Densities and Viscosities for Binary Mixtures of Chlorinated Polypropylene with Toluene, Tetrahydrofuran, Chloroform, Carbon Tetrachloride, and 2-Butanone at (298.15, 308.15, and 318.15) K

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The densities for binary mixtures of fractionated chlorinated polypropylene with toluene and 2-butanone have been determined. At a fixed temperature, concentration, and solvent, the densities for binary mixtures of fractionated and unfractionated chlorinated polypropylene with solvents are the same. The width of the molecular weight distribution of chlorinated polypropylene does not affect the densities of these mixtures. The densities and viscosities for binary mixtures of chlorinated polypropylene with toluene, tetrahydrofuran, chloroform, carbon tetrachloride, and 2-butanone have been measured at temperatures from (298.15 to 318.15) K. The apparent molar volumes and standard partial molar volumes of the chlorinated polypropylene repeat unit were calculated from experimental measurements. From the results, the repeat unit structure of chlorinated polypropylene has been determined.

Introduction

Chlorinated polypropylene (CPP) has excellent adhesion to polyolefin. As an adhesion promoter, CPP is widely used in polyolefin coatings, agglutinants, printing ink, etc.[1] CPP is usually used in solvents, so properties of CPP in various solvents are required.

Information on the volumetric and transport properties of polymer solutions is required for the design and operation of polymer processes. Among the properties of polymer solutions, density and viscosity data are especially important in a variety of applications.[2] Viscosity is also a significant parameter that influences not only the usual mixing and flow conditions and effectiveness of the heat and/or mass transfer operations but also the kinetics of phase separation, which are important to many applications. From a fundamental perspective, viscosity measurements give insight into polymer−solvent interactions.[3]

The Flory−Huggins lattice theory is one of the basic theories of polymer solution. According to this theory, one polymer repeat unit and one solvent molecule occupy one lattice, respectively. Polymer repeat unit and solvent molecule in polymer solution arrange according to these lattices. The size of each lattice is the same. Therefore, the volume of one polymer repeat unit is equal to that of one solvent molecule, and their ratio must be approximately equal to one. Accordingly, the polymer repeat unit structure can be determined by means of the ratio of volume of a solvent molecule to a polymer repeat unit.

After calculating the ratios of volumes of the solvent to polymer repeat unit structures for poly(styrene) + cyclohexane, poly(styrene) + ethylbenzene, poly(isobutylene) + diisobutyl ketone, poly(isobutylene) + ethylbenzene, and poly(methyl methacrylate) + 4-heptanone, Azevedo et al.[4] found that a monomeric polymer repeat unit corresponded to a solvent molecule for all but the poly(isobutylene) and diisobutyl ketone system, where a dimer repeat unit was required. Since CPP is not from polymerization of chlorinated propylene but from the reaction of chlorine and polypropylene, Azevedo's method cannot be used for CPP. In terms of material balance calculation, each chlorine atom corresponds to 6 carbon atoms and 11 hydrogen atoms in a CPP molecule, which contains a mass fraction of 30 % chlorine. However, CPP is from polypropylene, and polypropylene is from propylene polymerization. The repeat unit of CPP may be a propylene monomer ($C_3H_{5.5}Cl_{0.5}$), propylene dimmer ($C_6H_{11}Cl_1$), propylene trimer ($C_9H_{16.5}Cl_{1.5}$), or propylene tetramer ($C_{12}H_{22}Cl_2$). In order to determine the repeat unit structure of CPP, the volumes of repeat unit and solvent must be calculated.

Toluene, tetrahydrofuran, chloroform, carbon tetrachloride, and 2-butanone are widely used in practical application and are solvents of CPP. However, as far as we know, no thermodynamic data are available for binary mixtures of CPP with these solvents in the open literature.

The molecular weight distribution of CPP is wide. The CPP was separated into five fractions using fractional precipitations by solvent + nonsolvent technique. The objective of this work is to report densities and viscosities for binary mixtures of CPP and its fractions with toluene, tetrahydrofuran, chloroform, carbon tetrachloride, and 2-butanone at temperatures from (298.15 to 318.15) K. From measurements of densities, the apparent molar volumes and standard partial molar volumes of CPP were calculated. According to these results, the repeat unit of CPP was determined.

