

Excess volume and excess enthalpy of binary mixtures composed of 1,2-dichloropropane and 1-alkanol (C₅-C₈)

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Abstract—The excess molar volumes and excess molar enthalpies at T=298.15 K and atmospheric pressure for the binary systems {CH₃CHClCH₂Cl (1)+CH₃(CH₂)_{n-1}OH (2)} (n=5 to 8) have been determined over the whole range of composition from the density and heat flux measurements using a digital vibrating-tube densimeter and an isothermal calorimeter, respectively. The measured excess molar volumes of all binary mixtures showed positive symmetrical trend with values increasing with chain length of 1-alkanol. Similarly, excess enthalpy values of all binary mixtures showed skewed endothermic behavior with values increasing with chain length of 1-alkanol. The maxima of excess molar enthalpy values were observed around x₁=0.65 with excess enthalpy value ranging from 1,356.8 J/mol (1-pentanol) to 1,543.4 J/mol (1-octanol). The experimental results of both H_m^E and V_m^E are fitted to a modified version of Redlich-Kister equation using the Padé approximant to correlate the composition dependence. The experimental H_m^E data were also fitted to three local-composition models (Wilson, NRTL, and UNIQUAC). The correlation of excess enthalpy data in these binary systems using UNIQUAC model provides the most appropriate results.

Keywords: Excess Molar Properties (Volumes and Enthalpies), Padé Approximation, Thermodynamic Models, 1,2-Dichloropropane, 1-Alkanols

INTRODUCTION

Binary and ternary mixtures are very interesting because of their unusual behavior [1,2]. Thus data on physico-chemical properties associated with the liquids and liquid mixtures like excess enthalpy and excess volume are extensively applied in chemical engineering design, process simulation, solution theory and molecular dynamics [3]. These properties are important from practical and theoretical point of view to understand liquid theory and provide the intermolecular interaction between the various species present in the liquid mixtures. The variation about the excess volumes and excess enthalpies of these mixtures containing polar and hydrogen bonded components may be complex due to a decrease or an increase in hydrogen bonding interaction on mixing on the basis polarity and non-polarity of the constituent components.

As a part of continuing studies of the excess properties of the binary and ternary system containing 1,2-dichloropropane (1,2-DCP), several works on the excess enthalpies and volumes of the mixtures formed by 1,2-DCP have previously been reported [4-12]. A similar previous work [7] on binary mixtures between 1,2-DCP and 1-alkanols (C₁-C₄) shows the endothermic effect in excess enthalpy for all binary systems, and the endothermicity goes on increasing with chain length of alcohols. Similarly, excess volumes for these systems also increase with carbon number of 1-alkanols. In this work, an extension of the research program on thermody-

namic properties is presented for the measurement of the excess volume and enthalpy for the binary system of 1,2-DCP+1-alkanols (C₅-C₈) at 298.15 K. Literature survey showed that no measurements have been previously reported for the mixtures studied in this paper.

Generally, 1-alkanols are polar compounds with hydrophilic character and strongly self-associated by hydrogen bond through the hydroxyl group [13]. However, the polarity of 1-alkanol decreases with increase of chain length because the dielectric constants (ϵ , $\epsilon_{\text{vacuum}}=0$) of these alcohols containing more than four carbon chains at T=298.15 K are less than 20 and the value decreases with increasing chain length. The dielectric constants of 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol are 13.9, 13.3, 12.1 and 10.3, respectively. As a matter of fact, 1-alkanols containing five or more than five carbons behave like a non-polar solvent [14]. On the other hand, 1,2-DCP is a polar compound whose dipole moment is 1.87 (D) [15] at T=298.15 K and they are self-associated by dipole-dipole interaction.

Our aim was to collect set of values of excess properties, V_m^E and H_m^E of these binary mixtures of 1,2-DCP and 1-alkanols (C₅-C₈) at T=298.15 K and atmospheric pressure over the whole concentration range. The excess enthalpies and volumes were also compared to that of the previous work [7] to confirm whether it follows the same trend or not. The secondary aspect is to evaluate how V_m^E and H_m^E values of these binary mixtures are affected when chain length of 1-alknols are increased from C₅ to C₈. The experimental V_m^E and H_m^E values at T=298.15 K were correlated with a modified Redlich-Kister equation [16] using the Padé approximation [17]. Thermodynamic models (Wilson, NRTL, and UNIQUAC [18-20]) based on the local composition theory were also examined for the suitability by correlating experimental H_m^E data with compositions.

