

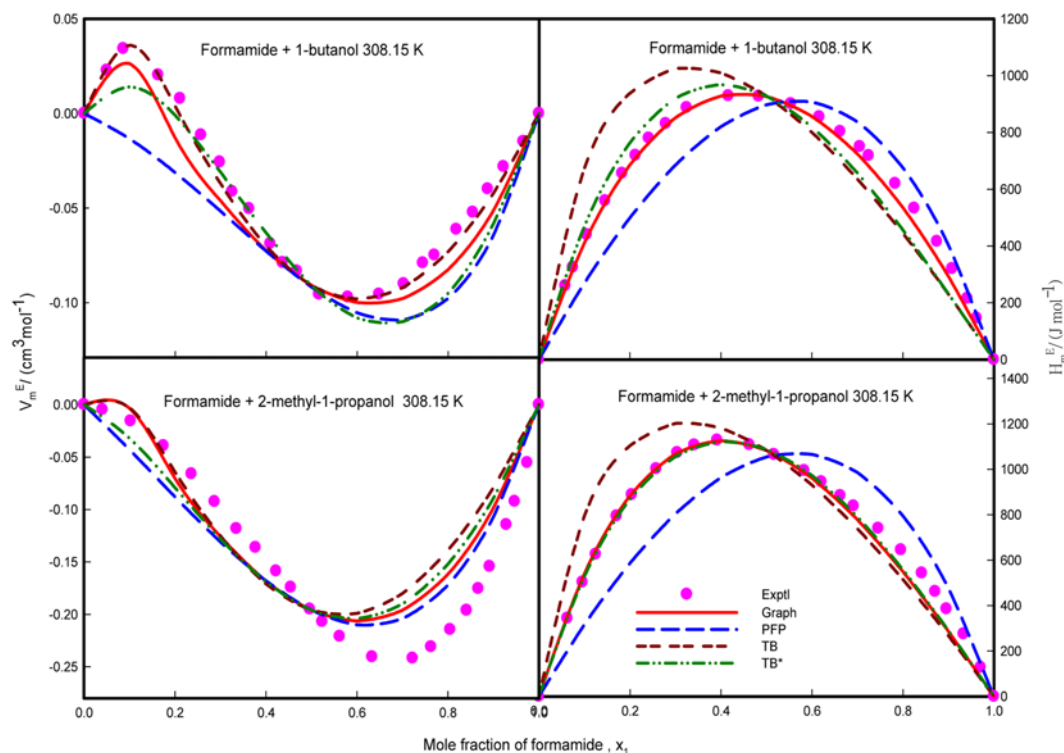
Thermodynamics of molecular interactions in binary mixtures containing associated liquids

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Abstract—Experimentally measured data of excess molar volumes and enthalpies at 308.15 K for binary mixtures of formamide with 1-butanol or 2-methyl-1-propanol were fitted to the Redlich-Kister polynomial equation. Thermodynamics of molecular interaction in these mixtures was discussed using Prigogine-Flory-Patterson theory, Treszczanowicz-Benson association model and Graph theoretical approach. Extent of inter-molecular H-bonding in formamide and butanol in their binary mixtures was also reflected in their molar enthalpy of association of H-bonding Δh_H^0 and association constant K_H calculated from Treszczanowicz-Benson association model. All the three theories predict the excess property data reasonably well.



Key words: Excess Molar Enthalpy, Excess Molar Volume, Prigogine-Flory-Patterson Theory, Treszczanowicz-Benson Association Model, Graph Theoretical Approach

INTRODUCTION

Formamide is the simplest amide that contains a peptide linkage which combines amino acids into polypeptide to form the building block of proteins. Addition of alkanol to amide may result in the intermolecular H-bonding [1-3]. Thus the thermo-physical properties

of binary mixtures of amide and alkanol would be of great importance in chemical designing and also for researchers to understand the nature of intermolecular interactions [3,4].

Addition of inert solvents like alkane to the self associated alkanol leads to pronounced thermodynamic non-ideal behavior [5-12]. Any excess thermodynamic property X_m^E for such binary systems may be considered to consist of two parts, one resulting from breaking up of the hydrogen bonded network and other due to van der Waals type interaction between the alkyl chain of alkanol and alkane [13].

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In our previous publications, we described the thermodynamics of alkanol+aromatic hydrocarbon in terms of Treszczanowicz-Benson (TB) association model [14-16]. Many researchers have interpreted binary systems containing one associated component [9,17-27], whereas systems containing both components of associated nature are relatively less [9,28-35] in literature. These considerations prompted us to study the thermodynamics of systems with formamide and butanol. In this paper, we report the excess molar enthalpies (H_m^E) and excess molar volumes (V_m^E) at 308.15 K for formamide (1)+1-butanol or 2-methyl-1-propanol (2) mixtures. The measured H_m^E and V_m^E data were also interpreted in terms of Prigogine-Flory-Patterson (PFP) model [36-42], Treszczanowicz-Benson (TB) association model [5,6] and Graph theoretical approach [43,44].

