Density and Viscosity of Ketones with Toluene at Different Temperatures and at Atmospheric Pressure

Krishnamurthy Rajagopal[†] and Subramonian Chenthilnath*[,‡]

Department of Physics, Government College of Engineering, Tirunelveli 627007, Tamilnadu, India, and Department of Physics, Satyam College of Engineering and Technology, Satyam Nagar, Aralvaimozhy, Nagercoil 629301, Tamilnadu, India

Densities and viscosities of binary mixtures of toluene with acetone, ethyl methyl ketone, and acetophenone including those of pure liquids are measured over the entire composition range at temperatures (298.15, 303.15, and 308.15) K, respectively, at atmospheric pressure. From these experimental data, the values of excess molar volume V_m^E and the deviations in viscosity $\Delta\eta$ are calculated and fitted to the Redlich−Kister polynomial equation. The variation of these properties shows strong interaction between the molecules of the mixtures.

Introduction

The present study is a continuation of our earlier studies[1,2] on understanding the thermodynamic properties of binary mixtures whose components have relevant industrial applications. A detailed search in the literature shows that binary mixtures of liquids belonging to the aliphatic and aromatic ketones (acetone, ethyl methyl ketone, and acetophenone) with toluene have not been reported using volumetric and viscometric data at various temperatures. In the present study, the data on density and viscosity of toluene + acetone/ethyl methyl ketone and acetophenone binary mixtures are reported at different temperatures and at atmospheric pressure. The excess molar volume V_m^E and the deviations in viscosity $\Delta\eta$ are determined and related to molecular interaction between unlike molecules.

Experimental Methods

Analytical reagent grade ketones (s.d. Fine Chemicals) and toluene (Ranbaxy) were distilled prior to use by standard procedures,[3,4] and only the middle fractions were used in the experiment. All of the chemicals were stored over 0.4 nm molecular sieves to remove water content, if any, and degassed just before use. The mixtures were prepared by mass and were kept in special airtight stopper bottles to avoid evaporation. Mass measurements were made using a single pan electronic balance (AND, Japan HR series 300) with a precision of ± 0.1 mg.

Densities of the pure liquids and their binary mixtures were measured by using a single capillary pycnometer (Borosil glass) having a bulb capacity of $8\cdot10^{-3}$ dm^3 having a graduated stem with $5\cdot10^{-7}$ dm^3 division.[5] The capillary with graduated stem marks has a uniform bore and could be closed by a well-fitted glass cap. The marks on the capillary were calibrated with triple-distilled water. The pycnometer was kept inside a thermostatic water bath (uncertainty = ± 0.01 K) for about 30 min to attain thermal equilibrium conditions. The reproducibility in the density measurements were ± 0.1 kg·m^{-3}. The viscosity of the pure liquids and binary mixture was measured by means of a suspended level Ubbelohde viscometer with a flow time of 174 s for distilled water at 308.15 K. As the flow time was greater than 100 s, the kinetic energy corrections are not necessary.[6] The time of flow was measured with an electronic stopwatch capable of recording ± 0.01 s. An average of three to four sets of flow times for each mixture was taken for the purpose of calculation of the viscosity. The overall experimental reproducibility was estimated to be within ± $1.9\cdot10^{-3}$ mPa·s.[5] The Ubbelohde viscometer filled with test liquids and mixtures was allowed to stand for about 30 min in a thermostatic water bath (uncertainty = ± 0.01 K) so as to minimize thermal fluctuations.

Table 1. Comparison of Experimental Density, ρ, and Viscosity, η, Values of Pure Liquids with Literature Values

	T	ρ/(10^3 kg·m^{-3})		η/(mPa·s)	
liquid	K	exptl	lit.	exptl	lit.
acetone	298.15	0.7843	0.78440[4]	0.3027	0.3029[4]
	303.15	0.7790	0.78033[4]	0.2918	0.2954[4]
	308.15	0.7735	0.7739[7]	0.2809	0.280[7]
ethyl methyl ketone	298.15	0.7982	0.7997[4]	0.3856	0.378[4]
	303.15	0.7947	0.7948[4]	0.3653	0.366[4]
	308.15	0.7885	0.7888[8]	0.3440	0.3441[8]
acetophenone	298.15	1.0224	1.02382[4]	1.6788	1.642[4]
	303.15	1.0179		1.5328	1.511[4]
	308.15	1.0135		1.4073	
toluene	298.15	0.8609	0.86219[4]	0.5635	0.5525[4]
	303.15	0.8560	0.85754[4]	0.5344	0.5187[9]
	308.15	0.8516	0.8574[10]	0.5091	0.4928[4]

The experimentally measured density and viscosity values of pure liquids have been compared with literature values in Table 1. A good comparison between the experimental values and the reported values show the validity of our experimental measurements. The uncertainty associated with the experimentally measured density and viscosity is given in Table 2.

