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Shear Viscosities of Methycyclohexane, Perfluoromethylcyclohexane, and Their Mixtures in the Vicinity of the Upper Critical Mixing Temperature. 1. Critical Isopleth and Coexistence Curve

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Shear viscosities η are reported for pure liquid methylcyclohexane (MCH) from 298.610 K to 333.694 K, for perfluoromethylcyclohexane (PFMCH) from 319.196 K to 333.114 K and for a MCH + PFMCH mixture of overall PFMCH near-critical mole fraction, $x_c = 0.3640$, from (T_{UCS}/K − 7) in the region of biphase liquid coexistence to (T_{UCS}/K + 20) in the uniphase region, where $T_{UCS} = 320.13$ K is the air-saturated upper liquid−liquid critical solution temperature. The measurements were made using a capillary rheometer that permits the measurement of the viscosity of thermally equilibrated coexisting-liquid phases. The results confirm that the near-critical viscosity exhibits a weak enhancement that strictly speaking becomes a divergence when account is taken of the finite shear gradients in the capillary during measurements. The viscosity of the uniphase mixture of critical composition is well-described after shear gradient correction by a multiplicative combination of an Arrhenius background and a critical power expression with an index close to the now-accepted universal value $y = 0.0435$. The chief objective of the work, in addition to contributing to knowledge of this aspect of near-critical rheology, is the development for the biphase of a simple expression for the temperature dependence of the viscosities of the coexisting phases, η_+ and η_-, that combines (a) an expression for the viscosity diameter $<\eta> = 1/2(\eta_+ + \eta_-)$ similar to that for the viscosity of the critical mixture in the uniphase region, with a similar best critical index y' between 0.041 and 0.0435, and (b) an expression for $\Delta\eta = (\eta_+ - \eta_-)$ that behaves like an order parameter, with an index β very close to the normal value $\beta = 0.325$ and as many Wegner correction terms as the data require. The best two-phase fit emerges from a freely fitted exponent $y' \approx 0.037$ with one Wegner-extended scaling term, but we believe that were shear gradient correction to be applied, the best y' would be the consensus value $y' = 0.0435$. The magnitude of y' notwithstanding, we believe that our primary objective has been satisfied, namely, the formulation of an expression that affords a good description of the shear and background viscosities of near-critical mixtures in the one- and two-liquid phases in relation to our estimates of the nano- or molecular-viscosity derived from measurements of fluorescence polarization decay rates.

Introduction

The viscosity of liquid mixtures has been the focus of much experimental and theoretical interest, but over the past 40 years perhaps the most intense scrutiny has been directed toward the investigation of the viscosity of mixtures near a liquid−liquid critical end point. The most cogent review of this material up to 20 years ago was written by Sengers.[1] Subsequent advances have been made by a variety of authors including Nieuwoudt and Sengers,[2] Zielesny and co-workers,[3,4] and Das and Bhattacharjee[5] but chiefly the Berg and Moldover group.[6−9] Very recent calculations by Hao et al. lend substantial support to the experimental findings.[10]

In much of this work, interest has attached chiefly to the divergence or enhancement of the viscosity at such a critical point along any of the experimentally convenient paths. This divergence is associated with the divergence of the correlation length ξ, especially in the single-phase or uniphase region of a mixture of critical composition, sometimes termed the critical isopleth, according to

$$\xi = \xi_0 \epsilon^{-\nu} \tag{1}$$

where for an upper critical solution point the reduced temperature $\epsilon = |T - T_{UCS}|/T_{UCS}$ with T_{UCS} as an upper critical temperature, ξ_0 is a system-dependent amplitude, and $\nu = 0.63$ is a universal critical exponent. From this expression, it has become customary to describe the viscosity η along the critical isopleth by

$$\eta = \eta_0 \epsilon^{-y} \tag{2}$$

where η_0 is again a system-dependent amplitude and y is a universal critical index for the viscosity. This expression is an approximation to the strictly correct form in which the right-hand term is $\eta_0(Q_0\xi_0)^{y/\nu}\epsilon^{-y}$, where the inverse length Q_0 depends on the fluid.[1] The factor $(Q_0\xi_0)^{y/\nu}$ is typically very close to but not exactly unity, and so for the present purpose it is taken as unity. Were the present purpose to engage in the precise experimental valuation of y and y' defined below, this approximation would be unavailable to us. Equation 2 applies when ϵ is sufficiently small to ignore the crossover to noncritical

