

# Densities, Refractive Indices, and Excess Properties of Binary Mixtures of 1,4-Dioxane with Benzene, Toluene, *o*-Xylene, *m*-Xylene, *p*-Xylene, and Mesitylene at Temperatures from (288.15 to 318.15) K

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The densities ( $\rho$ ) and refractive indices ( $n$ ) of binary mixtures of 1,4-dioxane with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene, including those of pure liquids, over the entire composition range expressed by mole fraction  $x_1$  of 1,4-dioxane were measured at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K under atmospheric pressure. From the experimental data, the excess molar volumes ( $V_m^E$ ), deviations in refractive indices ( $\Delta n$ ), partial molar volumes ( $V_{m,1}^\circ$  and  $V_{m,2}^\circ$ ), and excess partial molar volumes ( $V_{m,1}^{E,\infty}$  and  $V_{m,2}^{E,\infty}$ ) of the components at infinite dilution were calculated. The  $V_m^E$  values were negative for 1,4-dioxane + benzene, positive for 1,4-dioxane + *o*-xylene, + *m*-xylene, + *p*-xylene, and + mesitylene mixtures over the entire mole fraction range at all investigated temperatures, and exhibit a sigmoid trend for 1,4-dioxane + toluene mixtures wherein  $V_m^E$  changes sign from positive to negative as the mole fraction of 1,4-dioxane in the mixture is increased. The results indicate the presence of weak interactions between 1,4-dioxane and aromatic hydrocarbon molecules. The deviations in  $V_m^E$  values follow the order benzene < toluene < *p*-xylene < *m*-xylene < *o*-xylene < mesitylene. It is observed that  $V_m^E$  values depend on the number and position of the methyl groups in these aromatic hydrocarbons.

## Introduction

Knowledge of the composition and temperature dependence of physicochemical properties of multicomponent liquid mixtures provides information on the intermolecular interactions among component molecules.<sup>1–3</sup> Knowledge of physicochemical properties of nonaqueous binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in the design process (flow, mass transfer, or heat transfer calculations) of many chemical and industrial processes. As a part of our ongoing research focusing on experimental and theoretical studies of physicochemical properties of nonaqueous binary liquid mixtures,<sup>4–13</sup> we report here the results of our study on the binary mixtures of 1,4-dioxane with six aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) over the entire composition range at seven different temperatures.

1,4-Dioxane is an excellent aprotic solvent, has a zero dipole moment,<sup>14</sup> and is commercially used in polymerization and other chemical reactions in the cleaning of polymer surfaces and electronic materials. The aromatic hydrocarbon molecules possess large quadrupole moments,<sup>15</sup> which causes an orientational order in these liquids. The orientational order is thought of as a partial alignment of neighboring segments or possibly of whole molecules.<sup>15</sup> Also, binary mixtures containing aromatic hydrocarbons are interesting because they have applications in the study of polymer phase diagrams and the preferential interaction of polymers in mixed solvents.<sup>16,17</sup> 1,4-dioxane is cyclic ether that has electron-donor ability<sup>18</sup> toward the aromatic

rings that act like weak electron-acceptors.<sup>19</sup> Therefore, the 1,4-dioxane + aromatic hydrocarbon mixtures will be interesting because they involve charge-transfer interactions that may be influenced by the presence of alkyl groups on the ring.<sup>20</sup> A survey of literature indicates that there has been no temperature-dependent study on these systems from the point of view of their volumetric and refractive index behaviors. However, Khan and Subrahmanyam<sup>21</sup> reported excess volumes for 1,4-dioxane + benzene, and Francesconi and Comelli<sup>22</sup> reported excess volumes of 1,4-dioxane + toluene at 298.15 K.

In the present article, we report densities ( $\rho$ ) and refractive indices ( $n$ ) of 1,4-dioxane + benzene, + toluene, + *o*-xylene, + *m*-xylene, + *p*-xylene, and + mesitylene binary mixtures, including those of pure liquids at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K under atmospheric pressure, covering the entire composition range expressed by the mole fraction  $x_1$  of 1,4-dioxane ( $0 \leq x_1 \leq 1$ ). The experimental values of  $\rho$  and  $n$  have been used to calculate the excess molar volumes ( $V_m^E$ ), deviations in refractive index ( $\Delta n$ ), partial molar volumes ( $V_{m,1}^\circ$  and  $V_{m,2}^\circ$ ), and excess partial molar volumes ( $V_{m,1}^{E,\infty}$  and  $V_{m,2}^{E,\infty}$ ) of the components 1,4-dioxane and aromatic hydrocarbon at infinite dilution. The variation of these parameters with the composition and temperature of the mixtures has been discussed in terms of the molecular interactions in these mixtures. The effect of the number and position of the methyl groups in these aromatic hydrocarbons on molecular interactions in these mixtures has also been discussed.

## Experimental Section

1,4-dioxane and the aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) were products from Spectrochem Pvt., India and were purified by the methods

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**Table 1. Comparison of Experimental Values of Density ( $\rho$ ) and Refractive Index ( $n$ ) of Pure Liquids with the Corresponding Literature Values at 298.15 K**

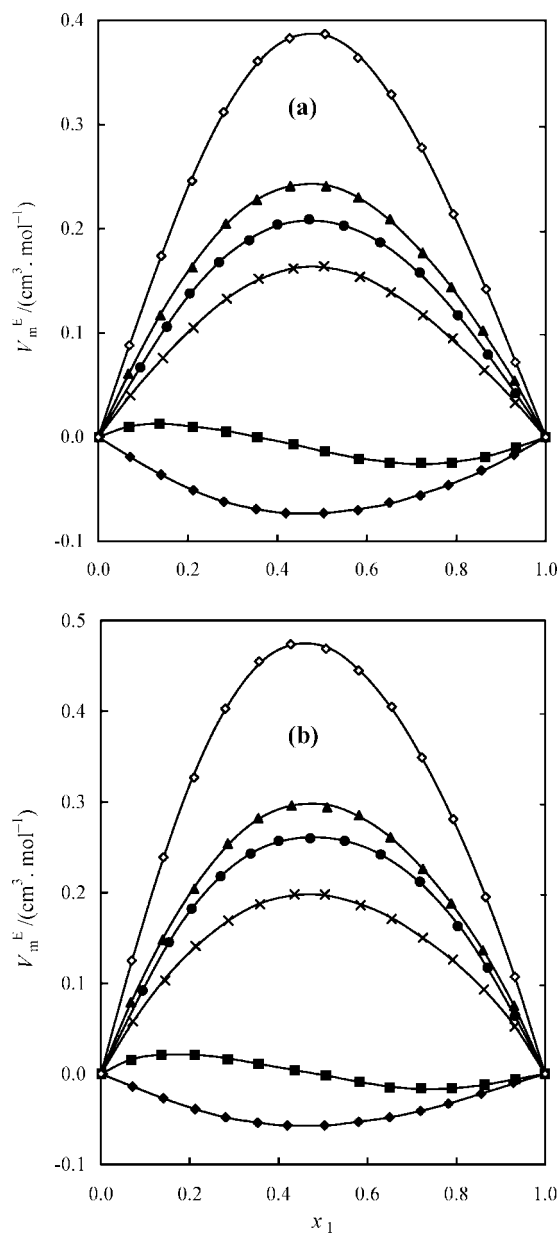
liquid	$\rho$		$n$	
	experimental	literature	experimental	literature
			$\text{g}\cdot\text{cm}^{-3}$	
1,4-dioxane	1.02795	1.02797 <sup>14</sup> 1.02787 <sup>25</sup>	1.4203	1.42025 <sup>14</sup> 1.419948 <sup>2</sup>
benzene	0.87361	0.8736 <sup>14</sup> 0.87362 <sup>1</sup> 0.87357 <sup>26</sup>	1.4980	1.49792 <sup>14</sup> 1.4979 <sup>17</sup>
toluene	0.86236	0.86219 <sup>14</sup> 0.86231 <sup>27</sup>	1.4942	1.49413 <sup>14</sup> 1.4941 <sup>17</sup>
<i>o</i> -xylene	0.87557	0.87594 <sup>14</sup> 0.87558 <sup>28</sup>	1.5029	1.50295 <sup>14</sup>
<i>m</i> -xylene	0.86002	0.86009 <sup>14</sup> 0.86000 <sup>29</sup>	1.4948	1.49494 <sup>14</sup> 1.4946 <sup>17</sup>
<i>p</i> -xylene	0.85682	0.85669 <sup>14</sup> 0.85685 <sup>30</sup>	1.4933	1.49325 <sup>14</sup>
mesitylene	0.86145	0.86111 <sup>14</sup> 0.86114 <sup>11</sup> 0.86150 <sup>17</sup>	1.4969	1.49684 <sup>14</sup>

described in the literature;<sup>14,23</sup> the mass fraction purities, as determined by gas chromatography, are: 1,4-dioxane > 0.997, benzene > 0.998, toluene > 0.998, *o*-xylene > 0.997, *m*-xylene > 0.997, *p*-xylene > 0.997, and mesitylene > 0.995. Before use, the pure chemicals were stored over 0.4 nm molecular sieves for 72 h to remove any water and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done using an electronic balance (model GR-202R, AND, Japan) with a precision of  $\pm 0.01$  mg. The uncertainty in the mole fraction was estimated to be less than  $\pm 0.0001$ .

We measured the densities of pure liquids and their binary mixtures by using a single-capillary pycnometer (made of Borosil glass) that had a bulb capacity of  $\sim 10$  mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated using triply distilled water. The uncertainty in density measurements was within  $\pm 2 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ . The refractive indices of pure liquids and their binary mixture were measured using a thermostatted Abbe refractometer. We calibrated the refractometer by measuring the refractive indices of triply distilled water and toluene at various temperatures. The values of refractive index were obtained using sodium D light. The temperature of the test liquids between the prisms of the refractometer during the measurements was maintained to an uncertainty of  $\pm 0.01$  K by circulating water through the jacket around the prisms from an electronically controlled thermostatic water bath, and the temperature was measured with a digital thermometer connected to the prism jacket. The uncertainty in refractive index measurements was within  $\pm 0.0001$ . The temperature of the test liquids during the measurements was maintained to an uncertainty of  $\pm 0.01$  K in an electronically controlled thermostatic water bath (JULABO, model ME-31A, Germany). The reliability of experimental measurements of  $\rho$  and  $n$  was ascertained by a comparison of the experimental data of pure liquids with the corresponding literature<sup>1,4,14,24–30</sup> values at 298.15 K (Table 1), and the agreement between the values was found to be good.

