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The Viscosities and Densities of Selected Organic Compounds and Mixtures of Interest in Coal Liquefaction Studies[1]

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Experimental measurements are presented for the density and viscosity of selected organic compounds and mixtures at ambient pressure (0.083 MPa) and at temperatures of 298, 318, 338, and 358 K. The compounds studied were decalin, 1-methylnaphthalene, tetralin, *m*-xylene, tetrahydrofuran, thiophene, quinoline 2,6-lutidine, and *m*-cresol. Measurements were also made on three mixtures of the compounds decalin, 1-methylnaphthalene, tetralin, *m*-xylene, and m-cresol. The experimental results are compared with predictions made using a modified corresponding states procedure called TRAPP. The density predictions for the individual compounds and mixtures are good in all cases. For the viscosity, however, the predictions are in reasonable agreement with experiment only for nonassociating compounds and mixtures at reduced densities less than 3. These results suggest that TRAPP may prove very useful as a screening test to distinguish between nonassociating and highly associating mixtures. Such a test would be extremely useful when dealing with mixtures of unknown composition, such as coal liquids.

KEY WORDS: corresponding states; decalin; density; *m*-cresol; *m*-xylene; 1-methylnaphthalene; quinoline; tetrahydrofuran; tetralin; thiophene; viscosity.

1. INTRODUCTION

The liquids produced by modern coal conversion processes represent an important class of industrial compounds whose physical and thermodynamic properties are as yet relatively unknown. Unfortunately, these

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liquids are undefined mixtures consisting of a variety of compound types, thus making the characterization of the liquid for correlation purposes quite difficult. This situation is, of course, completely analogous to the problem encountered with petroleum fluids.

A standard engineering method for dealing with this mixture problem is to measure the thermophysical properties of selected model compounds, chosen as representative of the chemical species believed present in the coal liquid or petroleum, in addition to measuring the properties of the undefined mixture itself. Successful correlation of thermophysical properties for the model compounds can then be scaled to the undefined mixture. This is the approach taken in this program. Our primary objective in this early work was to measure the viscosities and densities at ambient pressure and over a moderate temperature range for selected coal-liquid model compounds and defined mixtures. Our secondary objective was to investigate the suitability of using a modified corresponding-states predictive procedure for densities and viscosities (TRAPP) [1, 2], developed for use with nonpolar hydrocarbons, with pure model compounds, and three model coal liquids made by combining the pure materials. Since some coal liquids are known to contain compounds capable of hydrogen bonding, the failure of the procedure when applied to a specific sample might provide a means of identifying the presence of these bonds in the coal liquid. In other words, TRAPP could possibly be used as an effective screening tool to separate coal-liquid samples exhibiting significant hydrogen bonding or polarity from mixtures in which these effects are absent. Such a screening test would be very valuable, since coal liquids not exhibiting significant polarity or hydrogen bonding would be expected to follow the thermophysical properties correlations developed for petroleum fluids. Furthermore, an understanding of why TRAPP fails could lead to further development of the program.

The compounds selected for study were decalin, 1-methylnaphthalene, tetralin, *m*-xylene, tetrahydrofuran, thiophene, quinoline, 2, 6-lutidine, and *m*-cresol. Decalin, 1-methylnaphthalene, tetralin, and *m*-xylene represent typical nonpolar, nonassociating cyclic compounds encountered in coal liquids. Lutidine and quinoline model the heterocyclic nitrogen compounds and thiophene is the model sulfur compound. Heterocyclic nonassociative oxygen compounds are represented by tetrahydorfuran, while *m*-cresol contains oxygen and has a high degree of self-association.

