Viscosities of Binary and Ternary Mixtures of Polyaromatic Hydrocarbons

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Experimental measurements of the viscosities of the three binary-mixture combinations of the toluene/tetralin/1-methylnaphthalene system were performed over the entire concentration range for various temperatures ranging from 298 to 498 K. Viscosities were also determined for an equimolar mixture of the three components and for the binary naphthalene/tetralin system. Finally, the polar phenol/picoline mixture was found to have interesting associative properties. The viscosity data determined have an experimental uncertainty of 1.1%. The viscosity correlation of McAllister gave excellent representations of both binary and ternary data.

Introduction

For the successful design and operation of coal conversion plants, it is necessary to have methods for accurately predicting the transport coefficients of coal liquids over wide ranges of concentration and temperature. Accurate estimates of viscosities, for instance, are necessary for sizing of vessels, piping systems, pumps, and separating systems. The mixtures that occur in such operations are primarily aromatic and polyaromatic hydrocarbons as well as a wide variety of heterocyclic compounds. Viscosities of complex mixtures of these compounds must also be predicted over a wide range of temperature and composition in order to achieve optimum coal conversion conditions. In addition, viscosities of these compounds and their mixtures allow some insight into the energy relationships in these liquid mixtures. The need for such information is even more important for liquids at temperatures in the critical region, where most of the coal conversion reaction mechanisms operate, because of the rapid changes that occur in viscosity with changing temperature and pressure. A study of near-critical viscosities using dynamic laser-light-scattering techniques has recently been completed as part of the current program (*1*).

In a previously reported study (*2*), viscosities were reported for eight pure components that form a subgroup of the model compounds needed for characterizing typical midfraction coal conversion fluids (*3*). In this study, our objective is to examine the behavior of these components in nonpolar and polar mixtures. Since data on mixtures of the compounds in question are virtually nonexistent, this is an important base of experimental data that should be further developed both for immediate use and for formulating a more theoretically sound method for predicting mixture viscosities.

Experimental Section

The apparatus used in this study is described in detail in a previous paper (*2*, *3*). The major component is a glass Ubbelohde viscometer manufactured by Schott Geräte (Model Series 24500). Liquid efflux time can be determined electronically with fiber-optic detectors, with an accuracy of ∓0.01 s, essentially removing one of the persistent sources of experimental error in older devices. The operation and theory of capillary viscometers are discussed extensively in the literature (*4*–*6*).

Our experimental equipment also included a constant-temperature bath (a Haake, Model N2, recirculating unit placed in a well-insulated cylindrical glass container) and a piping system for drawing samples into the capillary tube. Because of the temperature range involved in the experiments and the possibility of oxidation, argon (at a pressure slightly greater than ambient) was selected as a blanket gas. The blanket also served to prevent evaporation of the fluids. In organic liquid mixtures, differences in vapor pressures can lead to changes in concentration during a run. As a check for this, the initial concentration measurement was repeated at the end of the series for each mixture.

Temperature measurements were made over the range from 298 to 498 K; it was possible to maintain the temperature constant to within 0.2 K. For convenience, water was used as the bath medium at temperatures ≤368 K, and Dow Corning's Silicone Fluid No. 550 (phenylmethylpolysiloxane) was used at higher temperatures. A calibrated, platinum, resistance thermometer connected to a digital Fluke RTD sensor (Model 2180A) made it possible to measure temperatures accurately to within 0.1 K. The entire experimental unit (except readout devices) was covered and heavily insulated to minimize temperature gradients.

The viscometer manufacturer (Schott Geräte) provided calibration constants which relate the efflux time, t, to the kinematic viscosity, ν, as

$$\nu = \mu/\rho = K_C\Delta t - K_E/\Delta t^2 \tag{1}$$

where the calibration constant, K_C, is expressed as

$$K_C = \left(\frac{\pi}{8}\right)\left(\frac{\bar{z}R^4}{L\,\Delta V}\right) \tag{2}$$

and K_E is the kinetic energy correction constant. The manufacturer's calibration values were confirmed in our laboratory and, in some cases, corrections were made, using both water and toluene as calibrating fluids. Recalibration involved corrections of <1% (*3*).

