Densities of *m*-Cresol + Quinoline and *m*-Cresol + 1-Methylnaphthalene Mixtures at (298 to 348) K and up to 30 MPa

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Densities were measured for mixtures of *m*-cresol + quinoline and *m*-cresol + 1-methylnaphthalene in a temperature range of (298.15 to 348.15) K and at pressures up to 30 MPa over the entire composition range. The Tait model correlated the density data accurately. Isothermal compressibilities of the pure fluids and their mixtures were calculated with the aid of the Tait model. Over the investigated conditions, the excess volumes of *m*-cresol + quinoline are negative, whereas those of *m*-cresol + 1-methylnaphthalene are positive.

Introduction

A series of density measurements were made in our laboratory for the mixtures containing several model compounds of coal liquids. In this paper we report the results of *m*-cresol + quinoline and *m*-cresol + 1-methylnaphthalene in a temperature range of (298.15 to 348.15) K and at pressures up to 30 MPa. While some density data have been published in the literature for pure *m*-cresol, quinoline, and 1-methylnaphthalene (Oshmyansky et al., 1986; TRC Tables, 1987, 1993), no density data are found under conditions similar to those of this work for these two binary mixtures.

Experimental Section

m-Cresol (99 mass %), quinoline (98 mass %), and 1-methylnaphthalene (98 mass %) were purchased from Aldrich. All the substances were used without further purification. The detailed description for the apparatus and operation procedure have been given elsewhere (Chang and Lee, 1995). Mixture samples (about 30 g) were prepared by mass with an accuracy better than 0.5 mg. A high-pressure densimeter (DMA-512, Anton Paar) with a DMA-60 processing unit (Anton Paar) was employed to make the measurements. High pressure was generated by a hand pump (model 2426-801, Ruska), and the pressure in the sample tube was monitored by a pressure transducer (model PDCR 330, 0−40 MPa, Druck) with a digital indicator (model DPI 261, Druck). The accuracy of the pressure readings was calibrated to 0.1%. The thermostated bath was controlled to within 0.03 K, and a precision digital thermometer (model 1506, Hart Scientific) incorporated with a thermister probe measured the temperature to an accuracy of 0.015 K. The oscillation period of sample i in the vibrating U tube (t_i) was converted into density (ρ_i) via

$$\varrho_i = A(t_i^2 - B) \qquad (1)$$

where A and B are apparatus constants determined by using pure water (Haar et al., 1984) and dry nitrogen (Vargaftik, 1975) as calibrated fluids. Calibrations were made over a pressure range from (0.1 to 30) MPa, and the apparatus constant A was correlated with a linear function of pressure at each temperature of interest. The calibrations reproduced water densities with a standard deviation of 5×10^{-5} g·cm^{-3} and an average absolute percent deviation of 0.004% over the entire range of the investigated conditions. The uncertainty of the density measurements was estimated to be less than 0.1%.

Table 1. Densities of Pure Liquids at 0.1 MPa

substance	T/K	ρ/g·cm^{-3} this work	ρ/g·cm^{-3} lit.	reference
quinoline	298.15	1.0892	1.0879	Oshmyansky et al. (1986)
			1.090	TRC Tables (1993)
	323.15	1.0692	1.070	TRC Tables (1993)
	348.15	1.0490	1.050[a]	TRC Tables (1993)
1-MNP[b]	298.15	1.0179	1.0142	Oshmyansky et al. (1986)
			1.01675[c]	TRC Tables (1987)
	323.15	0.9993	0.9989	TRC Tables (1987)
	348.15	0.9803	0.98065[a]	TRC Tables (1987)

[a] Average of the densities at 343.15 K and 353.15 K. [b] 1-Methylnaphthalene. [c] Average of the densities at 293.15 K and 303.15 K.