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Table 1. Densities ρ , refractive indices n_D^{25} , and purities of pure components at T=298.15 K and structural parameters q , stated purities, and suppliers

Components	ρ [g/cm ³]		n_D^{25}		q_i^c	Stated purities [mass%]	Suppliers
	Exptl.	Lit. ^a	Exptl.	Lit. ^a			
1,2-DCP	1.14903	1.14936	1.43653	1.43679	3.064	>99.0%	Fluka
1-Pentanol	0.81091	0.81080	1.40793	1.4080	4.208	>99.0%	Sigma-Aldrich
1-Hexanol	0.81517	0.81534	1.41609	1.4157	4.748	>99.0%	Sigma-Aldrich
1-Heptanol	0.81870	0.8187 ^b	1.42241	1.4224 ^b	5.288	>98.0%	Sigma-Aldrich
1-Octanol	0.82174	0.82157	1.42760	1.4276	5.828	>99.0%	Sigma-Aldrich

^aReference [15]^bReference [21]^cReference [22]

EXPERIMENTAL SECTION

1. Materials

1,2-DCP (Fluka, >99 wt%), 1-pentanol (Aldrich, >99 wt%), 1-hexanol (Aldrich, >99 wt%), 1-heptanol (Aldrich, >98 wt%), and 1-octanol (Aldrich, >99 wt%) were used without further purification but degassed by means of an ultrasonic bath. An analysis of all the chemicals by gas chromatography (model GC-17A, Shimadzu, Japan) has justified the stated purities of the compounds. Prior to experiments, densities ρ and refractive indices n_D^{25} of these chemicals were measured by a vibrating-tube densimeter (model DMA 58, Anton Paar, Graz, Austria) with an accuracy $\pm 1 \times 10^{-5}$ g/cm³ and a refractometer (model RA-620, Kyoto Electronics, Japan) with a resolution of $\pm 1 \times 10^{-5}$, respectively, at T=298.15 K and atmospheric pressure, and compared with their corresponding literature values [15,21] as shown in Table 1. The structural parameters (q) [22] of pure components used in UNIQUAC equation are also given in Table 1. The results of pure components are in good agreement with literature data.

2. Apparatus and Procedure

2-1. Densitometric Measurements

The densities of pure components and their binary mixtures were measured by a vibrating-tube densimeter operated under suction mode and equipped with automatic sample changer (model SP3, Anton Paar, Graz, Austria). The measuring method is based on the law of harmonic oscillation. A hollow U-shaped tube is electromagnetically forced into harmonic oscillation. The period of oscillation is dependent on the density of the sample in the tube. Therefore, by measuring the period of oscillation, the densities are automatically calculated. Prior to measurement, the densimeter was calibrated with air and bi-distilled water at T=(293.15 K and 298.15 K). The uncertainty of the density measurement for this work is about $(\rho \pm 0.00005)$ g/cm³. Binary mixtures were prepared by mass in approximately 50 cm³ well-sealed glass-vials. Cautions were taken to prevent evaporation, and for this 1,2-DCP was usually loaded first into the bottle. All the mass measurements were performed by a digital electronic balance with a precision $\pm 1.5 \times 10^{-5}$ g (model AT-201, Mettler Toledo, Switzerland). The uncertainty of mole fraction of the samples was estimated to be less than $\pm 1 \times 10^{-4}$. The experimental excess molar volumes V_m^E for these binary mixtures were obtained from the following relation:

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

where x_i , M_i , ρ_i and ρ are the mole fraction, molar mass, density of pure component i , and density of mixtures, respectively. The uncertainty for the excess volume measurement is less than $\pm 5 \times 10^{-4}$ cm³/mol.

2-2. Calorimetric Measurements

Excess molar enthalpies H_m^E were measured with an isothermal calorimeter (model CSC-4400, Calorimetry Sciences Corporation, UT, USA) with a newly designed flow-mixing assembly kit (model CSC-4442, CSC, UT, USA). Two ISCO high precision, positive displacement, syringe-type pumps (model 500D, Teledyne Isco Inc., USA) 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 flow calorimeter, the calibrations of a calorimeter and two pumps, the reliability of the apparatus, and the experimental procedure including the determination of baseline values of heat flux to obtain excess enthalpies H_m^E have been described in previous work [5-7,11]. The total volumetric flow rate of this study was set 0.2 cm³/min by observing the magnitude of the measured heat signal. The uncertainty in excess molar enthalpy measurement was estimated to be better than 1.0%. Similarly, the uncertainty of the mole fraction was estimated to be less than $\pm 1 \times 10^{-3}$.

