Densities, Viscosities, and Refractive Indices of Some Alkyl Esters with 4-Chlorotoluene Systems at (293.15, 298.15, and 303.15) K

Maria M. Palaiologou

Laboratory of Physical Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis, Athens 157-71, Greece

Densities, viscosities, and refractive indices have been measured for 4-chlorotoluene + methyl acetate, +ethyl acetate, and +propyl acetate at (293.15, 298.15, and 303.15) K. The results are correlated by means of a Redlich−Kister type equation and discussed in terms of molecular interactions. Excess volumes have been derived.

Introduction

A survey of the literature showed that excess properties of binary mixtures of toluene with some alkyl esters have been measured under different conditions (Grolier et al., 1974; Iloukhani et al., 1984; Qin et al., 1992; Oswall and Rathnan, 1984; Oswall and Rathnam, 1987; Wanhoo et al., 1988).

However, no attempt has been made to measure excess properties of binary mixtures of 4-chlorotoluene with alkyl esters. Introduction of a Cl group into the toluene molecule may influence both the sign and magnitude of excess properties. As a continuation of previous work in our laboratory (Palaiologou and Molinou, 1995) we here report excess volumes V^E, deviations in viscosity from a mole fraction average, $\Delta\eta$, and deviations in refractive index from a volume fraction average, ΔR, for binary mixtures of 4-chlorotoluene + methyl acetate, +ethyl acetate, and +propyl acetate, at (293.15, 298.15, and 303.15) K.

Experimental Section

Materials. All the chemicals used were Merck. p.a. The stated purity was better than 99.5 mass % for alkyl esters, and they were used without further purification. The stated purity of 4-chlorotoluene was better than 98 mass %, and it was purified by the method described by Vogel (1978). It was washed successively with concentrated sulfuric acid, water, 10% sodium carbonate, and water. Finally, it was dried over calcium chloride and distilled. The purity was checked by comparing the density and refractive index of the pure compound with the values reported in the literature (TRC, Jan 1996). Mixtures were prepared by mass in ground glass flasks to avoid evaporation during the mixing process. A set of nine compositions were prepared for each system, and their mole fractions were known to ±0.0001. The measured properties of the pure components are listed in Table 1 together with literature values.

Measurements. Densities, ρ, of pure liquids and binary mixtures were measured with a digital Anton Paar DMA10 densimeter equipped with a thermostat, and the temperature was maintained constant within ±0.01 K. The accuracy of the density was ±0.0002 g·cm⁻³. Under these experimental conditions the V^E values have been estimated to ±0.004 cm³·mol⁻¹.

Viscosities were measured by means of Cannon Fenske viscometers (sizes 50 and 75 ASTM D445) supplied by the Cannon Instrument Co., State College, PA. Kinetic energy corrections were made according to the recommended

Table 1. Comparison of Experimental Densities (ρ), Viscosities (η), and Refractive Indices (n_D) of Pure Liquids with Literature Values at 293.15 K

compd	ρ/g·cm⁻³ exptl	ρ/g·cm⁻³ lit.	η/mPa·s exptl	η/mPa·s lit.	n_D exptl	n_D lit.
methyl acetate	0.9333	0.9342[a]	0.3864	0.3876[c]	1.3611	1.3614[a]
ethyl acetate	0.9005	0.9003[a] 0.90099[b]	0.4544	0.4477[c]	1.3725	1.3723[a]
propyl acetate	0.8878	0.8883[a] 0.8878[b]	0.5881	0.580[d]	1.3840	1.3846[a]
4-chlorotoluene	1.0694	1.0691[a]	0.8893	0.8913[d]	1.5210	1.5209[a]

[a] TRC, Jan 1996. [b] From qin et al., 1992. [c] Interpolated from TRC data, March 1996. [d] Interpolated from CRC data, 1995−96.

method (Cannon et al., 1960). The estimated error was ±0.005 mPa·s.

