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EXCESS VOLUMES FOR BINARY MIXTURES FORMED BY METHYL ACETATE WITH AROMATIC HYDROCARBONS

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Abstract

Excess molar volumes for binary mixtures containing methyl acetate + methylbenzene, ethylbenzene, 1,4-dimethylethylbenzene, 1 methylbenzene, 1,-3,-5-trimethylbenzene or 1,-1-dimethylethylbenzene were determined from density measurements at 298.15 K using an Anton Paar DMA 58 vibrating tube densitometer. The excess molar volumes were positive throughout the concentration ranges. The excess molar volumes increase with the size of the hydrocarbon.

Keywords: aromatic hydrocarbon, excess volume, methyl acetate

Introduction

The binary mixture formed by methyl acetate + methanol, which arises in the direct synthesis of the ether from the corresponding alcohol, exhibits a minimum azeotrope at 101.3 kPa. The separation of this azeotropic mixture by extractive distillation is of importance for the preparation of pure products, the choice of the most appropriate solvents [1] and the calculation of the corresponding equilibrium [2]. This report is a continuation of the study of the thermodynamic properties of such systems; results on the densities and excess volumes of binary mixtures of methyl acetate with aromatic hydrocarbons are presented. Such data have not been found in the literature. The hydrocarbons studied were methylbenzene, ethylbenzene, 1,-4-dimethylbenzene, 1-methylethylbenzene, 1,-3,-5-trimethylbenzene and 1,-1-dimethylethylbenzene. These data are necessary for the design of the extractive distillation process.

Experimental

All the products were supplied by Riedel de Haën, with purities better than 99.5%. The purities were checked by gas chromatography, using a 14-B Shimadzu gas chromatograph. The column used was a Carbowax 20M one. The

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mixtures were prepared by mass, using a Salter ER-182A balance with a precision of ±0.0001 g. Densities were measured to a precision of ±0.00001 g cm^{-3} in an Anton Paar DMA 58 digital vibrating tube densitometer. All the measurements were made under thermostatized conditions at 298.15±0.01 K and atmospheric pressure.

The densitometer was calibrated with water and air, using the corresponding densities of water and air at each temperature. Excess volumes were accurate to ±2×10^{-3} cm^{-3} mol^{-1}. Temperatures were accurate to ±1×10^{-2} K. Experimental densities and refractive indices at 298.15 K of the solvents used, together with the corresponding literature values [3], are listed in Table 1.

Table 1 Densities and refractive indexes of the pure solvents at 298.15 K

Compound	ρ/g cm^{-3} (exp.)	ρ/g cm^{-3} [3]	n_D (exp.)	n_D (lit.) [3]
Methyl acetate	0.92705	0.92790	1.3595	1.3589
Methylbenzene	0.86220	0.86219	1.4935	1.49413
Ethylbenzene	0.86256	0.86253	1.4932	1.49320
1,-4-dimethylbenzene	0.85659	0.85661	1.4933	1.49325
1-methylethylbenzene	0.85741	0.85743	1.4887	1.48890
1,-3,-5-trimethylbenzene	0.86132	0.86111	1.4966	1.49684
1,-1-dimethylethylbenzene	0.86234	0.86240	1.4902	1.49024

Results and discussion

Densities and excess molar volumes of the prepared mixtures are listed in Tables 2 and 3. The excess molar volumes of the binary mixtures were fitted to Redlich-Kister polynomials of the form

$$V^E/\mathrm{cm^3mol^{-1}} = x_1x_2\sum_{k\geq 0} a_k(x_1-x_2)^k \tag{1}$$

where x_1 is the mole fraction of the more volatile compound, a_k are the adjustable parameters obtained by the least square method, and k is the degree of the polynomial expansion. Table 4 summarizes the values of the parameters a_k, together with the standard deviations $\sigma(V^E)$. The expression applied to compute the standard deviation was

Table 2 Densities ρ and excess molar volumes V^E for binary systems (methyl acetate + methylbenzene, methyl acetate + ethylbenzene, methyl acetate + 1,-4-dimethylbenzene) at 298.15 K