RESULTS AND DISCUSSION

Experimental values of both V_m^E and H_m^E for these binary mixtures {CH₃CHClCH₂Cl (1)+CH₃(CH₂)_{*n*-1}OH (2)} ($n=5$ to 8) at T=298.15 K and atmospheric pressure are listed in Tables 2 and 3, and the results are also reported graphically in Figs. 1 and 2, respectively.

1. Fitting to a Modified Redlich-Kister Equation

The composition dependence of experimental excess molar properties Q_m^E (V_m^E or H_m^E) of the binary mixtures was described by the following a modified Redlich-Kister equation using the Padé (m , n) approximant type:

Table 2. Excess molar volumes V_m^E for the binaries {x₁ 1,2-DCP + x₂ 1-alkanols (C₅-C₈)} at T=298.15 K and atmospheric pressure

x ₁	ρ (g/cm ³)	V_m^E (cm ³ /mol)	x ₁	ρ (g/cm ³)	V_m^E (cm ³ /mol)
x ₁ 1,2-DCP+x ₂ 1-pentanol					
0.0247	0.81837	0.0166	0.5495	0.98543	0.2982
0.0492	0.82580	0.0280	0.6001	1.00271	0.2955
0.0994	0.84107	0.0677	0.6509	1.02028	0.2884
0.1500	0.85661	0.1072	0.7024	1.03837	0.2739
0.1997	0.87203	0.1405	0.7502	1.05533	0.2598
0.2499	0.88771	0.1778	0.8003	1.07344	0.2312
0.3001	0.90361	0.2113	0.8503	1.09183	0.1918
0.3502	0.91967	0.2357	0.9004	1.11054	0.1470
0.4012	0.93616	0.2618	0.9491	1.12906	0.0920
0.4505	0.95234	0.2777	0.9743	1.13882	0.0529
0.5003	0.96885	0.2932			
x ₁ 1,2-DCP+x ₂ 1-hexanol					
0.0246	0.82146	0.0304	0.5510	0.97554	0.3826
0.0494	0.82786	0.0574	0.6011	0.99259	0.3788
0.0993	0.84104	0.1048	0.6505	1.00986	0.3704
0.1501	0.85469	0.1572	0.7006	1.02781	0.3592
0.1993	0.86824	0.2034	0.7505	1.04640	0.3276
0.2505	0.88272	0.2439	0.8008	1.06570	0.2876
0.3006	0.89715	0.2877	0.8492	1.08485	0.2425
0.3503	0.91193	0.3147	0.8998	1.10552	0.1854
0.4010	0.92736	0.3432	0.9506	1.12702	0.1112
0.4506	0.94281	0.3697	0.9744	1.13742	0.0702
0.5009	0.95901	0.3758			
x ₁ 1,2-DCP+x ₂ 1-heptanol					
0.0246	0.82414	0.0398	0.5504	0.96646	0.4658
0.0497	0.82983	0.0707	0.6001	0.98319	0.4573
0.0992	0.84132	0.1289	0.6515	1.00121	0.4430
0.1501	0.85351	0.1906	0.7012	1.01936	0.4210
0.2000	0.86585	0.2503	0.7493	1.03773	0.3906
0.2498	0.87861	0.3017	0.8002	1.05811	0.3468
0.3003	0.89197	0.3516	0.8500	1.07906	0.2844
0.3502	0.90574	0.3870	0.9000	1.10107	0.2162
0.3995	0.91983	0.4191	0.9495	1.12404	0.1305
0.4505	0.93497	0.4420	0.9747	1.13625	0.0754
0.5007	0.95053	0.4541			
x ₁ 1,2-DCP+x ₂ 1-octanol					
0.0248	0.82664	0.0346	0.5493	0.95863	0.5293
0.0499	0.83166	0.0746	0.6027	0.97626	0.5219
0.0993	0.84190	0.1430	0.6504	0.99294	0.5020
0.1496	0.85272	0.2160	0.7007	1.01144	0.4786
0.2010	0.86426	0.2808	0.7503	1.03072	0.4465
0.2499	0.87573	0.3398	0.8024	1.05234	0.3883
0.3001	0.88803	0.3926	0.8489	1.07280	0.3280
0.3507	0.90101	0.4392	0.9009	1.09722	0.2404
0.4005	0.91443	0.4730	0.9498	1.12175	0.1428
0.4519	0.92898	0.4999	0.9752	1.13533	0.0731
0.5009	0.94355	0.5167			

