

Short Articles

Densities and Surface Tensions of Propyl Acetate + Xylenes or + Ethylbenzene from (298.15 to 308.15) K

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Densities and surface tensions for binary systems of (propyl acetate + *o*-xylene, + *m*-xylene, + *p*-xylene, + ethylbenzene) were measured under normal atmospheric pressure over the entire mole fraction range from (298.15 to 308.15) K. The excess molar volumes V^E and surface tension deviations $\delta\sigma$ for the above systems were calculated and fitted to the Redlich–Kister polynomial equation. The V^E for the systems of (propyl acetate + *m*-xylene, + ethylbenzene) are nearly zero, but for the systems of (propyl acetate + *o*-xylene, + *p*-xylene) are negative. The $\delta\sigma$ values are negative for all of the four systems. The V^E of the four systems hardly change with increasing temperature, but their absolute values of $\delta\sigma$ decrease with increasing temperature.

Introduction

The molecular interaction properties of liquids and liquids mixtures are important in the mass and heat transfer of interface such as liquid–liquid extraction, gas absorption, distillation, and condensation. There are some experimental methods for understanding and interpreting the nature of interactions between molecules in liquid, the measurements of density and surface tension are of simplicity and precision. In the course of separation of mixed xylene and trimethylbenzene, we had measured excess functions of some solvents + trimethylbenzene.¹ Herein, excess molar volumes V^E and surface tensions $\delta\sigma$ for (propyl acetate + *o*-xylene, + *m*-xylene, + *p*-xylene, + ethylbenzene) from (298.15 to 308.15) K are determined. The results obtained are discussed from the viewpoint of the molecular interactions between different components.

Experimental Section

Propyl acetate (Acros Organic), *o*-xylene (Guangzhou Chem., China), *m*-xylene (Alfa Aesar), *p*-xylene (Guangzhou Chem., China), and ethylbenzene (Guangzhou Chem., China) are commercially available or purified by distillation. All the chemicals were stored over molecular sieve before use. The mass fractions determined by PE auto system XL gas chromatograph were as follows: propyl acetate (> 99.5 %), *o*-xylene (> 99.6 %), *m*-xylene (> 99.3 %), *p*-xylene (> 99.7 %), and ethylbenzene (> 99.7 %). The mole fraction of each mixture was obtained by measuring the masses of the components using an Ohaus E12140 balance; the uncertainty of the mole fraction is estimated to be less than ± 0.0001 .

Densities of the pure liquids and their mixtures were measured with an Anton Paar DMA 4500 vibrating tube densimeter whose thermostatic bath was controlled to within ± 0.01 K. Triplicate

Table 1. Physical Properties of the Pure Components

substance	T		$\rho/\text{g}\cdot\text{cm}^{-3}$		$\sigma/\text{mN}\cdot\text{m}^{-1}$	
	K		exptl	lit.	exptl	lit.
<i>o</i> -xylene	298.15		0.87505	0.87501 ²	29.89	29.76 ¹³
	303.15		0.87083	0.87066 ³	29.24	29.21 ¹³
	308.15		0.86662	0.86738 ⁴	28.57	28.66 ¹³
<i>m</i> -xylene	298.15		0.85980	0.86002 ²	28.47	28.47 ¹³
				0.85980 ³		
	303.15		0.85551	0.85551 ³	27.93	27.92 ¹³
<i>p</i> -xylene	308.15		0.85119	0.85140 ⁵	27.37	27.37 ¹³
	298.15		0.85692	0.85672 ²	28.08	28.01 ¹³
	303.15		0.85258	0.85235 ⁶	27.47	27.47 ¹³
ethylbenzene	308.15		0.84826	0.84791 ⁷	27.13	26.93 ¹³
	298.15		0.86225	0.86244 ⁸	28.79	28.75 ¹³
	303.15		0.85788	0.85780 ⁹	28.29	28.20 ¹³
propyl acetate	308.15		0.85343	0.85415 ⁴	27.85	27.65 ¹³
	298.15		0.88254	0.88201 ¹⁰	23.91	23.80 ¹³
	303.15		0.87699	0.87712 ¹¹	23.46	23.24 ¹³
		308.15	0.87135	0.8718 ¹²	22.79	22.68 ¹³

