

Ternary and constituent binary excess molar enthalpies of {1,2-dichloropropane + 2-pentanol + 3-pentanol} at $T=298.15$ K

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Abstract—Excess molar enthalpies for the ternary system of {1,2-dichloropropane (1,2-DCP)+2-pentanol+3-pentanol} and their constituent binary mixtures {1,2-DCP+2-pentanol}, {1,2-DCP+3-pentanol}, and {2-pentanol+3-pentanol} have been measured over the whole range of composition using an isothermal micro-calorimeter with flow-mixing cell at $T=298.15$ K and atmospheric pressure. The experimental excess molar enthalpies of all the binaries and ternary mixture, including three pseudo-binary mixtures, are positive (endothermic effect) throughout the mole fraction range, except for the binary mixture {2-pentanol+3-pentanol} in which shows a small negative values over the entire composition range. The experimental binary $H_{m,ij}^E$ data were fitted to Redlich-Kister equation, and the Cibulka and the Morris equations were employed to correlate the ternary $H_{m,123}^E$ data. Several empirical equations for predicting ternary excess enthalpies from constituent binary mixing data have been also examined and compared. The experimental results have been qualitatively discussed in terms of molecular interactions.

Keywords: Excess Molar Enthalpy, Ternary Mixture, 1,2-Dichloropropane, 2-Pentanol, 3-Pentanol, Empirical Equations

INTRODUCTION

In previous papers we reported the determination of some excess thermodynamic properties of several binary and ternary mixtures containing 1,2-dichloropropane (1,2-DCP) [1-8], which is used as a cleaning agent and a solvent for oil, fats, resin and rubber [9]. In continuation of the research program about determination of thermophysical properties on mixing, this paper is undertaken to measure the excess molar enthalpies over the whole range of composition at the temperature of 298.15 K and atmospheric pressure for the ternary mixture {1,2-DCP+2-pentanol+3-pentanol} and for the three constituent binary mixtures {1,2-DCP+2-pentanol}, {1,2-DCP+3-pentanol} and {2-pentanol+3-pentanol}, which are not available in literature survey. In a previous paper, ternary $H_{m,123}^E$ data of {1,2-DCP+2-propanol+2-butanol} measured at $T=298.15$ K and atmospheric pressure have been reported [8].

The aim of this study is to make a qualitative interpretation of the interactions including isomeric effect between different types of molecules, to correlate the experimental data, and to compare them with the values predicted by the several models.

The experimental $H_{m,ij}^E$ values of binary mixtures were fitted to the Redlich-Kister [10] equation. The measured values of ternary excess enthalpy $H_{m,123}^E$ were correlated using Cibulka [11] and Morris [12] equations. A number of researches have proposed empirical equations to predict excess thermodynamic properties for ternary mixtures from the results of corresponding binaries. In this work, Kohler [13], Rastogi et al. [14], Radojković [15], Jacob-Fitzner [16], Colinet [17], and Knobloch and Schwart [18], which are classified as symmetric equations and Tsao and Smith [19], Toop [20],

Scatchard et al. [21], Hillert [22], and Mathieson-Thynne [23], being classified as asymmetric ones, have been also examined and compared.

EXPERIMENTAL

1. Materials

The sources and purities of the chemicals employed were 1,2-DCP (Fluka, Switzerland, >99% (stated purity)), 2-pentanol (Aldrich, USA, >98.0% (stated purity)) and 3-pentanol (Aldrich, USA, >98.0% (stated purity)). Before measurements, all chemicals were subjected to no further purification but degassed using an ultrasonic bath. Gas chromatographic (Shimadzu GC-17A) analysis, using capillary fused silica column (i.d. 0.22 μ m, length 25 m) and a flame-ionization detector, showed that the major peak area for each pure component exceeds 99.0%. The purity of the chemicals was also checked by measuring and comparing the refractive indices and densities at $T=298.15$ K and atmosphere pressure with their corresponding literature values [24] as shown in Table 1. These results of pure components are in good agreement with literature values.

2. Apparatus and Procedure

Refractive indices were measured using a refractometer (RA-520, Kyoto Electronics, Japan) with a resolution of $\pm 2 \times 10^{-5}$ for values ranging from 1.32 to 1.58 and a temperature precision of $\pm 1 \times 10^{-2}$ K. The densities of pure components and their corresponding binary mixtures $\{x(2\text{-pentanol})+(1-x)3\text{-pentanol}\}$ having fixed molar ratios $x/(1-x) \approx 0.3, 1.0$ and 3.0 were measured by a vibrating-tube densimeter (DMA 58, Anton Paar, Graz, Austria) with an accuracy $\pm 1 \times 10^{-5}$ g/cm³, which is equipped with built-in electronic thermostat having an accuracy of $\pm 1 \times 10^{-2}$ K. Prior to measurements, both apparatuses were calibrated at working temperature and at atmospheric pressure using HPLC grade water (Fisher Scientific, USA, >99.7%) and dry air.

