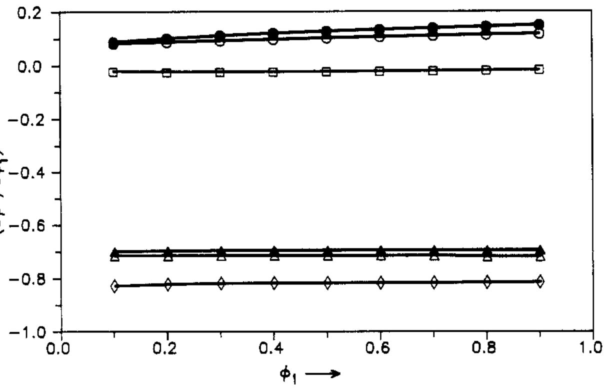

Figure 4. Dependence of density increment on volume fraction of the first-named component in the mixture at 20 °C: (○) benzene (1)-cyclohexane (2); (●) ethyl acetate (1)-cyclohexane (2); (△) benzene (1)-carbon tetrachloride (2); (▲) ethyl acetate (1)-carbon tetrachloride (2); (□) benzene (1)-ethyl acetate (2); (◇) cyclohexane (1)-carbon tetrachloride (2).

of cyclohexane with benzene or ethyl acetate.

Variation of refractive index for all the three wavelengths (589, 546, and 436 nm) as a function of ϕ_1 is shown in Figure 2. As expected, refractive index is higher for the mercury blue line (436 nm) than the mercury green line (546 nm). However, for sodium yellow line (589 nm) lower values of refractive indices than at either 546 or 436 nm are observed. For all the systems, the refractive index versus ϕ_1 curves are slightly deviated from a straight-line behavior.

Dependence of refractive index increment on ϕ_1 is shown in Figure 3. Mixtures of benzene with ethyl acetate, carbon tetrachloride or cyclohexane exhibit positive values for the increment for all the wavelengths. However, mixtures of ethyl acetate with cyclohexane or carbon tetrachloride and cyclohexane (1)-carbon tetrachloride (2) exhibit negative refractive index increments. In all the cases, the refractive index increments have shown increasing tendencies with a decrease in wavelength. The highest (and positive) values of refractive index increments are observed for the benzene (1)-ethyl acetate (2) system and the lowest (and negative) values are observed in the case of cyclohexane (1)-carbon tetrachloride (2) system. No strict linearity is observed for any of the systems as seen in Figure 3.

Dependence of density increment on volume fraction of the first component of the mixture is shown in Figure 4. For the systems benzene (1)-ethyl acetate (2), benzene (1)-carbon tetrachloride (2), ethyl acetate (1)-carbon tetrachloride (2), and cyclohexane (1)-carbon tetrachloride (2), the density increment is negative over the entire range of composition of the mixture. However, for the systems benzene (1)-cyclohexane (2) and ethyl acetate (1)-cyclohexane (2), the density increment is positive; for the latter system it is largest of all. For mixtures exhibiting positive refractive index increments the density increment is negative (see, for instance, mixtures I and II given in Table I). A reverse situation exists in the case of ethyl acetate (1)-cyclohexane (2) wherein the density increment is positive but refractive index increment is negative. On the other hand, for a few mixtures (see, for instance, mixtures V and VI given in Table I) both the increments are negative; in one case (mixture III) both the increments are positive. Thus, there appears to be no strict correlation between either the sign or magnitudes of these increments. From a general observation, it is apparent that if the first component of the mixture possesses higher values of either density or refractive index than the second component, then the increments are found to be positive. If on the other hand, the first component has lower values than the second then negative values of the increments are prevalent.

Acknowledgment

I thank Professor Petr Munk of the University of Texas (Austin) for the experimental facilities, Professor P. E. Cassidy of Southwest Texas State University for the facilities provided during the preparation of this manuscript, and Mrs. Sue Hall for typing the manuscript.

Registry No. Benzene, 71-43-2; cyclohexane, 110-82-7; ethyl acetate, 141-78-6; carbon tetrachloride, 56-23-5.

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Densities and Viscosities of Binary Liquid Mixtures at 45 °C

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Densities and viscosities for 14 binary liquid mixtures comprising carbon tetrachloride, cyclohexane, methyl ethyl ketone, benzene, *p*-xylene, bromobenzene, dimethyl sulfoxide, dimethylformamide, nitromethane, ethyl acetate, and methanol at 45 °C over the whole range of mixture compositions are presented.