Results and Discussion

Table 1 compares our measurements with literature values for the pure fluid densities at 0.1 MPa. Our results generally agree with the tabulated values in the TRC Tables (1987, 1993) to within 0.1%, except for the density of 1-methylnaphthalene at 298.15 K (+0.113%). The small amount of impurities may result in the discrepancy. The densities of quinoline and 1-methylnaphthalene reported by Oshmyansky et al. (1986) are obviously lower than others. Table 2 compiles the experimental densities and the calculated isothermal compressibilities (κ_T) of pure quinoline and 1-methylnaphthalene at temperatures from (298.15 to 348.15) K and pressures up to 30 MPa, while those of pure *m*-cresol have been reported in our previous paper (Chang and Lee, 1995). Tables 3 and 4 list the results of *m*-cresol + quinoline and *m*-cresol + 1-methylnaphthalene mixtures, respectively. The tabulated isothermal compressibilities were calculated from the following definition with the aid of the Tait equation:

$$\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,x} = \frac{V_0}{V}\left(\frac{C}{D + P}\right) \qquad (2)$$

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Table 2. Experimental Density and Calculated Isothermal Compressibility for Pure Quinoline and 1-Methylnaphthalene

	298.15 K		323.15 K		348.15 K	
P/MPa	ρ/(g·cm^{-3})	$10^4\kappa_T$/MPa^{-1}	ρ/(g·cm^{-3})	$10^4\kappa_T$/MPa^{-1}	ρ/(g·cm^{-3})	$10^4\kappa_T$/MPa^{-1}
			Quinoline			
0.1	1.0892	4.653	1.0692	5.313	1.0490	6.036
1.0	1.0896	4.628	1.0697	5.282	1.0496	5.993
2.0	1.0901	4.601	1.0703	5.249	1.0502	5.946
3.0	1.0906	4.575	1.0709	5.216	1.0508	5.899
4.0	1.0912	4.549	1.0714	5.183	1.0515	5.853
5.0	1.0917	4.523	1.0719	5.151	1.0520	5.808
6.0	1.0922	4.497	1.0725	5.119	1.0527	5.764
8.0	1.0931	4.447	1.0736	5.057	1.0539	5.678
10.0	1.0940	4.397	1.0747	4.996	1.0551	5.594
12.0	1.0950	4.349	1.0758	4.936	1.0563	5.513
14.0	1.0959	4.303	1.0768	4.878	1.0574	5.434
16.0	1.0969	4.257	1.0778	4.822	1.0586	5.357
18.0	1.0978	4.212	1.0789	4.767	1.0597	5.283
20.0	1.0987	4.168	1.0799	4.713	1.0607	5.211
25.0	1.1010	4.062	1.0824	4.584	1.0635	5.039
30.0	1.1032	3.962	1.0849	4.462	1.0661	4.878
			1-Methylnaphthalene			
0.1	1.0179	5.352	0.9993	5.916	0.9803	6.745
1.0	1.0184	5.314	0.9998	5.890	0.9809	6.699
2.0	1.0189	5.272	1.0004	5.862	0.9816	6.648
3.0	1.0195	5.231	1.0010	5.833	0.9822	6.599
4.0	1.0201	5.191	1.0016	5.805	0.9828	6.550
5.0	1.0206	5.151	1.0022	5.778	0.9835	6.502
6.0	1.0211	5.111	1.0028	5.750	0.9841	6.454
8.0	1.0220	5.035	1.0039	5.696	0.9854	6.362
10.0	1.0230	4.960	1.0051	5.643	0.9866	6.272
12.0	1.0242	4.889	1.0062	5.591	0.9879	6.185
14.0	1.0252	4.819	1.0073	5.540	0.9891	6.100
16.0	1.0261	4.751	1.0084	5.490	0.9903	6.018
18.0	1.0271	4.685	1.0095	5.441	0.9915	5.938
20.0	1.0280	4.621	1.0105	5.392	0.9926	5.860
25.0	1.0304	4.469	1.0132	5.276	0.9955	5.675
30.0	1.0328	4.327	1.0158	5.164	0.9983	5.501

Table 3. Experimental Density and Calculated Isothermal Compressibility for *m*-Cresol (1) + Quinoline (2)

