MOLAR EXCESS VOLUMES OF BINARY SOLUTIONS OF TOLUENE WITH C_3 - C_4 ALKANOLS

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abstract: Excess molar volumes, V^E, of mixtures of toluene + propane-2-ol, methyl-2-propane-1-ol, butane-2-ol and propane-1-ol were determined from density measurements at 20, 25, 30 and 35ºC, respectively. The V^E is positive over the entire composition range for all mixtures, with the exception of toluene + propane-1-ol system, where the V^E is negative at low toluene mole fractions. The experimental excess molar volumes were correlated by means of the Redlich - Kister equation.

Introduction

The thermodynamic and transportation macroscopic properties of liquid mixtures are the reflection of the intermolecular forces and microscopic structure of the liquids, too. It is very important to know some of the physic properties like density, refractive index, viscosity or dielectric constant, for a better understanding of the interaction between different molecules existing in the liquid solutions. The variations of these properties with concentration give important informations about intermolecular interactions and solvent structure.

It has been made some research regarding thermodynamic properties of these systems for understanding physical-chemical behavior of binary mixtures alkanol-aromatic hydrocarbons [1÷4].

There are a small number of studies regarding physical-chemical properties of the aromatic hydrocarbons and the isomers of alkanol [5,6].

In this paper it has been studied some of the physical properties of the C_3-C_4 alcohols in toluene to obtain new information about the nature of these solutions. In this purpose, density and molar volume have been determined at 293.15÷308.15 K.

Experimental

High purity chemicals (BDH) were employed. All the substances have been dried on the molecular sieves (Fluka 4 Å) before using. The substances purity has been verified by

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density, viscosity and refractive index measurement. The experimental data (density, refractive index) was analyzed comparing with theoretical data obtained from literature, regarding the reactive used in this research and there are presented in the Table 1.

The solutions (propane-1-ol, methyl-2-propane-1-ol, butane-2-ol and propane-2-ol in toluene) have been prepared by weighing at analytical balance and preserved in well-closed bottles. It has been prepared five different concentrations for each system, having molar fraction between 0.16 and 0.80. The pure substances and the solutions density have been determined by hydrostatic method (Mohr - Westphal balance) with an apparatus having a float and an analytical balance made in physical-chemistry laboratory [12÷14].

The precision of density determinations was ± 0.00005 g/cm^3. The refractive index has been determined at 20 and 25°C with Abbe refractometer (D sodium line).

Table 1. Pure substance properties comparing with dates from literature.

Substance	*t*,°C	Density, g/cm^3		Refractive index	
		Obs.	Lit.	Obs.	Lit.
toluene	20	0.8617			
	25	0.8589		1.4918	1.4941[11)]
	30	0.8554	0.8569[7)]		
	35	0.8526			
propane-1-ol	20	0.7996			
	25	0.7972	0.7996[8)]	1.3820	1.3832[9)]
	30	0.7939			
	35	0.7921	0.79158[8)]		
methyl-2-propane-1-ol	20	0.7971		1.3953	1.3955[10)]
	25	0.7950	0.79780[8)]		
	30	0.7919			
	35	0.7902	0.7902[8)]		
butane-2-ol	20	0.8025			
	25	0.7994	0.8024[8)]	1.3943	1.3853[8)]
	30	0.7961			
	35	0.7937			
propane-2-ol	20	0.7808		1.3769	1.3776[10)]
	25	0.7782	0.78126[8)]		
	30	0.7751			
	35	0.7726			

Results and discussions

The molar excess volume V^E (the difference between real volume V^R and ideal volume $V^{id.}$) was calculated with the following equation:

$$V^E = \frac{xM_1 + (1-x)M_2}{\rho} - \left[\frac{xM_1}{\rho_1} + \frac{(1-x)M_2}{\rho_2}\right] \quad (1)$$

where x and (1-x) represent the molar fraction of the component 1, 2 respectively; $\rho_{1,\,2}$ – the density of the pure component 1, 2 respectively; $M_{1,\,2}$ – the molar mass of the components.