To obtain the dynamic viscosity, μ, it is necessary to determine the density of the fluid at the temperature of the experiment. As was reported in the previous paper in this series the densities of all of the mixtures were measured by using calibrated pycnometers to an experimental accuracy of ~0.3%. In addition densities of pure components were predicted by using the method of Gunn and Yamada (*7*). The specific volume of a pure saturated liquid is given as a function of temperature, given critical data, acentric factor, and density data at one temperature in addition to the critical point. Data used to calculate densities for all the components in this study are those tabulated by Reid et al. (*8*). The liquids used in this study are chemically similar, and the pressure is low, so it is appropriate to select Amagat's law as a mixing rule. The molar volume of the mixture is given as

$$V_m^L = \sum_i x_i V_i^L \tag{3}$$

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Table I. Viscosity of Toluene (x = 0.8)/Tetralin

av temp, K	ν, m^2/s	μ, mPa·s	coeff of variation, %
298.2	0.792	0.7036	0.021
308.2	0.703	0.6177	0.033
318.2	0.636	0.5530	0.038
328.2	0.571	0.4909	0.012
338.2	0.517	0.4404	0.036
348.2	0.476	0.4004	0.017
358.2	0.439	0.3655	0.139
368.2	0.4112	0.3383	0.142
308.2	0.7004	0.6155	0.021
328.2	0.5679	0.4902	0.011
348.2	0.4789	0.4031	0.027
358.2	0.4417	0.3676	0.058
368.2	0.4094	0.3369	0.101

Table II. Viscosity of Toluene (x = 0.6)/Tetralin

av temp, K	ν, m^2/s	μ, mPa·s	coeff of variation, %
298.2	1.0106	0.9208	0.008
308.2	0.8904	0.8034	0.010
318.2	0.7874	0.7034	0.031
328.1	0.7101	0.6280	0.026
338.2	0.6412	0.5613	0.015
348.2	0.5843	0.5062	0.022
358.2	0.5350	0.4586	0.021
368.2	0.4949	0.4201	0.057

where x_j is the mole fraction of component j, and V_j^L is the molar volume of the pure components. This rule should be quite accurate for most mixtures in this study. The one possible exception is the picoline/phenol system. Even in this case, the basic molecular structures are sufficiently similar to make the chemical interaction a higher order density effect. A comparison of the prediction method with the density data for all mixtures revealed that the two were within the error of the experimental method for all of the mixtures used in the study. The data are tabulated elsewhere (*9*).

All organic chemicals used in the study were reagent grade (99+ wt % pure). There were problems associated with impurities found in two compounds. Tetralin was found to contain a peroxide that promoted coking, which caused yellowing of the solutions at high temperatures. As a result, it was considered necessary to purify the tetralin by extraction with aqueous ferrous ammonium sulfate (*3*). Impurities in the 2-methylnaphthalene caused a slight liquid discoloration, which was overcome by use of the argon blanket gas.

Results and Discussion

Two types of mixtures of the modeled coal conversion compounds were selected for study. First, fairly ideal mixtures involving three similar species were studied. The three components (studied in all possible binary combinations) were toluene, tetralin, and 1-methylnaphthalene. Because of its importance to coal processing, an additional binary of the type naphthalene/tetralin was studied over the range 358–458 K. Viscosities were also determined for a mixture of dissimilar species, a system in which interactions occur, namely the phenol/picoline mixture. The entire data base resulting from these investigations is tabulated in another report (*3*). A sampling of the data (the binary toluene/tetralin data base) is given in Tables I–V. Data for the other systems studied exhibit similar trends. All data were replicated, some several times. The coeffcient of variation column in each table indicates the variance between replicate runs. The definitions of all statistical terms used in the current work and tabulated in the previous work (*2*).

