

Excess molar volumes and molar enthalpies in the binary mixtures of $\{x_1\text{CH}_3\text{CHClCH}_2\text{Cl}+x_2\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}\}$ ($n=1$ to 4) at $T=298.15$ K

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Abstract—The excess molar volumes V_m^E and excess molar enthalpies H_m^E at $T=298.15$ K and atmospheric pressure for the binary systems $\{x_1\text{CH}_3\text{CHClCH}_2\text{Cl}+x_2\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}\}$ ($n=1$ to 4) have been determined from density measurements by using a digital vibrating-tube densimeter and an isothermal calorimeter with flow-mixing cell, respectively. The 1-alkanols are methanol, ethanol, 1-propanol and 1-butanol. The V_m^E values of the binary mixtures increase with chain length of the 1-alkanols, resulting in entire negative V_m^E values for methanol, ‘S-shaped’ for ethanol, being negative at low and positive at high mole fraction of 1,2-dichloropropane, and entire positive V_m^E values for both 1-propanol and 1-butanol. The H_m^E values for all systems show an endothermic effect (positive values), which exhibits a regular increase in magnitude when the number of $-\text{CH}_2-$ group in 1-alkanols is progressively increased and maximum values of H_m^E varying from $741 \text{ J}\cdot\text{mol}^{-1}$ (methanol) to $1,249 \text{ J}\cdot\text{mol}^{-1}$ (1-butanol) around $x_1=0.63-0.72$. The experimental results of both H_m^E and V_m^E were fitted to Redlich-Kister equation to correlate the composition dependence. The experimental H_m^E data were also used to test the suitability of the Wilson, NRTL, and UNIQUAC models. The correlation of excess enthalpy data in these binary systems using UNIQUAC model provides the most appropriate results except for the system containing methanol.

Key words: Excess Molar Properties, Redlich-Kister Equation, Thermodynamic Models, 1,2-Dichloropropane, 1-Alkanols

INTRODUCTION

Thermo-physical properties are beneficial for characterizing the type and magnitude of molecular interaction in these mixtures, giving important information in many practical problems concerning process design and simulation. In addition, knowledge of these excess molar properties can be useful in predicting the solution behavior of mixtures. This paper is part of our continuous research program based on the measurements of excess properties of binary mixtures containing 1,2-dichloropropane (1,2-DCP) [1-3], which is used as solvent for oil, fats, resin and rubber [4]. The literature offers experimental data of V_m^E and H_m^E for several mixtures of {1-chloroalkane+1-alkanols} [5,6] and $\{\alpha,\omega$ -dichloroalkane+1-butanol or 1-heptanol} [7] and only excess volume for binary mixture of {1,3-dichloropropane+isomeric butanols} [8]. To our knowledge, no efforts, however, have been made to provide V_m^E and H_m^E of these 1-alkanols: methanol, ethanol, 1-propanol, and 1-butanol with particular 1,2-DCP.

The excess thermodynamic properties of mixtures containing polar and self-associated components show significant deviations from ideality due to not only the difference in molecular size and shape but also hydrogen-bonding and dipolar interaction between unlike molecules. Obviously, 1-alkanols are polar compounds with hydrophilic character and strongly self-associated by hydrogen bond through the hydroxyl group [9]. The dipole moment and dielectric constant at $T=298.15$ K are as follows: $\mu=1.69$ D, $\epsilon=33.62$ for methanol, $\mu=1.69$ D, $\epsilon=25.0$ for ethanol, $\mu=1.67$ D, $\epsilon=22.2$ for 1-propanol, $\mu=1.66$ D, $\epsilon=17.8$ for 1-butanol [10]. This leads to a decrease

in polarity of $-\text{OH}$ in the longer chain 1-alkanols. Likewise, 1,2-DCP is a polar compound whose dipole moment is 1.87 (D) [10] at $T=298.15$ K and that is self-associated by dipole-dipole interaction. Polarity, self-association, and hydrogen bond are the main characteristics of the compounds, which cause the deviation from the ideality.

The aim of this paper is to collect set of values of excess properties, V_m^E and H_m^E of these binary mixtures at $T=298.15$ K and atmospheric pressure over the whole concentration range. The secondary aspect is to evaluate how chain length of 1-alkanols can affect on V_m^E and H_m^E values of these mixtures by the addition of 1,2-DCP. The V_m^E and H_m^E at $T=298.15$ K were correlated by Redlich-Kister equation [11]. Thermodynamic models (Wilson, NRTL, and UNIQUAC models [12-14]) based on the local-composition theory were also examined for the suitability by correlating experimental H_m^E data with compositions.