Refractive indices for the sodium D-line were measured with a thermostated Abbe refractometer (Carl-Zeiss Model A) with an accuracy of ±0.0005. In all measurements a thermostatically controlled bath (constant to 0.01 K) was used.

Results and Discussion

The experimental values of density, viscosity, and refractive index given in Table 2 were used to calculate the excess molar volume, V^E, as

$$V^E = V_m - \sum_{i=1}^{2} V_i x_i \qquad (1)$$

where V_i represents the molar volume and x_i the mole fraction of the ith component. The quantity V_m refers to the molar volume of the mixture which can be calculated from the mixture density, ρ_m, and the component molecular weights M_1 and M_2 as $V_m = (M_1 x_1 + M_2 x_2)/\rho_m$.

The V^E results were fitted to the Redlich−Kister equation

$$V^E/cm^3 \cdot mol^{-1} = x_1 x_2 \sum_{k=0}^{n} A_k (2x_1 - 1)^k \qquad (2)$$

where n is the number of parameters A_k. A nonlinear least squares method was used to estimate the parameters A_k. In each case, the optimum number of parameters was obtained through examination of the standard deviation according to the equation

$$\sigma_V^E = [\sum (V^E_{obsd} - V^E_{calcd})^2/(N - n)]^{1/2} \qquad (3)$$

Table 2. Experimental Densities (ρ), Viscosities (η), and Refractive Indices of the Binary Mixtures