The experimental excess molar enthalpies were measured with an isothermal calorimeter (CSC-4400, Calorimetry Sciences Cor-

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Table 1. Densities ρ , refractive indices n_D^{25} , and purities of pure liquids at T=298.15 K

Compound	ρ [g/cm ³]		n_D^{25}		GC analysis [mass%]	Stated purities [mass%]
	Exptl.	Lit. ^a	Exptl.	Lit. ^a		
1,2-DCP	1.14912	1.14936	1.43668	1.43679	99.0	>99.0
2-pentanol	0.80514	0.8054	1.40440	1.4044	99.0	>98.0
3-pentanol	0.81559	0.8160	1.40826	1.4079	99.0	>98.0

^aRef. [24]

poration (CSC), UT, USA) with a newly designed flow-mixing assembly kit (CSC-4442, CSC, UT, USA). Two high precision, positive displacement, syringe-type pumps (model 500D, Teledyne Isco Inc.) were used to establish constant flow rates through the mixing cell. Working pressure of the mixing cell in the calorimeter was controlled at P=101.3 kPa by a back-pressure regulator (Grove Valves & Regulator Co., Stafford, TX, USA). Details of an isothermal calorimeter, the calibrations of two pumps and a calorimeter, the reliability of the apparatus, and the experimental procedure including the determination of baseline values of heat flux to obtain excess molar enthalpies have been described in previous works [2-4,8]. Prior to measurements, the performance [8] of calorimeter was carried out at T=298.15 K with the endothermic system {cyclohexane hexane} and exothermic system {water+ethanol}, most widely employed as reference mixtures [25,26]. The uncertainty in excess molar enthalpy measurement is estimated to be better than 1.0%. Similarly, the uncertainty of the mole fraction was estimated to be less than $\pm 1 \times 10^{-3}$.

Each experimental run for the measurement of the ternary excess molar enthalpies was performed by adding one component (1,2-DCP) to a binary mixture of the other two (2-pentanol and 3-pentanol). A ternary mixture is regarded as pseudo-binary mixture made up of one binary mixture and the third component. In this ternary system, one mole of the ternary mixture was prepared by mixing $(1-x_1)$ of the binary mixture composed of $\{x'_1 \text{ 2-pentanol (2)} + x'_2 \text{ 3-pentanol (3)}\}$, where $x'_2 = 1 - x'_1$, and x_1 is the mole fraction of 1,2-DCP (1). For this purpose, binaries with fixed molar ratios $x'_1/x'_2 \approx 0.3, 1.0$ and 3.0 , were prepared by mass using an electronic balance with a precision $\pm 1.5 \times 10^{-5}$ g (AT-201, Mettler Toledo, Switzerland). The ternary excess molar enthalpy $H_{m,123}^E$ at the pseudo-binary composition x_1, x_2 , and $x_3 (= 1 - x_1 - x_2)$ was then obtained according to the following relation:

$$H_{m,123}^E = H_{m,1+23}^E + (1-x_1)H_{m,23}^E \quad (1)$$

where x_1 is the mole fraction of the component 1 (1,2-DCP) in the ternary mixture, and the $H_{m,1+23}^E$ is experimental excess enthalpy for pseudo-binary mixtures and $H_{m,23}^E$ is the excess molar enthalpy of a binary mixture composed of {2-pentanol+3-pentanol}. Values of $H_{m,23}^E$ at three specified composition (the approximate composition of these mixtures were 25, 50 and 75 mol% of component 2-pentanol) were obtained by Eq. (2) using parameters listed in Table 3. Eq. (1) does not involve any approximation.

RESULTS AND DISCUSSION

1. Experimental Results

The experimental excess molar enthalpies $H_{m,ij}^E$ ($i < j$), for the con-

stituent three binary mixtures of $\{x(1,2\text{-DCP}) + (1-x)2\text{-pentanol}\}$, $\{x(1,2\text{-DCP}) + (1-x)3\text{-pentanol}\}$ and $\{x(2\text{-pentanol}) + (1-x)3\text{-pen-}$

Table 2. Experimental excess molar enthalpies $H_{m,jk}^E$ for binary mixtures $\{x(1,2\text{-DCP}) + (1-x)2\text{-pentanol}\}$, $\{x(1,2\text{-DCP}) + (1-x)3\text{-pentanol}\}$ and $\{x(2\text{-pentanol}) + (1-x)3\text{-pentanol}\}$ at T=298.15 K