***Noninteractive Systems*.** Four binary mixtures (including all binary combinations of the system toluene/tetralin/1-methylnaphthalene as well as the naphthalene/tetralin binary) were investigated at several points over the range of possible concentrations and over the entire temperature range from ambient to 368 K (in the case of toluene mixtures) and from ambient to 458 K (for all others). Andrade coefficients were obtained for all mixtures over the entire range, and these values are given in Table VI. The Andrade coefficients were correlated as a function of the mole fraction of tetralin, using the relationship

Table III. Viscosity of Toluene (x = 0.5)/Tetralin

av temp, K	ν, m^2/s	μ, mPa·s	coeff of variation, %
303.2	1.0490	0.9625	0.023
313.1	0.9214	0.8373	0.017
323.5	0.8070	0.7260	0.055
323.1	0.8196	0.7376	0.016
333.1	0.7360	0.6558	0.014
340.1	0.6790	0.6009	0.860
343.1	0.6660	0.5875	0.040
353.7	0.5997	0.5234	0.689
353.1	0.6070	0.5300	0.015
364.6	0.5430	0.4685	0.431

Table IV. Viscosity of Toluene (x = 0.4)/Tetralin

av temp, K	ν, m^2/s	μ, mPa·s	coeff of variation, %
298.1	1.216	1.133	0.306
308.2	1.058	0.9772	0.132
318.1	0.9236	0.8532	0.064
328.3	0.8333	0.7550	0.059
338.4	0.7493	0.6723	0.133
348.4	0.6778	0.6021	0.049
358.4	0.6163	0.5420	0.207
365.4	0.5810	0.5074	0.162

Table V. Viscosity of Toluene (x = 0.2)/Tetralin

av temp, K	ν, m^2/s	μ, mPa·s	coeff of variation, %
298.0	1.629	1.550	0.066
313.1	1.288	1.209	0.004
328.3	1.047	0.9702	0.033
343.2	0.8798	0.8034	0.146
355.3	0.7731	0.6980	0.214
367.2	0.6927	0.6183	0.099

$$\mu(x,T) = (A_1 + A_2x)\exp[(B_1 + B_2x)/T] \tag{4}$$

where A_1 and A_2 have the units mPa·s and B_1 and B_2 are in kelvin. A least-squares analysis of the coefficients A and B gave the following values: A_1 = 0.015 66, A_2 = 0.003 33; B_1 = 1059.51, B_2 = 443.72. All of the data for this system were compared with the empirical correlation. The average prediction error is 1.25%, barely more than experimental error, with a maximum error of 3.62%. This represents an excellent fit of the data; therefore this method can be used with confidence to compute excess viscosities of the mixtures. An excess viscosity (μ_E) may be defined as

$$\mu_E = \mu_{mix} - (\mu^{\circ}_{mix}) \tag{5}$$

where μ°_{mix} is the mixture viscosity of an ideal solution of the same concentration.

Extensive tests on mixtures displaying thermodynamic ideality led Kendall and Monroe (*10*, *11*) to propose the following equation

$$\mu^{\circ}_{mix} = (x_1\mu_1^{1/3} + x_2\mu_2^{1/3})^3 \tag{6}$$

Deviations from this formula were generally less than 3%. Therefore, eq 6 provides a useful benchmark for comparison with results from real mixtures. Alexander and May also used this approach in a successful correlation of intrinsic viscosity with volumetric and enthalpy deviations from ideality (*12*).

Negative values for excess viscosity indicate some intermolecular repulsion, while positive values are attributed to attrac-

Table VI. Andrade Coefficients for Binary Mixtures

A/B	pure A	mole fraction B 0.2	0.4	0.6	0.8	pure B
toluene/tetralin	0.01535/1069.0	0.01539/1136.4	0.01434/1239.5	0.01438/1299.7	0.01166/1455.1	0.01292/1487.0
1-methylnaphthalene/tetralin	0.01169/1631.0	0.01018/1644.9	0.01079/1603.9	0.011493/1566.7	0.01177/1540.7	0.01292/1487.0
toluene/1-methylnaphthalene	0.01535/1069.0	0.01477/1166.3	0.01337/1298.3	0.01380/1386.6	0.00851/1630.2	0.01109/1631.0
naphthalene/tetralin	0.01975/1388.0	0.01294/1506.0	0.1302/1503.4	0.01326/1489	0.01355/1471.7	0.01292/1487.0
picoline/phenol[a]	0.01552/1192.0	0.01105/1442.3	0.00482/1890.5	0.00149/2431.0	0.000341/3009.5	0.000303/3028.0

[a] Additional data were collected for this binary mixture: 0.85 mole fraction B, 0.000294/3061.6; 0.091 mole fraction B, 0.000252/3109.6; 0.95 mole fraction B, 0.000227/3137.7.

tion or even bond formation between the two species. A maximum excursion of −0.1 mPa·s occurs at a tetralin mole fraction of 0.55, indicating a mild intermolecular repulsion effect. The system naphthalene/tetralin (two very similar compounds) represents a nearly ideal mixture. The excess viscosity for this system is negligible (<0.05 mPa·s), indicating intermolecular forces in the mixtures that are similar to those in the pure compounds. Between these pairs is the system 1-methylnaphthalene/tetralin. The methyl group tends to produce a charge difference between the two species, although their molecules are similar in size. This system exhibits a maximum excess viscosity of −0.05 mPa·s, thus indicating a modest net intermolecular repulsion.

