

Excess Molar Volumes and Enthalpies for 1,2-dichloropropane + 2-methoxyethanol at the Temperature 298.15K.

1,2-dichloropropane(1) - 2-methoxyethanol(2)계의 과잉 몰 부피 및 과잉 몰 엔탈피의 측정

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<요 약>

2성분계 혼합물(1,2-dichloropropane + 2-methoxyethanol)에 대해 과잉몰 부피(excess molar volumes) V^E 및 과잉 몰엔탈피(excess molar enthalpies) H^E 를 298.15K에서 측정하였다. 혼합물의 밀도측정은 digital vibrating tube densimeter를 이용하였고, 과잉 몰엔탈피는 isothermal flow microcalorimeter를 이용하였다. 측정된 과잉 몰부피는 전 조성 영역에서 양의 편차를 나타내었으며, 과잉 몰엔탈피는 S자형을 보였다. 또한 얻어진 data는 Nelder-Mead의 simplex method를 이용하여 Redlich-Kister 다항식에 접합(fitting)하였다.

Key words : *Excess molar volume, Excess molar enthalpy, 1,2-dichloropropane, 2-methoxyethanol(EGME)*

1. Introduction

The use of 1,2-dichloropropane is as a chemical intermediate in the production of carbon tetrachloride and perchloroethylene, lead scavenger for antiknock fluids. In addition, 1,2-dichloropropane is classified as pro-environmental material without environmental restrictions[VOCs(volatile organic compounds), ODS(ozone depletion substances), and toxic

substances] for use metal degreasing agent and solvent. It has lead to an increased interest in the thermodynamic properties of mixtures of 1,2-dichloropropane with additives for the purpose of wide applications

This paper reports excess molar volumes V^E using a digital vibrating-tube densimeter and excess molar enthalpies H^E by means of an isothermal microcalorimeter with a flow mixing cell for the binary mixture

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{1,2-dichloropropane + 2-methoxyethanol} at 298.15K under atmospheric pressure. The results of excess molar volumes and excess molar enthalpies were correlated by the model of Redlich-Kister polynomial by using Nelder-Mead[1]'s simplex pattern search method.

A survey of the literature reveals no studies of V^E and H^E for this mixture.

2. Experimental Section

2.1 Materials

The chemicals(1,2-dichloropropane and 2-methoxyethanol) in this present study were supplied by Fluka. The stated purity of all the chemicals exceeded 99.0%(Puriss grade) and 99.5% (Puriss, ACS grade) respectively. Since the impurities in chemicals were mostly water, it was dehydrated by molecular sieves (Aldrich, type 4Å, 1/8 in. pellets), and degassed by ultrasound (ultrasonic bath, Branson, Model 8210, U.S.A.). 1,2-Dichloropropane was further purified by fractional distillation under reduced pressure. The middle portion of distillate collected was used for the experimental investigation. From gas chromatographic analysis we found the resulting purity 99.0 mass% for 1,2-dichloropropane and 99.7 mass % for 2-methoxyethanol.

In order to check the purity of compounds, also density values, ρ and refractive indices, n_D^{20} (measured by a refractometer, Kyoto Electronics, model RA-520, with an accuracy of ± 0.00001) were determined and are listed in Table 1 in comparison with literature values^{2,3}.

2.2 Density Measurements.

Densities of the pure components and binary mixtures were determined using a vibrating-tube densimeter(model DMA 58, Anton Paar, Graz, Austria) equipped with an automatic sample changer(model SP3, Anton Paar, Graz, Austria) with a resolution $\pm 1 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. The apparatus was calibrated with double-distilled and degassed water, and dry air at atmospheric pressure. The temperature in the measuring cell was regulated to $\pm 0.01\text{K}$.

The sample solutions of different composition were prepared by mass in a sealed vial (approximately 50cm^3) using a Mettler balance (model AT-201, Switzerland) accurate to within $\pm 1 \times 10^{-5}\text{g}$. In order to prevent the error in composition, which may arise from evaporation during sampling procedure, more volatile component was directly charged into the bottle. The charged bottle was close and weighed. The second component was injected into the bottle through the vial cap by a digital buret(Walu Labortechnik, model Continuous RS), which can be fulfilled continuous pulse-free operation, for faster preparation to minimize the experimental error.