measurements of density were performed for all the mixtures and pure components. The uncertainty of reported densities is estimated to be $0.00005 \text{ g}\cdot\text{cm}^{-3}$. The surface tensions of the pure liquids and their mixtures were determined by the pendant drop method, using a Dataphysics OCA20 contact angle and surface tension measuring instrument.¹ The uncertainty of the surface tension measured is about $\pm 0.05 \text{ mN}\cdot\text{m}^{-1}$ (at $T = \pm 0.1$ K). The densities and surface tensions of the pure compounds are given in Table 1 and compared with the literature values. It can be seen that the measured results agree well with literature values.

Results and Discussion

Excess molar volumes were determined from the density data:

$$V^E = \frac{x_1 \cdot M_1 + x_2 \cdot M_2}{\rho} - x_1 \frac{M_1}{\rho_1} - x_2 \frac{M_2}{\rho_2} \quad (1)$$

where M_i is the molar mass of component i , ρ and ρ_i are the

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Table 2. Experimental Densities ρ and Excess Molar Volumes V^E

x	ρ g·cm ⁻³	V^E cm ³ ·mol ⁻¹	x	ρ g·cm ⁻³	V^E cm ³ ·mol ⁻¹	x	ρ g·cm ⁻³	V^E cm ³ ·mol ⁻¹	x	ρ g·cm ⁻³	V^E cm ³ ·mol ⁻¹
$T = 298.15$ K											
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>o</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.87505	0	0.2996	0.87783	-0.083	0.6004	0.88018	-0.096	0.9000	0.88203	-0.036
0.0998	0.87604	-0.038	0.4002	0.87867	-0.099	0.7002	0.88085	-0.084	1	0.88254	0
0.1995	0.87696	-0.065	0.5001	0.87945	-0.100	0.7999	0.88146	-0.063			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>m</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.85980	0	0.2986	0.86633	-0.006	0.6004	0.87306	0.005	0.9007	0.88011	0.005
0.0997	0.86198	-0.006	0.4002	0.86857	-0.003	0.6984	0.87531	0.008	1	0.88254	0
0.1999	0.86417	-0.008	0.4986	0.87076	0.001	0.8004	0.87770	0.008			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>p</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.85692	0	0.2981	0.86480	-0.085	0.6002	0.87251	-0.087	0.8999	0.88005	-0.031
0.1000	0.85960	-0.039	0.3986	0.86738	-0.092	0.6991	0.87500	-0.073	1	0.88254	0
0.1995	0.86222	-0.066	0.4993	0.86995	-0.093	0.7993	0.87752	-0.054			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + C ₆ H ₅ CH ₂ CH ₃ (1 - x)											
0	0.86225	0	0.3002	0.86816	-0.011	0.6002	0.87414	-0.002	0.9007	0.88038	0.004
0.1005	0.86423	-0.007	0.4005	0.87014	-0.009	0.6997	0.87617	0.001	1	0.88254	0
0.1994	0.86618	-0.011	0.5000	0.87212	-0.005	0.7998	0.87824	0.004			
$T = 303.15$ K											
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>o</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.87083	0	0.2992	0.87322	-0.083	0.6002	0.87517	-0.096	0.9020	0.87663	-0.036
0.1000	0.87168	-0.036	0.3998	0.87393	-0.097	0.6994	0.87570	-0.084	1	0.87699	0
0.1997	0.87248	-0.064	0.4993	0.87457	-0.100	0.8002	0.87619	-0.064			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>m</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.85551	0	0.2990	0.86169	-0.006	0.5994	0.86802	0.005	0.8992	0.87466	0.005
0.0999	0.85757	-0.005	0.4003	0.86380	-0.002	0.6998	0.87019	0.008	1	0.87699	0
0.1989	0.85962	-0.007	0.5000	0.86590	0.001	0.8006	0.87242	0.009			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>p</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.85258	0	0.2992	0.86013	-0.083	0.5998	0.86744	-0.085	0.8997	0.87463	-0.032
0.0994	0.85513	-0.039	0.3991	0.86258	-0.091	0.6999	0.86984	-0.072	1	0.87699	0
0.1992	0.85764	-0.065	0.5009	0.86505	-0.091	0.8009	0.87226	-0.054			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + C ₆ H ₅ CH ₂ CH ₃ (1 - x)											
0	0.85788	0	0.2995	0.86345	-0.012	0.5995	0.86908	-0.003	0.9007	0.87496	0.004
0.1001	0.85975	-0.009	0.4000	0.86532	-0.010	0.6999	0.87100	0.001	1	0.87699	0
0.1995	0.86159	-0.011	0.5004	0.86720	-0.007	0.8005	0.87296	0.004			
$T = 308.15$ K											
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>o</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.86662	0	0.3001	0.86859	-0.083	0.6008	0.87011	-0.096	0.9000	0.87112	-0.035
0.0999	0.86733	-0.036	0.3989	0.86915	-0.096	0.6998	0.87050	-0.084	1	0.87135	0
0.1999	0.86799	-0.064	0.5002	0.86966	-0.100	0.8007	0.87084	-0.063			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>m</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.85119	0	0.2998	0.85701	-0.005	0.6004	0.86295	0.006	0.9013	0.86920	0.006
0.0998	0.85312	-0.004	0.3993	0.85896	-0.003	0.6999	0.86497	0.009	1	0.87135	0
0.2000	0.85507	-0.006	0.5006	0.86096	0.001	0.7988	0.86702	0.009			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + <i>p</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)											
0	0.84826	0	0.2992	0.85543	-0.083	0.6000	0.86235	-0.084	0.9002	0.86914	-0.032
0.1001	0.85070	-0.038	0.4001	0.85777	-0.090	0.6996	0.86461	-0.072	1	0.87135	0
0.1999	0.85309	-0.065	0.4996	0.86006	-0.090	0.8003	0.86688	-0.053			
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) + C ₆ H ₅ CH ₂ CH ₃ (1 - x)											
0	0.85343	0	0.2999	0.85867	-0.012	0.5999	0.86395	-0.004	0.9003	0.86944	0.001
0.1000	0.85519	-0.009	0.3997	0.86041	-0.010	0.7001	0.86574	0.001	1	0.87135	0
0.2000	0.85693	-0.012	0.5003	0.86218	-0.007	0.8007	0.86758	0.003			