## Results and Discussion

The experimental values of densities ( $\rho$ ) and refractive indices ( $n$ ) of binary mixtures of 1,4-dioxane with benzene, toluene,



**Figure 1.** Variation of excess molar volume ( $V_m^E$ ) against mole fraction ( $x_1$ ) of 1,4-dioxane for the binary mixtures at (a)  $T = 298.15$  K and (b)  $T = 318.15$  K.  $\diamond$ , 1,4-dioxane + benzene;  $\blacksquare$ , 1,4-dioxane + toluene;  $\blacktriangle$ , 1,4-dioxane + *o*-xylene;  $\bullet$ , 1,4-dioxane + *m*-xylene;  $\blacktriangledown$ , 1,4-dioxane + *p*-xylene;  $\diamond$ , 1,4-dioxane + mesitylene;  $-$ , calculated from eq 3.

*o*-xylene, *m*-xylene, *p*-xylene, and mesitylene, with 1,4-dioxane as a common component, over the whole composition range expressed in the mole fraction  $x_1$  of 1,4-dioxane at the investigated temperatures are listed in Tables 2, 3, 4, 5, 6, and 7. The excess molar volumes ( $V_m^E$ ) and deviations in refractive indices ( $\Delta n$ )<sup>31</sup> of the mixtures were calculated using the following relations

$$V_m^E = xM_1(1/\rho - 1/\rho_1) + (1-x)M_2(1/\rho - 1/\rho_2) \quad (1)$$

$$\Delta n = n - [\phi n_1 + (1-\phi)n_2] \quad (2)$$

where  $M$  is the molar mass,  $\phi$  is the volume fraction (calculated using the molar volumes of the pure components obtained from the density data), and subscripts 1 and 2 stand for pure components 1,4-dioxane and aromatic hydrocarbons, respectively. The values of  $V_m^E$  and  $\Delta n$  calculated by the use of eqs 1 and 2 are included in Tables 2, 3, 4, 5, 6, and 7. The  $V_m^E$  and  $\Delta n$  values were fitted to a Redlich–Kister-type<sup>32</sup> polynomial equation

$$V_m^E/\text{cm}^3 \cdot \text{mol}^{-1} = x(1-x) \sum_{i=0}^j A_i(1-2x)^i \quad (3)$$

In case of  $\Delta n$ , volume fraction  $\phi$  has been used in place of  $x$  in eq 3. The values of coefficients,  $A_i$ , were evaluated by using the method of least-squares with all points weighted equally. The coefficients  $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_3$ , and  $A_4$  of  $V_m^E$  and  $\Delta n$  for the mixtures at all investigated temperatures are listed in Tables 8

and 9, respectively. The variations of  $V_m^E$  and  $\Delta n$  with mole fraction  $x_1$  of 1,4-dioxane along with the smoothed  $V_m^E$  and  $\Delta n$  values calculated by using eq 3 at (298.15 and 318.15) K are presented graphically in Figures 1 and 2.

The results presented in Tables 2, 3, 4, 5, 6, and 7 and Figure 1 indicate that  $V_m^E$  values are negative for 1,4-dioxane + benzene, positive for 1,4-dioxane + *o*-xylene, + *m*-xylene, + *p*-xylene, and + mesitylene mixtures over the entire mole

**Table 2. Mole Fractions ( $x_1$ ), Densities ( $\rho$ ), Refractive Indices ( $n$ ), Excess Molar Volumes ( $V_m^E$ ), and Deviations in Refractive Indices ( $\Delta n$ ) of 1,4-Dioxane (1) + Benzene (2) Mixtures at the Temperatures (288.15 to 318.15) K**

$x_1$	$\frac{\rho}{\text{g} \cdot \text{cm}^{-3}}$	$n$	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$100 \cdot \Delta n$	$x_1$	$\frac{\rho}{\text{g} \cdot \text{cm}^{-3}}$	$n$	$\frac{V_m^E}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$100 \cdot \Delta n$
$T = 288.15 \text{ K}$									
0.0000	0.88430	1.5042	0.000	0.000	0.5800	0.97348	1.4565	-0.077	0.145
0.0713	0.89516	1.4982	-0.022	0.047	0.6504	0.98443	1.4510	-0.071	0.139
0.1403	0.90571	1.4924	-0.042	0.079	0.7197	0.99523	1.4456	-0.062	0.128
0.2123	0.91674	1.4864	-0.057	0.108	0.7822	1.00500	1.4408	-0.052	0.113
0.2809	0.92728	1.4807	-0.069	0.126	0.8561	1.01658	1.4352	-0.037	0.082
0.3528	0.93834	1.4748	-0.076	0.138	0.9287	1.02799	1.4298	-0.019	0.050
0.4195	0.94863	1.4694	-0.080	0.144	1.0000	1.03923	1.4245	0.000	0.000
0.5037	0.96165	1.4626	-0.081	0.148					
$T = 293.15 \text{ K}$									
0.0000	0.87895	1.5011	0.000	0.000	0.5800	0.96789	1.4539	-0.074	0.138
0.0713	0.88977	1.4951	-0.021	0.043	0.6504	0.97882	1.4484	-0.068	0.133
0.1403	0.90028	1.4894	-0.039	0.074	0.7197	0.98961	1.4432	-0.059	0.121
0.2123	0.91128	1.4835	-0.055	0.102	0.7822	0.99937	1.4384	-0.049	0.106
0.2809	0.92179	1.4778	-0.066	0.118	0.8561	1.01094	1.4329	-0.035	0.077
0.3528	0.93282	1.4720	-0.073	0.129	0.9287	1.02235	1.4276	-0.018	0.045
0.4195	0.94309	1.4666	-0.077	0.136	1.0000	1.03359	1.4224	0.000	0.000
0.5037	0.95608	1.4599	-0.077	0.140					
$T = 298.15 \text{ K}$									
0.0000	0.87361	1.4980	0.000	0.000	0.5800	0.96230	1.4513	-0.070	0.131
0.0713	0.88438	1.4921	-0.019	0.039	0.6504	0.97321	1.4459	-0.063	0.125
0.1403	0.89485	1.4864	-0.036	0.069	0.7197	0.98399	1.4407	-0.056	0.113
0.2123	0.90582	1.4805	-0.051	0.093	0.7822	0.99374	1.4360	-0.046	0.098
0.2809	0.91630	1.4749	-0.062	0.109	0.8561	1.00530	1.4306	-0.032	0.071
0.3528	0.92731	1.4692	-0.069	0.122	0.9287	1.01671	1.4254	-0.017	0.040
0.4195	0.93755	1.4639	-0.073	0.129	1.0000	1.02795	1.4203	0.000	0.000
0.5037	0.95051	1.4573	-0.073	0.134					
$T = 303.15 \text{ K}$									
0.0000	0.86826	1.4949	0.000	0.000	0.5800	0.95671	1.4487	-0.065	0.124
0.0713	0.87899	1.4890	-0.018	0.034	0.6504	0.96760	1.4434	-0.059	0.117
0.1403	0.88942	1.4834	-0.033	0.063	0.7197	0.97837	1.4382	-0.052	0.104
0.2123	0.90036	1.4775	-0.048	0.086	0.7822	0.98811	1.4336	-0.043	0.090
0.2809	0.91081	1.4720	-0.058	0.101	0.8561	0.99966	1.4283	-0.029	0.064
0.3528	0.92180	1.4663	-0.066	0.114	0.9287	1.01107	1.4232	-0.015	0.035
0.4195	0.93201	1.4611	-0.069	0.121	1.0000	1.02232	1.4182	0.000	0.000
0.5037	0.94494	1.4546	-0.068	0.126					
$T = 308.15 \text{ K}$									
0.0000	0.86290	1.4918	0.000	0.000	0.5800	0.95112	1.4461	-0.062	0.116
0.0713	0.87360	1.4859	-0.018	0.030	0.6504	0.96200	1.4409	-0.056	0.109
0.1403	0.88399	1.4803	-0.032	0.057	0.7197	0.97275	1.4358	-0.049	0.095
0.2123	0.89490	1.4746	-0.046	0.078	0.7822	0.98248	1.4312	-0.040	0.081
0.2809	0.90532	1.4691	-0.056	0.092	0.8561	0.99402	1.4260	-0.027	0.056
0.3528	0.91628	1.4635	-0.063	0.106	0.9287	1.00543	1.4210	-0.014	0.030
0.4195	0.92647	1.4583	-0.066	0.113	1.0000	1.01668	1.4161	0.000	0.000
0.5037	0.93938	1.4519	-0.066	0.118					
$T = 313.15 \text{ K}$									
0.0000	0.85756	1.4887	0.000	0.000	0.5800	0.94554	1.4435	-0.058	0.111
0.0713	0.86822	1.4829	-0.016	0.027	0.6504	0.95640	1.4383	-0.052	0.102
0.1403	0.87858	1.4773	-0.030	0.051	0.7197	0.96713	1.4332	-0.044	0.090
0.2123	0.88945	1.4716	-0.043	0.071	0.7822	0.97685	1.4287	-0.036	0.076
0.2809	0.89984	1.4662	-0.052	0.086	0.8561	0.98839	1.4236	-0.025	0.053
0.3528	0.91077	1.4607	-0.059	0.101	0.9287	0.99979	1.4187	-0.012	0.028
0.4195	0.92094	1.4556	-0.062	0.108	1.0000	1.01105	1.4139	0.000	0.000
0.5037	0.93382	1.4492	-0.061	0.112					
$T = 318.15 \text{ K}$									
0.0000	0.85223	1.4856	0.000	0.000	0.5800	0.93996	1.4409	-0.053	0.105
0.0713	0.86284	1.4798	-0.014	0.023	0.6504	0.95080	1.4357	-0.048	0.097
0.1403	0.87317	1.4743	-0.027	0.045	0.7197	0.96152	1.4307	-0.041	0.084
0.2123	0.88400	1.4686	-0.039	0.064	0.7822	0.97123	1.4263	-0.033	0.070
0.2809	0.89436	1.4633	-0.048	0.080	0.8561	0.98276	1.4212	-0.022	0.048
0.3528	0.90526	1.4578	-0.054	0.094	0.9287	0.99415	1.4164	-0.010	0.025
0.4195	0.91541	1.4528	-0.057	0.102	1.0000	1.00542	1.4117	0.000	0.000
0.5037	0.92826	1.4465	-0.057	0.106					