Experimental Section

Materials. CPP, which contains a mass fraction of 30 % chlorine, was a commercial product purchased from Jin Zhujiang Chemical Factory in Guangdong (China). The number-average molecular weight (M_n) of CPP was 93010 g·mol^{-1}. CPP was purified with methanol.[5] A mixture of 45 g·L^{-1} CPP + toluene was prepared. Under stirring, the mixture was slowly dripped

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into methanol whose volume was five times the mixture until floccule precipitation appeared. The sample was allowed to stand undisturbed for about 24 h. Then the clear solution was poured out, and the residual precipitation was the purified CPP. The purified CPP was dried by vacuum to constant mass.

CPP was separated by fractional precipitations.[6] The mixture of 10 g·L^{-1} CPP + toluene was prepared and poured into a three-neck bottle. The bottle was immersed in a thermostatic water bath. Methanol was dripped into the mixture until turbidity appeared at 298.15 K after thermal stability was attained. Then the temperature was adjusted to 308.15 K to make precipitation and other impurity substances dissolve completely. Thirty minutes later, the three-neck bottle was taken out and the solution was poured into a pyriform separating funnel. The sample was allowed to stand undisturbed for about 24 h. Then the precipitation was tapped off from the bottom of the funnel. This was the first fraction (CPP1). By repeating the above steps, other fractions (CPP2 to CPP5) were obtained. The fractionated CPP were dried by vacuum to constant mass.

Toluene, carbon tetrachloride, 2-butanone, and methanol purchased from Tianjin BoDi Chemical Technology Co. Ltd were analytical grades. Their purities were greater than 0.995 by mass fraction. Analytical grade tetrahydrofuran and chloroform were purchased from Tianjin Kermel Chemical Reagents Development Center. Their purities were greater than 0.990 by mass fraction. All reagents were used directly without further purification. Water used in experiments was double-distilled water; the conductivity was less than 1×10^{-4} S·m^{-1}.

Apparatus and Procedure. A DAWNEOS multi-angle laser photometer from Wyatt Technology Corp. was used to measure molecular weights of CPP.

The binary mixtures of CPP with solvents were prepared by mass using an electronic balance (type AR2140, USA) and were stored in ground-glass-stoppered bottles of 60 cm^3. The balance has an uncertainty of ± 0.0001 g. It was ensured that the components were adequately mixed before being transferred to the density meter.

Densities were measured with a PAAR DMA60/ 602 vibrating-tube density meter, thermostatically controlled to within ± 0.01 K in the temperature range (298.15 to 318.15) K. Calibration was performed each time under atmospheric pressure, in accordance with specifications, using double-distilled water and dry air. The uncertainty of the density measurements was estimated to be $\pm 1 \times 10^{-5}$ g·cm^{-3}. At least three measurements were made, which had an average deviation of $\pm 8.19 \times 10^{-6}$ g·cm^{-3}. In order to avoid the effect of concentration on the density consistency, the densities for binary mixtures of fractions of CPP with solvents were determined at mass fractions of 1 % and 5 % CPP. In order to avoid the effect of solvents on the density consistency, the densities for binary mixtures of fractions of CPP with solvents were determined in both good solvent (toluene) and poor solvent (2-butanone), respectively.

Newtonian viscosity behavior was verified for all mixtures investigated before measurement of viscosity. It was found that the viscosities of all samples were independent of shear rate. Reference 7 reported that CPP + toluene mixtures at different concentrations were Newtonian fluids. The result was in agreement with this work.

The viscosity was measured using different Ubbelohde capillary viscometers. Their diameters were (0.52 to 0.53) mm (Beijing Glass Instruments Factory, China), (0.7 to 0.8) mm, and (1.0 to 1.1) mm (Shanghai Chemistry Reagent Corporation, Chinese Medicine Group), respectively. The viscometers were calibrated with toluene and carbon tetrachloride at temperatures of (298.15, 308.15, and 318.15) K. A thoroughly cleaned and perfectly dried viscometer, filled with experimental solution, was placed vertically in an insulated jacket wherein constant temperature (± 0.02 K) was maintained by circulating water from a thermoelectric controller (type 501, Shanghai Laboratory Instrument Works Co. Ltd.) at the required temperature. After thermal stability was attained, the flow times of the solutions were recorded with an electronic digital stopwatch correct to ± 0.01 s. At least five repetitions of each datum point obtained were reproducible to ± 0.06 s, and the results were averaged. The standard deviations for viscosity of five parallel measurements were less than 1.1×10^{-2} m Pa·s. Because the capillary diameter ((0.52 to 0.53), (0.7 to 0.8), and (1.0 to 1.1) mm) was far less than its length ((115, 93, and 93) mm), the end corrections were found to be negligible. The viscosity η was then calculated from the relationship[8]

$$\eta = kt\rho - \rho\frac{B}{t} \tag{1}$$

where η, ρ, and t are the viscosity, density, and flow time of the mixture, respectively. k and B are viscometer constants. The uncertainty in the viscosity measurement is estimated to be ± 0.6 %. There are three main sources of error in the measurement of the viscosity. The first is the propagation error resulting from the measurement of the density. The second is the measurement error resulting from the weighting process of the sample and the repeatability of the measurement. The third is the instrument error.

