

Densities and Viscosities of Binary Mixtures of Methyl 4-Chlorobutyrate with Aromatic Hydrocarbons at $T = (298.15 \text{ to } 318.15) \text{ K}$

Jian-Hai Yang, Li-Yan Dai,* Xiao-Zhong Wang, and Ying-Qi Chen

Institute of Pharmaceutical Engineering, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Densities and viscosities of the binary mixtures of methyl 4-chlorobutyrate with benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene have been measured at different temperatures (298.15, 308.15 and 318.15) K and atmospheric pressure over the whole range of compositions. The excess molar volumes were calculated from the experimental data and correlated by the Redlich–Kister polynomial equation. McAllister's three-body and four-body interaction models are also used to correlate the kinematic viscosities of these binary mixtures.

Introduction

Densities and viscosities are important fundamental data for the chemical design and the optimization of chemical processes. They are widely studied for many industrially interesting systems such as organic synthesis mixtures, ion extraction systems, and gas adsorption solvents, etc. Furthermore, excess thermodynamic and transport properties of binary mixtures can provide important information concerning the deeper understanding of the molecular liquid structure and intermolecular interactions. Methyl 4-chlorobutyrate has many applications in the chemical industry and is used in many organic synthesis mixtures.^{1–3} For an example, it is an indispensable intermediate in the industrial synthesis process of cyclopropanecarboxylic acid which is an important industrial chemical widely used for the preparation of crop protection agents and medicines.⁴ Aromatic hydrocarbons are important organic solvents in organic synthesis and extraction systems, such as in some synthesis processes where the mixture of methyl 4-chlorobutyrate with an aromatic hydrocarbon is necessary.^{5,6} So it is useful to know the physical properties of methyl 4-chlorobutyrate + aromatic hydrocarbons. In the last decades, much work has been devoted to study the deviations from ideality for binary liquid mixtures containing an aromatic hydrocarbon and a second component.^{7–9} However, despite its technological potential applications, a survey of the literature shows that there is no report on the densities and viscosities for methyl 4-chlorobutyrate with aromatic hydrocarbons.

This is a part of our ongoing program of research on the thermodynamic and transport properties of binary mixtures containing methyl 4-chlorobutyrate. In the present study, density and viscosity were measured for the binary mixtures of methyl 4-chlorobutyrate + benzene, + toluene, + *o*-xylene, + *m*-xylene, and + *p*-xylene at atmospheric pressure and temperatures in the range of (298.15 to 338.15) K. The excess molar volumes have been calculated from the experimental data and correlated by the Redlich–Kister polynomial equation.¹⁰ The kinematic viscosity data were correlated with McAllister's three-body and four-body interaction models.¹¹

Experimental Section

Materials. All chemicals used in this study were obtained from Sinopharm Chemical Reagent Co., Ltd. and were purified by standard procedures.¹² The mass fraction purities of these liquids tested by gas chromatography (Agilent Technologies 6820) were as follows: benzene (>0.995), toluene (>0.992), *o*-xylene (>0.995), *m*-xylene (>0.993), *p*-xylene (>0.996), and methyl 4-chlorobutyrate (>0.998). These liquids were dried over 4 Å molecular sieves and partially degassed by ultrasound prior to use. The measured viscosity and density data of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene were compared with the literature data and are shown in Table 1.

Airtight stoppered bottles were used for the preparation of the mixtures. The weight of the dry bottle was first determined. The less volatile component of the binary mixtures was introduced first in the sample tube followed by a second component, and the weight at each step was taken using an electronic balance (BS224S, The Sartorius Group, Germany) accurate to $\pm 0.1 \text{ mg}$. Each mixture was immediately used after it was well mixed by shaking. The uncertainty in the mole fraction is estimated to be lower than $\pm 1 \cdot 10^{-4}$. All mole quantities were based on the IUPAC relative atomic mass table.¹³

Apparatus and Procedure. The density of these pure compounds and the binary mixtures was measured by an Anton Paar DMA 4500 oscillating U-tube densitometer at (298.15 to 318.15) K. The temperature in the cell was regulated to $\pm 0.01 \text{ K}$ with a solid-state thermostat (Peltier). The temperature in the cell was measured by means of two integrated Pt 100 platinum thermometers. The densitometer was calibrated once a day with dry air and double-distilled freshly degassed water. The density of water was taken from the literature.¹⁴ The uncertainty in density measurements was $\pm 5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$.

