Densities and Viscosities of Binary Mixtures of Ethylbenzene + *N*-Methyl-2-pyrrolidone, Ethylbenzene + Sulfolane, and Styrene + Octane from (303.15 to 353.15) K and Atmospheric Pressure

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The experimental densities and viscosities of ethylbenzene + sulfolane and ethylbenzene + *N*-methyl-2-pyrrolidone at temperatures of (303.15 to 353.15) K and of styrene + octane at temperatures of (293.15 to 363.15) K were determined using a vibrating-tube density meter and Ubbelohde viscometer. From these data, excess molar volumes and viscosity deviations have been calculated. The computed quantities have been fitted to the Redlich−Kister equation to derive the coefficients and estimate the standard error values. The results are discussed in terms of the intermolecular interactions.

Introduction

The physical properties and the thermodynamic behavior of binary mixtures have been studied for many reasons, one of the most important of which is that these properties may provide information about molecular interactions. This paper is part of our systematic program of research on the measurement of physical and transport properties of binary liquid mixtures containing sulfolane and NMP, which are both widely used in the extraction of aromatics in petrochemical processing. In this work, we present density and viscosity data for the binary systems ethylbenzene + sulfolane and ethylbenzene + *N*-methyl-2-pyrrolidone (NMP) at (303.15 to 353.15) K and over the whole mole fraction range. The densities and viscosities for system styrene + octane from (293.15 to 363.15) K are also reported.

A survey of the literature shows that very few measurements have been made on the densities and viscosities for these binary mixtures. There are no experimental data available in the literature for NMP + ethylbenzene and styrene + octane at these temperatures. For the binary mixture of ethylbenzene + sulfolane, Chen and Knapp[1] measured densities at 313.15 K and 333.15 K, and Yu et al.[2] reported excess molar volumes at 298.15 K. Nevertheless, to our knowledge, no viscosity data on this mixture were previously reported in the literature.

The experimental values were used to calculate excess molar volumes and the deviation in viscosity over the entire mole fraction range for the binary mixtures. The computed quantities have been fitted to the Redlich−Kister equation to derive the coefficients and estimate the standard error values. The results are discussed in terms of the intermolecular interactions.

Table 1. Comparison of Experimental and Literature Values of Densities (ρ) and Viscosities (η) for Pure Compounds

liquid	T/K	ρ/g·cm^{-3} exptl	ρ/g·cm^{-3} lit	η/mPa·s exptl	η/mPa·s lit
N-methyl-2-pyrrolidinone	298.15	1.02794	1.0279[3]	1.683	1.687[3]
			1.02851[4]		1.656[5]
			1.02872[5]		
	303.15	1.02347	1.02340[6]	1.554	
	313.15	1.01455	1.0157[7]	1.332	1.322[5]
			1.01519[5]		
	323.15	1.00566	1.0054[7]	1.160	1.175[5]
			1.00627[5]		
	333.15	0.99671	0.9974[7]	1.022	1.035[5]
			0.99741[5]		
	343.15	0.98775	0.98846[5]	0.908	0.921[5]
Ethylbenzene	298.15	0.86433	0.86289[1]	0.629	0.6293[8]
			0.8625[10]		
	303.15	0.85995	0.86454[9]	0.598	0.5923[8]
					0.5976[9]
	313.15	0.85114	0.85976[9]	0.537	0.5369[8]
	323.15	0.84227	0.85471[9]	0.483	0.4797[8]
					0.4852[9]
	333.15	0.83334	0.8318[2]	0.437	0.4410[9]
			0.84975[9]		
Sulfolane	298.15	1.26540	1.26654[1]	10.074	10.356[13]
			1.2640[11]		10.284[14]
	303.15	1.26080	1.26224[12]		
			1.26184[13]		
	313.15	1.25190	1.2532[2]		
	323.15	1.24336			
	333.15	1.23462	1.2359[2]		
Styrene	293.15	0.90629		0.749	
	298.15	0.90186	0.9016[15]	0.699	0.709[15]
			0.90197[16]		0.697[17]
	303.15	0.89745	0.8971[15]	0.654	0.662[15]
Octane	293.15	0.70388	0.7026[18]	0.534	0.5436[18]
	298.15	0.69983	0.6984[19]	0.501	0.506[19]
			0.6986[18]		0.5113[18]
	303.15	0.69579	0.6943[19]	0.472	0.477[19]
	313.15	0.68759	0.68634[20]	0.422	0.431[20]
			0.6862[19]		0.425[19]

Experimental Section

Materials. Ethylbenzene, styrene, and octane obtained from Shanghai Chemical Reagent Co. were purified by distillation, and their middle fraction was collected. The mass fraction purities tested by gas chromatography were as follows: ethylbenzene (>0.993), styrene (>0.995), and octane (>0.993). Analytical grade NMP and sulfolane obtained from Tianjin Reagent Company were used without further purification. These liquids were dried over 0.4 nm molecular sieves and partially degassed by ultrasound prior