The densities ρ of mixture were used to calculate the excess molar volume V^E according to x_i

$$V^E = (x_1M_1 + x_2M_2) / \rho - x_1M_1 / \rho_1 - x_2M_2 / \rho_2 \quad (1)$$

where x_i , M_i , and ρ_i are the mole fraction, molar mass, and density of component i , respectively.

Table 1. Densities and refractive indices of pure components and comparison with literature values

component	$\rho / \text{g} \cdot \text{cm}^{-3}$		n_D^{20}	
	exptl.	lit.	exptl.	lit.
1,2-dichloropropane	1.15458	1.1560	1.43856	1.4394 ^[2]
		1.1558		1.4390 ^[3]
2-methoxyethanol	0.96458	0.9647	1.40178	1.4024 ^[2]
		0.9646		1.4021 ^[3]

2.3 Calorimetric measurement

The excess molar enthalpies H^E were determined using an isothermal microcalorimeter with a flow mixing cell (Calorimetry Sciences Corporation, CSC-4400, Utah, U.S.A). The measuring unit of the calorimeter is a large heat sink (approximately 66 liters) incorporating two test wells. The water bath of the calorimeter provided temperature control of $\pm 0.0005\text{K}$. The measurement principle is quite simple as follows: heat that is produced or absorbed by any reaction in a test well is completely exchanged with the heat sink which is kept at a constant temperature. A heat change occurring in a sample will create a temperature difference between the sample and the heat sink. The thermoelectric sensors located between the sample and the aluminium block will generate a voltage that is proportional to the temperature gradient across the sensors, and the temperature gradient is directly dependent on the heat flux. A block diagram showing the main components of the calorimeter is given in Fig. 1⁴⁾.

Liquid components studied were pumped into the mixing cell of the calorimeter by means of digital HPLC pump (Acuflo Series II, Fisher Scientific, U.S.A) operated in a steady-state (fixed composition) mode at

atmospheric pressure. The pumps were calibrated by determining the volumetric flow rate of bi-distilled water, and an empirical correction equation was fitted for each pump.

And the excess molar enthalpies from an experiment were obtained by subtracting heat effect from baseline values. The baseline is determined by running pump I at total flow rate while pump II is turned off, then repeating with pump I off and pump II at the total flow rate. Baseline values Φ of each mixture are calculated according to following relation;

$$\Phi = \dot{q}_1 \cdot \dot{v}_1 / \dot{v}_T + \dot{q}_2 \cdot \dot{v}_2 / \dot{v}_T \quad (2)$$

where \dot{q}_i , \dot{v}_i , and \dot{v}_T are heat flux, volumetric flow rate of component i , and total flow rate, respectively.

The total volumetric flow rate was 0.5ml min^{-1} depending on the magnitude of the measured heat signal. From volumetric flow rates (\dot{v}_1 and \dot{v}_2), the molar mass (M_1 and M_2) and the densities (ρ_1 and ρ_2) of the pure components, the compositions (x_1 and x_2) of the mixture in the mixing cell, and the excess molar enthalpies can be determined:

$$x_1 = (\dot{v}_1 \cdot \rho_1 / M_1) / \{(\dot{v}_1 \cdot \rho_1 / M_1) + (\dot{v}_2 \cdot \rho_2 / M_2)\} \quad (3)$$

$$H^E = \Phi - \dot{h} / \{(\dot{v}_1 \cdot \rho_1 / M_1) + (\dot{v}_2 \cdot \rho_2 / M_2)\} \quad (4)$$