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behavior. A very great deal of attention has been attached to the exact determination of the value of y along the critical isopleth. After repeated measurements in many laboratories, there now appears to be very good reason to believe that the optimum value is $y = 0.0435$, chiefly from the astounding measurements over an unparalleled range of ϵ very close to the gas−liquid critical point of the viscosity of xenon in zero gravity reported by Berg et al.[9] supported by the recent theoretical result reported by Hao et al.[10] However, here we do not focus primarily on this critical isopleth y-evaluation exercise, although we return to the matter in the discussion section below. Instead, our main attention falls on the description of the viscosity along other pathways leading to the critical point with our present interest concerned with the behavior of the viscosities, canonical η_+ and η_- (i.e., at the same temperature) along the two limbs of the coexistence curve in the two-phase or biphase region. We propose a simple expression that appears to describe the data well and allows safe interpolation to obtain the viscosity of the coexisting phases as a function of ϵ. If the $(T - x)$ coexistence curve, where x is mixture mole fraction, is known well, we can obtain η as a function of the coexisting canonical mole fractions x_+ and x_-.

Although methylcyclohexane + perfluoromethylcyclohexane (MCH + PFMCH) has been greatly studied in the critical mixing region,[11−21] its transport properties, like those of many other mixtures studied in this region, have been much less thoroughly explored than the equilibrium properties. Partly in an effort to redress this imbalance, we have determined the near-critical shear viscosity and the thermal conductivity in the upper critical mixing region. However, until now, none of the results of our viscosity measurements have been published in full, and only some of the outcomes emerging from the analysis of all our results have been reported.[22,23] Our principal purpose here therefore is to present in full the results of our viscosity measurements for an air-saturated MCH + PFMCH mixture of close-to-critical mole fraction composition x_c (a) in the two-liquid-phase region from 7 K below the upper critical solution temperature $T_{UCS} = 320.13$ K and (b) in the one-liquid-phase region from T_{UCS} to 20 K above T_{UCS}. Our secondary purpose is to describe briefly the successful application of a recently developed representation of the near-critical viscosity in the two-liquid phase region.[24]

Experimental Section

Materials. Methylcyclohexane obtained from BDH Chemicals was purified by a series of steps involving treatment with a sulfuric acid−nitric acid nitrating mixture, followed in turn by 0.5 mol·dm^{-3} aqueous sodium hydroxide solution, 0.07 mol·dm^{-3} acidified aqueous iron(II) sulfate solution to remove traces of peroxide, and distilled water. The sample was dried over 5 Å molecular sieve and finally fractionated in a spinning-band column. UV absorption revealed no trace of aromatic impurity, and gas−liquid chromatography indicated a level impurity of below 0.01 % in mole fraction. Purum grade perfluoromethylcyclohexane of estimated purity around mole fraction of 97 % was obtained from Fluorochem Ltd and fractionated in a spinning-band column. Gas−liquid chromatography analysis confirmed that the original five impurities of unknown identity had been thereby removed. This purification confirmed one particularly useful advantage of cyclic perfluorocarbons over open-chain, especially unbranched, perfluorocarbons (namely, their greater ease of purification).

The sample mixture was made up by weighing to yield a 275 cm^3 sample of PFMCH mole fraction $x_F = 0.3640 \pm 0.0004$ in close agreement with the accurate critical mole composition $x_c = 0.364$ reported by Kumaran.[16] The volume of sample in the sealed viscosity cell sufficiently exceeded that of the vapor space in the cell to render entirely negligible changes in liquid composition caused by differential vaporization as the measurement temperature changed. The marked positive azeotropy of the mixture, the near-equality of the vapor pressures of the components across the working temperature range, and the flatness of the near-critical vapor pressure isotherm all further contributed to the composition stability.[11]

