Influence of Temperature on the Densities of Binary Mixtures of Benzene with Methanol and Ethanol

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The densities of the binary mixtures benzene + methanol and benzene + ethanol have been measured at 288.15, 293.15, 298.15, 303.15, 308.15 K and atmospheric pressure over the whole composition range. The correlation of the density of these solutions with temperature and composition was performed with Emmerling et al. and Jouyban-Acree models. 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: density, excess volumes, benzene, methanol, ethanol

The present work is a part of our systematic studies on thermodynamic properties for mixtures of great interest in industry [1–7]. Benzene is an important constituent of petroleum compounds. The binary mixtures of benzene with alcohols present interest because these solutions exhibit molecular interactions and also are used in industry [8]. The present work reports densities for the Methanol + Bezene and Etahnol + Benzene binary systems 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 is only a report on the density measurements for the mixtures studied in this paper in the temperature range 288.15 – 313.15 K [9]. Reports on density and excess volumes for these mixtures are available only for one or two temperatures [10-18]. This article is aimed to improve correlation of the density of binary mixtures liquid with temperature and composition using two models.

Experimental part

All chemicals were purchased from Merck and were used without further purification. The purity (GC) was as follows: Benzene (> 99.7 %), methanol (> 99.8 %) and ethanol (> 99.9%). The chemicals were dried over molecular sieves (Fluka type 4 Å). 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 [19], the temperature of thermostatic water bath being controlled to ± 0.05 K.

Results and discussions

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

Densities and excess molar volumes of the binary mixtures of Benzene + alcohols are reported in tables 2 and 3.

The densities (ρ/gcm^{-3}) of the binary mixtures ALCOHOLS (x_1)+ BENZENE (x_2) were correlated with composition using eq. (1) proposed in [21]:

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

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

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

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 4 shows the fitting parameters A_i B_i, C_i, for the pure substances and P1 – P9 for the binary solutions BENZENE + ALCOHOLS.

The model Jouyban-Acree [22] was also tested for correlating the density of liquid mixtures at various temperatures. The proposed equation is:

$$ln\,\rho = x_1\,ln\rho_1 + x_2\,ln\,\rho_2 + x_1x_2\sum_{j=0}^{2}\left[\frac{J_j(x_1 - x_2)^j}{T}\right] \quad (3)$$

where ρ, ρ_i and ρ_2 is density of the mixture and pure compounds 1 and 2 at temperature *T*, respectively, x_1 and x_2 are the mole fraction, and J_j are the model constants.

Table1
COMPARISON OF EXPERIMENTAL DENSITIES OF PURE LIQUIDS WITH LITERATURE VALUES AT 298.15 K

Component	Density, g cm^{-3}	
	Experimental	Literature
Benzene	0.8739	0.873582 [9], 0.87362[10], 0.87364[17]
Methanol	0.7874	0.786694 [9], 0.78664[17], 0.78666[20]
Ethanol	0.7856	0.785164[9], 0.78525[10], 0.78508[14]