x	$H_{m,jk}^E$ (J/mol)	x	$H_{m,jk}^E$ (J/mol)
x(1,2-DCP)+(1-x)2-pentanol			
0.030	219.2	0.546	1966.7
0.052	362.7	0.596	1962.9
0.096	704.5	0.654	1920.1
0.151	979.3	0.703	1816.7
0.205	1234.0	0.751	1689.4
0.247	1413.4	0.798	1558.5
0.300	1596.1	0.845	1360.6
0.352	1720.4	0.901	1035.7
0.404	1843.7	0.947	634.8
0.445	1895.0	0.974	399.6
0.496	1949.6		
x(1,2-DCP)+(1-x)3-pentanol			
0.029	300.8	0.553	2312.2
0.051	492.5	0.602	2275.7
0.095	816.8	0.652	2205.8
0.149	1174.5	0.700	2090.5
0.202	1516.6	0.748	1945.4
0.245	1725.1	0.796	1749.4
0.297	1929.7	0.853	1440.5
0.349	2083.3	0.900	1094.4
0.401	2184.8	0.946	673.0
0.452	2274.9	0.974	435.2
0.503	2312.8		
x(2-pentanol)+(1-x)3-pentanol			
0.028	-6.2	0.548	-28.3
0.048	-8.4	0.598	-26.9
0.098	-13.3	0.649	-25.1
0.148	-17.5	0.699	-22.7
0.197	-21.4	0.750	-20.1
0.247	-24.4	0.800	-17.0
0.297	-26.3	0.851	-13.8
0.347	-28.3	0.902	-10.2
0.397	-29.3	0.952	-5.0
0.447	-29.9	0.983	-2.4
0.498	-29.5		

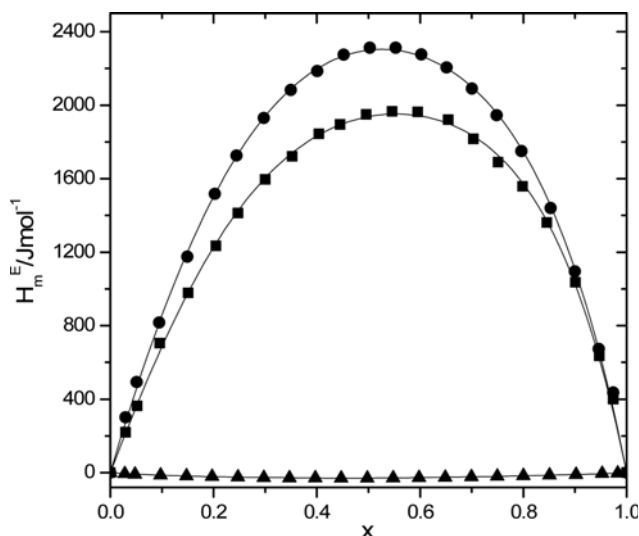


Fig. 1. Excess molar enthalpies, $H_{m,jk}^E$ (J/mol) of binary mixtures at $T=298.15$ K and atmospheric pressure. Experimental results: (●, $H_{m,12}^E$), $x(1,2\text{-DCP})+(1-x)3\text{-pentanol}$; (■, $H_{m,13}^E$), $x(1,2\text{-DCP})+(1-x)2\text{-pentanol}$; (▲, $H_{m,23}^E$), $x(2\text{-pentanol})+(1-x)3\text{-pentanol}$. Solid lines: calculated with Eq. (2) using parameters listed in Table 3.

tanol} at $T=298.15$ K and atmospheric pressure, are listed in Table 2 and the results are also presented graphically in Fig. 1.

The experimental excess molar enthalpies $H_{m,ij}^E$ of three binary mixtures and three pseudo-binary mixtures has been fitted to Redlich-Kister [10] equation:

$$H_{m,ij}^E(\text{J/mol}) = x_i(1-x_i) \sum_{p=1}^n A_p (2x_i - 1)^{p-1} \quad (2)$$

where x_i is the mole fraction of the first component in the binary mixture and n is the number of parameters. A_p is the adjustable parameters determined by minimizing the sum of squares of the differences between experimental values of $H_{m,ij}^E$ and the corresponding values calculated by Eq. (2) using a linear regression procedure. The optimal number of the adjustable parameters A_p was determined by applying an F -test [27], based on the F -distribution, with an examination of the variation of the standard deviation σ defined by

$$\sigma = \left[\frac{\sum_{i=1}^N (H_{m,ij}^E(\text{exp}) - H_{m,ij}^E(\text{calc}))^2}{N - n} \right]^{1/2} \quad (3)$$

where N is the number of experimental points and n is the number of adjustable parameters. All the parameters of Eq. (2) are listed in Table 3 along with the corresponding standard deviations σ of the fits.

As shown in Fig. 1, the excess molar enthalpies $H_{m,ij}^E$ for the binary

mixtures $\{x(1,2\text{-DCP})+(1-x)2\text{-pentanol}\}$ and $\{x(1,2\text{-DCP})+(1-x)3\text{-pentanol}\}$ are positive, while the binary mixture $\{x(2\text{-pentanol})+(1-x)3\text{-pentanol}\}$ is slightly negative over the whole range of composition.