	298.15 K		323.15 K		348.15 K			298.15 K		323.15 K		348.15 K	
P/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	P/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}
							$x_1 = 0.2$						
0.1	1.0839	4.685	1.0643	5.236	1.0443	5.798	10.0	1.0888	4.381	1.0697	4.928	1.0502	5.508
1.0	1.0843	4.656	1.0648	5.206	1.0448	5.770	12.0	1.0897	4.325	1.0707	4.871	1.0514	5.454
2.0	1.0849	4.623	1.0653	5.174	1.0454	5.740	14.0	1.0907	4.270	1.0718	4.814	1.0525	5.400
3.0	1.0854	4.592	1.0659	5.142	1.0461	5.710	16.0	1.0916	4.216	1.0728	4.760	1.0537	5.347
4.0	1.0859	4.560	1.0664	5.110	1.0467	5.680	18.0	1.0925	4.164	1.0738	4.706	1.0547	5.295
5.0	1.0863	4.529	1.0670	5.079	1.0473	5.651	20.0	1.0934	4.113	1.0748	4.653	1.0558	5.245
6.0	1.0869	4.499	1.0675	5.048	1.0479	5.622	25.0	1.0956	3.992	1.0773	4.528	1.0585	5.123
8.0	1.0879	4.440	1.0686	4.987	1.0491	5.564	30.0	1.0978	3.877	1.0797	4.409	1.0611	5.006
							$x_1 = 0.4$						
0.1	1.0778	4.676	1.0581	5.214	1.0381	5.948	10.0	1.0826	4.357	1.0635	4.939	1.0440	5.522
1.0	1.0783	4.645	1.0586	5.187	1.0386	5.906	12.0	1.0836	4.298	1.0645	4.888	1.0451	5.443
2.0	1.0788	4.611	1.0591	5.158	1.0392	5.861	14.0	1.0845	4.240	1.0655	4.837	1.0463	5.367
3.0	1.0792	4.577	1.0597	5.130	1.0398	5.816	16.0	1.0854	4.184	1.0666	4.787	1.0474	5.293
4.0	1.0797	4.544	1.0603	5.102	1.0405	5.772	18.0	1.0863	4.130	1.0676	4.739	1.0485	5.221
5.0	1.0802	4.512	1.0608	5.074	1.0411	5.729	20.0	1.0872	4.077	1.0686	4.691	1.0495	5.151
6.0	1.0807	4.480	1.0613	5.046	1.0416	5.686	25.0	1.0894	3.951	1.0710	4.577	1.0522	4.985
8.0	1.0817	4.417	1.0624	4.992	1.0429	5.603	30.0	1.0916	3.832	1.0734	4.468	1.0548	4.829
							$x_1 = 0.6$						
0.1	1.0673	4.747	1.0476	5.333	1.0274	6.035	10.0	1.0722	4.442	1.0530	5.021	1.0334	5.626
1.0	1.0677	4.717	1.0481	5.303	1.0279	5.995	12.0	1.0732	4.385	1.0541	4.962	1.0345	5.550
2.0	1.0682	4.685	1.0487	5.270	1.0285	5.952	14.0	1.0741	4.330	1.0551	4.905	1.0357	5.476
3.0	1.0687	4.653	1.0492	5.237	1.0291	5.909	16.0	1.0749	4.276	1.0561	4.849	1.0368	5.405
4.0	1.0692	4.621	1.0498	5.205	1.0298	5.867	18.0	1.0759	4.223	1.0571	4.795	1.0379	5.335
5.0	1.0698	4.591	1.0503	5.173	1.0304	5.825	20.0	1.0768	4.172	1.0581	4.742	1.0390	5.267
6.0	1.0703	4.560	1.0509	5.142	1.0310	5.784	25.0	1.0790	4.050	1.0606	4.614	1.0416	5.104
8.0	1.0712	4.500	1.0519	5.081	1.0323	5.704	30.0	1.0812	3.935	1.0630	4.494	1.0442	4.952
							$x_1 = 0.8$						
0.1	1.0502	4.817	1.0304	5.618	1.0101	6.395	10.0	1.0551	4.600	1.0360	5.254	1.0163	5.917
1.0	1.0506	4.796	1.0309	5.582	1.0106	6.348	12.0	1.0560	4.559	1.0371	5.186	1.0175	5.829
2.0	1.0511	4.774	1.0315	5.544	1.0113	6.297	14.0	1.0570	4.519	1.0381	5.120	1.0186	5.744
3.0	1.0516	4.751	1.0321	5.506	1.0119	6.247	16.0	1.0580	4.479	1.0392	5.056	1.0198	5.661
4.0	1.0521	4.729	1.0326	5.468	1.0125	6.197	18.0	1.0589	4.440	1.0402	4.994	1.0209	5.581
5.0	1.0526	4.707	1.0332	5.431	1.0132	6.148	20.0	1.0599	4.402	1.0412	4.933	1.0221	5.503
6.0	1.0531	4.686	1.0337	5.395	1.0138	6.101	25.0	1.0622	4.309	1.0438	4.787	1.0247	5.317
8.0	1.0542	4.643	1.0349	5.323	1.0151	6.007	30.0	1.0643	4.219	1.0463	4.650	1.0274	5.145