Introduction

In our earlier studies (*1-3*) densities and viscosities have been measured at 25 and 35 °C for several binary mixtures comprising carbon tetrachloride, cyclohexane, methyl ethyl ketone, dimethyl sulfoxide, dimethylformamide, nitromethane, benzene, bromobenzene, ethyl acetate, *p*-xylene, and methanol. In continuation of this research we now present additional data of densities and viscositites of 14 binary mixtures comprising the same solvents. The properties were studied over the entire range of composition of the mixture.

Experimental Section

All chemicals used were of commercial products of the highest available purity (BDH). These were further purified by

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Table I. Data for Pure Components at 25 °C

solvent	boiling point, °C			viscosity, cP			density, g/cm^3		
	found	lit.	ref	found	lit.	ref	found	lit.	ref
benzene	80.00	80.10	*8*	0.6010	0.5990	*8*	0.8742	0.8737	*9*
carbon tetrachloride	76.2	76.75	*8*	0.8920	0.9020	*8*	1.5787	1.5840	*4*
cyclohexane	80.10	80.74	*8*	0.8830	0.8860	*8*	0.7759	0.7740	*4*
methyl ethyl ketone	79.00	79.6	*13*	0.4750	0.4800	*4*	0.8008	0.7997	*4*
dimethyl sulfoxide	190.00	189.85	*13*	2.0240	2.0210	*11*	1.0965	1.0960	*10*
ethyl acetate	77.10	77.26	*8*	0.4390	0.4240	*12*	0.8948	0.8945	*12*
methanol	64.20	65.15	*13*	0.5900	0.5470	*13*	0.7857	0.7865	*4*
nitromethane	100.20	100.80	*13*	0.6270	0.6200	*13*	1.1255	1.1313	*4*
dimethylformamide	152.80	153.00	*13*	0.8050	0.8001	*14*	0.9481	0.9440	*4*
bromobenzene	155.90	156.05	*4*	1.0810	1.0400	*14*	1.4982	1.4980	*12*
p-xylene	137.50	138.00	*14*	0.6150	0.6000	*14*	0.8561	0.8567	*9*

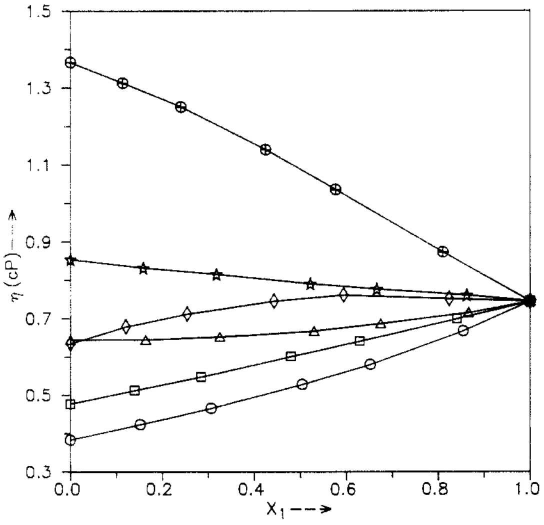

FIGURE 1

Figure 1. Dependence of viscosity on mole fraction of carbon tetrachloride at 45 °C: (⊕) carbon tetrachloride (1)–dimethyl sulfoxide (2); (☆) carbon tetrachloride (1)-bromobenzene (2); (◇) carbon tetrachloride (1)-dimethylformamide (2); (△) carbon tetrachloride (1)-cyclohexane (2); (□) carbon tetrachloride (1)-benzene (2); (○) carbon tetrachloride (1)-ethyl acetate (2).

standard methods (*4*, *5*). The purity of the final samples was checked by measuring their densities and viscosities at 25 °C and these agreed well with the corresponding literature values (*5*). These data are given in Table I.

Mixtures were made by weighing an appropriate volume of each solvent using special airtight stoppered bottles. When once the mixtures were made, all measurements were done on the same day. However, keeping the mixtures overnight and remeasuring them on the subsequent days indicated an error of about 0.5–1.5% in viscosity and approximately 1% error in density measurements. The mole fractions (X_i) of the components in the mixtures were calculated from the volumes and densities of individual components.