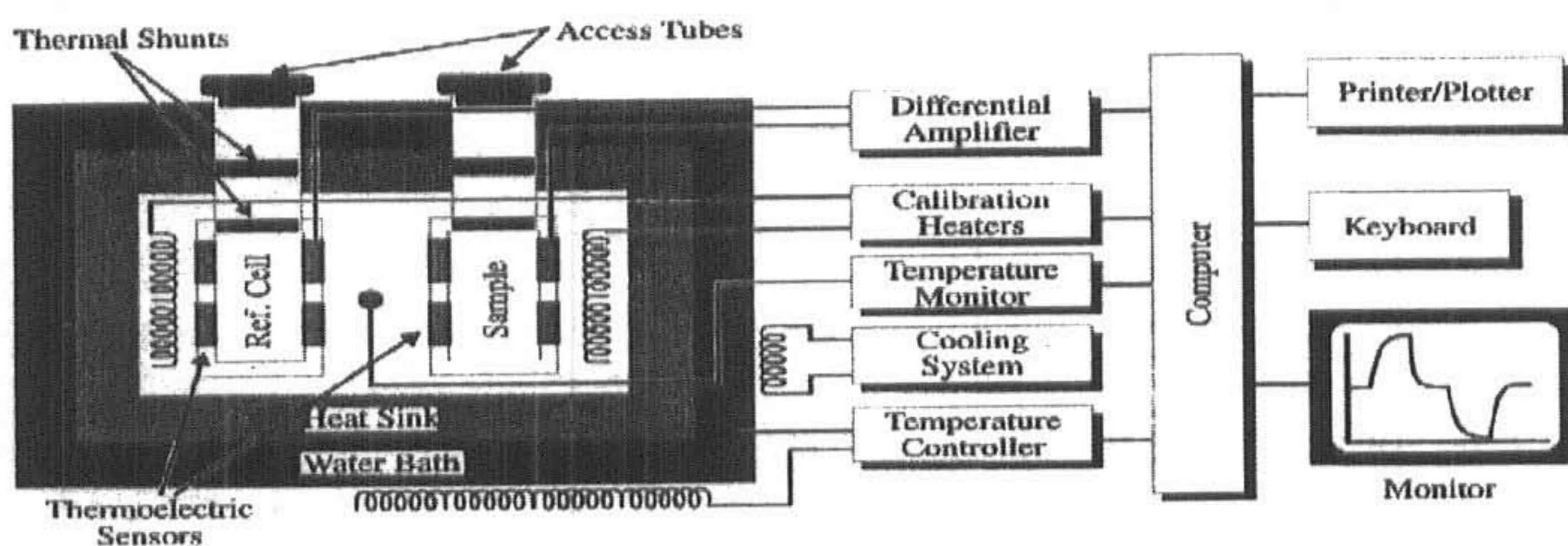


Fig. 1. The block diagram of the isothermal microcalorimeter.