2. EXPERIMENT

Viscosity measurements at atmospheric pressure (approximately 0.083 MPa) were made with Zeitfuchs cross-arm viscometers, using a

Table I. Comparison Between Experimental Measurements and Values Calculated from TRAPP: Viscosities and Densities of the Liquids at 298 K

Substance	T(K)	Viscosity (Pa · s 10^3)		Density (kg · dm^{-3})	
		η_{calc}	η_{exp}	ρ_{calc}	ρ_{exp}
m-Cresol	298.03	2.055	13.56	1.0928	1.0275
Decalin	298.10	1.008	2.469	0.8582	0.8839
2, 6-Lutidine	298.00	0.893	0.795	0.9523	0.9210
1-Methylnaphthalene	298.11	1.970	2.940	0.9756	1.0142
Quinoline	298.10	3.638	3.375	1.3837	1.0879
Tetralin	298.01	1.288	1.991	0.9246	0.9641
Tetrahydrofuran	298.13	0.397	0.451	0.8632	0.8802
Thiophene	297.86	0.534	0.617	1.0472	1.0559
m-Xylene	298.08	0.722	0.559	0.8416	0.8592

slightly modified ASTM D-445 testing procedure. The viscometers were calibrated using fluids supplied by the manufacturer, and distilled water was used to establish the accuracy of the apparatus. Our experimental results for water agreed with literature values to within $\pm 2\%$.

A bicapillary pycnometer was used, with a slightly modified ASTM D-3505 testing procedure, for the density determinations. Water could not be used to establish the experimental accuracy since it was the calibrating fluid for the pycnometer, but the availability of excellent data for *m*-xylene allowed its use in evaluating the accuracy of our density measurements. Complete details on the experimental procedure and calibrations and the

Table II. Comparison Between Experimental Viscosities and Values Calculated from TRAPP (All Values Are in Pa · s 10^3)

Substance	318.15 K		338.15 K		358.15 K	
	η_{calc}	η_{exp}	η_{calc}	η_{exp}	η_{calc}	η_{exp}
m-Cresol	1.531	5.210	1.186	2.653	0.946	1.646
Decalin	0.801	1.700	0.654	1.231	0.544	0.959
2, 6-Lutidine	0.692	0.619	0.561	0.495	0.464	0.410
1-Methylnaphthalene	1.492	1.932	1.166	1.366	0.937	1.038
Quinoline	2.722	2.201	2.116	1.563	1.693	1.195
Tetralin	1.000	1.395	0.801	1.040	0.657	0.829
Tetrahydrofuran	0.329	0.380	—	—	—	—
Thiophene	0.440	0.488	0.370	0.394	—	—
m-Xylene	0.577	0.460	0.472	0.377	0.393	0.322

Table III. Comparison Between Experimental Densities and Values Calculated from TRAPP (All Values Are in $kg \cdot dm^{-3}$)

	318.15 K		338.15 K		358.15 K	
Substance	ρ_{calc}	ρ_{exp}	ρ_{calc}	ρ_{calc}	ρ_{calc}	ρ_{exp}
m-Cresol	1.0696	1.0115	1.047	1.0248	1.0248	0.9795
Decalin	0.8426	0.8668	0.8270	0.8115	0.8115	0.8367
2, 6-Lutidine	0.9307	0.8996	0.9094	0.8880	0.8880	0.8629
1-Methylnaphthalene	0.9587	0.9983	0.9421	0.9254	0.9254	0.9700
Quinoline[a]	1.3608	1.0729	1.3384	1.3162	1.3162	1.0409
Tetralin	0.9077	0.9487	0.8911	0.8745	0.8745	0.9165
Tetrahydrofuran	0.8411	0.8588	—	—	—	—
Thiophene	1.0233	1.0324	0.9992	—	—	—
m-Xylene	0.8229	0.8422	0.8042	0.7854	0.7854	0.8059

[a] Calculated using the method of Riedel given in Ref. 6.

results of the water and *m*-xylene measurements are given by Oshmyansky [3].

The purity of the organic compounds used was greater than 99 mol%, with the exception of the decalin, which was a mixture of cis and trans isomers with approximately 2% of other materials.

The values for the viscosities and densities are summarized in Tables I–III. All measurements were made at ambient pressure (0.083 MPa).

3. COMPARISON OF EXPERIMENTAL DATA WITH TRAPP

3.1. Pure Fluids

TRAPP requires the following data for each compound: critical pressure, critical volume, critical temperature, molecular weight, and Pitzer's accentric factor. With this information TRAPP predicts the viscosity and density of the pure compound or a mixture at the specified temperature and pressure. The required properties for the compounds of this study (Table IV) were obtained from Refs. 4–7 with the exception of the critical volumes for 2, 6-lutidine and quinoline. For these compounds it was necessary to estimate the volumes using the method of Riedel, as outlined by Reid *et al.* [6]. The results of the TRAPP calculations are presented in Tables I–III and Figs. 1 and 2. It should be noted that TRAPP was not optimized for the compounds of this study.