Viscosities were measured at 45 °C with an Ostwald viscometer by comparing the flow times of pure liquid or the mixture with that of double distilled water (*6*). Viscosities were calculated from flow times (in seconds) for all the mixtures. Flow times for water as well as for pure solvents were quite consistent during the entire period of measurement. Densities were measured by means of a pycnometer. A single-arm-type pycnometer was used with a volume capacity of about 20 cm^3 having an internal diameter of about 1 mm. The calibration of the pycnometer was done at 45 °C using doubly distilled water (*7*).

A Toshniwal constant temperature bath with a precision of ±0.05 °C was used. Triplicate measurements of each composition of the mixture showed reproducibility to within ±0.0005 cP for viscosity and ±0.000 05 g/cm^3 for density. Only the average values of the densities and viscosities from three independent measurements are presented in Table II.

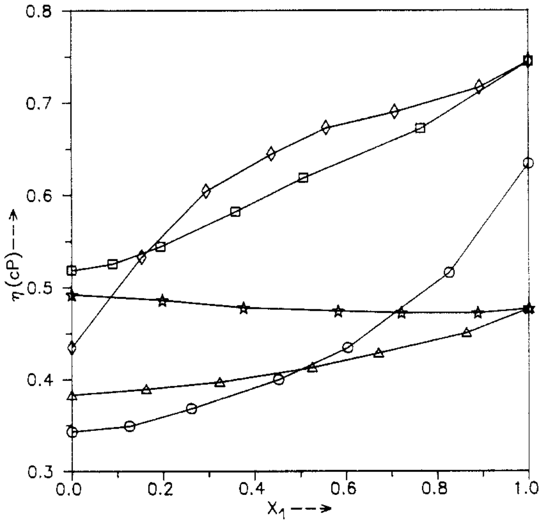

FIGURE 2

Figure 2. Dependence of viscosity on mole fraction of the second-named component in the mixture at 45 °C: (○) cyclohexane (1)-methyl ethyl ketone (2); (△) benzene (1)–ethyl acetate (2); (☆) benzene (1)-xylene (2); (◇) carbon tetrachloride (1)-methanol (2); (□) carbon tetrachloride (1)-nitromethane (2).

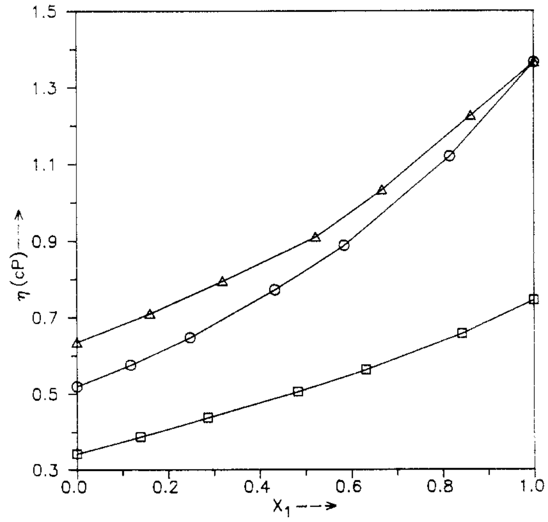

FIGURE 3

Figure 3. Dependence of viscosity on mole fraction of the second-named component in the mixture at 45 °C: (○) dimethyl sulfoxide (1)-nitromethane (2); (△) dimethyl sulfoxide (1)-dimethylformamide (2); (□) carbon tetrachloride (1)-methyl ethyl ketone (2).

Results and Discussion

The dependence of viscosity on mole fraction for carbon tetrachloride containing mixtures is presented in Figure 1. For

