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Excess Volumes of Binary Mixtures of Ethyl Acetate with *o*-Xylene, *p*-Xylene, Dioxane & Tetrahydrofuran

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The excess volumes (V^E) for binary mixtures of ethyl acetate with *o*-xylene, *p*-xylene, dioxane and tetrahydrofuran have been determined at 303.15 K and 313.15 K. Excess volumes are negative over the whole range of composition for the mixtures of ethyl acetate with *o*-xylene, *p*-xylene and dioxane while it is positive for mixture with tetrahydrofuran. However with increase in temperature the sign of V^E changes for the mixtures of ethyl acetate with *o*-xylene and *p*-xylene.

Presently we have measured the excess volumes of mixing in the title binary mixtures at 303.15 K and 313.15 K. The results have been interpreted in terms of molecular interactions. To the best of our knowledge the excess volume data on the title binary systems are not available in literature.

Ethyl acetate, *o*-xylene and *p*-xylene (all BDH, AR) were purified by the procedure given by Riddick and Bunger[1]. Dioxane and tetrahydrofuran were purified, dried and distilled before use. The purity of the solvents was checked by measuring their densities and comparing the data with those reported in literature[2].

Densities were determined with the help of a pycnometer (capacity 11 cm^3), calibrated against water and benzene. The density data are correct to ± 0.0001

Table 1—Densities (d) and Excess Volumes (V^E) for Ethyl Acetate-*o*-Xylene/*p*-Xylene/Dioxane/Tetrahydrofuran Binaries at Different Temperatures

Ethyl acetate(1) + *o*-xylene (2)

Temp = 303.15 K			Temp = 313.15 K		
X_1	d (g cm^3)	V^E (cm^3 mol^{-1})	X_1	d (g cm^3)	V^E (cm^3 mol^{-1})
0.0000	0.8717		0.0000	0.8632	—
0.0599	0.8727	−0.024	0.2056	0.8656	−0.011
0.1789	0.8745	−0.036	0.4079	0.8678	+0.025
0.2918	0.8763	−0.056	0.5023	0.8690	+0.027
0.4303	0.8786	−0.064	0.5988	0.8701	+0.051
0.4994	0.8798	−0.072	0.8018	0.8732	+0.025
0.5537	0.8806	−0.057	1.0000	0.8765	
0.6001	0.8814	−0.057			
0.6951	0.8830	−0.046			
0.7859	0.8846	−0.037			
0.8730	0.8862	−0.028			
0.9583	0.8878	−0.017			
1.000	0.8885				

Ethyl acetate(1) + *p*-xylene (2)

0.0000	0.8523		0.0000	0.8436	
0.0624	0.8542	−0.011	0.2063	0.8493	−0.006
0.1828	0.8579	−0.018	0.4077	0.8552	+0.010
0.2938	0.8615	−0.026	0.5061	0.8582	+0.027
0.4031	0.8656	−0.043	0.5991	0.8612	+0.039
0.5056	0.8689	−0.046	0.8016	0.8685	+0.026
0.5520	0.8707	−0.060	1.0000	0.8765	
0.6041	0.8726	−0.056			
0.6976	0.8761	−0.044			
0.7887	0.8797	−0.037			
0.8757	0.8832	−0.021			
0.9585	0.8868	−0.019			
1.0000	0.8885				

Ethyl acetate(1) + *p*-dioxane(2)

Temp = 303.15 K			Temp = 313.15 K		
X_1	d (g cm^3)	V^E (cm^3 mol^{-1})	X_1	d (g cm^3)	V^E (cm^3 mol^{-1})
0.0000	1.0223		0.0000	1.0111	
0.0451	1.0156	−0.016	0.2090	0.9801	−0.041
0.0948	1.0083	−0.035	0.4050	0.9525	−0.059
0.1332	1.0027	−0.044	0.5144	0.9379	−0.083
0.1779	0.9962	−0.051	0.6020	0.9263	−0.078
0.2236	0.9897	−0.063	0.7994	0.9012	−0.071
0.3187	0.9763	−0.075	1.0000	0.8765	
0.4670	0.9558	−0.065			
0.5155	0.9492	−0.053			
0.6182	0.9356	−0.037			
0.7243	0.9220	−0.025			
0.8297	0.9089	−0.015			
0.9411	0.8955	−0.011			
1.0000	0.8885				