Table 3. Excess molar enthalpies H_m^E for the binaries {x₁ 1,2-DCP + x₂ 1-alkanols (C₅-C₈)} at T=298.15 K and atmospheric pressure

x ₁	H_m^E (J/mol)	x ₁	H_m^E (J/mol)
x ₁ 1,2-DCP+x ₂ 1-pentanol			
0.026	65.4	0.550	1322.9
0.048	145.5	0.599	1353.5
0.097	295.6	0.648	1356.8
0.151	465.3	0.701	1322.8
0.199	617.9	0.749	1279.4
0.247	758.7	0.802	1174.9
0.300	898.4	0.849	1060.9
0.352	1030.1	0.900	863.6
0.398	1124.1	0.951	539.0
0.449	1215.9	0.973	331.2
0.500	1284.9		
x ₁ 1,2-DCP+x ₂ 1-hexanol			
0.023	78.7	0.550	1389.2
0.049	165.8	0.599	1417.0
0.098	326.1	0.652	1413.8
0.146	492.7	0.698	1391.9
0.200	646.9	0.748	1329.8
0.246	788.7	0.802	1225.7
0.297	915.3	0.849	1104.7
0.347	1047.3	0.900	878.4
0.401	1159.4	0.949	569.1
0.448	1244.5	0.977	292.4
0.500	1316.5		
x ₁ 1,2-DCP+x ₂ 1-heptanol			
0.019	70.1	0.551	1434.5
0.048	159.4	0.600	1451.8
0.096	318.7	0.652	1458.3
0.150	528.7	0.702	1446.2
0.201	688.8	0.750	1384.6
0.251	837.5	0.800	1286.2
0.300	993.1	0.849	1148.8
0.347	1119.1	0.899	930.0
0.398	1218.3	0.951	572.2
0.447	1315.3	0.976	311.2
0.500	1389.5		
x ₁ 1,2-DCP+x ₂ 1-octanol			
0.021	88.1	0.548	1510.0
0.045	179.7	0.598	1540.1
0.099	374.2	0.649	1543.4
0.150	558.6	0.699	1509.8
0.199	731.9	0.749	1442.2
0.247	867.3	0.802	1329.4
0.298	1034.7	0.851	1183.1
0.348	1156.9	0.902	948.6
0.402	1276.8	0.949	613.6
0.447	1361.5	0.975	345.4
0.501	1453.1		

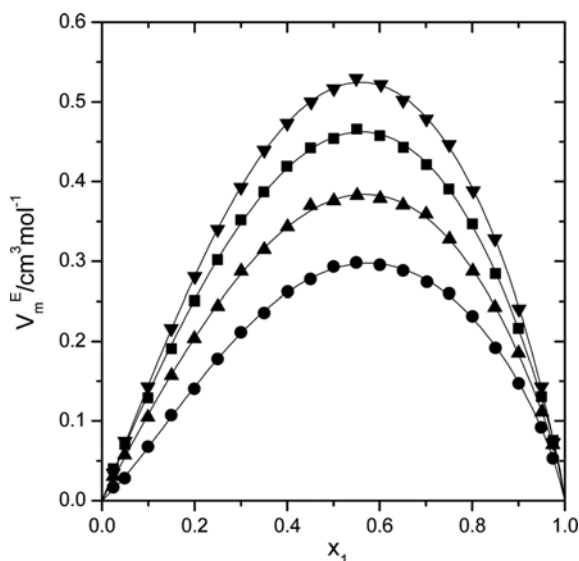


Fig. 1. Excess molar volumes V_m^E for the binaries $\{x_1$ 1,2-DCP + x_2 1-alkanols (C_5 - C_8) at $T=298.15$ K. Experimental results: (●), 1-pentanol; (▲), 1-hexanol; (■), 1-heptanol; and (▼), 1-octanol; (—), calculated with Padé Approximation using parameters listed in Table 4.