EXPERIMENTAL SECTION

The methods of purification of formamide, 1-butanol and 2-methyl-1-propanol (Sigma-Aldrich) and their analysis to check purities were described in our previous publication [35,45,46]. Their purities were found to be better than 99.7 wt% when analyzed by gas chromatography.

Excess molar enthalpy of mixing (H_m^E) data at 308.15 for the binary mixtures was measured using flow micro calorimeter (LKB-2107, Bromma, Sweden) in the manner described by Monk and Wadso [47]. Details and the operating procedure of the calorimeter were described elsewhere [48,49]. The uncertainty in the measured H_m^E

values was $\pm 1\%$.

Excess molar volumes (V_m^E), at 308.15 K for the binary mixtures, were measured by V-shaped dilatometer in the manner described elsewhere [50]. The uncertainty in the measured V_m^E values was $\pm 1\%$.

RESULTS

The measured X_m^E ($X=V$ or H) data, which are recorded in Table 1, were fitted to the following Redlich and Kister equation:

$$X_m^E = x_1 x_2 \left[\sum_{n=0}^3 X^{(n)} (x_1 - x_2)^n \right] \quad (1)$$

where $X^{(n)}$ ($X=V$ or H) are the adjustable parameters, and x_1 and x_2 are the mole fractions of formamide (1) and butanol (2) in mixture. These parameters were evaluated by fitting X_m^E data to Eq. (1) by least squares method and recorded in Table 2 along with the standard deviations of X_m^E , ($\sigma(X_m^E)$) [35].

DISCUSSION

The V_m^E data for formamide+1-butanol were reported at 308.15 K [58]. A comparison of present data with reported values is shown in Fig. 1. Our V_m^E values are somewhat lower than those reported for the mole fraction ($0.2 < x_1 < 0.7$) but little higher thereafter ($x_1 >$

Table 1. Measured excess molar volumes, V_m^E , and excess molar enthalpies, H_m^E , data for (1+2) binary mixtures as functions of mole fractions of formamide, x_1 , at 308.15 K

x_1	V_m^E (cm ³ mol ⁻¹)	x_1	V_m^E (cm ³ mol ⁻¹)	x_1	H_m^E (J mol ⁻¹)	x_1	H_m^E (J mol ⁻¹)
Formamide (1)+1-butanol (2)							
0.0499	0.023	0.5166	-0.095	0.0582	260	0.5540	901
0.0862	0.034	0.5799	-0.097	0.0750	325	0.6166	855
0.1629	0.020	0.6482	-0.095	0.1052	440	0.6624	803
0.2111	0.008	0.7025	-0.090	0.1458	559	0.7054	750
0.2571	-0.011	0.7446	-0.079	0.1832	656	0.7250	718
0.2983	-0.026	0.7699	-0.075	0.2124	719	0.7832	620
0.3254	-0.041	0.8183	-0.061	0.2416	780	0.8250	533
0.3629	-0.050	0.8544	-0.052	0.2790	831	0.8750	416
0.4092	-0.069	0.8873	-0.040	0.3250	887	0.9082	320
0.4363	-0.079	0.9218	-0.028	0.4166	929	0.9416	215
0.4675	-0.083	0.9654	-0.015	0.4832	927	0.9624	146
Formamide (1)+2-methyl-1-propanol (2)							
0.0408	-0.005	0.5622	-0.221	0.0624	344	0.5832	994
0.1027	-0.016	0.6334	-0.241	0.0958	503	0.6208	945
0.1751	-0.039	0.7224	-0.242	0.1250	626	0.6624	884
0.2364	-0.066	0.7631	-0.231	0.1708	794	0.6916	838
0.2873	-0.093	0.8051	-0.215	0.2040	888	0.7458	740
0.3353	-0.118	0.8412	-0.196	0.2580	1002	0.7958	645
0.3772	-0.136	0.8669	-0.176	0.3040	1073	0.8416	543
0.4225	-0.159	0.8917	-0.154	0.3416	1107	0.8708	462
0.4548	-0.174	0.9285	-0.114	0.3918	1128	0.8958	385
0.4967	-0.195	0.9469	-0.092	0.4624	1108	0.9332	275
0.5238	-0.207	0.9745	-0.055	0.5166	1065	0.9708	128

Table 2. Values of adjustable parameters, $X^{(n)}$, of Redlich-Kister equation along with standard deviation, $\sigma(X_m^E)$, (where $X=V$ or H) of the molar excess volumes or enthalpy for the various (1+2) binary mixtures at 308.15 K

System	Property	$X^{(0)}$	$X^{(1)}$	$X^{(2)}$	$X^{(3)}$	$\sigma(X_m^E)$
Formamide (1)+1-butanol (2)	V_m^E	-0.3634	-0.3247	0.5270	-0.2283	0.0018
	H_m^E	3705.6	-642.0	837.6	216.5	2.728
Formamide (1)+2-methyl-1-propanol (2)	V_m^E	-0.7840	-0.8365	-0.1702	-0.1297	0.0030
	H_m^E	4330.1	-1618.2	1070.8	979.3	3.010