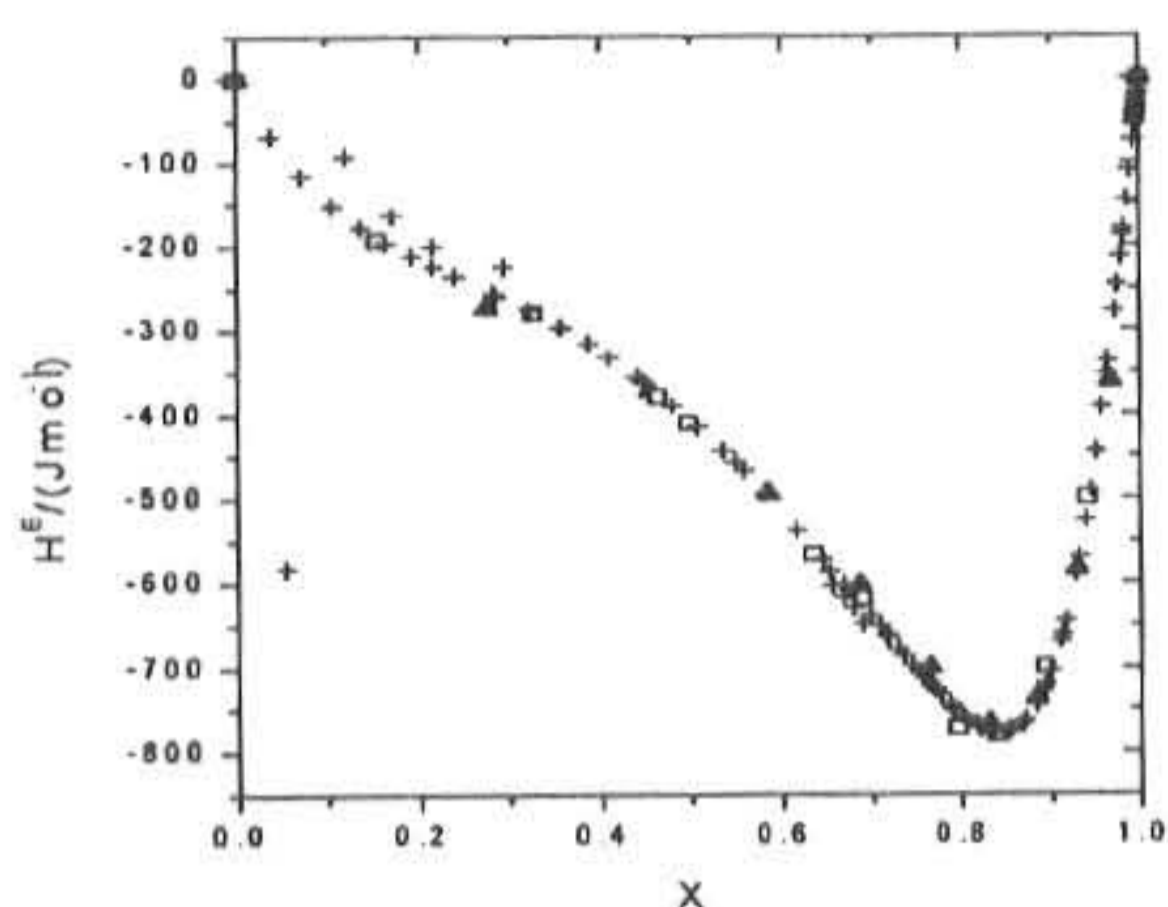


Fig. 2. Comparisons of the experimental results for $(x\text{H}_2\text{O} + (1-x)\text{C}_2\text{H}_5\text{OH})$ with literature values at 298.15K : \square , Chand and Fenby(1978); $+$, Costigan et. al.(1980); \blacktriangle , this work.

where h is the heat effect upon mixing.

The performance of the calorimeter was examined by means of enthalpies of mixing for the systems cyclohexane+n-hexane (particularly for the endothermic processes) and water+ethanol(particularly for the exothermic processes) recommended as a reference mixture in isothermal microcalorimeter^{5,6)}. Fig. 2 and Fig. 3 show the comparisons of experimental results of Chand and Fenby⁷⁾ and Costigan et. al.⁸⁾ for the system water+ ethanol, and Tanaka et. al.⁹⁾ for the system cyclohexane+n-hexane with those from this investigation, respectively. In all cases the smoothed results agreed within 1.6% of previously published values.

3. Results and Discussions

Experimental excess molar volumes V^E and excess molar enthalpies H^E at 298.15K for the binary mixture of 1,2-dichloropropane and 2-methoxyethanol are listed in Tables 2 and 3, and their dependences on mole fraction were shown in Fig. 4 and 5 together with the results of model calculations. From Fig. 4, the mixture 1,2-dichloropropane + 2-methoxyethanol has positive V^E over the entire composition range. These positive deviations from ideal