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Table 2
THE DENSITIES (ρ) AND MOLAR EXCESS VOLUMES (V^E) OF THE BINARY MIXTURES METHANOL (x_1) + BENZENE ($1- x_1$) 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	0.8847	0.000	0.6241	0.8470	-0.014
	0.0932	0.8806	0.019	0.7132	0.8381	-0.016
	0.2112	0.8750	0.011	0.7983	0.8282	-0.013
	0.3056	0.8699	0.006	0.9013	0.8139	-0.009
	0.4157	0.8631	0.004	1.0000	0.7966	0.000
	0.5019	0.8571	-0.006			
293.15	0.0000	0.8792	0.000	0.6241	0.8419	-0.014
	0.0932	0.8751	0.024	0.7132	0.8331	-0.017
	0.2112	0.8695	0.020	0.7983	0.8233	-0.014
	0.3056	0.8645	0.011	0.9013	0.8091	-0.008
	0.4157	0.8578	0.006	1.0000	0.7920	0.000
	0.5019	0.8519	-0.007			
298.15	0.0000	0.8739	0.000	0.6241	0.8369	-0.013
	0.0932	0.8698	0.028	0.7132	0.8281	-0.011
	0.2112	0.8642	0.029	0.7983	0.8184	-0.010
	0.3056	0.8592	0.022	0.9013	0.8044	-0.008
	0.4157	0.8526	0.014	1.0000	0.7874	0.000
	0.5019	0.8468	-0.003			
303.15	0.0000	0.8686	0.000	0.6241	0.8317	-0.009
	0.0932	0.8644	0.039	0.7132	0.8230	-0.012
	0.2112	0.8588	0.041	0.7983	0.8134	-0.014
	0.3056	0.8539	0.028	0.9013	0.7994	-0.008
	0.4157	0.8474	0.017	1.0000	0.7825	0.000
	0.5019	0.8415	0.005			
308.15	0.0000	0.8633	0.000	0.6241	0.8265	-0.004
	0.0932	0.8591	0.041	0.7132	0.8179	-0.011
	0.2112	0.8535	0.046	0.7983	0.8083	-0.011
	0.3056	0.8486	0.034	0.9013	0.7941	-0.007
	0.4157	0.8421	0.021	1.0000	0.7776	0.000
	0.5019	0.8363	0.007			

Table 3
THE DENSITIES (ρ) AND MOLAR EXCESS VOLUMES (V^E) OF THE BINARY MIXTURES ETHANOL (x_1) + BENZENE ($1- x_1$) 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	0.8847	0.000	0.5877	0.8413	-0.035
	0.1088	0.8774	0.062	0.7122	0.8292	-0.050
	0.1971	0.8714	0.073	0.8048	0.8192	-0.058
	0.2866	0.8652	0.056	0.9132	0.8060	-0.035
	0.4078	0.8563	0.023	1.0000	0.7941	0.000
	0.4969	0.8490	0.004			
293.15	0.0000	0.8792	0.000	0.5877	0.8364	-0.031
	0.1088	0.8719	0.073	0.7122	0.8244	-0.040
	0.1971	0.8660	0.083	0.8048	0.8146	-0.053
	0.2866	0.8599	0.065	0.9132	0.8016	-0.032
	0.4078	0.8511	0.034	1.0000	0.7899	0.000
	0.4969	0.8440	0.007			
298.15	0.0000	0.8739	0.000	0.5877	0.8315	-0.023
	0.1088	0.8660	0.080	0.7122	0.8196	-0.031
	0.1971	0.8608	0.092	0.8048	0.8099	-0.042
	0.2866	0.8547	0.074	0.9132	0.7971	-0.026
	0.4078	0.8460	0.044	1.0000	0.7856	0.000
	0.4969	0.8390	0.017			
303.15	0.0000	0.8686	0.000	0.5877	0.8266	-0.016
	0.1088	0.8613	0.089	0.7122	0.8148	-0.019
	0.1971	0.8555	0.102	0.8048	0.8052	-0.030
	0.2866	0.8496	0.080	0.9132	0.7926	-0.020
	0.4078	0.8409	0.053	1.0000	0.7813	0.000
	0.4969	0.8340	0.026			
308.15	0.0000	0.8633	0.000	0.5877	0.8158	-0.008
	0.1088	0.8551	0.090	0.7122	0.8026	-0.010
	0.1971	0.8486	0.111	0.8048	0.7918	-0.023
	0.2866	0.8418	0.085	0.9132	0.7779	-0.015
	0.4078	0.8320	0.063	1.0000	0.7771	0.000
	0.4969	0.8242	0.034			

The constants J_j were estimated using the experimental density data and a non-linear regression analysis employing the Levenberg-Marquardt algorithm. The values of the constants J_j are reported in table 4. The deviations between experimental (exp.) and calculated (calc.) values are shown as the standard deviation, σ, defined by:

$$\sigma = \left[\frac{\sum (X_{exp.} - X_{calc.})^2}{m-n} \right]^{1/2}, \qquad (4)$$

