Influence of Temperature on Densities of 2-Methoxy-2-Methylpropane + Xylenes Solutions

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The densities of the binary mixtures methoxy-2-methylpropane (MTBE) + xylenes (o-xylene, m-xylene and p-xylene respectively) have been measured at 288.15, 293.15, 298.15, 303.15, 308.15 K and atmospheric pressure over the whole composition range. The temperature dependence of the density of these solutions as a function of molar fraction is presented. Values of excess molar volume were calculated from experimental measurements of density and a Redlich-Kister equation type was used to correlate this excess property. Knowledge of these mixing properties has relevance in both theoretical and applied areas of research because such results are useful in design and simulation processes for petrochemical industry.

Key words: binary liquid mixtures, density, excess volumes, 2-methoxy-2-methylpropane, xylenes

The present work is a part of our systematic studies on thermodynamic properties for mixtures of great interest in industry [1 – 7]. Methoxy-2-methylpropane (MTBE) is used as gasoline additive to improve the octane rating and reduce pollution. The present work reports densities for the MTBE + xylenes binary system at 288.15, 293.15, 298.15, 303.15, and 308.15 K at atmospheric pressure over the whole composition range, as well as the corresponding excess molar volumes. A survey of the literature shows that there are very few reports on the density measurements for the mixtures studied in this paper [8, 9].

Experimental part

All chemicals were purchased from Merck (> 99.5 % purity) and were used without further purification. The chemicals were dried over molecular sieves (Fluka type 4 Å). The purity was checked through chromatographic and refractive index methods. The mole fractions were determined by weighing and precision of the mole fraction was ± 0.00005. The densities were determined by hydrostatic weighing method of Kohlrausch with a precision of ± 0.00005 g/cm^3. The experimental technique has been previously described [10], the temperature of thermostatic water bath being controlled to ± 0.05 K.

Results and discussion

The measured densities of the pure component liquids are listed in table 1 together with published values [9,11,12]. All measured values show good agreement with data given in the literature.

Densities and excess molar volumes of the binary mixtures of MTBE + xylenes are reported in tables 2 - 4. The densities (ρ/gcm^{-3}) of the binary mixtures MTBE (x_1) + xylenes (x_2) were correlated with composition using equation (1) [13].

$$\rho = x_1\rho_1 + x_2\rho_2 + x_1x_2\left[\begin{array}{l} P_1 + P_2T + P_3T^2 + (P_4 + P_5T + P_6T^2)(x_1 - x_2) + \\ + (P_7 + P_8T + P_9T^2)(x_1 - x_2)^2 \end{array}\right] \quad (1)$$

The temperature dependence of the densities (ρ_i) of each pure substance *i* involved in eq. (1) is expressed using equation (2).

$$\rho_i = A_i + B_i T + C_i T^2 \quad (i = 1, 2) \quad (2)$$

In these two equations P_1, P_2, P_3, P_4, P_5, P_6, P_7, P_8, P_9 and A_i, B_i, C_i, are fitted parameters.

Table 5 shows the fitting parameters for the pure substances and for the binary solutions MTBE + xylenes.

The deviations between experimental (exp.) and calculated (calc.) values are shown as the standard deviation, σ, defined by:

$$\sigma = \left[\frac{\sum (X_{exp.} - X_{calc.})^2}{m - n}\right]^{1/2}, \quad (3)$$

where *m* is the number of data points, *n* is the number of estimated parameters and X is the density or the excess molar volume. The results in table 5 reveal that the calculated values of densities using equation (1) and (2) are very good for all the solutions analyzed in this work. As

Table1
COMPARISON OF EXPERIMENTAL DENSITIES OF PURE LIQUIDS WITH LITERATURE VALUES

Component	Density, g cm^{-3}		Density, g cm^{-3}	
	Experimental (298.15 K)	Literature (298.15 K)	Experimental (308.15 K)	Literature (308.15 K)
MTBE	0.7345	0.73517 [11] 0.734406 [9]	0.7239	0.72726 [11]
o-xylene	0.8748	0.874708 [9]	0.8664	0.86741 [12]
m-xylene	0.8598	0.859471 [9]	0.8512	0.85153 [12]
p-xylene	0.8566	0.856589 [9]	0.8479	0.84791 [12]