The viscosities of pure liquids and the binary mixtures were measured at atmospheric pressure and different temperatures using an Ubbelohde capillary viscometer (Shanghai Glass Instruments Factory, China). The viscometer was filled with experimental liquid and immersed vertically in a DF-02 transparent thermostatic water bath (Fangao Scientific Co., Ltd., Nanjing, China) with temperature regulated within $\pm 0.01 \text{ K}$. An electronic digital stopwatch with a readability of $\pm 0.01 \text{ s}$

* Corresponding author. E-mail: dailiyang@zju.edu.cn. Fax: +86-571-87952693. Telephone: +86-571-87952693.

Table 1. Comparison of Experimental Density and Viscosity of Pure Liquids with Literature Values at 298.15 K

component	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
		this paper	lit.	this paper	lit.
benzene	298.15	0.87361	0.87357 ¹⁵	0.603	0.604 ¹⁵
			0.87344 ¹⁶		0.598 ¹⁶
			0.87365 ¹⁷		
toluene	298.15	0.86218	0.87360 ¹⁸	0.561	
			0.8622 ²¹		0.523 ²¹
			0.8516 ²¹		0.471 ²¹
	308.15	0.85281	0.86301 ¹⁵	0.499	0.523 ²¹
			0.86160 ¹⁶		0.449 ²¹
			0.86222 ¹⁷		0.446
o-xylene	298.15	0.87508	0.86219 ¹⁸	0.758	0.754 ¹⁵
			0.8529 ²¹		0.748 ¹⁶
			0.8435 ²¹		
	308.15	0.86662	0.87487 ¹⁵	0.665	0.690 ²¹
			0.87516 ¹⁶		0.611 ²¹
			0.87593 ¹⁷		0.589 ¹⁵
m-xylene	298.15	0.85983	0.87594 ¹⁸	0.587	
			0.8677 ²¹		0.524
			0.8597 ²¹		0.471
	308.15	0.85119	0.85980 ¹⁶	0.524	0.520 ²¹
			0.86007 ¹⁷		0.481 ²¹
			0.86009 ¹⁸		0.608 ¹⁵
p-xylene	298.15	0.85668	0.8511 ²¹	0.609	0.597 ¹⁶
			0.8424 ²¹		0.608 ¹⁹
			0.85670 ¹⁵		0.611 ²⁰
	308.15	0.84796	0.85654 ¹⁶	0.541	0.537 ²¹
			0.85663 ¹⁷		0.488 ²¹
			0.85661 ¹⁸		
methyl 4-chlorobutyrate	298.15	1.11624	0.85670 ¹⁹	1.519	
			0.85663 ²⁰		
			0.8477 ²¹		
	308.15	1.10523	0.8387 ²¹	1.279	
			-----		-----
			-----		-----
318.15	1.09413	-----	1.089	-----	
		-----		-----	

was used for flow time measurement. Experiments were repeated at least four times at each temperature for all mixtures, and the results were averaged. The viscosity (η) of these pure liquids and binary mixtures was then calculated from the following relationship

$$v = \frac{\eta}{\rho} = At - \frac{B}{t} \quad (1)$$

where t is the flow time; v is the kinematic viscosity; and A and B are the viscometer constants. The values of these