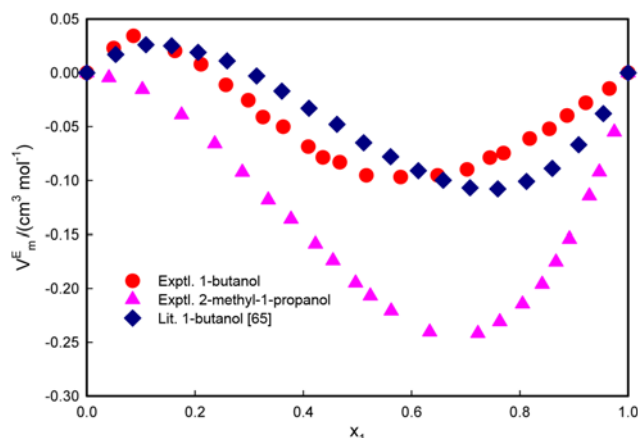


Fig. 1. Measured excess molar volumes (V_m^E) of formamide (1)+alkanol (2) as function of mole fraction of formamide (x_1) at 308.15 K.

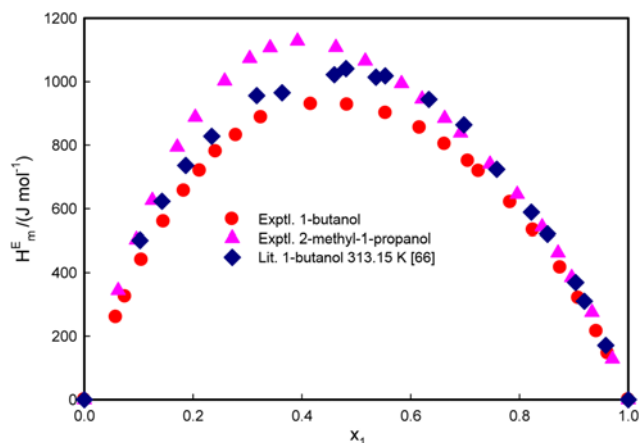


Fig. 2. Measured excess molar enthalpies (H_m^E) of formamide (1)+alkanol (2) as function of mole fraction of formamide (x_1) at 308.15 K.

0.7). The H_m^E data for these systems were reported for formamide+1-butanol at 313.15 K by Pikkarainen [51] and compared with present H_m^E data in Fig. 2. The H_m^E values were lower than those reported by Pikkarainen [51], and that might be due to our lower experimental temperature. The V_m^E values for formamide+butanol systems are negative over the whole composition range (Fig. 3) and the H_m^E values are positive for these systems (Fig. 4). At the simplest qualitative level, the observed X_m^E ($X=V$ or H) values may be attributed to the resultant of two opposing effects/contributions. The positive contribution arises from the breaking of intermolecular hydrogen bonding in self associated pure components, physical dipole-

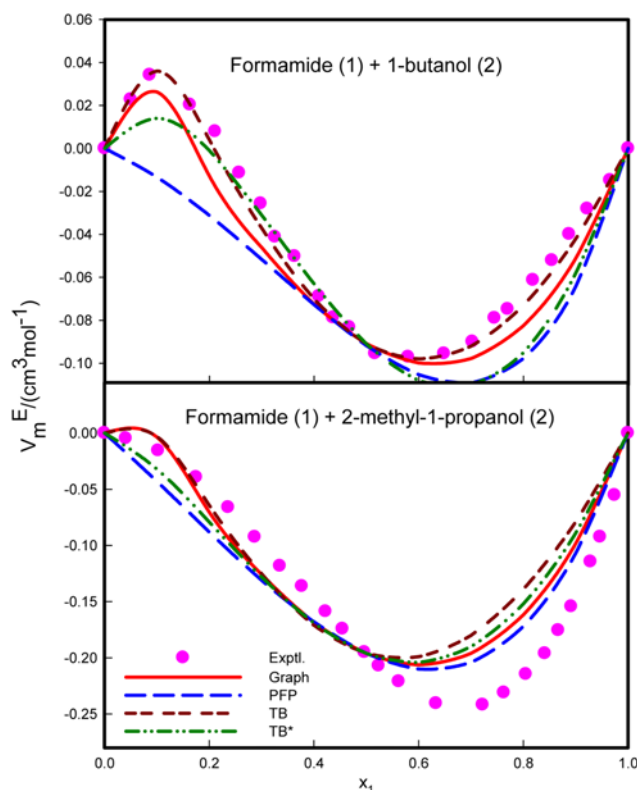


Fig. 3. Excess molar volume (V_m^E) of formamide (1)+alkanol (2) as function of mole fraction of formamide (x_1) at 308.15 K.

dipole interactions between monomers and multimers, and also due to disruption in favorable orientation order of pure components; the negative contribution is due to the formation of hydrogen bonded interactions between formamide and butanol. At higher temperature the positive contribution decreases due to weakening of self association/interaction in pure components, and negative contribution also decreases owing to lesser interaction in unlike molecules. The higher value of H_m^E (Fig. 2) at higher temperature indicates that the decrease in negative contribution outweighs the decrease in positive contribution. Similar effect of temperature was also observed for formamide+propanol mixtures [45]. The measured V_m^E and H_m^E data were next analyzed in terms of PFP theory, TB association model and Graph theoretical approach.

