

Review

Excess parameters of binary and ternary mixtures of {1-Butanol + hexylamine + *n*-heptane} at different temperatures and comparison with the Flory theory

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In this work, we calculated α (thermal expansion coefficients), α^E (excess thermal expansion coefficients) and $(\partial H_m^E / \partial P)_T$ (isothermal coefficient of pressure excess molar enthalpy) for the binary and ternary mixtures of {1-butanol + hexylamine + *n*-heptane} from experimental densities (Djordjevic et al., 2010) at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K. The trends of α^E and $(\partial H_m^E / \partial P)_T$ for the binary mixture 1-butanol + hexylamine are S-shaped dependence on composition, and for the binary mixture 1-butanol + *n*-heptane the trends of α^E and $(\partial H_m^E / \partial P)_T$ are positive and negative, respectively over the mole fraction range. For the binary mixture of hexylamine + *n*-heptane, the trends of α^E and $(\partial H_m^E / \partial P)_T$ are negative and S-shaped, respectively. The values of α^E and $(\partial H_m^E / \partial P)_T$ of binary mixtures were correlated as a function of the mole fraction by using the Redlich-Kister equation and the ternary mixture was fitted by using the Cibulka equation. By using Flory theory, we calculated the values of α^E and $(\partial H_m^E / \partial P)_T$ at different temperature; the results show a good agreement between Flory theory and experimental data.

Key words: Thermal expansion coefficients, excess thermal expansion coefficients, isothermal coefficient of pressure excess molar enthalpy, Flory.

INTRODUCTION

Research activities of our laboratory comprise, among others, the systematic measurements of volumetric properties of different groups of organic compounds (Rezaei-Sameti et al., 2010; Rezaei-Sameti et al., 2009, 2010; Iloukhani and Rakhshi, 2009). Thermodynamic properties of liquid mixtures can be utilized to extract information about the existence of molecular interactions among the constituents of mixtures. Knowledge of thermodynamic properties is essential for the proper design of industrial processes, chemical engineering and also for optimizing thermodynamic model/theories development. In this work, we used the experimental

densities ρ of Djordjevic et al. (2010) for the binary systems formed by {1-butanol + hexylamine and + *n*-heptane} and {hexylamine + *n*-heptane} and ternary system of {1-butanol + hexylamine + *n*-heptane} at (288.15 to 323.15) K for the liquid region at ambient pressure for the whole composition range.

The excess parameters of these mixtures such as α , α^E (and $(\partial H_m^E / \partial P)_T$) were calculated. These excess parameters in combination with other mixing properties provide valuable information for qualitatively analyzing the molecular interactions between molecules. The α^E , $(\partial H_m^E / \partial P)_T$, of binary mixtures have been fitted to the Redlich and Kister (1948) and ternary mixtures have been fitted to the Cibulka (1982), equation to determine the coefficients.

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Table 1. Coefficient a_i of Equation 1 for the fits of the pure components densities.

Component	a_0	a_1	a_2	a_3	a_4
1-butanol	-0.39031	0.01821	-0.00009	2.1210×10^{-7}	-1.7878×10^{-7}
hexylamine	1.68242	-0.00962	0.00004	-9.2367×10^{-8}	7.4242×10^{-11}
<i>n</i> -heptane	1.71220	-0.01110	0.00005	-1.08234×10^{-7}	8.6363×10^{-11}

Table 2. Coefficient B_i of Cibulka (1982) equation of α^E and $(\partial H_m^E / \partial P)_{T,x}$ for ternary mixture 1-butanol + hexylamine + *n*-heptane.

$T/(K)$	B_0	B_1	B_2
	α_{123}^E / K^{-1}		
288.15	-0.066	0.076	0.058
323.15	-0.071	$0.079 (\partial H / \partial P)_{T,P,x} / JPa.s^{-1}$	0.068
288.15	21.058	-101.181	45.193
323.15	38.702	-3.794	-146.420

RESULTS AND DISCUSSION

Thermal expansion coefficient and their excess values

The temperature dependence of density of the pure components was fitted to the equation:

$$\rho(T) / g.cm^3 = \sum_{i=0}^4 a_i T^i \quad (1)$$

The parameters a_i , for the pure components are listed in Table 1. The thermal expansion coefficient, α , as in the case of pure components was obtained by analytical differentiation of the density fitting equation:

$$\alpha = -\rho^{-1} (\partial \rho / \partial T)_P \quad (2)$$

The thermal expansion coefficients of pure components at different temperature are presented in Table 2. The average uncertainty in the thermal expansion coefficient is estimated to be 5.10^{-6} K.

The basic expression relating the thermal expansion coefficient is:

$$\alpha = V^{-1} \left[(\partial V_m^E / \partial T)_{P,x_i} + \sum_{i=1}^N \alpha_i x_i V_i \right] \quad (3)$$

Where α and α_i are the thermal expansion coefficient of the mixture and a pure component, respectively. From this expression, the excess thermal expansion coefficient can be rewritten as:

$$\alpha^E = \alpha - \sum_{i=1}^n \phi_i \alpha_i \quad (4)$$

Where

$$\phi_i = x_i V_i / \sum_{i=1}^2 x_i V_i \quad (5)$$

And ϕ_i is the volumetric fraction of the components of the mixture. This property can be described as the variation of density with temperature due to the non ideality of the mixture. The thermal expansion coefficient (α) and excess thermal expansion coefficient (α^E) are for all binary and ternary mixtures calculated and results graphically represented in Figure 1.