Theory

The excess molar volume V_m^E and deviations in viscosity $\Delta\eta$ are calculated using the general relation

$$Y^E = Y - [x_1Y_1 + x_2Y_2] \quad (1)$$

where Y represents V_m or η of the mixture, x is the mole fraction, and subscripts 1 and 2 refer to solvent and solute,

* Corresponding author: E-mail: chenthilnaths@rediffmail.com. Tel.: 91-9443418697. Fax: 91-4652-227621.
[†] Government College of Engineering. E-mail: krpal25@yahoo.com.
[‡] Satyam College of Engineering and Technology.

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Table 2. Density, ρ, and Viscosity, η, Values for the Binary Mixtures of Toluene (1) + Ketones (2) at (298.15, 303.15, and 308.15) K

mole fraction	T/K = 298.15		T/K = 303.15		T/K = 308.15	
x_1	ρ/(10^3 kg·m^{-3})	η/(mPa·s)	ρ/(10^3 kg·m^{-3})	η/(mPa·s)	ρ/(10^3 kg·m^{-3})	η/(mPa·s)
			Toluene (1) + Acetone (2)			
0.0000	0.7843	0.3027	0.7790	0.2918	0.7735	0.2809
0.0702	0.7925	0.3418	0.7876	0.3218	0.7828	0.3021
0.1468	0.8013	0.3759	0.7967	0.3527	0.7922	0.3267
0.2269	0.8100	0.4076	0.8057	0.3810	0.8013	0.3517
0.3135	0.8187	0.4383	0.8144	0.4098	0.8101	0.3785
0.4051	0.8270	0.4662	0.8227	0.4358	0.8183	0.4040
0.5072	0.8344	0.4893	0.8300	0.4553	0.8259	0.4250
0.6160	0.8412	0.5092	0.8369	0.4750	0.8329	0.4443
0.7355	0.8479	0.5293	0.8436	0.4947	0.8396	0.4638
0.8629	0.8543	0.5462	0.8498	0.5144	0.8458	0.4848
1.0000	0.8609	0.5635	0.8560	0.5344	0.8516	0.5091
Uncertainty	0.0023	0.0078	0.0023	0.0073	0.0024	0.0069
			Toluene (1) + Ethyl Methyl Ketone (2)			
0.0000	0.7982	0.3856	0.7947	0.3653	0.7885	0.3440
0.0856	0.8053	0.4052	0.8020	0.3822	0.7963	0.3593
0.1724	0.8123	0.4244	0.8091	0.3996	0.8038	0.3756
0.2624	0.8193	0.4439	0.8160	0.4176	0.8109	0.3922
0.3370	0.8248	0.4594	0.8214	0.4320	0.8165	0.4061
0.4330	0.8314	0.4781	0.8278	0.4494	0.8230	0.4230
0.5555	0.8388	0.4987	0.8350	0.4688	0.8304	0.4417
0.6600	0.8446	0.5145	0.8407	0.4844	0.8362	0.4575
0.7690	0.8503	0.5308	0.8462	0.5002	0.8419	0.4738
0.8831	0.8558	0.5472	0.8514	0.5168	0.8472	0.4909
1.0000	0.8609	0.5635	0.8560	0.5344	0.8516	0.5091
Uncertainty	0.0019	0.0054	0.0019	0.0051	0.0019	0.0050
			Toluene (1) + Acetophenone (2)			
0.0000	1.0224	1.6788	1.0179	1.5328	1.0135	1.4073
0.1093	1.0068	1.5606	1.0027	1.4257	0.9987	1.3102
0.2145	0.9917	1.4457	0.9874	1.3225	0.9835	1.2170
0.3206	0.9759	1.3292	0.9717	1.2180	0.9678	1.1228
0.4281	0.9595	1.2105	0.9551	1.1121	0.9511	1.0272
0.5229	0.9445	1.1055	0.9400	1.0180	0.9360	0.9425
0.6213	0.9282	0.9949	0.9237	0.9188	0.9196	0.8535
0.7157	0.9121	0.8879	0.9076	0.8233	0.9035	0.7678
0.8392	0.8904	0.7472	0.8859	0.6978	0.8818	0.6554
0.9074	0.8780	0.6694	0.8735	0.6286	0.8695	0.5933
1.0000	0.8609	0.5635	0.8560	0.5344	0.8516	0.5091
Uncertainty	0.0049	0.0338	0.0049	0.0303	0.0049	0.0272

respectively. The values of V_m are calculated using standard relation

$$V_m = M_{eff}/\rho \quad (2)$$

where $[M_{eff} = (x_1M_1 + x_2M_2)]$, M_1 and M_2 are the molecular weights of pure components, and ρ is the density of the mixture.