Table 4. Experimental Density and Calculated Isothermal Compressibility for the *m*-Cresol (1) + 1-Methylnaphthalene (2)

	298.15 K		323.15 K		348.15 K			298.15 K		323.15 K		348.15 K	
P/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	P/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$ MPa^{-1}
							$x_1 = 0.2$						
0.1	1.0198	5.190	1.0006	6.075	0.9812	6.900	10.0	1.0249	4.888	1.0064	5.664	0.9877	6.351
1.0	1.0204	5.162	1.0011	6.035	0.9818	6.846	12.0	1.0259	4.832	1.0076	5.588	0.9890	6.251
2.0	1.0210	5.130	1.0018	5.992	0.9825	6.786	14.0	1.0269	4.777	1.0086	5.514	0.9902	6.154
3.0	1.0213	5.098	1.0023	5.948	0.9832	6.729	16.0	1.0280	4.723	1.0098	5.443	0.9914	6.060
4.0	1.0218	5.067	1.0029	5.906	0.9839	6.672	18.0	1.0288	4.670	1.0109	5.373	0.9926	5.969
5.0	1.0224	5.036	1.0035	5.864	0.9846	6.617	20.0	1.0298	4.619	1.0119	5.305	0.9937	5.881
6.0	1.0229	5.006	1.0041	5.823	0.9852	6.561	25.0	1.0321	4.495	1.0146	5.142	0.9966	5.672
8.0	1.0239	4.946	1.0053	5.743	0.9864	6.454	30.0	1.0344	4.378	1.0171	4.989	0.9994	5.478
							$x_1 = 0.4$						
0.1	1.0216	5.291	1.0023	6.182	0.9825	6.774	10.0	1.0269	4.978	1.0082	5.688	0.9889	6.310
1.0	1.0220	5.261	1.0028	6.133	0.9830	6.729	12.0	1.0277	4.919	1.0094	5.598	0.9902	6.225
2.0	1.0226	5.228	1.0033	6.080	0.9837	6.679	14.0	1.0288	4.862	1.0105	5.551	0.9913	6.141
3.0	1.0231	5.195	1.0039	6.027	0.9844	6.631	16.0	1.0298	4.806	1.0115	5.426	0.9925	6.060
4.0	1.0236	5.163	1.0046	5.977	0.9850	6.583	18.0	1.0308	4.751	1.0126	5.344	0.9937	5.981
5.0	1.0242	5.131	1.0052	5.926	0.9857	6.536	20.0	1.0317	4.698	1.0136	5.264	0.9949	5.904
6.0	1.0246	5.099	1.0057	5.876	0.9863	6.489	25.0	1.0342	4.570	1.0165	5.078	0.9979	5.721
8.0	1.0257	5.038	1.0071	5.781	0.9876	6.399	30.0	1.0365	4.449	1.0189	4.903	1.0006	5.549
							$x_1 = 0.6$						
0.1	1.0238	5.166	1.0043	6.024	0.9842	6.890	10.0	1.0289	4.934	1.0101	5.658	0.9907	6.321
1.0	1.0243	5.144	1.0048	5.989	0.9846	6.833	12.0	1.0299	4.889	1.0113	5.590	0.9918	6.217
2.0	1.0249	5.120	1.0054	5.950	0.9853	6.772	14.0	1.0310	4.846	1.0123	5.523	0.9930	6.117
3.0	1.0252	5.095	1.0059	5.912	0.9861	6.713	16.0	1.0319	4.803	1.0134	5.458	0.9943	6.021
4.0	1.0258	5.072	1.0066	5.874	0.9867	6.653	18.0	1.0329	4.761	1.0145	5.395	0.9955	5.927
5.0	1.0263	5.048	1.0071	5.837	0.9874	6.595	20.0	1.0339	4.720	1.0156	5.333	0.9966	5.836
6.0	1.0269	5.025	1.0077	5.800	0.9880	6.538	25.0	1.0364	4.621	1.0183	5.185	0.9996	5.622
8.0	1.0279	4.979	1.0089	5.728	0.9894	6.428	30.0	1.0386	4.525	1.0209	5.045	1.0023	5.423
							$x_1 = 0.8$						
0.1	1.0264	5.350	1.0064	6.142	0.9864	6.543	10.0	1.0316	4.912	1.0123	5.720	0.9926	6.235
1.0	1.0269	5.307	1.0070	6.101	0.9869	6.513	12.0	1.0326	4.833	1.0135	5.642	0.9939	6.176
2.0	1.0274	5.260	1.0077	6.056	0.9875	6.481	14.0	1.0336	4.756	1.0146	5.566	0.9951	6.119
3.0	1.0280	5.214	1.0083	6.012	0.9881	6.449	16.0	1.0345	4.681	1.0157	5.493	0.9964	6.063
4.0	1.0286	5.169	1.0089	5.969	0.9888	6.418	18.0	1.0355	4.609	1.0168	5.421	0.9976	6.008
5.0	1.0290	5.123	1.0095	5.926	0.9894	6.386	20.0	1.0365	4.539	1.0179	5.351	0.9988	5.954
6.0	1.0295	5.079	1.0101	5.884	0.9900	6.355	25.0	1.0388	4.374	1.0206	5.185	1.0016	5.823
8.0	1.0305	4.994	1.0112	5.801	0.9913	6.294	30.0	1.0411	4.221	1.0232	5.029	1.0044	5.698