Apparatus. The viscosity measurements were made in a sealed combined thermal conductivity/capillary rheometer made of Pyrex glass incorporating a Veridia precision bore rheometer capillary. The design belongs to the modified Ubbelohde suspended-column class and was based on that described by Pegg and McLure.[25] A feature of both designs was the facility to readily conduct measurements on the coexisting liquid phases of a thermally equilibrated biphase mixture, a characteristic that before our instruments were first described appears to have been reported only by Chu and Lin and then solely for ternary mixtures.[26] The inner diameter of the rheometer capillary was 0.25 mm, and its length was 22.1 cm yielding a length/radius ratio of 884 that is much larger than the threshold recommended by Bogue to render end-effects negligible.[27] The temperature was determined to ± 0.01 K using a platinum thermometer calibrated against a secondary standard itself calibrated at the National Physical Laboratory, London. Details of the instrument and its mode of operation are available.[28]

Results

Upper Critical Solution Temperature. The rheometer was originally designed for the determination of orthobaric viscosities (i.e., under the equilibrium vapor pressure of the mixture in the absence of air). Used in this mode with a freeze−pump−thaw degassed sample, we obtained $T_{UCS} = (319.26 \pm 0.01)$ K, in quite astonishingly good agreement with the orthobaric $T_{UCS} = 319.26$ K reported by Kumaran and McGlashan.[15] An early inadvertent opening of one of the taps on the rheometer allowed air to access our sample whereupon its T_{UCS} rose to 320.13 K. As a general rule, the extent of the partial mixing region of a liquid mixture increases with the ingress of a further component more soluble in one of the two components of the original mixture (i.e., for a mixture exhibiting an upper critical endpoint T_{UCS} rises). The observed rise in T_{UCS} in the present case is therefore consistent with the known very much higher solubility of simple gases, notably air, in perfluoroalkanes than in alkanes. Although the presence of a small amount of air rendered the mixture slightly impure, the effect on the near-critical physical properties was believed to be of limited significance for our purposes. So we undertook no redegassing measures. In any event, it proved much easier to implement the viscosity-measuring protocol with the fluid pressure within the instrument close to atmospheric pressure, not least because the mixture positive azeotropy readily brought about boiling when the mixture was subjected to reduced pressure during fluid manipulation when in the biphase region.[11]

Shear Viscosity. The design and dimensions of the instrument and the physical properties of the sample combined to yield a small Reynold's number, never exceeding 5, such that corrections arising from turbulence, kinetic energy (Hagenbach's and Cannon's corrections), the Couette effect, drainage, and surface tension effects were unnecessary.

This was confirmed for the calibration runs using twice-distilled and ion-exchanged water. The flow times t_F at five

Table 1. Shear Viscosities η for Pure Methylcyclohexane and Perfluoromethylcyclohexane at Temperatures T

methylcyclohexane		perfluoromethylcyclohexane	
T/K	η/mPa·s	T/K	η/mPa·s
298.610	0.7341	319.196	1.0313
303.632	0.6844	320.161	1.0114
308.955	0.6360	323.176	0.9582
317.714	0.5669	328.128	0.8787
323.657	0.5268	333.114	0.8074
328.768	0.4964		
333.694	0.4690		

Table 2. Values of the Fitting Parameters η_0 and B for Expressions of the Form of Equation 5 for Pure Methylcyclohexane and Perfluoromethylcyclohexane

pure liquid	η_0/mPa·s	B/K	RMS % deviation
methylcyclohexane	0.01023	1275.96	0.035
perfluoromethylcyclohexane	0.00299	1864.47	0.030

Table 3. Temperatures T, Liquid Densities ρ, and Shear Viscosities η for MCH + PFMCH in the One-Liquid Phase Region for $T > T_{UCS} = 320.13$ K

T/K	ρ/g·cm^{-3}	η/mPa·s	T/K	ρ/g·cm^{-3}	η/mPa·s
One-Liquid Phase Region					
320.16	1.1736	0.7472	325.50	1.1629	0.5617
320.19	1.1735	0.7280	326.98	1.1601	0.5452
320.34	1.1732	0.6890	328.41	1.1573	0.5313
320.50	1.1729	0.6723	330.08	1.1541	0.5170
320.74	1.1724	0.6544	331.60	1.1511	0.5034
321.00	1.1719	0.6428	333.21	1.1481	0.4923
321.39	1.1711	0.6292	334.85	1.1449	0.4806
321.96	1.1699	0.6151	336.69	1.1414	0.4679
322.62	1.1686	0.6018	338.48	1.1381	0.4558
324.05	1.1658	0.5798	340.38	1.1345	0.4438