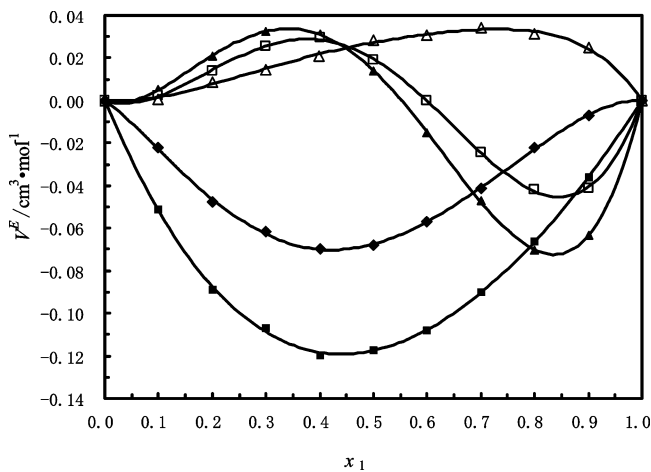


Figure 1. Excess molar volumes V^E at 298.15 K for (x_1) methyl 4-chlorobutyrate + $(1 - x_1)$ aromatic hydrocarbons: ▲, benzene; ■, toluene; □, *o*-xylene; Δ, *m*-xylene; ◆, *p*-xylene. The symbols represent experimental values, and solid curves were correlated by the Redlich–Kister equation.

constants A and B were obtained by using double-distilled water at 5 K intervals from (298.15 to 318.15) K. During the heating, to minimize the evaporation losses, the viscometer's limbs are closed with Teflon caps. During the measurements of flow time, the caps of the limbs were removed. The uncertainty of viscosity measurements was found to be within ± 0.003 mPa·s.

Results and Discussion

The experimental values of density and viscosity for the binary mixtures at different temperatures and at atmospheric pressure are listed in Table 2. Excess molar volumes were calculated from the measured density data according to the following equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (2)$$

where x_1 and x_2 are mole fractions; M_1 and M_2 are the molar masses; and ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively. Quantities without subscripts refer to the mixture.

The values of V^E for each mixture were fitted to the Redlich–Kister equation

$$Y = x_1(1 - x_1) \sum_{i=0}^n A_i (2x_1 - 1)^i \quad (3)$$

where $Y = V^E$ and A_i are the adjustable parameters, and x_1 is the mole fraction of component 1. In each case, the optimum

Table 2. Densities (ρ), Viscosities (η), and Excess Molar Volumes V^E for the Binary Mixtures of Methyl 4-Chlorobutyrate (1) + Aromatic Hydrocarbons (2) at Different Temperatures