The α^E values for binary mixture of 1-butanol + hexylamine are negative over the entire concentration range. Negative values of α^E are due to hydrogen bonding of components in the mixtures. The excess thermal expansion coefficients α^E , are positive over the mole fraction range for binary mixture of 1-butanol + *n*-heptane and increase with increasing temperatures from (288.15 to 323.15) K. Positive values of α^E due to self-association of components in the mixtures, and the components of mixture are strongly associated in the pure state and in mixtures. The α^E amount may reflect the molecular orientation and packing of mixtures. Molecular orientation effects are ascribed to shapes of molecules for no polar solvents and dipole moments, higher multi pole moments, and special interactions such as hydrogen bonds for polar solvents. In the binary

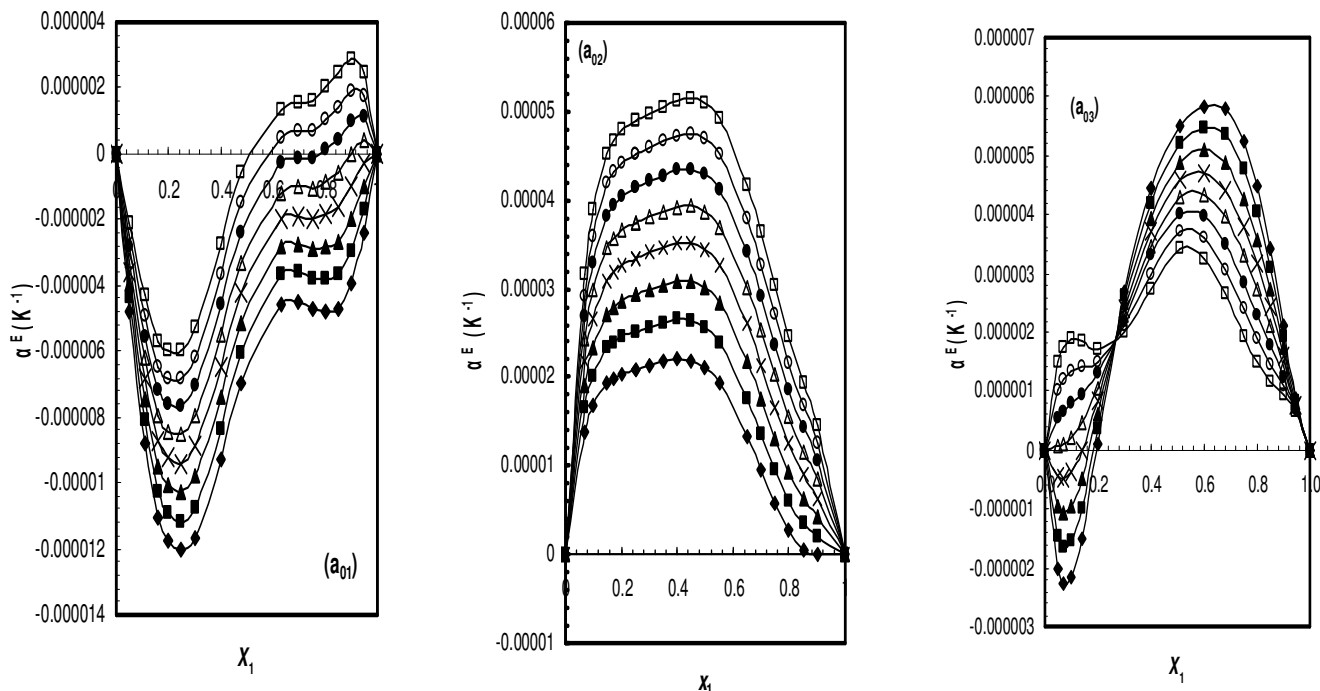


Figure 1. Plot of excess thermal expansion coefficients α^E against mole fraction for $\{(a_{01}); 1\text{-butanol} + \text{hexylamine}, (a_{02}); 1\text{-butanol} + n\text{-heptane}, (a_{03}); \text{hexylamine} + n\text{-heptane}\}$ at 288.15 K (■), 293.15 K (□), 298.15 K (●), 303.15 K (○), 308.15 K (▲), 313.15 K (△), 318.15 K (◇), 323.15 K (◆).

mixture of hexylamine + *n*-heptane the α^E values are S-shape and decrease with increasing temperatures from (288.15 to 323.15) K. The α_{123}^E values for the ternary system {1-butanol (1) + hexylamine (2) + *n*-heptane (3)} are calculated.

The dependence of α_{123}^E values of ternary mixtures on the composition is expressed by Cibulka (1982):

$$Y_{123} = Y_{bin} + x_1 x_2 (1 - x_1 - x_2) (B_0 + B_1 x_1 + B_2 x_2) \quad (6)$$

Where $Y \equiv \alpha^E, \text{ or } \left(\frac{\partial H}{\partial p}\right)_T$ and $Y_{bin} = Y_{12} + Y_{13} + Y_{23}$

known as the binary contribution to the excess thermal expansion coefficients $\alpha^E, \text{ or } \left(\frac{\partial H}{\partial p}\right)_T$ are given by the

Redlich–Kister, x_1 , x_2 and x_3 are mole fractions of component, respectively. The coefficients, B_p Equation 6 are obtained by the least-squares method and given in Table 2.

Figure 2 shows the curves of constant α_{123}^E for the ternary system {1-butanol (1) + hexylamine (2) + *n*-heptane (3)} at 288.15 K. The lines present results calculated by Cibulka (1982) as functions of mole fraction composition of ternary system.

Isothermal coefficient of pressure excess molar enthalpy

The isothermal coefficient of pressure excess molar enthalpy can be derived accurately from volumetric measurements by application of the following expression:

$$\left(\frac{\partial H_m^E}{\partial p}\right)_T = V_m^E - T \left(\frac{\partial V_m^E}{\partial T}\right)_p \quad (7)$$

This quantity represents the dependence of the excess molar enthalpy of mixing with pressure at fixed composition and temperature.

The isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial p)_{T,x}$ for all binary and ternary mixtures calculated and results graphically represented in Figure 3. The isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial p)_T$ for the binary mixtures {1-butanol + hexylamine} and {1-butanol + *n*-heptane} are negative over the mole fraction range and decrease with increasing temperatures from (288.15 to 323.15)K, and S-shaped for binary mixture of {hexylamine + *n*-heptane} and increase with increasing temperatures from (288.15 to 323.15)K. The results are given in supplementary data.

Negative values of $(\partial H_m^E / \partial p)_T$ are due to the presence of significant interactions between 1-butanol, hexylamine and *n*-heptane in these mixtures. With increasing

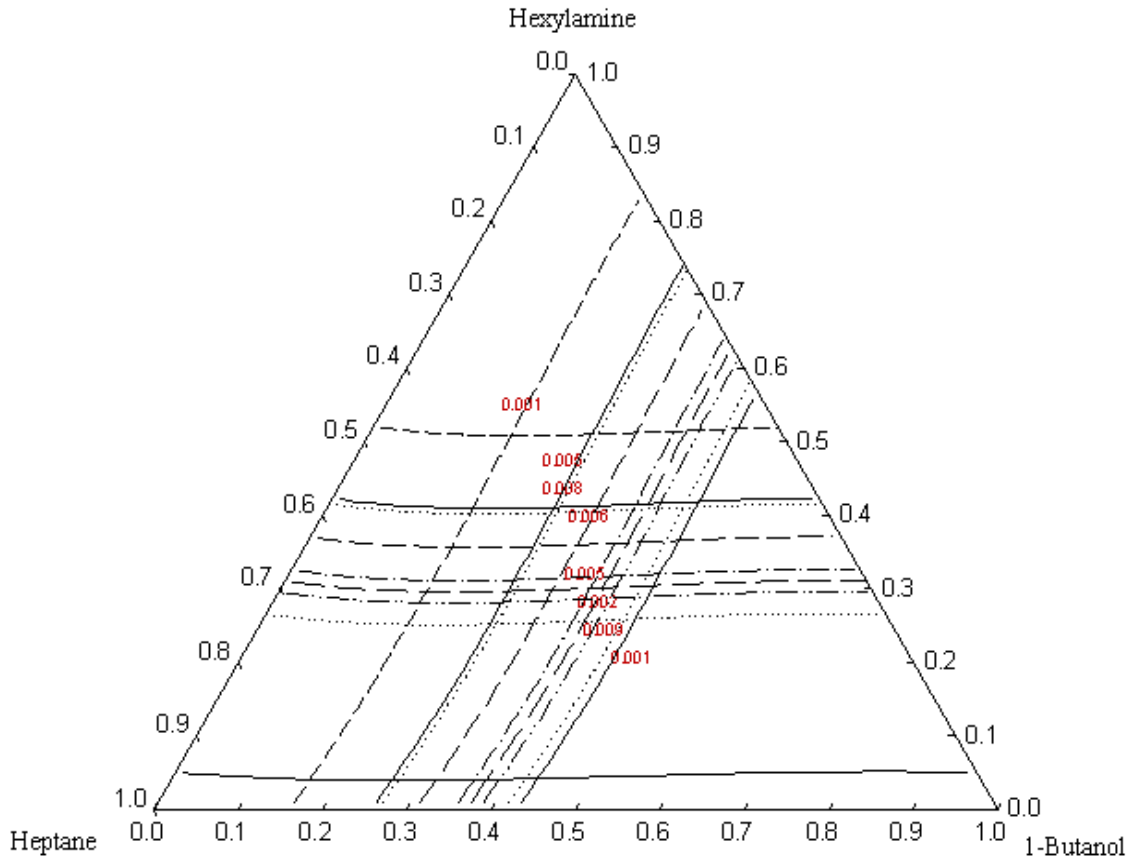


Figure 2. Isoline curves of α_{123}^E , for the ternary system 1-butanol (1) + hexylamine (2) + n-heptane (3), at 288.15 K. The lines present results calculated by Cibulka (1982), equation.