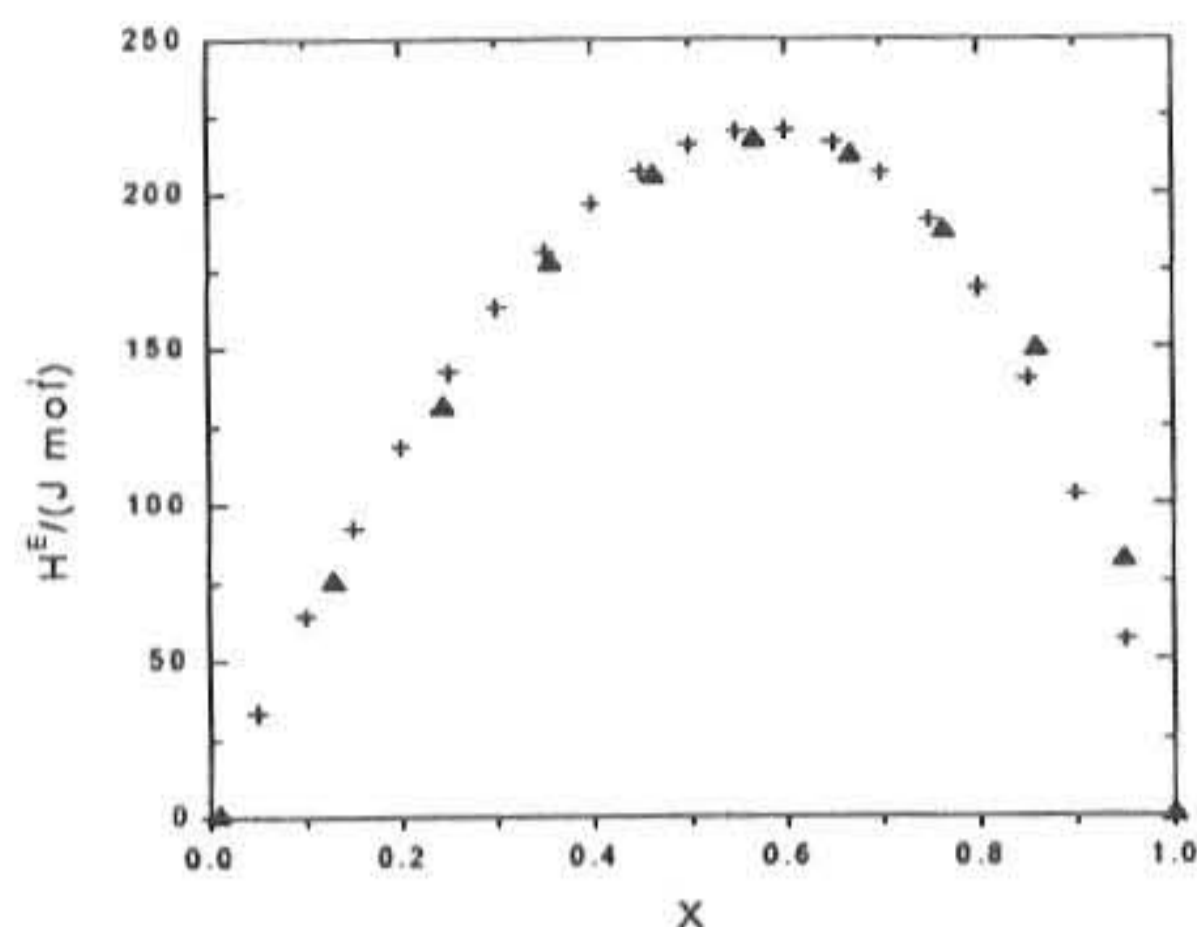


Fig. 3. Comparisons of the experimental results for $(xC_6H_{12} + (1-x)C_6H_{14})$ with literature values at 298.15K : $+$, Tanaka et. al.(1975); \blacktriangle , this work.

behavior are coincident with loosening of intermolecular interaction of a component with weak self-association(2-methoxyethanol). The maximum value of this mixture is found to be about $0.2 \text{ cm}^3 \cdot \text{mol}^{-1}$ at $x_1=0.724$. The dependence of H^E on compositions has an S-shaped curve, being negative for poor and positive for rich component of 1,2-dichloropropane.