x_1	ρ g·cm ⁻³	η mPa·s	V^E cm ³ ·mol ⁻¹	x_1	ρ g·cm ⁻³	η mPa·s	V^E cm ³ ·mol ⁻¹
Methyl 4-Chlorobutyrate (1) + Benzene (2)							
$T = 298.15$ K							
0.0000	0.87361	0.603	0.0000	0.5000	1.01366	0.960	0.0140
0.1000	0.90557	0.669	0.0051	0.5999	1.03689	1.054	-0.0151
0.2001	0.93529	0.731	0.0208	0.7000	1.05882	1.157	-0.0473
0.3000	0.96299	0.799	0.0326	0.8000	1.07942	1.271	-0.0703
0.4001	0.98908	0.875	0.0313	0.9000	1.09860	1.391	-0.0634
				1.0000	1.11624	1.519	0.0000
$T = 308.15$ K							
0.0000	0.86228	0.533	0.0000	0.5000	1.00277	0.828	-0.0019
0.1000	0.89474	0.579	0.0047	0.5999	1.02601	0.907	-0.0343
0.2001	0.92442	0.634	0.0164	0.7000	1.04797	0.990	-0.0644
0.3000	0.95212	0.690	0.0223	0.8000	1.06849	1.080	-0.0851
0.4001	0.97820	0.754	0.0176	0.9000	1.08762	1.180	-0.0712
				1.0000	1.10522	1.279	0.0000
$T = 318.15$ K							
0.0000	0.85208	0.466	0.0000	0.5000	0.99175	0.719	-0.0123
0.1000	0.88387	0.507	0.0007	0.5999	1.01499	0.785	-0.0470
0.2001	0.91349	0.553	0.0105	0.7000	1.03694	0.853	-0.0836
0.3000	0.94113	0.601	0.0165	0.8000	1.05755	0.927	-0.1075
0.4001	0.96718	0.661	0.0105	0.9000	1.07665	1.007	-0.0886
				1.0000	1.09413	1.089	0.0000
Methyl 4-Chlorobutyrate (1) + Toluene (2)							
$T = 298.15$ K							
0.0000	0.86218	0.561	0.0000	0.5000	0.99881	0.919	-0.1172
0.1000	0.89128	0.614	-0.0510	0.6000	1.02369	1.021	-0.1059
0.2000	0.91947	0.680	-0.0887	0.7000	1.04784	1.123	-0.0902
0.3000	0.94673	0.753	-0.1072	0.8000	1.07131	1.246	-0.0664
0.4001	0.97321	0.829	-0.1195	0.8998	1.09405	1.380	-0.0358
				1.0000	1.11624	1.519	0.0000
$T = 308.15$ K							
0.0000	0.85281	0.499	0.0000	0.5000	0.98849	0.796	-0.1189
0.1000	0.88171	0.551	-0.0535	0.6000	1.01323	0.883	-0.1095
0.2000	0.90969	0.599	-0.0908	0.7000	1.03722	0.962	-0.0922
0.3000	0.93679	0.662	-0.1130	0.8000	1.06054	1.062	-0.0668
0.4001	0.96307	0.731	-0.1228	0.8998	1.08316	1.170	-0.0370
				1.0000	1.10522	1.279	0.0000
$T = 318.15$ K							
0.0000	0.84340	0.446	0.0000	0.5000	0.97814	0.700	-0.1238
0.1000	0.87209	0.486	-0.0553	0.6000	1.00274	0.767	-0.1166
0.2000	0.89987	0.530	-0.0937	0.7000	1.02657	0.831	-0.0979
0.3000	0.92677	0.582	-0.1153	0.8000	1.04974	0.913	-0.0712
0.4001	0.95289	0.635	-0.1278	0.8998	1.07221	1.001	-0.0391
				1.0000	1.09413	1.089	0.0000
Methyl 4-Chlorobutyrate (1) + <i>o</i> -Xylene (2)							
$T = 298.15$ K							
0.0000	0.87508	0.758	0.0000	0.4992	0.99583	1.074	0.0190
0.1000	0.89936	0.814	0.0025	0.6000	1.02027	1.153	-0.0004
0.2001	0.92355	0.872	0.0136	0.7000	1.04453	1.235	-0.0245
0.3000	0.94767	0.935	0.0254	0.8000	1.06871	1.322	-0.0421
0.3998	0.97175	1.001	0.0297	0.9000	1.09268	1.415	-0.0411
				1.0000	1.11624	1.519	0.0000
$T = 308.15$ K							
0.0000	0.86662	0.665	0.0000	0.4992	0.98599	0.920	0.0329
0.1000	0.89063	0.710	0.0048	0.6000	1.01017	0.983	0.0131
0.2001	0.91454	0.757	0.0195	0.7000	1.03419	1.050	-0.0138
0.3000	0.93839	0.808	0.0335	0.8000	1.05813	1.120	-0.0340
0.3998	0.96219	0.863	0.0409	0.9000	1.08188	1.194	-0.0376
				1.0000	1.10522	1.279	0.0000
$T = 318.15$ K							
0.0000	0.85812	0.589	0.0000	0.4992	0.97614	0.800	0.0419
0.1000	0.88184	0.627	0.0097	0.6000	1.00007	0.855	0.0200
0.2001	0.90546	0.668	0.0291	0.7000	1.02383	0.907	-0.0076
0.3000	0.92903	0.707	0.0461	0.8000	1.04753	0.965	-0.0308
0.3998	0.95259	0.752	0.0512	0.9000	1.07102	1.025	-0.0347
				1.0000	1.09413	1.089	0.0000
Methyl 4-Chlorobutyrate (1) + <i>m</i> -Xylene (2)							
$T = 298.15$ K							
0.0000	0.85983	0.587	0.0000	0.4999	0.98721	0.928	0.0282
0.0999	0.88523	0.639	0.0008	0.5995	1.01273	1.022	0.0305
0.1999	0.91066	0.700	0.0088	0.6996	1.03843	1.128	0.0343