Ethyl acetate(1) + tetrahydrofuran(2)

0.0000	0.8768		0.0000	0.8668	
0.0431	0.8773	0.010	0.2044	0.8683	0.079
0.0837	0.8778	0.015	0.4059	0.8702	0.103
0.1718	0.8789	0.023	0.5072	0.8711	0.113
0.2625	0.8799	0.031	0.6002	0.8720	0.112
0.3504	0.8810	0.041	0.7996	0.8741	0.082
0.4097	0.8816	0.054	1.0000	0.8765	
0.4521	0.8822	0.044			
0.6544	0.8846	0.035			
0.7669	0.8859	0.026			
0.8229	0.8865	0.025			
0.8817	0.8872	0.014			
0.9396	0.8878	0.012			
1.0000	0.8885				

Table 2—Values of Parameters of Eq (2) and Standard Deviation [$\sigma(V^E)$] by Method of Least Squares at Different Temperatures for Different Binary Systems

System	Temp. (K)	A_0	A_1	A_2	$\sigma(V^E)$ ($cm^3\ mol^{-1}$)
Ethyl acetate +	303.15	−0.2349	0.0263	−0.1709	0.009
o-xylene	313.15	0.1452	0.1968	−0.2714	0.012
Ethyl acetate +	303.15	−0.1718	−0.1028	−0.1196	0.009
p-xylene	313.15	0.1054	0.1839	−0.1227	0.006
Ethyl acetate +	303.15	−0.2352	0.1604	−0.0479	0.007
dioxane	313.15	−0.3276	−0.1707	−0.0327	0.010
Ethyl acetate +	303.15	0.1665	−0.0208	0.0344	0.005
tetrahydrofuran	313.15	0.4261	0.0762	0.3123	0.004

units. The temperature of the water thermostat was maintained with an accuracy of ±0.01 K.

The excess volumes, calculated from the measured densities were reproducible within ±0.003 $cm^3\ mol^{-1}$.

The excess volumes (V^E) were calculated from the measured densities using the relation (1).

$$V^E = [(MX_1 + M_2X_2)/d_{12}] - (M_1X_1/d_1 + M_2X_2/d_2) \quad ...(1)$$

where M_1, X and d_1 represent molecular weight, mol fraction and density respectively; subscripts 1, 2 and 12 refer to pure components and their mixtures respectively. The density and excess volume data are given in Table 1. The values of V^E have been fitted to an empirical equation of the form (2)

$$V^E = X_1(1 - X_1)[A_0 + A_1(2X_1 - 1) + A_2(2X_1 - 1)^2] \quad ...(2)$$

where A_0, A_1 and A_2 are adjustable parameters and X_1 is the mol fraction of the principal component of the mixture namely, ethyl acetate. The values of the parameters obtained by least-squares analysis are given in Table 2 together with the standard deviation, $\sigma(V^E)$.

Excess volumes are negative for the binary mixtures of ethyl acetate with *o*-xylene, *p*-xylene, and dioxane over the entire composition range indicating strong specific interactions. The V^E values are positive for ethyl acetate + tetrahydrofuran mixture. However with increase in temperature, V^E values become positive for binary mixtures of ethyl acetate with *o*- and *p*-xylenes indicating that 1-2 interactions are weaker in these mixtures as compared to 1-1 and 2-2 interactions. In the case of ethyl acetate + tetrahydrofuran mixture, the magnitude of V^E becomes large and positive, with increase in temperature.

The observed negative V^E for ethyl acetate + dioxane mixture may be explained qualitatively by postulating the existence of (i) acceptor-donor interaction and (ii) the interaction between ethyl acetate and oxygen lone-pair electrons. This may involve a charge-transfer mechanism. The large positive values of V^E for ethyl acetate + tetrahydrofuran mixture indicate that the interactions between unlike molecules are weaker as compared to those in the pure liquid state and give rise to positive deviation.

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References

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