The binary mixture of toluene/1-methylnaphthalene shows a larger negative deviation (~0.45 mPa·s) in excess viscosity at 0.5 mole fraction 1-methylnaphthalene (see Figure 1). This is attributable to the difference in molecular size of the species and the fact that both species have very active methyl groups. Therefore this system, which is expected to be only mildly interactive, exhibits a considerable departure from ideality.

One method for predicting the viscosity of binary mixtures is the technique proposed by McAllister (*13*). The basis for the equation form is the Eyring reaction-rate theory (*14*). In a manner similar to that used for successful gas-phase viscosity correlation (*15*), the theory of molecular motion is used as a basis for viscosity prediction. For a binary mixture, the McAllister equation has the form

$$\ln \nu_M = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 + R^0 \qquad (7)$$

where

$$R^0 = x_2^3 \ln \left(\frac{M_2}{M_1}\right) + 3x_1x_2^2 \ln \left(\frac{1 + 2M_2/M_1}{3}\right) + 3x_1^2x_2 \ln \left(\frac{2 + M_2/M_1}{3}\right) - \ln \left[x_1 + x_2\left(\frac{M_2}{M_1}\right)\right] \qquad (8)$$

and x is the mole fraction of each component, M is the molecular weight, ν_{21} and ν_{12} are interaction coefficients.

To predict mixture viscosities, four values (ν_1, ν_2, ν_{12}, and ν_{21}) must be obtained. The former two may be predicted from available pure-component correlations (or from data), but the latter two must be assessed from data for the binary system with which one is dealing. Since our data extended over a wide temperature range, the temperature functionality for each constant was obtained by the assumption of an Andrade form:

$$\nu_{12} = A_{12} \exp(B_{12}/T), \quad \nu_{21} = A_{21} \exp(B_{21}/T) \qquad (9)$$

Table VII shows the A and B values for the various systems of the current study. Data for all pure components were obtained from the previous study (*2*). For naphthalene, data were taken from Landolt and Bornstein (*16*). In comparisons of the experimentally determined data with the four-constant fit that was derived by McAllister's method, the average error was 1.05% (approximately equivalent to experimental error).

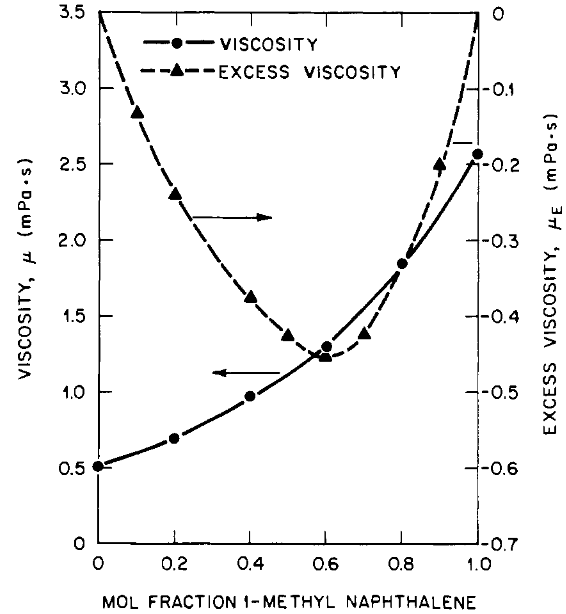

Figure 1. Viscosity and excess viscosity data for toluene/1-methylnaphthalene binary mixtures at 303 K.