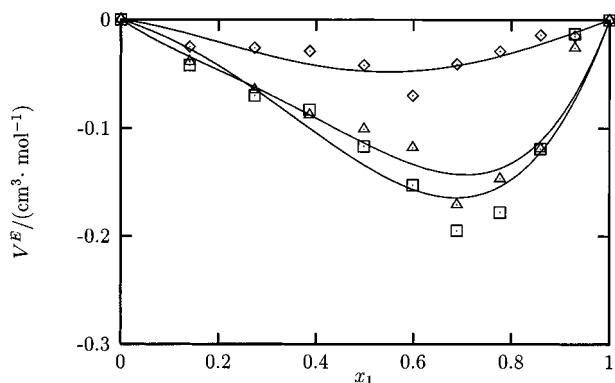| x_1	ρ/g·cm⁻³	η/mPa·s	n_D	x_1	ρ/g·cm⁻³	η/mPa·s	n_D
Methyl Acetate (1) + 4-Chlorotoluene (2)						
T = 293.15 K						
0.0000	1.0694	0.8893	1.5210	0.6890	0.9885	0.5305	1.4270
0.1404	1.0562	0.8139	1.5080	0.7771	0.9744	0.4887	1.4109
0.2737	1.0422	0.7448	1.4905	0.8597	0.9601	0.4490	1.3960
0.3871	1.0292	0.6857	1.4755	0.9295	0.9473	0.4181	1.3790
0.4985	1.0154	0.6266	1.4575	1.000	0.9333	0.3864	1.3611
0.5985	1.0021	0.5751	1.4436				
T = 298.15 K						
0.0000	1.0645	0.8348	1.5188	0.6890	0.9837	0.5039	1.4290
0.1404	1.0512	0.7655	1.5075	0.7771	0.9693	0.4650	1.4100
0.2737	1.0372	0.7014	1.4913	0.8597	0.9547	0.4282	1.3918
0.3871	1.0242	0.6474	1.4752	0.9295	0.9407	0.3974	1.3750
0.4985	1.0102	0.5907	1.4601	1.0000	0.9264	0.3704	1.3580
0.5985	0.9966	0.5431	1.4440				
T = 303.15 K						
0.0000	1.0595	0.7854	1.5160	0.6895	0.9777	0.4762	1.4315
0.1404	1.0460	0.7175	1.5018	0.7771	0.9632	0.4438	1.4120
0.2737	1.0318	0.6597	1.4865	0.8597	0.9481	0.4120	1.3917
0.3871	1.0185	0.6085	1.4725	0.9295	0.9338	0.3831	1.3730
0.4985	1.0045	0.5600	1.4580	1.0000	0.9195	0.3576	1.3560
0.5985	0.9909	0.5143	1.4430				
Ethyl Acetate (1) + 4-Chlorotoluene (2)						
T = 293.15 K						
0.0000	1.0694	0.8893	1.5210	0.6425	0.9703	0.6092	1.4337
0.1173	1.0537	0.8411	1.5080	0.7318	0.9541	0.5667	1.4190
0.2313	1.0373	0.7933	1.4940	0.8281	0.9356	0.5273	1.4060
0.3409	1.0209	0.7478	1.4805	0.9153	0.9183	0.4918	1.3880
0.4471	1.0040	0.7001	1.4640	1.0000	0.9005	0.4544	1.3725
0.5460	0.9874	0.6551	1.4490				
T = 298.15 K						
0.0000	1.0645	0.8348	1.5188	0.6425	0.9652	0.5738	1.4310
0.1173	1.0491	0.7911	1.5054	0.7318	0.9488	0.5358	1.4190
0.2313	1.0323	0.7453	1.4905	0.8281	0.9304	0.5005	1.4010
0.3409	1.0156	0.7018	1.4760	0.9153	0.9124	0.4628	1.3855
0.4471	0.9986	0.6564	1.4600	1.0000	0.8944	0.4297	1.3695
0.5460	0.9820	0.6148	1.4455				
T = 303.15 K						
0.0000	1.0595	0.7854	1.5160	0.6425	0.9596	0.5419	1.4310
0.1173	1.0438	0.7445	1.5025	0.7318	0.9430	0.5071	1.4140
0.2313	1.0266	0.7015	1.4885	0.8281	0.9243	0.4714	1.3980
0.3409	1.0099	0.6604	1.4748	0.9153	0.9063	0.4380	1.3833
0.4471	0.9929	0.6192	1.4580	1.0000	0.8881	0.4071	1.3670
0.5460	0.9763	0.5800	1.4442				
Propyl Acetate (1) + 4-Chlorotoluene (2)						
T = 293.15 K						
0.0000	1.0694	0.8893	1.5210	0.6084	0.9622	0.7255	1.4393
0.1018	1.0521	0.8693	1.5070	0.7065	0.9437	0.6924	1.4263
0.2029	1.0347	0.8432	1.4949	0.8045	0.9251	0.6620	1.4115
0.3052	1.0171	0.8175	1.4810	0.9035	0.9061	0.6242	1.3976
0.4088	0.9988	0.7890	1.4670	1.0000	0.8878	0.5881	1.3840
0.5143	0.9794	0.7550	1.4520				
T = 298.15 K						
0.0000	1.0645	0.8348	1.5188	0.6084	0.9573	0.6775	1.4376
0.1018	1.0471	0.8141	1.5050	0.7065	0.9391	0.6491	1.4245
0.2029	1.0299	0.7895	1.4924	0.8045	0.9209	0.6176	1.4090
0.3052	1.0115	0.7651	1.4780	0.9035	0.9011	0.5848	1.3960
0.4088	0.9929	0.7370	1.4633	1.0000	0.8821	0.5556	1.3820
0.5143	0.9739	0.7055	1.4516				
T = 303.15 K						
0.0000	1.0595	0.7854	1.5160	0.6065	0.9519	0.6351	1.4350
0.1037	1.0416	0.7624	1.5030	0.7066	0.9333	0.6063	1.4210
0.2044	1.0200	0.7402	1.4890	0.8044	0.9147	0.5779	1.4072
0.3034	1.0069	0.7160	1.4772	0.9025	0.8956	0.5494	1.3930
0.4075	0.9885	0.6879	1.4630	1.0000	0.8763	0.5181	1.3790
0.5071	0.9708	0.6635	1.4489				

where N is the number of measurements and n the number of parameters. The results of A_k and σ for V^E are presented in Table 3.