The excess enthalpies are influenced by two opposing effects: (i) absorption of heat due to depolymerization of self-associated alcohols by 1,2-DCP and reduction in dipole-dipole interactions between like molecules; (ii) liberation of heat as a result of possible hydrogen bonding interaction between the halogenated group of the alkane and the hydroxyl group of the alcohol or the formation of hydrogen-bonded complexes between unlike alkanol molecules. The actual values of $H_{m,ij}^E$ would depend upon the relative strength of the two opposing effects. The positive experimental $H_{m,ij}^E$ values in the binary mixtures for {1,2-DCP+2-pentanol, and +3-pentanol} suggest that the former effect is more predominant than the latter, which is consistent with previous works [4,8,28]. Combining the results of this work and previous works [4,8,28,29], the isomeric effects for the binary mixtures 1,2-DCP with 1-, and 2-propanols and 1-, and 2-butanols and 2-, and 3-pentanols can be also examined. The obtained results can be explained in terms of degree of branching in the chain and relative position of the alkyl and OH group in the alcohol. The trend in positive values of $H_{m,ij}^E$ in the order 1-alkanols (1-propanol < 1-butanol) < 2-alkanols (2-propanol < 2-butanol < 2-pentanol) < 3-pentanol suggests that steric hindrance mainly due to branching, predominates over that of specific interaction of unlike molecules. As the chain length of alkanols increases in length, the mixture becomes more endothermic, even though they do not have much difference in polarity (1,2-DCP; 1.87D, 2-pentanol; 1.66D, 3-pentanol; 1.64D [30]). Comparing these results with Lafuente et al. [28] and Rambabu et al. [29], a similar trend was found in both cases.

The experimental pseudo-binary excess enthalpy $H_{m,1+23}^E$ and the corresponding ternary excess enthalpy $H_{m,123}^E$, calculated from Eq. (1), for the system $\{x_1(1,2\text{-DCP})+x_2(2\text{-pentanol})+(1-x_1-x_2)(3\text{-pentanol})\}$ at $T=298.15$ K are listed in Table 4. The values of $H_{m,1+23}^E$ are plotted in Fig. 2, along with curves of the constituent binary systems for comparison. The $H_{m,1+23}^E$ values also indicate that the prevailing effect is the disruption of the associated hydrogen bonding of 2- and 3-alkanols against the formation of hydrogen bonds between 2-pentanol and 3-pentanol molecules during mixing process. The maximum values of $H_{m,12}^E$, $H_{m,13}^E$ and $H_{m,1+23}^E$ occur near $x_1=0.5$, and at constant composition of x_1 , the excess enthalpies $H_{m,1+23}^E$ of the pseudo-binary mixtures also gradually increase with an increase of the relative amount of the 3-pentanol in the binary mixture composed of {2-pentanol (2)+3-pentanol (3)} as expected.

Experimental results of $H_{m,123}^E$ for the ternary system were correlated as the sum of binary and ternary contributions:

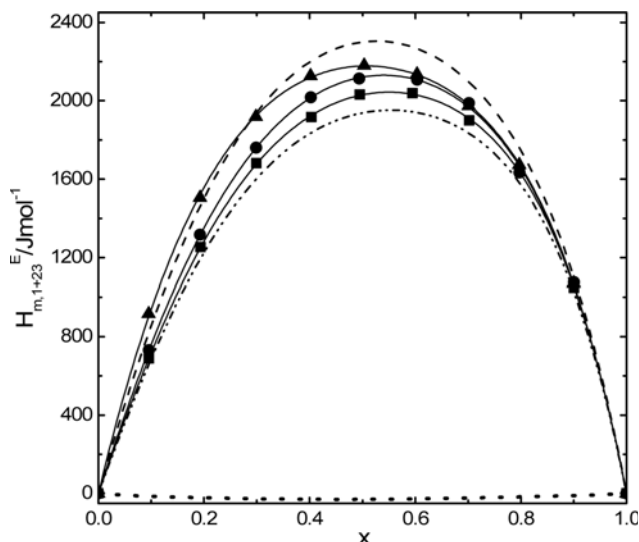
$$H_{m,123}^E(\text{J/mol}) = H_{m,bin}^E + x_1 x_2 (1-x_1-x_2) \Delta_{123} \quad (4)$$

Table 3. Adjustable parameters A_i of Redlich-Kister equation in Eq. (2) with standard deviation σ (J/mol) for constituent binary systems at $T=298.15$ K

Binary systems	A_1	A_2	A_3	A_4	A_5	σ (J/mol)
$x(1,2\text{-DCP})+(1-x)2\text{-pentanol}$	7751.9	1056.0	2755.3	2060.0		26.6
$x(1,2\text{-DCP})+(1-x)3\text{-pentanol}$	9199.5	684.5	2633.3	1624.5		26.1
$x(2\text{-pentanol})+(1-x)3\text{-pentanol}$	-118.0	22.0	18.2	7.0	-69.2	0.4

Table 4. Experimental excess molar enthalpies, $H_{m,123}^E$ for the ternary mixture $\{x_1(1,2\text{-DCP})+x_2(2\text{-pentanol})+(1-x_1-x_2)3\text{-pentanol}\}$ at $T=298.15$ K and atmospheric pressure