Figure 1 shows that for all compounds studied except quinoline, the density predictions were within $\pm 7\%$, a reasonable deviation in the con-

Table IV. Thermophysical Property Data

Compound	Ref. No.	P_c (MPa)	V_c (ml · mol^{-1})	T_c (K)	ω	Temperature (K) at the normal boiling point (0.101325 MPa)
m-Cresol	5	4.56	309.	705.8	0.454	475.42
cis-Decalin	4	3.20	576.1	702.3	0.287	468.96
trans-Decalin	4	2.615	543.5	687.1	0.27	460.46
2, 6-Lutidine	4	3.900	343.1[a]	623.8	0.367	417.2
1-Methylnaphthalene	5	3.25	462.	772.	0.310	517.8
Quinoline	4	3.80	456.7[a]	782.0	0.262	510.78
	7	5.78	—	800.2	0.318	510.85
	5	—	—	782.	—	510.78
Tetrahydrofuran	5	5.19	224.	540.1	0.217	338.
Tetralin	4	3.515	427.9	719.2	0.303	480.7
Thiophene	5	5.69	219.	579.4	0.196	357.15
m-Xylene	6	3.55	376.	617.0	0.331	412.3

[a] Calculated using the method of Riedel given in Ref. 6.

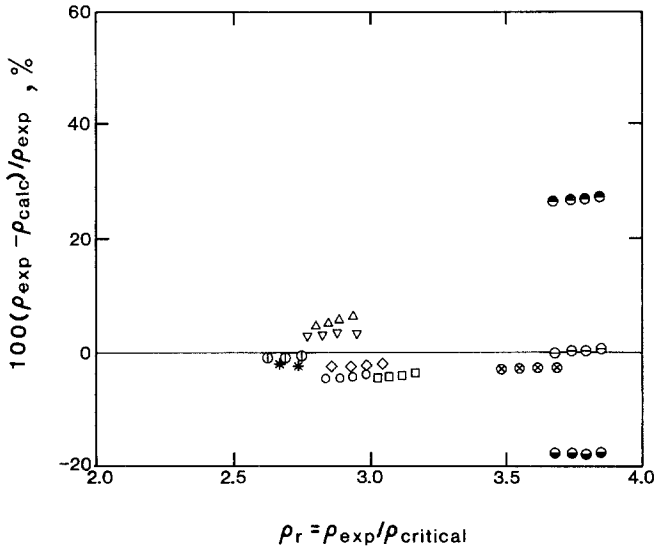

Fig. 1. Comparison of calculated and experimental densities. (△) *m*-Cresol; (⊗) decalin; (□) 1-methylnaphthalene; (⏀) thiophene; (◇) *m*-xylene; (∗) tetrahydrofuran; (▽) 2, 6-lutidine; (○) tetralin; (◓) quinoline, critical values from Ref. 4; (◒) quinoline, critical values from Ref. 7; (⊖) quinoline, critical values from Ref. 4 with critical pressure = 4.54 MPa.