densities of the mixture and component i , and x_i is the molar fraction of component i . Experimental excess molar volumes V^E for four binary mixtures (propyl acetate + *o*-xylene, + *m*-xylene, + *p*-xylene, + ethylbenzene) at (298.15, 303.15, and 308.15) K are listed in Table 2. The variations of V^E with the mole fraction for these four binary systems at $T = 298.15$ K are presented in Figure 1. Figure 2 shows the plot of V^E against temperature for the four systems at equimolar composition.

The surface tension deviations $\delta\sigma$ are defined by

$$\delta\sigma = \sigma - x_1\sigma_1 - x_2\sigma_2 \quad (2)$$

The surface tensions σ and surface tension deviations $\delta\sigma$ for four binary mixtures (propyl acetate + *o*-xylene, + *m*-xylene, + *p*-xylene, + ethylbenzene) at (298.15, 303.15, and 308.15) K are listed in Table 4. The variations of $\delta\sigma$ with the mole fraction for the four systems at $T = 298.15$ K are presented in Figure 3. Figure 4 shows the plot of $\delta\sigma$ against temperature for the four systems at equimolar composition.

The experimental results were fitted by the method of least-squares with all points weighted equally to the smoothing equation:¹

Table 3. Least-Squares Coefficients (A_i), Associated Errors (S_{A_i}), and Standard Deviations (S_{V^E}) for Excess Molar Volumes at 298.15 K from Equation 3

$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$ (x) +	A_0 $\text{cm}^3\cdot\text{mol}^{-1}$	S_{A0} $\text{cm}^3\cdot\text{mol}^{-1}$	A_1 $\text{cm}^3\cdot\text{mol}^{-1}$	S_{A1} $\text{cm}^3\cdot\text{mol}^{-1}$	A_2 $\text{cm}^3\cdot\text{mol}^{-1}$	S_{A2} $\text{cm}^3\cdot\text{mol}^{-1}$	A_3 $\text{cm}^3\cdot\text{mol}^{-1}$	S_{A3} $\text{cm}^3\cdot\text{mol}^{-1}$	A_4 $\text{cm}^3\cdot\text{mol}^{-1}$	S_{A4} $\text{cm}^3\cdot\text{mol}^{-1}$	S_{V^E} $\text{cm}^3\cdot\text{mol}^{-1}$
<i>o</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)	-0.402	0.002	0.009	0.006							0.001
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)	0.0051	0.0008	0.082	0.002	-0.014	0.003					0.002
<i>p</i> -C ₆ H ₄ (CH ₃) ₂ (1 - x)	-0.372	0.001	0.063	0.003	-0.019	0.007					0.001
C ₆ H ₅ CH ₂ CH ₃ (1 - x)	-0.0216	0.0008	0.072	0.003	-0.020	0.009	0.010	0.007	0.04	0.02	0.005

Table 4. Surface Tensions σ and Surface Tension Deviations $\delta\sigma$

x	σ $\text{mN}\cdot\text{m}^{-1}$	$\delta\sigma$ $\text{mN}\cdot\text{m}^{-1}$	x	σ $\text{mN}\cdot\text{m}^{-1}$	$\delta\sigma$ $\text{mN}\cdot\text{m}^{-1}$	x	σ $\text{mN}\cdot\text{m}^{-1}$	$\delta\sigma$ $\text{mN}\cdot\text{m}^{-1}$	x	σ $\text{mN}\cdot\text{m}^{-1}$	$\delta\sigma$ $\text{mN}\cdot\text{m}^{-1}$
$T = 298.15 \text{ K}$											
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + o\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	29.89	0	0.2996	27.47	-0.63	0.6004	25.71	-0.59	0.9000	24.25	-0.26
0.0998	28.94	-0.35	0.4002	26.85	-0.65	0.7002	25.18	-0.52	1	23.91	0
0.1995	28.14	-0.56	0.5001	26.27	-0.63	0.7999	24.69	-0.42			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + m\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	28.47	0	0.2986	26.70	-0.41	0.6004	25.30	-0.43	0.9007	24.25	-0.11