EXPERIMENTAL SECTION

1. Materials

1,2-DCP (Fluka, >99 mass%), methanol (Aldrich, >99.9%), ethanol (Aldrich, >99.9%), 1-propanol (Aldrich, >99.7%), and 1-butanol (Aldrich, >99.8%) were used without further purification but degassed by means of an ultrasonic bath. HPLC grade water (Fisher Scientific, >99.7%) has been used for calibration of the refractometer and densimeter. An analysis of the chemicals by gas chromatography (Shimadzu, model 17A chromatograph with capillary column type, CBP-10 and FID) showed that all cases were better than 0.99 by mass fraction. 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 corre-

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Table 1. Densities ρ , refractive indices n_D^{25} , and molar volumes v_i for pure components at $T=298.15$ K and structural parameters q_i stated purities, and suppliers

Compounds	$\rho/\text{g}\cdot\text{cm}^{-3}$		n_D^{25}		$v_i/\text{cm}^3\cdot\text{mol}^{-1}$ [15]	q_i [16]	Stated purities (mass%)	Suppliers
	Exptl.	Lit. [10]	Exptl.	Lit.[10]				
1,2-DCP	1.14884	1.14936	1.43653	1.43679	98.29	3.064	>99.0	Fluka
Methanol	0.78653	0.78637	1.32675	1.32652	40.70	1.432	>99.9	Sigma-Aldrich
Ethanol	0.78492	0.78493	1.35935	1.35941	58.51	2.588	>99.9	Sigma-Aldrich
1-Propanol	0.79955	0.79960	1.38315	1.38370	74.94	3.128	>99.7	Sigma-Aldrich
1-Butanol	0.80561	0.80575	1.39733	1.39741	91.94	3.668	>99.8	Sigma-Aldrich

sponding literature values [10] as shown in Table 1. These results are in good agreement with literature data. The molar volumes and structural parameters of pure components used in Wilson and UNIQUAC models, respectively [15,16], are also given in Table 1.

2. Apparatus and Procedure

Refractive indices were measured by using a refractometer (model RA-520, Kyoto Electronics, Japan) with a resolution of $\pm 2 \cdot 10^{-5}$ for values ranging from 1.32 to 1.58. The densities of pure components and their binary mixtures were measured by a vibrating-tube densimeter (model DMA 58, Anton Paar, Graz, Austria) with an accuracy $\pm 1 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$, which was operated under suction mode and equipped with automatic sample changer (model SP3, Anton Paar, Graz, Austria). Prior to measuring the refractive index and density, calibrations were done by using HPLC grade water for refractometer and HPLC grade water and air for densimeter at working condition. Samples were prepared by weighing the liquids in 50 cm^3 well-sealed glass-vials, taking due precaution to minimize the evaporation losses. All the weighings were performed by a digital electronic balance with a precision $\pm 3 \cdot 10^{-5} \text{ g}$ (model AT-201, Mettler Toledo, Switzerland). The uncertainty of mole fraction of the samples was estimated to be less than $\pm 1 \cdot 10^{-4}$. From these data, excess molar volumes of the binary mixtures were determined according to the following relation:

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = \sum_{i=1}^2 (x_i M_i) / \rho - \sum_{i=1}^2 (x_i M_i / \rho_i) \quad (1)$$

where x_i , M_i , ρ , and ρ_i are the mole fraction, molar mass, density of mixtures and density of component i , respectively. The uncertainty for the excess volume measurement can be estimated to be $(V_m^E \pm 5 \cdot 10^{-4}) \text{ cm}^3\cdot\text{mol}^{-1}$.