Table 4. Liquid Densities ρ and Shear Viscosities ρ at Temperatures T for MCH + PFMCH in the Two-Liquid Phase Region for $T < T_{UCS} = 320.13$ K

T/K	ρ/g·cm^{-3}	η/mPa·s	T/K	ρ/g·cm^{-3}	η/mPa·s
Upper MCH-Rich Phase					
313.50	0.9111	0.5402	319.16	1.0381	0.5795
315.17	0.9593	0.5477	319.62	1.0656	0.5973
316.53	0.9599	0.5516	319.85	1.0943	0.6255
318.48	1.0104	0.5724	320.03	1.1130	0.6477
Lower PFMCH-Rich Phase					
313.50	1.4199	0.7520	319.62	1.2774	0.6711
315.17	1.3961	0.7216	319.85	1.2525	0.6805
316.53	1.3728	0.7032	320.03	1.2346	0.6903
318.48	1.3267	0.6780	320.11	1.2099	0.7159
319.16	1.3019	0.6696			

different equispaced temperatures between 295 K and 345 K were fitted first to the equation suggested by Cannon et al.:[29]

$$\eta = A\rho t_F - E t_F^{\,2} \tag{3}$$

where A and E are instrument constants, and ρ is the density of the liquid under examination, in this case water.[30] The water viscosity came from the IUPAC recommendation.[31]The results were also fitted to the simpler expression

$$\eta = A\rho t_F \tag{4}$$

The values of A and E were obtained using the nonlinear least-squares fitting routine of Bevington.[32] The small magnitude and ill-characterization of E and the resulting small size of E/t_F^2, the second term in eq 3, never exceeded 0.15 % of At_F, thus suggesting that no corrections need be applied to the simple proportionality between η and t_F. Accordingly, the shear viscosity was invariably calculated thereafter from eq 4 with $A = (0.005798 \pm 0.00002)$ cm^2·s^{-2}. Although the absolute uncertainty of the resulting viscosity thus never exceeded 0.3 % (i.e., $\sim \pm 0.0020$ mPa·s in η), in the tables of results η is quoted to ± 0.0001 mPa·s which is a better reflection of the precision of our measurements.

The densities of the uniphase mixture and of the coexisting phases were determined from the densities reported by Kumaran[16] and the excess volumes and liquid−liquid coexistence curve reported by Kumaran and McGlashan.[15]

The viscosities η of the pure MCH and PFMCH listed in Table 1 are well-represented by the Arrhenius expression:

$$\eta = \eta_0 \exp(B/T) \tag{5}$$

with the fitting parameters η_0 and B shown in Table 2. The densities and viscosities of the mixture for 20 temperatures in the one-liquid phase region above T_{UCS} are shown in Table 3 and for nine temperatures in the two-liquid phase region below T_{UCS} in Table 4 where η_+ is the higher and η_- is the lower of the viscosities of the coexisting liquid phases. The fitting expressions are discussed below.

Discussion

Figure 1 shows η as a function of ϵ along the uniphase critical isopleth and both limbs of the biphase coexistence region. For useful comparison, we also show η for pure MCH and pure PFMCH.[33,34] The results are very similar to those we have recorded for the closely related mixture hexane + perfluorohexane.[35,36] The diagram shows that except over a limited range of temperature just below T_{UCS} the viscosity of the methylcyclohexane-rich phase is lower than that of pure methylcyclohexane indicating a minimum in the shear viscosity critical isotherm that is confirmed by our subsequent measurements. At higher temperatures outside our current working temperature range, the viscosity of the critical mixture also falls below that of pure methylcyclohexane, further confirming that the viscosity isotherm exhibits a minimum. Although upward concavity appears to be a characteristic of many mixtures in the near-critical region, the presence of a minimum, although not uncommon, is not, as the viscosity measurements reported by Reed for a variety of alkane + perfluorocarbon mixtures confirm.[37]