Table 5. Results of the Density Correlations with the Tait Equation

		m-cresol (1) + quinoline (2)				*m*-cresol (1) + 1-MNP (2)			
T/K	x_1	C	D/MPa	$10^2\pi^a$	$10^5\sigma^b$ (g·cm^{-3})	C	D/MPa	$10^2\pi^a$	$10^5\sigma^b$ (g·cm^{-3})
298.15	0.0	0.073 41	157.67	0.002	3.68	0.062 74	117.12	0.004	6.19
298.15	0.2	0.062 60	133.51	0.001	1.81	0.076 63	147.54	0.003	6.19
298.15	0.4	0.059 33	126.79	0.002	2.33	0.076 60	144.67	0.003	3.97
298.15	0.6	0.063 89	134.49	0.004	4.49	0.097 62	188.85	0.004	5.03
298.15	0.8	0.091 70	190.27	0.004	5.37	0.056 01	104.60	0.004	5.76
298.15	1.0	0.082 75	159.34	0.005	7.22	0.082 75	159.36	0.005	7.22
323.15	0.0	0.076 29	143.49	0.001	1.93	0.107 51	181.63	0.005	6.26
323.15	0.2	0.076 47	145.95	0.001	1.56	0.076 42	125.70	0.002	2.83
323.15	0.4	0.084 83	162.61	0.002	2.32	0.065 58	105.98	0.006	7.87
323.15	0.6	0.078 09	146.33	0.001	1.35	0.084 17	139.62	0.003	4.08
323.15	0.8	0.074 13	131.86	0.001	1.60	0.076 02	123.68	0.006	7.38
323.15	1.0	0.092 60	155.98	0.004	5.20	0.092 63	156.05	0.004	5.21
348.15	0.0	0.070 11	116.05	0.003	3.50	0.081 15	120.22	0.001	1.25
348.15	0.2	0.098 06	169.03	0.005	7.48	0.072 99	105.69	0.004	4.77
348.15	0.4	0.070 72	118.81	0.002	2.66	0.083 27	122.82	0.004	5.16
348.15	0.6	0.075 59	125.14	0.003	4.64	0.070 09	101.62	0.005	6.38
348.15	0.8	0.072 33	112.99	0.003	4.08	0.115 45	176.34	0.007	7.61
348.15	1.0	0.075 68	111.13	0.004	5.88	0.095 27	141.94	0.007	9.14

[a] π as defined in eq 4. [b] σ (g·cm^{-3}) = $[[\sum_{k=1}^{n}(\Delta\rho_k - \Delta\bar{\rho})^2]/(n-2)]^{1/2}$ where $\Delta\rho_k = \rho_{k,\mathrm{calc}} - \rho_{k,\mathrm{expt}}$ and $\Delta\bar{\rho} = (\sum_{k=1}^{n}\Delta\rho_k)/n$.

where V is the molar volume, V_o is the molar volume at 0.1 MPa, T is temperature, and x is the mole fraction. The constants C and D are parameters of the Tait model:

$$\frac{\varrho - \varrho_o}{\varrho} = C \ln\left(\frac{D + P}{D + 0.1}\right) \tag{3}$$

where ρ_o is the density at 0.1 MPa. The optimized C and D were determined from fitting the Tait model to the isothermal density data at a given composition by minimization of the objective function π (i.e., average absolute deviations) with a modified Levenberg−Marquardt algorithm.