0.0997	27.86	-0.16	0.4002	26.16	-0.49	0.6984	24.94	-0.35	1	23.91	0
0.1999	27.26	-0.30	0.4986	25.71	-0.49	0.8004	24.59	-0.23			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + p\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	28.08	0	0.2981	26.54	-0.30	0.6002	25.23	-0.35	0.8999	24.23	-0.10
0.1000	27.56	-0.10	0.3986	26.05	-0.37	0.6991	24.89	-0.27	1	23.91	0
0.1995	27.04	-0.21	0.4993	25.61	-0.39	0.7993	24.56	-0.19			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 (1 - x)$											
0	28.79	0	0.3002	26.89	-0.44	0.6002	25.50	-0.36	0.9007	24.30	-0.09
0.1005	28.15	-0.15	0.4005	26.35	-0.49	0.6997	25.10	-0.28	1	23.91	0
0.1994	27.51	-0.31	0.5000	25.91	-0.44	0.7998	24.70	-0.19			
$T = 303.15 \text{ K}$											
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + o\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	29.24	0	0.2992	26.92	-0.59	0.6002	25.20	-0.57	0.9020	23.81	-0.22
0.0999	28.41	-0.25	0.3998	26.30	-0.63	0.6994	24.70	-0.50	1	23.46	0
0.1997	27.60	-0.49	0.4993	25.74	-0.61	0.8002	24.24	-0.37			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + m\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	27.93	0	0.2990	26.25	-0.32	0.5994	24.88	-0.37	0.8992	23.81	-0.10
0.0999	27.35	-0.13	0.4003	25.73	-0.41	0.6998	24.51	-0.29	1	23.46	0
0.1989	26.79	-0.25	0.5000	25.27	-0.42	0.8006	24.15	-0.20			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + p\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	27.47	0	0.2992	25.99	-0.28	0.5998	24.76	-0.30	0.8997	23.78	-0.08
0.0994	26.98	-0.09	0.3991	25.52	-0.35	0.6999	24.43	-0.23	1	23.46	0
0.1992	26.48	-0.19	0.5009	25.10	-0.36	0.8009	24.10	-0.16			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 (1 - x)$											
0	28.29	0	0.2995	26.49	-0.35	0.5995	25.07	-0.32	0.9007	23.85	-0.09
0.1001	27.70	-0.11	0.4000	25.95	-0.41	0.6999	24.65	-0.26	1	23.46	0
0.1995	27.10	-0.23	0.5004	25.49	-0.38	0.8005	24.24	-0.18			
$T = 308.15 \text{ K}$											
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + o\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	28.57	0	0.3001	26.35	-0.49	0.6008	24.60	-0.50	0.9000	23.20	-0.17
0.0999	27.80	-0.19	0.3989	25.73	-0.53	0.6998	24.10	-0.43	1	22.79	0
0.1999	27.05	-0.36	0.5002	25.14	-0.54	0.8007	23.63	-0.31			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + m\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	27.37	0	0.2998	25.71	-0.29	0.6004	24.27	-0.35	0.9013	23.15	-0.09
0.0998	26.80	-0.11	0.3993	25.19	-0.35	0.6999	23.89	-0.27	1	22.79	0
0.2000	26.25	-0.20	0.5006	24.70	-0.38	0.7988	23.52	-0.19			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + p\text{-C}_6\text{H}_4(\text{CH}_3)_2 (1 - x)$											
0	27.13	0	0.2992	25.57	-0.26	0.6000	24.23	-0.30	0.9002	23.15	-0.07
0.1001	26.61	-0.09	0.4001	25.06	-0.33	0.6996	23.87	-0.22	1	22.79	0
0.1999	26.09	-0.17	0.4996	24.62	-0.34	0.8003	23.51	-0.15			
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 (x) + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 (1 - x)$											
0	27.85	0	0.2999	26.01	-0.32	0.5999	24.52	-0.29	0.9003	23.22	-0.07
0.1000	27.24	-0.10	0.3997	25.46	-0.37	0.7001	24.08	-0.23	1	22.79	0
0.2000	26.62	-0.22	0.5003	24.97	-0.35	0.8007	23.65	-0.15			