The measured densities and viscosities of toluene, tetrahydrofuran, chloroform, carbon tetrachloride, and 2-butanone together with literature values at 298.15 K are included in Table 1.

Table 1. Comparison of Experimental Densities, ρ, and Viscosities, η, of Toluene, Tetrahydrofuran, Chloroform, Carbon Tetrachloride, and 2-Butanone with Literature Values at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s	
solvent	exptl	lit	exptl	lit
toluene	0.86197	0.86198[9]	0.5475	0.5497[14]
tetrahydrofuran	0.88207	0.88199[10]	0.4661	0.4610[15]
chloroform	1.47899	1.47924[11]	0.5275	0.5273[16]
carbon tetrachloride	1.58390	1.58397[12]	0.8975	0.9170[17]
2-butanone	0.79965	0.79961[13]	0.3899	0.3920[13]

Results and Discussion

Table 2 lists the experimental densities for binary mixtures of five fractionated and unfractionated CPP with solvents at (298.15, 308.15, and 318.15) K. The average absolute deviation (AAD) of density between CPP1 to CPP5, CPP, and their average value is defined by

$$\mathrm{AAD} = (1/n)\sum_{i=1}^{n} |(\rho_{\mathrm{ave}} - \rho_i)/\rho_i| \tag{2}$$

where ρ_i is the densities for binary mixtures of CPP1 to CPP5 and CPP with solvents. ρ_{ave} is the average value of ρ_i. n is the experimental point.

Table 2 shows that the AAD of mass fraction $w = 0.01$ fractioned and unfractionated CPP + toluene mixtures are 7.0×10^{-5}, 6.0×10^{-5}, and 7.0×10^{-5} for (298.15, 308.15, and 318.15) K, respectively. These results indicate that, at a fixed temperature, there is no difference between the densities. The AAD of mass fraction $w = 0.05$ fractioned and unfractionated

Table 2. Densities, ρ, for Fractionated and Unfractionated Chlorinated Polypropylene (1) + Toluene and 2-Butanone (2) from T = (298.15 to 318.15) K

	M_n		ρ/gcm^{-3}		
no.	g·mol^{-1}	M_w[a]/M_n	T/K = 298.15	T/K = 308.15	T/K = 318.15
			w = 0.01 Fractionated CPP + Toluene		
CPP1	282200	1.047	0.86404	0.85485	0.84563
CPP2	194400	1.026	0.86397	0.85477	0.84550
CPP3	136700	1.038	0.86400	0.85480	0.84553
CPP4	100600	1.016	0.86413	0.85493	0.84566
CPP5	48960	1.478	0.86405	0.85486	0.84559
CPP	93010	1.972	0.86417	0.85496	0.84566
ρ_{ave}			0.86406	0.85486	0.84560
AAD			7.0×10^{-5}	6.0×10^{-5}	7.0×10^{-5}
			w = 0.05 Fractionated CPP + Toluene		
CPP1	282200	1.047	0.87246	0.86334	0.85416
CPP2	194400	1.026	0.87213	0.86300	0.85386
CPP3	136700	1.038	0.87232	0.86317	0.85411
CPP4	100600	1.016	0.87249	0.86336	0.85429
CPP5	48960	1.478	0.87213	0.86298	0.85390
CPP	93010	1.972	0.87286	0.86372	0.85449
ρ_{ave}			0.87240	0.86326	0.85414
AAD			2.4×10^{-4}	2.4×10^{-4}	2.1×10^{-4}
			w = 0.01 Fractionated CPP + 2-Butanone		
CPP1	282200	1.047	0.80258	0.79225	0.78182
CPP2	194400	1.026	0.80208	0.79172	0.78129
CPP3	136700	1.038	0.80212	0.79173	0.78130
CPP4	100600	1.016	0.80217	0.79179	0.78138
CPP5	48960	1.478	0.80213	0.79176	0.78134
CPP	93010	1.972	0.80209	0.79173	0.78122
ρ_{ave}			0.80220	0.79183	0.78139
AAD			1.6×10^{-4}	1.8×10^{-4}	1.8×10^{-4}

[a] M_w is the weight average molecular weight.