Excess molar enthalpies H_m^E were determined with an isothermal calorimeter (model CSC-4400, Calorimetry Sciences Corporation, Utah, U.S.A) with a newly designed flow-mixing assembly kit (model CSC-4442, CSC, Utah, U.S.A). Two digital HPLC pumps with a precision of 0.2% (Acuflow Series II, Fisher Scientific, U.S.A) were used to deliver liquid components at constant volumetric flow rates to the mixing cell of the calorimeter. Working pressure of the mixing cell in the calorimeter was controlled at $P=101.3 \text{ kPa}$ by a back-pressure regulator (Grove Valves & Regulator Co., Stafford, TX, U.S.A). The block diagram of the isothermal calorimeter was already mentioned in a previous paper [17]. The magnitude of the measured heat signal is an important factor that has to be taken into account when determining the total volumetric flow rate for a set of experiments; in this study, the values were determined: $0.3 \text{ cm}^3\cdot\text{min}^{-1}$ for methanol and ethanol, $0.2 \text{ cm}^3\cdot\text{min}^{-1}$ for 1-propanol and 1-bu-

tanol. To eliminate the uncertainties in the volumetric flow rate due to the fluctuations in ambient temperature, liquid components were kept in double glass-lined jacketed bottles controlled by circulating coolant from a Haake digital circulating bath (model Series-9100, PolyScience, IL., U.S.A.) with an accuracy of $\pm 0.01 \text{ K}$. Details of the isothermal flow calorimeter, operating procedure, and calibrations of pumps and calorimeter have been described in previous work [2,3,17]. The performance of the calorimeter has been checked by test mixtures $\{\text{cyclohexane}+\text{n-hexane}\}$ and $\{\text{water}+\text{ethanol}\}$. The excess molar enthalpies H_m^E have been determined within an error of $\pm 1.6\%$ of the maximum values of the reported H_m^E [18-20]. The uncertainty of our calorimetric measurements can be estimated to be $(H_m^E \pm 0.5 \text{ to } 1.0 \text{ J}\cdot\text{mol}^{-1})$.

Baseline values were determined by running pump I at total flow rate while pump II was turned off, then repeating with pump I off and pump II at the total flow rate. Knowing the heat flux (\dot{q}_i) of component i , volumetric flow rate (\dot{v}_i) of component i , and total flow rate (\dot{v}_T), the baseline values (Φ) were determined at each composition by the following equations:

$$\Phi/(\text{J}\cdot\text{mol}^{-1}) = \sum_{i=1}^2 (\dot{q}_i \cdot \dot{v}_i) / \dot{v}_T \quad (2)$$

$$x_i = (\dot{v}_i \cdot \rho_i / M_i) / \sum_{i=1}^2 (\dot{v}_i \cdot \rho_i / M_i) \quad (3)$$

From volumetric flow rates (\dot{v}_i), the molar masses (M_i), the densities (ρ_i) of the pure component i , the excess molar enthalpies can be determined by Eq. (4):

$$H_m^E/(\text{J}\cdot\text{mol}^{-1}) = (\dot{q} - \Phi) / \sum_{i=1}^2 (\dot{v}_i \cdot \rho_i / M_i) \quad (4)$$

where $\dot{q}/(\text{J}\cdot\text{mol}^{-1})$ is the heat flux upon mixing.

RESULTS AND DISCUSSION

The experimental results for the excess molar properties (V_m^E and H_m^E) of the four binary systems $\{x_1\text{CH}_3\text{CHClCH}_2\text{Cl}+x_2\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}\}$ ($n=1$ to 4) at $T=298.15 \text{ K}$ are listed in Tables 2 and 3, and shown graphically in Figs. 1 and 2.

1. Fitting to Redlich-Kister Equation

The composition dependence of experimental molar excess properties of the binary systems Q_m^E (V_m^E or H_m^E) is described by the following Redlich-Kister equation:

$$Q_m^E/(\text{cm}^3\cdot\text{mol}^{-1} \text{ or } \text{J}\cdot\text{mol}^{-1}) = x_1 x_2 \sum_{j=1}^p A_j (2x_1 - 1)^{j-1} \quad (5)$$

Table 2. Densities ρ and excess molar volumes V_m^E for the binary mixtures of $\{x_1\text{CH}_3\text{CHClCH}_2\text{Cl}+x_2\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}\}$ ($n=1$ to 4) at $T=298.15$ K