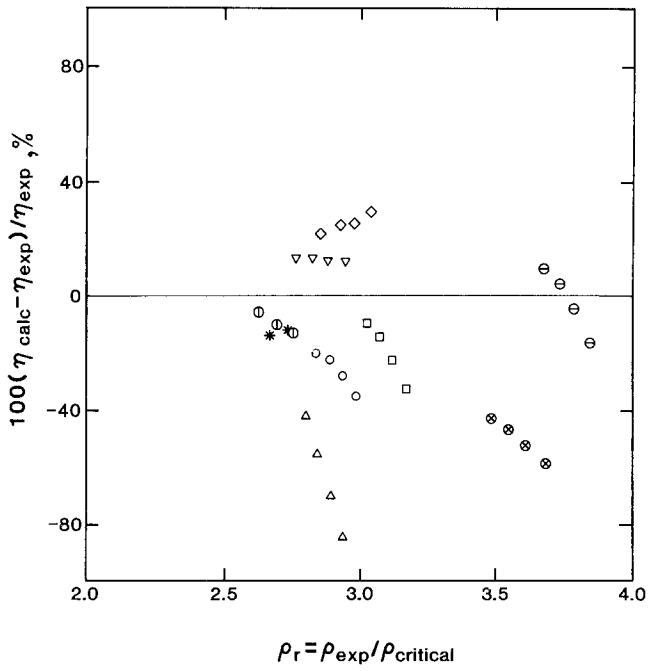

Fig. 2. Comparison of calculated and experimental viscosities. Symbols are the same as in Fig. 1.

text of this study. The difficulty with quinoline is attributed to uncertainty in the critical properties. For example, values from Refs. 4 and 7 are in substantial disagreement. Between the above-mentioned data sets critical pressures differed by 0.198 MPa, critical temperatures by 18.2 K, and the accentric factor by 0.56. The critical volume was not reported in either reference and, as mentioned previously, was calculated using the method of Riedel. A comparison of the effects of varying different critical parameters on the TRAPP predictions demonstrated that the critical pressure variation between the two data sets was the major source of the deviation between predicted and experimental results. Therefore, a critical pressure was selected (4.54 MPa) that produced density deviations of 0.5% or less. The viscosity predictions obtained using this critical pressure are compared with the experimental results in Fig. 2.

TRAPP gave approximate but acceptable results for the majority of the compounds used in this investigation (typically 10 to 40% deviation). The differences between the experimental and the calculated viscosity values for decalin and quinoline can be explained by the physical limitation of TRAPP; the TRAPP program, using methane as a reference compound,

is designed to work in a reduced density range of less than 3.4. Since both the decalin and the quinoline data were taken at reduced densities above this limit, the accuracy of TRAPP's predictions is questionable. Figure 2 shows that as the reduced density of the compound decreases, the results from TRAPP agree more closely with the experimental data for the majority of the compounds.

The TRAPP viscosity values for *m*-cresol, a highly self-associating compound, show a large deviation from the experimental data. This is the expected result, since it was anticipated that association in liquids will lead to large errors in the TRAPP predictions, thus suggesting the use of the TRAPP predictions to distinguish between associating and nonassociating compounds.

3.2. Mixtures

To test further the idea of using TRAPP as a screening test for the presence of associating compounds, a series of measurements was made on three "synthetic" coal liquids. These mixtures were meant to mimic coal liquids with association effects ranging from negligible to very high. The first mixture, called base "syn" coal liquid throughout this paper, was composed of nonassociating compounds and had the following composition: 26.4 wt% decalin, 27.9 wt% 1-methylnaphthalene, 25.4 wt% tetralin, and 20.3 wt% *m*-xylene. The second mixture, having 3.5 wt% oxygen, was prepared by taking the base "syn" coal liquid and adding enough *m*-cresol to reach the following composition: 20.2 wt% decalin, 21.3 wt% 1-

Table V. Comparison Between Experimental Measurements and Values Calculated from Trapp

Substance	T(K)	Viscosity (Pa · s 10^3)		Density (kg · dm^{-3})	
		η_{calc}	η_{exp}	ρ_{calc}	ρ_{exp}
Base "syn" coal liquid	297.99	1.175	1.498	0.9042	0.9310
	318.15	0.925	1.090	0.8872	0.9148
	338.15	0.826	0.613	0.8705	0.8997
	358.15	0.613	0.675	0.8538	0.8843
3.5 wt% oxygen "syn" coal liquid	298.15	1.374	2.051	0.9502	0.9510
	358.15	0.693	0.758	0.8958	0.9028
10.0 wt% oxygen "syn" coal liquid	298.15	1.733	5.274	1.0320	0.9934
	358.15	0.832	1.149	0.9701	0.9452