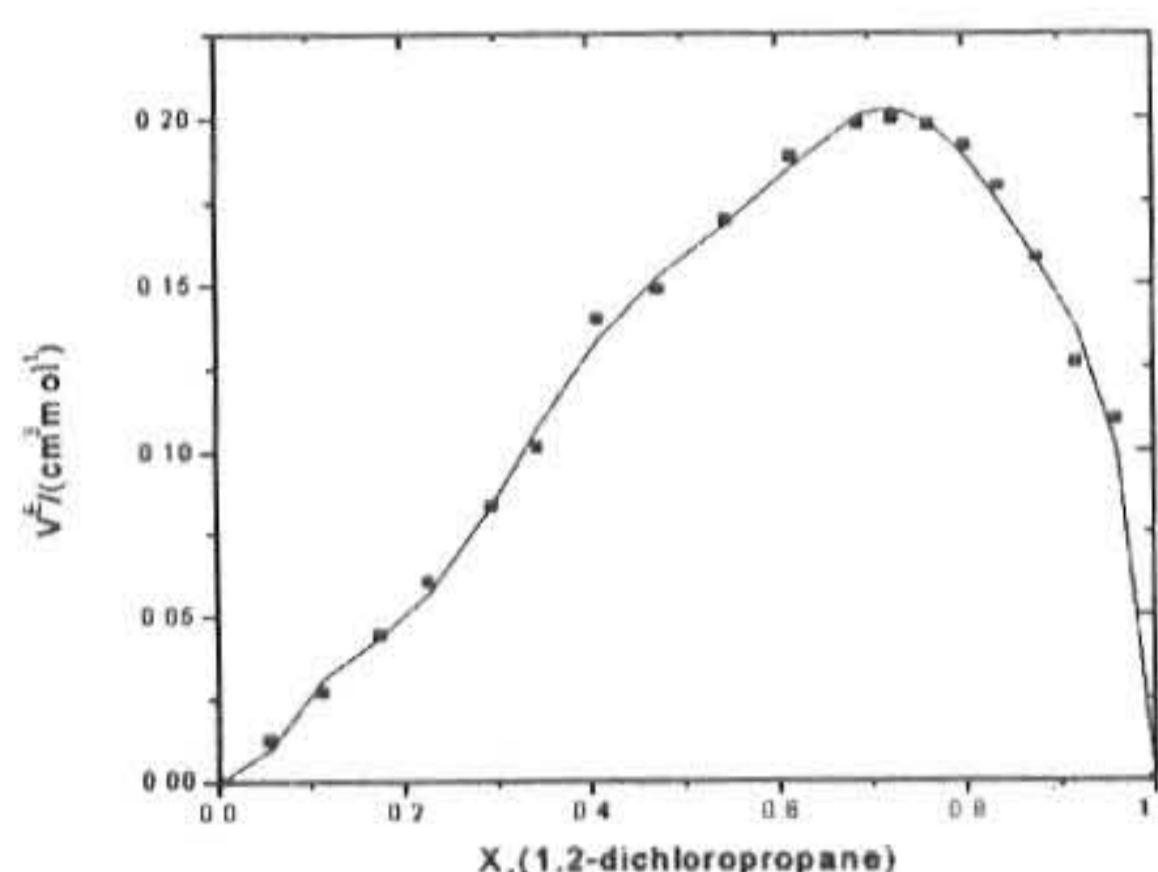


Fig. 4. Excess molar volumes V^E for binary mixture of (1,2-dichloropropane(1) and 2-methoxyethanol(2)) at 298.15K : \blacksquare , this work; —, Redlich-Kister model using parameters listed in Table 4.

This shows that a relatively high energy is needed to break hydrogen bonds of 2-methoxyethanol with an increase of halogenated hydrocarbon

molecular during mixing.

