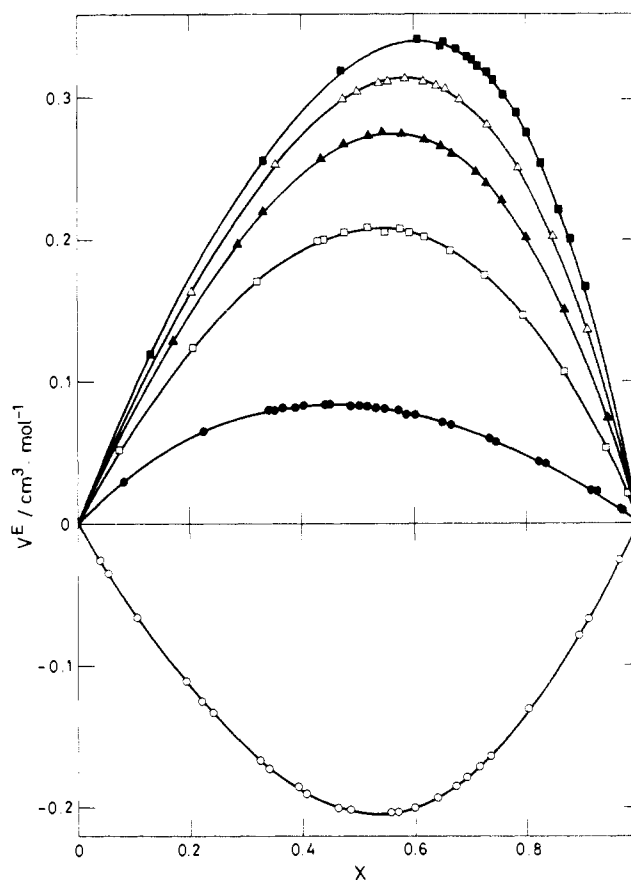


Figure 1. Excess volumes  $V^E$  against the mole fraction,  $x$ , of *o*-xylene: (O) *o*-xylene + *n*-hexane; (●) *o*-xylene + *n*-octane; (□) *o*-xylene + *n*-decane; (▲) *o*-xylene + *n*-dodecane; (Δ) *o*-xylene + *n*-tetradecane; (■) *o*-xylene + *n*-hexadecane.

We are now working in binary mixtures of *n*-alkanes with toluene and ethylbenzene. Our first results on these systems show that a methyl or ethyl group on the aromatic ring has a very similar effect on the  $V^E$ . The values of  $V^E$  for those systems are always smaller than those for benzene + *n*-alkanes and larger than, but closer to, those for binary mixtures of *n*-alkanes with any of the three xylenes. The very small differences between the experimental  $V^E$  of binary mixtures of *n*-alkanes with toluene and ethylbenzene show that the number of carbon atoms of the aliphatic group on the aromatic ring has little influence on the value of  $V^E$ . It seems that it is the number of aliphatic groups on the aromatic ring which has the more important effect on the  $V^E$ .

We are now preparing a theoretical treatment for these systems which will be published soon.

**Registry No.** *m*-Xylene, 108-38-3; *n*-hexane, 110-54-3; *n*-octane, 111-65-9; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; *n*-tetradecane, 629-59-4; *n*-hexadecane, 544-76-3.

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