Excess Volumes of Ethyl Acetate + Toluene, + o-Chlorotoluene, and + p-Chlorotoluene from 283.15 to 303.15 K

Maria M. Palaiologou and Ioanna E. Molinou*

Physical Chemistry Laboratory, Department of Chemistry, University of Athens, Panepistimiopolis, Athens 77 751, Greece

Excess volumes (V^E) of binary mixtures of ethyl acetate with toluene and its o- and p-chloro derivatives have been determined from density measurements from 283.15 to 303.15 K over the entire composition range. Excess volumes are negative for all mixtures at all temperatures. The V^E values are close to zero for the ethyl acetate + toluene system. The values decrease in the order toluene, o-chlorotoluene, and p-chlorotoluene. The effect of temperature on the excess volume is $(\partial V^E/\partial T)_p$, being generally negative.

Introduction

In this paper we report measurements of densities for three binary systems, ethyl acetate + toluene, ethyl acetate + o-chlorotoluene, and ethyl acetate + p-chlorotoluene at 283.15, 288.15, 293.15, 298.15, and 303.15 K. The aim of this work is to investigate the effect on V^E of the introduction of a Cl− group into the toluene molecule in mixtures with ethyl acetate. A survey of the literature showed that V^E has been measured only for the system ethyl acetate + toluene at 293.15, 298.15, and 313.15 K (Grolier et al., 1974; Iloukhani et al., 1984; Qin et al., 1992).

We have extended our studies to the three systems at a series of temperatures, and we report the equimolar excess volume dependence on the temperature. The excess volumes of ethyl acetate with o-chlorotoluene and p-chlorotoluene have not been reported previously.

Experimental Section

All the chemicals were Merck p.a. The stated purity was better than 99.5 mass % for ethyl acetate and toluene and better than 98 mass % for o-chloro- and p-chlorotoluene. Toluene and ethyl acetate were used without further purification, whereas o-chlorotoluene and p-chlorotoluene were purified by the method described by Vogel (1978). Each one of the chloro derivatives 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 densities of the pure compounds with the values reported in the literature (*Lange's Handbook of Chemistry*, 1972). The agreement was very satisfactory. The solutions were prepared by mass in ground glass flasks (with a precision of ± 0.1 mg), and care was taken to avoid evaporation during the mixing process. The mole fractions were known to ±0.0001.

The densities 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 ±0.00025 g cm^{-3}. Under these experimental conditions the V^E values have been estimated to ±0.004 cm^3 mol^{-1}. The density values of the pure components are shown in Table 1 together with the literature data.

Results and Discussion

The excess molar volumes of a binary system are defined by the equation

$$V^E = (x_1M_1 + x_2M_2)/\varrho - (x_1V_1 + x_2V_2) \quad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, V_1 and V_2 are the molar volumes of the corresponding pure components, and ϱ is the density of the solution.

The V^E results were fitted to the equation

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x_1x_2\sum_{k=0}^{n}A_k(2x - 1)^k \quad (2)$$

where A_k are parameters and V^E is the excess molar volume of the mixture.

The optimum number of coefficients was obtained through examination of the standard deviation according to the equation

$$\sigma_{VE} = [\sum(V^E_{\text{calcd}} - V^E_{\text{obsd}})^2/(N - n)]^{1/2} \quad (3)$$

where N is the number of measurements and n the number of parameters.

In Table 2 are listed the experimental values of the binary mixtures ethyl acetate + toluene, ethyl acetate + o-chlorotoluene, and ethyl acetate + p-chlorotoluene as functions of the mole fraction x_1 of ethyl acetate at each of the following temperatures: 283.15, 288.15, 293.15, 298.15, and 303.15 K. The results are presented graphically in Figure 1 for 298.15 K.

The coefficients A_k of eq 2 are listed in Table 3 together with the standard deviation σ for each system.

In Table 4 are presented our experimental values of equimolar V^E as a function of temperature, together with the ones appearing in previous works. In the literature for the ethyl acetate + toluene system the values −0.021 at 293.15 K (Qin et al., 1992) and −0.026 at 298.15 K (Grolier et al., 1974) appear. The agreement with our results is good. We were not able to find any other values in the literature concerning the other systems and temperatures.