For the binary mixture V^E and H^E values were fitted to the Redlich-Kister equation to correlate the composition dependence of both excess of properties

$$Q^E = x_1(1-x_1) \sum_{j=1}^n A_j(1-2x_1)^{j-1} \quad (5)$$

where $Q^E = H^E/J \cdot \text{mol}^{-1}$ or $V^E/\text{cm}^3 \cdot \text{mol}^{-1}$ and x_1 is the mole fraction of 1,2-dichloropropane. The Redlich-Kister model gives an almost quantitative description of V^E and H^E for the system. Values of the coefficients A_j , determined by a Nelder-Mead simplex pattern search method, minimizing a function of n variables, are given in Table 4 along with standard deviations σ for the representation according to following equation (6)

$$\sigma = [\sum (Q_{calcd}^E - Q_{exptl}^E)^2 / (N - n)]^{1/2} \quad (6)$$

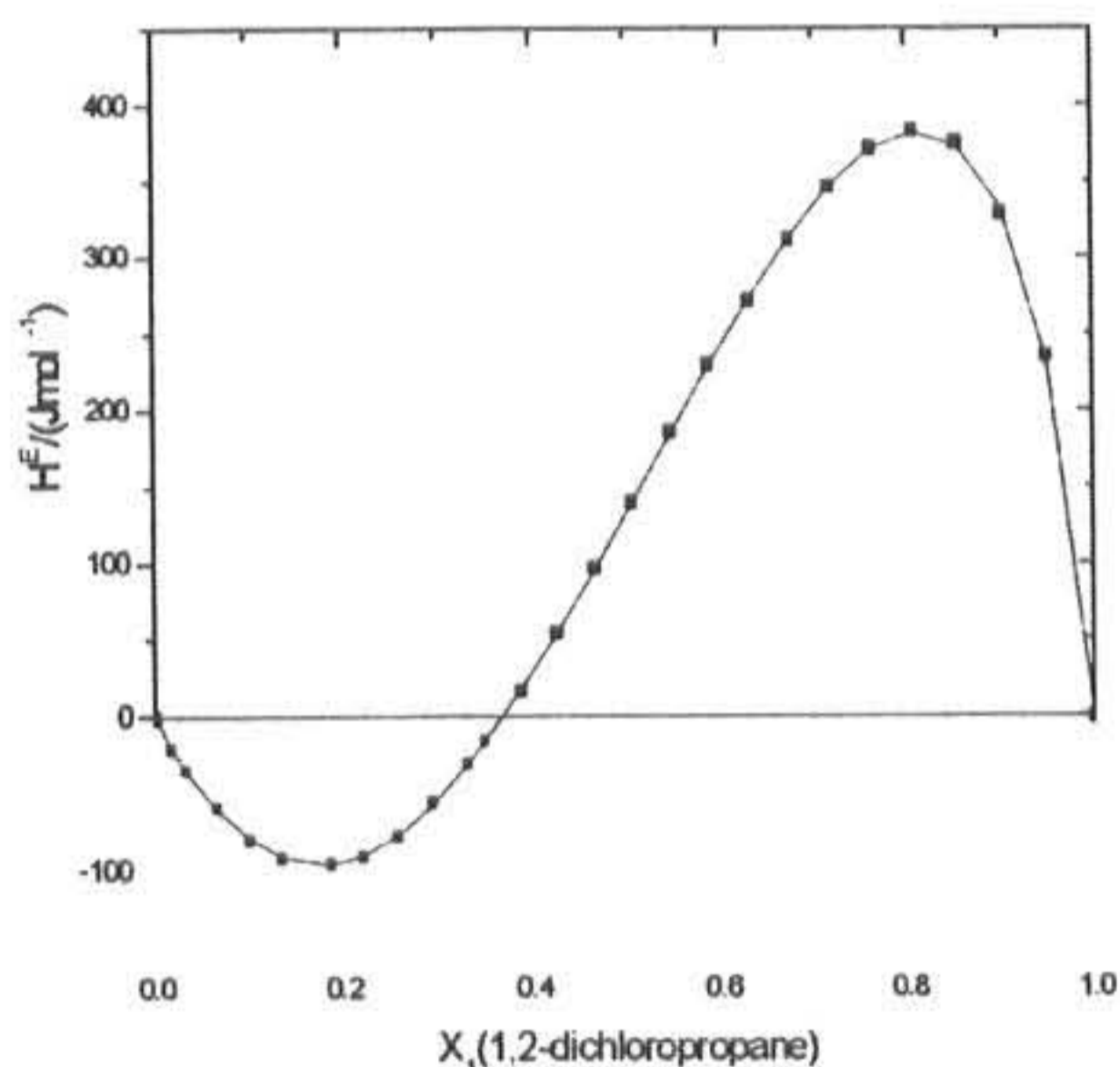


Fig. 5 Excess molar enthalpies H^E for the system of (1,2-dichloropropane(1) and 2-methoxyethanol(2)) at 298.15K : ■, this work; —, Redlich-Kister model using parameters listed in Table 4.