Table II. Density (ρ) and Viscosity (η) Data for Binary Mixtures at 45 °C

x_1	ρ, g/cm^3	η, cP	x_1	ρ, g/cm^3	η, cP
I. Cyclohexane (1)–Methyl Ethyl Ketone (2)			VIII. Carbon Tetrachloride (1)–Methyl Ethyl Ketone (2)		
0.0	0.78661	0.34293	0.0	0.78661	0.34293
0.1257	0.77964	0.34900	0.1385	0.90108	0.38773
0.2611	0.77356	0.36816	0.2858	1.02030	0.43788
0.4518	0.76730	0.39962	0.4821	1.17606	0.50517
0.6033	0.76365	0.43429	0.6311	1.29034	0.56253
0.8254	0.76132	0.51566	0.8418	1.44622	0.65722
1.0	0.76249	0.63377	1.0	1.56169	0.74444
II. Dimethyl Sulfoxide (1)–Nitromethane (2)			IX. Carbon Tetrachloride (1)–Benzene (2)		
0.0	1.10562	0.51870	0.0	0.86706	0.47653
0.1170	1.10215	0.57526	0.1399	0.96511	0.51247
0.2468	1.09779	0.64709	0.2838	1.07043	0.54780
0.4324	1.09423	0.77168	0.4793	1.21033	0.60114
0.5837	1.09137	0.88779	0.6289	1.31381	0.64114
0.8156	1.08793	1.11970	0.8405	1.45659	0.69928
1.0	1.08693	1.36580	1.0	1.56169	0.74444
III. Dimethyl Sulfoxide (1)–Dimethylformamide (2)			X. Carbon Tetrachloride (1)–Nitromethane (2)		
0.0	0.93468	0.63484	0.0	1.10562	0.51870
0.1590	0.95736	0.70946	0.0897	1.17114	0.52558
0.3184	0.98078	0.79479	0.1941	1.23870	0.54422
0.5210	1.01056	0.91009	0.3589	1.32855	0.58220
0.6667	1.03357	1.03220	0.5073	1.39656	0.61885
0.8614	1.06441	1.22590	0.7644	1.49087	0.67188
1.0	1.08693	1.36580	1.0	1.56169	0.74444
IV. Benzene (1)–Ethyl Acetate (2)			XI. Carbon Tetrachloride (1)–Dimethylformamide (2)		
0.0	0.87911	0.38292	0.0	0.93468	0.63484
0.1624	0.87582	0.38942	0.1208	1.03042	0.67888
0.3233	0.87239	0.39710	0.2535	1.12884	0.71180
0.5251	0.86893	0.41290	0.4423	1.25660	0.74497
0.6710	0.86636	0.42866	0.5937	1.35024	0.76076
0.8633	0.86308	0.45048	0.8235	1.47544	0.75062
1.0	0.86076	0.47653	1.0	1.56131	0.74485
V. Carbon Tetrachloride (1)–Ethyl Acetate (2)			XII. Carbon Tetrachloride (1)–Dimethyl Sulfoxide (2)		
0.0	0.87911	0.38292	0.0	1.08693	1.36580
0.1518	0.98024	0.42291	0.1140	1.16089	1.31170
0.3052	1.08374	0.46552	0.2398	1.23513	1.24980
0.5035	1.21826	0.52789	0.4240	1.33317	1.13930
0.6517	1.31950	0.57972	0.5763	1.40400	1.03520
0.8540	1.45897	0.66741	0.8096	1.49751	0.87254
1.0	1.56169	0.74444	1.0	1.56169	0.74444
VI. Carbon Tetrachloride (1)–Bromobenzene (2)			XIII. Carbon Tetrachloride (1)–Methanol (2)		
0.0	1.47639	0.85355	0.0	0.77590	0.43453
0.1581	1.49038	0.83129	0.1527	1.01066	0.53284
0.3169	1.50542	0.81470	0.2949	1.16802	0.60435
0.5212	1.52281	0.78977	0.4375	1.28522	0.64464
0.6657	1.53525	0.77584	0.5566	1.36419	0.67293
0.8618	1.55137	0.76001	0.7077	1.44509	0.68995
1.0	1.56169	0.74444	0.8931	1.52454	0.71638
VII. Carbon Tetrachloride (1)–Cyclohexane (2)			1.0	1.56169	0.74444
0.0	0.76292	0.64449	XIV. Benzene (1)–Xylene (2)		
0.1636	0.87995	0.64446	0.0	0.84257	0.49188
0.3244	1.00023	0.65220	0.1977	0.84442	0.48564
0.5293	1.15969	0.66696	0.3756	0.84637	0.47750
0.6744	1.27906	0.68689	0.5821	0.84966	0.47391
0.8658	1.44253	0.71484	0.7212	0.85313	0.47199
1.0	1.56169	0.74444	0.8882	0.85686	0.47179
			1.0	0.86076	0.47653

the remaining mixtures the viscosity dependence is shown in Figures 2 and 3. For carbon tetrachloride (1)–bromobenzene (2) (see Figure 1) a more or less linear dependence was observed; however, the remaining mixtures have shown deviations from linearity.