x_1	x_2	$H_{m,1+23}^E$ (J/mol)	$H_{m,123}^E$ (J/mol)	x_1	x_2	$H_{m,1+23}^E$ (J/mol)	$H_{m,123}^E$ (J/mol)
$x_1/x_2=0.3336, H_{m,23}^E$ (J/mol)=-24.3							
0.095	0.226	916.7	894.7	0.603	0.099	2135.8	2126.1
0.192	0.202	1506.4	1486.8	0.701	0.075	1974.0	1966.7
0.298	0.176	1919.7	1902.7	0.797	0.051	1673.9	1668.9
0.402	0.150	2126.4	2111.9	0.900	0.025	1070.5	1068.1
0.504	0.124	2179.9	2167.8				
$x_1/x_2=0.9809, H_{m,23}^E$ (J/mol)=-29.5							
0.096	0.448	730.4	703.7	0.604	0.196	2107.6	2095.9
0.193	0.400	1315.9	1292.1	0.702	0.148	1987.7	1978.8
0.299	0.347	1759.7	1739.0	0.797	0.100	1634.1	1628.1
0.403	0.296	2018.0	2000.3	0.900	0.049	1075.6	1072.6
0.494	0.250	2113.1	2098.2				
$x_1/x_2=2.9443, H_{m,23}^E$ (J/mol)=-20.1							
0.096	0.675	688.8	670.6	0.595	0.302	2039.0	2030.9
0.193	0.602	1253.2	1237.0	0.702	0.222	1899.9	1894.0
0.300	0.523	1681.6	1667.6	0.798	0.151	1639.3	1635.2
0.403	0.445	1916.0	1904.1	0.901	0.074	1048.0	1046.1
0.495	0.377	2032.0	2021.9				

**Fig. 2. Excess molar enthalpies, $H_{m,1+23}^E$ (J/mol) for the ternary mixture $\{x_1(1,2\text{-DCP})+x_2(2\text{-pentanol})+x_3(3\text{-pentanol})\}$ at $T=298.15$ K and atmospheric pressure. Experimental results: (\blacktriangle), $x_1/x_2=0.3336$; (\bullet), $x_1/x_2=0.9809$; (\blacksquare), $x_1/x_2=2.9443$. Solid lines: calculated using Redlich-Kister equation. Dotted lines: (---), $x(1,2\text{-DCP})+(1-x)3\text{-pentanol}$; (- - -), $x(1,2\text{-DCP})+(1-x)2\text{-pentanol}$; (- · -), $x(2\text{-pentanol})+(1-x)3\text{-pentanol}$.**

where $H_{m,bin}^E$, as the binary contribution to the excess molar enthalpy of a ternary system, is expressed by:

$$H_{m,bin}^E(\text{J/mol}) = \sum_{i=1}^2 \sum_{j=2}^3 H_{m,ij}^E = H_{m,12}^E + H_{m,13}^E + H_{m,23}^E \quad (5)$$

where $H_{m,ij}^E$ is the binary excess enthalpies calculated from the correlation (by Eq. (2)) of the constituting binary combination i - j pairs

Table 5. Fitting parameters c_i for ternary contributions in Eq. (6) and (7), and standard deviation σ (J/mol)

Ternary system		Adjustable parameters	
		by Eq. (6)	by Eq. (7)
$x_1(1,2\text{-DCP})$	c_0	9829.9	17.2
$+x_2(2\text{-pentanol})$	c_1	-24977.3	-64.0
$+(1-x_1-x_2)3\text{-pentanol}$	c_2	-7381.4	-61.5
	c_3		59.1
	c_4		194.8
	c_5		52.4
	c_6		-24.2
	c_7		-103.1
	c_8		-133.0
	σ (J/mol)	43.6	15.1

using the ternary mole fractions. The last term in Eq. (4) stands for the ternary contribution to the ternary excess enthalpy $H_{m,123}^E$. Several correlations for the ternary contribution are suggested in the literature. In this work, and the ternary contribution term to Δ_{123} excess molar enthalpy of the ternary system was fitted to the expression suggested by Cibulka,

$$\Delta_{123} = (c_0 + c_1x_1 + c_2x_2) \quad (6)$$

and the one suggested by Morris et al.,

$$\frac{\Delta_{123}}{RT} = (c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + c_6x_1^3 + c_7x_1^2x_2 + c_8x_1x_2^2 + c_9x_2^3 \dots) \quad (7)$$

which differs from the number of adjustable parameters. The parameters c_i of Eqs. (6)-(7) computed by the unweighted least-squares method using a linear regression procedure similar to that for the

binary parameters are listed in Table 5. It can be observed that the prediction model to calculate adequately the ternary contribution for this mixture needs more parameters than that of Cibulka. The optimal number of the parameters c_i was also determined with an optimization algorithm similar to that of the binary systems. The lines of constant ternary excess molar enthalpy, $H_{m,123}^E$ calculated using Eqs. (4), (5) and (7) are presented in Fig. 3. The excess molar enthalpy $H_{m,123}^E$ for the ternary system is positive over the whole range of composition, and the maximum value is 2,250 J/mol around at $x_1=0.5-0.55$.