CPP + toluene mixtures at (298.15, 308.15, and 318.15) K are 2.4×10^{-4}, 2.4×10^{-4}, and 2.1×10^{-4}, respectively. These results indicate that, at a fixed temperature, there is also no difference between the densities. Therefore, at a fixed temperature and concentration, there is no effect of molecular weights on their densities of fractionated and unfractionated CPP + toluene mixtures.

In the same way, the AAD of mass fraction $w = 0.01$ fractioned and unfractionated CPP + 2-butanone mixtures at (298.15, 308.15, and 318.15) K are 1.6×10^{-4}, 1.8×10^{-4}, and 1.8×10^{-4}, respectively. At a fixed temperature and concentration, there is also no effect of molecular weights on their densities of fractionated and unfractionated CPP + 2-butanone mixtures.

Accordingly, at a fixed temperature, concentration, and solvent, the densities for binary mixtures of fractionated and unfractionated CPP that contains 30 % chlorine with solvents have only one value. In other words, the width of molecular weight distribution of CPP does not affect the densities of these mixtures.

Since different fractions have identical density, densities for binary mixtures of CPP with solvents can be directly determined using CPP purified with methanol rather than a fractionated one. The densities for binary mixtures of CPP with solvents at (298.15, 308.15, and 318.15) K are listed in Table 3.

As described above, density is independent of molecular weight distribution of CPP. It only relates to the molecular structure. Nevertheless, the minimum unit that reflects the character of molecular structure is the polymer repeat unit. Among a monomeric propylene repeat unit ($C_3H_{5.5}Cl_{0.5}$), a dimer repeat unit ($C_6H_{11}Cl$), a trimer repeat unit ($C_9H_{16.5}Cl_{1.5}$), or a tetramer repeat unit ($C_{12}H_{22}Cl_2$), which one is the correct? It is necessary to calculate the volumes of the repeat unit and the solvent molecules. Then the correct result is judged by the Flory−Huggins lattice theory.

Table 3. Densities, ρ, and Viscosities, η, for Chlorinated Polypropylene (1) + Different Solvents (2) from T = (298.15 to 318.15) K

100 w	ρ/g·cm^{-3}	η/mPa·s	100 w	ρ/g·cm^{-3}	η/mPa·s
		T/K = 298.15			
		CPP + Toluene			
1.0	0.86415	1.0483	4.0	0.87065	4.5064
2.0	0.86631	1.7657	5.0	0.87286	6.5543
3.0	0.86849	3.1329	10.0	0.88402	30.8535
		CPP + Tetrahydrofuran			
1.0	0.88414	1.0490	4.0	0.89042	5.9834
2.0	0.88620	2.0079	5.0	0.89254	9.5162
3.0	0.88836	4.2259	10.0	0.90337	59.0705
		CPP + Chloroform			
1.0	1.47484	2.0125	4.0	1.46246	14.6482
2.0	1.47066	5.4896	5.0	1.45850	29.2209
3.0	1.46657	9.8086	10.0	1.43900	218.7208
		CPP + Carbon Tetrachloride			
1.0	1.57789	2.9658	4.0	1.56032	30.2659
2.0	1.57193	7.1188	5.0	1.55438	54.2427
3.0	1.56608	14.9723	10.0	1.52689	698.6607
		CPP + 2-Butanone			
0.5	0.80101	0.6431	2.0	0.80473	0.8849
1.0	0.80233	0.7253	2.5	0.80583	1.1086
1.5	0.80369	0.7982			
		T/K = 308.15			
		CPP + Toluene			
1.0	0.85496	0.9551	4.0	0.86149	4.0960
2.0	0.85712	1.6102	5.0	0.86372	5.4014
3.0	0.85937	2.7001	10.0	0.87500	26.6990
		CPP + Tetrahydrofuran			
1.0	0.87334	0.9612	4.0	0.87971	5.2290
2.0	0.87542	1.8620	5.0	0.88186	8.6111
3.0	0.87762	3.7750	10.0	0.89283	51.7895
		CPP + Chloroform			
1.0	1.45606	1.7716	4.0	1.44441	11.0878
2.0	1.45216	4.8888	5.0	1.44048	23.1054
3.0	1.44825	7.5870	10.0	1.42175	154.1783
		CPP + Carbon Tetrachloride			
1.0	1.55892	2.6530	4.0	1.54185	25.0470
2.0	1.55316	6.1613	5.0	1.53628	42.5198
3.0	1.54752	12.9538	10.0	1.50948	566.8490
		CPP + 2-Butanone			
0.5	0.79062	0.5954	2.0	0.79432	0.7977
1.0	0.79192	0.6894	2.5	0.79549	0.9822
1.5	0.79319	0.7161			
		T/K = 318.15			
		CPP + Toluene			
1.0	0.84563	0.8807	4.0	0.85230	3.5444
2.0	0.84779	1.4791	5.0	0.85449	4.8049
3.0	0.84997	2.4955	10.0	0.86592	21.5484
		CPP + Tetrahydrofuran			
1.0	0.86243	0.8948	4.0	0.86895	4.7293
2.0	0.86461	1.6949	5.0	0.87108	7.4353
3.0	0.86674	3.4850	10.0	0.88217	42.8651
		CPP + Chloroform			
1.0	1.43719	1.5779	4.0	1.42611	9.4973
2.0	1.43344	4.1961	5.0	1.42234	18.6844
3.0	1.42980	6.4334	10.0	1.40387	119.4367
		CPP + Carbon Tetrachloride			
1.0	1.53961	2.3580	4.0	1.52316	21.5184
2.0	1.53406	5.6429	5.0	1.51763	35.6082
3.0	1.52860	11.2897	10.0	1.49110	453.1655
		CPP + 2-Butanone			
0.5	0.78016	0.5519	2.0	0.78381	0.7140
1.0	0.78144	0.6171	2.5	0.78488	0.8716
1.5	0.78265	0.6609			