Table 2. (Continued)

x_1	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{\eta}{\text{mPa}\cdot\text{s}}$	$\frac{V^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	x_1	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{\eta}{\text{mPa}\cdot\text{s}}$	$\frac{V^E}{\text{cm}^3\cdot\text{mol}^{-1}}$
0.2999	0.93614	0.769	0.0147	0.7992	1.06411	1.238	0.0312
0.3990	0.96141	0.843	0.0209	0.8999	1.09015	1.368	0.0250
				1.0000	1.11624	1.519	0.0000
$T = 308.15 \text{ K}$							
0.0000	0.85119	0.524	0.0000	0.4999	0.97732	0.807	0.0357
0.0999	0.87633	0.571	0.0037	0.5995	1.00260	0.882	0.0383
0.1999	0.90149	0.624	0.0159	0.6996	1.02806	0.966	0.0422
0.2999	0.92672	0.674	0.0232	0.7992	1.05351	1.062	0.0381
0.3990	0.95174	0.737	0.0311	0.8999	1.07930	1.163	0.0330
				1.0000	1.10522	1.279	0.0000
$T = 318.15 \text{ K}$							
0.0000	0.84249	0.471	0.0000	0.4999	0.96737	0.706	0.0427
0.0999	0.86738	0.512	0.0051	0.5995	0.99239	0.770	0.0481
0.1999	0.89227	0.550	0.0217	0.6996	1.01763	0.839	0.0495
0.2999	0.91726	0.596	0.0288	0.7992	1.04283	0.920	0.0468
0.3990	0.94203	0.649	0.0385	0.8999	1.06838	1.004	0.0415
				1.0000	1.09413	1.089	0.0000
Methyl 4-Chlorobutyrate (1) + <i>p</i> -Xylene (2)							
$T = 298.15 \text{ K}$							
0.0000	0.85668	0.609	0.0000	0.4999	0.98616	0.927	-0.0679
0.0999	0.88247	0.662	-0.0221	0.6000	1.01209	1.023	-0.0571
0.2001	0.90843	0.714	-0.0479	0.7000	1.03803	1.133	-0.0412
0.3000	0.93433	0.775	-0.0619	0.8000	1.06399	1.255	-0.0221
0.4001	0.96027	0.847	-0.0698	0.9000	1.09006	1.385	-0.0072
				1.0000	1.11624	1.519	0.0000
$T = 308.15 \text{ K}$							
0.0000	0.84796	0.541	0.0000	0.4999	0.97620	0.806	-0.0588
0.0999	0.87348	0.586	-0.0173	0.6000	1.00191	0.886	-0.0492
0.2001	0.89917	0.629	-0.0387	0.7000	1.02762	0.978	-0.0329
0.3000	0.92484	0.679	-0.0534	0.8000	1.05337	1.077	-0.0156
0.4001	0.95054	0.738	-0.0606	0.9000	1.07925	1.179	-0.0046
				1.0000	1.10523	1.279	0.0000
$T = 318.15 \text{ K}$							
0.0000	0.83920	0.484	0.0000	0.4999	0.96620	0.705	-0.0523
0.0999	0.86445	0.522	-0.0129	0.6000	0.99169	0.772	-0.0445
0.2001	0.88987	0.561	-0.0303	0.7000	1.01719	0.846	-0.0308
0.3000	0.91530	0.600	-0.0451	0.8000	1.04271	0.926	-0.0134
0.4001	0.94077	0.651	-0.0534	0.9000	1.06837	1.008	-0.0035
				1.0000	1.09413	1.089	0.0000

Table 3. Coefficients of the Redlich–Kister Equation and Standard Deviation for Excess Molar Volumes of the Binary Mixtures

T/K	property	A_0	A_1	A_2	σ
Methyl 4-Chlorobutyrate (1) + Benzene (2)					
298.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.0577	-0.4759	-0.5908	0.0003
308.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.0103	-0.5257	-0.5647	0.0006
318.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.0490	-0.6087	-0.6953	0.0008
Methyl 4-Chlorobutyrate (1) + Toluene (2)					
298.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.4681	0.1118	-0.0303	0.0011
308.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.4807	0.1237	-0.0360	0.0007
318.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.5028	0.1121	-0.0346	0.0010
Methyl 4-Chlorobutyrate (1) + <i>o</i> -Xylene (2)					
298.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.0773	-0.2972	-0.4603	0.0007
308.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.1303	-0.2841	-0.4924	0.0008
318.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.1675	-0.3144	-0.4787	0.0004
Methyl 4-Chlorobutyrate (1) + <i>m</i> -Xylene (2)					
298.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.1081	0.1260	0.0500	0.0018
308.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.1414	0.1300	0.0875	0.0032
318.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.1717	0.1521	0.1228	0.0042
Methyl 4-Chlorobutyrate (1) + <i>p</i> -Xylene (2)					
298.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.2714	0.1239	0.1589	0.0010
308.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.2353	0.1137	0.1809	0.0010
318.15	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.2106	0.0826	0.1948	0.0009