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Table 2
THE DENSITIES (ρ) AND MOLAR EXCESS VOLUMES (V^H) OF THE BINARY MIXTURES MTBE (x_1) + *o*-XYLENE AT DIFFERENT TEMPERATURES

T, K	x_1	ρ g/cm³	V^E cm³/mol	x_1	ρ g/cm³	V^E cm³/mol
	0.0000	0.8832	0.0000	0.5973	0.8044	- 0.4864
	0.1088	0.8697	- 0.1746	0.6897	0.7912	- 0.4391
288.15	0.1859	0.8599	- 0.2905	0.7796	0.7781	- 0.3579
	0.2931	0.8460	- 0.4086	0.8950	0.7609	- 0.1984
	0.3895	0.8331	- 0.4667	1.0000	0.7449	0.0000
	0.5089	0.8168	- 0.5022			
	0.0000	0.8790	0.0000	0.5973	0.7997	- 0.5175
	0.1088	0.8654	- 0.1815	0.6897	0.7864	- 0.4678
293.15	0.1859	0.8556	- 0.3118	0.7796	0.7732	- 0.3470
	0.2931	0.8415	- 0.4207	0.8950	0.7559	- 0.2205
	0.3895	0.8286	- 0.4950	1.0000	0.7397	0.0000
	0.5089	0.8122	- 0.5350			
	0.0000	0.8748	0.0000	0.5973	0.7950	- 0.5497
	0.1088	0.8611	- 0.1888	0.6897	0.7816	- 0.4977
298.15	0.1859	0.8512	- 0.3196	0.7796	0.7683	- 0.4084
	0.2931	0.8371	- 0.4478	0.8950	0.7508	- 0.2274
	0.3895	0.8241	- 0.5243	1.0000	0.7345	0.0000
	0.5089	0.8076	- 0.5690			
	0.0000	0.8706	0.0000	0.5973	0.7902	- 0.5775
	0.1088	0.8569	- 0.2122	0.6897	0.7767	- 0.5243
303.15	0.1859	0.8469	- 0.3450	0.7796	0.7633	- 0.4320
	0.2931	0.8327	- 0.4805	0.8950	0.7456	- 0.2331
	0.3895	0.8196	- 0.5609	1.0000	0.7292	0.0000
	0.5089	0.8029	- 0.5973			
	0.0000	0.8664	0.0000	0.5973	0.7855	- 0.6217
	0.1088	0.8526	- 0.2220	0.6897	0.7718	- 0.5519
308.15	0.1859	0.8425	- 0.3568	0.7796	0.7583	- 0.4565
	0.2931	0.8282	- 0.4994	0.8950	0.7405	- 0.2555
	0.3895	0.8150	- 0.5837	1.0000	0.7239	0.0000
	0.5089	0.7982	- 0.6266			

Table 3
THE DENSITIES (ρ) AND MOLAR EXCESS VOLUMES (V^E) OF THE BINARY MIXTURES MTBE (x_1) + *m*-XYLENE AT DIFFERENT TEMPERATURES