1. Prigogine-flory-patterson Theory

According to PFP theory [39], excess molar volume (V_m^E) is the result of three contributions: (i) due to interaction between unlike molecules that is proportional to interaction parameter (χ_{12}^*), (ii) the free volume contribution owing to the dependence of reduced volume upon reduced temperature due to the difference between the

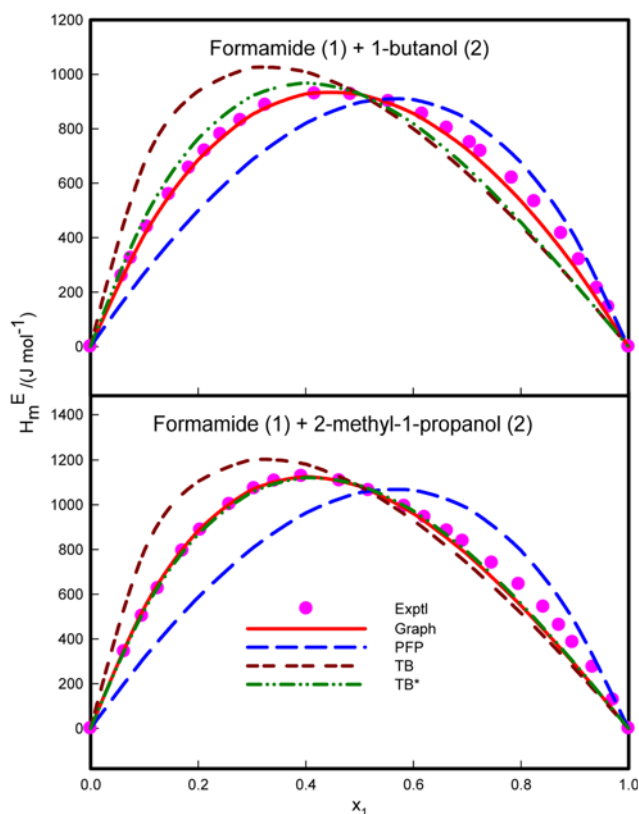


Fig. 4. Excess molar enthalpies (H_m^E) of formamide (1)+alkanol (2) as function of mole fraction of formamide (x_1) at 308.15 K.

degree of expansion of the components, and (iii) the P^* contribution that depends on the difference of internal pressures as well as the difference of reduced volumes of the components. Similarly, excess molar enthalpy is expressed as the sum of only two contributions: interactional contribution, and free volume contribution. Thus V_m^E and H_m^E may be expressed as

$$V_m^E = V_{inter}^E + V_{free vol}^E + V_P^E \quad (2)$$

$$\frac{V_m^E}{x_1 V_1^* + x_2 V_2^*} = \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\psi_1\theta_2(\chi_{12}^*/P_1^*)}{((4/3)\tilde{V}^{-1/3} - 1)} - \frac{(\tilde{V}_1 - \tilde{V}_2)^2((14/9)\tilde{V}^{-1/3} - 1)\psi_1\psi_2}{((4/3)\tilde{V}^{-1/3} - 1)\tilde{V}} + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\psi_1\psi_2}{P_2^*\psi_1 + P_2^*\psi_2} \quad (3)$$

$$H_m^E = H_{inter}^E + H_{free vol}^E \quad (4)$$

$$H_m^E = (x_1 U_1^* + x_2 U_2^*)[-\tilde{U}(\tilde{T}) + \tilde{T}\tilde{C}_p(\tilde{T})]\chi_{12}\psi_1\theta_2/P_1^*$$

$$+ (x_1 U_1^* + x_2 U_2^*)\tilde{C}_p(\tilde{T})(\psi_1\tilde{T}_1 + \psi_2\tilde{T}_2 - \tilde{T}) \quad (5)$$

where all the terms have their usual meanings [36,37]. The characteristic pressure, volume and temperature (P_i^* , V_i^* and T_i^*) of the pure components are reported in Table 3. Calculation of V_m^E and H_m^E from Eq. (2) and Eq. (4) requires the knowledge of Flory interaction parameters χ_{12}^* (for excess volume) and χ_{12} (for excess enthalpy). These interaction parameters were computed employing equimolar experimental data of V_m^E and H_m^E and were subsequently used to calculate V_m^E and H_m^E at other mole fraction (x_1). The calculated V_m^E and H_m^E values are recorded in Table 4, respectively. The calculated values of various contributions to the values of V_m^E and H_m^E for equimolar mixture, Flory interaction parameters χ_{12}^* (for excess volumes) and χ_{12} (for excess enthalpies) are recorded in Table 5. Calculated V_m^E values were found to agree well with respective experimental data as shown in Fig. 3. But the comparison between calculated and experimental H_m^E values is reasonably good for $x_1 > 0.5$ (Fig. 4) and for $x_1 < 0.5$ the calculated H_m^E values are less (at the most 150 J mol^{-1} at $x_1 = 0.3$) than corresponding experimental data (Fig. 4). In these binary mixtures, $P_1^* > P_2^*$ and $\tilde{V}_1 < \tilde{V}_2$ results in the large negative contribution of V_P^E which determines the sign of excess molar volume [52]. The larger P^* and \tilde{V} smaller values of formamide as compared to butanol lead to negative value of V_m^E as well as positive H_m^E . The branching of alkyl chain in butanol further decreases the P_2^* and increases the \tilde{V}_2 . This further increases the negative contribution of V_P^E term as well as dominant H_{inter}^E (Table 5), thus making V_m^E more negative and H_m^E more positive (Fig. 3 and 4).