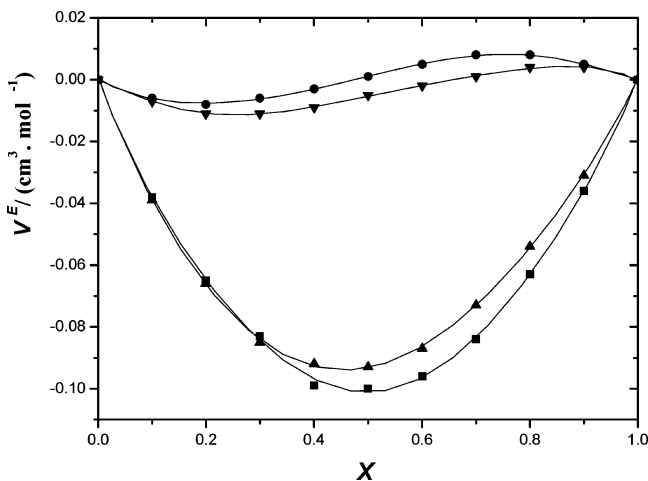
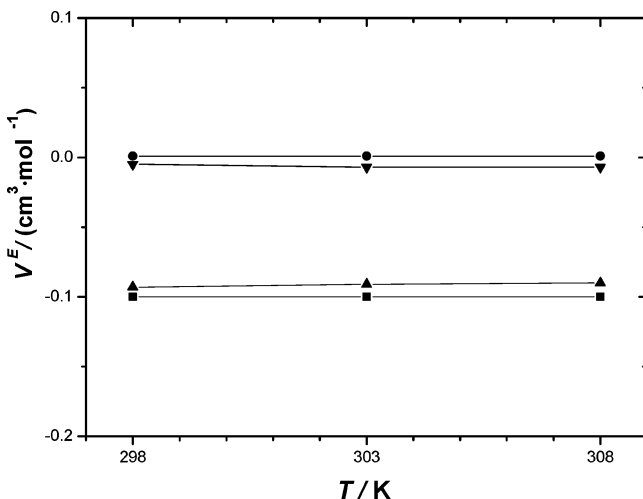
The coefficients A_i , associated errors S_{A_i} , and standard deviations S_Y are given in Table 3 ($Y = V^E$) and in Table 5 ($Y = \delta\sigma$).