T, K	x_1	ρ g/cm³	V^E cm³/mol	x_1	ρ g/cm³	V^E cm³/mol
	0.0000	0.8684	0.0000	0.5843	0.7994	- 0.3275
	0.1128	0.8558	- 0.1329	0.7129	0.7830	- 0.2769
288.15	0.1985	0.8460	- 0.2127	0.8031	0.7713	- 0.2225
	0.3095	0.8330	- 0.2861	0.8852	0.7604	- 0.1412
	0.4153	0.8203	- 0.3259	1.0000	0.7449	0.0000
	0.4905	0.8111	- 0.3372			
	0.0000	0.8641	0.0000	0.5843	0.7947	- 0.3589
	0.1128	0.8514	- 0.1377	0.7129	0.7782	- 0.3095
293.15	0.1985	0.8415	- 0.2170	0.8031	0.7663	- 0.2346
	0.3095	0.8285	- 0.3078	0.8852	0.7553	- 0.1462
	0.4153	0.8157	- 0.3487	1.0000	0.7397	0.0000
	0.4905	0.8064	- 0.3558			
	0.0000	0.8598	0.0000	0.5843	0.7899	- 0.3760
	0.1128	0.8470	- 0.1426	0.7129	0.7733	- 0.3275
298.15	0.1985	0.8371	- 0.2362	0.8031	0.7614	- 0.2631
	0.3095	0.8240	- 0.3302	0.8852	0.7503	- 0.1676
	0.4153	0.8111	- 0.3722	1.0000	0.7345	0.0000
	0.4905	0.8018	- 0.3903			
	0.0000	0.8555	0.0000	0.5843	0.7851	- 0.4034
	0.1128	0.8427	- 0.1643	0.7129	0.7683	- 0.3421
303.15	0.1985	0.8327	- 0.2592	0.8031	0.7563	- 0.2737
	0.3095	0.8194	- 0.3434	0.8852	0.7451	- 0.1726
	0.4153	0.8065	- 0.4034	1.0000	0.7292	0.0000
	0.4905	0.7971	- 0.4186			
	0.0000	0.8512	0.0000	0.5843	0.7803	- 0.4317
	0.1128	0.8383	- 0.1717	0.7129	0.7634	- 0.3734
308.15	0.1985	0.8282	- 0.2679	0.8031	0.7513	- 0.3010
	0.3095	0.8149	- 0.3722	0.8852	0.7400	- 0.1935
	0.4153	0.8018	- 0.4202	1.0000	0.7239	0.0000
	0.4905	0.7923	- 0.4323			

an example, figure 1 shows experimental and calculated values of density at 298.15 K constant temperature for all three systems.

Table 4

THE DENSITIES (ρ) AND MOLAR EXCESS VOLUMES ((V^E)) OF THE BINARY MIXTURES MTBE (x_1) + *p*-XYLENE AT DIFFERENT TEMPERATURES

T, K	x_1	ρ g/cm^3	V^E cm^3/mol	x_1	ρ g/cm^3	V^E cm^3/mol
288.15	0.0000	0.8653	0.0000	0.6089	0.7955	- 0.3730
	0.0936	0.8553	- 0.1295	0.6835	0.7862	- 0.3421
	0.2145	0.8420	- 0.2604	0.8129	0.7697	- 0.2484
	0.2897	0.8335	- 0.3194	0.9081	0.7572	- 0.1359
	0.4129	0.8192	- 0.3782	1.0000	0.7449	0.0000
	0.5130	0.8072	- 0.3848			
293.15	0.0000	0.8610	0.0000	0.6089	0.7907	- 0.3927
	0.0936	0.8509	- 0.1311	0.6835	0.7814	- 0.3713
	0.2145	0.8375	- 0.2673	0.8129	0.7647	- 0.2618
	0.2897	0.8290	- 0.3382	0.9081	0.7521	- 0.1434
	0.4129	0.8146	- 0.4008	1.0000	0.7397	0.0000
	0.5130	0.8025	- 0.4067			
298.15	0.0000	0.8566	0.0000	0.6089	0.7859	- 0.4188
	0.0936	0.8465	- 0.1459	0.6835	0.7765	- 0.3905
	0.2145	0.8330	- 0.2859	0.8129	0.7597	- 0.2784
	0.2897	0.8244	- 0.3530	0.9081	0.7470	- 0.1526
	0.4129	0.8099	- 0.4177	1.0000	0.7345	0.0000
	0.5130	0.7978	- 0.4364			
303.15	0.0000	0.8523	0.0000	0.6089	0.7811	- 0.4501
	0.0936	0.8421	- 0.1494	0.6835	0.7715	- 0.4013
	0.2145	0.8285	- 0.2971	0.8129	0.7546	- 0.2903
	0.2897	0.8198	- 0.3628	0.9081	0.7418	- 0.1594
	0.4129	0.8053	- 0.4487	1.0000	0.7292	0.0000
	0.5130	0.7930	- 0.4530			
308.15	0.0000	0.8479	0.0000	0.6089	0.7762	- 0.4724
	0.0936	0.8376	- 0.1515	0.6835	0.7666	- 0.4332
	0.2145	0.8240	- 0.3203	0.8129	0.7495	- 0.3054
	0.2897	0.8152	- 0.3834	0.9081	0.7366	- 0.1678
	0.4129	0.8006	- 0.4738	1.0000	0.7239	0.0000
	0.5130	0.7883	- 0.4931			