The experimental results at 298.15 K in Table 2 are shown in Figure 1. In Figure 2 the equimolar V^E values are plotted against temperature and the literature data are also shown.

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Table 1. Densities of the Pure Components at Various Temperatures

	ϱ/(g cm^{-3})							
	ethyl acetate		toluene		o-chlorotoluene		p-chlorotoluene	
T/K	obsd	lit.	obsd	lit.	obsd	lit.	obsd	lit.
283.15	0.9126		0.8762		1.0921		1.0792	
288.15	0.9064	0.9066[a]	0.8713		1.0871		1.0743	
293.15	0.9005	0.9006[a]	0.8670	0.8660[a]	1.0825	1.0826[a]	1.0694	1.0697[a]
298.15	0.8944		0.8621	0.86234[a]	1.0774		1.0645	
303.15	0.8881		0.8576		1.0726		1.0595	

[a] From *Lange's Handbook of Chemistry* (1972).

Table 2. Excess Volumes (V^E) for Ethyl Acetate (1) + Toluene (2), Ethyl Acetate (1) + o-Chlorotoluene (2), and Ethyl Acetate (1) + p-Chlorotoluene (2)[a]

	EA + toluene		EA + o-chlorotoluene			EA + p-chlorotoluene		
x_1	ϱ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	x_1	ϱ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	x_1	ϱ/(g cm^{-3})	V^E/(cm^3 mol^{-1})
				283.15 K				
0.1070	0.8798	−0.004	0.1180	1.0746	−0.045	0.1207	1.0630	−0.079
0.3172	0.8872	−0.006	0.2322	1.0576	−0.170	0.2395	1.0464	−0.159
0.4241	0.8909	−0.007	0.3452	1.0390	−0.178	0.3432	1.0307	−0.179
0.5210	0.8945	−0.007	0.4362	1.0236	−0.193	0.4575	1.0130	−0.220
0.6170	0.8980	−0.006	0.5440	1.0044	−0.180	0.5459	0.9985	−0.228
0.7130	0.9015	−0.004	0.6411	0.9863	−0.164	0.6447	0.9814	−0.207
0.8081	0.9051	−0.001	0.7405	0.9720	−0.148	0.7290	0.9661	−0.181
0.9031	0.9088	−0.001	0.8280	0.9498	−0.145	0.8316	0.9468	−0.134
			0.9151	0.9312	−0.067	0.9160	0.9301	−0.083
				288.15 K				
0.1070	0.8749	−0.005	0.1180	1.0697	−0.085	0.1207	1.0580	−0.080
0.2150	0.8786	−0.015	0.2322	1.0520	−0.136	0.2395	1.04121	−0.163
0.3172	0.8820	−0.018	0.3452	1.0336	−0.177	0.3432	1.0256	−0.198
0.4241	0.8856	−0.017	0.4362	1.0183	−0.209	0.4575	1.0074	−0.213
0.5210	0.8890	−0.014	0.6411	0.9807	−0.189	0.5459	0.9932	−0.262
0.6170	0.8924	−0.010	0.7405	0.9614	−0.167	0.6447	0.9760	−0.256
0.7130	0.8958	−0.003	0.8280	0.9437	−0.139	0.7383	0.9590	−0.224
0.8081	0.8992	−0.001	0.9151	0.9250	−0.053	0.8316	0.9411	−0.176
						0.9160	0.9238	−0.069
				293.15 K				
0.1070	0.8703	−0.002	0.1180	1.0649	−0.070	0.1207	1.0531	−0.097
0.2144	0.8738	−0.012	0.2322	1.0469	−0.122	0.2395	1.0363	−0.194
0.4201	0.8806	−0.020	0.3452	1.0283	−0.165	0.3432	1.0205	−0.227
0.5180	0.8838	−0.015	0.4362	1.0128	−0.199	0.4575	1.0022	−0.238
0.6143	0.8870	−0.010	0.5440	0.9935	−0.203	0.5459	1.0393	−0.265
0.7130	0.8904	−0.007	0.6411	0.9752	−0.189	0.6447	0.9700	−0.210
0.7171	0.8905	−0.004	0.7405	0.9557	−0.163	0.7383	0.9528	−0.177
0.8120	0.8938	−0.003	0.8280	0.9386	−0.131	0.8316	0.9491	−0.134
0.9071	0.8972	−0.002	0.9151	0.9200	−0.093	0.9160	0.9181	−0.075
				298.15 K				
0.1070	0.8654	−0.015	0.1180	1.0597	−0.086	0.1207	1.0480	−0.098
0.2152	0.8688	−0.022	0.2322	1.0416	−0.131	0.2395	1.0306	−0.142
0.3172	0.8721	−0.038	0.3452	1.0226	−0.144	0.3432	1.0145	−0.154
0.4240	0.8755	−0.031	0.4362	1.0072	−0.198	0.4575	0.9967	−0.236
0.5182	0.8783	−0.023	0.5440	0.9879	−0.217	0.5459	0.9818	−0.241
0.5210	0.8782	−0.022	0.6411	0.9696	−0.204	0.6447	0.9647	−0.260
0.6170	0.8816	−0.021	0.7405	0.9499	−0.172	0.7383	0.9477	−0.250
0.7131	0.8847	−0.011	0.8280	0.9323	−0.168	0.8316	0.9294	−0.172
0.8080	0.8879	−0.010	0.9151	0.9132	−0.067	0.9160	0.9124	−0.119
0.9071	0.8912	−0.002						
				303.15 K				
0.1070	0.8607	−0.013	0.1180	1.0545	−0.057	0.1207	1.0428	−0.091
0.2152	0.8639	−0.022	0.2322	1.0364	−0.129	0.2395	1.0254	−0.156
0.3172	0.8669	−0.023	0.3452	1.0174	−0.155	0.3432	1.0094	−0.198
0.4201	0.8701	−0.029	0.4362	1.0018	−0.209	0.4575	0.9915	−0.286
0.5210	0.8731	−0.032	0.5440	0.9823	−0.221	0.5459	0.9765	−0.290
0.6143	0.8759	−0.021	0.6411	0.9637	−0.202	0.6447	0.9592	−0.303
0.7130	0.8789	−0.009	0.7405	0.9441	−0.186	0.7383	0.9510	−0.278
0.7322	0.8795	−0.006	0.8280	0.9260	−0.150	0.8316	0.9233	−0.172
0.907	0.8851	0.001						