The apparent molar volume of CPP repeat unit, $V_{\phi,2}$, is given by the equation[18−20]

$$V_{\phi,2} = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \qquad (3)$$

Table 4. Standard Partial Molar Volumes, $V^0_{\phi,2}$, of CPP Repeat Unit and Molar Volume, V_m, of Solvents from T = (298.15 to 318.15) K

T	$V^0_{\phi,2}$/cm^3·mol^{-1}				V_m	
K	monomeric propylene	dimeric propylene	trimeric propylene	tetrameric propylene	cm^3·mol^{-1}	$(V^0_{\phi,2})_2/V_m$[a]
			Toluene			
298.15	30.61	102.92	154.34	276.79	106.89	0.96
308.15	77.36	103.61	155.37	279.78	108.05	0.96
318.15	78.24	104.67	157.00	282.89	109.24	0.96
			Tetrahydrofuran			
298.15	74.76	102.94	154.34	270.49	81.75	1.26
308.15	75.69	103.29	154.83	273.85	82.77	1.25
318.15	76.63	103.66	155.47	277.31	83.82	1.24
			Chloroform			
298.15	25.13	102.82	154.21	156.47	80.72	1.27
308.15	26.24	103.32	154.94	158.69	81.76	1.26
318.15	27.12	103.59	155.38	160.89	82.85	1.25
			Carbon Tetrachloride			
298.15	15.94	103.36	155.06	144.23	97.11	1.06
308.15	17.06	103.81	155.68	146.23	98.31	1.06
318.15	17.83	104.57	156.90	148.19	99.54	1.05
			2-Butanone			
298.15	75.72	96.37	144.64	296.34	90.18	1.07
308.15	75.37	96.58	144.64	300.25	91.36	1.06
318.15	76.70	97.02	145.90	304.26	92.59	1.05

[a] $(V^0_{\phi,2})_2/V_m$ is the ratio of $V^0_{\phi,2}$ of dimer propylene to V_m.

where M is the molar mass of the CPP repeat unit. If the repeat unit is $C_3H_{5.5}Cl_{0.5}$, $C_6H_{11}Cl$, $C_9H_{16.5}Cl_{1.5}$, or $C_{12}H_{22}Cl_2$, M is 59.225, 118.450, 177.675, and 236.900, respectively. ρ is the density of mixtures, and ρ_0 is the density of the solvent. m is the molality of the CPP repeat unit, and its value changes with M.

The relation between apparent molar volume of CPP repeat unit, $V_{\phi,2}$, and its molality, m, is given by[21−23]

$$V_{\phi,2} = V^0_{\phi,2} + S_V m \tag{4}$$

where S_V is the slope. $V^0_{\phi,2}$ is standard partial molar volume of the CPP repeat unit. Since the partial molar quantity of pure solvent is equal to its molar quantity, the physical quantity that corresponds to $V^0_{\phi,2}$ is the molar volume of pure solvent, V_m, which is a character parameter of pure solvent. $V^0_{\phi,2}$ is obtained by fitting eq 4 to experimental results using a least-squares regression method. Table 4 gives $V^0_{\phi,2}$ together with the molar volume of pure solvents, V_m.