**Table 3. Mole Fractions ( $x_1$ ), Densities ( $\rho$ ), Refractive Indices ( $n$ ), Excess Molar Volumes ( $V_m^E$ ), and Deviations in Refractive Indices ( $\Delta n$ ) of 1,4-Dioxane (1) + Toluene (2) Mixtures at the Temperatures (288.15 to 318.15) K**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$n$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$100 \cdot \Delta n$	$x_1$	$\rho$ g·cm <sup>-3</sup>	$n$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$100 \cdot \Delta n$
$T = 288.15$ K									
0.0000	0.87179	1.4998	0.000	0.000	0.5819	0.96038	1.4611	-0.026	0.102
0.0688	0.88109	1.4955	0.008	-0.009	0.6506	0.97239	1.4557	-0.029	0.100
0.1373	0.89067	1.4914	0.009	0.016	0.7212	0.98511	1.4499	-0.031	0.091
0.2112	0.90134	1.4869	0.006	0.044	0.7903	0.99793	1.4440	-0.029	0.078
0.2858	0.91247	1.4822	0.001	0.067	0.8640	1.01202	1.4374	-0.022	0.058
0.3552	0.92315	1.4775	-0.005	0.082	0.9336	1.02574	1.4310	-0.012	0.032
0.4361	0.93602	1.4719	-0.013	0.093	1.0000	1.03923	1.4245	0.000	0.000
0.5064	0.94757	1.4668	-0.019	0.099					
$T = 293.15$ K									
0.0000	0.86708	1.4970	0.000	0.000	0.5819	0.95515	1.4586	-0.023	0.095
0.0688	0.87632	1.4927	0.009	-0.015	0.6506	0.96710	1.4533	-0.027	0.094
0.1373	0.88584	1.4886	0.011	0.009	0.7212	0.97974	1.4475	-0.028	0.086
0.2112	0.89645	1.4842	0.008	0.037	0.7903	0.99249	1.4417	-0.026	0.072
0.2858	0.90751	1.4795	0.004	0.060	0.8640	1.00651	1.4352	-0.020	0.052
0.3552	0.91813	1.4749	-0.002	0.075	0.9336	1.02016	1.4288	-0.011	0.028
0.4361	0.93092	1.4693	-0.009	0.086	1.0000	1.03359	1.4224	0.000	0.000
0.5064	0.94241	1.4643	-0.016	0.093					
$T = 298.15$ K									
0.0000	0.86236	1.4942	0.000	0.000	0.5819	0.94992	1.4561	-0.021	0.089
0.0688	0.87154	1.4899	0.010	-0.020	0.6506	0.96180	1.4508	-0.025	0.089
0.1373	0.88100	1.4858	0.013	0.001	0.7212	0.97437	1.4451	-0.025	0.081
0.2112	0.89155	1.4814	0.010	0.030	0.7903	0.98706	1.4393	-0.025	0.066
0.2858	0.90255	1.4768	0.005	0.053	0.8640	1.00100	1.4329	-0.019	0.047
0.3552	0.91311	1.4722	-0.000	0.069	0.9336	1.01458	1.4266	-0.010	0.025
0.4361	0.92582	1.4667	-0.007	0.079	1.0000	1.02795	1.4203	0.000	0.000
0.5064	0.93725	1.4617	-0.014	0.086					
$T = 303.15$ K									
0.0000	0.85764	1.4913	0.000	0.000	0.5819	0.94469	1.4536	-0.018	0.083
0.0688	0.86676	1.4870	0.012	-0.022	0.6506	0.95650	1.4483	-0.021	0.081
0.1373	0.87616	1.4829	0.015	-0.008	0.7212	0.96901	1.4427	-0.023	0.076
0.2112	0.88665	1.4786	0.012	0.020	0.7903	0.98163	1.4370	-0.022	0.061
0.2858	0.89758	1.4740	0.009	0.043	0.8640	0.99550	1.4306	-0.017	0.043
0.3552	0.90808	1.4695	0.003	0.062	0.9336	1.00901	1.4244	-0.009	0.023
0.4361	0.92072	1.4640	-0.003	0.073	1.0000	1.02232	1.4182	0.000	0.000
0.5064	0.93209	1.4591	-0.011	0.080					
$T = 308.15$ K									
0.0000	0.85293	1.4884	0.000	0.000	0.5819	0.93946	1.4510	-0.015	0.077
0.0688	0.86199	1.4841	0.013	-0.024	0.6506	0.95121	1.4458	-0.019	0.075
0.1373	0.87133	1.4800	0.017	-0.017	0.7212	0.96365	1.4403	-0.021	0.068
0.2112	0.88175	1.4757	0.016	0.011	0.7903	0.97620	1.4346	-0.021	0.056
0.2858	0.89262	1.4712	0.012	0.034	0.8640	0.98999	1.4283	-0.015	0.038
0.3552	0.90306	1.4668	0.006	0.053	0.9336	1.00344	1.4222	-0.008	0.019
0.4361	0.91563	1.4614	-0.001	0.066	1.0000	1.01668	1.4161	0.000	0.000
0.5064	0.92693	1.4565	-0.008	0.074					
$T = 313.15$ K									
0.0000	0.84821	1.4855	0.000	0.000	0.5819	0.93423	1.4484	-0.012	0.070
0.0688	0.85721	1.4812	0.014	-0.028	0.6506	0.94592	1.4433	-0.017	0.069
0.1373	0.86649	1.4771	0.019	-0.025	0.7212	0.95829	1.4378	-0.019	0.061
0.2112	0.87685	1.4729	0.018	0.001	0.7903	0.97077	1.4322	-0.018	0.051
0.2858	0.88766	1.4684	0.014	0.025	0.8640	0.98449	1.4260	-0.014	0.035
0.3552	0.89804	1.4640	0.009	0.046	0.9336	0.99787	1.4199	-0.007	0.018
0.4361	0.91054	1.4587	0.002	0.059	1.0000	1.01105	1.4139	0.000	0.000
0.5064	0.92177	1.4539	-0.005	0.067					
$T = 318.15$ K									
0.0000	0.84349	1.4826	0.000	0.000	0.5819	0.92900	1.4458	-0.009	0.063
0.0688	0.85243	1.4783	0.015	-0.032	0.6506	0.94063	1.4408	-0.015	0.063
0.1373	0.86165	1.4742	0.021	-0.033	0.7212	0.95293	1.4353	-0.016	0.055
0.2112	0.87195	1.4700	0.021	-0.010	0.7903	0.96534	1.4298	-0.016	0.047
0.2858	0.88270	1.4655	0.016	0.016	0.8640	0.97899	1.4236	-0.012	0.031
0.3552	0.89302	1.4613	0.011	0.038	0.9336	0.99230	1.4176	-0.006	0.017
0.4361	0.90545	1.4560	0.004	0.053	1.0000	1.00542	1.4117	0.000	0.000
0.5064	0.91661	1.4512	-0.002	0.061					

fraction range at all investigated temperatures, and exhibit a sigmoid trend for 1,4-dioxane + toluene mixtures wherein  $V_m^E$  changes sign from positive to negative as the concentration of 1,4-dioxane in the mixture is increased. The  $V_m^E$  values obtained in the present work compare well with those reported by other investigators for 1,4-dioxane + benzene<sup>21</sup> and 1,4-dioxane + toluene<sup>22</sup> mixtures at 298.15 K. The extent of deviation in  $V_m^E$  from linear dependence on mole fraction

(Figure 1) follows the sequence benzene < toluene < *p*-xylene < *m*-xylene < *o*-xylene < mesitylene. This suggests that there is an expansion in volume of the mixtures as we move from benzene to mesitylene.

The behavior of  $V_m^E$  with the composition of the mixture can be qualitatively examined by considering the nature of the component molecules in the pure state and in the mixture. The molecules of 1,4-dioxane are nonpolar, and those of the