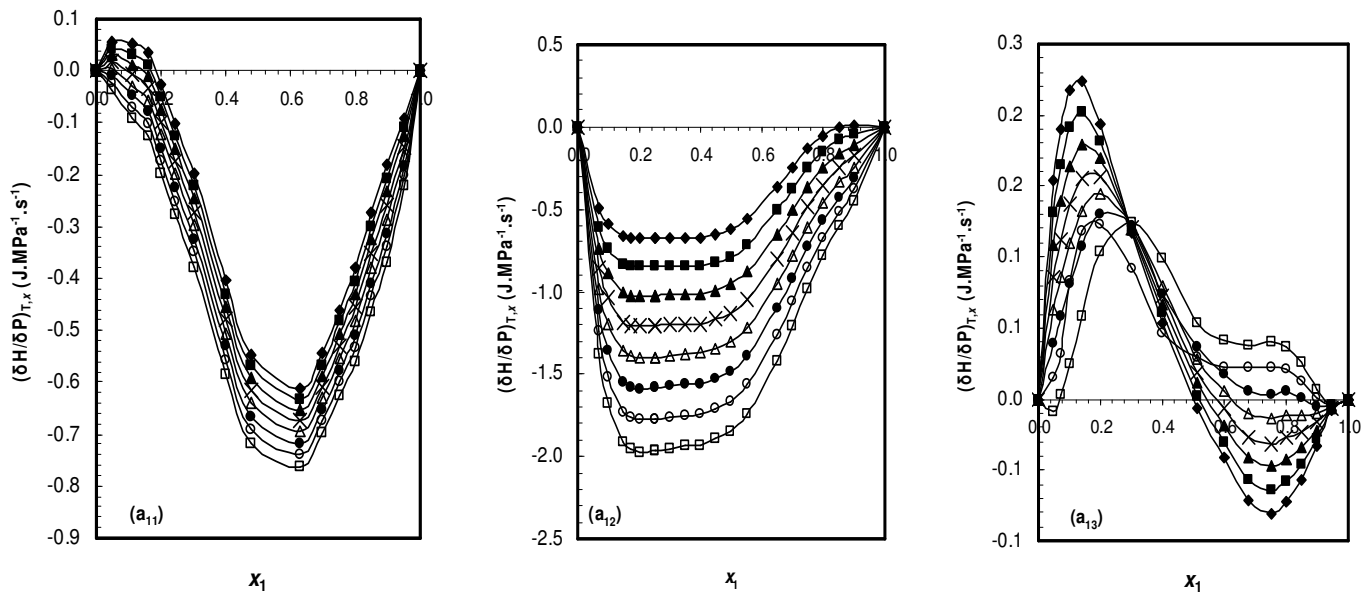


Figure 3. Plot of isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_T$, against mole fraction for $\{(a_{11})$; 1-butanol + hexylamine, (a_{12}) ; 1-butanol + *n*-heptane, (a_{13}) ; hexylamine + *n*-heptane $\}$ at 288.15 K (\blacklozenge), 293.15 K (\blacksquare), 298.15 K (\blacktriangle), 303.15 K (\times), 308.15 K (Δ), 313.15 K (\bullet), 318.15 K (\circ), 323.15 K (\square).

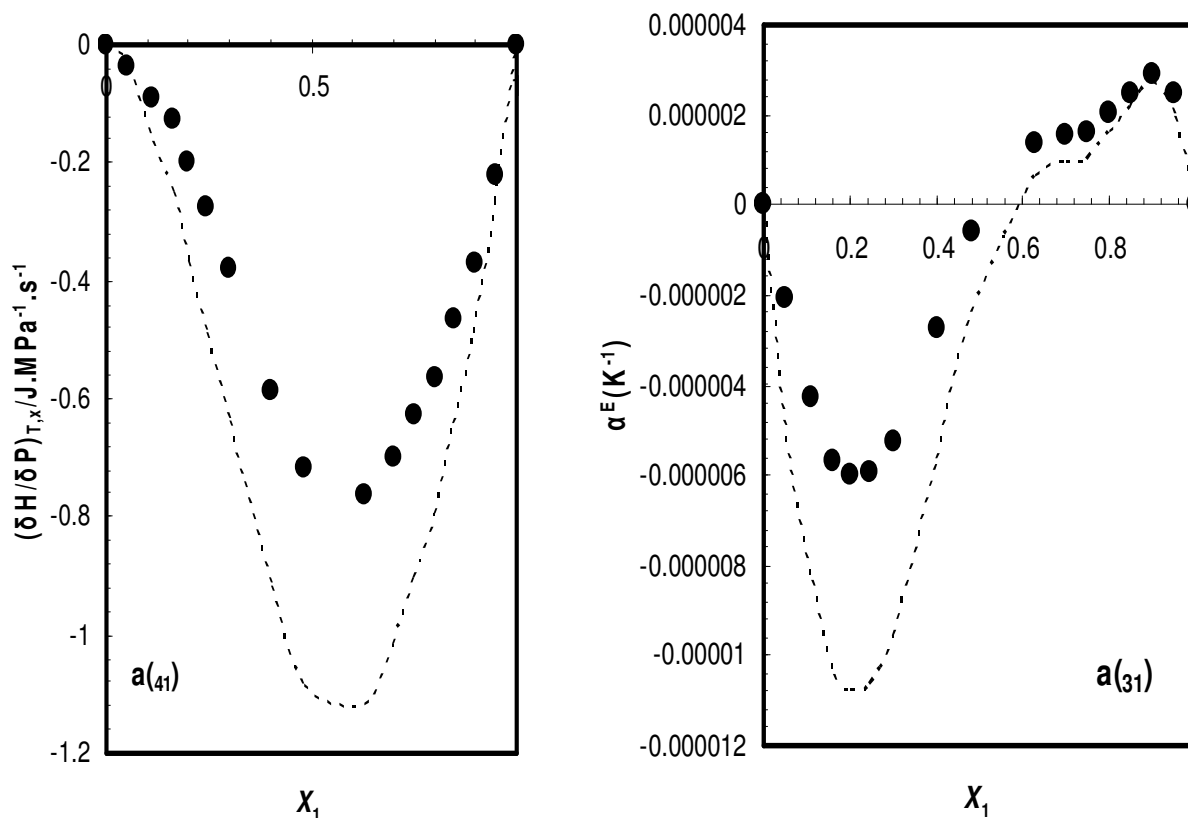


Figure 4. Plot of α^E , and $(\partial H_m^E / \partial P)_T$ against mole fraction for {1-butanol + hexylamine, 323.15 K. (o) Experimental; calculated by using Flory theory.

temperature the interactions of molecular mixtures increased and so the values of $(\partial H_m^E / \partial P)_T$ are more negative.

Figure 4 shows the curves of constant $(\partial H_m^E / \partial P)_T$, for the ternary system {1-butanol (1) + hexylamine (2) + n-heptane (2)} at 288.15 and 323.15 K. The lines present results are calculated by Cibulka (1982) as functions of mole fraction composition of ternary system.