Table 5

VALUES OF PARAMETERS IN THE RANGE 288.15 – 308.15 K AND STANDARD DEVIATIONS FOR DENSITIES FOR PURE SUBSTANCES AND FOR THE BYNARY SYSTEMS MTBE + XYLENES[a]

MTBE			
A_i = 0.971345995	B_i = - 0.000538886	C_i = - 8.571428571 E-7	σ = 0.0041
o- xylene			
A_i = 1.125246	B_i = - 0.00084	C_i = - 6.369687763 E-19	σ = 8.8 E-9
m - xylene			
A_i = 1.116209	B_i = - 0.00086	C_i = - 6.369687763 E-19	σ = 8.9 E-9
p - xylene			
A_i = 1.090626665	B_i = - 0.000699629	C_i = - 2.857142857 E-7	σ = 0.0058
MTBE +*o*- xylene			
P_1 = - 0.02012	P_4 = - 0.11695	P_7 = - 0.02011	σ = 2.5 E-5
P_2 = 0.00015	P_5 = 0.00078	P_8 = 0.00015	
P_3 = - 3.9797 E-7	P_6 = -1.3005 E-6	P_9 = - 4.2003E-10	
MTBE +*m*- xylene			
P_1 = - 0.0198	P_4 = - 0.06199	P_7 = - 0.01988	σ = 3.0 E-5
P_2 = 0.00015	P_5 = 0.00041	P_8 = 0.00015	
P_3 = -3.8684E-7	P_6 = - 6.6658 E-7	P_9 = 1.2486E-9	
MTBE +*p*- xylene			
P_1 = 0.02248	P_4 = - 0.09182	P_7 = 0.00654	σ = 2.8 E-5
P_2 = - 0.00007	P_5 = 0.00061	P_8 = - 0.00008	
P_3 = 3.3391E-7	P_6 = - 1.0042 E -6	P_9 = - 9.507 E -10	

[a]Units: A_i, P_1, P_4, P_7, σ , g/cm^3; B_i, P_2, P_5, P_8, g/cm^{3}K; C_i, P_3, P_6, P_9, g/cm^{3}K^2;

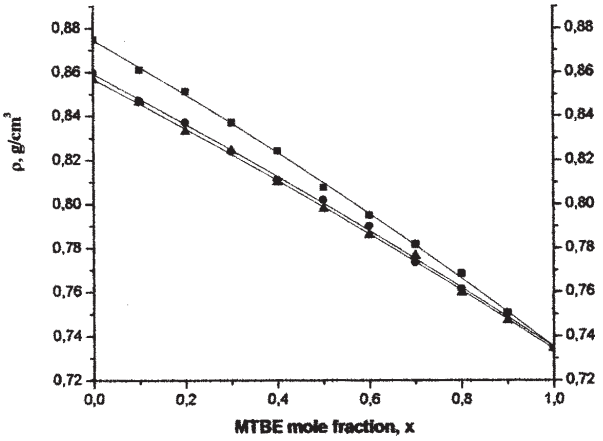

Fig. 1. Values for experimental densities ρ and fitting lines at 298.15 K for the systems ■, MTBE + *o*-xylene; ●, MTBE + *m*-xylene; ▲, MTBE + *p*-xylene

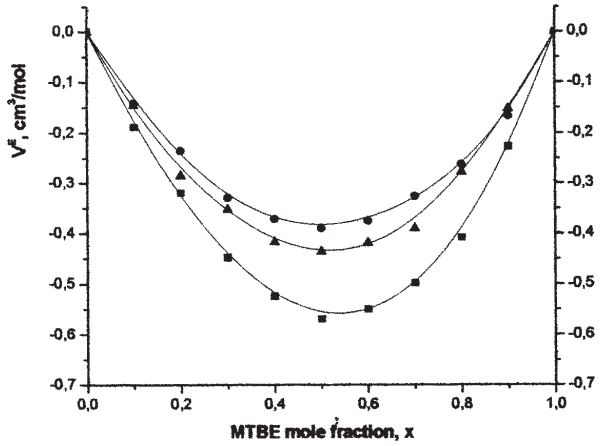

Fig. 2. Values for experimental molar excess volumes and fitting lines at 298.15 K for the systems ■, MTBE + *o*-xylene; ●, MTBE + *m*-xylene; ▲, MTBE + *p*-xylene

