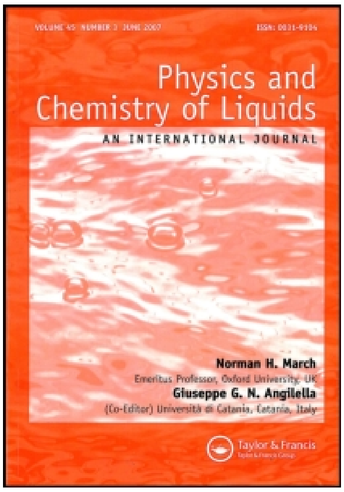

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Viscosities and Molar Volumes of Some Specially Selected Liquid Mixtures at 298.15 K

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Reliable viscosities and molar volumes are reported for some binary and ternary liquid mixtures containing carbon tetrachloride, tetrachloroethylene, benzene, toluene and pyridine. Similarities are observed in the shapes of the viscosity and vapor pressure curves for the binary systems. Systems exhibiting linear vapor pressure vs. mole fraction curves also exhibit, with some exceptions, linear viscosity vs. mole fraction curves. Maxima and minima found for some systems on the vapor pressure vs. mole fraction curves are often observed on the viscosity vs. mole fraction curves. This is especially true for systems containing species close in viscosity values. The viscosity vs. mole fraction data for the binary systems are well correlated with a modified Katti–Heric equation. One ternary constant, in addition to the respective binary system constants, predicts the viscosities of ternary systems well.

KEY WORDS: Solution, viscosity, molar volume, correlation, carbon tetrachloride, tetrachloroethylene, benzene, pyridine, toluene.

INTRODUCTION

A lot of attention has been paid to the study of viscosities of pure liquids and liquid mixtures[1–8]. Some similarities have been found in the viscosity and vapor pressure behavior. The temperature dependence of viscosity is described reasonably well by a "Clausius–Clapeyron" type of equation, in spite of the fact that viscosity is a transport property, and, moreover, that viscosity decreases and vapor pressure increases with temperature. Viscosity vs. mole fraction curves often exhibit

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features similar to those observed for the vapor pressure vs. mole fraction curves. Attempts were made to define an ideal solution in terms of viscosities and to derive expressions that would accurately correlate the excess viscosity with the mole fraction of binary and ternary solutions.

In the present study, we further investigate this problem. For our treatment we have chosen the following relatively simple systems:

1) Carbon tetrachloride (1) + Tetrachloroethylene (2)
2) Carbon tetrachloride (1) + Benzene (2)
3) Benzene (1) + Tetrachloroethylene (2)
4) Carbon tetrachloride (1) + Pyridine (2)
5) Tetrachloroethylene (1) + Pyridine (2)
6) Benzene (1) + Toluene (2)
7) $CCl_4(1) + C_2Cl_4(2) + C_5H_5N(3)$
8) $C_6H_6(1) + CCl_4(2) + C_2Cl_4(3)$

EXPERIMENTAL

Fisher and Aldrich analytical grade chemicals were used in the investigation. The quality of the chemicals was tested by gas liquid chromatography and by density and boiling point measurements. If needed, further purification was performed by distillation in a 60-plate column until no trace impurities were detected by gas liquid chromatography and the physical properties were in agreement with those given in the literature[9,10]. The pyridine has shown small, but definite, deviation in its physical properties with time. For this reason, the pyridine was freshly distilled prior to each measurement.

The density of the purified chemicals and their binary and ternary mixtures were measured pycnometrically at 298.15 K. A pycnometer of about 25 cm^3, calibrated with deionized water which was twice distilled, was employed in the measurement. The air dissolved in the water was expelled by boiling prior to the calibration. Buoyancy corrections were applied in all the weighings. Special precaution was taken to prevent the evaporation of the sample during the measurement. The pycnometer was placed in a thermostated water bath for approximately one hour. The temperature of the water bath was monitored with an NBS certified mercury in glass thermometer. The accuracy of the temperature reading is estimated to be better than ±0.01°C.