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Table 2. Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E), and Viscosity Deviations ($\Delta\eta$) for the Binary Mixtures at Different Temperatures

x_1	ρ / $g \cdot cm^{-3}$	η / mPa·s	V^E / $cm^3 \cdot mol^{-1}$	$\Delta\eta$ / mPa·s	x_1	ρ / $g \cdot cm^{-3}$	η / mPa·s	V^E / $cm^3 \cdot mol^{-1}$	$\Delta\eta$ / mPa·s
				(x_1)Ethylbenzene + (1 − x_1)*N*-Methyl-2-pyrrolidinone					
				T = 303.15 K					
0.0000	1.02347	1.554	0.000	0.000	0.5835	0.92322	0.884	−0.556	−0.113
0.0940	1.00625	1.415	−0.185	−0.049	0.6854	0.90691	0.796	−0.465	−0.103
0.1901	0.98943	1.301	−0.372	−0.071	0.7888	0.89073	0.722	−0.317	−0.078
0.2859	0.97261	1.188	−0.471	−0.093	0.8937	0.87471	0.660	−0.111	−0.040
0.3839	0.95598	1.081	−0.548	−0.107	1.0000	0.85995	0.598	0.000	0.000
0.4839	0.93938	0.975	−0.576	−0.117					
				T = 313.15 K					
0.0000	1.01455	1.332	0.000	0.000	0.5835	0.91435	0.772	−0.572	−0.096
0.0940	0.99735	1.216	−0.192	−0.041	0.6854	0.89804	0.705	−0.477	−0.082
0.1901	0.98053	1.124	−0.383	−0.057	0.7888	0.88186	0.643	−0.322	−0.061
0.2859	0.96371	1.033	−0.485	−0.072	0.8937	0.86585	0.588	−0.110	−0.033
0.3839	0.94711	0.940	−0.565	−0.087	1.0000	0.85114	0.537	0.000	0.000
0.4839	0.93052	0.846	−0.595	−0.101					
				T = 323.15 K					
0.0000	1.00566	1.160	0.000	0.000	0.5835	0.9054	0.688	−0.587	−0.077
0.0940	0.98846	1.057	−0.198	−0.040	0.6854	0.8891	0.629	−0.490	−0.067
0.1901	0.97163	0.982	−0.394	−0.050	0.7888	0.8730	0.576	−0.332	−0.050
0.2859	0.95481	0.904	−0.499	−0.062	0.8937	0.8569	0.525	−0.107	−0.030
0.3839	0.93820	0.829	−0.581	−0.072	1.0000	0.8423	0.483	0.000	0.000
0.4839	0.92164	0.750	−0.615	−0.082					
				T = 333.15 K					
0.0000	0.99671	1.022	0.000	0.000	0.5835	0.89646	0.618	−0.601	−0.063
0.0940	0.97951	0.932	−0.205	−0.035	0.6854	0.88017	0.565	−0.503	−0.056
0.1901	0.96267	0.868	−0.405	−0.043	0.7888	0.86400	0.520	−0.339	−0.041
0.2859	0.94585	0.801	−0.513	−0.054	0.8937	0.84793	0.474	−0.104	−0.026
0.3839	0.92924	0.735	−0.598	−0.063	1.0000	0.83334	0.437	0.000	0.000
0.4839	0.91270	0.671	−0.635	−0.068					
				T = 343.15 K					
0.0000	0.98775	0.908	0.000	0.000	0.5835	0.88745	0.559	−0.627	−0.051
0.0940	0.97056	0.833	−0.215	−0.028	0.6854	0.87113	0.514	−0.523	−0.044
0.1901	0.95371	0.774	−0.422	−0.037	0.7888	0.85497	0.472	−0.357	−0.033
0.2859	0.93687	0.714	−0.534	−0.048	0.8937	0.83891	0.430	−0.117	−0.021
0.3839	0.92025	0.658	−0.622	−0.054	1.0000	0.82426	0.397	0.000	0.000
0.4839	0.90371	0.603	−0.663	−0.058					
				T = 353.15 K					
0.0000	0.97876	0.813	0.000	0.000	0.5835	0.87835	0.505	−0.643	−0.047
0.0940	0.96156	0.746	−0.222	−0.025	0.6854	0.86201	0.468	−0.534	−0.038
0.1901	0.94470	0.695	−0.437	−0.033	0.7888	0.84586	0.430	−0.365	−0.030
0.2859	0.92786	0.643	−0.554	−0.042	0.8937	0.82976	0.391	−0.112	−0.023
0.3839	0.91120	0.596	−0.642	−0.045	1.0000	0.81518	0.366	0.000	0.000
0.4839	0.89464	0.547	−0.682	−0.049					
				(x_1)Ethylbenzene + (1 − x_1)Sulfolane					
				T = 303.15 K					
0.0000	1.26080	10.07	0.000	0.0000	0.6293	0.99333	1.324	−0.918	−2.787
0.1118	1.20927	6.224	−0.379	−2.7906	0.7254	0.95717	1.057	−0.793	−2.144
0.2205	1.16040	4.155	−0.620	−3.8296	0.8194	0.92309	0.861	−0.622	−1.448
0.3267	1.11466	2.942	−0.802	−4.0360	0.9106	0.89045	0.716	−0.306	−0.730
0.4301	1.07165	2.185	−0.901	−3.8133	1.0000	0.85995	0.598	0.000	0.000
0.5309	1.03119	1.536	−0.928	−3.5069					
				T = 313.15 K					
0.0000	1.25190	7.808	0.000	0.0000	0.6293	0.98445	1.135	−0.962	−2.097
0.1118	1.20044	4.943	−0.403	−2.0524	0.7254	0.94831	0.924	−0.832	−1.610
0.2205	1.15153	3.385	−0.652	−2.8199	0.8194	0.91423	0.757	−0.650	−1.093
0.3267	1.10577	2.452	−0.842	−2.9807	0.9106	0.88160	0.632	−0.320	−0.555
0.4301	1.06277	1.835	−0.947	−2.8463	1.0000	0.85114	0.537	0.000	0.000
0.5309	1.02232	1.316	−0.976	−2.6323					
				T = 323.15 K					
0.0000	1.24336	6.194	0.000	0.000	0.6293	0.97558	0.993	−1.004	−1.607
0.1118	1.19164	4.007	−0.406	−1.548	0.7254	0.93943	0.813	−0.870	−1.239
0.2205	1.14270	2.801	−0.670	−2.134	0.8194	0.90536	0.660	−0.680	−0.849
0.3267	1.09692	2.048	−0.872	−2.280	0.9106	0.87272	0.564	−0.330	−0.430
0.4301	1.0539	1.561	−0.984	−2.176	1.0000	0.84227	0.483	0.000	0.000
0.5309	1.01347	1.136	−1.019	−2.026					