Theoretical model

The Flory (Dominguez et al., 2000; Flory, 1965; Flory et al., 1964; Flory, 1970; Prigogine, 1957; Van and Patterson, 1982; Abe and Flory, 1965) model has been commonly employed to analyze the molar volume of the mixture and the excess molar volume parting from the equation of the state in function of the reduced variables:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \left[\frac{\tilde{v}^{-1/3}}{\tilde{v}^{-1/3}-1} \right] - \left[\frac{1}{\tilde{v}\tilde{T}} \right] \quad (8)$$

Where

$$\tilde{v} = \frac{v}{v^*} = \left[\frac{1 + (\frac{4}{3})\alpha T}{(1 + \alpha T)} \right]^3 \quad (9)$$

$$\tilde{T} = \frac{T}{T^*} = \left[\frac{\tilde{v}^{-1/3}-1}{(\tilde{v}^{-1/3})} \right] \quad (10)$$

Theoretical values of $\left[\frac{\partial V_m^E}{\partial T} \right]$ were calculated from the Flory theory using:

$$T \left[\frac{\partial V_m^E}{\partial T} \right] = \left[\sum_{i=1}^2 x_i V_i^* \left[\tilde{T} \left(\frac{\partial \tilde{v}}{\partial T} \right) \right] - \left[\sum_{i=1}^2 x_i V_i^* \left(\tilde{T} \left(\frac{\partial \tilde{v}}{\partial T} \right) \right) \right] \right] \quad (11)$$

Where

$$\tilde{T} \left[\frac{\partial \tilde{v}}{\partial T} \right] = \left[\frac{\tilde{v}^{-1/3} (1 - \tilde{v}^{-1/3})}{\left[\left(\frac{4}{3} \right) \tilde{v}^{-1/3} - 1 \right]} \right] \quad (12)$$

Table 3. The parameters of Flory theory for pure components at different temperature.

	T K	$10^4 \alpha$ K ⁻¹	ρ g · cm ⁻³ [5]	V^* (cm ³ · mol ⁻¹)	T^* K ⁻¹	\tilde{v}	\tilde{T}
1-Butanol	288.15	9.298	0.813373	74.2960	5423.6663	1.2265	0.0531
	298.15	9.403	0.809573	74.3126	5427.9153	1.2320	0.0540
	298.15	9.504	0.805762	74.3362	5434.2134	1.2375	0.0549
	303.15	9.609	0.801923	74.3601	5440.2914	1.2430	0.0557
	308.15	9.724	0.798053	74.3759	5444.0982	1.2487	0.0566
	313.15	9.857	0.794147	74.3755	5443.7562	1.2549	0.0575
	318.15	10.013	0.790231	74.3482	5437.7377	1.2616	0.0585
	323.15	10.201	0.786238	74.2902	5424.4009	1.2690	0.0596
hexylamine	288.15	11.055	0.768637	104.3629	4924.9229	1.2616	0.0585
	298.15	11.132	0.764385	104.5136	4946.9672	1.2668	0.0593
	298.15	11.219	0.760128	104.6514	4966.7462	1.2722	0.0600
	303.15	11.316	0.755856	104.7819	4984.9756	1.2778	0.0608
	308.15	11.418	0.751573	104.9092	5002.3994	1.2835	0.0616
	313.15	11.523	0.747276	105.0382	5019.6681	1.2893	0.0624
	318.15	11.629	0.742962	105.1746	5037.4684	1.2951	0.0632
	323.15	11.732	0.738636	105.3227	5056.3912	1.3009	0.0639
<i>n</i> -Heptane	288.15	12.249	0.687954	113.4265	4670.3564	1.2842	0.0617
	298.15	12.372	0.683733	113.5744	4687.3641	1.2905	0.0625
	298.15	12.512	0.679494	113.7034	4701.8264	1.2970	0.0634
	303.15	12.666	0.675229	113.8201	4714.5297	1.3039	0.0643
	308.15	12.830	0.670941	113.9311	4726.3264	1.3109	0.0652
	313.15	13.001	0.666621	114.0434	4737.8907	1.3181	0.0661
	318.15	13.175	0.662273	114.1634	4749.9265	1.3254	0.0670
	323.15	13.349	0.657896	114.2979	4763.044	1.3326	0.0678

In the present study the values of the reduced volume for the liquids and their mixtures were determined for α values of the mixtures using the Equation (8). The Flory parameters for pure components at different temperatures are given in Table 3.

The excess thermal expansion coefficients and isothermal coefficient of pressure excess molar enthalpies for all binary mixtures at different temperatures are calculated by Flory theory. The results are given in Tables 4 and 5. The comparison between theoretical and experimental of the excess thermal expansion coefficients and isothermal coefficient of pressure excess molar enthalpies at the temperature 323.15 K are shown in Figures (4 and 5). Comparisons between the experimental and theoretical data are obtained by Flory

theory show a good agreement.

Conclusion

In this work thermal expansion coefficients α , their excess values α^E , isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$ were calculated from experimental densities. The results are shown that:

1- The α^E values for binary mixture of 1-butanol + hexylamine is negative over the entire concentration range. Negative values of α^E are due to hydrogen bonding of components in the mixtures. The excess thermal

Table 4. Excess thermal expansion coefficients (α^E) for binary mixtures of 1-butanol + hexylamine, *n*-heptane and hexylamine + *n*-heptane at different temperatures calculated by Flory theory.