[a] EA = ethyl acetate.

Figure 2 shows that the temperature coefficient of V^E has a slight tendency to negative values for the three systems. V^E is negative for all systems over the entire range of composition and at each temperature. For ethyl acetate + toluene the values are close to zero whereas the negative deviation of V^E is enhanced when toluene is replaced by either o-chlorotoluene or p-chlorotoluene.

Among the factors that might give rise to negative V^E values is the fact that interactions occur between unlike molecules which are stronger than the interactions between

Table 3. Values of Parameters A_k of Eq 2 and Standard Deviation (σ)

T/K	system[a]	A_0	A_1	A_2	σ/(cm^3 mol^{-1})
283.15	EA + toluene	−0.0273	0.0157	0.0118	±0.001
	EA + *o*-chlorotoluene	−0.7589	−0.0125	−0.1615	±0.021
	EA + *p*-chlorotoluene	−0.8825	−0.1190	0.1806	±0.011
288.15	EA + toluene	−0.0612	0.0694	0.0580	±0.001
	EA + *o*-chlorotoluene	−0.8290	−0.0855	0.0015	±0.009
	EA + *p*-chlorotoluene	−0.9848	−0.3237	−0.0345	±0.011
293.15	EA + toluene	−0.0638	0.0450	0.0667	±0.002
	EA + *o*-chlorotoluene	−0.7913	−0.1757	−0.0396	±0.008
	EA + *p*-chlorotoluene	−0.9962	0.0734	0.0727	±0.011
298.15	EA + toluene	−0.1059	0.0965	0.0070	±0.008
	EA + *o*-chlorotoluene	−0.8025	−0.2585	−0.1792	±0.015
	EA + *p*-chlorotoluene	−0.9334	−0.4847	−0.3034	±0.016
303.15	EA + toluene	−0.1100	0.0866	0.1065	±0.003
	EA + *o*-chlorotoluene	−0.8439	−0.2910	0.0457	±0.009
	EA + *p*-chlorotoluene	−1.1517	−0.4949	0.1647	±0.017

[a] EA = ethyl acetate.