The viscosity deviations, $\Delta\eta$, are obtained by

$$\Delta\eta/\text{mPa·s} = \eta_m - \sum_{i=1}^{2} \eta_i x_i \qquad (4)$$

Table 3. Estimated Parameters of Excess Functions for the Mixtures

function	A_0	A_1	A_2	σ
Methyl Acetate (1) + 4-Chlorotoluene (2), T = 293.15 K			
V^E/cm³·mol⁻¹	−0.1897	−0.0516	0.0802	0.0009
$\Delta\eta$/mPa·s	−0.0470	−0.0227	−0.0005	<10⁻⁴
ΔR/cm³·mol⁻¹	−6.3662	1.3323	1.0152	0.0123
Methyl Acetate (1) + 4-Chlorotoluene (2), T = 298.15 K			
V^E/cm³·mol⁻¹	−0.4562	−0.4474	−0.2893	0.0032
$\Delta\eta$/mPa·s	−0.0454	−0.0251	−0.0021	<10⁻⁴
ΔR/cm³·mol⁻¹	−5.8033	0.6023	0.2056	0.0224
Methyl Acetate (1) + 4-Chlorotoluene (2), T = 303.15 K			
V^E/cm³·mol⁻¹	−0.5384	−0.5480	−0.1554	0.0060
$\Delta\eta$/mPa·s	−0.0533	−0.0093	−0.0018	<10⁻⁴
ΔR/cm³·mol⁻¹	−5.0321	1.4300	−2.8349	0.1059
Ethyl Acetate (1) + 4-Chlorotoluene (2), T = 293.15 K			
V^E/cm³·mol⁻¹	−0.9524	0.0679	−0.0774	0.0006
$\Delta\eta$/mPa·s	0.0139	−0.0400	−0.0139	<10⁻⁴
ΔR/cm³·mol⁻¹	−1.9685	−0.0545	0.9818	0.0206
Ethyl Acetate (1) + 4-Chlorotoluene (2), T = 298.15 K			
V^E/cm³·mol⁻¹	−1.0412	0.1206	−0.6597	0.0017
$\Delta\eta$/mPa·s	0.0065	−0.0326	0.0144	<10⁻⁴
ΔR/cm³·mol⁻¹	−2.0735	0.4027	0.6032	0.0121
Ethyl Acetate (1) + 4-Chlorotoluene (2), T = 303.15 K			
V^E/cm³·mol⁻¹	−1.0589	−0.3926	−0.5076	0.0034
$\Delta\eta$/mPa·s	0.0067	−0.0271	0.0096	<10⁻⁴
ΔR/cm³·mol⁻¹	1.7515	−0.0466	−0.0051	0.0162
Propyl Acetate (1) + 4-Chlorotoluene (2), T = 293.15 K			
V^E/cm³·mol⁻¹	−1.0756	0.1614	0.6941	0.0006
$\Delta\eta$/mPa·s	0.0851	−0.0143	0.0207	<10⁻⁴
ΔR/cm³·mol⁻¹	0.0825	−0.0155	−0.0159	0.0052
Propyl Acetate (1) + 4-Chlorotoluene (2), T = 298.15 K			
V^E/cm³·mol⁻¹	−1.0471	−0.6205	−0.7806	0.0070
$\Delta\eta$/mPa·s	0.0611	−0.0253	−0.0031	<10⁻⁴
ΔR/cm³·mol⁻¹	0.1418	0.4011	−0.2146	0.0107
Propyl Acetate (1) + 4-Chlorotoluene (2), T = 303.15 K			
V^E/cm³·mol⁻¹	−1.3436	−0.3546	0.3175	0.0027
$\Delta\eta$/mPa·s	0.0508	−0.0048	0.0060	<10⁻⁴
ΔR/cm³·mol⁻¹	0.2302	−0.1647	−0.0682	0.0039

where x_i, η_i, and η_m refer respectively to the mole fraction and viscosities of pure components and of the mixtures.