Table 2 (Continued)

x_1	ρ / $g \cdot cm^{-3}$	η / mPa·s	V^E / $cm^3 \cdot mol^{-1}$	$\Delta\eta$ / mPa·s	x_1	ρ / $g \cdot cm^{-3}$	η / mPa·s	V^E / $cm^3 \cdot mol^{-1}$	$\Delta\eta$ / mPa·s
				$T = 333.15$ K					
0.0000	1.23462	5.009	0.000	0.000	0.6293	0.96666	0.876	−1.055	−1.256
0.1118	1.18285	3.330	−0.425	−1.167	0.7254	0.93050	0.724	−0.914	−0.968
0.2205	1.13386	2.350	−0.703	−1.650	0.8194	0.89641	0.597	−0.712	−0.666
0.3267	1.08806	1.763	−0.916	−1.752	0.9106	0.86376	0.505	−0.349	−0.341
0.4301	1.04502	1.347	−1.034	−1.695	1.0000	0.83334	0.437	0.000	0.000
0.5309	1.00457	0.995	−1.072	−1.587					
				$T = 343.15$ K					
0.0000	1.22592	4.126	0.000	0.000	0.6293	0.95762	0.772	−1.106	−1.007
0.1118	1.17393	2.796	−0.433	−0.914	0.7254	0.92143	0.646	−0.958	−0.775
0.2205	1.12489	2.005	−0.727	−1.299	0.8194	0.88732	0.536	−0.745	−0.534
0.3267	1.07906	1.541	−0.953	−1.367	0.9106	0.85467	0.459	−0.36	−0.271
0.4301	1.03602	1.177	−1.083	−1.345	1.0000	0.82426	0.397	0.000	0.000
0.5309	0.99554	0.882	−1.123	−1.264					
				$T = 353.15$ K					
0.0000	1.21680	3.440	0.000	0.000	0.6293	0.94863	0.692	−1.180	−0.813
0.1118	1.16514	2.371	−0.484	−0.725	0.7254	0.91240	0.583	−1.018	−0.627
0.2205	1.11608	1.736	−0.795	−1.026	0.8194	0.87828	0.484	−0.792	−0.437
0.3267	1.07018	1.319	−1.028	−1.116	0.9106	0.84558	0.417	−0.387	−0.224
0.4301	1.02710	1.039	−1.162	−1.079	1.0000	0.81518	0.366	0.000	0.000
0.5309	0.98658	0.785	−1.201	−1.023					
				(x_1)Styrene + $(1 - x_1)$Octane					
				$T = 293.15$ K					
0.0000	0.70388	0.534	0.000	0.000	0.6220	0.81207	0.593	0.120	−0.075
0.1085	0.71952	0.537	0.091	−0.021	0.7189	0.83364	0.619	0.099	−0.070
0.2151	0.73618	0.537	0.122	−0.044	0.8145	0.85659	0.649	0.063	−0.060
0.3202	0.7537	0.541	0.156	−0.062	0.9081	0.88084	0.694	0.017	−0.035
0.4223	0.77201	0.551	0.167	−0.074	1.0000	0.90629	0.749	0.000	0.000
0.5230	0.79151	0.565	0.146	−0.081					
				$T = 298.15$ K					
0.0000	0.69983	0.501	0.000	0.000	0.6220	0.80778	0.560	0.120	−0.064
0.1085	0.71545	0.502	0.086	−0.020	0.7189	0.82930	0.576	0.101	−0.067
0.2151	0.73206	0.508	0.120	−0.036	0.8145	0.85222	0.608	0.064	−0.055
0.3202	0.74953	0.510	0.156	−0.055	0.9081	0.87643	0.647	0.019	−0.034
0.4223	0.76781	0.518	0.165	−0.067	1.0000	0.90186	0.699	0.000	0.000
0.5230	0.78727	0.533	0.144	−0.072					
				$T = 303.15$ K					
0.0000	0.69579	0.472	0.000	0.000	0.6220	0.80350	0.527	0.121	−0.059
0.1085	0.71138	0.475	0.085	−0.017	0.7189	0.82498	0.544	0.102	−0.059
0.2151	0.72794	0.477	0.121	−0.034	0.8145	0.84787	0.571	0.064	−0.050
0.3202	0.74538	0.480	0.154	−0.050	0.9081	0.87203	0.609	0.021	−0.029
0.4223	0.76363	0.489	0.162	−0.060	1.0000	0.89745	0.654	0.000	0.000
0.5230	0.78303	0.503	0.145	−0.064					
				$T = 313.15$ K					
0.0000	0.68759	0.422	0.000	0.000	0.6220	0.79486	0.480	0.116	−0.038
0.1085	0.70313	0.423	0.079	−0.016	0.7189	0.81628	0.486	0.096	−0.047
0.2151	0.71960	0.427	0.118	−0.028	0.8145	0.83909	0.511	0.060	−0.037
0.3202	0.73700	0.431	0.144	−0.041	0.9081	0.86315	0.541	0.023	−0.022
0.4223	0.75516	0.439	0.154	−0.049	1.0000	0.88853	0.577	0.000	0.000
0.5230	0.77446	0.451	0.141	−0.052					
				$T = 323.15$ K					
0.0000	0.67934	0.380	0.000	0.000	0.6220	0.78622	0.427	0.108	−0.036
0.1085	0.69484	0.381	0.071	−0.013	0.7189	0.80756	0.437	0.091	−0.039
0.2151	0.71123	0.385	0.111	−0.024	0.8145	0.83031	0.460	0.055	−0.029
0.3202	0.72858	0.388	0.132	−0.034	0.9081	0.85431	0.484	0.019	−0.017
0.4223	0.74666	0.396	0.145	−0.041	1.0000	0.87962	0.513	0.000	0.000
0.5230	0.76588	0.406	0.134	−0.044					
				$T = 333.15$ K					
0.0000	0.67098	0.343	0.000	0.000	0.6220	0.77749	0.387	0.098	−0.030
0.1085	0.68643	0.351	0.066	−0.005	0.7189	0.79877	0.395	0.081	−0.034
0.2151	0.70274	0.351	0.108	−0.018	0.8145	0.82146	0.413	0.047	−0.027
0.3202	0.72006	0.352	0.120	−0.029	0.9081	0.84537	0.438	0.018	−0.013
0.4223	0.73807	0.359	0.133	−0.034	1.0000	0.87064	0.462	0.000	0.000
0.5230	0.75721	0.368	0.125	−0.038					

Table 2 (Continued)