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 4 reveal that the

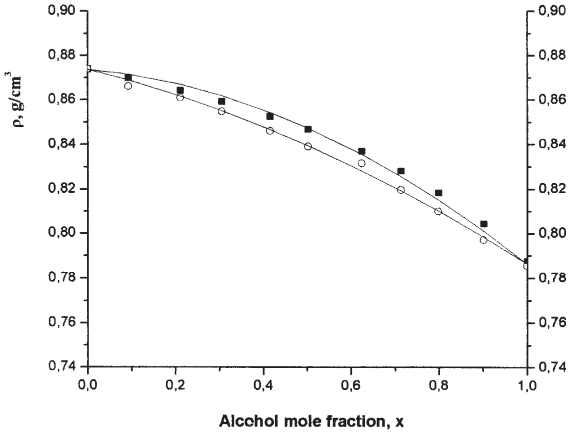

Fig. 1. Values for experimental densities ρ and fitting lines at 298.15 K for the systems ■, methanol + benzene; o, ethanol + benzene.

Table 4

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

	BENZENE		
A_i = 1.2939	B_i = - 0.00175	C_i = 1.1429 E-6	σ = 4.8 E-5
	METHANOL		
A_i = 0.84201	B_i = 0.00058	C_i = - 2.5714 E-6	σ = 5.1 E-5
	ETHANOL		
A_i = 0.95283	B_i = -0.00026	C_i = -1 E-6	σ = 2.2 E-5
	METHANOL +	BENZENE (Eq.1)	
P_1 = 0.01345	P_4 = - 0.17608	P_7 = 0.17607	σ = 2.5 E-3
P_2 = -0.00021	P_5 = 0.00083	P_8 = -0.00083	
P_3 = 1.0371 E-6	P_6 = -8.3788 E-7	P_9 = 1.0374 E-6	
	ETHANOL +	BENZENE (Eq.1)	
P_1 = -1.33391	P_4 = 5.33565	P_7 = -5.33564	σ = 2.0 E-3
P_2 = 0.00911	P_5 = -0.03642	P_8 = 0.03642	
P_3 = -0.00005	P_6 = 0.00005	P_9 = -0.00005	
	METHANOL +	BENZENE (Eq.3)	
	J_0 =8.8134		
	J_1 = - 8.80729	σ = 3.1 E-3	
	J_2 =8.8134		
	ETHANOL +	BENZENE (Eq.3)	
	J_0 =4.11325		
	J_1 = -4.06189	σ = 3.2 E-3	
	J_2 =4.0884		

[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;

calculated values of densities using eq. (1) are very good for pure compounds. It is observed also that 2.5 x 10^{-3} the standard deviation value for all binary systems is less than cm^3/mol for Emmerling et al. model and less than 3.2 x 10^{-3}cm^3/mol for Jouyban-Acree model.

Figure 1 shows experimental and calculated values (eq. (1) of density at 298.15 K constant temperature for all two systems.

Values of excess molar volumes V^E were obtained from densities using the relation (5):

$$V^E = [x_1 M_1 + x_2 M_2]/\rho - [x_1 M_1/\rho_1 + x_2 M_2/\rho_2] \quad (5)$$

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 excess volumes values V^E in the temperature interval of 288.15-308.15 K for each binary mixture are also given in tables 2-3, over the complete range of concentrations. The excess molar volumes are positive at lower mole fraction of alkanol and are negative at higher mole fraction of alcohol. The positive V^E values at lower concentrations of alkanol can be interpreted by the breaking of the hydrogen bonding in alcohol molecules during the mixing process. The major contribution to negative V^E values is attributed of more efficient packing in the mixture than in the pure liquids. The negative values of excess molar volumes show that hydrogen-bonding interactions prevail at higher alcohol concentration and that the benzene molecules are located in the structure created by hydrogen bonds. The interaction between the –OH group of an alcohol and π electrons of aromatic ring of benzene can contribute also to the negative values of V^E [9]. The effect of temperature on the V^E shows a systematic increase with temperature for all the mixtures. The experimental values of V^E for benzene-methanol system are smaller than the