Table VII. McAllister Constants for Binary Mixtures[a]

mixture	ν_{12} A_{12}	B_{12}	ν_{21} A_{21}	B_{21}
toluene/tetralin	0.025 99	1043.9	0.0226	1228.5
1-methylnaphthalene/tetralin	0.009 21	1687.2	0.0289	1271.9
naphthalene/tetralin	0.009 94	1590.9	0.0414	1078.1
toluene/1-methylnaphthalene	0.025 90	1040.9	0.0100	1652.1
phenol/picoline	0.000 1	3423.2	0.0367	1094.2

[a] The temperature functionality for each constant is obtained by the assumption of an Andrade equation form (*13*) [$\nu_{12} = A_{12} \exp(B_{12}/T)$, $\nu_{21} = A_{21} \exp(B_{21}/T)$].

Interactive Binary Mixtures. To study the effects of weak bonding on the viscosity of mixtures, the phenol/picoline system was selected. Since phenol is weakly acidic and picoline is mildly basic, some bonding was expected to occur, thus increasing viscosity. Pure-component and binary-mixture data for this system were collected over the temperature range 300–378 K; the Andrade coefficients are given in Table VII. The data for this system plotted in Figure 2 indicate a maximum viscosity at a phenol mole fraction of ~0.85. The excess viscosity curve for the system is shown in Figure 3. Data are insufficient to precisely place extrema of the curves.

At least two types of molecular interaction are evident in this system. Samples submitted for infrared spectra gave indications of a mild acid–base reaction such as the disappearance of the phenol OH$^-$ stretching-vibration characteristic, shifting of the picoline bond at 1604 cm^{-1}, and shifting of the phenol C–O bond (*2*). The second set of molecular forces involved are those causing negative interactions such as disruption of the hydrogen-bonding network in phenol and steric effects. The net

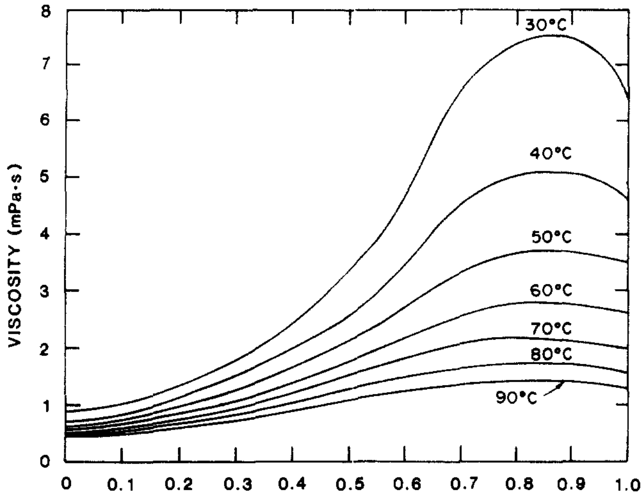

Figure 2. Viscosity of the phenol/picoline system.

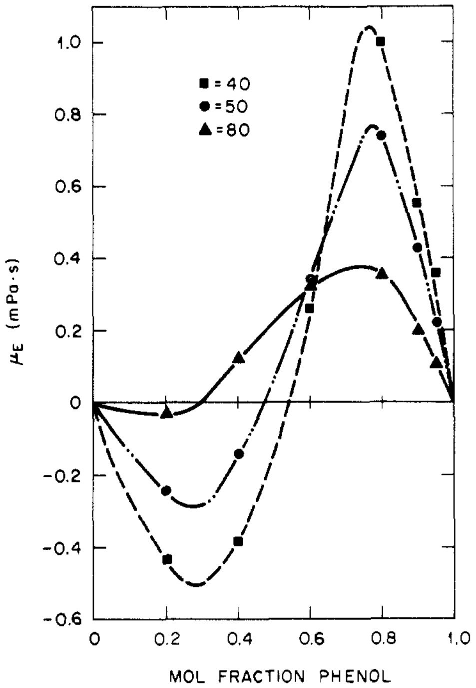

Figure 3. Excess viscosity data for phenol/picoline binary mixtures at various temperatures.

result of these molecular interactions is a tendency toward the disruption of hydrogen bonds at low phenol concentrations and by the dominance of the acid–base reaction at high concentrations of phenol.

Another important consideration involves the behavior of liquids in the supercooled state. At temperatures <315 K, pure phenol was subcooled; at these conditions, it is possible to measure viscosity of the liquid, presumably in a supersaturated condition. Viscosity data for this region are sparse, but there is an interesting indication that the energy constant for the Andrade correlation under these conditions is substantially higher than that for the normal liquid. This indicates confirmation of previous reports that higher intermolecular forces exist at supercooled conditions (*17*, *18*).