The viscosity in the one-phase region is well-described as a function of temperature T along the critical isopleth (i.e., along the path of constant critical composition x_c) by the by-now-standard expression, apparently first described by Debye[38] and more recently given greater theoretical strength by Ohta:[39]

$$\eta = \eta_{back}\eta_{anom} \tag{6}$$

For the mixtures of relatively simple liquids studied hitherto, the background term η_{back} takes the same form of the Arrhenius function of T shown in eq 5 that was used for the pure components; the values of the composition-dependent constants η_0 and B are characteristic of a given mixture. The background contribution is shown in Figure 1 by dotted lines. The critical or divergent anomaly term η_{anom} is well-described by

$$\eta_{anom} = \eta^{-y} \tag{7}$$

The anomalous part of the viscosity is a weak divergence that is reflected, as Siggia et al.[40] and Calmettes[41] showed many years ago, by the small value $y \sim 0.04$. This value has subsequently

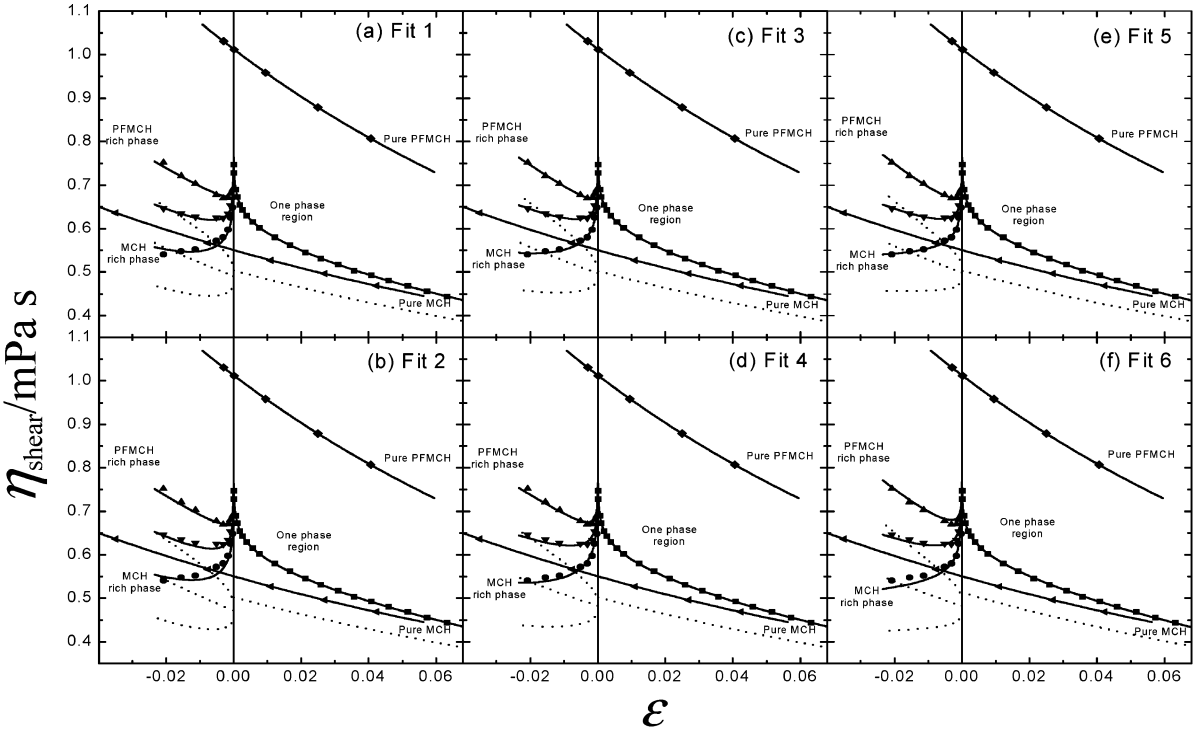

Figure 1. (a−f) Shear viscosities η as a function of scaled temperature $|T - T_{\mathrm{UCS}}|/T_{\mathrm{UCS}}$ of (left-pointing filled triangle), MCH; ◆, PFMCH; and a MCH + PFMCH mixture of overall critical mole fraction of x_c(PFMCH) = 0.3640 along ■, the critical isopleth; ▼, the MCH-rich; ▲, and the PFMCH-rich branches of the liquid−liquid coexistence curve, and ▼, the viscosity diameter $<\eta> = 1/2(\eta_+ + \eta_-)$. The curves are drawn using the fitting eqs 4, 5, and 6. The background contributions are shown as dotted lines. The fitting parameters are listed in Table 6.

Table 5. Values of the Fitting Parameters for Expressions of the Form of Equation 5 in the One-Phase Liquid Region[a]

parameter	fit 1	fit 2
$10^4 A_{\mathrm{visc}}$/mPa·s	83.6	82.0
	(0.2)	(0.4)
B/K	1311	1318
	(8)	(17)
y	0.0435	0.0432
	fixed	(0.0008)
χ^2	0.18	0.18
RMS	0.04 %	0.03 %

[a] The quantities in parentheses represent the uncertainties of the fitted parameters.

been confirmed experimentally using capillary rheometers such as that used in this project for a number of mixtures.[22] However, for mixtures very close to the critical point $y \sim 0.04$ is found only after taking the correct account of the influence of shear gradients.[42] In the absence of this near-critical correction, the viscosity of some critical mixtures appears not to diverge but rather to exhibit an enhancement; unconstrained fits of the data then usually yield values y less than 0.04. The apparent absence of need for a shear correction may arise either from an off-critical mixture composition or, more usually, from a measurement temperature range insufficiently close to T_{UCS}. Table 5 contains the results of our fitting of the uniphase region η that we discuss in the next section.