x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s	x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s
				T = 343.15 K					
0.0000	0.66259	0.314	0.000	0.000	0.6220	0.76875	0.355	0.092	−0.025
0.1085	0.67799	0.321	0.061	−0.004	0.7189	0.78997	0.362	0.077	−0.028
0.2151	0.69424	0.325	0.102	−0.011	0.8145	0.81263	0.376	0.041	−0.023
0.3202	0.71151	0.322	0.110	−0.026	0.9081	0.8365	0.398	0.010	−0.011
0.4223	0.72946	0.328	0.124	−0.030	1.0000	0.86172	0.419	0.000	0.000
0.5230	0.74855	0.337	0.114	−0.032					
				T = 353.15 K					
0.0000	0.65405	0.287	0.000	0.000	0.6220	0.75993	0.322	0.074	−0.024
0.1085	0.66939	0.293	0.059	−0.005	0.7189	0.78111	0.333	0.059	−0.021
0.2151	0.6856	0.295	0.094	−0.013	0.8145	0.80368	0.349	0.033	−0.015
0.3202	0.70281	0.295	0.101	−0.022	0.9081	0.82751	0.362	0.007	−0.010
0.4223	0.72071	0.301	0.113	−0.026	1.0000	0.85268	0.381	0.000	0.000
0.5230	0.73976	0.308	0.100	−0.028					
				T = 363.15 K					
0.0000	0.64568	0.261	0.000	0.000	0.6220	0.75134	0.294	0.060	−0.022
0.1085	0.66098	0.270	0.055	0.000	0.7189	0.77248	0.304	0.049	−0.020
0.2151	0.67715	0.268	0.086	−0.012	0.8145	0.79504	0.318	0.022	−0.015
0.3202	0.69432	0.273	0.090	−0.016	0.9081	0.81882	0.333	0.005	−0.007
0.4223	0.71219	0.277	0.099	−0.021	1.0000	0.84399	0.349	0.000	0.000
0.5230	0.7312	0.285	0.086	−0.022					

Table 3. Coefficients of the Redlich−Kister Equation and Standard Deviation for Excess Molar Volumes and Viscosity Deviations of Mixtures

T/K	property	A_0	A_1	A_2	A_3	A_4	σ	T/K	property	A_0	A_1	A_2	A_3	A_4	σ
							(x_1)Ethylbenzene + (1 − x_1)*N*-Methyl-2-pyrrolidinone								
303.15	V^E/cm^3·mol^{-1}	−2.285	0.102	−0.117	0.928	1.720	0.0046	333.15	V^E/cm^3·mol^{-1}	−2.496	0.085	−0.070	1.248	1.986	0.0053
	$\Delta\eta$/mPa·s	−0.467	−0.086	0.073	0.279	−0.178	0.0019		$\Delta\eta$/mPa·s	−0.273	−0.017	0.188	0.151	−0.453	0.0015
313.15	V^E/cm^3·mol^{-1}	−2.357	0.111	−0.048	0.998	1.703	0.0048	343.15	V^E/cm^3·mol^{-1}	−2.601	0.101	−0.030	1.195	1.861	0.0058
	$\Delta\eta$/mPa·s	−0.397	−0.074	0.255	0.227	−0.435	0.0015		$\Delta\eta$/mPa·s	−0.226	0.030	0.128	0.033	−0.315	0.0052