2. Treszczanowicz and Benson Association Model

Treszczanowicz-Benson association model [5] was proposed for alkane (1)+alkanol (2) mixtures, and it assumes that the mode of self association of alkanol is of Mecke-Kempton type in which linear multimers A are formed due to the consecutive association reaction,



The consecutive thermodynamic association constant K_{i-1} can be expressed in terms of the association parameters for standard enthalpy $\Delta h_{i,i-1}^0$ and entropy $\Delta s_{i,i-1}^0$ of H-bond formation. In TB association model, these parameters are taken to be independent of the degree of association i . Kehiaian [53] observed that standard entropy of H-bond formation $\Delta s_{i,i-1}^0$ for alkanol depends on the number of segment r_2 in a molecule of monomer. Thus, for an alkanol

$$\Delta h_{i,i-1}^0 = \Delta h_H^0 \quad (7)$$

$$\Delta s_{i,i-1}^0 = \Delta s_H^0 - R \ln r_2 \quad (8)$$

These assumptions indicate that

$$K_{i,i-1} = \frac{K_H}{r_2} \quad (9)$$

Table 3. Molar volume, V , isobaric expansivity, α , and isothermal compressibility, κ_T , characteristic pressure, P^* , characteristic molar volume, V^* , and characteristic temperature, T^* , obtained from Flory theory for the pure liquids at 308.15 K

Compound	$V \text{ (cm}^3 \text{ mol}^{-1}\text{)}$	$10^3 \times \alpha \text{ (K}^{-1}\text{)}$	$10^6 \times \kappa_T \text{ (cm}^3 \text{ J}^{-1}\text{)}$	$P^* \text{ (J cm}^{-3}\text{)}$	$V^* \text{ (cm}^3 \text{ mol}^{-1}\text{)}$	$T^* \text{ (K)}$
Formamide	40.20	0.758	417	808.69	33.46	6236.52
1-Butanol	92.88	1.041	1004	509.72	73.53	5196.82
2-Methyl-1-propanol	93.76	1.066	1116	473.41	73.93	5132.24

Table 4. Comparison of excess property, X_m^E (X=V or H) calculated from Prigogine-Flory-Patterson theory and Treszczanowicz-Benson association model with their corresponding experimental values (calculated from Eq. (1) at round mole fractions) for the binary mixtures as functions of mole fraction of formamide, x_1 , at 308.15 K. TB and TB* represent the values of X_m^E when either butanol or formamide was assumed to be associated, respectively

V_m^E (cm ³ mol ⁻¹)						H_m^E (J mol ⁻¹)				
Exptl	PFP	TB	TB*	Graph	Exptl	PFP	TB	TB*	Graph	
Formamide (1)+1-butanol (2)										
0.1	0.032	-0.009	0.036	0.014	0.026	418	269	673	469	410
0.2	0.011	-0.026	0.004	-0.001	-0.013	695	499	938	763	685
0.3	-0.028	-0.047	-0.037	-0.031	-0.046	857	685	1025	920	852
0.4	-0.066	-0.069	-0.070	-0.063	-0.072	928	820	1009	968	928
0.5	-0.091	-0.091	-0.091	-0.091	-0.091	926	897	928	928	926
0.6	-0.098	-0.107	-0.098	-0.108	-0.100	867	907	800	819	856
0.7	-0.089	-0.112	-0.092	-0.110	-0.098	755	837	636	657	724
0.8	-0.067	-0.102	-0.073	-0.095	-0.082	587	676	445	457	535
0.9	-0.036	-0.067	-0.042	-0.058	-0.051	346	404	231	232	293
Formamide (1)+2-methyl-1-propanol (2)										
0.1	-0.014	-0.043	-0.003	-0.032	-0.003	523	316	794	529	541
0.2	-0.050	-0.088	-0.064	-0.079	-0.070	876	586	1104	868	883
0.3	-0.098	-0.131	-0.125	-0.128	-0.126	1068	804	1202	1056	1068
0.4	-0.149	-0.168	-0.171	-0.169	-0.168	1125	963	1181	1121	1125
0.5	-0.196	-0.196	-0.196	-0.196	-0.196	1083	1054	1083	1087	1083
0.6	-0.230	-0.210	-0.199	-0.204	-0.206	974	1065	930	972	961
0.7	-0.242	-0.204	-0.180	-0.190	-0.196	823	985	738	790	778
0.8	-0.220	-0.172	-0.139	-0.152	-0.162	633	795	515	558	549
0.9	-0.147	-0.107	-0.079	-0.089	-0.098	380	476	267	290	286