**Table 4. Mole Fractions ( $x_1$ ), Densities ( $\rho$ ), Refractive Indices ( $n$ ), Excess Molar Volumes ( $V_m^E$ ), and Deviations in Refractive Indices ( $\Delta n$ ) of 1,4-Dioxane (1) + *o*-Xylene (2) Mixtures at the Temperatures (288.15 to 318.15) K**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$n$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$100 \cdot \Delta n$	$x_1$	$\rho$ g·cm <sup>-3</sup>	$n$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$100 \cdot \Delta n$
$T = 288.15$ K									
0.0000	0.88409	1.5083	0.000	0.000	0.5810	0.95889	1.4606	0.202	-0.625
0.0672	0.89120	1.5029	0.053	-0.134	0.6518	0.97057	1.4545	0.183	-0.610
0.1391	0.89918	1.4972	0.102	-0.252	0.7248	0.98338	1.4482	0.153	-0.561
0.2103	0.90748	1.4914	0.144	-0.364	0.7888	0.99525	1.4427	0.122	-0.484
0.2853	0.91669	1.4853	0.181	-0.458	0.8595	1.00911	1.4365	0.085	-0.376
0.3543	0.92567	1.4796	0.202	-0.530	0.9298	1.02375	1.4305	0.042	-0.210
0.4293	0.93600	1.4734	0.213	-0.583	1.0000	1.03923	1.4245	0.000	0.000
0.5092	0.94769	1.4667	0.214	-0.617					
$T = 293.15$ K									
0.0000	0.87983	1.5055	0.000	0.000	0.5810	0.95386	1.4580	0.216	-0.638
0.0672	0.88685	1.5001	0.057	-0.141	0.6518	0.96544	1.4520	0.196	-0.623
0.1391	0.89473	1.4944	0.110	-0.262	0.7248	0.97814	1.4457	0.165	-0.575
0.2103	0.90295	1.4886	0.154	-0.375	0.7888	0.98991	1.4402	0.133	-0.504
0.2853	0.91206	1.4825	0.193	-0.472	0.8595	1.00366	1.4342	0.093	-0.387
0.3543	0.92095	1.4769	0.215	-0.541	0.9298	1.01819	1.4282	0.048	-0.222
0.4293	0.93118	1.4707	0.227	-0.596	1.0000	1.03359	1.4224	0.000	0.000
0.5092	0.94277	1.4641	0.227	-0.630					
$T = 298.15$ K									
0.0000	0.87557	1.5029	0.000	0.000	0.5810	0.94883	1.4554	0.230	-0.661
0.0672	0.88250	1.4974	0.061	-0.153	0.6518	0.96031	1.4495	0.209	-0.641
0.1391	0.89029	1.4917	0.117	-0.276	0.7248	0.97290	1.4433	0.177	-0.586
0.2103	0.89842	1.4858	0.163	-0.397	0.7888	0.98457	1.4378	0.144	-0.519
0.2853	0.90743	1.4798	0.205	-0.492	0.8595	0.99821	1.4318	0.102	-0.401
0.3543	0.91623	1.4742	0.228	-0.566	0.9298	1.01263	1.4259	0.054	-0.237
0.4293	0.92636	1.4681	0.241	-0.618	1.0000	1.02795	1.4203	0.000	0.000
0.5092	0.93785	1.4615	0.241	-0.645					
$T = 303.15$ K									
0.0000	0.87131	1.5002	0.000	0.000	0.5810	0.94381	1.4528	0.243	-0.680
0.0672	0.87815	1.4946	0.065	-0.160	0.6518	0.95519	1.4469	0.222	-0.658
0.1391	0.88585	1.4889	0.125	-0.287	0.7248	0.96766	1.4408	0.190	-0.604
0.2103	0.89389	1.4831	0.173	-0.411	0.7888	0.97923	1.4354	0.155	-0.537
0.2853	0.90280	1.4771	0.218	-0.510	0.8595	0.99277	1.4295	0.110	-0.414
0.3543	0.91151	1.4714	0.242	-0.583	0.9298	1.00708	1.4236	0.059	-0.251
0.4293	0.92155	1.4654	0.255	-0.637	1.0000	1.02232	1.4182	0.000	0.000
0.5092	0.93293	1.4589	0.255	-0.665					
$T = 308.15$ K									
0.0000	0.86705	1.4975	0.000	0.000	0.5810	0.93879	1.4502	0.257	-0.698
0.0672	0.87380	1.4918	0.070	-0.173	0.6518	0.95007	1.4444	0.234	-0.676
0.1391	0.88141	1.4861	0.133	-0.303	0.7248	0.96243	1.4383	0.201	-0.627
0.2103	0.88936	1.4803	0.183	-0.425	0.7888	0.97390	1.4329	0.165	-0.554
0.2853	0.89817	1.4743	0.230	-0.527	0.8595	0.98733	1.4271	0.118	-0.432
0.3543	0.90679	1.4687	0.256	-0.604	0.9298	1.00153	1.4213	0.065	-0.265
0.4293	0.91674	1.4627	0.268	-0.657	1.0000	1.01668	1.4161	0.000	0.000
0.5092	0.92802	1.4562	0.267	-0.684					
$T = 313.15$ K									
0.0000	0.86279	1.4948	0.000	0.000	0.5810	0.93377	1.4476	0.271	-0.712
0.0672	0.86945	1.4890	0.074	-0.185	0.6518	0.94495	1.4418	0.248	-0.694
0.1391	0.87697	1.4833	0.140	-0.322	0.7248	0.95720	1.4357	0.213	-0.644
0.2103	0.88483	1.4775	0.194	-0.447	0.7888	0.96857	1.4304	0.176	-0.575
0.2853	0.89355	1.4715	0.242	-0.547	0.8595	0.98189	1.4246	0.127	-0.452
0.3543	0.90208	1.4659	0.269	-0.622	0.9298	0.99599	1.4190	0.070	-0.274
0.4293	0.91193	1.4600	0.282	-0.673	1.0000	1.01105	1.4139	0.000	0.000
0.5092	0.92311	1.4535	0.281	-0.701					
$T = 318.15$ K									
0.0000	0.85853	1.4921	0.000	0.000	0.5810	0.92875	1.4450	0.285	-0.725
0.0672	0.86510	1.4862	0.079	-0.197	0.6518	0.93983	1.4392	0.261	-0.711
0.1391	0.87253	1.4804	0.148	-0.342	0.7248	0.95197	1.4332	0.226	-0.660
0.2103	0.88030	1.4746	0.204	-0.470	0.7888	0.96324	1.4279	0.188	-0.590
0.2853	0.88893	1.4687	0.254	-0.567	0.8595	0.97645	1.4221	0.136	-0.472
0.3543	0.89737	1.4632	0.282	-0.640	0.9298	0.99045	1.4166	0.075	-0.284
0.4293	0.90712	1.4573	0.296	-0.689	1.0000	1.00542	1.4117	0.000	0.000
0.5092	0.91820	1.4509	0.294	-0.718					

aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) have a large quadrupole moment,<sup>15</sup> which causes molecular order in the pure state. Mixing 1,4-dioxane with the aromatic hydrocarbons would induce a decrease in the molecular order in the latter, resulting in an

expansion in volume and hence positive  $V_m^E$  values. There is a possibility of electron donor–acceptor-type interactions<sup>26</sup> between electronegative oxygen atoms of 1,4-dioxane (acting as donor) and the  $\pi$  electrons of the ring of aromatic hydrocarbon molecules (acting as acceptor), which would

**Table 5. Mole Fractions ( $x_1$ ), Densities ( $\rho$ ), Refractive Indices ( $n$ ), Excess Molar Volumes ( $V_m^E$ ), and Deviations in Refractive Indices ( $\Delta n$ ) of 1,4-Dioxane (1) + *m*-Xylene (2) Mixtures at the Temperatures (288.15 to 318.15) K**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$n$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$100 \cdot \Delta n$	$x_1$	$\rho$ g·cm <sup>-3</sup>	$n$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$100 \cdot \Delta n$
T = 288.15 K									
0.0000	0.86859	1.4999	0.000	0.000	0.5487	0.94500	1.4598	0.178	-0.561
0.0938	0.87961	1.4933	0.055	-0.155	0.6300	0.95944	1.4536	0.160	-0.547
0.1532	0.88695	1.4890	0.087	-0.249	0.7182	0.97623	1.4468	0.131	-0.494
0.2046	0.89354	1.4852	0.114	-0.328	0.8035	0.99374	1.4401	0.094	-0.405
0.2698	0.90226	1.4805	0.142	-0.402	0.8708	1.00847	1.4348	0.061	-0.299
0.3374	0.91176	1.4755	0.164	-0.472	0.9324	1.02271	1.4299	0.032	-0.174
0.4002	0.92105	1.4709	0.178	-0.515	1.0000	1.03923	1.4245	0.000	0.000
0.4714	0.93218	1.4656	0.183	-0.548					
T = 293.15 K									
0.0000	0.86431	1.4974	0.000	0.000	0.5487	0.94002	1.4574	0.191	-0.573
0.0938	0.87520	1.4907	0.062	-0.167	0.6300	0.95433	1.4512	0.173	-0.563
0.1532	0.88246	1.4864	0.097	-0.268	0.7182	0.97098	1.4444	0.145	-0.509
0.2046	0.88898	1.4826	0.126	-0.349	0.8035	0.98836	1.4378	0.105	-0.419
0.2698	0.89762	1.4779	0.155	-0.419	0.8708	1.00299	1.4325	0.070	-0.311
0.3374	0.90705	1.4730	0.177	-0.487	0.9324	1.01715	1.4277	0.037	-0.179
0.4002	0.91626	1.4684	0.191	-0.531	1.0000	1.03359	1.4224	0.000	0.000
0.4714	0.92730	1.4631	0.196	-0.563					
T = 298.15 K									
0.0000	0.86002	1.4948	0.000	0.000	0.5487	0.93504	1.4549	0.203	-0.585
0.0938	0.87079	1.4880	0.067	-0.181	0.6300	0.94922	1.4487	0.187	-0.574
0.1532	0.87797	1.4837	0.106	-0.279	0.7182	0.96573	1.4420	0.158	-0.525
0.2046	0.88442	1.4799	0.138	-0.361	0.8035	0.98298	1.4354	0.117	-0.435
0.2698	0.89298	1.4753	0.168	-0.434	0.8708	0.99751	1.4302	0.079	-0.322
0.3374	0.90234	1.4704	0.189	-0.499	0.9324	1.01159	1.4255	0.042	-0.189
0.4002	0.91147	1.4658	0.204	-0.541	1.0000	1.02795	1.4203	0.000	0.000
0.4714	0.92242	1.4606	0.209	-0.576					
T = 303.15 K									
0.0000	0.85574	1.4922	0.000	0.000	0.5487	0.93006	1.4524	0.217	-0.597
0.0938	0.86638	1.4853	0.074	-0.194	0.6300	0.94411	1.4462	0.201	-0.590
0.1532	0.87348	1.4811	0.116	-0.289	0.7182	0.96049	1.4395	0.172	-0.541
0.2046	0.87987	1.4772	0.149	-0.378	0.8035	0.97760	1.4329	0.129	-0.457
0.2698	0.88835	1.4726	0.181	-0.449	0.8708	0.99203	1.4279	0.089	-0.337
0.3374	0.89763	1.4677	0.203	-0.516	0.9324	1.00603	1.4232	0.048	-0.199
0.4002	0.90668	1.4632	0.218	-0.556	1.0000	1.02232	1.4182	0.000	0.000
0.4714	0.91755	1.4580	0.222	-0.589					
T = 308.15 K									
0.0000	0.85145	1.4896	0.000	0.000	0.5487	0.92508	1.4498	0.229	-0.614
0.0938	0.86197	1.4826	0.080	-0.207	0.6300	0.93901	1.4437	0.214	-0.606
0.1532	0.86899	1.4783	0.125	-0.309	0.7182	0.95525	1.4371	0.184	-0.557
0.2046	0.87532	1.4745	0.160	-0.395	0.8035	0.97223	1.4305	0.140	-0.478
0.2698	0.88372	1.4699	0.193	-0.468	0.8708	0.98656	1.4255	0.098	-0.353
0.3374	0.89292	1.4651	0.215	-0.534	0.9324	1.00048	1.4209	0.053	-0.214
0.4002	0.90190	1.4606	0.230	-0.571	1.0000	1.01668	1.4161	0.000	0.000
0.4714	0.91268	1.4555	0.234	-0.602					
T = 313.15 K									
0.0000	0.84717	1.4870	0.000	0.000	0.5487	0.92010	1.4473	0.243	-0.626
0.0938	0.85756	1.4799	0.087	-0.219	0.6300	0.93391	1.4412	0.228	-0.617
0.1532	0.86450	1.4756	0.136	-0.328	0.7182	0.95001	1.4346	0.198	-0.572
0.2046	0.87077	1.4718	0.172	-0.411	0.8035	0.96686	1.4280	0.152	-0.492
0.2698	0.87909	1.4672	0.206	-0.486	0.8708	0.98109	1.4231	0.107	-0.370
0.3374	0.88821	1.4624	0.229	-0.549	0.9324	0.99493	1.4186	0.058	-0.220
0.4002	0.89712	1.4580	0.244	-0.588	1.0000	1.01105	1.4139	0.000	0.000
0.4714	0.90781	1.4529	0.247	-0.617					
T = 318.15 K									
0.0000	0.84288	1.4844	0.000	0.000	0.5487	0.91512	1.4447	0.257	-0.639
0.0938	0.85316	1.4772	0.092	-0.232	0.6300	0.92881	1.4387	0.242	-0.628
0.1532	0.86001	1.4728	0.145	-0.347	0.7182	0.94477	1.4321	0.212	-0.587
0.2046	0.86622	1.4691	0.182	-0.426	0.8035	0.96150	1.4256	0.163	-0.506
0.2698	0.87447	1.4645	0.218	-0.503	0.8708	0.97562	1.4206	0.117	-0.388
0.3374	0.88350	1.4597	0.243	-0.568	0.9324	0.98938	1.4163	0.064	-0.226
0.4002	0.89234	1.4553	0.257	-0.605	1.0000	1.00542	1.4117	0.000	0.000
0.4714	0.90294	1.4503	0.260	-0.631					