The dependence of density on mole fraction is shown in Figures 4 and 5. A linear behavior is seen for carbon tetrachloride (1)–ethyl acetate (2), carbon tetrachloride (1)–methyl ethyl ketone (2), cyclohexane (1)–methyl ethyl ketone (2), benzene (1)–ethyl acetate (2), benzene (1)–p-xylene (2), dimethyl sulfoxide (1)–nitromethane (2), and dimethyl sulfoxide (1)–dimethylformamide (2). For the remaining mixtures, slight deviations from the straight-line behavior has been observed.

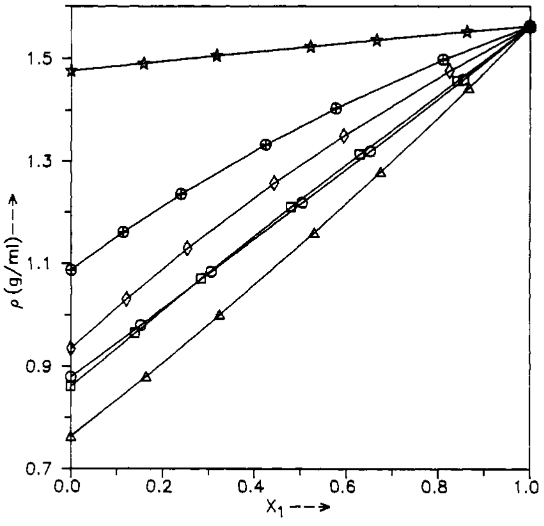

FIGURE 4

Figure 4. Dependence of density on mole fraction of carbon tetrachloride at 45 °C: (△) carbon tetrachloride (1)–methyl ethyl ketone (2); (□) carbon tetrachloride (1)–benzene (2); (○) carbon tetrachloride (1)–ethyl acetate (2); (◇) carbon tetrachloride (1)–dimethylformamide (2); (⊕) carbon tetrachloride (1)–dimethyl sulfoxide (2); (☆) carbon tetrachloride (1)–bromobenzene (2).

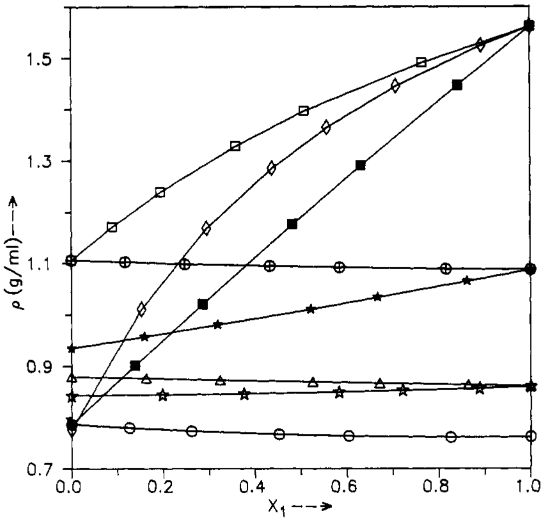

FIGURE 5

Figure 5. Dependence of density on mole fraction of the second-named component in the mixture at 45 °C: (○) cyclohexane (1)–methyl ethyl ketone (2); (☆) benzene (1)–xylene (2); (△) benzene (1)–ethyl acetate (2); (■) carbon tetrachloride (1)–methanol (2); (★) dimethyl sulfoxide (1)–dimethylformamide (2); (◇) carbon tetrachloride (1)–cyclohexane (2); (⊕) dimethyl sulfoxide (1)–nitromethane (2); (□) carbon tetrachloride (1)–nitromethane (2).

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Registry No. Carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7; benzene, 71-43-2; p-xylene, 106-42-3; methanol, 67-56-1; ethyl acetate, 141-78-6; methyl ethyl ketone, 78-93-3; dimethyl sulfoxide, 67-68-5; bromobenzene, 108-86-1; nitromethane, 75-52-5.