x_1	ρ^l ($\text{g}\cdot\text{cm}^{-3}$)	V_m^E ($\text{cm}^3\cdot\text{mol}^{-1}$)	x_1	ρ^l ($\text{g}\cdot\text{cm}^{-3}$)	V_m^E ($\text{cm}^3\cdot\text{mol}^{-1}$)
{ x_1 1,2-DCP+ x_2 methanol}					
0.0311	0.81285	-0.0122	0.4794	1.03752	-0.0713
0.0630	0.83756	-0.0224	0.5060	1.04556	-0.0706
0.0982	0.86255	-0.0336	0.5314	1.05289	-0.0660
0.1324	0.88489	-0.0458	0.5881	1.06824	-0.0608
0.2046	0.92640	-0.0596	0.6453	1.08242	-0.0555
0.2467	0.94760	-0.0642	0.7041	1.09579	-0.0495
0.2866	0.96610	-0.0691	0.7461	1.10465	-0.0436
0.3309	0.98489	-0.0716	0.7756	1.11054	-0.0360
0.3781	1.00320	-0.0744	0.8492	1.12430	-0.0233
0.4263	1.02030	-0.0756	0.8869	1.13085	-0.0154
0.4454	1.02672	-0.0745	0.9425	1.13997	-0.0047
{ x_1 1,2-DCP+ x_2 ethanol}					
0.0449	0.81185	-0.0280	0.5163	1.01816	0.0129
0.0882	0.83625	-0.0440	0.5677	1.03480	0.0255
0.1338	0.86048	-0.0531	0.6204	1.05102	0.0389
0.1797	0.88342	-0.0568	0.6748	1.06694	0.0488
0.2279	0.90606	-0.0525	0.7268	1.08146	0.0567
0.2738	0.92647	-0.0474	0.7802	1.09569	0.0628
0.3194	0.94567	-0.0427	0.8281	1.10797	0.0631
0.3692	0.96546	-0.0272	0.8832	1.12153	0.0586
0.4155	0.98294	-0.0146	0.9421	1.13542	0.0457
0.4681	1.00179	0.0004			
{ x_1 1,2-DCP+ x_2 1-propanol}					
0.0623	0.82747	-0.0001	0.5734	1.02080	0.1240
0.1621	0.86999	0.0093	0.6232	1.03696	0.1288
0.2163	0.89195	0.0244	0.6728	1.05266	0.1320
0.2688	0.91254	0.0403	0.7181	1.06671	0.1308
0.3206	0.93223	0.0572	0.7686	1.08201	0.1277
0.3728	0.95153	0.0725	0.8159	1.09608	0.1181
0.4237	0.96980	0.0892	0.8613	1.10934	0.1056
0.4743	0.98749	0.1009	0.9093	1.12314	0.0824
0.5239	1.00435	0.1150	0.9543	1.13593	0.0495
{ x_1 1,2-DCP+ x_2 1-butanol}					
0.0664	0.82970	0.0176	0.6214	1.02200	0.2090
0.1272	0.85147	0.0421	0.6685	1.03784	0.2058
0.1908	0.87402	0.0731	0.7156	1.05368	0.1970
0.2487	0.89432	0.1027	0.7578	1.06780	0.1858
0.3062	0.91439	0.1285	0.8015	1.08237	0.1711
0.3634	0.93415	0.1559	0.8425	1.09607	0.1506
0.4190	0.95323	0.1771	0.8843	1.10997	0.1266
0.4703	0.97080	0.1911	0.9227	1.12280	0.0963
0.5226	0.98856	0.2029	0.9618	1.13590	0.0567
0.5734	1.00579	0.2077			

where x_1 is the mole fraction of 1,2-DCP, A_j are adjustable parameters determined by minimizing the sum of squares of the differences between experimental values of Q_m^E and the corresponding values calculated by Eq. (5) using a linear regression procedure. The

Table 3. Excess molar enthalpies H_m^E for the binary mixtures of $\{x_1\text{CH}_3\text{CHClCH}_2\text{Cl}+x_2\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}\}$ ($n=1$ to 4) at $T=298.15$ K