The parameters A_k and standard deviation, σ, for $\Delta\eta$ as obtained from equations similar to eqs 2 and 3 are listed in Table 3.

Deviations in refractive index, ΔR, were calculated from the Lorentz−Lorenz mixing rule (Lorentz, 1909) as

$$\Delta R/\text{cm}^3\cdot\text{mol}^{-1} = R_m - \sum_{i=1}^{2} R_i \Phi_i \qquad (5)$$

where R_i and R_m represent the pure component and mixture molar refractions, respectively, and $\Phi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i$ is the volume fraction of the ith component.

The molar refraction, R_i, was obtained using the Lorentz−Lorenz equation

$$R_i = \frac{n_D^2 - 1}{n_D^2 + 2} V_i \qquad (6)$$

where n_D is the refractive index for a pure liquid. Equation 6 can be rearranged for a binary mixture as

$$R_m = \frac{\eta_{D(m)}^2 - 1}{\eta_{D(m)}^2 + 2} V_m \qquad (7)$$

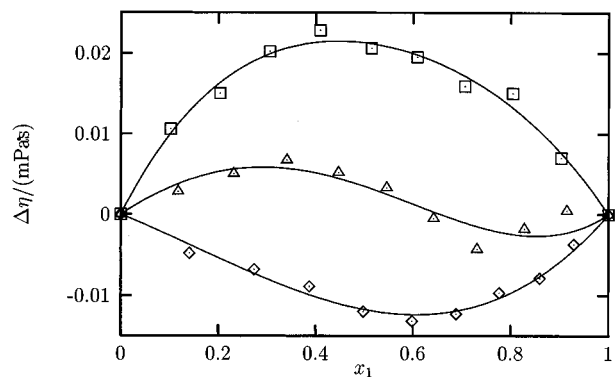where $\eta_{D(m)}$ is the refractive index of the mixture and R_m is the molar refraction of the mixture.

Figure 1. Excess molar volumes of methyl acetate (1) + 4-chlorotoluene (2) ($\diamond$), ethyl acetate (1) + 4-chlorotoluene (2) ($\triangle$), and propyl acetate (1) + 4-chlorotoluene (2) ($\square$) at 293.15 K.
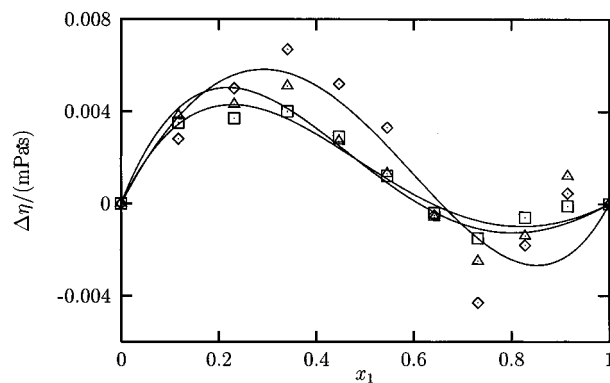