Table 1 The CCl_4 (1) + C_6H_6(2) system at 298.15 K

mole fraction x_1	molar volume V	excess volume V^E	viscosity η_{exp}	η_{calc}	st. dev. σ
	$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}$	cp		
0.0000	89.442	0.000	0.6000	0.6000	±0.0003
0.0951	90.172	0.000	0.6268	0.6267	
0.1690	90.741	0.002	0.6474	0.6477	
0.2559	91.442	0.016	0.6726	0.6727	
0.3734	92.321	0.014	0.7073	0.7072	
0.4917	93.226	0.011	0.7429	0.7427	
0.5951	94.029	0.021	0.7742	0.7741	
0.6135	94.166	0.017	0.7803	0.7799	
0.7561	95.255	0.011	0.8236	0.8243	
0.9264	96.555	0.005	0.8783	0.8783	
1.0000	97.115	0.000	0.9019	0.9019	

Considering all the uncertainties in the measurement, we estimate the error in density to be about ±5 × 10^{-5} g/cm^3. The density values listed in Tables 1 through 6 are averages of at least two measurements. The viscosities were measured with an Ostwald-Ubbelohde viscosimeter, made from pyrex glass in our glassblowing shop. More than usual attention was paid in mounting the viscosimeter in the thermostated bath (the one described above) to ensure that the capillary was vertical.

Table 2 The CCl_4 (1) + C_2Cl_4(2) system at 298.15 K

mole fraction x_1	molar volume V	excess volume V^E	viscosity η_{exp}	η_{calc}	st. dev. σ
	$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}$	cp		
0.0000	102.725	0.000	0.8486	0.8426	±0.0008
0.0973	102.185	0.006	0.8311	0.8311	
0.1594	101.837	0.006	0.8241	0.8249	
0.2440	101.362	0.006	0.8182	0.8182	
0.3103	100.990	0.006	0.8153	0.8145	
0.4139	100.409	0.006	0.8130	0.8118	
0.4636	100.130	0.006	0.8122	0.8121	
0.5633	99.570	0.005	0.8140	0.8161	
0.6300	99.196	0.005	0.8216	0.8215	
0.6339	99.174	0.005	0.8211	0.8219	
0.7582	98.477	0.006	0.8392	0.8389	
0.8009	98.237	0.005	0.8470	0.8469	
0.8067	98.205	0.006	0.8482	0.8481	
0.9135	97.605	0.005	0.8744	0.8742	
1.0000	97.115	0.000	0.9019	0.9019	

Table 3 The $C_6H_6(1) + C_2Cl_4(2)$ system at 298.15 K

mole fraction x_1	molar volume V	excess volume V^E	viscosity η_{exp}	η_{calc}	st. dev. σ
	$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}$	cp		
0.0000	102.725	0.000	0.8426	0.8426	±0.0003
0.0876	101.675	0.114	0.8015	0.8016	
0.1609	100.772	0.184	0.7710	0.7708	
0.2500	99.672	0.268	0.7371	0.7371	
0.3555	98.326	0.323	0.7018	0.7022	
0.4520	97.085	0.364	0.6743	0.6744	
0.6216	94.830	0.362	0.6351	0.6354	
0.6602	94.306	0.350	0.6286	0.6283	
0.7080	93.653	0.332	0.6209	0.6205	
0.7810	92.629	0.278	0.6115	0.6109	
0.8752	91.287	0.187	0.6029	0.6026	
0.9037	90.877	0.156	0.6011	0.6010	
1.0000	89.442	0.000	0.6000	0.6000	

The flow times, measured with an electric timer (Precision Scientific Company) were reproducible to ±0.1 second. Because of the relatively high fluid velocities, kinetic energy corrections were employed in the calculations of viscosities. We estimate that the overall error in the viscosity measurements is about $\pm 7 \times 10^{-4}$ cp. The values reported in Tables 1 through 6 represent averages of three measurements.