x_1	H_m^E /($\text{J}\cdot\text{mol}^{-1}$)	x_1	H_m^E /($\text{J}\cdot\text{mol}^{-1}$)
{ x_1 1,2-DCP+ x_2 methanol}			
0.033	24.6	0.386	488.1
0.049	35.7	0.455	570.3
0.065	54.2	0.492	610.8
0.082	72.5	0.532	649.2
0.099	93.9	0.575	681.9
0.156	166.6	0.620	717.4
0.177	196.0	0.669	733.1
0.199	227.1	0.722	741.4
0.245	293.9	0.840	677.8
0.297	368.5	0.906	572.0
0.355	446.9		
{ x_1 1,2-DCP+ x_2 ethanol}			
0.069	77.2	0.476	802.4
0.113	154.1	0.510	842.1
0.160	243.3	0.583	905.8
0.185	292.4	0.621	928.5
0.210	341.0	0.661	938.9
0.263	448.4	0.702	944.6
0.291	500.4	0.745	924.2
0.319	554.3	0.835	827.7
0.379	661.6	0.883	711.9
0.410	709.4	0.933	552.0
{ x_1 1,2-DCP+ x_2 1-propanol}			
0.090	190.8	0.487	1050.2
0.130	267.8	0.537	1101.1
0.171	388.4	0.588	1134.8
0.213	494.6	0.640	1157.0
0.256	606.8	0.693	1136.0
0.300	709.4	0.748	1090.1
0.345	812.2	0.804	1005.4
0.391	897.9	0.862	868.5
0.439	981.7	0.922	667.6
{ x_1 1,2-DCP+ x_2 1-butanol}			
0.108	273.2	0.538	1212.3
0.155	377.1	0.586	1242.3
0.202	530.8	0.636	1250.0
0.249	659.8	0.685	1244.3
0.297	791.5	0.734	1188.7
0.344	901.7	0.784	1113.7
0.392	1006.1	0.834	1010.6
0.440	1087.1	0.885	838.8
0.489	1159.9	0.935	617.6

optimal number of parameters A_j was determined by applying an F-test [21] with an examination of the variation of the standard deviations σ :

$$\sigma/(\text{cm}^3\cdot\text{mol}^{-1} \text{ or } \text{J}\cdot\text{mol}^{-1}) = \left[\frac{\sum_{i=1}^N (Q_{m,exp,i}^E - Q_{m,calc}^E)^2 / (N-p)}{N} \right]^{1/2} \quad (6)$$

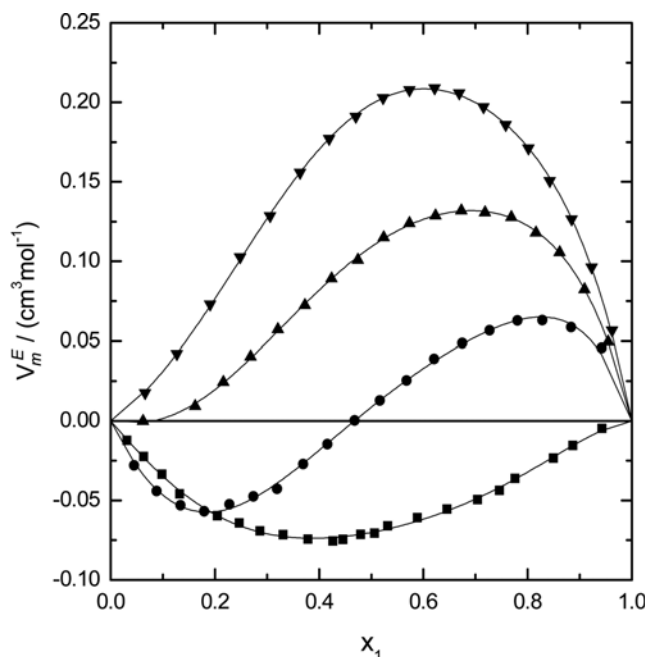


Fig. 1. Excess molar volume V_m^E for the binary mixtures of $\{x_1\text{CH}_3\text{CHClCH}_2\text{Cl}+x_2\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}\}$ ($n=1$ to 4) at $T=298.15$ K as a function of mole fraction x_1 : (■), methanol; (●), ethanol; (▲), 1-propanol; (▼), 1-butanol; (—), calculated with Eq. (5) using parameters listed in Table 4.

where N is the number of experimental points and p is the number of coefficients. All the parameters of Eq. (5) are reported in Tables 4 and 5 for V_m^E and H_m^E , respectively, together with the standard deviations of the fits.