1-butanol + hexylamine							
$10^6 \cdot \alpha^E / K^{-1}$							
<i>T</i> =288.15K	<i>T</i> =293.15K	<i>T</i> =298.15K	<i>T</i> =303.15K	<i>T</i> =308.15K	<i>T</i> =313.15K	<i>T</i> =318.15K	<i>T</i> =323.15K
-8.62	-8.10	-7.61	-7.11	-6.61	-6.11	-5.63	-5.15
-14.29	-13.42	-12.58	-11.73	-10.87	-10.02	-9.18	-8.34
-17.43	-16.42	-15.43	-14.40	-13.40	-12.38	-11.39	-10.41
-18.42	-17.34	-16.24	-15.13	-14.03	-12.94	-11.87	-10.79
-18.76	-17.61	-16.45	-15.26	-14.10	-12.93	-11.76	-10.63
-18.09	-16.88	-15.65	-14.41	-13.20	-11.96	-10.75	-9.53
-14.52	-13.26	-11.98	-10.72	-9.42	-8.15	-6.90	-5.61
-11.12	-9.88	-8.64	-7.39	-6.13	-4.85	-3.61	-2.35
-7.52	-6.37	-5.22	-4.05	-2.89	-1.69	-0.56	0.64
-7.43	-6.23	-5.08	-3.88	-2.68	-1.48	-0.30	0.92
-7.79	-6.55	-5.29	-4.06	-2.78	-1.51	-0.27	1.02
-7.87	-6.53	-5.17	-3.82	-2.47	-1.11	0.24	1.62
-7.82	-6.42	-5.00	-3.59	-2.15	-0.73	0.67	2.13
-6.79	-5.43	-4.08	-2.74	-1.38	0.00	1.33	2.70
-4.68	-3.72	-2.76	-1.79	-0.84	0.12	1.03	2.00
1-butanol + <i>n</i>-heptane							
14.60	17.75	20.84	23.87	26.85	29.75	32.58	35.35
18.14	22.06	25.89	29.68	33.39	37.01	40.54	43.99
21.30	25.89	30.41	34.87	39.24	43.51	47.68	51.75
22.00	26.75	31.42	36.04	40.55	44.97	49.27	53.45
22.65	27.53	32.34	37.07	41.72	46.26	50.69	54.99
23.41	28.40	33.32	38.14	42.88	47.52	52.04	56.43
23.45	28.40	33.33	38.18	42.91	47.57	52.09	56.49
24.07	29.10	34.05	38.94	43.74	48.43	52.99	57.44
24.75	29.82	34.82	39.76	44.60	49.36	53.97	58.44
25.17	30.32	35.39	40.40	45.33	50.16	54.84	59.42
25.03	30.25	35.40	40.50	45.50	50.41	55.17	59.79
24.16	29.45	34.65	39.81	44.87	49.83	54.66	59.36
22.07	27.34	32.55	37.69	42.76	47.73	52.56	57.26
15.23	20.21	25.15	30.03	34.84	39.58	44.18	48.69
10.78	15.47	20.10	24.71	29.25	33.71	38.05	42.30
6.38	10.65	14.91	19.13	23.29	27.38	31.34	35.24
2.77	6.57	10.35	14.09	17.80	21.45	24.98	28.47
0.27	3.50	6.71	9.89	13.06	16.16	19.16	22.13
-0.71	1.80	4.28	6.74	9.19	11.59	13.90	16.23
Hexylamine + <i>n</i>-heptane							
-7.97	-7.74	-7.54	-7.32	-7.13	-6.91	-6.71	-6.52
-12.42	-12.25	-12.11	-11.97	-11.83	-11.67	-11.52	-11.36
-15.46	-15.54	-15.62	-15.69	-15.77	-15.81	-15.86	-15.90
-18.76	-19.30	-19.83	-20.35	-20.85	-21.34	-21.80	-22.24
-20.70	-21.57	-22.44	-23.27	-24.08	-24.88	-25.64	-26.38
-22.76	-23.90	-25.01	-26.09	-27.16	-28.18	-29.17	-30.14
-23.58	-24.74	-25.88	-26.99	-28.07	-29.11	-30.12	-31.11
-25.02	-26.04	-27.04	-28.01	-28.97	-29.89	-30.78	-31.63
-25.32	-26.24	-27.16	-28.04	-28.91	-29.72	-30.53	-31.30

Table 4. Contd.

-25.31	-26.10	-26.88	-27.62	-28.35	-29.05	-29.71	-30.37
-24.98	-25.61	-26.23	-26.82	-27.40	-27.95	-28.47	-28.98
-22.43	-22.71	-22.97	-23.23	-23.46	-23.69	-23.90	-24.10
-15.81	-15.78	-15.74	-15.70	-15.65	-15.61	-15.54	-15.48

Table 5. Isothermal coefficient of pressure excess molar enthalpies for binary mixtures of 1-butanol + hexylamine, *n*-heptane and hexylamine + *n*-heptane at Different Temperatures calculated by Flory theory.