The density and excess volumes values of the toluene in C_3-C_4 alcohols solutions have been studied at 20÷35°C and the results are shown in the Table 2-5. Figs. 1 and 2 show the variation of the density with the temperature for the pure substances and equimolar solutions of alcohols in toluene, respectively. In this figures there are the equations and corresponding correlation coefficients, too.

The table and the figures lead to the following observations:

1- there is a good conformity between the experimental and tabular densities and the refractive index for the majority of the substances, having the relative error 0.38% maximum;

2- the pure components densities vary in this order:

$\rho_{\text{toluene}} > \rho_{\text{-butane-2-ol}} > \rho_{\text{-propane-1-ol}} > \rho_{\text{-methyl-2-propane-1-ol}} > \rho_{\text{-propane-2-ol}}$

3- the density of the pure substances and of the all analyzed solutions have a linear decrease with the temperature enhance (Figs. 1, 2);

4- the solutions density increase with the toluene concentration enhance, at the constant temperature, for all hydrocarbons-alcohol systems;

5- the results of this study are in conformity with the data published by Nikam [5] for the toluene + propan-1-ol system. It hasn't been found published data for the other studied solutions to verify them;

6- the following mixtures: toluene + propane-2-ol and methyl-2-propane-1-ol + butane-2-ol, have positive values for the molar excess volume in the whole concentration and temperature studied domain;

7- the molar excess volume of toluene + propane-1-ol has positive value for small concentrations and negative value for bigger alcohol concentrations;

8- the molar excess volume increase with the enhance of the temperatures.