Table 4 The $CCl_4\ (1) + C_5H_5N$ system at 298.15 K

mole fraction x_1	molar volume V	excess volume V^E	viscosity η_{exp}	η_{calc}	st. dev. σ
	$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}$	cp		
0.0000	80.900	0.000	0.8890	0.8890	±0.0007
0.0900	82.173	−0.186	0.9206	0.9213	
0.1492	83.029	−0.290	0.9404	0.9397	
0.2381	84.345	−0.416	0.9623	0.9619	
0.2930	85.195	−0.456	0.9729	0.9719	
0.3700	86.391	−0.509	0.9819	0.9813	
0.4337	87.413	−0.519	0.9847	0.9846	
0.4561	87.782	−0.514	0.9841	0.9848	
0.4972	88.456	−0.506	0.9842	0.9841	
0.6006	90.203	−0.436	0.9751	0.9758	
0.7380	92.581	−0.286	0.9538	0.9539	
0.7863	93.427	−0.223	0.9430	0.9443	
0.8636	94.779	−0.124	0.9286	0.9282	
0.9447	96.176	−0.042	0.9120	0.9118	
1.0000	97.115	0.000	0.9019	0.9019	

Table 5 The C_2Cl_4 (1) + C_5H_5N (2) system at 298.15 K

mole fraction x_1	molar volume V	excess volume V^E	viscosity η_{exp}	η_{calc}	st. dev. σ
	$cm^3 mol^{-1}$	$cm^3 mol^{-1}$	cp		
0.0000	80.892	0.000	0.8891	0.8891	±0.0009
0.0296	81.533	−0.005	0.8879	0.8875	
0.1254	83.648	0.018	0.8794	0.8807	
0.1862	84.988	0.031	0.8750	0.8755	
0.2246	85.830	0.034	0.8719	0.8721	
0.2887	87.238	0.043	0.8657	0.8661	
0.4448	90.701	0.098	0.8496	0.8508	
0.5638	93.333	0.132	0.8411	0.8404	
0.6271	94.732	0.149	0.8370	0.8359	
0.7214	96.812	0.170	0.8324	0.8313	
0.8420	99.435	0.160	0.8315	0.8306	
0.9127	100.936	0.117	0.8331	0.8338	
0.9559	101.832	0.070	0.8373	0.8374	
1.0000	102.725	0.000	0.8426	0.8426	

RESULTS AND DISCUSSION

The molar volumes of the samples were evaluated from the formula

$$V = \sum_{i=1}^{n} (x_i M_i)/\rho \qquad (1)$$

where x_i and M_i are the mole fractions and molar masses of compo-

Table 6 The C_6H_6 (1) + C_7H_8(2) system at 298.15 K

mole fraction x_1	molar volume V	excess volume V^E	viscosity η_{exp}	η_{calc}	st. dev. σ
	$cm^3 mol^{-1}$	$cm^3 mol^{-1}$	cp		
0.0000	106.850	0.000	0.5530	0.5530	±0.0001
0.1153	104.923	0.036	0.5560	0.5559	
0.2022	103.401	0.031	0.5584	0.5585	
0.2965	101.785	0.061	0.5613	0.5613	
0.4076	99.852	0.068	0.5651	0.6552	
0.5405	97.549	0.085	0.5703	0.5705	
0.7237	94.319	0.053	0.5802	0.5800	
0.8593	91.948	0.050	0.5888	0.5887	
0.9637	90.078	0.002	0.5968	0.5969	
1.0000	89.442	0.000	0.6000	0.6000	

nents i and ρ is the measured density of the solution. From the molar volumes, we evaluated the excess volumes, V^E, for each solutions

$$V^E = V - \sum_{i=1}^{n} x_i V_i \tag{2}$$

The molar volumes and the excess volumes are summarized in Tables 1 through 6.

The viscosities of the samples were obtained from a modified Poiseuille equation[11, 12]

$$\eta/\rho = d\tau - E/\tau^2 \tag{3}$$

where η is the viscosity, ρ the density, τ the flow time and d and E are constants (see Table 7). The value of the constant d is practically the same for all systems; it depends only on the design and structure of the viscosimeter. The constant E depends also on the nature of the solution. E/τ^2 is the kinetic energy correction term. The Poiseuille equation assumes that all the friction in the viscosimeter is caused by the liquid passing through the capillary (laminar flow). This, however, is not the case of liquids with high flow velocities and in such cases viscosity corrections are required. The viscosities listed in Tables 1 through 6 are those obtained from Eq. (3).