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Modelling of Impurity Effects in Fluids and Fluid Mixtures

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An extended corresponding-states model of the Helmholtz free energy for two-component mixtures, based upon existing accurate representations of the principal component as the reference function, has been used to model the effects of impurities. The results give a clearer and more accurate view of the errors in the measurement of thermodynamic properties caused by small amounts of impurity. The model is also extended to include three-component mixtures to allow the estimation of the effects of impurities in two-component mixtures. The model is applied to two systems of practical importance: methane as an impurity in ethylene, and *n*-butane as an impurity in isobutane–isopentane mixtures. Both of these systems are of commercial importance and commonly used in their critical regions, where the effect of impurities on thermodynamic values is large, and where existing procedures for the estimation of the impurity effects are not accurate. New experimental determinations of the critical line for ethylene containing small amounts of methane have improved the ability to predict the behavior of the impure ethylene near its critical point.

Introduction

There is a growing awareness of the need for more accurate methods for the prediction of properties of fluids used in commercial quantities where there are likely to be significant amounts of impurities, particularly if the region of use of the material is near the critical region. In custody transfer, for instance, the density ρ of the fluid is often calculated, at measured pressure p and temperature T, from a known equation of state formulation. In the limit of infinite dilution, $x \longrightarrow 0$, where x is the mole fraction of impurity

$$(\partial V/\partial x)_{pT} = VK_T(\partial p/\partial x)_{VT} \quad (1)$$

where K_T is the compressibility of the pure fluid. $(\partial p/\partial x)_{VT}$, in general, is a finite quantity. At the critical point of the pure fluid, it reaches the value

$$(\partial p/\partial x)_{VT} = \mathrm{d}p/\mathrm{d}x|_{\mathrm{crl}} - \mathrm{d}p/\mathrm{d}T]_\sigma^{\mathrm{c}}\,\mathrm{d}T/\mathrm{d}x|_{\mathrm{crl}} \quad (2)$$

where $\mathrm{d}p/\mathrm{d}x|_{\mathrm{crl}}$ and $\mathrm{d}T/\mathrm{d}x|_{\mathrm{crl}}$ are the initial slopes of the critical line of the mixture in $p-x$ and $T-x$ space, respectively, and $\mathrm{d}p/\mathrm{d}T|_\sigma^{\mathrm{c}}$ is the limiting slope of the solvent's vapor pressure curve. Thus, the change in molar volume, at constant p and T, due to a small admixture x is

$$\begin{aligned}\delta V &= (\partial V/\partial x)_{pT}x + ... \\ &\propto xK_T\end{aligned} \quad (3)$$

Equation 3 is based on a Taylor expansion at constant p,T (*1-4*). It shows that the effect of the impurity on molar volume or molar density is proportional to the solvent's compressibility, and therefore becomes very large in the critical region. The compressibility diverges at the critical point, where expression 3 becomes invalid. It therefore seems worthwhile to model the impurity effects by means of a Helmholtz free energy representation for the mixture. As long as this is done in a consistent way, a classical equation of state for the major component, combined with the classical principle of corresponding states, the impurity effects can be calculated at any point in the $p-T$ plane. We find that impurity effects on the density are very large and not linear in x in a large region around the critical point of the fluid. Also, we find that impurities can induce a phase transition and therefore, if the pure-fluid equation of state is used, one may even predict the wrong phase.

The two examples studied here are that of ethylene, for the purpose of custody transfer, and that of a 90%-10% isobutane–isopentane mixture used in a Rankine cycle for geothermal power generation. Ethylene is produced in very large quantities and is transferred from producer to consumer through pipelines in which the fluid, whose critical temperature is 9 °C, may assume conditions not too far from criticality. Commercial ethylene is at least 99.85% pure, the most volatile contaminant being methane. We will estimate the errors in the density, at given pressure and temperature, caused by a worst-case scenario of 0.15 mol % methane. Another system modelled is the isobutane–isopentane mixture containing *n*-butane as an impurity. These mixtures are used as working fluids in geothermal binary power cycles, and the interest here is in the effect of impurities on the thermodynamic properties of the working fluid which affect the efficiency of the power cycle. Since the commercial grade of isobutane, the major component of the mixture, may contain up to 5% impurity, principally *n*-butane, the location of the critical point and the phase boundaries can be significantly affected. Before extending the treatment to the 3-component system, we calculate the effect of a small amount of isopentane in pure isobutane.

In both of the examples we have the advantage of the availability of an excellent classical equation of state for the major component. Using this equation as a reference, we have modelled the mixture properties using principles of extended corresponding states.