Figure 2. Effect of temperature on excess molar volume for the methyl acetate (1) + 4-chlorotoluene mixture at ($\diamond$) 293.15 K, ($\triangle$) 298.15 K, and ($\square$) 303.15 K.
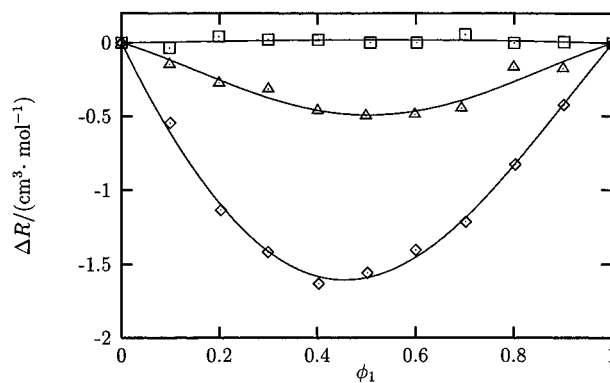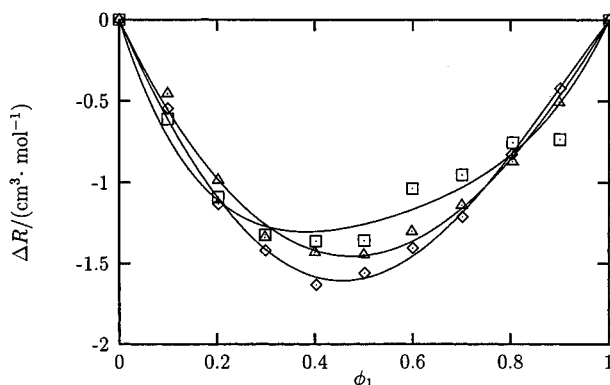

Figure 3. Deviations in viscosity of methyl acetate (1) + 4-chlorotoluene (2) ($\diamond$), ethyl acetate (1) + 4-chlorotoluene (2) ($\triangle$), and propyl acetate (1) + 4-chlorotoluene (2) ($\square$) at 293.15 K.

Figure 4. Effect of temperature on deviations in viscosity for the ethyl acetate + 4-chlorotoluene mixture at ($\diamond$) 293.15 K, ($\triangle$) 298.15 K, and ($\square$) 303.15 K.

Figure 5. Dependence of the deviations in molar refraction on volume fraction at 293.15 K of methyl acetate (1) + 4-chlorotoluene (2) ($\diamond$), ethyl acetate (1) + 4-chlorotoluene (2) ($\triangle$), and propyl acetate (1) + 4-chlorotoluene (2) ($\square$) at 293.15 K.

Figure 6. Effect of temperature on deviations in molar refraction of the methyl acetate (1) + 4-chlorotoluene (2) mixture at ($\diamond$) 293.15 K, ($\triangle$) 298.15 K, and ($\square$) 303.15 K.

The parameters A_k and standard deviation, σ, for ΔR as obtained from equations similar to eqs 2 and 3 are listed in Table 3.

Plots of excess molar volume at 293.15 K versus mole fraction for the three systems are shown in Figure 1. For all mixtures, the values of V^E are negative, suggesting specific interactions between alkyl esters and 4-chlorotoluene. The V^E results of the mixtures follow the sequence methyl < ethyl < propyl acetate, and the minima of the curves are at equimolar compositions for the ethyl acetate + 4-chlorotoluene and propyl acetate + 4-chlorotoluene systems. The interactions in these mixtures may be classified as dipole−dipole type forces resulting from the polarizability of ester molecules by the dipoles of 4-chlorotoluene molecules. On the other hand, a complex formation between free electrons of the carboxylic group of the ester and the aromatic ring might give rise to a negative contribution (Grolier et al., 1974). The observed values of

V^E in Figure 1 show similar types of interactions for the mixtures of ethyl acetate + and propyl acetate + 4-chlorotoluene. An explanation could be given by considering the dipole moments of the three esters which are 1.72 D for methyl acetate, 1.81 D for ethyl acetate, and 1.86 D for propyl acetate.

The effect of temperature on V^E is noteworthy. There is a systematic decrease in V^E with a rise in temperature for all mixtures, as shown in Figure 2.

Figure 3 indicates that the deviations in viscosity, $\Delta\eta$, follow the sequence methyl < ethyl < propyl acetate with negative values of $\Delta\eta$ for the mixture of methyl acetate + 4-chlorotoluene and positive values for the mixture propyl acetate + 4-chlorotoluene. However, the ethyl acetate + 4-chlorotoluene system shows a sign inversion around x_1 = 0.63.