numerical values of coefficients (A_i) were selected from an examination of the variation of the standard deviation

$$\sigma(Y) = \left[\sum (Y_{\text{calcd}} - Y_{\text{exptl}})^2 / (n - m) \right]^{(1/2)} \quad (4)$$

where n is the total number of number of data points and m is the number of parameters. The subscripts “calcd” and “exptl” denote correlated and experimental values. Table 3 lists the values of the parameters A_i together with the standard deviations.

We have calculated the V^E at several temperatures, but graphically the results are shown only at 298.15 K since at

other temperatures the variation of curves is similar. The density, viscosity, and excess molar volume data are presented in Table 2. Table 3 lists the values of the parameters A_i together with the standard deviations. The variation of V^E with the mole fraction x_1 of methyl 4-chlorobutyrate for the five binary mixtures at 298.15 K is presented in Figure 1. It is seen that the V^E values are negative for binary mixtures of methyl 4-chlorobutyrate + toluene, + *p*-xylene, and it is positive for the binary mixture of methyl 4-chlorobutyrate + *m*-xylene over the whole composition range at particular temperatures. However, for the system of methyl 4-chlo-

Table 4. Parameters of McAllister's Model together with the Standard Deviations (σ) at Different Temperatures

T/K	four-body interaction model				three-body interaction model		
	ν_{1112} ($\text{mm}^2 \cdot \text{s}^{-1}$)	ν_{1122} ($\text{mm}^2 \cdot \text{s}^{-1}$)	ν_{222} ($\text{mm}^2 \cdot \text{s}^{-1}$)	σ ($\text{mm}^2 \cdot \text{s}^{-1}$)	ν_{12} ($\text{mm}^2 \cdot \text{s}^{-1}$)	ν_{21} ($\text{mm}^2 \cdot \text{s}^{-1}$)	σ ($\text{mm}^2 \cdot \text{s}^{-1}$)
Methyl 4-Chlorobutyrate (1) + Benzene (2)							
298.15	1.1567	0.9224	0.8261	0.0015	1.0706	0.8594	0.0030
308.15	0.9898	0.8290	0.7003	0.0015	0.9425	0.7347	0.0015
318.15	0.8546	0.7397	0.6164	0.0012	0.8233	0.6519	0.0015
Methyl 4-Chlorobutyrate (1) + Toluene (2)							
298.15	1.1218	0.9267	0.7549	0.0025	1.0602	0.8002	0.0025
308.15	0.9703	0.8068	0.6843	0.0035	0.9139	0.7206	0.0035
318.15	0.8429	0.7195	0.6025	0.0027	0.8042	0.6353	0.0027
Methyl 4-Chlorobutyrate (1) + <i>o</i> -Xylene (2)							
298.15	1.2054	1.0829	0.09645	0.0011	1.1618	1.0035	0.0012
308.15	1.0301	0.9396	0.8422	0.0008	0.9970	0.8744	0.0011
318.15	0.9108	0.8119	0.7530	0.0013	0.8772	0.7706	0.0015
Methyl 4-Chlorobutyrate (1) + <i>m</i> -Xylene (2)							
298.15	1.1067	0.9551	0.7801	0.0015	1.0515	0.8304	0.0027
308.15	0.9763	0.8091	0.7126	0.0018	0.9126	0.7406	0.0020
318.15	0.8698	0.7058	0.6387	0.0013	0.8131	0.6530	0.0024
Methyl 4-Chlorobutyrate (1) + <i>p</i> -Xylene (2)							
298.15	1.1697	0.8858	0.8144	0.0012	1.0687	0.8193	0.0047
308.15	1.0301	0.7715	0.7243	0.0013	0.9440	0.7201	0.0049
318.15	0.8954	0.6851	0.6508	0.0011	0.8249	0.6467	0.0042

robutyrate with benzene and *o*-xylene, V^E curves at measured temperatures are sigmoid in nature, and there is an inversion in sign (Figure 1).