From Table 4, the ratio of $V^0_{\phi,2}$ of dimer propylene $[(V^0_{\phi,2})_2]$ to V_m is between 0.96 and 1.27. It is obvious that the ratios are approximately one. The result accords with Flory−Huggins lattice model. This result is also very close to the J. Azevedo's result[4] that the volume ratios of solvent to polymer repeat unit were between 0.91 and 1.25. The ratios of $V^0_{\phi,2}$ of other CPP repeat unit to V_m is clearly far from one. These results do not accord with lattice model. Therefore, the CPP repeat unit is the dimer repeat unit ($C_6H_{11}Cl$).

The experimental viscosities at (298.15, 308.15, and 318.15) K are also listed in Table 3. Comparing the viscosity between the different binary mixtures, the viscosities of CPP + toluene solution and CPP + tetrahydrofuran solution are lower than that of CPP + chloroform solution and CPP + carbon tetrachloride solution. This indicates that the fluid of CPP + toluene solution and CPP + tetrahydrofuran solution are better than that of CPP + chloroform solution and CPP + carbon tetrachloride solution. Although the viscosity of CPP + 2-butanone solution is also low, the solubility of CPP in it is small. Therefore, toluene and tetrahydrofuran are common solvents of CPP. Since the price of toluene is lower than that of tetrahydrofuran, toluene is the optimal solvent for CPP.

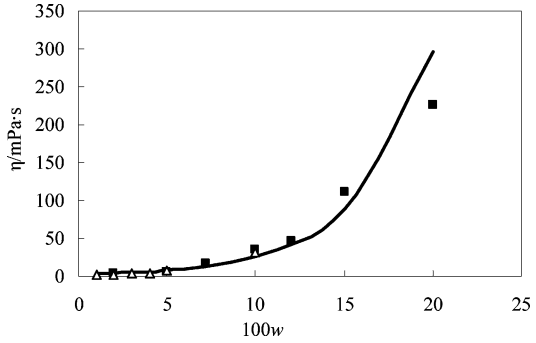

Figure 1. Comparison of viscosity of CPP + toluene mixtures with literature: △, experimental data; ■, literature data; −, fitting curve.

Variation of viscosity with concentration can be described by either an exponential-type or a power-type relationship. Kar and Arslan considered that the exponential model seems to describe well than the power-type relationship when they discussed the viscosity of pectin solutions:[24]

$$\eta = K \exp(AC) \tag{5}$$

where K and A are constants, and C is the concentration of solutions.

Ou et al. found that the CPP + toluene system also presented an exponential-type function when they studied the solution viscosity of CPP and petroleum resin.[7] In their study, the unit of concentration was mass percent. According to experimental data, Ou et al. gave the following expression:

$$\eta = 2.336 \exp(24.2C) \tag{6}$$

If the experimental results of this work are plotted in the fitting curve of eq 6, it is found that the experimental points are located on the fitting curve. Figure 1 shows the result. This indicates that the results in this work are consistent with previous literature and that the conclusion of CPP + toluene mixtures are Newtonian flow described in this work is credible.

According to Table 3, the relations of viscosity for binary mixtures of CPP with other solvents and concentration can also be described by an exponential-type relationship. The regression K and A of eq 5 along with standard deviations at different temperatures are listed in Table 5.

The standard deviation is defined by

$$\sigma = [\sum_{i=1}^{p} (Y_i^{\text{exptl}} - Y_i^{\text{calcd}})^2/(n-p)]^{1/2} \tag{7}$$

where n is the number of experimental points and p is the number of parameters. Y_i^{calcd} and Y_i^{exptl} refer to the calculated values from the equation and to the experimental value.

It is necessary to note that standard deviation (σ) is an absolute value. It relates to viscosity value of solution. Among these binary mixtures, the viscosities of CPP+ chloroform solution and CPP + carbon tetrachloride solution are obviously higher than that of CPP + toluene solution and of CPP + tetrahydrofuran solution. The higher the concentration, the bigger is the difference between viscosities of CPP solutions. When concentration is at $w = 0.10$, the viscosities of CPP + chloroform solution and CPP + carbon tetrachloride solution are 3 to 10 times higher than that of CPP + toluene solution

Table 5. Regression *K, A,* and Standard Deviation, σ, of Equation 5 as Well as the Ratio of σ to η_{max}