Figure 1 also shows that $<\eta> = 1/2(\eta_+ + \eta_-)$, the viscosity diameter or mean of the canonical viscosities η_+ and η_-, exhibits a weak divergence similar to that of the viscosity of the critical mixture in the uniphase region, so suggesting that $<\eta>$ can be represented by an expression similar to that for the viscosity along the critical isopleth. This similarity has been taken into account in the formulation of $\eta_\pm$ along both limbs of the coexistence curve[43] of the following expression for the viscosities:

$$\eta_\pm = <\eta> \pm 1/2\Delta\eta = (A_{\mathrm{visc}} \exp(B/T)\epsilon^{-y'}) \pm 1/2(H\epsilon^{\beta} + H_1\epsilon^{\beta+\Delta_1} + H_2\epsilon^{\beta+2\Delta_1}) \quad (8)$$

The development of this expression will be reported shortly;[24] but, briefly, its derivation rests on two observations. The first is that the viscosity diameter $<\eta>$ exhibits the same form of temperature dependence as the viscosity of the mixture of critical composition in the uniphase region (i.e., eq 5 but with a possibly different index, say y'). Although we know of no theoretical reason for a particular value for y', it appears from our study of this and other mixtures that it is close to the value $y = 0.04$. Recent very exact measurements of near-critical liquid mixture viscosity, chiefly by highly precise measurements by Berg et al.[9] and more recently by Hao et al.,[10] suggest authoritatively that the correct value for y (i.e., for the uniphase region) is very close to 0.0435. The second observation is the recognition that the difference in the canonical viscosities $\Delta\eta = (\eta_+ - \eta_-)$ behaves as an order parameter and so, unsurprisingly, can be described by the same expressions as describe near-critical liquid−liquid coexistence curves for mixtures[44] and vapor−liquid densities for pure substances[45] with the same universal order-parameter exponent, $\beta = 0.325$[46] along with as many corrections to the order-parameter expression of the kind introduced by Wegner,[47] with the gap-exponent $\Delta_1 = 0.5$, as the data require for good description of the coexistence curve outside the critical region.[47] The viscosities were fitted to eq 6 by nonlinear least-squares fitting. Table 6 contains the details of the biphasic region η fitting that we discuss in the section below. In Figure 1, the background terms are shown using dotted lines, illustrating the order parameter-like behavior of the canonical background viscosities for $<\eta>$ and for $\Delta\eta$ that are revealed by our fitting procedure.