McAllister's multibody interaction model, which takes into account interactions of both like and unlike molecules, is widely used for correlating the kinematic viscosity (ν) of binary mixtures with mole fraction. The three-body model is defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln \left(x_1 + \frac{x_2 M_2}{M_1} \right) + 3x_1^2 x_2 \ln \left(\frac{2 + M_2/M_1}{3} \right) + 3x_1 x_2^2 \ln \left(\frac{1 + 2M_2/M_1}{3} \right) + x_2^3 \ln \left(\frac{M_2}{M_1} \right) \quad (5)$$

and the four-body model is given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln \left(x_1 + \frac{x_2 M_2}{M_1} \right) + 4x_1^3 x_2 \ln \left(\frac{3 + M_2/M_1}{4} \right) + 6x_1^2 x_2^2 \ln \left(\frac{1 + M_2/M_1}{2} \right) + 4x_1 x_2^3 \ln \left(\frac{1 + 3M_2/M_1}{4} \right) + x_2^4 \ln \left(\frac{M_2}{M_1} \right) \quad (6)$$

where ν , ν_1 , and ν_2 are the kinematic viscosities of the mixture and the kinematic viscosities of pure components 1 and 2, respectively. ν_{12} , ν_{21} , ν_{1112} , ν_{1122} , and ν_{2221} are the model parameters. The calculated results are presented in Table 4. The correlating ability of eqs 5 and 6 was tested by calculating the standard deviation (σ) between the experimental and calculated kinematic viscosities. From Table 4, it is clear that McAllister's four-body interaction model gives a better result than the three-body model for correlating the kinematic viscosities of the systems of methyl 4-chlorobutyrate with *m*-xylene and *p*-xylene. For the other three systems, the correlating results have no significant difference by using McAllister's three-body and four-body interaction models.

Conclusion

This paper reports new experimental data for the densities and viscosities of the binary mixtures of methyl 4-chlorobutyrate with benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene over the whole composition range at different temperatures ranging from (298.15 to 318.15) K and atmospheric pressure. Excess molar volumes V^E for the binary mixtures were derived from the experimental data. The V^E values are negative for binary mixtures of methyl 4-chlorobutyrate with toluene and *p*-xylene, and it is positive for the binary mixture of methyl 4-chlorobutyrate with *m*-xylene over the whole composition range at a particular temperature. For the system of methyl 4-chlorobutyrate with benzene and *o*-xylene, V^E curves at measured temperatures are sigmoid in nature, and there is an inversion in sign. The values of V^E were correlated by using the Redlich–Kister equation. The binary kinematic viscosities were correlated by the McAllister three- and four-body interaction equations. Both the Redlich–Kister equation and the McAllister equation can represent data very well.