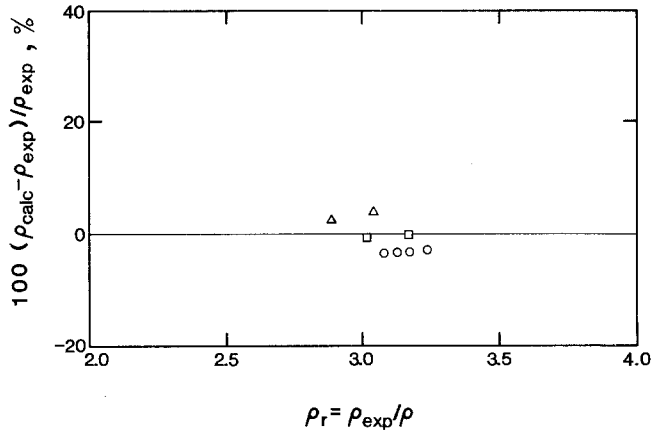

Fig. 3. Comparison of calculated and experimental densities for "synthetic" coal liquids. (○) Base "syn" coal liquid; (□) 3.5 wt% oxygen "syn" coal liquid; (△) 10 wt% oxygen "syn" coal liquid.

methylnaphthalene, 19.4 wt% tetralin, 15.4 wt% *m*-xylene, and 23.7 wt% *m*-cresol. The last mixture was selected to simulate a highly associated coal liquid and was prepared by adding *m*-cresol to the base "syn" coal liquid until the mixture contained 10% oxygen by weight. The composition of this mixture was 8.5 wt% decalin, 9.0 wt% 1-methylnaphthalene, 8.2 wt% tetralin, 6.6 wt% *m*-xylene, and 67.7 wt% *m*-cresol.

TRAPP results for the densities were excellent for all three mixtures (Table V and Fig. 3). The results for the base "syn" coal liquid showed reasonable deviation for the viscosity data (under 21% error; Fig. 4). On

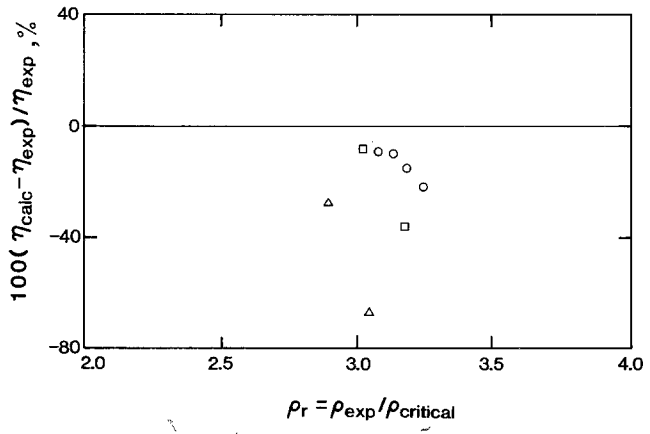

Fig. 4. Comparison of calculated and experimental viscosities for "synthetic" coal liquids. Symbols are the same as in Fig. 3.

the other hand, the mixture containing 10 wt% oxygen, which was supplied by highly self-associating *m*-cresol, showed a large deviation (about 67%). The mixture with an intermediate amount of *m*-cresol (3.5 wt% oxygen) showed a significant viscosity deviation (36%), but not sufficient to enable TRAPP to judge the degree of association. These results demonstrate that TRAPP can be used to distinguish highly associated liquids from nonassociating liquids, but it is unclear if it can be used with any success for the liquids with small to intermediate association.

4. CONCLUSIONS

TRAPP can be used to predict the densities of individual compounds and complex mixtures at all values of reduced density with an accuracy acceptable for many engineering calculations. The viscosity predictions are somewhat poorer, but at reduced densities below 3.0 for nonassociating compounds and mixtures the results are generally reasonable.

The results of this study demonstrate that when TRAPP is used as a screening test, it can distinguish between highly associated liquids and nonassociated liquids, but it is doubtful if it can be used successfully in its present form for those liquids with small to intermediate association. TRAPP has two problems that must be solved before it can be used with confidence as a screening test. First, TRAPP tends to underpredict the viscosity for both branched-chain and naphthenic compounds, and second, the program begins to fail as the freezing line is approached. It seems likely that both of these problems can be overcome, and thus future versions of TRAPP may well prove to be an effective and general tool for determining the presence of associating compounds in undefined mixtures.

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