Table 6. Values of the Fitting Parameters of the Form of Equation 6 in the Two-Phase Region

parameter	fit 1	fit 2	fit 3	fit 4	fit 5	fit 6
$10^4 A_{\text{visc}}$/mPa·s	11.520 (0.002)	5.852 (0.002)	18.098 (0.020)	24.040 (0.104)	17.952 (0.048)	21.927 (0.008)
B/K	1938.8 (0.1)	2145.6 (0.1)	1797.7 (0.3)	1697.7 (1.3)	1801.7 (0.5)	1727.0 (0.1)
H/mPa·s	0.667 (0.001)	0.667 (0.002)	0.486 (0.006)	0.494 (0.010)	0.603 (0.010)	0.696 (0.003)
H_1/mPa·s			1.67 (0.05)	1.60 (0.08)	−1.28 (0.18)	−1.96 (0.02)
H_2/mPa·s					15.7 (1.0)	19.2 (0.2)
y'	0.03850 (0.00002)	0.0435 fixed	0.0372 (0.0002)	0.0435 fixed	0.0365 (0.0004)	0.0435 fixed
χ^2	49	50	12	47	9	49
RMS	0.27 %	0.30 %	0.14 %	0.36 %	0.11 %	0.33 %

[a] The quantities in parentheses represent the uncertainties of the fitted parameters.

It is evident that the background terms for the diameter and the one-*critical* phase do not coincide at T_{UCS} as one might expect. This we attribute tentatively, despite our confidence in the preparation of the mixture, to a slight departure of the actual composition from x_c. As we shall show later, the isothermal viscosity at T_{UCS} also exhibits a divergence that makes it very hard to target the *critical* part and so can lead to a slight mismatching of the background terms. For this reason, we did not apply a constraint to equality of $A_{\text{visc}} \exp(B/T_{\text{UCS}})$ from each side of the critical point. Perversely, we have somewhat greater faith in the diameter term despite the complication of the analysis that leads to the biphasic pathway background, at least in terms of mixture composition since there is an automatic independence of η along the two branches of the coexistence curve from the overall mixture composition.

The ratios of the limiting amplitudes for different paths of approach to the critical point at $\epsilon = 0$ have been studied, and the results have been discussed elsewhere[22] in terms of the Calmettes treatment for limiting amplitudes for transport properties.[41,48] The experimental results are in good agreement with Calmettes' predictions.

Results of Data Fitting

Uniphase Region. In relation to the effect of shear gradients on our results, the simple (log η vs log ϵ) plot shows very little flattening at the lowest $\epsilon \approx 10^{-4}$ reached—although it can just be discerned at $(T - T_{\text{UCS}}) \sim 0.03$ K, suggesting that within our experimental temperature range shear gradient effects can be neglected in the light of our present purpose (namely, the description of η along the two conjugate paths to the critical point). However, forcing the fitting procedure to take account of shear gradients results in a correlation length amplitude $\xi_0 \approx 3$ Å, perhaps associated with the relatively high mass density of the MCH + PFMCH mixture—and the consequent increase in the shear gradient as compared to the case of less dense mixtures in the same viscometer—and an exponent of $y = 0.043$, not far from the Berg et al. result. The results in Table 5 were, however, calculated incorporating a finite shear gradient effect.

We turn now to the results shown in Table 5 of our fitting of the uniphase data to eqs 4 and 5. In the first column we show the results of a forced fit with the Berg and Moldover $y = 0.0435$. The results of the totally free fit shown in the second column yields $y = 0.0432$, in effect indistinguishable from the Berg and Moldover recommendation that we therefore endorse unreservedly for uniphase mixtures.

Biphase Region. Table 6 shows the results of the more complex fit of the biphase data to eq 6. The fitting strategy broadly follows that for the uniphase data except for the obvious need for judgment in the use of Wegner correction terms for the order parameter contribution in the fitting expression (eq 6). We list separately the results for two choices of y', namely, a freely fitted y' and the current most widely accepted value for η along the critical isopleth, $y' = 0.0435$. For each of these elections, we illustrate the result of using either no, one, or two Wegner correction terms; thus, we have six sets of result that we shall discuss in terms of increasing numbers of Wegner terms.