x_1	ρ/g cm^{-3}	V^E/cm^3 mol^{-1}	x_1	ρ/g cm^{-3}	V^E/cm^3 mol^{-1}
Methyl acetate + methylbenzene					
0.0516	0.86447	0.032	0.5457	0.89090	0.206
0.1140	0.86721	0.082	0.5998	0.89442	0.208
0.1559	0.86932	0.089	0.6548	0.89820	0.203
0.2073	0.87186	0.110	0.6906	0.90080	0.192
0.2661	0.87484	0.136	0.7471	0.90506	0.172
0.2972	0.87641	0.155	0.8070	0.90978	0.146
0.3487	0.87925	0.166	0.8419	0.91264	0.129
0.4155	0.88301	0.184	0.8920	0.91695	0.097
0.4544	0.88528	0.193	0.9478	0.92206	0.048
0.4951	0.88765	0.209			
Methyl acetate + ethylbenzene					
0.0501	0.86443	0.037	0.5640	0.88908	0.324
0.1024	0.86633	0.093	0.6115	0.89217	0.324
0.1558	0.86843	0.138	0.6508	0.89486	0.320
0.2072	0.87055	0.179	0.6907	0.89780	0.305
0.2608	0.87288	0.218	0.7499	0.90237	0.282
0.3091	0.87516	0.240	0.8039	0.90700	0.238
0.3430	0.87683	0.254	0.8569	0.91180	0.195
0.4035	0.87987	0.285	0.8939	0.91541	0.155
0.4627	0.88306	0.307	0.9489	0.92118	0.084
0.5135	0.88596	0.322			
Methyl acetate + 1,-4-dimethylbenzene					
0.0521	0.85888	0.018	0.5451	0.88536	0.219
0.1025	0.86111	0.043	0.5998	0.88891	0.224
0.1589	0.86351	0.099	0.6541	0.89329	0.214
0.1923	0.86513	0.112	0.6934	0.89637	0.210
0.2464	0.86777	0.142	0.7530	0.90139	0.192
0.2940	0.87019	0.168	0.7999	0.90556	0.176
0.3373	0.87256	0.180	0.8525	0.91069	0.139
0.3879	0.87547	0.191	0.8973	0.91526	0.108
0.4479	0.87900	0.212	0.9379	0.91972	0.070
0.4935	0.88182	0.227			

Table 3 Densities ρ and excess molar volumes V^E for binary systems (methyl acetate + 1-methylethylbenzene, methyl acetate + 1,-3,-5-trimethylbenzene, methyl acetate + 1,-1-dimethylbenzene) at 298.15 K

x_1	ρ(g cm^{-3})	V^E(cm^{3}mol^{-1})	x_1	ρ(g cm^{-3})	V^E(cm^{3}mol^{-1})
Methyl acetate + 1-methylethylbenzene					
0.0495	0.85915	0.043	0.5506	0.88310	0.357
0.1065	0.86119	0.101	0.5920	0.88599	0.348
0.1679	0.86351	0.163	0.6574	0.89077	0.342
0.2152	0.86549	0.196	0.7031	0.89440	0.330
0.2546	0.86716	0.230	0.7584	0.89923	0.300
0.3366	0.87105	0.273	0.8060	0.90377	0.265
0.3715	0.87295	0.272	0.8634	0.90975	0.211
0.4167	0.87519	0.312	0.8960	0.91343	0.174
0.4493	0.87694	0.332	0.9583	0.92123	0.079
0.5156	0.88096	0.341			
Methyl acetate + 1,-3,-5-trimethylbenzene					
0.0474	0.86266	0.076	0.5502	0.88419	0.508
0.1036	0.86431	0.168	0.5984	0.88719	0.515
0.1514	0.86592	0.225	0.6579	0.89128	0.506
0.1867	0.86710	0.275	0.7003	0.89443	0.493
0.2609	0.86982	0.364	0.7444	0.89815	0.452
0.3219	0.87231	0.422	0.7984	0.90313	0.388
0.3611	0.87406	0.450	0.8477	0.90805	0.325
0.4164	0.87669	0.484	0.8964	0.91339	0.247
0.4536	0.87857	0.503	0.9432	0.91915	0.150
0.5023	0.88118	0.524			
Methyl acetate + 1,-1-dimethylethylbenzene					
0.0639	0.86423	0.053	0.5740	0.88623	0.326
0.1030	0.86539	0.095	0.6113	0.88861	0.325
0.1583	0.86721	0.137	0.6543	0.8915	0.325
0.2397	0.87008	0.202	0.6919	0.89435	0.306
0.2517	0.8705	0.215	0.7468	0.89874	0.284
0.3003	0.87245	0.240	0.8131	0.90467	0.247
0.3618	0.87506	0.274	0.8425	0.90751	0.230
0.3939	0.87663	0.273	0.9073	0.91473	0.181
0.4605	0.87986	0.302	0.9446	0.91854	0.141
0.4952	0.8817	0.310			

Table 4 Adjustable parameters and standard deviation for the studied systems

System	A_0	A_1	A_2	σ/cm^{3}mol^{-1} 10^3
Methyl acetate-methylbenzene	0.8095	–0.2118	0.0422	4.6
Methyl acetate-ethylbenzene	1.2685	–0.3953	0.0850	3.6
Methyl acetate-1,-4-dimethylbenzene	0.8857	–0.2914	0.0099	6.8
Methyl acetate-1-methylethylbenzene	1.3572	–0.4690	0.1784	6.1
Methyl acetate-1,-3,-5-trimethylbenzene	2.0642	–0.5142	0.2190	6.1
Methyl acetate-1,-1-dimethylethylbenzene	1.2426	–0.4819	0.3974	12.3

$$\sigma = \left(\frac{\sum_{i}^{n_{dat}} V_{exp}^{E} - V_{pred}^{F}}{n_{dat}} \right)^{1/2} \tag{2}$$

where n_{dat} is the number of experimental data, and V^E_{pred} is the excess molar volume calculated for each of the experimental data by means of Eq. (1). The coefficients a_k were used to calculate the solid curves in Fig. 1. In Fig. 1, the excess molar volumes for the binary mixtures of methyl acetate + hydrocarbons are plotted *vs.* the mole fraction of methyl acetate.