Table 6

VALUES OF A_i COEFFICIENTS (cm³/mol) OF EQ. (5) FOR EXCESS MOLAR VOLUMES AND STANDARD DEVIATIONS σ (cm³/mol) IN ACCORDANCE WITH EQ. (3) FOR MTBE + XYLENES SOLUTIONS AT DIFFERENT TEMPERATURES

Temperature, K	A_0	A_1	A_2	A_3	σ
		MTBE +	*o*-xylene		
288.15	- 2.00653	- 0.09379	0.03024	- 0.14498	0.0032
293.15	- 2.12382	- 0.06376	0.11674	- 0.18557	0.0122
298.15	- 2.26172	- 0.17484	0.07977	- 0.17542	0.0031
303.15	-2.38913	- 0.14927	0.02417	- 0.082	0.0032
308.15	- 2.51216	- 0.23657	0.00928	- 0.04492	0.0032
		MTBE +	*m*-xylene		
288.15	- 1.34508	- 0.01839	- 0.03976	-0.05731	0.0019
293.15	- 1.45595	- 0.12483	0.05626	0.11772	0.0045
298.15	- 1.5539	- 0.04833	- 0.02066	- 0.19879	0.0032
303.15	- 1.65932	- 0.07514	- 0.01302	0.03233	0.0045
308.15	- 1.74829	- 0.12309	- 0.12405	- 0.04671	0.0032
		MTBE +	*p*-xylene		
288.15	- 1.55462	- 0.03005	- 0.06716	- 0.07074	0.0022
293.15	- 1.65197	- 0.06059	- 0.00996	- 0.09552	0.0054
298.15	- 1.74279	- 0.12371	- 0.0595	0.0713	0.0019
303.15	- 1.83874	- 0.11845	0.02467	0.01765	0.0054
308.15	- 1.96735	- 0.12522	0.09328	0.00078	0.0032

Values of excess molar volumes V^E were obtained from densities using the relation (4):

$$V^E = [x_1M_1 + x_2M_2]/\rho - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (4)$$

where x_1 and x_2 are the mole fractions of the components, M_1 and M_2 are the corresponding molecular masses and ρ, ρ_1 and ρ_2 are densities of the solution and of the pure components, respectively. The V^E in the temperature interval of 288.15-308.15 K for each binary mixtures are also given in tables 2-4, over the complete range of concentrations. We notice that the results of this study are in close agreement with the works of Sharma and Kaur [8] with regard to the systems composed of MTBE with xylene at 303.15 K. The excess molar volumes are negative for all solutions studied in this work over the entire range of mole fractions and at all the temperatures. The negative excess volumes values can be assigned to the interactions between π ring electrons of xylenes and n electrons belonging to oxygen atoms of MTBE. The strength of n-π interactions follows the sequence *o*-xylene > *p*-xylene > m-xylene. When temperature increases excess molar volumes (in absolute values) also increase for all solutions studied in this work. This behaviour can be explained by more intense n- interactions at higher temperatures that produce a more efficient packing of molecules in the mixture than in the pure liquids. The values of V^E have been fitted to the Redlich-Kister [14] equation:

$$V^E = x(1-x)\sum_{i=0}^{i=3} A_i(2x-1)^i \quad (5)$$

to estimate the coefficients A_i by the method of least squares. The values of the coefficients A_i are listed in Table 6 together with the standard deviations σ calculated with equation (3). As an exemple, figure 2 shows experimental and calculated values of excess molar volumes at 298.15 K for all three systems.

Conclusions

The densities of the binary solutions MTBE + xylenes in the temperature range 288.15-308.15 K at atmospheric pressure over the whole composition range were correlated by means of a polynomial temperature dependence equation which gave a very good fit. The excess values of molar volume have been computed and fitted by using the Redlich-Kister equation. The obtained negative V^E values are interpreted in terms of molecular interactions between

π ring electrons of xylenes and n electrons of oxygen atoms in MTBE.

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