First, it is clear analytically that a free fit always describes the data better than a fit using y' fixed at the consensus value $y' = 0.0435$. However, this better description of the data is obtained at the cost of free fit y' values that are significantly smaller than the consensus value and that fall even further below the consensus value as one and then two Wegner-extended scaling terms are added to the fitting expression. Unsurprisingly, little extra benefit results from using more than one Wegner term; these observations are illustrated in fits 1, 3, and 5 shown in Figure 1. The fit with the consensus y' allowing extended scaling makes little change in either χ^2 or the RMS deviation, but as fits 2, 4, and 6 show, the addition of one Wegner term makes the fit look better than either none or two terms. Arguably the essential indifference of χ^2 to extended scaling for the consensus y' suggests that the consensus y' is basically correct, and the seemingly improved fit brought about by freely fitting y' reflects only the benefit of greater parametrization. Some of the difference, of course, may arise from our inability here to take advantage of shear gradient correction in the two-phase region. In the one-phase region it is now well-known that correctly introducing this correction causes y to increase toward the consensus value, and there seems to be no reason why matters should be different in this regard in the two-phase region. Overall, the best fit to our results comes from a freely fitted y' and *one* Wegner term, but the fit with the consensus y' with one extended scaling term looks almost equally good. Thus we are inclined to the view that our results are not inconsistent with $y' = 0.0435$. These numerical matters aside, it appears fair to claim that our fitting expression (eq 6) is a good one for representing the shear viscosities along the coexistence curve.

During the final preparation of this article, the work of Drozd-Rzoska came to our attention.[49] One of the object of her work, as in ours, was the description of the coexistence curve behavior of η. Her measurements of η for nitrobenzene + decane were made in an ingenious instrument, and the results are numerous. Among the welcome features of her approach were the separate examination of the values of y'_+ and y'_- (her ϕ) along the two branches of the coexistence curve. She found, in contrast to our conclusion, common values for both y'_+ and y'_- and y along the critical isopleth. This agreement was reached, however, at the expense of a very small value of 0.033. A further reservation on our part is the use of an arbitrary expression as a function of mole fraction, which has been much used in the past for the ideal viscosity of a liquid mixture but not universally accepted, as a descriptor of the background viscosity. In our approach, we preferred to use the canonical viscosities to elaborate an order parameter expression so introducing the Wegner corrections to facilitate usages far from the critical point. As in our investigation, shear rate corrections were applied to the biphase data but appeared unnecessary for the uniphase data. We should add that the Drozd-Rzoska paper was published after the thesis of E.M.-P. was published.[43] The foregoing notwithstanding, it seems clear that there exists for now a good case for accepting our eq 6 as an acceptable description of coexistence curve viscosities with the same critical index as for the mixture of critical composition in the uniphase region. This was our main purpose in analyzing our data in this way.

Conclusions

The shear viscosities of a methylcyclohexane + perfluoromethylcyclohexane liquid mixture of critical composition and its components are reported at temperatures above and below T_{UCS}. The viscosities of the pure liquids are well-described by the standard Arrhenius expression for the shear viscosity of relatively simple liquids. The viscosity of the critical mixture and the viscosity diameter $\langle\eta\rangle$ require critical enhancement factors ϵ^{-y} and $\epsilon^{-y'}$, respectively, with $y = 0.0435$, the currently favored value. The best y' lies in the range 0.0385 to 0.0365, depending on the number of Wegner terms, but the fit is not inconsistent with $y' = 0.0435$. The viscosities along the two limbs of the liquid–liquid coexistence curve, η_+ and η_-, are well-described by a combination of the expression for $\langle\eta\rangle$ with the addition of an order parameter term with the standard critical exponent $\beta = 0.325$. The limiting Calmettes amplitudes that emerge from the outcome of these fitting maneuvers have been shown previously to agree well with theoretical predictions.[22] Last, we now have an expression that allows us confidently to describe the viscosities of coexisting phases of a binary liquid mixture just inside the region of biphase stability.

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