	T				σ
solvent	K	K	A	σ	η_{max}
toluene	298.15	0.9277	0.0412	2.36	0.077
	308.15	0.8379	0.0409	1.72	0.065
	318.15	0.7926	0.0396	1.51	0.070
tetrahydrofuran	298.15	0.9381	0.0478	5.76	0.097
	308.15	0.8611	0.0478	4.92	0.095
	318.15	0.8128	0.0468	3.88	0.091
chloroform	298.15	1.8029	0.0347	23.79	0.109
	308.15	1.5934	0.0334	15.13	0.098
	318.15	1.4227	0.0327	10.61	0.089
carbon tetrachloride	298.15	2.1526	0.0390	65.85	0.094
	308.15	1.8977	0.0388	48.33	0.085
	318.15	1.7336	0.0383	35.36	0.078
2-butanone	298.15	0.5551	0.0318	0.04	0.040
	308.15	0.5291	0.0288	0.04	0.041
	318.15	0.4917	0.0270	0.03	0.036

and CPP + tetrahydrofuran solution. Therefore, the standard deviations of CPP + chloroform solution and CPP + carbon tetrachloride solution are higher than that of other solutions. If the ratio of the standard deviation (σ) to the viscosity of CPP solution at maximal concentration (η_{max}) is used as evaluation index, the values of CPP + chloroform solution and CPP + carbon tetrachloride solution are not the highest. There is no evident difference between the ratio values. The results are also listed in Table 5. Consequently, if the viscosities of CPP + chloroform solution and CPP + carbon tetrachloride solutions are taken into account, their standard deviations are reasonable.

Conclusion

Densities of fractionated CPP + toluene and CPP + 2-butanone mixtures were measured in the temperature range (298.15 to 318.15) K. The effect of molecular weights on their densities of fractionated CPP + toluene and CPP + 2- butanone mixtures were studied. At a fixed temperature, concentration, and solvent, densities for binary mixtures of fractions of CPP, which contains 30 % chlorine, are independent of molecular weight distribution. It only relates to the molecular structure. Densities for binary mixtures of CPP with toluene, tetrahydrofuran, chloroform, carbon tetrachloride, and 2-butanone at temperatures from (298.15 to 318.15) K have been measured. The apparent molar volumes and standard partial molar volumes of the CPP repeat unit have been calculated. From the results, the repeat unit structure of CPP ($C_6H_{11}Cl$) has been determined. Viscosities for binary mixtures of CPP with toluene, tetrahydrofuran, chloroform, carbon tetrachloride, and 2-butanone at temperatures from (298.15 to 318.15) K have been measured. The relation between viscosity and concentration can be expressed by an exponential-type function.

Literature Cited

(1) Zhong, L. F.; Tang, S. Y.; Liu, D. Z.; Zhu, D. S. Research progress of chlorinated polypropylene. *China Mod. Chem. Ind.* (*China*) **2004**, *12*, 16−19.

(2) Yeo, S. D.; Kiran, E. High-pressure density and viscosity of polystyrene solutions in methylcyclohexane. *J. Supercrit. Fluid* **1999**, *15*, 261−272.

(3) Xiong, Y.; Kiran, E. Miscibility, density and viscosity of polystyrene in *n*-hexane at high pressures. *Polymer* **1997**, *38*, 5185−5193.

(4) Azevedo, J. A. T.; Mello Cardoso, M. J. E.; Silva, E. C. Theoretical determination of the theta temperature for solvent−polymer systems. *J. Mol. Struct.-THEOCHEM* **1999**, *464*, 95−105.

(5) Ma, L. Q.; Zhang, X. H.; Wang, Y. Z. *Minisize Polymer Chemistry Experimental Technology*; China Weave Press: Beijing, China, 1999.

(6) Feng, K. C.; Li, G.; Fu, R. W.; Liu, Z. S. *Polymer Physics Experiment*; Chemistry Industry Press: Beijing, China, 2004.

(7) Ou, Y. J.; Fan, Z. L.; Liu, D. Z.; Liu, Q. Z. Study on solution viscosity of chlorinated polypropylenbe and petroleum resin. *Synth. Resin Plast.* (*China*) **2004**, *21*, 10−13.

(8) Yoshidaa, K.; Tsuchihashib, N.; Ibukib, K.; Ueno, M. NMR and viscosity B coefficients for spherical nonelectrolytes in nonaqueous solvents. *J. Mol. Liq.* **2005**, *119*, 67−75.

(9) Yang, X. Y.; Yi, G. L. Excess molar volumes of sulfolane in binary mixtures with six aromatic hydrocarbons at 298.15 K. *Fluid Phase Equilib.* **1998**, *147*, 207−213.