result in negative  $V_m^E$  values. The observed trends in  $V_m^E$  values suggest the presence of weak donor–acceptor (charge-transfer) interactions between 1,4-dioxane and aromatic hydrocarbon molecules in these mixtures, which follows the order benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. Recently, Ma et al.<sup>26</sup> have also reported a similar type of donor–acceptor interactions between the oxygen atom of sulfolane and the  $\pi$  electrons of the aromatic

hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene), and Ali et al.<sup>12</sup> also reported similar interactions between the oxygen atom of dimethyl sulfoxide and the  $\pi$  electrons on the ring of the aromatic hydrocarbon (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) binary mixtures.

It is observed that  $V_m^E$  values increase as the number of  $-\text{CH}_3$  groups in the ring increase from benzene (without

**Table 6. Mole Fractions ( $x_1$ ), Densities ( $\rho$ ), Refractive Indices ( $n$ ), Excess Molar Volumes ( $V_m^E$ ), and Deviations in Refractive Indices ( $\Delta n$ ) of 1,4-Dioxane (1) + *p*-Xylene (2) Mixtures at the Temperatures (288.15 to 318.15) K**

$x_1$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$n$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$100\cdot\Delta n$ $\text{g}\cdot\text{cm}^{-3}$	$x_1$	$\frac{\rho}{\text{cm}^3\cdot\text{mol}^{-1}}$	$n$	$V_m^E$	$100\cdot\Delta n$
T = 288.15 K									
0.0000	0.86552	1.4985	0.000	0.000	0.5846	0.94987	1.4569	0.138	-0.511
0.0716	0.87409	1.4937	0.030	-0.106	0.6543	0.96276	1.4516	0.123	-0.496
0.1445	0.88322	1.4887	0.061	-0.206	0.7249	0.97661	1.4462	0.102	-0.453
0.2132	0.89223	1.4839	0.089	-0.293	0.7923	0.99062	1.4410	0.079	-0.385
0.2871	0.90241	1.4787	0.116	-0.369	0.8623	1.00605	1.4355	0.052	-0.289
0.3582	0.91276	1.4736	0.133	-0.430	0.9311	1.02214	1.4301	0.025	-0.156
0.4358	0.92473	1.4680	0.143	-0.474	1.0000	1.03923	1.4245	0.000	0.000
0.5042	0.93590	1.4629	0.146	-0.506					
T = 293.15 K									
0.0000	0.86117	1.4959	0.000	0.000	0.5846	0.94484	1.4544	0.146	-0.525
0.0716	0.86964	1.4911	0.036	-0.113	0.6543	0.95763	1.4492	0.131	-0.509
0.1445	0.87869	1.4861	0.068	-0.216	0.7249	0.97138	1.4438	0.109	-0.465
0.2132	0.88763	1.4813	0.097	-0.305	0.7923	0.98527	1.4386	0.087	-0.401
0.2871	0.89773	1.4761	0.124	-0.384	0.8623	1.00060	1.4332	0.058	-0.299
0.3582	0.90800	1.4710	0.142	-0.443	0.9311	1.01658	1.4279	0.029	-0.166
0.4358	0.91988	1.4655	0.153	-0.486	1.0000	1.03359	1.4224	0.000	0.000
0.5042	0.93097	1.4604	0.155	-0.516					
T = 298.15 K									
0.0000	0.85682	1.4933	0.000	0.000	0.5846	0.93981	1.4520	0.154	-0.534
0.0716	0.86520	1.4884	0.040	-0.120	0.6543	0.95250	1.4467	0.139	-0.521
0.1445	0.87416	1.4834	0.076	-0.226	0.7249	0.96615	1.4414	0.117	-0.476
0.2132	0.88303	1.4786	0.105	-0.318	0.7923	0.97992	1.4362	0.095	-0.416
0.2871	0.89305	1.4734	0.133	-0.400	0.8623	0.99515	1.4309	0.064	-0.309
0.3582	0.90324	1.4684	0.152	-0.457	0.9311	1.01103	1.4256	0.033	-0.175
0.4358	0.91503	1.4629	0.162	-0.498	1.0000	1.02795	1.4203	0.000	0.000
0.5042	0.92604	1.4579	0.164	-0.525					
T = 303.15 K									
0.0000	0.85247	1.4907	0.000	0.000	0.5846	0.93478	1.4495	0.163	-0.543
0.0716	0.86076	1.4858	0.045	-0.128	0.6543	0.94738	1.4443	0.147	-0.534
0.1445	0.86964	1.4808	0.083	-0.236	0.7249	0.96092	1.4390	0.125	-0.493
0.2132	0.87843	1.4760	0.114	-0.330	0.7923	0.97458	1.4338	0.104	-0.432
0.2871	0.88837	1.4708	0.143	-0.415	0.8623	0.98970	1.4286	0.071	-0.324
0.3582	0.89849	1.4658	0.161	-0.470	0.9311	1.00548	1.4234	0.038	-0.185
0.4358	0.91019	1.4604	0.171	-0.510	1.0000	1.02232	1.4182	0.000	0.000
0.5042	0.92112	1.4554	0.172	-0.535					
T = 308.15 K									
0.0000	0.84812	1.4881	0.000	0.000	0.5846	0.92976	1.4470	0.170	-0.557
0.0716	0.85632	1.4831	0.049	-0.135	0.6543	0.94226	1.4418	0.155	-0.547
0.1445	0.86512	1.4781	0.089	-0.246	0.7249	0.95569	1.4365	0.133	-0.509
0.2132	0.87383	1.4733	0.122	-0.348	0.7923	0.96925	1.4314	0.111	-0.448
0.2871	0.88369	1.4681	0.152	-0.430	0.8623	0.98425	1.4262	0.078	-0.340
0.3582	0.89374	1.4632	0.169	-0.483	0.9311	0.99993	1.4211	0.042	-0.200
0.4358	0.90535	1.4578	0.180	-0.521	1.0000	1.01668	1.4161	0.000	0.000
0.5042	0.91620	1.4529	0.180	-0.549					
T = 313.15 K									
0.0000	0.84377	1.4855	0.000	0.000	0.5846	0.92474	1.4445	0.178	-0.566
0.0716	0.85188	1.4805	0.054	-0.142	0.6543	0.93714	1.4394	0.163	-0.554
0.1445	0.86060	1.4754	0.096	-0.260	0.7249	0.95046	1.4341	0.141	-0.520
0.2132	0.86923	1.4706	0.131	-0.359	0.7923	0.96392	1.4290	0.118	-0.456
0.2871	0.87902	1.4655	0.161	-0.444	0.8623	0.97880	1.4238	0.086	-0.352
0.3582	0.88899	1.4606	0.178	-0.499	0.9311	0.99438	1.4188	0.047	-0.206
0.4358	0.90051	1.4552	0.189	-0.535	1.0000	1.01105	1.4139	0.000	0.000
0.5042	0.91128	1.4503	0.189	-0.559					
T = 318.15 K									
0.0000	0.83942	1.4830	0.000	0.000	0.5846	0.91972	1.4420	0.186	-0.577
0.0716	0.84744	1.4778	0.058	-0.154	0.6543	0.93202	1.4369	0.171	-0.563
0.1445	0.85608	1.4727	0.103	-0.279	0.7249	0.94523	1.4316	0.150	-0.532
0.2132	0.86463	1.4680	0.141	-0.374	0.7923	0.95859	1.4266	0.126	-0.466
0.2871	0.87435	1.4628	0.169	-0.461	0.8623	0.97335	1.4214	0.093	-0.365
0.3582	0.88424	1.4580	0.187	-0.513	0.9311	0.98883	1.4165	0.052	-0.213
0.4358	0.89567	1.4526	0.198	-0.551	1.0000	1.00542	1.4117	0.000	0.000
0.5042	0.90636	1.4478	0.198	-0.572					

$-\text{CH}_3$  groups) to mesitylene (with three  $-\text{CH}_3$  groups). This is due to the fact that the methyl group ( $-\text{CH}_3$ ) is an electron-releasing group that would enhance the electron density of the benzene ring of the aromatic molecules; however, the electron-accepting tendency of the aromatic ring would decrease as we move from benzene to mesitylene, resulting in decreased donor-acceptor interaction between unlike molecules with an increase in the number of methyl groups

( $-\text{CH}_3$ ) in the aromatic hydrocarbon molecule, which would cause an expansion in the volume of the mixture. This would cause an increase in  $V_m^E$  values in the sequence benzene < toluene < xylenes < mesitylene as we move from benzene to mesitylene.