Figure 1 shows the plot of V^E against the mole fraction for these four binary systems at $T = 298.15 \text{ K}$. The V^E behaviors

at $T = (303.15 \text{ and } 308.15) \text{ K}$ are similar to that observed at $T = 298.15 \text{ K}$. The V^E curves for propyl acetate + *m*-xylene or ethylbenzene are *S*-shaped and nearly zero and for propyl acetate + *o*-xylene or *p*-xylene are negative. The minimum values of

Table 5. Least-Squares Coefficients (A_i), Associated Errors (S_{A_i}), and Standard Deviations ($S_{\delta\sigma}$) for Surface Tensions at 298.15 K from Equation 3

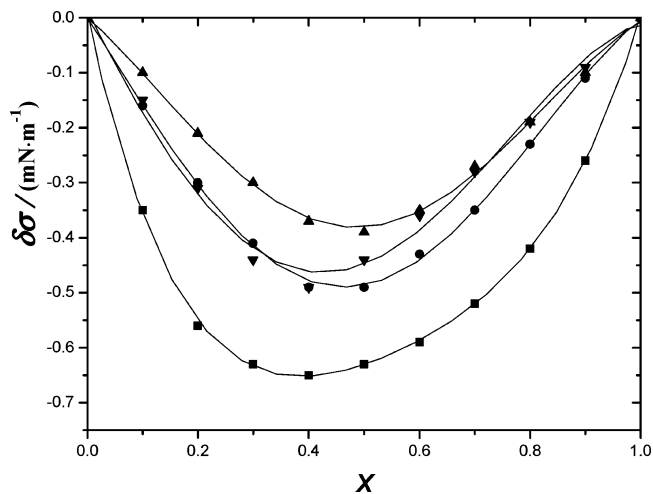
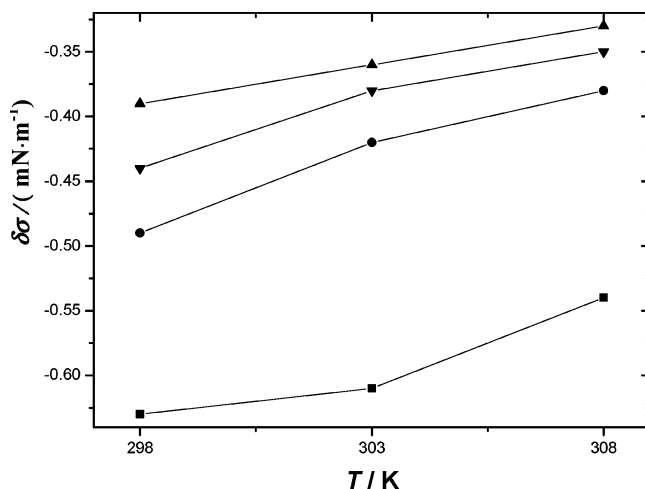
	A_0	S_{A0}	A_1	S_{A1}	A_2	S_{A2}	A_3	S_{A3}	$S_{\delta\sigma}$
CH ₃ COOCH ₂ CH ₂ CH ₃ (x) +	mN·m ⁻¹	mN·m ⁻¹	mN·m ⁻¹	mN·m ⁻¹	mN·m ⁻¹	mN·m ⁻¹	mN·m ⁻¹	mN·m ⁻¹	mN·m ⁻¹
<i>o</i> -C ₆ H ₄ (CH ₃) ₂ ($1-x$)	-2.52	0.01	0.68	0.02	-1.42	0.05			0.002
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ ($1-x$)	-1.95	0.02	0.39	0.03	0.76	0.07			0.002
<i>p</i> -C ₆ H ₄ (CH ₃) ₂ ($1-x$)	-1.52	0.02	0.12	0.04	0.74	0.09			0.002
C ₆ H ₅ CH ₂ CH ₃ ($1-x$)	-1.79	0.02	1.19	0.08	0.65	0.09	-1.3	0.2	0.005