The excess functions V_m^E and $\Delta\eta$ are fitted to a Redlich−Kister type polynomial equation,[11]

$$Y^E = x_1(1 - x_1)\sum_{i=1}^{5} A_i(1 - 2x_1)^{i-1} \quad (3)$$

where Y^E is V_m^E and $\Delta\eta$. The values of A_i are evaluated by using least-squares method with all points weighed equally, and the corresponding standard deviations $\sigma(Y^E)$ are calculated by using the relation

$$\sigma(Y^E) = \sum((Y_{cal}^E - Y_{exp}^E)^2/(n - j))^{1/2} \quad (4)$$

where n is the number of experimental data points and j is the number of A_i coefficients considered. The values of Y_{cal}^E were obtained from eq 3 by using the best fit values of A_i coefficients. The uncertainties for the V_m^E values for the temperatures T = (298.15, 303.15, and 308.15) K are as follows: for the toluene + acetone binary mixture, 0.0166, 0.0196, and 0.0221; for the toluene + ethyl methyl ketone binary mixture, 0.0132, 0.0155, and 0.0180; and for the toluene + acetophenone binary mixture, 0.0109, 0.0120, and 0.0136, respectively.

Results

The experimental values of density (ρ) and viscosity (η) of the binary mixtures of toluene with acetone/ethyl methyl ketone and acetophenone with toluene as a common component over the whole composition range expressed in mole fraction x_1 of toluene ($0 \le x_1 \le 1$) at different temperatures are listed in Table 2. The values of coefficients A_0, A_1, A_2, A_3, and A_4 of V_m^E and $\Delta\eta$ along with the standard deviation $\sigma(Y^E)$ are listed in Table 3. The variations of V_m^E and $\Delta\eta$ with the composition of the mixtures along with smoothed values using eq 3 at 298.15 K are presented graphically in Figures 1 and 2.

Discussion

The results shown in Figures 1 and 2 indicate that V_m^E values are negative, while $\Delta\eta$ are positive over the entire mole fraction range and at all temperatures reported. Generally, dispersive forces and improper interstitial accommodation of molecules of a binary mixture will be reflected in positive V_m^E and negative $\Delta\eta$ values. However, strong interactions taking place between unlike molecules through charge transfer forces, the formation of new hydrogen bonds, and proper interstitial accommodation will yield negative V_m^E and positive $\Delta\eta$ values.

Table 3. Coefficients of A_i of Equation 3 and Standard Deviations $\sigma(Y^E)$ for the Binary Mixtures at Different Temperatures

T/K	A_0	A_1	A_2	A_3	A_4	σ
Toluene (1) + Acetone (2)						
			$V_m^E/(10^{-6}\ m^3 \cdot mol^{-1})$			
298.15	−1.9224	−0.9872	2.3450	1.4860	−1.6635	0.0082
303.15	−2.2686	−1.0140	1.6468	1.4092	−0.9604	0.0101
308.15	−2.6057	−0.8674	1.0659	0.9284	−0.9258	0.0034
			$\Delta\eta$/(mPa·s)			
298.15	0.2216	0.1046	−0.0939	−0.0294	0.1765	0.0003
303.15	0.1684	0.1056	−0.0729	−0.0859	0.0943	0.0009
308.15	0.1171	0.0684	−0.1316	−0.0844	0.1036	0.0005
Toluene (1) + Ethyl Methyl Ketone (2)						
			$V_m^E/(10^{-6}\ m^3 \cdot mol^{-1})$			
298.15	−1.5965	−0.3040	0.9209	0.6892	−0.8566	0.0028
303.15	−1.8597	−0.3201	0.3294	0.6563	−0.4370	0.0038
308.15	−2.1559	−0.4652	0.0428	0.8964	−0.5529	0.0046
			$\Delta\eta$/(mPa·s)			
298.15	0.0610	0.0192	−0.0471	−0.0188	0.0477	0.0000
303.15	0.0423	0.0182	−0.0412	−0.0184	0.0258	0.0000
308.15	0.0281	0.0173	−0.0405	−0.0215	0.0285	0.0002
Toluene (1) + Acetophenone (2)						
			$V_m^E/(10^{-6}\ m^3 \cdot mol^{-1})$			
298.15	−1.2979	0.2301	0.8311	0.0876	−0.5183	0.0034
303.15	−1.4402	0.1594	0.3688	0.1868	−0.8120	0.0032
308.15	−1.6536	−0.0388	0.1964	0.5702	−1.4043	0.0056
			$\Delta\eta$/(mPa·s)			
298.15	0.0389	−0.0014	−0.0189	0.0094	0.0196	0.0000
303.15	0.0290	−0.0022	−0.0371	0.0035	0.0382	0.0001
308.15	0.0191	−0.0011	−0.0229	0.0001	0.0188	0.0000

The volume of the liquid mixture depends upon the structural arrangement as well as intermolecular interactions. An increase in the strength of the heteromolecular forces manifests in a decrease in adiabatic compressibility and volume and, hence, the size of the cluster. Thus, the negative V_m^E values account for the strong interactions between the unlike molecules.[12] Further, Fort and Moore[13] used the positive deviation in viscosity values to account for the presence of strong interactions in binary mixtures. Thus, the excess molar volume and deviation in viscosity compliments the presence of strong interactions in the mixtures reported in this paper.