Table 4. Equimolar Excess Volumes[a]

	V^E/(cm^3 mol^{-1})			
	EA + toluene		EA +	EA +
T/K		lit.	*o*-chlorotoluene	*p*-chlorotoluene
283.15	−0.007		−0.190	−0.221
288.15	−0.015		−0.207	−0.246
293.15	−0.016	−0.021[b]	−0.199	−0.249
298.15	−0.026	−0.026[c]	−0.201	−0.233
303.15	−0.027		−0.211	−0.289

[a] EA = ethyl acetate. [b] From Qin et al. (1992). [c] From Grolier et al. (1974).

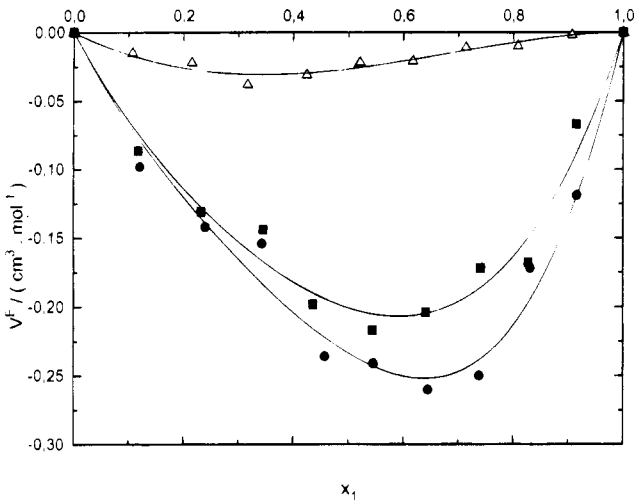

Figure 1. Excess volumes of ethyl acetate (1) with toluene (2) (△), *o*-chlorotoluene (2) (■), and *p*-chlorotoluene (2) (●) at 298.15 K.

like ones. 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 tendency to negative values might also be enhanced by a dipole−dipole interaction caused by the strong polar character of the carbonyl of the ester and the toluene (or chlorotoluene) molecules. The V^E values decrease from toluene to *p*-chlorotoluene mixtures as clearly shown in Figure 1. The same conclusion is held for the corresponding figures at the other temperatures. An explanation could be given by considering the dipole moments of the

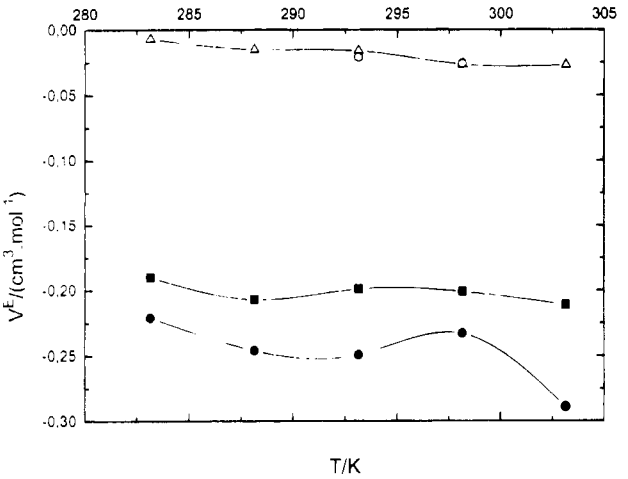

Figure 2. Temperature dependence of the equimolar excess volumes for ethyl acetate + toluene (△), ethyl acetate + *o*-chlorotoluene (■), and ethyl acetate + *p*-chlorotoluene (●) and reference values of ethyl acetate + toluene (○).

three pure solvents which are 2.21 D for *p*-chlorotoluene, 1.56 D for *o*-chlorotoluene, and 0.45 D (Qin et al., 1992) for toluene. *p*-Chlorotoluene yields the more negative value of the excess volume at each temperature, and that might be due to the fact that it also has the larger dipole moment which enhances the dipole−dipole interaction.

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