2. Fitting to Thermodynamic Models

The experimental H_m^E data were also used to test the suitability of thermodynamic models (Wilson, NRTL, and UNIQUAC equations) for representing experimental H_m^E data over the entire range of compositions. The excess enthalpy, which indicates the temperature dependence of the excess Gibbs free energy, can be correlated via the Gibbs-Helmholtz equation:

$$H_m^E = -RT^2[\partial(G^E/RT)/\partial T]_{P,x} \quad (7)$$

From Eq. (7), the resulting expressions for the excess enthalpy can be derived by substituting G^E/RT for the corresponding excess Gibbs free energy equations. The Wilson, NRTL and UNIQUAC expressions of H_m^E are given by the following Eqs. (8)-(10), respectively:

$$\frac{H_m^E}{RTx_1x_2} = \frac{\lambda_{12}A_{12}}{x_1 + A_{12}x_2} + \frac{\lambda_{21}A_{21}}{x_2 + A_{21}x_1} \quad (8)$$

where $A_{12} = V_2/V_1 \exp(-\lambda_{12}/RT)$, $A_{21} = V_1/V_2 \exp(-\lambda_{21}/RT)$, and V_i is

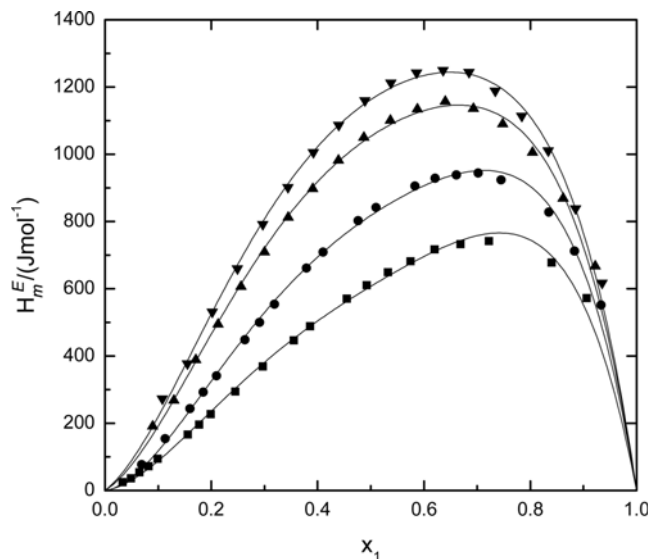


Fig. 2. Excess molar enthalpies H_m^E for the binary mixtures of $\{x_1\text{CH}_3\text{CHClCH}_2\text{Cl}+x_2\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}\}$ ($n=1$ to 4) at $T=298.15$ K as a function of mole fraction x_1 : (■), methanol; (●), ethanol; (▲), 1-propanol; (▼), 1-butanol; (—), calculated with Eq. (5) using parameters listed in Table 5.

the molar volume of the component i ,

$$H_m^E = RTx_1x_2 \left[\frac{x_2 + x_1 \exp(\alpha\tau_{21}) \cdot (1 - \alpha\tau_{21})}{\{x_1 \exp(\alpha\tau_{21}) + x_2\}^2} \cdot \tau_{21} + \frac{x_1 + x_2 \exp(\alpha\tau_{12}) \cdot (1 - \alpha\tau_{12})}{\{x_2 \exp(\alpha\tau_{12}) + x_1\}^2} \cdot \tau_{12} \right] \quad (9)$$

where $\tau_{12} = \Delta g_{12}/RT$, $\tau_{21} = \Delta g_{21}/RT$ and α is the non-randomness parameter.

$$H_m^E = q_1x_1 \left(\frac{\theta_2\tau_{21}\Delta u_{21}}{\theta_1 + \theta_2\tau_{21}} \right) + q_2x_2 \left(\frac{\theta_1\tau_{12}\Delta u_{12}}{\theta_2 + \theta_1\tau_{12}} \right) \quad (10)$$

where q_i is a structural parameter of component i , $\tau_{12} = \exp(-\Delta u_{12}/RT)$, $\tau_{21} = \exp(-\Delta u_{21}/RT)$, and $\theta_i = x_i q_i / \sum_{i=1}^2 x_i q_i$. The adjustable parameters of each model, $\lambda_{12} (= a_{21} - a_{11})$ and $\lambda_{21} (= a_{12} - a_{22})$ in the Wilson equation, $\Delta g_{12} (= g_{12} - g_{22})$, $\Delta g_{21} (= g_{21} - g_{11})$ and α in the NRTL equation, and $\Delta u_{12} (= u_{12} - u_{22})$ and $\Delta u_{21} (= u_{21} - u_{11})$ in the UNIQUAC equation, are summarized in Table 6 together with standard deviations.