Excess volumes mainly depend on two effects:

– the variation in intermolecular forces when two components come into contact,

– the variation in molecular packing as a consequence of the different sizes and shapes of the molecules of the components.

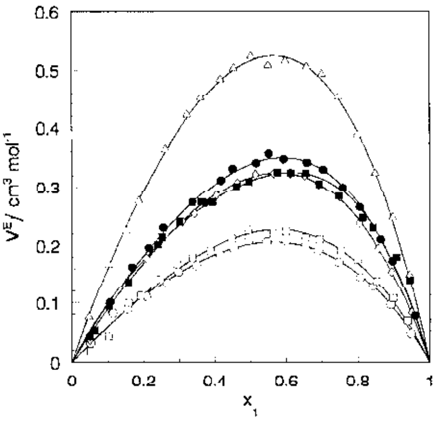

Fig. 1 Excess volumes of binary mixtures of methyl acetate + hydrocarbons (○ – methylbenzene, ◇ – ethylbenzene, □ – 1,-4-dimethylbenzene, ● – 1-methylethylbenzene, △ – 1,-3,-5-trimethylbenzene, ■ – 1,-1-dimethylethylbenzene) *vs.* mole fraction of methyl acetate

When two components are mixed, if the interactions between their molecules are weaker than the interactions between the molecules of the pure compounds, then the excess volumes of the mixtures will be higher than zero. This usually occurs when one of the components consists of polar molecules and the other of non-polar or weakly polar molecules.

The methyl acetate molecule is weakly polar, while the aromatic hydrocarbon molecules are nearly non-polar, although they can show slight polarizability. The nearness of polar molecules can induce weak temporary dipoles. When the molecules of the pure compounds are mixed, the non-plar molecules of the hydrocarbons are situated among the methyl acetate molecules, and decrease the interactions between the dipoles of the acetate. As the interactions diminish, the inter molecular length grow and the excess volume will be higher than zero. The experimental results agree with this explanation because all the studied mixtures displayed excess volumes higher than zero.

The fact that all the excess volumes are higher than zero shows that the variation in the intermolecular forces is higher than the packing caused by geometric effects. This determines the differences in the excess volumes from one hydrocarbon to another. If we compare the maximum excess volumes in Fig. 2 (ca x=0.05), it can be observed that the lower values correspond to the mixtures with hydrocarbons which have flat geometry with small substituents or separated ones (methylbenzene, 1,-4-dimethylbenzene), the intermediate values correspond to mixtures with hydrocarbons whose geometry is not flat (1,-1-dimethylethylbenzene, 1-methylbenzene, ethylbenzene) and the highest volume appears for the acetate for 1,-3,-5-trimethylbenzene mixture. 1,-3,-5-Trimethylbenzene has flat geometry, but contains three substituents in meta positions.

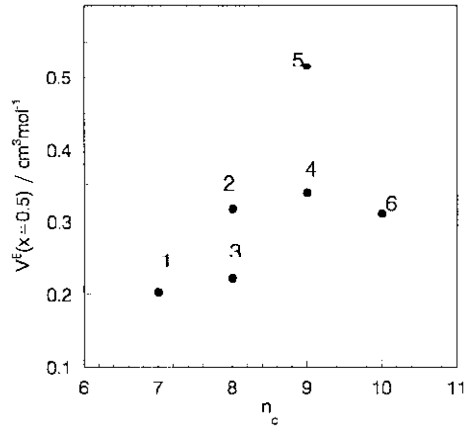

Fig. 2 Variation in V^E at the equimolecular composition for the studied mixtures *vs.* the number of carbon atoms in the hydrocarbon (1 – methylbenzene, 2 – ethylbenzene, 3 – 1,-4-dimethylbenzene, 4 – 1-methylethylbenzene, 5 – 1,-3,-5-trimethylbenzene, 6 – 1,-1-dimethylethylbenzene)

These results can be interpreted qualitatively as a consequence of the diminution of the molecular interaction between the methyl acetate and the different hydrocarbons.

For $x=0.5$, mixture contains 50% of molecules of each compound, which will be homogeneously distributed. The hydrocarbon molecules added to the acetate molecules will reduce the interactions the more, the bigger they are. If the molecules are flat or possess a few bulky substituents (methylbenzene, 1,-4-dimethylbenzene), some interactions can remain and the excess volume will not be very large. If the hydrocarbon molecules possess a bulky substituent or one situated in another plane than the aromatic ring, then the interactions between the acetate molecules will be disabled and the excess volume will be higher than in the previous case. The presence of three methyl in meta positions obstructs the approach to the acetate molecules from the ring and the steric volume will be higher. The interaction between the acetate molecules will be lower and the excess volume will increase. The increase in excess volume with the size of the molecules is shown in other mixtures of non-polar + polar compounds, such as those of acetone with ethers [4].

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