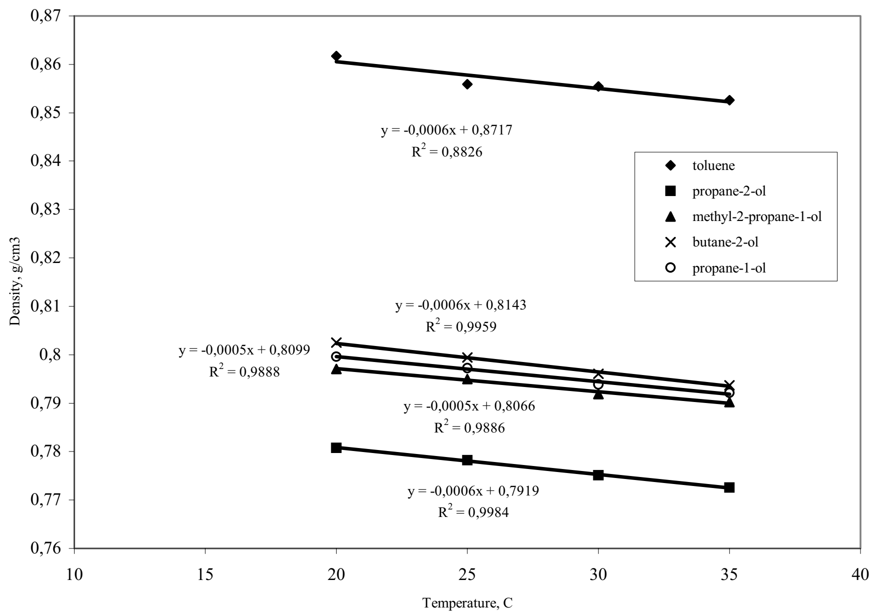

Fig. 1: *The variation of pure substances densities with temperature.*

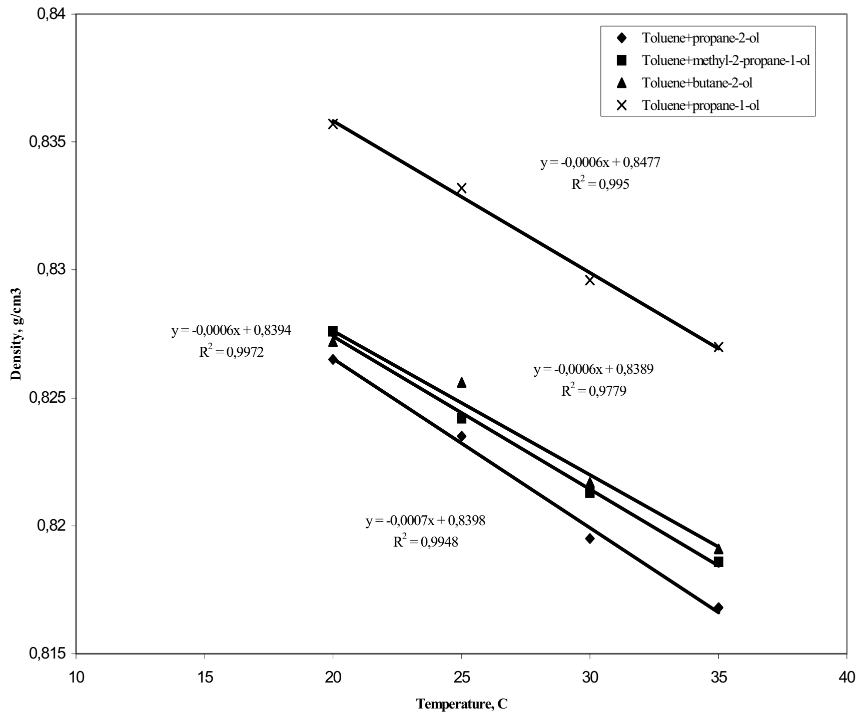

Fig. 2: *The variation of the equimolar solutions densities of toluene in alcohols with temperature.*

The positive values of molar excess volume in dilute solution are caused by the hydrogen bonds breaking between the alcohol molecules and unfavorable interactions between the components molecules. The negative excess volumes in the concentrated alcohol solutions could be explained if they are considered to be the results of the: a) structural contribution; b) alkanes molecules locating in the ramified interstitials structures of the associated alcohol molecules; c) alcohol molecules auto-associations by hydrogen bonds.

The molar excess volumes values were associated with polynomial equation Redlich-Kister type [15]:

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

where x and (1-x), respectively, represent the molar fraction of the components; A_i - the polynomial equation coefficients. The values of A_i coefficients have been calculated with a computerized program and the results are shown in Table 6.

The standard deviation, σ, has been calculated with the following equation:

$$\sigma = \left[\frac{\sum(V^E_{\text{exp.}} - V^E_{\text{calc.}})^2}{m-n}\right]^{1/2} \qquad (3)$$

where m is the number of experimental points; n - the number of A_i estimated coefficients.

Table 2. The densities and molar volumes of the toluene and propane-2-ol (x) solutions.

t, ºC	x	ρ, g/cm^3	V^R, cm^3/mol	$V^{id.}$ cm^3/mol	V^E cm^3/mol
20	0.0000	0.8617	106.917	106.917	0.000
	0.2038	0.8477	100.982	100.814	0.168
	0.3880	0.8358	95.361	95.298	0.062
	0.5004	0.8265	92.078	91.933	0.145
	0.5990	0.8175	89.228	88.980	0.248
	0.8013	0.8015	82.925	82.922	0.003
	1.000	0.7808	76.972	76.972	0.000
25	0.0000	0.8559	107.265	107.265	0.000
	0.2038	0.8451	101.293	101.144	0.149
	0.3880	0.8327	95.716	95.611	0.104
	0.5004	0.8235	92.413	92.235	0.178
	0.5990	0.8159	89.403	89.274	0.129
	0.8013	0.7985	83.237	83.198	0.039
	1.000	0.7782	77.230	77.230	0.000
30	0.0000	0.8554	107.704	107.704	0.000
	0.2038	0.8416	101.714	101.556	0.158
	0.3880	0.8291	96.131	95.999	0.132
	0.5004	0.8195	92.864	92.609	0.255
	0.5990	0.8122	89.810	89.635	0.176
	0.8013	0.7994	83.615	83.520	0.094
	1.000	0.7751	77.538	77.538	0.000
35	0.0000	0.8526	108.058	108.058	0.000
	0.2038	0.8393	101.993	101.889	0.104
	0.3880	0.8268	96.399	96.314	0.085
	0.5004	0.8168	93.171	92.911	0.260
	0.5990	0.8094	90.121	89.927	0.194
	0.8013	0.7922	83.899	83.804	0.095
	1.000	0.7726	77.789	77.789	0.000