$$\pi = [\sum_{k=1}^{n}|\varrho_k^{(\mathrm{calc})} - \varrho_k|/\varrho_k]/n \tag{4}$$

where n is the number of data points and $\rho_k^{(\mathrm{calc})}$ and ρ_k

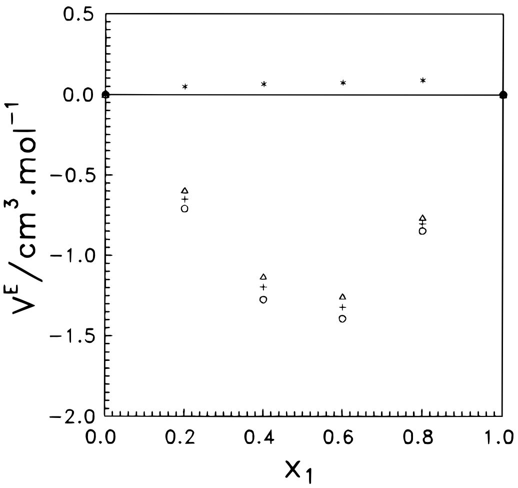

Figure 1. Temperature effects on the molar excess volumes at 0.1 MPa: (*) *m*-cresol (1) + 1-methylnaphthalene (2) at 323.15 K; *m*-cresol (1) + quinoline (2) at (△) 298.15 K, (+) 323.15 K, and (○) 348.15 K.

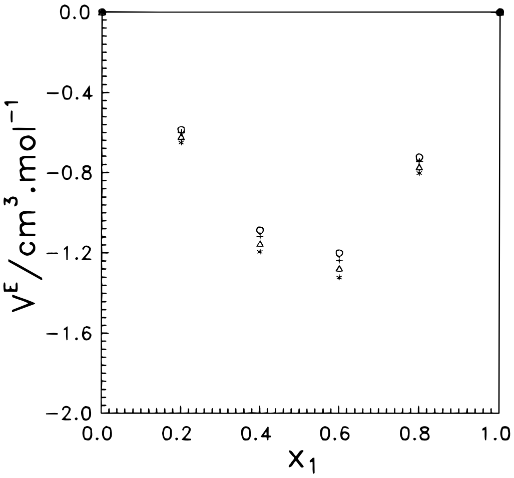

Figure 2. Pressure effects on the molar excess volumes for the *m*-cresol (1) + quinoline (2) system at 323.15 K: (*) 0.1 MPa, (△) 10 MPa, (+) 20 MPa, (○) 30 MPa.

represent the calculated and experimental densities for the *k*th point, respectively. Table 5 summarizes the calculated results including the optimized values of *C* and *D*, π, and the standard deviations of the fits (σ). It appears that the Tait model is capable of correlating the densities over the entire pressure range accurately. The tabulated values show the isothermal compressibility increasing with temperature and decreasing with pressure. The molar excess volumes (V^E) can be calculated from the experimental density data via

$$V^E = V_m - x_1V_1° - x_2V_2° \tag{5}$$

with

$$V_m = \frac{x_1M_1 + x_2M_2}{\varrho} \tag{6}$$

where V_m denotes the molar volume of a mixture, $V_i°$ refers to the molar volume of component *i* at the same temperature and pressure of the mixture, and M_i is the molecular weight of component *i*. Figure 1 illustrates the variations of molar excess volumes with the mole fraction of *m*-cresol at 0.1 MPa. Three isotherms are shown in the figure for the *m*-cresol + quinoline system. However, only the isotherm of 323.15 K is given for the *m*-cresol + 1-methylnaphthalene system because the temperature effects on these excess volumes are too small to be represented in the graph. It is evident that the volumes would contract significantly upon mixing *m*-cresol with quinoline and would expand slightly upon mixing *m*-cresol with 1-methylnaphthalene; that is, the excess volumes of the *m*-cresol + quinoline system are negative, and those of *m*-cresol + 1-methylnaphthalene are positive. Over the entire investigated conditions, the absolute value of the excess volume increases with temperature. The pressure effects on the excess volume of the *m*-cresol + quinoline system are illustrated in Figure 2, which shows the contraction of the volume decreasing with pressure.

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