323.15	V^E/cm^3·mol^{-1}	−2.424	0.087	−0.083	1.138	1.878	0.0050	353.15	V^E/cm^3·mol^{-1}	−2.673	0.125	−0.100	1.306	2.113	0.0061
	$\Delta\eta$/mPa·s	−0.324	−0.046	0.216	0.196	−0.495	0.0014		$\Delta\eta$/mPa·s	−0.198	0.025	0.125	−0.002	−0.364	0.0041
							(x_1)Ethylbenzene + (1 − x_1)Sulfolan								
303.15	V^E/cm^3·mol^{-1}	−3.706	−0.713	−0.980	1.065	1.226	0.0096	333.15	V^E/cm^3·mol^{-1}	−4.267	−0.865	−1.004	1.210	1.424	0.0105
	$\Delta\eta$/mPa·s	−14.117	9.460	−7.338	4.452		0.0505		$\Delta\eta$/mPa·s	−6.324	3.956	−2.732	1.428		0.305
313.15	V^E/cm^3·mol^{-1}	−3.894	−0.752	−0.991	1.197	1.205	0.0099	343.15	V^E/cm^3·mol^{-1}	−4.472	−0.929	−0.944	1.182	1.476	0.0105
	$\Delta\eta$/mPa·s	−10.546	6.805	−5.282	3.285		0.0461		$\Delta\eta$/mPa·s	−5.021	2.979	−2.077	1.248		0.0262
323.15	V^E/cm^3·mol^{-1}	−4.058	−0.819	−0.998	1.132	1.359	0.0101	353.15	V^E/cm^3·mol^{-1}	−4.783	−0.931	−1.092	1.433	1.498	0.0116
	$\Delta\eta$/mPa·s	−8.092	5.1117	−3.867	2.347		0.0372		$\Delta\eta$/mPa·s	−4.0576	2.387	−1.599	0.826		0.0204
							(x_1)Styrene + (1 − x_1)Octane								
293.15	V^E/cm^3·mol^{-1}	0.218	3.886	−7.637	3.637		0.0190	333.15	V^E/cm^3·mol^{-1}	0.097	3.883	−7.586	3.694		0.0180
	$\Delta\eta$/mPa·s	−0.372	−0.182	0.278	0.155		0.0092		$\Delta\eta$/mPa·s	−0.170	−0.093	0.140	0.082		0.0037
298.15	V^E/cm^3·mol^{-1}	0.209	3.892	−7.631	3.642		0.0186	343.15	V^E/cm^3·mol^{-1}	0.066	3.862	−7.576	3.715		0.0183
	$\Delta\eta$/mPa·s	−0.335	−0.181	0.241	0.165		0.0086		$\Delta\eta$/mPa·s	−0.145	−0.084	0.123	0.074		0.0030
303.15	V^E/cm^3·mol^{-1}	0.201	3.900	−7.623	3.647		0.0186	353.15	V^E/cm^3·mol^{-1}	0.033	3.819	−7.572	3.742		0.0184
	$\Delta\eta$/mPa·s	−0.301	−0.164	0.221	0.142		0.0079		$\Delta\eta$/mPa·s	−0.119	−0.041	0.098	0.029		0.0023
313.15	V^E/cm^3·mol^{-1}	0.173	3.903	−7.610	3.660		0.0183	363.15	V^E/cm^3·mol^{-1}	0.000	3.771	−7.561	3.783		0.0188
	$\Delta\eta$/mPa·s	−0.243	−0.101	0.108	0.090		0.0057		$\Delta\eta$/mPa·s	−0.099	−0.056	0.089	0.045		0.0024
323.15	V^E/cm^3·mol^{-1}	0.134	3.897	−7.599	3.673		0.0176								
	$\Delta\eta$/mPa·s	−0.203	−0.075	0.155	0.066		0.0043								