1-butanol + hexylamine							
$(\partial H_m^E / \partial P)_{T,x} / (\text{J. MPa}^{-1} \cdot \text{s}^{-1})$							
<i>T</i> =288.15K	<i>T</i> =293.15K	<i>T</i> =298.15K	<i>T</i> =303.15K	<i>T</i> =308.15K	<i>T</i> =313.15K	<i>T</i> =318.15K	<i>T</i> =323.15K
-0.030	-0.014	0.001	0.017	0.032	0.047	0.062	0.076
-0.164	-0.136	-0.108	-0.081	-0.053	-0.027	-0.002	0.024
-0.247	-0.214	-0.182	-0.149	-0.118	-0.086	-0.057	-0.027
-0.366	-0.329	-0.294	-0.259	-0.224	-0.190	-0.156	-0.124
-0.488	-0.451	-0.412	-0.374	-0.337	-0.299	-0.265	-0.231
-0.634	-0.592	-0.553	-0.513	-0.474	-0.435	-0.399	-0.362
-0.916	-0.871	-0.831	-0.790	-0.748	-0.709	-0.671	-0.633
-1.086	-1.043	-1.003	-0.962	-0.922	-0.883	-0.846	-0.809
-1.121	-1.081	-1.047	-1.009	-0.974	-0.939	-0.905	-0.872
-1.016	-0.977	-0.943	-0.907	-0.872	-0.838	-0.806	-0.772
-0.900	-0.860	-0.826	-0.790	-0.753	-0.720	-0.686	-0.653
-0.793	-0.752	-0.716	-0.678	-0.642	-0.606	-0.571	-0.537
-0.641	-0.599	-0.564	-0.526	-0.488	-0.452	-0.418	-0.383
-0.486	-0.448	-0.416	-0.380	-0.346	-0.314	-0.282	-0.250
-0.268	-0.242	-0.223	-0.199	-0.177	-0.154	-0.132	-0.111
1-butanol + <i>n</i>-heptane							
-0.491	-0.623	-0.758	-0.895	-1.034	-1.173	-1.312	-1.456
-0.599	-0.764	-0.931	-1.103	-1.276	-1.450	-1.625	-1.802
-0.687	-0.877	-1.071	-1.269	-1.471	-1.674	-1.877	-2.083
-0.699	-0.894	-1.093	-1.298	-1.503	-1.711	-1.919	-2.127
-0.700	-0.898	-1.100	-1.305	-1.514	-1.725	-1.936	-2.148
-0.702	-0.900	-1.104	-1.308	-1.516	-1.727	-1.937	-2.148
-0.705	-0.900	-1.104	-1.310	-1.517	-1.730	-1.940	-2.153
-0.706	-0.902	-1.101	-1.305	-1.511	-1.720	-1.928	-2.139
-0.720	-0.913	-1.108	-1.310	-1.514	-1.722	-1.927	-2.133
-0.724	-0.916	-1.111	-1.312	-1.516	-1.721	-1.925	-2.134
-0.707	-0.897	-1.091	-1.291	-1.493	-1.698	-1.900	-2.104
-0.677	-0.867	-1.058	-1.256	-1.455	-1.657	-1.858	-2.061
-0.602	-0.786	-0.973	-1.163	-1.358	-1.554	-1.750	-1.947
-0.389	-0.553	-0.720	-0.891	-1.065	-1.243	-1.418	-1.597
-0.258	-0.408	-0.559	-0.716	-0.875	-1.036	-1.196	-1.360
-0.134	-0.264	-0.399	-0.537	-0.678	-0.821	-0.961	-1.104
-0.043	-0.155	-0.270	-0.389	-0.511	-0.634	-0.753	-0.879
0.022	-0.071	-0.166	-0.263	-0.365	-0.467	-0.565	-0.668
0.036	-0.035	-0.106	-0.180	-0.257	-0.333	-0.406	-0.487
Hexylamine + <i>n</i>-heptane							
0.115	0.137	0.159	0.181	0.204	0.226	0.248	0.270
0.140	0.169	0.193	0.220	0.246	0.272	0.296	0.322

Table 5. Contd.

0.179	0.206	0.232	0.260	0.287	0.312	0.338	0.364
0.233	0.256	0.276	0.299	0.320	0.341	0.362	0.382
0.301	0.310	0.317	0.327	0.335	0.344	0.351	0.359
0.334	0.326	0.317	0.309	0.301	0.293	0.284	0.277
0.302	0.287	0.256	0.258	0.244	0.230	0.215	0.201
0.235	0.219	0.203	0.187	0.169	0.154	0.138	0.123
0.205	0.185	0.166	0.146	0.127	0.108	0.089	0.071
0.183	0.161	0.136	0.113	0.089	0.067	0.044	0.024
0.169	0.144	0.118	0.094	0.069	0.048	0.023	0.001
0.155	0.132	0.111	0.088	0.065	0.045	0.023	0.003
0.131	0.111	0.095	0.077	0.060	0.044	0.027	0.012