Fig. 4 represents the ternary contribution, $x_1x_2(1-x_1-x_2)\Delta_{123}$, to the ternary excess molar enthalpy, correlated with Eq. (7). At the poor and rich region of 1,2-DCP on the Gibbs triangle, positive and negative contribution values were found, respectively, which can

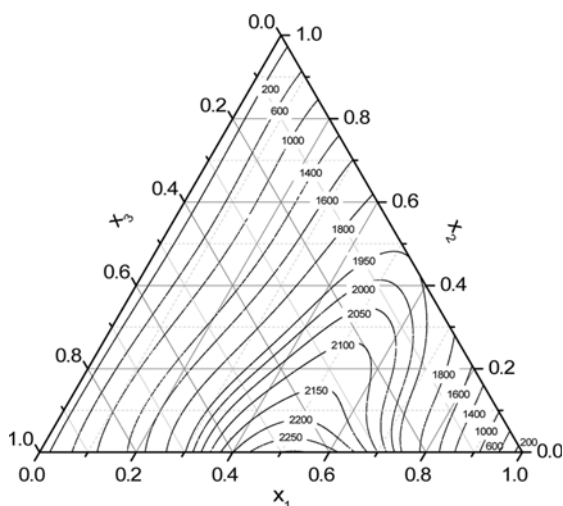


Fig. 3. Lines of constant excess molar enthalpies $H_{m,123}^E$ (J/mol) for ternary mixture $\{x_1(1,2\text{-DCP})+x_2(2\text{-pentanol})+x_3(3\text{-pentanol})\}$ at $T=298.15$ K calculated from correlation of the experimental results by Eqs. (4) and (7) using parameters listed in Tables 3 and 5.

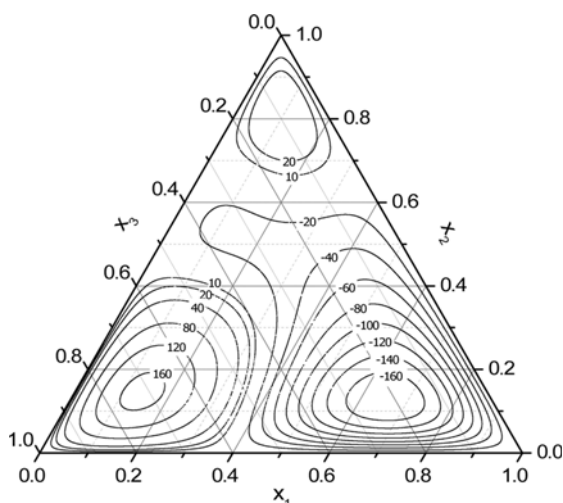


Fig. 4. Ternary contribution, $x_1x_2(1-x_1-x_2)\Delta_{123}$, for ternary mixture $\{x_1(1,2\text{-DCP})+x_2(2\text{-pentanol})+x_3(3\text{-pentanol})\}$ at $T=298.15$ K calculated from correlation of the experimental results by Eq. (7) using parameters listed in Table 5.

be explained as follows: some energy is needed to break intermolecular hydrogen bonds of 2- or 3-alkanols during mixing while some heat is liberated due to possible intermolecular complexes [31-33] between the halogenated group of the 1,2-DCP and the hydroxyl group of the 2 or 3-alkanols.

2. Prediction of H^E by Empirical Models

A wide variety of empirical methods have been proposed to estimate excess properties of ternary mixtures from experimental results of their constituent binaries. These methods can be divided into symmetric and asymmetric, depending on whether the assumption of the three binaries contributing equally to the ternary mixture magnitude is accepted or not. The symmetric equations tested were those suggested by Kohler, Rastogi, Radojkovic, Jacob and Fitzner, Colinet, and Knobloch and Schwartz, while the asymmetric ones were by Tsao and Smith, Toop, Scatchard et al., Hillert, and Mathieson and Thynne. In this work, all models described above have been examined and compared, which take only the binary contributions into account.

i) The Kohler model [13]

$$H_{123}^E = (x_1 + x_2)^2 H_{12}^E(x_1^b, x_2^b) + (x_1 + x_3)^2 H_{13}^E(x_1^b, x_3^b) + (x_2 + x_3)^2 H_{23}^E(x_2^b, x_3^b) \quad (8)$$

where H_{ij}^E is excess molar enthalpies for the binary mixtures at binary compositions x_i^b and x_j^b , such that $x_i^b = 1 - x_j^b = x_i/(x_i + x_j)$, x_i and x_j refers to ternary compositions. The same meanings of symbols mentioned in Kohler model apply to all models unless otherwise stated.

ii) The Rastogi et al. model [14]

$$H_{123}^E = 0.5[(x_1 + x_2)H_{12}^E(x_1^b, x_2^b) + (x_1 + x_3)H_{13}^E(x_1^b, x_3^b) + (x_2 + x_3)H_{23}^E(x_2^b, x_3^b)] \quad (9)$$

where the binary mole fractions are computed as in the Kohler equation (Eq. (8)).

iii) The Radojković model [15]

$$H_{123}^E(\text{J/mol}) = H_{12}^E + H_{13}^E + H_{23}^E \quad (10)$$

This model is used with only binary contributions evaluated by Redlich-Kister equation (Eq. (2)) using the parameters in Table 3, where x_1 , x_2 , and x_3 are mole fractions of the ternary mixture.