3. Qualitative Explanation

For the mixtures examined, several factors such as differences in self-association (inter- or intramolecular interaction) and physical interaction (van der Waals interaction and dipole-dipole interaction) between like molecules increase the volume. On the other hand, charge transfer type forces, a structural effect that arises from the

Table 4. Adjustable parameters, A_j , of in Eq. (5) and standard deviations, $\sigma(V_m^E)$ in Eq. (6) for $\{x_1\text{CH}_3\text{CHClCH}_2\text{Cl} (1)+x_2\text{CH}_3(\text{CH}_2)_{n-1}\text{OH} (2)\}$ ($n=1$ to 4) at $T=298.15$ K

System: 1,2-DCP(1)	A_1	A_2	A_3	A_4	A_5	$\sigma(\text{cm}^3 \cdot \text{mol}^{-1})$
+methanol(2)	-0.2805	0.1229	-0.0523	0.0433	0.1182	0.0014
+ethanol(2)	0.0346	0.5223	-0.1202	0.3060	0.2420	0.0020
+1-propanol(2)	0.4365	0.4551	-0.0717	0.2216	0.2556	0.0010
+1-butanol(2)	0.7953	0.3837	-0.1548	0.3133	0.2852	0.0012

Table 5. Adjustable parameters, A_j of in Eq. (5) and standard deviations, $\sigma(H_m^E)$ in Eq. (6) for $\{CH_3CHClCH_2Cl(1)+x_2CH_3(CH_2)_{n-1}OH(2)\}$ ($n=1$ to 4) at $T=298.15$ K

System:	A_1	A_2	A_3	A_4	$\sigma(J\cdot mol^{-1})$
1,2-DCP(1)					
+methanol(2)	2429.7	1916.4	1764.2	2044.9	14.5
+ethanol(2)	3271.3	2107.2	1587.3	2528.7	18.3
+1-propanol(2)	4214.1	2097.8	1364.8	2502.8	21.4
+1-butanol(2)	4651.1	2101.4	1284.2	2641.9	22.0

geometrical fitting of one component into other component due to the different molar volumes and free volumes of pure components or interactions between unlike molecules are the most common factors that contribute to volume contraction.

Fig. 1 shows that experimental excess molar volumes at $T=298.15$ K for the binary mixture of $\{1,2\text{-DCP}+\text{methanol}\}$ are negative over the entire composition range. On the basis of dipole moment and dielectric constant value, methanol is found to be more polar than other remaining 1-alkanols. Moreover, 1,2-DCP is larger than methanol and creates an empty space when its molecules are self-associated among themselves. Accordingly, the empty space may easily accommodate methanol molecules because of dipole-dipole interaction between the unlike molecules. As a result, contraction effect can be observed to show the negative value of V_m^E . As the size of 1-alkanols increases from 1-propanol to 1-butanol, unlike the methanol molecule which can easily be admitted into the environment of 1,2-DCP, admission of 1-propanol and 1-butanol into the environment of 1,2-DCP is difficult during the mixing process. Additionally, absorption of energy to break the hydrogen bonds in higher alcohol may be the secondary reason leading to volume expansion. As a consequence, increasingly positive values of V_m^E were found for the higher 1-alkanols i.e. 1-propanol and 1-butanol.

In the case of $\{1,2\text{-DCP}+\text{ethanol}\}$, both polarity effect and steric hindrance effect due to their size of molecules fall between the aforementioned mixtures. That is why this binary mixture gives both negative (low mole fraction of 1,2-DCP) and positive (high mole fraction of 1,2-DCP) values of V_m^E . Thus, V_m^E values for $\{1,2\text{-DCP}+1\text{-alkanols}\}$ are found to vary in the following order:

$$\text{methanol} < \text{ethanol} < 1\text{-propanol} < 1\text{-butanol}.$$

Fig. 2 shows the experimental values of H_m^E plotted against x_1 together with fitted curves by using the Redlich-Kister polynomial. For all the mixtures examined, the H_m^E values are positive over the whole composition range and the maximum of $H_m^E(x_1)$ curves being

slightly shifted around the rich composition in 1,2-DCP, and the values are $741.4 J\cdot mol^{-1}$ for methanol at ($x_1=0.722$), $944.6 J\cdot mol^{-1}$ for ethanol at ($x_1=0.702$), $1,157.0 J\cdot mol^{-1}$ for 1-propanol at ($x_1=0.636$), and $1,250.0 J\cdot mol^{-1}$ for 1-butanol at ($x_1=0.63$). H_m^E values of mixtures containing 1,2-DCP increase in the sequence:

$$\text{methanol} < \text{ethanol} < 1\text{-propanol} < 1\text{-butanol}.$$

Usually the H_m^E values are positive when the interactions between the like molecules are stronger than that of unlike molecules and vice versa [22]. The positive values of H_m^E for the present work indicate that interaction between like molecules is stronger than that of unlike molecules. The enthalpy of mixing H_m^E is the result of three effects: the dissociation of alcohol, which is the endothermic effect; dissociation of 1,2-DCP is also an endothermic effect; and cross interaction of alcohol and 1,2-DCP, which is an exothermic effect. It is well known that 1-alkanols and 1,2-DCP molecules are associated by hydrogen bond and dipole-dipole interaction in pure state, respectively. The opposing effect, cross-association contributed by the formation of weak hydrogen bonds between the Cl-atoms of 1,2-DCP and H-atom on the hydroxyl group of 1-alkanols may be predominated by the dissociation effect of the compounds. As a result, the system should absorb an additional amount of energy from the surroundings to break the hydrogen bond of 1-alkanols in the mixing process, causing a positive deviation from ideality. This may be one of the strongest reasons why all H_m^E values obtained are positive.

Contrary to the combined results obtained from the binary mixtures of $\{\text{alkan-1-ol}+n\text{-alkane}\}$ [23-26], H_m^E values in our cases surprisingly increase when the carbon-atom number of 1-alkanol increases. As the size of alkyl group increases from methanol to 1-butanol, the polarity of the hydroxyl group decreases. On the basis of diminution of polarity, a decrease of H_m^E values with size of 1-alkanols is natural to some degree. However, the impact of polarity on H_m^E in our case is reduced due to the cross association effect produced by weak hydrogen bond between Cl-atoms of 1,2-DCP and the H-atom on the hydroxyl group of 1-alkanols. Furthermore, the cross association effect decreases from the binary mixture containing methanol to 1-butanol due to the electron-releasing tendency (+I effect), reducing the maximum polarity effect in the case of methanol, and therefore energy required for breaking the hydrogen bond during the mixing process also increases from the binary mixture containing methanol to 1-butanol. Ultimately, this fact leads to increasingly positive H_m^E values for higher 1-alkanols.

CONCLUSIONS

Table 6. Adjustable parameters: (λ_{12} and λ_{21}), Wilson equation in Eq. (8); (Δg_{12} and Δg_{21} and α), NRTL equation in Eq. (9); (Δu_{12} and Δu_{21}), UNIQUAC equation in Eq. (10) and standard deviations, $\sigma(H_m^E/J\cdot mol^{-1})$ in Eq. (6) for $\{x_1CH_3CHClCH_2Cl(1)+x_2CH_3(CH_2)_{n-1}OH(2)\}$ ($n=1$ to 4) at $T=298.15$ K

System: 1,2-DCP(1)	Wilson			NRTL				UNIQUAC		
	λ_{12}	λ_{21}	σ	Δg_{12}	Δg_{21}	α	σ	Δu_{12}	Δu_{21}	σ
+methanol(2)	320.0	5795.3	78.4	7527.3	661.8	0.28	21.2	6013.4	-153.3	23.8
+ethanol(2)	2090.4	4604.2	197.4	8381.3	855.2	0.23	30.1	4134.2	-228.8	25.4
+1-propanol(2)	2888.4	3897.8	352.1	8516.8	1115.3	0.20	34.1	3358.9	-23.8	30.2
+1-butanol(2)	3047.4	3723.9	454.4	8774.5	1460.4	0.19	35.3	2869.0	67.0	30.6

Both V_m^E and H_m^E increase as the carbon number of 1-alkanols increases. H_m^E values of all binary mixtures are positive for the whole composition range due to the breakdown of the hydrogen bonding in the pure 1-alkanol molecules. But the V_m^E values of the mixtures have been shown to be positive over the whole composition range for both 1-propanol and 1-butanol, 's-shaped' being negative only in the low mole fraction of 1,2-DCP for ethanol, and negative over the entire composition range of 1,2-DCP for methanol.

The Redlich-Kister polynomial was successfully correlated with both the experimental V_m^E and H_m^E data. For all mixtures, good agreement between experimental H_m^E and calculated H_m^E values as a function of mole fraction derived from NRTL and UNIQUAC models except Wilson model was obtained in accordance with standard deviations. Of the two models, the UNIQUAC equation was found to be more appropriate for correlating the enthalpy of mixing data than the NRTL model for all systems except the system containing methanol.

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