Table 3. The densities and molar volumes of the toluene and methyl-2 propane-1-ol (x) solutions.

t, ºC	*x*	ρ, g/cm^3	V^R cm^3/mol	$V^{id.}$ cm^3/mol	V^E cm^3/mol
	0.0000	0.8617	106.917	106.917	0.000
	0.1691	0.8517	104.596	104.561	0.035
	0.3511	0.8406	102.078	102.026	0.052
20	0.4499	0.8336	100.801	100.650	0.151
	0.5548	0.8276	99.249	99.189	0.060
	0.7658	0.8146	96.167	96.249	-0.082
	1.0000	0.7971	92.987	92.987	0.000
	0.0000	0.8589	107.265	107.265	0.000
	0.1691	0.8489	104.941	104.892	0.049
	0.3511	0.8368	102.542	102.338	0.203
25	0.4499	0.8305	101.177	100.952	0.225
	0.5548	0.8242	99.658	99.480	0.178
	0.7658	0.8114	96.547	96.519	0.028
	1.0000	0.7950	93.233	93.233	0.000
	0.0000	0.8554	107.704	107.704	0.000
	0.1691	0.8449	105.438	105.319	0.119
	0.3511	0.8324	103.084	102.751	0.332
30	0.4499	0.8271	101.593	101.358	0.235
	0.5548	0.8213	100.010	99.878	0.132
	0.7658	0.8079	96.965	96.901	0.063
	1.0000	0.7919	93.598	93.598	0.000
	0.0000	0.8526	108.058	108.058	0.000
	0.1691	0.8424	105.751	105.647	0.104
	0.3511	0.8308	103.282	103.052	0.231
35	0.4499	0.8242	101.950	101.643	0.307
	0.5548	0.8186	100.340	100.147	0.193
	0.7658	0.8058	97.218	97.138	0.079
	1.0000	0.7902	93.799	93.799	0.000

Table 4. The densities and molar volumes of the toluene and butane-2-ol (x) solutions.

t, ºC	*x*	ρ, g/cm^3	V^R, cm^3/mol	$V^{id.}$ cm^3/mol	V^E cm^3/mol
	0.0000	0.8617	106.917	106.917	0.000
	0.1705	0.8505	104.714	104.435	0.279
	0.3496	0.8401	102.171	101.828	0.343
20	0.4474	0.8345	100.746	100.405	0.351
	0.5492	0.8272	99.418	98.923	0.496
	0.7663	0.8163	95.956	95.763	0.193
	1.0000	0.8025	92.361	92.361	0.000
	0.0000	0.8589	107.265	107.265	0.000
	0.1705	0.8475	105.085	104.785	0.300
	0.3496	0.8369	102.562	102.180	0.382
25	0.4474	0.8318	101.073	100.757	0.315
	0.5492	0.8256	99.611	99.277	0.334
	0.7663	0.8133	96.310	96.119	0.191
	1.0000	0.7994	92.720	92.720	0.000
	0.0000	0.8554	107.704	107.704	0.000
	0.1705	0.8431	105.633	105.215	0.481
	0.3496	0.8329	103.054	102.600	0.454
30	0.4474	0.8286	101.463	101.172	0.291
	0.5492	0.8217	100.084	99.686	0.398
	0.7663	08102	96.679	96.516	0.163
	1.0000	0.7961	93.104	93.104	0.000