$$Q_m^E (\text{cm}^3/\text{mol or J/mol}) = \frac{x_1 x_2 \sum_{i=0}^m A_i (2x_1 - 1)^i}{1 + \sum_{j=1}^n B_j (2x_1 - 1)^j} \quad (2)$$

where A_i and B_j are adjustable parameters calculated by unweighted least-squares using a Levenberg-Marquardt algorithm, and m and n are the number of parameters. Fitted results by Eq. (2) showed a much better goodness-of-fit than those using an original Redlich-Kister equation, where the representation of data is asymmetric. The optimal number (m and n) of parameters (A_i and B_j) was determined by applying an F-test [23] with an examination of the variation of the standard deviation σ :

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

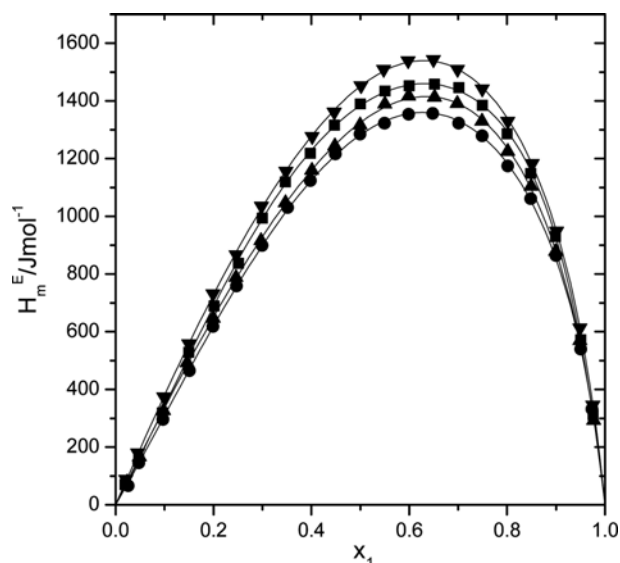


Fig. 2. Excess molar enthalpies H_m^E for the binaries $\{x_1$ 1,2-DCP + x_2 1-alkanols (C_5 - C_8) at $T=298.15$ K. Experimental results: (●), 1-pentanol; (▲), 1-hexanol; (■), 1-heptanol; and (▼), 1-octanol; (—), calculated with Padé Approximation using parameters listed in Table 4.

where N is the experimental data points. All parameters of Eq. (2) are shown in Table 4 for both V_m^E and H_m^E together with standard deviations of the fits.

2. Fitting to Thermodynamic Models

The experimental H_m^E data of these mixtures were also correlated with thermodynamic models (Wilson, NRTL, and UNIQUAC equations) to examine the suitability for representing 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:

$$H_m^E = -RT^2 [\partial(G^E/RT)/\partial T]_{P, x} \quad (4)$$

From Eq. (4), the resulting expressions for the excess molar 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 expressed by the following Eqs. (5)–(7), respectively:

Table 4. Adjustable parameters A_i and B_j of a modified Redlich-Kister equation in Eq. (2) with standard deviations, σ (V_m^E or H_m^E) in Eq. (3) for the binaries $\{x_1$ 1,2-DCP + x_2 1-alkanols (C_5 - C_8) at $T=298.15$ K and atmospheric pressure

	x_1 1,2-DCP	A_0	A_1	A_2	A_3	B_1	B_2	σ cm ³ /mol or J/mol
V_m^E	+ x_2 1-Pentanol	1.1622		−0.7406		−0.3158	−0.5166	0.0019
	+ x_2 1-Hexanol	1.5076	−1.0732	−0.3354		−0.9840		0.0028
	+ x_2 1-Heptanol	1.8223	−1.3279	−0.3550		−0.9713		0.0031
	+ x_2 1-Octanol	2.0694		−0.9051		−0.2349	−0.4101	0.0024
H_m^E	+ x_2 1-Pentanol	5129.5		−1813.2		−0.4591	−0.3328	6.6
	+ x_2 1-Hexanol	5299.2	−1848.4	−871.3		−0.8317		6.5
	+ x_2 1-Heptanol	5537.6	−935.7		1426.4	−0.5793		7.9
	+ x_2 1-Octanol	5803.5	−2231.6	−826.0		−0.8384		5.6

Table 5. Adjustable parameters: (λ_{12} and λ_{21}), Wilson equation in Eq. (5); (Δg_{12} , Δg_{21} and α), NRTL equation in Eq. (6); (Δu_{12} and Δu_{21}), UNIQUAC equation in Eq. (7) with standard deviations σ (H_m^E J/mol) in Eq. (3) for the binaries {x₁ 1,2-DCP+x₂ 1-alkanols (C₅-C₈)} at T=298.15 K