The viscosity vs. mole fraction data for the 6 systems are summarized in Tables 1 through 6 and plotted in Figure 1. As is seen from the figure, the curves for the $CCl_4(1) + C_6H_6(2)$ and $C_6H_6(1) + C_7H_8(2)$ systems exhibit only minor deviation from linearity. For all practical purposes the viscosities of these two systems can be considered to be additive: $\eta_s = x_1\eta_1 + x_2\eta_2$. The V^E and G^E values of these systems are relatively small and therefore from a thermodynamic point of view these systems are practically ideal. (The $CCl_4(1) + C_6H_6(2)$ system is often treated as a regular solution.) Do these facts justify the conclusion that all systems obeying the equation (ideal) $\mu_i = \mu_i^0 + RT \ln x_i$ will follow the additivity rule for viscosities? The answer to this question is obvious from the $CCl_4(1) + C_2Cl_4(2)$ system. This system exhibit only minor deviations from ideality[12] and yet its viscosity vs. mole fraction curve goes through a minimum. Notice that the pure constituents of this system have very close viscosity values. Such systems often exhibit a minimum or a maximum on the viscosity vs. mole fraction curves. Similar behavior is observed for the nonideal $CCl_4(1) + C_5H_5N(2)$ and $C_2Cl_4(1) + C_5H_5N(2)$ systems[13, 14] (see Figure 1). Other systems exhibiting this kind of behavior are available in the literature[5, 15]. The

Table 7 Summary of constants for all systems

System	Eq. (3)		Eq. (4)		Eq. (5)	
	d	E	a_{ij}	b_{ij}	c_{ij}	A_{123}
$CCl_4 + C_6H_6$	0.003720	156.7	0.05551	−0.00145	0.002467	
$CCl_4 + C_2Cl_4$	0.003805	471.2	−0.2770	−0.05429	−0.006581	
$C_6H_6 + C_2Cl_4$	0.003739	277.3	−0.2604	−0.06026	−0.02686	
$CCl_4 + C_5H_5N$	0.003734	207.9	0.3711	−0.09885	−0.06321	
$C_2Cl_4 + C_5H_5N$	0.003738	274.5	−0.05936	−0.09814	−0.01385	
$C_6H_6 + C_7H_8$	0.003654	−268.2	−0.03072	−0.01563	0.001089	
$C_6H_6 + CCl_4 + C_2Cl_4$	0.003755*	301.8*	—	—	—	−0.07029
$CCl_4 + C_2Cl_4 + C_5H_5N$	0.003759*	317.9*	—	—	—	−0.3177

* average values

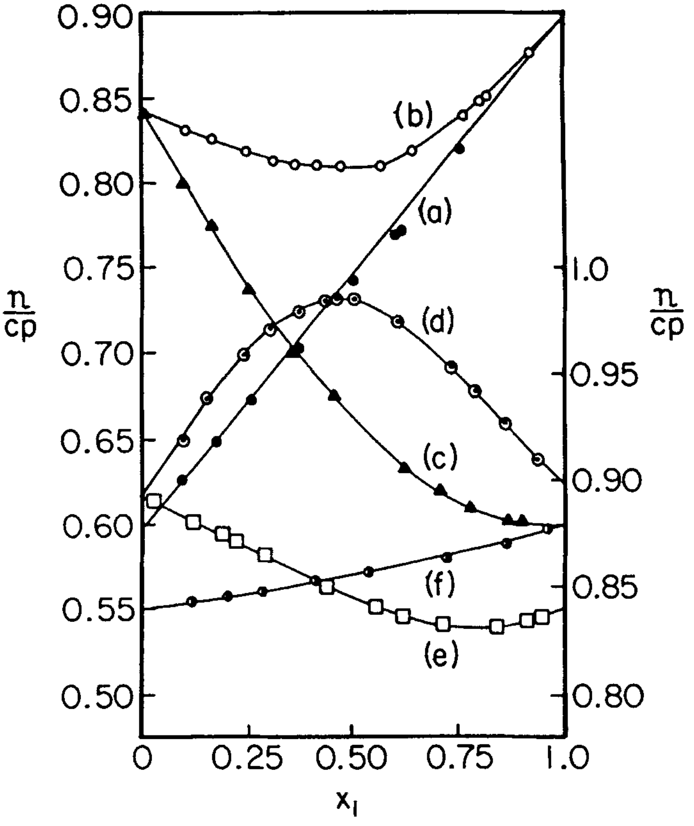

Figure 1 The viscosity of the various binary solutions as a function of mole fraction. (a) The $CCl_4(1) + C_6H_6(2)$ system. (b) The $CCl_4(1) + C_2Cl_4(2)$ system. (c) The $C_6H_6(1) + C_2Cl_4(2)$ system. (d) The $CCl_4(1) + C_5H_5N(2)$ system (scale on the right). (e) The $C_2Cl_4(1) + C_5H_5N(2)$ system (scale on the right). (f) The $C_6H_6(1) + C_7H_8(2)$ system.

nonideal $C_6H_6(1) + C_2Cl_4(2)$ system exhibits a zero tangent in the limit of $x_1 \to 1$. It is well known that binary solution containing species of close vapor pressures or boiling points often form azeotropes with maximum or minimum boiling points.