Another factor that would cause an increase in  $V_m^E$  values is the steric hindrance due to  $-\text{CH}_3$  groups of the rings. As the number of methyl groups in the ring increase from

**Table 7. Mole Fractions ( $x_1$ ), Densities ( $\rho$ ), Refractive Indices ( $n$ ), Excess Molar Volumes ( $V_m^E$ ), and Deviations in Refractive Indices ( $\Delta n$ ) of 1,4-Dioxane (1) + Mesitylene (2) Mixtures at the Temperatures (288.15 to 318.15) K**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$n$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$100 \cdot \Delta n$	$x_1$	$\rho$ g·cm <sup>-3</sup>	$n$	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$100 \cdot \Delta n$
$T = 288.15$ K									
0.0000	0.86928	1.5020	0.000	0.000	0.5801	0.94434	1.4584	0.327	-0.806
0.0696	0.87628	1.4969	0.070	-0.170	0.6548	0.95796	1.4525	0.291	-0.783
0.1408	0.88383	1.4916	0.143	-0.332	0.7227	0.97144	1.4470	0.243	-0.733
0.2098	0.89162	1.4865	0.207	-0.465	0.7936	0.98675	1.4412	0.181	-0.638
0.2800	0.90004	1.4812	0.269	-0.588	0.8663	1.00378	1.4354	0.117	-0.469
0.3558	0.90987	1.4755	0.315	-0.689	0.9319	1.02049	1.4300	0.056	-0.275
0.4276	0.91997	1.4701	0.338	-0.755	1.0000	1.03923	1.4245	0.000	0.000
0.5066	0.93203	1.4641	0.347	-0.796					
$T = 293.15$ K									
0.0000	0.86537	1.4995	0.000	0.000	0.5801	0.93954	1.4558	0.346	-0.832
0.0696	0.87224	1.4942	0.080	-0.192	0.6548	0.95301	1.4500	0.310	-0.808
0.1408	0.87967	1.4889	0.160	-0.355	0.7227	0.96636	1.4445	0.261	-0.756
0.2098	0.88736	1.4838	0.227	-0.490	0.7936	0.98151	1.4388	0.197	-0.660
0.2800	0.89568	1.4786	0.291	-0.609	0.8663	0.99839	1.4330	0.129	-0.489
0.3558	0.90540	1.4729	0.338	-0.713	0.9319	1.01496	1.4277	0.064	-0.290
0.4276	0.91540	1.4675	0.361	-0.781	1.0000	1.03359	1.4224	0.000	0.000
0.5066	0.92735	1.4615	0.367	-0.820					
$T = 298.15$ K									
0.0000	0.86145	1.4969	0.000	0.000	0.5801	0.93474	1.4532	0.364	-0.854
0.0696	0.86820	1.4915	0.088	-0.203	0.6548	0.94806	1.4474	0.329	-0.828
0.1408	0.87552	1.4862	0.174	-0.369	0.7227	0.96128	1.4420	0.278	-0.775
0.2098	0.88310	1.4811	0.246	-0.506	0.7936	0.97627	1.4363	0.214	-0.679
0.2800	0.89132	1.4758	0.312	-0.633	0.8663	0.99300	1.4306	0.142	-0.508
0.3558	0.90093	1.4702	0.361	-0.735	0.9319	1.00943	1.4254	0.072	-0.304
0.4276	0.91083	1.4648	0.383	-0.801	1.0000	1.02795	1.4203	0.000	0.000
0.5066	0.92267	1.4589	0.387	-0.837					
$T = 303.15$ K									
0.0000	0.85754	1.4944	0.000	0.000	0.5801	0.92994	1.4506	0.384	-0.880
0.0696	0.86416	1.4888	0.099	-0.225	0.6548	0.94312	1.4449	0.348	-0.853
0.1408	0.87137	1.4835	0.191	-0.398	0.7227	0.95621	1.4395	0.295	-0.798
0.2098	0.87884	1.4784	0.267	-0.536	0.7936	0.97104	1.4338	0.230	-0.705
0.2800	0.88696	1.4731	0.335	-0.665	0.8663	0.98761	1.4282	0.156	-0.534
0.3558	0.89646	1.4675	0.385	-0.763	0.9319	1.00391	1.4231	0.081	-0.319
0.4276	0.90626	1.4622	0.406	-0.827	1.0000	1.02232	1.4182	0.000	0.000
0.5066	0.91799	1.4563	0.408	-0.861					
$T = 308.15$ K									
0.0000	0.85363	1.4918	0.000	0.000	0.5801	0.92514	1.4480	0.404	-0.901
0.0696	0.86013	1.4861	0.108	-0.237	0.6548	0.93818	1.4423	0.367	-0.873
0.1408	0.86722	1.4807	0.207	-0.416	0.7227	0.95114	1.4370	0.313	-0.822
0.2098	0.87459	1.4756	0.287	-0.557	0.7936	0.96581	1.4313	0.247	-0.729
0.2800	0.88260	1.4703	0.358	-0.688	0.8663	0.98223	1.4257	0.168	-0.558
0.3558	0.89200	1.4648	0.408	-0.785	0.9319	0.99839	1.4208	0.089	-0.338
0.4276	0.90170	1.4595	0.428	-0.846	1.0000	1.01668	1.4161	0.000	0.000
0.5066	0.91332	1.4537	0.428	-0.884					
$T = 313.15$ K									
0.0000	0.84971	1.4893	0.000	0.000	0.5801	0.92034	1.4454	0.424	-0.923
0.0696	0.85610	1.4834	0.115	-0.258	0.6548	0.93325	1.4397	0.386	-0.897
0.1408	0.86307	1.4779	0.222	-0.449	0.7227	0.94607	1.4344	0.330	-0.844
0.2098	0.87034	1.4729	0.306	-0.585	0.7936	0.96058	1.4288	0.264	-0.748
0.2800	0.87825	1.4676	0.380	-0.718	0.8663	0.97685	1.4233	0.181	-0.576
0.3558	0.88754	1.4621	0.431	-0.811	0.9319	0.99287	1.4184	0.098	-0.350
0.4276	0.89714	1.4568	0.450	-0.874	1.0000	1.01105	1.4139	0.000	0.000
0.5066	0.90865	1.4510	0.448	-0.909					
$T = 318.15$ K									
0.0000	0.84580	1.4868	0.000	0.000	0.5801	0.91554	1.4428	0.445	-0.945
0.0696	0.85207	1.4807	0.125	-0.279	0.6548	0.92832	1.4371	0.405	-0.921
0.1408	0.85892	1.4751	0.239	-0.481	0.7227	0.94100	1.4318	0.349	-0.871
0.2098	0.86609	1.4701	0.327	-0.613	0.7936	0.95535	1.4263	0.281	-0.773
0.2800	0.87390	1.4648	0.403	-0.747	0.8663	0.97147	1.4208	0.195	-0.593
0.3558	0.88308	1.4593	0.455	-0.842	0.9319	0.98735	1.4161	0.107	-0.361
0.4276	0.89258	1.4542	0.474	-0.897	1.0000	1.00542	1.4117	0.000	0.000
0.5066	0.90398	1.4484	0.469	-0.934					

benzene to mesitylene, the closer approach of the 1,4-dioxane molecule to the aromatic ring becomes increasingly difficult, resulting in decreased interaction between 1,4-dioxane and aromatic hydrocarbon molecules. Among the xylenes, the magnitude of negative  $V_m^E$  values follows the order *o*-xylene < *m*-xylene < *p*-xylene, which suggests that the position of  $-\text{CH}_3$  groups on the aromatic ring plays a substantial role

in deciding the magnitude of  $V_m^E$  and hence the order of interaction between the component molecules of the mixtures. The more negative  $V_m^E$  values for 1,4-dioxane + *p*-xylene are observed because 1,4-dioxane molecules could more closely approach the ring of *p*-xylene from two directions, as compared with *o*- and *m*-xylenes; this shows a maximum interaction of 1,4-dioxane molecule with the former xylene



**Table 8. Coefficients ( $A_i$ ) from Equation 3 for  $V_m^E$  and Standard Deviations ( $\sigma$ ) for 1,4-Dioxane + Aromatic Hydrocarbon Mixtures at Temperatures (288.15 to 318.15) K**