iv) The Jacob and Fitzner model [16]

$$H_{123}^E = \frac{x_1x_2H_{12}^E(x_1^b, x_2^b)}{\left(x_1 + \frac{x_3}{2}\right)\left(x_2 + \frac{x_3}{2}\right)} + \frac{x_1x_3H_{13}^E(x_1^b, x_3^b)}{\left(x_1 + \frac{x_2}{2}\right)\left(x_3 + \frac{x_2}{2}\right)} + \frac{x_2x_3H_{23}^E(x_2^b, x_3^b)}{\left(x_2 + \frac{x_1}{2}\right)\left(x_3 + \frac{x_1}{2}\right)} \quad (11)$$

where $x_i^b = 1 - x_j^b = (1 + x_i - x_j)/2$.

v) The Colinet model [17]

$$H_{123}^E = 0.5 \left[\frac{x_2}{1-x_1} H_{12}^E(x_1, 1-x_1) + \frac{x_1}{1-x_2} H_{12}^E(1-x_2, x_2) + \frac{x_3}{1-x_1} H_{13}^E(x_1, 1-x_1) + \frac{x_1}{1-x_3} H_{13}^E(1-x_3, x_3) + \frac{x_3}{1-x_2} H_{23}^E(x_2, 1-x_2) + \frac{x_2}{1-x_3} H_{23}^E(1-x_3, x_3) \right] \quad (12)$$

vi) The Knobloch and Schwartz model [18]

$$H_{123}^E = \frac{1}{3}(\Delta_1 H_{123}^E + \Delta_2 H_{123}^E + \Delta_3 H_{123}^E) \quad (13)$$

where $\Delta_1 H_{123}^E$, $\Delta_2 H_{123}^E$ and $\Delta_3 H_{123}^E$ are determined as follows:

$$\begin{aligned} \Delta_1 H_{123}^E &= \frac{x_2}{1-x_1} H_{12}^E(x_1^b, x_2^b) + \frac{x_3}{1-x_1} H_{13}^E(x_1^b, x_3^b) \\ &\quad + (1-x_1)^{1/2} H_{23}^E(x_2^b, x_3^b) \\ \Delta_2 H_{123}^E &= \frac{x_1}{1-x_2} H_{12}^E(x_2^b, x_1^b) + \frac{x_3}{1-x_2} H_{23}^E(x_2^b, x_3^b) \\ &\quad + (1-x_2)^{1/2} H_{13}^E(x_1^b, x_3^b) \\ \Delta_3 H_{123}^E &= \frac{x_1}{1-x_3} H_{13}^E(x_3^b, x_1^b) + \frac{x_2}{1-x_3} H_{23}^E(x_3^b, x_2^b) \\ &\quad + (1-x_3)^{1/2} H_{12}^E(x_1^b, x_2^b) \end{aligned} \quad (14)$$

Eqs. (9)-(14) are symmetric due to the application of an equal contribution of the constituent three binaries to the ternary mixture. Their numerical predictions do not depend on the arbitrary designation of component numbering. Contrarily, the following equations including Tsao and Smith equation are asymmetric:

vii) The Tsao-Smith model [19]

$$\begin{aligned} H_{123}^E &= \frac{x_2}{1-x_1} H_{12}^E(x_1^b, x_2^b) + \frac{x_3}{1-x_1} H_{13}^E(x_1^b, x_3^b) \\ &\quad + (1-x_1) H_{23}^E(x_2^b, x_3^b) \end{aligned} \quad (15)$$

where $H_{ij}^E(x_i^b, x_j^b)$ refers to the excess enthalpies of the binary mixtures at binary compositions (x_i^b, x_j^b) where $x_i^b = x_i$ and $x_j^b = 1 - x_i^b$ for 1-2 and 1-3 binaries, and $x_2^b = x_2/(x_2 + x_3)$ and $x_3^b = 1 - x_2^b$ for 2-3 binary system.

viii) The Toop model [20]

$$\begin{aligned} H_{123}^E &= \frac{x_2}{1-x_1} H_{12}^E(x_1^b, x_2^b) + \frac{x_3}{1-x_1} H_{13}^E(x_1^b, x_3^b) \\ &\quad + (1-x_1)^2 H_{23}^E(x_2^b, x_3^b) \end{aligned} \quad (16)$$

where the binary mole fractions x_i^b and x_j^b are computed as in the Tsao-Smith equation (Eq. (15)).

ix) The Scatchard et al. model [21]

$$H_{123}^E = \frac{x_2}{1-x_1} H_{12}^E(x_1^b, x_2^b) + \frac{x_3}{1-x_1} H_{13}^E(x_1^b, x_3^b) + H_{23}^E(x_2, x_3) \quad (17)$$

where the binary mole fractions x_i^b and x_j^b are computed as in the Tsao-Smith equation (Eq. (15)).

x) The Hillert model [22]

$$\begin{aligned} H_{123}^E &= \frac{x_2}{1-x_1} H_{12}^E(x_1^b, x_2^b) + \frac{x_3}{1-x_1} H_{13}^E(x_1^b, x_3^b) \\ &\quad + \frac{x_3}{1-x_2} H_{23}^E(x_2, 1-x_2) + \frac{x_3}{1-x_3} H_{23}^E(1-x_3, x_3) \end{aligned} \quad (18)$$

xi) The Mathieson and Thynne model [23]

$$H_{123}^E = \frac{x_1 x_2}{x_1 x_2} H_{12}^E(x_1^b, x_2^b) + \frac{x_1 x_3}{x_1 x_3} H_{13}^E(x_1^b, x_3^b) + H_{23}^E(x_2, x_3) \quad (19)$$

where $x_1^b - x_2^b = x_1 - x_2 - x_3/2$ and $x_1^b - x_3^b = x_1 - x_3 - x_2/2$.