(10) Zeng, X. S.; Ou Yang, G. F.; Zhang, M. Y.; Huang, Z. Q. Excess molar volumes of binary mixtures of tetrahydrofuran with o- , m- , p-xylene and ethylbenzene at 298115 K. *Acta Sci. Nat. Univ. Sunyatseni* (*China*) **2002**, *41*, 111−113.

(11) Lu, G. Z.; OuYang, G. F.; Deng, G. R.; Yang, Y. Y.; Huang, Z. Q. Excess molar volumes of binary liquid mixtures of trichloromethane or nitrobenzene with 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene at 298115 K. *Acta Sci. Nat. Univ. Sunyatseni* (*China*) **2002**, *43*, 55−58.

(12) Wang, H. J. Volumetric properties of ternary pseudo-binary mixtures at the temperature 298.15 K. II. (Benzene + chloroform, or carbon tetrachloride) + (acrylonitrile + chloroform, or carbon tetrachloride). *J. Chem. Thermodyn.* **2000**, *32*, 963−972.

(13) Martnez, S.; Garriga, R.; Perez, P.; Gracia, M. Densities and viscosities of binary mixtures of butanone with butanol isomers at several temperatures. *Fluid Phase Equilib.* **2000**, *168*, 267−279.

(14) George, J.; Sastry, N. V. Measurements of densities, viscosities, speeds of sound and relative permittivities and excess molar volumes, excess isentropic compressibilities and deviations in relative permittivities and molar polarizations for dibutyl ether + benzene, + toluene and + *p*-xylene at different temperatures. *J. Chem. Thermodyn.* **2003**, *35*, 1837−1853.

(15) Gascon, I.; Lafuente, C.; Cea, P.; Royo, F. M.; Urieta, J. S. Viscosities of the ternary mixture (cyclohexane + tetrahydrofuran + chlorocyclohexane) at 298.15 and 313.15 K. *Fluid Phase Equilib.* **1999**, *164*, 143−155.

(16) Lu, H. Z.; Bi, L. Y.; Wu, Z. P.; Shi, C. Y. *Handbook of Petrochemical Basic Data*; Chemistry Industry Press: Beijing, China, 1984.

(17) Biswas, R. K.; Banu1, R. A.; Islam, M. N. Some physico-chemical properties of D2EHPA. Part 2. Distribution, dimerization and acid dissociation constants in n-hexane/1 M (Na^+,H^+)SO_4^{2-}system, interfacial adsorption and excess properties. *Hydrometallurgy* **2003**, *69*, 157−168.

(18) Wang, L. C.; Xu, H. S.; Zhao, J. H.; Song, C. Y.; Wang, F. A. Densities and viscosities of niacin + 3-picoline + sulfuric acid + water from (293.15 to 343.15) K. *J. Chem. Eng. Data* **2005**, *50*, 643−646.

(19) Krakowiak, J.; Koziel, H.; Grzybkowski, W. Apprent molar volumes of divalent transition metal perchlorates and chlorides in *N*,*N*-dimethylacetamide. *J. Mol. Liq.* **2005**, *118*, 7−65.

(20) Yan, Z. N.; Wang, J. J.; Kong, W.; Lu, J. S. Effect of temperature on volumetric and viscosity properties of some α-amino acids in aqueous calcium chloride solutions. *Fluid Phase Equilib.* **2004**, *215*, 143−150.

(21) Wang, L.C.; Xu, H. S.; Zhao, J. H.; Song, C. Y.; Wang, F. A. Densities and viscosities of niacin + 3-picoline + water mixtures from (293.15 to 343.15) K. *J. Chem. Eng. Data* **2005**, *50*, 254−257.

(22) Zhao, C. W.; Ma, P. S.; Li, J. D. Partial molar volumes and viscosity B-coefficients of arginine in aqueous glucise, sucrose and L-ascorbic acid solutions at T = 298.15 K. *J. Chem. Thermodyn.* **2005**, *37*, 37−42.

(23) Jiang, Y. C.; Hu, M. C.; Wang, J. J.; Zhuo, K. L.; Xia, S. P. Volumetric propertoes and volumetric interaction parameters for the CsCl-monosaccharide (D-galactose, D-xylose and D-arabinose)−water systems at T = 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 671−676.

(24) Kar, F.; Arslan, N. Effect of temperature and concentration on viscosity of orange peel pectin solution and intrinsic viscosity−molecular weight relationship. *Carbohyd. Polym.* **1999**, *40*, 277−284.

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