to use. Their purity was check by measuring and comparing the densities and viscosities with their corresponding literature values as shown in Table 1.

Apparatus and Procedure. The densities of the pure components and their mixtures were measured with a high-precision vibrating-tube digital density meter (density/specific gravity meter DA 505, KEM, Japan) whose measurement cell temperature was controlled automatically to within ±0.01 K of the selected value. Before each series of measurements, the instrument was calibrated at atmospheric pressure with double-distilled water and dry air. Densities both in water and dry air at the various working temperatures were given by the manufacturer in the instruction manual. The calibration was accepted if the measurements were within $\pm 5 \times 10^{-5}$ g·cm^{-3} of the published values. The uncertainty in the density measurements was $\pm 5 \times 10^{-5}$ g·cm^{-3}. Density measurements were reproducible to $\pm 3 \times 10^{-5}$ g·cm^{-3}.

The liquid mixtures were prepared by weight using a BP210s balance that was accurate to within ±0.01 mg. The average uncertainty in the mole fraction of the mixtures was estimated to be less than ±0.0001. The molar excess volumes were calculated from composition−density data with an uncertainty better than ±0.002 cm^3·mol^{-1}. All molar quantities were based on the IUPAC relative atomic mass table.

The viscosities of the pure liquids and the mixtures were measured at atmospheric pressure and at different temperatures using several Ubbelohde suspended-level viscometers. The viscometer was immersed in a well-stirred water bath (Lauda, Germany) with temperature control to within ±0.01 K. An electronic digital stopwatch with a