To compare the correlating ability of Eqs. (8)-(19), the standard

Table 6. Standard deviations of Eqs. (8)-(19) in estimating excess molar enthalpies with the empirical models for the ternary mixture

Predictive models	Standard deviations, σ (J/mol), for the ternary mixture		
Kohler	90.6		
Rastogi	538.6		
Radojkovic	95.9		
Jacob-Fitzner	95.9		
Colinet	119.6		
Knobloch and Schwartz	410.9		
Tsao and Smit	42.6 ^a	449.2 ^b	393.4 ^c
Toop	42.8 ^a	171.7 ^b	131.6 ^c
Scatchard	42.7 ^a	152.0 ^b	131.6 ^c
Hillert	42.8 ^a	173.5 ^b	144.4 ^c
Mathieson-Tynne	60.9 ^a	114.1 ^b	105.7 ^c

For the asymmetric models the values depend on the component ordering:

^a1,2-DCP+2-pentanol+3-pentanol

^b2-Pentanol+3-pentanol+1,2-DCP

^c3-Pentanol+1,2-DCP+2-pentanol

deviations between the experimental and predicted H_{123}^E for the ternary mixture have been calculated and listed in Table 6. In this case, the symmetric models show less predictive ability than the asymmetric ones. The Kohler equation of these symmetric models presents the lowest deviation, while the asymmetric models such as Tsao and Smith, Toop, Scatchard et al., and Hillert except Mathieson and Thynne show the best predictions when 1,2-DCP is taken as component 1. The asymmetric models give more weight to the binary contributions 1-2 and 1-3, and therefore component 1 plays a more important role. The rule for selecting the numbering of the components in this mixture was given by Pando [34]: component 1 is designated as the common component of these two mixtures which exhibit the largest absolute values of H_{ij}^E in their maxima or minima. In this case, the two largest absolute values of binary H_{ij}^E for this ternary mixture of {1,2-DCP+2-pentanol+3-pentanol} are {1,2-DCP+2-pentanol} and {1,2-DCP+3-pentanol}. According to this rule, 1,2-DCP must be component 1, which coincides with these results for all the asymmetric equations.

CONCLUSIONS

Experimental excess molar enthalpies for the binary and ternary mixtures of {1,2-DCP+2-pentanol+3-pentanol} at T=298.15 K and atmospheric pressure were measured using an isothermal flow-calorimeter. The $H_{m,ij}^E$ values for the binary mixtures {1,2-DCP+2-pentanol} and {1,2-DCP+3-pentanol} show an endothermic effect (positive values), while the binary mixture {2-pentanol+3-pentanol} is formed slightly exothermally (negative values) over the whole range of composition. The ternary system shows an endothermic behavior over the whole ternary composition range with a maximum value $H_{m,123}^E \approx 2,250$ J/mol. The Redlich-Kister equation was used to correlate the binary $H_{m,ij}^E$ data, while the Cibulka and Morris equations were employed to correlate the ternary $H_{m,123}^E$ data. In the

case of three pseudo-binary mixtures, $H_{m,1+23}^E$ shows all positive values and the magnitude in $H_{m,1+23}^E$ increases gradually with an increase of the relative amount of the 3-pentanol in the binary mixture composed of {2-pentanol (2)+3-pentanol (3)}. Ternary predictions using the Morris equation show better agreement with experimental data for this ternary system. Several methods to predict the ternary excess enthalpies from constituent binary results were employed to test their applicability. The empirical expressions of Kohler, Rastogi, Radojkovic, Jacob and Fitzner, Colinet, Knobloch and Schwartz, Tsao and Smith, Toop, Scatchard et al., Hillert, and Mathieson and Thynne were also applied to predict the ternary excess enthalpies from constituent binary results. The best results from asymmetric equations were obtained with Tsao and Smith, Toop, Scatchard et al., and Hillert equations with 1,2-DCP as the first component in the numbering. The best agreement with experimental data was achieved by the symmetric equation from the Kohler equation.

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NOMENCLATURE

List of Symbols

A_j, c_i : adjustable parameters for Redlich-Kister, Cibulka and Morris equations, respectively
 $H_{m,ij}^E, H_{m,1+23}^E$, and $H_{m,123}^E$: excess molar enthalpy of binary, pseudo-binary, and ternary mixtures, respectively [J/mol]
 n : number of adjustable parameters
 N : number of experimental data points
 n_D^{25} : refractive index at $T=298.15$ K
 P : pressure [kPa]
 R : universal gas constant [J/mol K]
 T : temperature [K]
 x_i, x_i^b : liquid mole fraction of component i

Greek Letters

Δ_{123} : ternary contribution term
 ρ : density [g/cm³]
 σ : standard deviation [J/mol]

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