Table 5. PFP interaction parameters χ_{12}^* , χ_{12} and equimolar values of the contributions to excess volume and excess enthalpy at 308.15 K

System	V_{inter}^E	$V_{free vol}^E$	$V_{p^*}^E$	χ_{12}^*	H_{inter}^E	$H_{free vol}^E$	χ_{12}
Formamide (1)+1-butanol (2)	0.334	-0.074	-0.351	54.65	926.40	-29.51	84.93
Formamide (1)+2-methyl-1-propanol (2)	0.337	-0.088	-0.445	52.29	1082.54	-33.48	99.04

where

$$K_H = \exp\left[\frac{-(\Delta h_H^0 - T\Delta s_H^0)}{RT}\right] \quad (10)$$

is a constant for a homologous series of self-associating components. The number of segments in an alkanol molecule was calculated from the relation,

$$r_2 = \frac{V_2^*}{17.12} \quad (11)$$

where V_2^* is the characteristic molar volume of the alkanol and 17.12 cm³mol⁻¹ is the van der Waals molar volume for methane [54].

This model was developed for alkane+alkanol mixtures where the alkane behaves as an inert solvent [5]. It assumes that the X_m^E (X=V or H) are composed of a chemical contribution (Mecke-Kempton type of association of alkanol) term and a physical contribution described by Flory theory [36,37]:

$$H_m^E = H_{MK}^E + H_F^E \quad (12)$$

$$V_m^E = V_{MK}^E + V_F^E \quad (13)$$

The chemical contribution is given by

$$H_{MK}^E = \Delta h_H^0 x_2 h(K^\phi, \phi_2) \quad (14)$$

$$V_{MK}^E = \Delta v_H^0 x_2 h(K^\phi, \phi_2) \quad (15)$$

where

$$h(K^\phi, \phi_2) = \frac{[\phi_2 \ln(1+K^\phi) - \ln(1+K^\phi \phi_2)]}{K^\phi \phi_2} \quad (16)$$

$$\ln K^\phi = 1 + \ln(K_H/r_2) \quad (17)$$

In these equations R is the gas constant, T is the temperature and K^ϕ is the volume fraction based association constant and x_2 and V_2^* are mole fraction and hard core molar volume of associating component. Δv_H^0 , Δh_H^0 and Δs_H^0 are the standard volume, enthalpy and entropy of association of alkanol.

The physical contribution is obtained from Flory theory [36,37], which contains the effect of nonspecific interaction between the real molecular species in the mixture, together with the free volume term. According to Flory theory [36,37]

$$H_F^E = x_2 \theta_1 \left(\frac{V_2^*}{V} \right) \chi_{12} + \sum_{i=1}^2 [x_i P_i^* V_i^* (\tilde{V}_i^{-1} - \tilde{V}^{-1})] \quad (18)$$

$$V_F^E = V^* [\tilde{V} - (\tilde{V}_1 \phi_1 + \tilde{V}_2 \phi_2)] \quad (19)$$

where χ_{12} is Flory's interaction parameter, $V^* = x_1 V_1^* + x_2 V_2^*$ is the characteristic molar volume for the mixture, α and κ_T are the isobaric expansivity and isothermal compressibility of pure components and were taken from literature [55-57] and recorded in Table 3.

The association parameters (Δv_H^0 , Δh_H^0 and Δs_H^0) for butanol in these mixtures were calculated as suggested elsewhere [58]. As the experimental C_p^E values for these mixtures were not available in literature, C_p^E data ($0.925 \text{ J mol}^{-1} \text{ K}^{-1}$) for an equimolar mixture of dimethylformamide+ethanol at 298.15 K reported by Conti et al. [59] was used for the calculation of association parameters for the present binary systems at 308.15 K. The most suitable value for Δv_H^0 that predicts V_m^E data close to experimental is $-5 \text{ cm}^3 \text{ mol}^{-1}$. The same value was also reported by Liu et al. [60], though Treszczanowicz and Benson [5] and Stoke [61] calculated -10 and $-7.5 \text{ cm}^3 \text{ mol}^{-1}$ for alkane+alcohol mixtures. The values of association parameters (Δv_H^0 , Δh_H^0 and Δs_H^0), association constants, K_H and K^ϕ , and Flory interaction parameter χ_{12} for the present binary systems, when butanol is assumed to be associated, are recorded in Table 6. It has been observed from Fig. 3 and Fig. 4 that calculated and experimental V_m^E and H_m^E values are in good agreement for these systems. The agreement would have been much better if the exact experimental values of C_p^E for all these systems were known. This model was again applied on these systems by assuming that formamide is associated and association parameters (Δv_H^0 , Δh_H^0 and Δs_H^0), K_H and K^ϕ , and Flory interaction parameter χ_{12} were again calculated by the same procedure and reported in Table 6 as TB*. The calculated V_m^E and H_m^E , when formamide was assumed to be associated, were reported in Table 4 and plotted in Fig. 3 and Fig. 4 as TB*. It can be seen from the Fig. 3 and Fig. 4 that the comparison between calculated and experimental V_m^E and H_m^E values was better when formamide was assumed to be associated. Since inter-molecular H-bonding in formamide is weaker than butanol, enthalpy of association of H-bonding Δh_H^0 and association constant K_H should also be less in formamide than butanol in these systems. This is indeed true in our case as evident from Table 6. The same was also observed by Funke et al. [9].