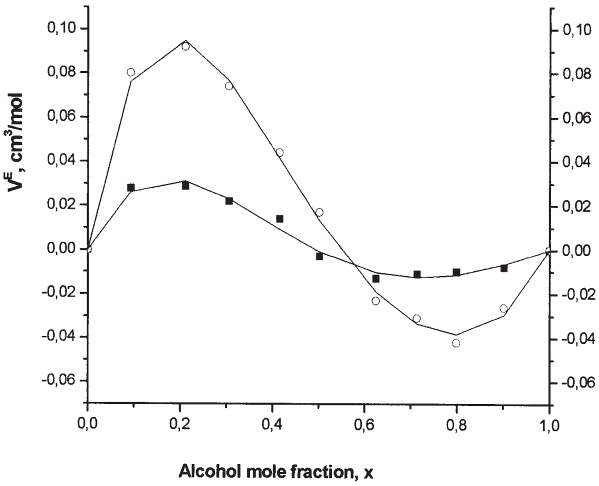

Fig. 2. Values for experimental molar excess volumes and fitting lines at 298.15 K for the systems ■, methanol + benzene; o, ethanol + benzene.

Table 5
VALUES OF A_i COEFFICIENTS (cm^3/mol) OF EQ. (5) FOR EXCESS MOLAR VOLUMES AND STANDARD DEVIATIONS σ (cm^3/mol) IN ACCORDANCE WITH EQ. (3) FOR BENZENE + ALCOHOLS SOLUTIONS AT DIFFERENT TEMPERATURES

Temperature, K	A_0	A_1	A_2	A_3	σ
		BENZENE +	METHANOL		
288.15	-0.0286	-0.12332	0.07994	-0.07293	0.0032
293.15	-0.02574	-0.16368	0.14742	-0.08057	0.0025
298.15	-0.00268	-0.20864	0.18287	-0.04249	0.0026
303.15	0.01376	-0.23109	0.22135	-0.16005	0.0021
308.15	0.02869	-0.24824	0.23786	-0.14757	0.0015
		BENZENE +	ETHANOL		
288.15	-0.01796	-0.61863	0.18558	-0.11536	0.0044
293.15	0.00602	-0.62568	0.26953	-0.16892	0.0044
298.15	0.04225	-0.62983	0.33158	-0.15008	0.0044
303.15	0.0739	-0.60052	0.42134	-0.20556	0.0063
308.15	0.10869	-0.60513	0.43879	-0.16623	0.0070

values of V^E for benzen-ethanol mixture. We notice that the results of this study are in close agreement with the works of Šerbanović et al. [9].

The values of V^E have been fitted to the Redlich-Kister [23] equation:

$$V^E = x(1-x)\sum_{i=0}^{i=3} A_i(2x-1)^i \tag{6}$$

to estimate the coefficients A_i by the method of least squares. The values of the coefficients A_i are listed in table 5 together with the standard deviations σ calculated with eq. (4). As an exemple, figure 2 shows experimental and calculated values of excess molar volumes at 298.15 K for all two systems.

Conclusions

The densities of the binary solutions benzene + methanol and bezene+ethanol in the temperature range 288.15-308.15 K at atmospheric pressure over the whole composition range were correlated by means of Emmerling et al. and Jouyban-Acree temperature dependence equations. The proposed models provide reasonably accurate calculations for the density of binary liquids mixtures analyzed in this work at various temperatures. The model Jouyban-Acree and also the model proposed by Emmerling et al. could be used in data modeling. The excess values of molar volume have been computed and fitted by using the Redlich-Kister equation.

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