McAllister (*13*) reported that his equation was applicable to interactive systems such as acetone–water with an average deviation of 6.4%. Other interactive systems have been tested with similar results (*19*). The McAllister correlation was applied to the picoline phenol system. The interaction parameters ν_{12} and ν_{21} are reported in Table VII. The average deviation between the predicted and the experimental kinematic viscosities was 2.0% with a maximum error of 7.4%. The maximum in the viscosity–mole fraction curve was reproduced at all temperatures and occurs, as closely as can be ascertained from the data, very near the experimentally observed maximum. The greatest errors occurred below 40 °C. This is possibly due to the fact that pure phenol is supercooled in this region and has a significantly different viscosity behavior.

Table VIII. Viscosity Data for a Ternary Mixture of 1-Methylnaphthalene (x = 0.333), Tetralin (0.334), and Toluene (0.333)

av temp, K	ν, m^2/s	μ, mPa·s	coeff of variation, %
278.1	0.863	0.798	0.081
347.9	0.773	0.708	0.037
358.1	0.700	0.635	0.043
368.1	0.638	0.574	0.101
378.2	0.586	0.522	0.062
303.2	1.378	1.316	0.012
313.2	1.193	1.129	0.021
323.2	1.044	0.979	0.044
333.2	0.925	0.859	0.085
343.2	0.828	0.762	0.093
353.2	0.748	0.682	0.057

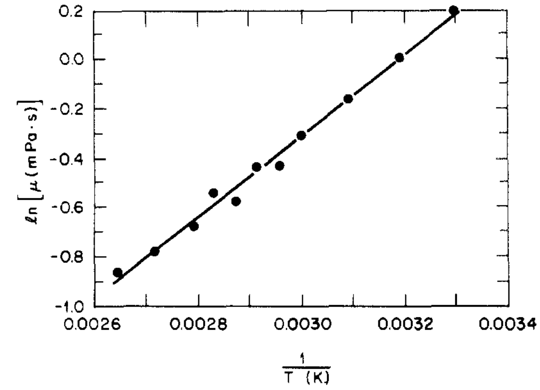

Figure 4. Correlation of the McAllister ternary coefficient (μ_{123}) as a function of reciprocal temperature: $\mu_{123} = A_{123} \exp(B_{123}/T)$. Data points (●) and regression line are displayed.

Viscosities of Ternary Mixtures. Viscosity measurements for multicomponent mixtures of known composition have only rarely been reported (*20*). For our investigations, an equimolar mixture of toluene, tetralin, and 1-methylnaphthalene was studied over the temperature range 303–378 K. The results are given in Table VIII. These data are more scattered than those for our previously reported binary runs, but are generally consistent with our prior measurements.

Correlation of the ternary liquid viscosity data, using the McAllister method, is discussed by Kalidas and Laddha (*20*), who considered three-body interactions in ternary-mixture viscosity. If ratios of molecular diameter are >1.5, even higher order interactions must be considered; however, the largest disparity in this study (between toluene and 1-methylnaphthalene) is <1.5, so it may be assumed that three-body interactions adequately describe the mixtures. The equation that predicts the ternary-mixture behavior is given elsewhere (*2*). To use this equation for predictive correlation, data must be available for all three components as well as for six binary-interaction parameters and one ternary-interaction parameter. Data extensive enough for such a prediction scheme have seldom been available but were gathered as part of the current program.

Following the Andrade form established in predicting the binary coefficients, it is possible to correlate the ternary interaction coefficient in terms of the following equation:

$$\mu_{123} = A_{123} \exp(B_{123}/T) \qquad (10)$$

Table IX. McAllister Ternary Coefficients[a]

	Andrade coeff	
	A, mPa·s	B, K
pure components		
ν_1	0.0153	1069
ν_2	0.0129	1487
ν_3	0.0110	1631
binary mixtures		
ν_{12}	0.0259	1043
ν_{13}	0.0179	1160
ν_{21}	0.0226	1228
ν_{23}	0.0288	1271
ν_{31}	0.00627	1677
ν_{32}	0.00921	1687
ternary mixtures		
ν_{123}	0.00525	1644

[a] Components: toluene (1), tetralin (2), 1-methylnaphthalene (3).