T/K	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma$
1,4-dioxane + benzene						
288.15	-0.3241	-0.0394	-0.0063	0.0167	0.0243	0.0002
293.15	-0.3091	-0.0401	0.0001	0.0195	0.0201	0.0002
298.15	-0.2921	-0.0426	0.0044	0.0353	0.0311	0.0002
303.15	-0.2752	-0.0475	0.0092	0.0394	0.0406	0.0004
308.15	-0.2631	-0.0466	0.0237	0.0294	0.0187	0.0004
313.15	-0.2469	-0.0499	0.0368	0.0258	0.0083	0.0002
288.15	-0.3241	-0.0394	-0.0063	0.0167	0.0243	0.0002
1,4-dioxane + toluene						
288.15	-0.0750	0.1781	-0.0014	0.0092	0.0691	0.0002
293.15	-0.0631	0.1813	-0.0008	-0.0006	0.0798	0.0004
298.15	-0.0529	0.1794	-0.0026	0.0060	0.1000	0.0005
303.15	-0.0402	0.1841	0.0019	0.0014	0.1011	0.0005
308.15	-0.0291	0.1892	0.0131	0.0000	0.0944	0.0003
313.15	-0.0182	0.1882	0.0156	0.0058	0.1086	0.0003
318.15	-0.0071	0.1871	0.0183	0.0122	0.1226	0.0004
1,4-dioxane + <i>o</i> -xylene						
288.15	0.8579	0.1327	-0.1596	-0.0401	-0.0017	0.0008
293.15	0.9129	0.1341	-0.1488	-0.0530	0.0276	0.0008
298.15	0.9689	0.1367	-0.1380	-0.0727	0.0489	0.0009
303.15	1.0247	0.1392	-0.1091	-0.0936	0.0465	0.0010
308.15	1.0786	0.1473	-0.0846	-0.1148	0.0453	0.0013
313.15	1.1342	0.1449	-0.0615	-0.1189	0.0519	0.0014
318.15	1.1911	0.1424	-0.0395	-0.1239	0.0605	0.0015
1,4-dioxane + <i>m</i> -xylene						
288.15	0.7294	0.0943	-0.2364	-0.0268	0.0248	0.0005
293.15	0.7814	0.0952	-0.1540	-0.0304	-0.0377	0.0005
298.15	0.8313	0.0945	-0.0676	-0.0431	-0.1167	0.0008
303.15	0.8860	0.0917	0.0010	-0.0493	-0.1454	0.0007
308.15	0.9353	0.0878	0.0744	-0.0486	-0.2067	0.0006
313.15	0.9903	0.0844	0.1516	-0.0443	-0.2544	0.0006
318.15	1.0436	0.0799	0.2188	-0.0553	-0.3102	0.0009
1,4-dioxane + <i>p</i> -xylene						
288.15	0.5830	0.0550	-0.2445	-0.0293	0.0302	0.0004
293.15	0.6183	0.0626	-0.2235	-0.0351	0.0784	0.0007
298.15	0.6535	0.0717	-0.1844	-0.0461	0.0820	0.0009
303.15	0.6874	0.0791	-0.1379	-0.0644	0.0831	0.0010
308.15	0.7194	0.0914	-0.0897	-0.0823	0.0785	0.0010
313.15	0.7536	0.0987	-0.0511	-0.0997	0.0972	0.0008
318.15	0.7890	0.1069	-0.0145	-0.1192	0.1212	0.0009
1,4-dioxane + mesitylene						
288.15	1.3829	0.1340	-0.6036	-0.0336	0.0804	0.0013
293.15	1.4659	0.1659	-0.5175	-0.0591	0.0708	0.0013
298.15	1.5471	0.1976	-0.4309	-0.1046	0.0381	0.0014
303.15	1.6346	0.2369	-0.3558	-0.1500	0.0445	0.0016
308.15	1.7179	0.2721	-0.2609	-0.1860	0.0011	0.0018
313.15	1.8004	0.3038	-0.1752	-0.2386	-0.0287	0.0018
318.15	1.8878	0.3383	-0.0884	-0.2832	-0.0426	0.0019

compared with the latter two xylenes. These trends are in good agreement with the  $V_m^E$  values reported<sup>33</sup> for dimethyl sulfoxide + xylene binary mixtures.

The values of  $V_m^E$  increase with the increase in temperature of the mixture (Figure 1) for all six binary systems under study. The increase in  $V_m^E$  is attributed to the breaking of donor-acceptor interactions between unlike molecules with the rise in temperature, which leads to an expansion in volume and therefore results in an increase in  $V_m^E$  values.

The results presented in Figure 2 indicate that  $\Delta n$  values are positive for 1,4-dioxane + benzene, negative for 1,4-dioxane + *o*-xylene, + *m*-xylene, + *p*-xylene, and + mesitylene mixtures over entire mole fraction range at all investigated temperatures, and exhibit a sigmoid trend for 1,4-dioxane + toluene mixtures wherein  $\Delta n$  changes sign from negative to positive as the concentration of 1,4-dioxane in the mixture is increased. The extent of negative deviation in  $\Delta n$  from linear dependence on

**Table 9. Coefficients ( $A_i$ ) from Equation 3 for  $V_m^E$  and Standard Deviations ( $\sigma$ ) for 1,4-Dioxane + Aromatic Hydrocarbon Mixtures at Temperatures (288.15 to 318.15) K**

T/K	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$100 \cdot \sigma$
1,4-dioxane + benzene						
288.15	0.5899	0.0055	0.2020	0.0085	-0.0523	0.0013
293.15	0.5589	-0.0076	0.1883	0.0392	-0.0923	0.0011
298.15	0.5332	-0.0134	0.1015	0.0526	-0.0318	0.0006
303.15	0.5030	-0.0101	0.0437	0.0548	-0.0156	0.0007
308.15	0.4702	-0.0095	-0.0075	0.0617	-0.0111	0.0008
313.15	0.4449	-0.0020	-0.0532	0.0214	0.0179	0.0006
318.15	0.4266	-0.0088	-0.1049	0.0261	0.0319	0.0005
1,4-dioxane + toluene						
288.15	0.4018	0.0111	0.1191	-0.3103	-0.5449	0.0030
293.15	0.3758	0.0129	0.1056	-0.3465	-0.6197	0.0033
298.15	0.3511	0.0097	0.0860	-0.3725	-0.6797	0.0034
303.15	0.3266	0.0049	0.0291	-0.4158	-0.6607	0.0027
308.15	0.3030	-0.0074	-0.0632	-0.4342	-0.5971	0.0021
313.15	0.2777	-0.0074	-0.1212	-0.4993	-0.5660	0.0017
318.15	0.2532	-0.0211	-0.1889	-0.5420	-0.5244	0.0014
1,4-dioxane + <i>o</i> -xylene						
288.15	-2.5002	-0.1825	-0.1995	-0.0708	0.0641	0.0027
293.15	-2.5545	-0.1611	-0.2745	-0.0889	0.0268	0.0019
298.15	-2.6279	-0.2194	-0.3203	-0.0224	-0.1532	0.0039
303.15	-2.7044	-0.2375	-0.3440	0.0222	-0.2551	0.0042
308.15	-2.7835	-0.2296	-0.3828	0.0011	-0.4001	0.0047
313.15	-2.8429	-0.1992	-0.5746	-0.1290	-0.3703	0.0041
318.15	-2.9030	-0.1855	-0.7215	-0.2311	-0.4139	0.0039
1,4-dioxane + <i>m</i> -xylene						
288.15	-2.2248	-0.3702	-0.2779	0.0796	0.3195	0.0022
293.15	-2.2807	-0.3500	-0.3810	-0.0650	0.2900	0.0029
298.15	-2.3315	-0.3151	-0.4476	-0.1534	0.2261	0.0023
303.15	-2.3867	-0.2745	-0.6262	-0.2451	0.3211	0.0036
308.15	-2.4487	-0.2469	-0.7341	-0.3223	0.2094	0.0036
313.15	-2.4968	-0.2327	-0.8993	-0.4158	0.2542	0.0020
318.15	-2.5440	-0.2296	-1.1056	-0.4933	0.3651	0.0021
1,4-dioxane + <i>p</i> -xylene						
288.15	-2.0422	-0.2020	-0.0140	-0.0909	0.1182	0.0018
293.15	-2.0901	-0.1938	-0.1047	-0.1246	0.1091	0.0019
298.15	-2.1306	-0.1837	-0.2513	-0.1621	0.1748	0.0027
303.15	-2.1723	-0.1521	-0.4437	-0.2221	0.3016	0.0029
308.15	-2.2252	-0.1430	-0.5456	-0.2171	0.2376	0.0030
313.15	-2.2600	-0.1644	-0.6781	-0.2235	0.2795	0.0027
318.15	-2.3057	-0.1782	-0.7660	-0.2865	0.1998	0.0021
1,4-dioxane + mesitylene						
288.15	-3.1964	-0.5998	-0.6148	-0.1695	0.4500	0.0036
293.15	-3.3009	-0.5944	-0.5531	-0.2674	0.0478	0.0035
298.15	-3.3789	-0.5963	-0.6423	-0.2928	-0.0297	0.0043
303.15	-3.4770	-0.5706	-0.7837	-0.4754	-0.1890	0.0520
308.15	-3.5625	-0.5455	-0.8986	-0.5271	-0.3164	0.0051
313.15	-3.6587	-0.5481	-0.9239	-0.7197	-0.6156	0.0058
318.15	-3.7567	-0.5081	-1.0133	-1.0040	-0.7924	0.0072

composition follows the sequence benzene < toluene < *p*-xylene < *m*-xylene < *o*-xylene < mesitylene. In general, the positive deviations in  $\Delta n$  values (on a volume fraction dependence basis) are considered to be due to the presence of significant interactions in the mixtures, whereas negative deviations in  $\Delta n$  values indicate weak interactions between the components of the mixture.<sup>31,34</sup> The observed trends (Figure 2) of  $\Delta n$  values indicate the presence of weak interactions in these mixtures, which follow the order benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. The  $\Delta n$  values decrease with the increase in temperature for each binary mixture, indicating that the interactions between unlike molecules weaken with a rise in temperature. Also, the deviations in  $\Delta n$  values are found to be opposite to the sign of excess molar volumes  $V_m^E$  for all six binary mixtures (Figure 1), which is in agreement with the view proposed by Brocos et al.<sup>31,34</sup> This further reinforces our earlier conclusions regarding the intermolecular

**Table 10.**  $V_{m,1}^{\circ}$ ,  $V_{m,1}^{\circ E,\infty}$ ,  $V_{m,2}^{\circ}$ , and  $V_{m,2}^{\circ E,\infty}$  Values for 1,4-Dioxane + Aromatic Hydrocarbon Mixtures at Temperatures  $T = (288.15 \text{ to } 318.15) \text{ K}$ 