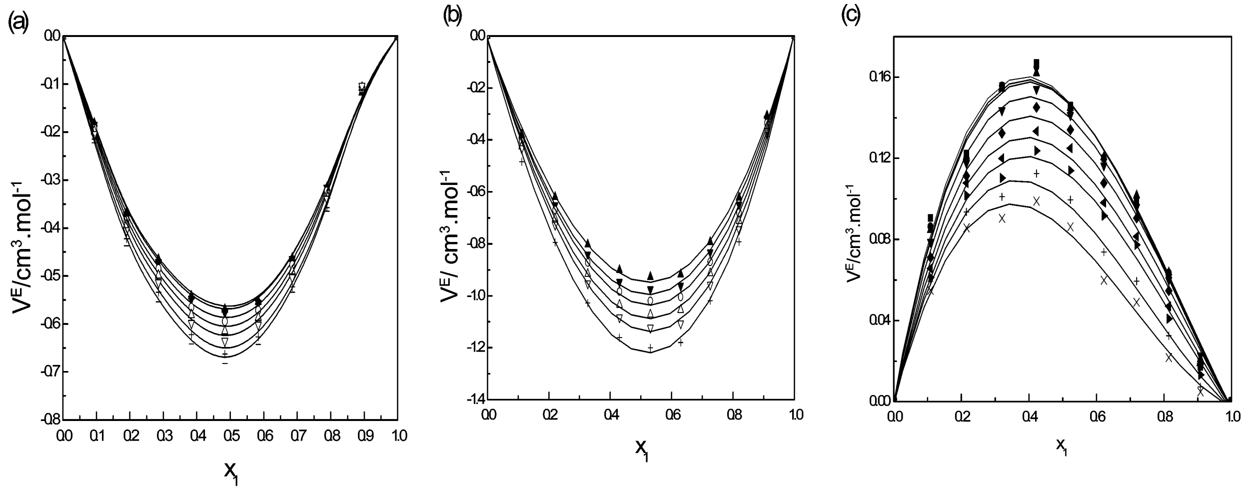

Figure 1. Excess volume variation with mole fraction for the following systems: (a) ethylbenzene (1) + *N*-methyl-2-pyrrolidone (2); (b) ethylbenzene (1) + sulfolane (2); (c) styrene (1) + octane (2) at ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 313.15 K; ○, 323.15 K; △, 333.15 K; ▽, 343.15 K; +, 353.15 K; and −, 363.15 K. Solid curves, calculated with the Redlich−Kister equation; symbols, experimental values.

readability of ±0.01 s was used for flow-time measurements. Experiments were repeated a minimum of four times at each temperature for all compositions, and the results were averaged. The viscosity η of the liquid was then calculated from the following relationship

$$\nu = \frac{\eta}{\rho} = k(t - \theta) \qquad (1)$$

where t is the flow time, ν is the kinematic viscosity, and k and θ are the viscometer constant and the Hagenbach correction factor, respectively.

The calibration of the viscometer was carried out with double-distilled water and double-distilled benzene. Care was taken to reduce evaporation during the measurements. The uncertainty in the values is within ±0.003 mPa·s.

In the experiment, the density and viscosity for the one-composition sample were measured at different temperatures. Densities and viscosities of pure compounds are reported in Table 1 together with the corresponding literature values.

Results and Discussion

Excess volumes and viscosity deviations were calculated from our measurements according to the following equation[21]

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \qquad (2)$$

where x_1 and x_2 are mole fractions, M_1 and M_2 are 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 viscosity deviations were calculated from the following relation

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (3)$$

where η is the viscosity of the mixtures and η_1 and η_2 are the viscosities of components 1 and 2, respectively.

The values of V^E and $\Delta\eta$ for each mixture were fitted to the Redlich−Kister polynomial equation[22,23]

$$Y = x_1(1 - x_1)\sum_{i=0}^{n} A_i(2x_1 - 1)^i \qquad (4)$$

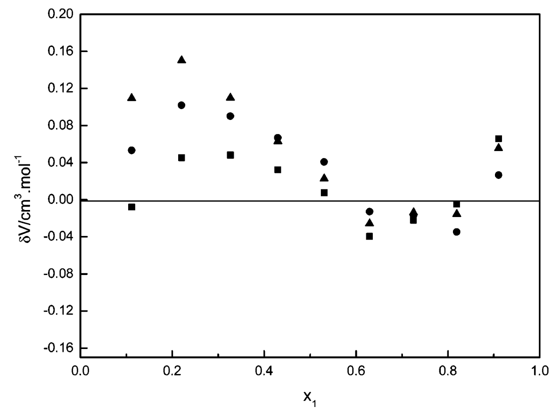

Figure 2. Deviation of experimental values of excess volume from those calculated from the Redlich−Kister equation fitted by literature data for ethylbenzene (1) + sulfolane (2): ■, 298.15 K, Yu and Li[2]; ●, 313.15 K, Chen et al.;[1] ▲, 333.15 K, Chen et al.[1]

where $Y = V^E$ or $\Delta\eta$, A_i are adjustable parameters, and x_1 is the fraction of component 1.

In each case, the optimum number of coefficients A_i was determined from an examination of the variation of the standard derivation[24]

$$\sigma(Y) = \left[\sum\frac{(Y_{calcd} - Y_{exptl})^2}{n - m}\right]^{1/2} \qquad (5)$$

where n is the total number of experimental values and m is the number of parameters.

The excess molar volume data and the viscosity deviations are presented in Table 2. Table 3 lists the values of parameters A_i together with the standard deviations.

V^E against x_1 plots of the three systems are shown in Figure 1. The values for the binary mixtures of ethylbenzene + NMP and ethylbenzene + sulfolane are negative over the whole composition range, and a parabolic composition dependence is found. For the mixtures of styrene + octane, the V^E values are positive. Figure 2 gives the deviation of experimental values of the excess volume from those calculated from the Redlich−Kister equation fitted by literature data for ethylbenzene + sulfolane at 298.15 K, 313.15 K, and 333.15 K. It can be seen that V^E values at $x = 0.5309$ are in agreement with those of Yu et al.[2] at 298.15 K; the deviation is 0.008 cm^3·mol^{-1}, but the V^E values are 0.041 cm^3·mol^{-1} higher at 313.15 K and 0.023