There are some similarities in the viscosities and vapor pressures of binary solutions. These similarities do not come as a surprise. After all, intermolecular forces dominate the viscosity as well as the vapor pressure behavior of solutions. In spite of this, it is necessary to realize that a solution obeying the ideal requirement, $\mu_i = \mu_i^0 + RT \ln x_i$, will not necessarily obey the additivity rule for viscosities.

For the correlation of the viscosity vs. mole fraction data of the

Table 8 Ternary systems

$CCl_4(1) + C_2Cl_4(2) + C_5H_5N(3)$

mole fractions		molar volume V	viscosity		
x_1	x_2	$cm^3\ mol^{-1}$	η_{exp}	η[Eq.(5)]	$\eta(A_{123} = 0)$
			cp		
0.3240	0.3590	93.931	0.8611*	0.8611	0.8712
0.5423	0.2822	95.789	0.8579	0.8582	0.8656
0.4585	0.1518	91.386	0.9164	0.9165	0.9244
$C_6H_6(1) + CCl_4(2) + C_2Cl_4(3)$					
0.5733	0.2814	93.708	0.6845	0.6847	0.6858
0.5340	0.2505	94.447	0.6824*	0.6824	0.6838
0.5532	0.0782	93.683	0.6673	0.6674	0.6682
0.2820	0.4721	96.493	0.7513	0.7523	0.7540

* These values were used for evaluating A_{123}

binary systems, we have employed an extended form of the Katti-Heric equation[16]

$$\ln[\eta_s V_s] = x_1 \ln[\eta_1 V_1] + x_2 \ln[\eta_2 V_2] + x_1 x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2] \qquad (4)$$

where a, b and c are constants. Their values for the various binary mixtures are given in Table 7. To correlate the data within the limits of experimental error only the $CCl_4(1) + C_5H_5N(2)$ requires three parameters. The $CCl_4(1) + C_2Cl_4(2)$, $C_6H_6(1) + C_2Cl_4(2)$ and the $C_2Cl_4(1) + C_5H_5N(2)$ systems require only two parameters and the $CCl_4(1) + C_6H_6(2)$ and $C_6H_6(1) + C_7H_8(2)$ require only one parameter.

For the two ternary systems we have used the equation

$$\begin{aligned}\ln[\eta_s V_s] = {} & x_1 \ln[\eta_1 V_1] + x_2 \ln[\eta_2 V_2] + x_3 \ln[\eta_3 V_3] \\ & + x_1 x_2[a_{12} + b_{12}(x_1 - x_2) + c_{12}(x_1 - x_2)^2] \\ & + x_1 x_3[a_{13} + b_{13}(x_1 - x_3) + c_{13}(x_1 - x_3)^2] \\ & + x_2 x_3[a_{23} + b_{23}(x_2 - x_3) + c_{23}(x_2 - x_3)^2] \\ & + x_1 x_2 x_3 A_{123} \end{aligned} \qquad (5)$$

where the subscripts are used to indicate the various components. The a_{ij}, b_{ij} and c_{ij} constants are those for the different binary systems. The constant A_{123} is a ternary constant which is determined from one ternary viscosity measurement. The constants for the two ternary systems are listed in Table 7. As can be seen from this table, the calculated values of the ternary viscosities compare quite favorably with the experimental values. The $C_6H_6(1) + CCl_4(2) + C_2Cl_4(3)$ system is correlated well even by using binary data only ($A_{123} = 0$). The similarities in the viscosity and vapor pressure behavior are again obvious from Eqs. (4) and (5). Expressions of this kind are used to correlate vapor pressure data, or better, excess Gibbs free energy data[17].

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