Figure 4 shows the effect of temperature on $\Delta\eta$ for the ethyl acetate + 4-chlorotoluene system. The higher the temperature, $\Delta\eta$ is less positive and less negative. However, for systems methyl acetate + 4-chlorotoluene and propyl acetate + 4-chlorotoluene it was found that $\Delta\eta$ decreases with the increase of temperature over the entire scale of the mixtures composition.

The plots of ΔR vs volume fraction at 293.15 K are given in Figure 5. The ΔR values for the propyl acetate + 4-chlorotoluene system are very close to zero, while for the methyl + and ethyl + 4-chlorotoluene mixtures they increase in the negative direction. While the effect of temperature on ΔR is not very systematic with the systems of ethyl acetate + and propyl acetate + 4-chlorotoluene, the methyl acetate + 4-chlorotoluene mixture shows a decrease in ΔR values with an increase in temperature, as shown in Figure 6.

Literature Cited

Cannon, M. R.; Manning, R. E.; Bell, J. D. Viscosity Measurement. The kinetic Energy Correction and a new Viscometer. *Anal. Chem.* **1960**, *32*, 355.

CRC Handbook of Chemistry and Physics, 76th ed.; CRC Press, Inc.: Boca Raton, FL, 1995−96.

Grolier, J. P. E.; Ballet, D.; Viallard, A. Thermodynamics of ester-containing mixtures. Excess enthalpies and excess volumes for alkyl acetates and alkyl benzates + alkyl benzoates + alkanes, + benzene, + toluene, and + ethylbenzene. *J. Chem. Thermodyn.* **1974**, *6*, 895−908.

Iloukhani, H.; Reddy, K. D.; Rao, M. V. P. Excess Volumes of the Binary Mixtures of Substituted Benzenes with Ethyl Acetate and Butyl Acetate. *J. Chem. Eng. Data* **1984**, *29*, 474−478.

Lorentz, H. A. *Theory of electrons*; Teubner; Leipzig, 1909.

Oswall, S.; Rathnam, M. V. Viscosity data of binary mixtures: Ethyl acetate − cyclohexane, + benzene, + toluene, + ethylbenzene, carbon tetrachloride, and + chloroform at 303.15 K. *Can. J. Chem.* **1984**, *62*, 2851.

Oswall, S.; Rathnam, M. V. Study of Dielectric Constants and Refractive Indices of Binary Mixtures of Ethyl Acetate with toluene, Ethylbenzene, o-Xylene, p-Xylene and p-Dioxane. *Indian J. Chem.* **1987**, *26A*, 29−32.

Palaiologou, M. M.; Molinou, J. E. Excess Volumes of Ethyl Acetate + Toluene, + o-Chlorotoluene, and o-Chlorotoluene from 283.15 to 303.15 K. *J. Chem. Eng. Data* **1995**, *40*, 880.

Qin, A.; Hoffman, D. E.; Munk, P. Excess volume of mixtures of selected Alkyl Esters and Ketones with Aromatic Hydrocarbons. *J. Chem. Eng. Data* **1992**, *37*, 66−70.

TRC Data Bases for Chemistry and Engineering − TRC Thermodynamic Tables, version 1996−1S; Texas Engineering Experiment Station, Texas A&M University System: College Station, TX, Jan 1996.

TRC Data Bases for Chemistry and Engineering − TRC source Database, version 1996−1; Texas Engineering Experiment Station, Texas A&M University System: College Station, TX, March 1996.

Vogel, A. *A Textbook of Practical Organic Chemistry*; Longman: Birmingham, AL, 1978.

Wanhoo, R. K.; Narayan, J.; Raina, G. K.; Wani, G. A. Viscosity and surface tension of toluene − Ethylacetate liquid mixture. *Chem. Eng. Commun.* **1988**, *68*, 225.