where N is the number of data points for system and n is the number of adjustable parameters.

Table 2. Experimental values of densities ρ and excess molar volume V^E for the system of $(x\text{CH}_3\text{CHClCH}_2\text{Cl} + (1-x)\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH})$ at 298.15K.

x	ρ	V^E
	($\text{g} \cdot \text{cm}^{-3}$)	($\text{cm}^3 \cdot \text{mol}^{-1}$)
0.056	0.97282	0.01253
0.112	0.98504	0.02720
0.174	0.99834	0.04452
0.226	1.00927	0.06065
0.293	1.02295	0.08304
0.343	1.03271	0.10142
0.409	1.04523	0.14001
0.474	1.05741	0.14870
0.544	1.07024	0.16963
0.615	1.08268	0.18859
0.688	1.09530	0.19828
0.724	1.10153	0.19987
0.762	1.10793	0.19783
0.801	1.11446	0.19164
0.836	1.12020	0.17972
0.877	1.12704	0.15811
0.918	1.13388	0.12708
0.960	1.14055	0.10969

Table 3. Experimental values of excess molar enthalpies H^E for binary mixture of $(x\text{CH}_3\text{CHClCH}_2\text{Cl} + (1-x)\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH})$ at 298.15K.

x	H^E	x	H^E
	($\text{J} \cdot \text{mol}^{-1}$)		($\text{J} \cdot \text{mol}^{-1}$)
0.017	-20.40474	0.466	97.05380
0.033	-33.91812	0.506	140.43762
0.066	-58.71698	0.547	185.74484
0.100	-79.48286	0.588	229.79842
0.134	-90.90786	0.631	271.85717
0.186	-94.98906	0.674	312.14149
0.221	-90.11456	0.718	346.78725
0.257	-76.98142	0.763	371.72856
0.293	-55.51850	0.808	383.51075
0.331	-30.09691	0.855	375.66895
0.349	-15.05974	0.902	329.13223
0.388	16.88956	0.950	234.98787
0.426	54.62745		

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Table 4. Coefficients A_i and standard deviations σ for least-squares representations of $V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$ and $H^E/(\text{J} \cdot \text{mol}^{-1})$ for binary mixture of $(x\text{CH}_3\text{CHClCH}_2\text{Cl} + (1-x)\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH})$ at 298.15K by eqn. (5)

	V^E	H^E
	$(\text{cm}^3 \cdot \text{mol}^{-1})$	$(\text{J} \cdot \text{mol}^{-1})$
A_1	0.63478	533.01458
A_2	-0.44372	-2167.50029
A_3	0.44428	814.77498
A_4	-2.47732	-909.35213
A_5	-1.01208	95.35616
A_6	7.00296	704.65264
A_7	1.77179	1284.09547
A_8	-6.36789	-1592.50734
σ	0.00597	1.63033

University grant.

Nomenclature

- A_j : adjustable parameters in the equation (5)
 \dot{h} , H^E : heat effect upon mixing and excess molar enthalpy, respectively
 M_i : molecular weight of component i
 n : number of adjustable parameter
 N : number of experimental data point
 \dot{q}_i : heat flux of component i
 \dot{v}_i , \dot{v}_T : heat flux, volumetric flow rate of component i , and total flow rate, respectively.
 x_i : liquid phase mole fraction of component i

Greek letters

- ρ , ρ_i : densities of binary mixture and component i , respectively
 σ : standard deviation
 Φ : baseline values

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