The possible strong interactions observed in the above mixtures may result because of the charge transfer complex formed between ketones and toluene molecules. It is well-known that ketones are electron acceptors. Toluene molecules exhibit a positive charge on the hydrogen atom because of the resonance structure phenomena which result from the possibility of the interaction between the σ and the π systems. Thus, in aliphatic ketone + toluene binary mixtures, there may be an interaction between the hydrogen atom of the toluene molecule and the oxygen atom of the carbonyl group of the ketones.[10]

In the toluene + acetophenone mixture similar charge transfer type interaction is also possible. The toluene molecule has an alternate π bond system which overlaps to form a π cloud of electrons located centrally above and below the ring, making it highly susceptible to interaction with electrophilic or electron

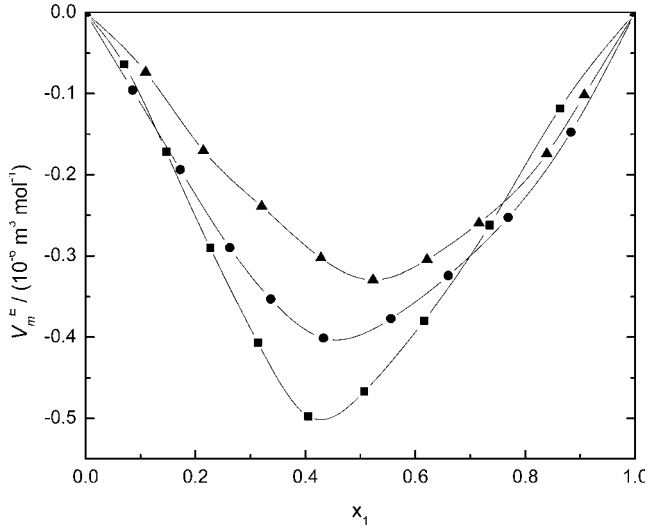

Figure 1. Plots of V_m^E against the mole fraction, x_1, of toluene for binary mixtures of toluene with ■, acetone; ●, ethyl methyl ketone; and ▲, acetophenone at 298.15 K.

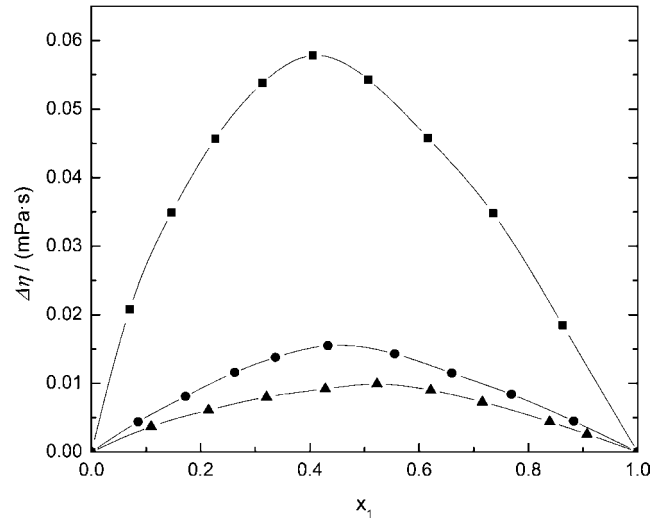

Figure 2. Plots of $\Delta\eta$ against the mole fraction, x_1, of toluene for binary mixtures of toluene with ■, acetone; ●, ethyl methyl ketone; and ▲, acetophenone at 298.15 K.

deficient solvents.[10] So, interaction is possible with the π-clouds of electron-rich toluene and electron-deficient acetophenone, which is a donor−acceptor type interaction.[10] Thus, in all of the studied binary mixtures, the electron donor−acceptor type of interaction is possible, and formation of some complex leads to the negative variations in V_m^E values and vice versa trends in $\Delta\eta$ values. The strength of interaction due to polarizability values and steric hindrance is very well-reflected in excess molar volume values (V_m^E), that is, acetone < ethyl methyl ketone < acetophenone.

Conclusion

In this paper, data on density and viscosity are reported for three binary mixtures, taking toluene as a common component with acetone, ethyl methyl ketone, and acetophenone as the other component, at three different temperatures.

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