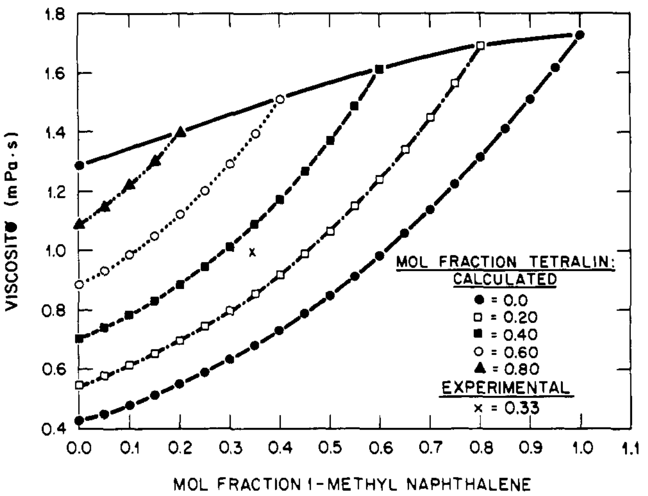

Figure 5. Two-dimensional representation of the viscosity of the toluene/tetralin/1-methylnaphthalene ternary system at 50 °C.

The fit of this ternary data with the correlation is shown in Figure 4. The coefficient of correlation is 0.997, indicating justification for the use of this equation form. Table IX is a compilation of all constants used for the three-component system of toluene/tetralin/1-methylnaphthalene. It is evident that the requirement for such a data base is a serious deterrent to using the McAllister prediction method although, with the 20 constants from Table IX, it is possible to predict the entire viscosity topography for the temperature range of the data. As an example, Figure 5 presents viscosity prediction data for 323 K. Viscosities for mixtures with a constant tetralin mole fraction are plotted as functions of the mole fraction of 1-methylnaphthalene. The construction of other curves simply requires the application of the constants in Table IX to the Kalidas and Laddha equation. Testing the proposed correlation has required that more data be taken on several ternary mixtures of the toluene, tetralin, and 1-methylnaphthalene. Data were collected throughout the concentration range and from 296 to 358 K. These data were compared with the predictions obtained by applying the constants in Table IX to the Kalidas and Laddha equation. The average error of the predictions is <2%, with a maximum error of 9%. Figure 6 shows the experimental data for two ternary systems along with the predicted curves. As shown, the agreement is excellent. Therefore, for this system which has significant variations from ideal conditions, the correlation is a viable means of predicting mixture viscosities.

The simplistic approach of linearly adding the contributions based upon mole fraction gave errors in the 20% range for these mixtures. Therefore, it is not acceptable for most purposes.

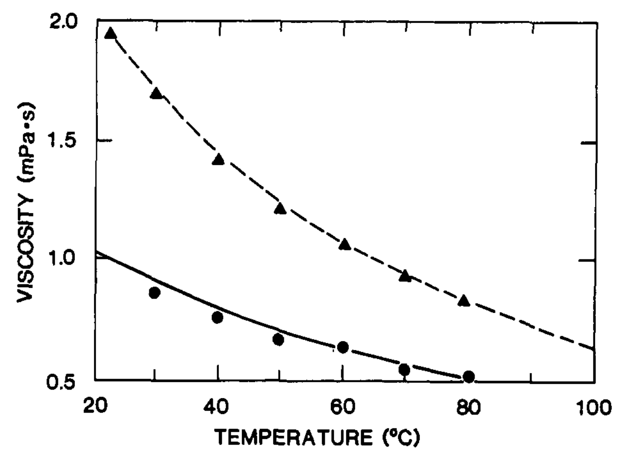

Figure 6. Viscosities of two toluene/tetralin/methylnaphthalene mixtures as compared with the predictions of the McAllister equation: for 0.6 mole fraction toluene, 0.2 mole fraction tetralin (▲, data prediction); and 0.2 mole fraction toluene, 0.2 mole fraction tetralin (O, data prediction).