**Figure 1.** Excess molar volumes V^E for propyl acetate (x) + \blacksquare , *o*-xylene ($1-x$); + \bullet , *m*-xylene ($1-x$); + \blacktriangle , *p*-xylene ($1-x$); + \blacktriangledown , ethylbenzene ($1-x$) at 298.15 K.**Figure 2.** Excess molar volumes V^E against temperature for propyl acetate (x) + \blacksquare , *o*-xylene ($1-x$); + \bullet , *m*-xylene ($1-x$); + \blacktriangle , *p*-xylene ($1-x$); + \blacktriangledown , ethylbenzene ($1-x$) at $x = 0.5$.

$$Y = x(1-x) \sum_{i=0}^k A_i (1-2x)^i \quad (3)$$

V^E for the four systems follow the order: propyl acetate + *o*-xylene < propyl acetate + *p*-xylene < propyl acetate + ethylbenzene < propyl acetate + *m*-xylene. Figure 2 shows the plot of V^E against temperature for the four systems at equimolar composition. It can be seen that V^E values for these binary systems hardly vary with increasing temperature.

Treszczanowicz et al.¹⁴ suggested that V^E is the result of contributions from several opposing effects, which may be divided into three types: physical, chemical, and structural effect. Physical effects make a positive contribution to V^E ; chemical and structural effects make a negative contribution.

**Figure 3.** Surface tension deviations $\delta\sigma$ for propyl acetate (x) + \blacksquare , *o*-xylene ($1-x$); + \bullet , *m*-xylene ($1-x$); + \blacktriangle , *p*-xylene ($1-x$); + \blacktriangledown , ethylbenzene ($1-x$) at 298.15 K.**Figure 4.** Surface tension deviations $\delta\sigma$ against temperature for propyl acetate (x) + \blacksquare , *o*-xylene ($1-x$); + \bullet , *m*-xylene ($1-x$); + \blacktriangle , *p*-xylene ($1-x$); + \blacktriangledown , ethylbenzene ($1-x$) at $x = 0.5$.

The negative V^E values for propyl acetate + *o*-xylene or *p*-xylene indicate that the chemical contributions are dominant. The absolute values of V^E for propyl acetate + *m*-xylene or ethylbenzene are nearly zero, which implies that the interactions between unlike molecules are very similar to the intramolecular interactions. The V^E values for propyl acetate + *o*-xylene or *p*-xylene are more negative than propyl acetate + *m*-xylene or ethylbenzene, probably because of steric factor; the packing effects of propyl acetate + *m*-xylene or ethylbenzene are stronger than that of propyl acetate + *o*-xylene or *p*-xylene.

Figure 3 shows the surface tension deviation $\delta\sigma$ for these four binary systems at $T = 298.15$ K. They are all negative, and the minimum values of $\delta\sigma$ follow the order: propyl acetate + *o*-xylene < propyl acetate + *m*-xylene < propyl acetate +

ethylbenzene < propyl acetate + *p*-xylene. The curves of $\delta\sigma$ against composition at the temperatures of (303.15 and 308.15) K are similar to those at $T = 298.15$ K. Tsierkezos and Filippou¹⁵ thought that the surface tension deviations indicate different distributions of unlike components between the surface and the bulk region. The negative values of $\delta\sigma$ indicate that the surface concentration of the lower surface tension component is higher than its bulk concentration. For these binary systems, the value of the surface tension of propyl acetate is smaller than that of *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene; it suggests that the surface concentration of propyl acetate is higher than its bulk concentration. Figure 4 shows the surface tension deviations $\delta\sigma$ against temperature for the four systems at equimolar composition. It can be observed that the values of $\delta\sigma$ increase with increasing temperature.

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