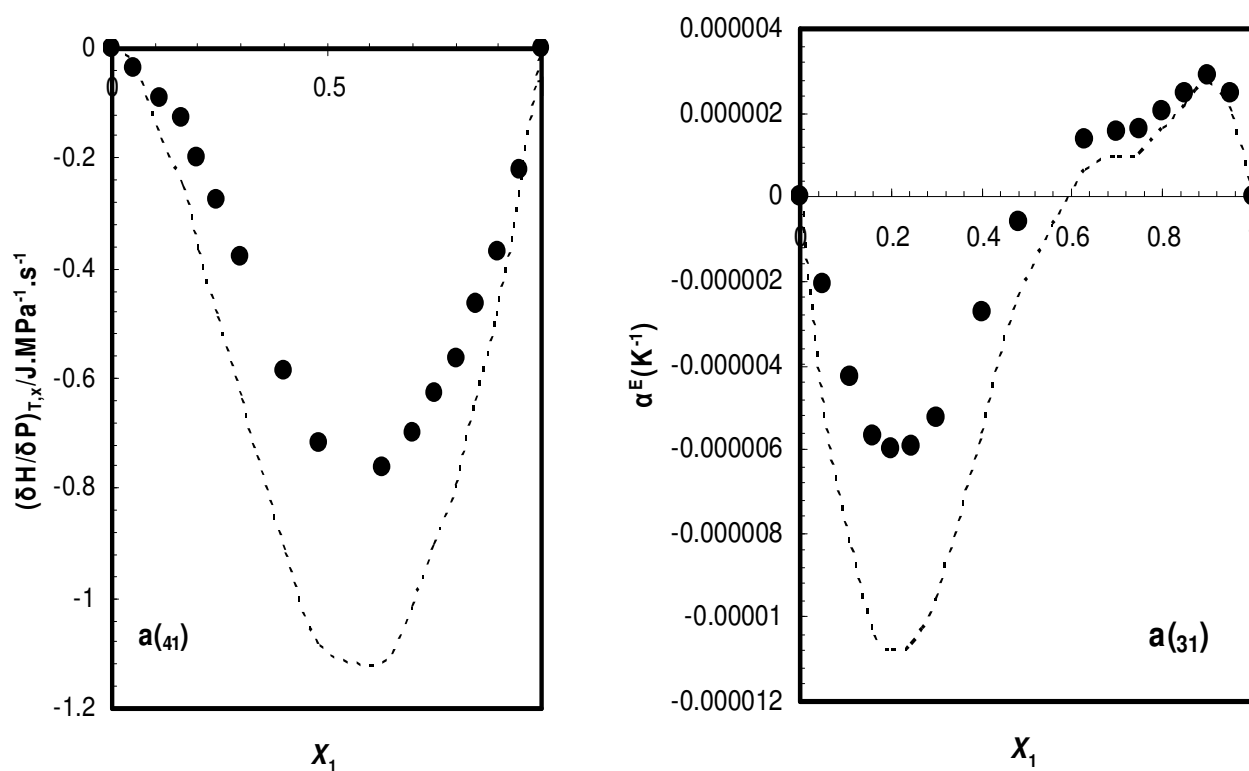


Figure 4. Plot of α^E , and $(\partial H_m^E / \partial P)_T$ against mole fraction for {1-butanol + hexylamine, 323.15 K. (o) Experimental; (.....) calculated by using Flory theory.

expansion coefficients α^E , are positive over the mole fraction range for binary mixture of 1-butanol + *n*-heptane and increase with increasing temperatures from (288.15 to 323.15) K.

2- The values of $(\partial H_m^E / \partial P)_{T,x}$ for the binary mixtures {1-butanol + hexylamine} and {1-butanol + *n*-heptane} are negative over the mole fraction range and decrease with increasing temperatures from (288.15 to 323.15)K, and S-shaped for binary mixture of {hexylamine + *n*-heptane} and increase with increasing temperatures from (288.15 to 323.15)K.

3- The comparison between Flory theory and experimental of the excess thermal expansion coefficients and isothermal coefficient of pressure excess molar enthalpies at the temperature 323.15 K show a good agreement.

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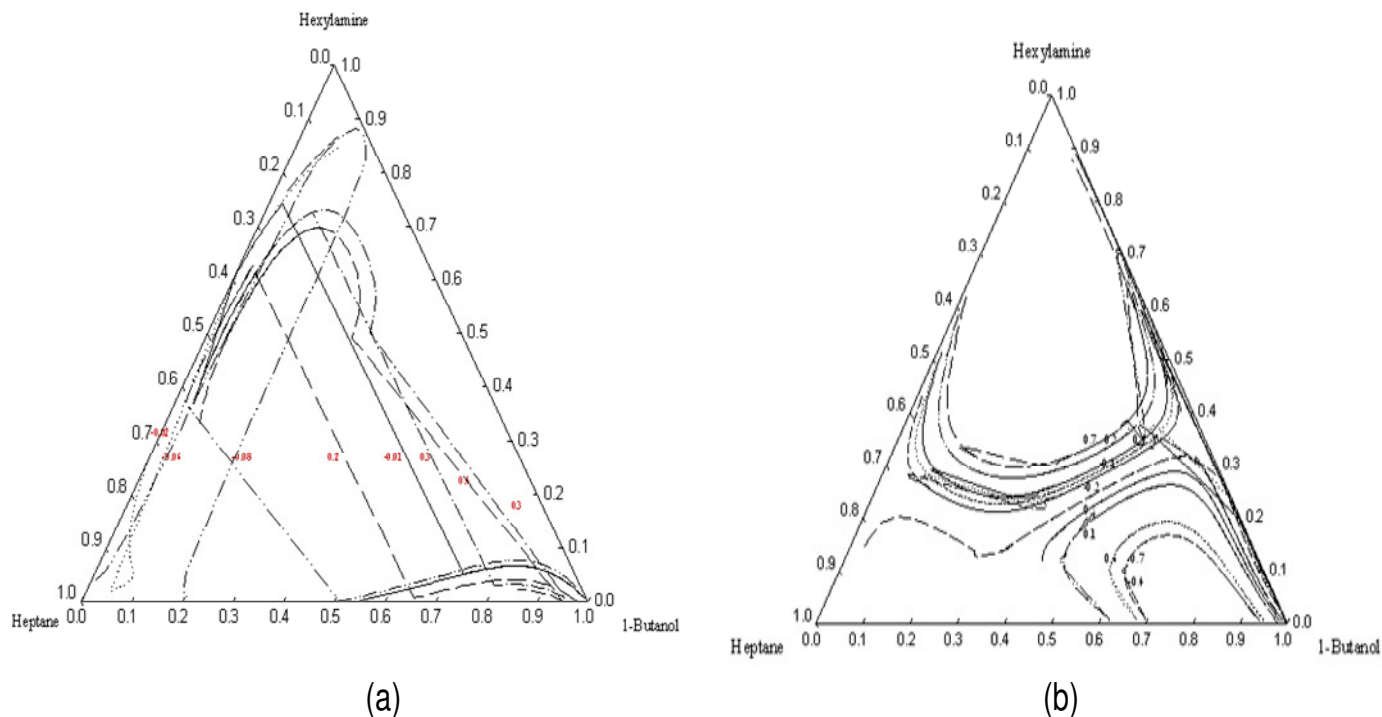


Figure 5. Isoline Curves of $(\partial H_m^E / \partial P)_T$, for the ternary system 1-butanol (1) + hexylamine (2) + n-heptane (2), at (a) 288.15 K and (b) 323.15 K. The lines present results calculated by Cibulka (1982), equation

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