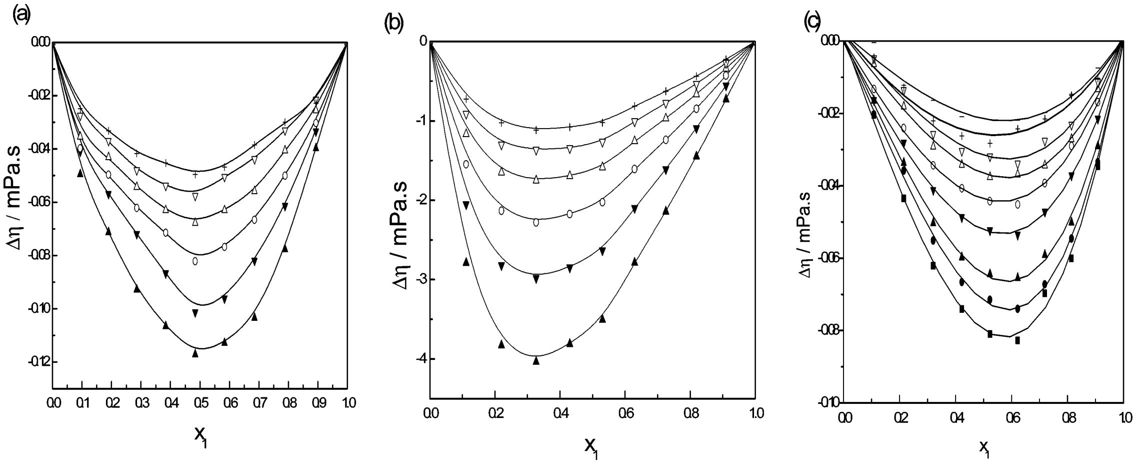

Figure 3. Viscosity deviation with mole fraction for the following systems: (a) ethylbenzene (1) + *N*-methyl-2-pyrrolidone (2); (b) ethylbenzene (1) + sulfolane (2); (c) styrene (1) + octane (2) at ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 313.15 K; ○, 323.15 K; △, 333.15 K; ▽, 343.15 K; +, 353.15 K; and −, 363.15 K. Solid curves, calculated with Redlich−Kister equation; symbols, experimental values.

$cm^3 \cdot mol^{-1}$ higher at 333.15 K than those reported by Chen et al.[1] The deviations for V^E are in the range of −0.040 to 0.066 $cm^3 \cdot mol^{-1}$ at 298.15 K, −0.035 to 0.102 $cm^3 \cdot mol^{-1}$ at 313.15 K, and −0.026 to 0.110 $cm^3 \cdot mol^{-1}$ at 333.15 K.

It is well known[25] that in addition to physical intermolecular forces there are chemical forces of attraction. In many cases, chemical forces are of major importance in determining the thermodynamic properties of solutions. There is a lone pair of electrons on the sulfur and nitrogen atoms of the sulfolane and *N*-methyl-2-pyrrolidone. That is to say that *N*-methyl-2-pyrrolidone and sulfolane are electron donors and aromatic hydrocarbons are electron acceptors. Therefore, *N*-methyl-2-pyrrolidone and sulfolane form charge-transfer complexes with ethylbenzene. The complex formation leads to a volumetric contraction, and V^E values are negative for mixtures of ethylbenzene + *N*-methyl-2-pyrrolidone and ethylbenzene + sulfolane. For mixture of styrene + octane, these two molecules are nonpolar. There are only physical intermolecular forces between unlike molecules. Owing to the difference in shape, size, and free volume, the excess volumes are positive for mixtures of styrene with octane.

Figure 3 shows viscosity deviations for these three binary mixtures, plotted against mole fraction together with the fitted curve, obtained from the Redlich−Kister equation. The viscosity deviations for these systems at selected temperatures are negative over the entire composition. For ethylbenzene + *N*-methyl-2-pyrrolidone and styrene + octane mixtures, the curves are almost symmetrical, and the minimum in $\Delta\eta$ occurs at a mole fraction of about x = 0.5. For mixtures of ethylbenzene + sulfolane, the curves are asymmetrical in nature and skewed to the sulfolane-rich range. At the same temperatures, the absolute viscosity deviations for ethylbenzene with sulfolane are much larger than for the other two systems.

Conclusions

Densities and viscosities for ethylbenzene + sulfolane, ethylbenzene + NMP at temperatures of (303.15 to 353.15) K, and styrene + octane at temperatures of (293.15 to 363.15) K have been experimentally determined over the entire mole fraction range. The excess molar volume and viscosity deviations were correlated using the Redlich−Kister polynomial equation. The excess molar volumes for the binary mixtures of ethylbenzene + NMP and ethylbenzene + sulfolane are negative over the whole composition range, and for the mixtures of styrene + octane, the V^E values are positive. On the contrary, the deviations in viscosity for these systems at selected temperatures are all negative over the entire composition. The absolute viscosity deviations for ethylbenzene + sulfolane are much larger than for the other two systems.

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