$T/\text{K}$	$V_{m,1}^{\circ}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$V_{m,1}^{\circ E,\infty}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$V_{m,2}^{\circ}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$V_{m,2}^{\circ E,\infty}$ $\text{cm}^3 \cdot \text{mol}^{-1}$
1,4-dioxane + benzene				
288.15	84.451	-0.329	88.046	-0.283
293.15	84.933	-0.310	88.599	-0.268
298.15	85.446	-0.264	89.161	-0.249
303.15	85.949	-0.234	89.744	-0.217
308.15	86.423	-0.238	90.317	-0.204
313.15	86.917	-0.226	90.906	-0.178
318.15	87.443	-0.189	91.515	-0.139
1,4-dioxane + toluene				
288.15	84.960	0.180	105.496	-0.195
293.15	85.439	0.197	106.100	-0.165
298.15	85.940	0.230	106.705	-0.141
303.15	86.431	0.248	107.312	-0.123
308.15	86.928	0.268	107.917	-0.111
313.15	87.443	0.300	108.541	-0.088
318.15	87.964	0.333	109.171	-0.066
1,4-dioxane + <i>o</i> -xylene				
288.15	85.569	0.789	120.694	0.604
293.15	86.115	0.873	121.382	0.711
298.15	86.654	0.944	122.074	0.816
303.15	87.190	1.008	122.768	0.916
308.15	87.732	1.072	123.456	1.007
313.15	88.294	1.151	124.153	1.099
318.15	88.862	1.231	124.858	1.194
1,4-dioxane + <i>m</i> -xylene				
288.15	85.365	0.585	122.683	0.450
293.15	85.897	0.654	123.363	0.525
298.15	86.409	0.698	124.046	0.596
303.15	86.966	0.784	124.767	0.699
308.15	87.503	0.842	125.457	0.764
313.15	88.071	0.928	126.171	0.847
318.15	88.608	0.977	126.889	0.928
1,4-dioxane + <i>p</i> -xylene				
288.15	85.174	0.394	123.009	0.343
293.15	85.743	0.501	123.731	0.446
298.15	86.287	0.577	124.437	0.525
303.15	86.830	0.647	125.162	0.618
308.15	87.378	0.717	125.882	0.699
313.15	87.942	0.799	126.629	0.801
318.15	88.514	0.883	127.388	0.908
1,4-dioxane + mesitylene				
288.15	85.740	0.960	139.035	0.759
293.15	86.369	1.126	139.813	0.912
298.15	86.958	1.247	140.593	1.061
303.15	87.593	1.410	141.405	1.236
308.15	88.205	1.544	142.182	1.372
313.15	88.805	1.662	142.991	1.531
318.15	89.443	1.812	143.816	1.702

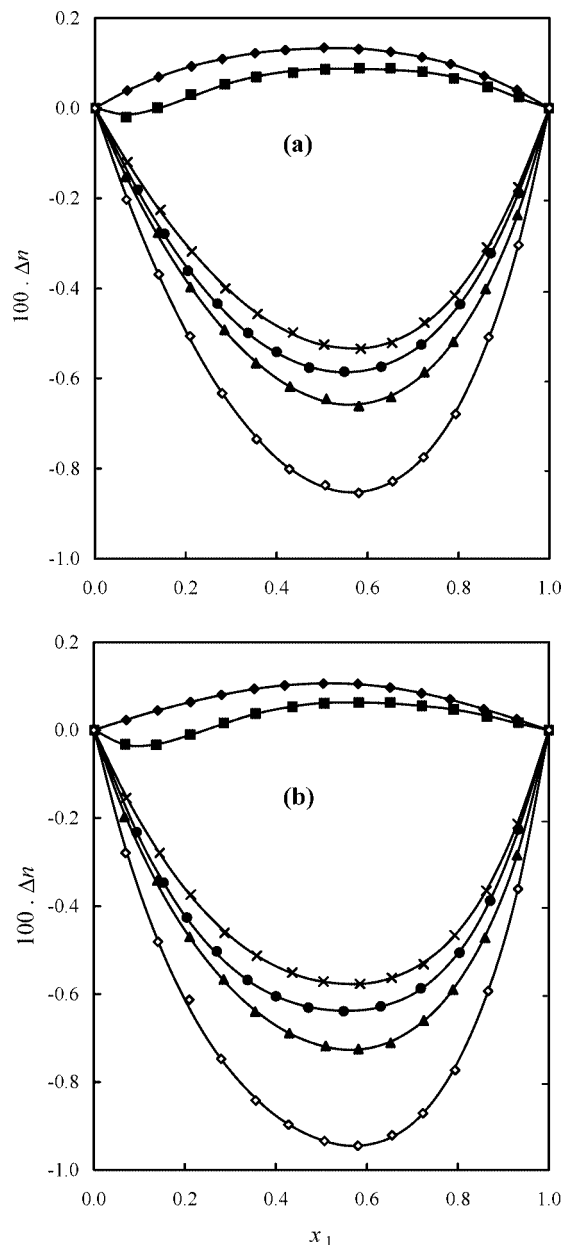
interactions from the variations of  $V_m^E$  values of these mixtures.

The partial molar volumes,  $V_{m,1}^{\circ}$  of component 1 (1,4-dioxane) and  $V_{m,2}^{\circ}$  of component 2 (aromatic hydrocarbon), in these mixtures over the entire composition range were calculated by using the following relations<sup>33</sup>

$$V_{m,1}^{\circ} = V_m^E + V_{m,1} + x_2(\partial V_m^E / \partial x_1)_{T,p} \quad (4)$$

$$V_{m,2}^{\circ} = V_m^E + V_{m,1} - x_1(\partial V_m^E / \partial x_1)_{T,p} \quad (5)$$

where  $V_{m,1}$  and  $V_{m,2}$  are the molar volumes of pure components 1,4-dioxane and aromatic hydrocarbon, respectively, and  $x_1$  and  $x_2$  are the mole fractions of components in the mixture. The derivative  $(\partial V_m^E / \partial x_1)_{T,p}$  in eqs 4 and 5 was obtained by the



**Figure 2.** Deviations in refractive index ( $\Delta n$ ) versus mole fraction ( $x_1$ ) of 1,4-dioxane for the binary mixtures at (a)  $T = 298.15 \text{ K}$  and (b)  $T = 318.15 \text{ K}$ .  $\diamond$ , 1,4-dioxane + benzene;  $\blacksquare$ , 1,4-dioxane + toluene;  $\blacktriangle$ , 1,4-dioxane + *o*-xylene;  $\bullet$ , 1,4-dioxane + *m*-xylene;  $\Delta$ , 1,4-dioxane + *p*-xylene;  $\diamond$ , 1,4-dioxane + mesitylene; —, calculated from eq 3.

differentiation of eq 3, which leads to the following equations for  $V_{m,1}^{\circ}$  and  $V_{m,2}^{\circ}$

$$V_{m,1}^{\circ} = V_{m,1} + x_2^2 \sum_{i=0}^j A_i (1 - 2x_1)^i - 2x_1 x_2^2 \sum_{i=1}^j A_i (1 - 2x_1)^{i-1} \quad (6)$$

$$V_{m,2}^{\circ} = V_{m,2} + x_1^2 \sum_{i=0}^j A_i (1 - 2x_1)^i + 2x_1^2 x_2 \sum_{i=1}^j A_i (1 - 2x_1)^{i-1} \quad (7)$$

Using the values of partial molar volumes  $V_{m,1}^{\circ}$  and  $V_{m,2}^{\circ}$  of the components at infinite dilution obtained from eqs 4, 5, 6, and 7, we calculated the excess partial molar volumes  $V_{m,1}^{\circ E,\infty}$  and  $V_{m,2}^{\circ E,\infty}$  of the components at infinite dilution by using the following relations<sup>35</sup>

$$V_{m,1}^{E,\infty} = V_{m,1}^{\infty} - V_{m,1} \quad (8)$$

$$V_{m,2}^{E,\infty} = V_{m,2}^{\infty} - V_{m,2} \quad (9)$$

The values  $V_{m,1}^{\infty}$ ,  $V_{m,1}^{E,\infty}$ ,  $V_{m,2}^{\infty}$ , and  $V_{m,2}^{E,\infty}$  for all six binary systems at the investigated temperatures are listed in Table 10. A close perusal of Table 10 indicates that the values of  $V_{m,1}^{E,\infty}$  and  $V_{m,2}^{E,\infty}$  calculated using eqs 8 and 9 are negative for 1,4-dioxane + benzene and are positive for 1,4-dioxane + *o*-xylene, + *m*-xylene, + *p*-xylene, and + mesitylene mixtures;  $V_{m,1}^{E,\infty}$  values are positive, whereas  $V_{m,2}^{E,\infty}$  values are negative for 1,4-dioxane + toluene mixtures at each investigated temperature. This suggests that the molar volumes of each component in the mixture are less than their respective molar volumes in the pure state; that is, there is a contraction in volume on mixing 1,4-dioxane with benzene, whereas the molar volumes of each component in the mixture are more than their respective molar volumes in the pure state (i.e., there is an expansion in volume on mixing 1,4-dioxane with *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene). For the 1,4-dioxane + toluene system, there is an expansion in volume in the toluene-rich region, whereas there is a contraction in volume in the 1,4-dioxane-rich region, which is well reflected in the sigmoid trend in  $V_m^E$  values. This further supports the trends observed in  $V_m^E$  values for these binary systems. Also, the values of  $V_{m,1}^{E,\infty}$  and  $V_{m,2}^{E,\infty}$  increase with the increase in temperature of the mixture for each system investigated, which indicates the breaking of donor–acceptor interactions between unlike molecules with the rise in temperature, leading to an expansion in volume. This further supports the trends observed in  $V_m^E$  values for these binary systems.

## Conclusions

The densities and refractive indices for 1,4-dioxane + benzene, + toluene, + *o*-xylene, + *m*-xylene, + *p*-xylene, and + mesitylene mixtures, including those of pure liquids, have been measured at different temperatures. The values of  $V_m^E$  and  $\Delta n$  for the mixtures and  $V_{m,1}^{\infty}$ ,  $V_{m,1}^{E,\infty}$ ,  $V_{m,2}^{\infty}$ , and  $V_{m,2}^{E,\infty}$  for the components were calculated. The observed trends in  $V_m^E$  and  $\Delta n$  values indicate the presence of specific interactions between MA + benzene, + toluene, + *o*-xylene, + *m*-xylene, and + *p*-xylene and weak interactions in MA + mesitylene mixtures, and this interaction decreases with the increase in temperature. The extent of negative deviation in  $V_m^E$  values shows that the interactions in these mixtures follows the order benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. It is observed that the magnitude of  $V_m^E$  depends on the number and position of methyl groups in these aromatic hydrocarbon molecules.

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