Literature Cited

- (1) Kulinkovich, O. G.; Kananovich, D. G. Advanced Procedure for the Preparation of Cis-1,2-Dialkylcyclopropanols - Modified Ate Complex Mechanism for Titanium-Mediated Cyclopropanation of Carboxylic Esters with Grignard Reagents. *Eur. J. Org. Chem.* **2007**, 212, 1–2132.
- (2) Mourtas, S.; Gatos, D.; Kalaitzi, V.; Katakoulou, C.; Barlos, K. S-4-Methoxytrityl Mercapto Acids: Synthesis and Application. *Tetrahedron Lett.* **2001**, 42, 6965–6967.
- (3) Venkatesan, H.; Greenberg, M. M. Improved Utility of Photolabile Solid Phase Synthesis Supports for the Synthesis of Oligonucleotides Containing 3'-Hydroxyl Termini. *J. Org. Chem.* **1996**, 61, 525–529.
- (4) Tatsuya, M.; Kazuya, U.; Osamu, M.; Kazunori, Y.; Noritada, M. Synthetic Studies of Fluorine-containing Compounds for Household Insecticides. *J. Fluorine Chem.* **2007**, 128, 1174–1181.
- (5) Zakharkin, L. I.; Aniline, E. V. Friedel-Craft Alkylation of Benzene by Normal -Chloroalkanoic Acids, Their Methyl Esters and Nitriles. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 36, 7–71.
- (6) Liu, Q. Y.; Zhuo, J. L.; Xi, H. T.; Sun, X. Q. Stability of Ether Bond of *O*-nitro Aryl Ether in the Alkaline Medium. *Guangzhou Huaxue* **2005**, 30, 26–29.
- (7) Nain, A. K.; Chandra, P.; Pandey, J. D.; Gopal, S. 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. *J. Chem. Eng. Data* **2008**, *53*, 2654–2665.
- (8) Singh, S.; Sethi, B. P. S.; Katyal, R. C.; Rattan, V. K. Viscosities, Densities, and Speeds of Sound of Binary Mixtures of *o*-Xylene, *m*-Xylene, *p*-Xylene, and Isopropylbenzene with 2-Butanone at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 125–127.
 - (9) Singh, S.; Sethi, B. P. S.; Katyal, R. C.; Rattan, V. K. Viscosities, Densities, and Speeds of Sound of *o*-Xylene, *m*-Xylene, *p*-Xylene, and Isopropylbenzene with 4-Methylpentane at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 1373–1375.
 - (10) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and The Classification of Solutions[J]. *Ind. Eng. Chem.* **1948**, *40*, 345–348.
 - (11) McAllister, R. A. The Viscosity of Liquid Mixtures. *AIChE J.* **1960**, *6* (3), 427–431.
 - (12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents; Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.
 - (13) IUPAC Commission on Atomic Weight and Isotopic Abundances, 1985. *Pure Appl. Chem.* **1986**, *58*, 1677–1692.
 - (14) *Perry's Chemical Engineering' Handbook*, 8/E Section 1&2, 2007.
 - (15) Yang, C. S.; Ma, P. S.; Zhou, Q. Excess Molar Volumes and Viscosities of Binary Mixtures of Sulfolane with Benzene, Toluene, Ethylbenzene, *p*-Xylene, *o*-Xylene, and *m*-Xylene at 303.15 and 323.15 K and Atmospheric Pressure. *J. Chem. Eng. Data* **2004**, *49*, 881–885.
 - (16) Chevaller, J. L. E.; Pei, P. J.; Gaston-Bonhomme, Y. H. Viscosity and Density of Some Aliphatic, Cyclic, and Aromatic Hydrocarbons Binary Liquid Mixtures. *J. Chem. Eng. Data* **1990**, *35*, 206–212.
 - (17) Verma, N.; Maken, S.; Deshwal, B. R.; Singh, K. C.; Park, J. W. Molar Excess Volume of *sec*- and *tert*-Butyl Chloride with Aromatic Hydrocarbons at $T = 298.15$ K. *J. Chem. Eng. Data* **2007**, *52*, 2083–2085.
 - (18) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents-Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.
 - (19) Yang, C. S.; Xu, W.; Ma, P. S. Thermodynamic Properties of Binary Mixtures of *p*-Xylene with Cyclohexane, Heptane, Octane, and *N*-Methyl-2-pyrrolidone at Several Temperatures. *J. Chem. Eng. Data* **2004**, *49*, 1794–1801.
 - (20) Exarchos, N. C.; Tasioula-Margar, M.; Demetropoulos, I. N. Viscosities and Densities of Dilute Solutions of Glycerol Trioleate + Octane, + *p*-Xylene, + Toluene, and + Chloroform. *J. Chem. Eng. Data* **1995**, *40*, 567–571.
 - (21) Song, C. Y.; Shen, H. Z.; Zhao, J. H.; Wang, L. C.; Wang, F. A. Densities and Viscosities of Binary Mixtures of Vitamin K3 with Benzene, Toluene, Ethylbenzene, *o*-Xylene, *m*-Xylene, and *p*-Xylene from (303.15 to 333.15) K. *J. Chem. Eng. Data* **2008**, *53*, 1110–1115.

Received for review February 18, 2009. Accepted April 14, 2009.

JE900194V