Table 4. ***Continued***

T, ºC	*x*	ρ, g/cm^3	V^R, cm^3/mol	$V^{id.}$ cm^3/mol	V^E cm^3/mol
	0.0000	0.8526	108.058	108.058	0.000
	0.1705	0.8413	105.859	105.556	0.303
	0.3496	0.8305	103.352	102.928	0.424
35	0.4474	0.8243	101.992	101.493	0.499
	0.5492	0.8191	100.402	100.000	0.402
	0.7663	0.8072	97.038	96.814	0.224
	1.0000	0.7937	93.385	93.385	0.000

Table 5. The densities and molar volumes of the toluene and propane-1-ol (x) solutions.

t, ºC	*x*	ρ, g/cm^3	V^R, cm^3/mol	$V^{id.}$ cm^3/mol	V^E cm^3/mol
	0.0000	0.8617	106.917	106.917	0.000
	0.2447	0.8499	99.179	99.146	0.033
	0.5066	0.8357	90.826	90.830	-0.004
20	0.6341	0.8280	86.739	86.781	-0.043
	0.7541	0.8196	82.938	82.971	-0.033
	0.7986	0.8194	81.219	81.558	-0.339
	1.0000	0.7996	75.163	75.163	0.000
	0.0000	0.8589	107.265	107.265	0.000
	0.2447	0.8468	99.542	99.465	0.0077
	0.5066	0.8332	91.099	91.117	-0.018
25	0.6341	0.8251	87.044	87.052	-0.009
	0.7541	0.8170	83.202	83.227	-0.025
	0.7986	0.8164	81.517	81.809	-0.291
	1.0000	0.7972	75.389	75.389	0.000
	0.0000	0.8554	107.704	107.704	0.000
	0.2447	0.8427	100.027	99.873	0.153
	0.5066	0.8296	91.494	91.492	0.002
30	0.6341	0.8224	87.330	87.412	-0.082
	0.7541	0.8138	83.529	83.572	-0.042
	0.7986	0.8135	81.808	82.147	-0.340
	1.0000	0.7939	75.702	75.702	0.000
	0.0000	0.8526	108.058	108.058	0.000
	0.2447	0.8409	100.241	100.182	0.058
	0.5066	0.8270	91.782	91.754	0.028
35	0.6341	0.8189	87.703	87.650	0.053
	0.7541	0.8110	83.818	83.788	0.029
	0.7986	0.8109	82.070	82.356	-0.286
	0.0000	0.7921	75.874	75.874	0.000

Table 6. The A_i coefficients and standard deviations, σ, of the molar excess volume V^E (cm^3/mol), according to the 4th equation, at different temperatures.

t, °C	A_0	A_1	A_2	σ
Propane-2-ol (x) + toluene (1-x)				
20	0.63770	-0.27317	-0.32655	0.084
25	0.57548	-0.38653	-0.05795	0.034
30	0.79475	-0.15343	-0.15565	0.044
35	0.78096	0.21081	-0.60198	0.055
Methyl-2- propane-1-ol (x) + toluene (1-x)				
20	0.37375	-0.68493	-1,.59126	0.034
25	0.85673	-0.46343	-1.72733	0.011
30	0.89344	-0.91969	-0.74137	0.057
35	1.02011	-0.50870	-1.31253	0.031

Table 6. *Continued.*

t, °C	A_0	A_1	A_2	σ
		Butane-2-ol (x) + toluene (1-x)		
20	1.63092	-0.40571	-0.51418	0.069
25	1.32178	-0.77854	0.66160	0.022
30	1.35171	-1.57785	1.94530	0.068
35	1.78487	-0.78403	-0.45947	0.025
		Propane-1-ol (x) + toluene (1-x)		
20	0.17972	-1.03223	-2.31931	0.100
25	0.15447	-0.72109	-2.16812	0.091
30	0.69369	-0.00588	-0.43588	0.020
35	0.69369	-0.00588	-0.43588	0.078

Conclusion

It has been determined the densities and molar excess volumes for four systems containing toluene and C_3-C_4 at different temperatures, in the whole domain of concentrations.

The molar excess volumes are positives for all investigated systems, excepting toluene solutions in propane-1-ol, at bigger alcohol concentration.

The molar excess volumes have been correlated with Redlich-Kister polynomial equations.

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