3. Graph Theoretical Approach

According to this theory V_m^E may be expressed by [43].

$$V_m^E = \alpha_{12} \left[\sum_{i=1}^2 [x_i (\xi_i^3 \xi_i)_m]^{-1} - \sum_{i=1}^2 \frac{x_i}{\xi_i^3} \right] \quad (20)$$

where α_{12} is the constant characteristic of the (1+2) mixture and can be evaluated using equimolar experimental V_m^E value (ξ_i^3) and $(\xi_i^3 \xi_i)_m$ and ($i=1$ or 2) are the connectivity parameter of third order in pure state and in mixtures. These ξ parameters were evaluated by fitting experimental V_m^E data to Eq. (20). Only those values of (ξ_i^3) and $(\xi_i^3 \xi_i)_m$ were retained that best reproduced the V_m^E data. The values of ($i=1$ or 2) parameters are recorded in Table 7 and their significance was discussed elsewhere [35]. The V_m^E values obtained from Eq. (20) for the various binary mixtures as a function of x_1 are recorded in Table 5 and found to compare well with experimental data (Fig. 3).

To understand the energetics of the various interactions present in these binary formamide (1)+alcohol (2) mixtures, it is assumed that the process of mixtures formation requires:

- mixing of (1) with (2) to establish (1)-(2) contacts with an interaction energy χ_{12}^* per mole of (1)-(2) contacts
- these (1)-(2) contacts between formamide and butanol would then cause rupture of
 - intermolecular association in formamide to yield monomers of formamide with an interactional energy χ_{11} per mole
 - intermolecular association in butanol to yield monomers of butanol with an interactional energy χ_{22} per mole
- the monomers of formamide then interact with butanol to give 1-2 molecular entity with an interaction energy χ_{12} per mole

The change in enthalpy due to processes (a), (b)(i), (b)(ii) and (c) would then be expressed [49,62-64] by

$$\Delta H_u = x_1 \chi_{12}^* S_2 \quad (21)$$

where S_2 is the surface fraction of butanol involved in (1)-(2) contact and is defined [62,63] by:

$$S_2 = \frac{x_2 V_2}{\sum x_i V_i} \quad (22)$$

Similarly enthalpy changes due to processes (b) and (c) would be given by:

$$\Delta H_{b(i)} = x_1 \chi_{11} S_2' \quad (23)$$

$$\Delta H_{b(ii)} = x_1 \chi_{22} S_2' \quad (24)$$

where S_2' is the surface fraction of butanol that brings about changes in formamide and, following our earlier work has been expressed by

Table 6. Values of association parameters, Δh_H^0 , Δs_H^0 and Δv_H^0 , association constants, K_H and K^ϕ , of Treszczanowicz-Benson (TB) association model and Flory interaction parameter, χ_{12} , for the binary systems at 308.15 K. TB and TB* represent the values of parameters when either butanol or formamide is assumed to be associated, respectively

System		Δh_H^0 (J mol ⁻¹)	Δs_H^0 (J K ⁻¹ mol ⁻¹)	Δv_H^0 (cm ³ mol ⁻¹)	K_H	K^ϕ	χ_{12}
Formamide (1)+1-butanol (2)	TB	-17513	-43.56	-5	4.93	3.12	16.74
	TB*	-11865	-28.51	-5	3.32	4.62	-47.06
Formamide (1)+2-methyl-1-propanol (2)	TB	-21562	-57.15	-5	4.67	2.94	16.30
	TB*	-12895	-32.05	-5	3.25	4.52	-44.42

Table 7. Value of parameters involved in graph theoretical approach

System	ξ_1^3	ξ_2^3	$(\xi_1^3)_m$	$(\xi_2^3)_m$	α_{12}	χ_{12}	χ^*
Formamide (1)+1-butanol (2)	0.8	1.49	0.8	1.4	1.7269	2453.42	2341.43
Formamide (1)+2-methyl-1-propanol (2)	0.8	1.4	0.8	1.36	3.4865	3277.89	718.93

$$S_2' \propto x_1 S_2 = \frac{K x_1 x_2 V_2}{\sum x_i V_i} \quad (25)$$

and

$$\Delta H_c = x_2 \chi_{12} S_2' \quad (26)$$

The total enthalpy change due to processes (a), (b) and (c) is given by:

$$H_m^E = \left[\frac{x_1 x_2 V_2}{\sum x_i V_i} \right] [\chi_{12}^* + K x_1 \chi_{11} + K x_1 \chi_{22} + K x_2 \chi_{12}] \quad (27)$$

$$H_m^E = \left[\frac{x_1 x_2 (\xi_1^3 / \xi_2)}{x_1 + x_2 (\xi_1^3 / \xi_2)} \right] [\chi_{12}^* + K x_1 \chi_{11} + K x_1 \chi_{22} + K x_2 \chi_{12}] \quad (28)$$