The method of Kendall and Monroe (*10*) is simpler than the other techniques that have been discussed in this report. The mixture viscosity is given by the equation

$$\mu_M = (\sum_i x_i \mu_i^{1/3})^3 \qquad (11)$$

For our ternary system, the average error in this method's prediction of viscosity is <6%, using the data base we have accumulated. The Kendall–Monroe method makes no theoretical claims; it is based strictly upon observation. It does provide a prediction base for multicomponent systems which, at least in our case, gives reasonable results. The Kendall–Monroe correlation is recommended for obtaining a rough estimate of mixture viscosity when no mixture data are available. Only for fairly ideal mixtures will these estimates be accurate. In interactive systems, like picoline–phenol, the Kendall–Monroe method cannot predict a maximum. McAllister's is the method of choice when accurate mixture viscosity estimation is needed, especially where interactive systems are involved.

Conclusions

1. In this study, data for several interactive and noninteractive binary mixtures were collected over a wide temperature range. Computations of excess viscosity have shown a net repulsion effect for most nominally noninteractive systems. The picoline/phenol system showed intense positive interaction due to acid–base bonding (which was confirmed by infrared spectra).

2. The McAllister method for predicting binary mixture viscosities has been shown to be effective for both interacting and noninteracting systems. The extensive data base requirements limit its use for most purposes. Ternary-mixture viscosity measurements for an equimolar mixture of toluene, tetralin, and 1-methylnaphthalene were accumulated as a function of temperature. An extension of the McAllister correlation is effective, though tedious, for predicting ternary viscosity data.

Glossary

A	Andrade coefficient, mPa·s (cP)
B	Andrade coefficient, K
C	Andrade coefficient, dimensionless

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K	viscometer calibration constants
L	viscometer tube length, m
P	pressure, Pa
R	tube radius, m
R^0	McAllister equation constant
t	time, s
T	temperature, K
V	mole volume, m^3/mol
V	volume, m^3
x	mole fraction
$\bar{z}$	average hydrostatic level, m

Greek Letters

Γ	Gunn-Yamada parameter
γ	shear force, g/(cm^2·s)
Δ	change in (e.g., ΔP = pressure change)
μ	viscosity, mPa·s
ν	kinematic viscosity, m^2/s
ρ	fluid density, kg/m^3
ω	acentric factor

Subscripts

c	critical point
C	calibration constant
E	excess viscosity property, kinetic energy constant
i, j	refers to components i, j
m	mixture
r	reduced
sc	scaling parameter
123	refers to ternary mixture
1, 2, 3	refers to pure components 1, 2, 3
21, 12 etc.	indicates binary mixture interaction

Superscripts

0	referring to an ideal mixture
0	at zero pressure
R	at the reference point
L	of mixture

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Liquid-Liquid Equilibrium for the Ternary System 1,3-Dioxolane-Ethyl Acetate-Ethylene Glycol at T = 291.15, 301.15, and 311.15 K

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Ternary liquid-liquid equilibrium data for the 1,3-dioxolane-ethyl acetate-ethylene glycol system are obtained at 291.15, 301.15, and 311.15 K and are correlated by the Bachman, Hand, Othmer-Tobias, and selectivity plots. We conclude that ethylene glycol can be used as a solvent for extracting ethyl acetate from its binary mixtures with 1,3-dioxolane, a separation not obtained by distillation since 1,3-dioxolane and ethyl acetate are a closely boiling pair.

Introduction

The wide use of ethylene glycol (G) in technology justifies the extensive study of its chemical properties, with particular regard to solubility. It is well-known that G is slightly soluble in hydrocarbons or similar compounds and in many esters, whereas alcohols, aldehydes, and ketones are good solvents for G (*1*). Reference *2* in the literature reports data on ternary mixtures of G with a good solvent and with a compound practically insoluble in G.

The aims of the present paper are the following:

1. To study the ternary mixtures of G with ethyl acetate (A) and 1,3-dioxolane (D) on account of the good solubility of D in the other two compounds and in their binary mixtures.

2. To find the experimental conditions that will allow the use of G as a solvent for extracting A from the binary mixtures with D: separation of these compounds via distillation indeed would be difficult since their boiling points are nearly the same (T = 351.15 K at 102 kPa and T = 350.21 K at 103.1 kPa for D and A, respectively) (*3*).

Experimental Section

Chemicals. 1,3-Dioxolane, Fluka product (analytical grade 99%), was purified by refluxing on sodium under inert gas flow

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