Systems	Wilson			NRTL				UNIQUAC		
	λ_{12}	λ_{21}	σ	Δg_{12}	Δg_{21}	α	σ	Δu_{12}	Δu_{21}	σ
x ₁ 1,2-DCP	J/mol	J/mol	J/mol	J/mol	J/mol		J/mol	J/mol	J/mol	J/mol
+x ₂ 1-Pentanol	3174.7	3614.2	478.7	9694.8	2662.1	0.20	31.9	2592.0	185.4	27.3
+x ₂ 1-Hexanol	3253.2	3524.7	511.0	10066.7	2786.0	0.19	23.4	2331.1	229.3	20.2
+x ₂ 1-Heptanol	3330.7	3448.3	548.5	10460.7	3100.2	0.18	29.0	2083.6	303.0	26.6
+x ₂ 1-Octanol	3405.8	3385.0	587.1	10920.0	3344.8	0.18	26.4	1893.1	383.3	25.9

$$H_m^E = x_1 x_2 \left[\frac{\lambda_{12} A_{12}}{x_1 + A_{12} x_2} + \frac{\lambda_{21} A_{21}}{x_2 + A_{21} x_1} \right] \quad (5)$$

where $A_{ij} = V_j/V_i \exp(-\lambda_{ij}/RT)$ and V_i is the molar volume of pure component i.

$$H_m^E = RT x_1 x_2 \left[\frac{x_2 + x_1 \exp(\alpha \tau_{21}) \cdot (1 - \alpha \tau_{21})}{\{x_1 \exp(\alpha \tau_{21}) + x_2\}^2} \cdot \tau_{21} + \frac{x_1 + x_2 \exp(\alpha \tau_{12}) \cdot (1 - \alpha \tau_{12})}{\{x_2 \exp(\alpha \tau_{12}) + x_1\}^2} \cdot \tau_{12} \right] \quad (6)$$

where α is the non-randomness parameter; $\tau_{ij} = \Delta g_{ij}/RT$.

$$H_m^E = q_1 x_1 \left(\frac{\theta_2 \tau_{21} \Delta u_{21}}{\theta_1 + \theta_2 \tau_{21}} \right) + q_2 x_2 \left(\frac{\theta_1 \tau_{12} \Delta u_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) \quad (7)$$

where q_i is a structural parameter of component i, $\tau_{ij} = \exp(-\Delta u_{ij}/RT)$, and $\theta_i = x_i q_i / \sum_{i=1}^n x_i q_i$.

The adjustable parameters of each model, $\lambda_{ij} (= a_{ji} - a_{ii})$ in the Wilson equation, $\Delta g_{ij} (= g_{ji} - g_{ii})$ and α in the NRTL equation, and $\Delta u_{ij} (= u_{ji} - u_{ii})$ in the UNIQUAC equation, are summarized in Table 5 together with standard deviations.

3. Qualitative Explanation

3-1. Experimental Excess Volumes

There are 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 can cause to increase in resultant volume. On the contrary, charge transfer type of force, structural effect that arises from the geometrical fitting of one component into other component due to the different molar volumes and free volume of pure components or interaction between unlike molecules are the most general factors that contribute to decrease in volume of the system.

Fig. 1 shows that all experimental V_m^E values are found to be positive over the whole range of composition in all binary mixtures. Changes in excess volume with an increase of chain-length of alcohols are regular as in our previous works [7], which increase with an increase in the alkylated part of the alcohols. The net expansion effect after mixing alcohols with 1,2-DCP can be explained on the basis of dipole-dipole interaction and van der Waals force of attraction. 1,2-DCP is polar compound which is self-associated by the both dipole-dipole interaction and van der Waals force of attraction where 1-alkanols in this experiments are non-polar compounds and only associated by van der Waals force of attraction.

When they are brought to mix with each other, a global reduction in contact surface may happen in the mixture than in their pure state because of the formation of asymmetric structure to minimize the internal energy for stabilization of the molecules in the mixtures. Moreover, molecules in the mixture are associated with each other by only the van der Waals force of attraction, which is very weak. This, in turn, leads to volume expansion in the mixtures. This explains, therefore, why all the processes have expansive effects, $V_m^E > 0$. As size of 1-alkanol increases, non-polarity behavior also increases in 1-alcohols, which causes the values of excess volume also to go on increasing in the binary mixtures containing higher alcohols.