For these mixtures, it would be reasonable to assume that $\chi_{12}^* = K \chi_{12}$ and $K \chi_{22} = K \chi_{11} = \chi^*$, then Eq. (12) reduces to

$$H_m^E = \left[\frac{x_1 x_2 (\xi_1^3 / \xi_2)}{x_1 + x_2 (\xi_1^3 / \xi_2)} \right] [(1 + \chi_2) \chi_{12}^* + \chi_1 \chi^*] \quad (29)$$

Calculation of H_m^E from Eq. (13) requires the knowledge of two unknown interaction parameters χ_{12}^* and χ^* . These parameters are calculated using H_m^E data at two compositions ($x_1=0.4$ and 0.5) for various binary mixtures, and were subsequently used to evaluate H_m^E at other mole fraction (x_1). Such values of H_m^E along with parameters χ_{12}^* and χ^* are recorded in Table 6 along with previously reported (ξ) values [49]. The calculated H_m^E were found to compare well with their corresponding experimental values (Fig. 4). This gives additional support to the assumptions made in derivation of Eq. (29).

CONCLUSION

The thermodynamics of binary mixtures of formamide (1)+1-butanol or 2-methyl-1-propanol (2) was discussed in terms of Prigogine-Flory-Patterson theory, Treszczanowicz-Benson association model and Graph theoretical approach. Measured excess molar enthalpies (H_m^E) and volumes (V_m^E) data of these mixtures were predicted reasonably well using these models. The Mecke-Kempton type TB association model was developed for binary alkane+alkanol systems having one associated component. For the first time, this TB association model was applied to systems containing both the components associated through H-bonding by considering either of them to be associated at a time. In both cases, when either formamide or butanol was assumed to be associated, the calculated H_m^E and V_m^E values compared reasonably well with corresponding experimental data. The extent of inter-molecular H-bonding in formamide and butanol in their binary mixtures was reflected in their molar association of H-bonding Δh_3^0 and association constant K_H .

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LIST OF SYMBOLS

C_p^E	: molar excess isobaric heat capacity
$\Delta H_a, \Delta H_{b(i)}, \Delta H_{b(ii)}, \Delta H_c$: enthalpy of processes in graph theory
Δh_H^0	: standard enthalpy of association
K^ϕ	: volume fraction based association constant
n	: number of adjustable parameters in Eq. (1)
P	: pressure
P_i^*	: characteristic pressure
\tilde{P}_i	: reduced pressure
P^*	: characteristic pressure of mixture
r_1	: number of segment in a molecule of monomer
R	: gas constant
ΔS_H^0	: standard entropy of association
S_i	: contact sites per segment
S_2	: surface fraction of butanol involved in (1)-(2) contact
S_2'	: surface fraction of butanol (2) that brings about changes in formamide (1)
T	: temperature
T_i^*	: characteristic temperature
T^*	: characteristic temperature of mixture
\tilde{T}_i	: reduced temperature
\tilde{T}	: reduced temperature of mixture
U_i^*	: characteristic configurational energy
\tilde{U}_i	: reduced configurational energy
$\tilde{U}(\tilde{T})$: reduced configurational energy of mixture
V	: molar volume
V_i^*	: characteristic volume
\tilde{V}_i	: reduced volume
V^*	: characteristic volume of mixture
\tilde{V}	: reduced volume of mixture
Δv_H^0	: standard volume of association
x_i	: mole fraction
X_m^E	: excess molar property
$X^{(n)}$: adjustable parameters of Redlich and Kister equation

Greek Letters

α	: isobaric expansivity
α_{12}	: constant characteristics of binary mixture in graph theory
ϕ_i	: hard core volume fraction
κ_T	: isothermal compressibility
ψ_i	: molar contact energy fraction
σ	: standard deviations of X_m^E
θ_i	: molecular surface fraction
${}^3\xi_i$: connectivity parameter of third order in pure state
$({}^3\xi_i)_m$: connectivity parameter of third order in binary mixture
χ_{12}	: flory interaction parameter for excess enthalpies
χ_{12}^*	: flory interaction parameter for excess volume

Subscript

Expt.	: experimental
F	: flory theory
free vol.	: free volume contribution
i	: pure component
Inter.	: interactional contribution
MK	: Mecke-Kempton type of association
TB	: Treszczanowicz-Benson association model when butanol

is assumed to be associated

TB* : Treszczanowicz-Benson association model when formamide is assumed to be associated

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