3-2. Experimental Excess Enthalpies

Fig. 2 shows the experimental values of H_m^E plotted against x_1 together with fitted curves by using a modified Redlich-Kister equation. 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 has been shifted towards the slightly 1,2-DCP rich region. The maximum H_m^E values are 1,356.8 J/mol at $x_1=0.648$ for 1-pentanol, 1,417.0 J/mol at $x_1=0.599$ for 1-hexanol, 1,458.3 J/mol at $x_1=0.652$ for 1-heptanol, 1,543.4 J/mol at $x_1=0.649$ for 1-octanol. The H_m^E values for binary mixtures containing 1,2-DCP and 1-alkanols (C₅-C₈) increase with increase of chain length of alcohols.

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 [24]. The enthalpy of mixing is the result of three effects: the dissociation of alcohol, which is the endothermic effect; dissociation of 1,2-DCP, also an endothermic effect; and cross interaction of alcohol and 1,2-DCP, which is an exothermic effect. Since higher alcohols are non-polar compound, the cross-association effect between 1-alkanols and 1,2-DCP is very slim. Moreover, 1,2-DCP is polar compound and they are associated by the dipole-dipole interaction where 1-alkanols are associated by van der Waals force of attraction. As a matter of fact, the interaction between like molecules is stronger than that of unlike molecules, leads to the positive H_m^E values for all these binary mixtures over the whole composition range.

As the molecular size of the alcohols increases, van der Waals force of attraction increases and self-association between the like molecules in higher size of alcohols also become stronger than that of smaller size of alcohols. As a result, larger sizes of alcohols absorb higher energy from the surrounding to overcome the van der Waals force of attraction for the dissociation of the alcohols. For this rea-

son, H_m^E values of binary mixtures containing 1-alkanols (C_5 - C_8) increase with chain length of alcohols.

CONCLUSIONS

The experimental results have shown that H_m^E values are endothermic and V_m^E values are positive in all cases. The endothermicity is due to the breakdown of the van der Waals force of attraction between the like molecules of alcohols and dipole-dipole interaction between the like molecules of 1,2-DCP. Both V_m^E and H_m^E values go on increasing with alkyl chain length of 1-alkanols.

The modified Redlich-Kister equation using the Padé (m,n) approximation was successfully correlated with both the experimental V_m^E and H_m^E data. For all mixtures, agreement between the experimental H_m^E and calculated H_m^E by using Wilson, NRTL, and UNIQUAC models was not found so much satisfactory. Of the three models, the UNIQUAC equation was found to be most appropriate for correlating the enthalpy of mixing data than either Wilson or NRTL model for all the systems.

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NOMENCLATURE

List of Symbols

A_i	: adjustable parameters for a modified Redlich-Kister equation [J/mol or cm^3/mol]
B_j	: adjustable parameters for a modified Redlich-Kister equation
Δg_{ij}	: energy parameters in NRTL model [J/mol]
G^E	: excess Gibbs free energy [J/mol]
H_m^E	: excess molar enthalpy of binary mixtures [J/mol]
m	: number of adjustable parameters in Eq. (2)
M_i	: molar mass of pure component i
n	: number of adjustable parameters in Eq. (2)
N	: number of experimental data points
n_D^{25}	: refractive index at $T=298.15$ K
P	: total pressure [kPa]
q_i	: structural parameter of pure component i
R	: universal gas constant [J/mol K]
T	: temperature [K]
Δu_{ij}	: energy parameters in UNIQUAC model [J/mol]
V_i	: molar volume of pure component i
V_m^E	: excess molar volume of binary mixtures [cm^3/mol]
x_i	: liquid mole fraction of pure component i

Greek Letters

α	: parameter in NRTL related to nonrandomness in the mixture
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θ_i	: area fraction of component i
ρ, ρ_i	: density of mixture and pure component i [g/cm^3]
λ_{ij}	: energy parameters in Wilson model [J/mol]
Λ_{ij}	: binary parameters in Wilson model
σ	: standard deviation [cm^3/mol or J/mol]
τ_{ij}	: binary parameters in NRTL and UNIQUAC

Subscripts/Superscripts

E	: excess properties
i, j	: components of a mixture

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