Excess molar enthalpies for the binary and ternary mixtures of ether compounds (*di*-isopropyl ether, *di*-butyl ether, propyl vinyl ether) with ethanol and isooctane at 298.15 K

Moon-Gab Kim*, So-Jin Park**,†, and In-Chan Hwang**

*School of Applied Chemical Engineering, Sangju National University, Sangju 742-711, Korea
**Department of Chemical Engineering, Chungnam National University, Daejeon 305-764, Korea

Abstract−Excess molar enthalpy (H^E) data at 298.15 K are reported for the binary systems *di*-isopropyl ether (1)+ethanol (2), *di*-isopropyl ether (1)+isooctane (2), ethanol (1)+isooctane (2), *di*-butyl ether (1)+ethanol (2), *di*-butyl ether (1)+isooctane (2), propyl vinyl ether (1)+ethanol (2) and propyl vinyl ether (1)+isooctane (2). These data were obtained by using an isothermal flow calorimeter. The experimental binary H^E data were well correlated with the Redlich-Kister model, and infinitely dilute partial excess molar enthalpies for each binary were calculated with the fitted Redlich-Kister parameters. Additionally, the isoclines of H^E for ternary systems *di*-isopropyl ether (1)+ethanol (2)+isooctane (3), *di*-butyl ether (1)+ethanol (2)+isooctane (3) and propyl vinyl ether (1)+ethanol (2)+isooctane (3) at 298.15 K were calculated by using the Radojkovič equation. H^E for all the measured systems in this work shows that mixing is endothermic.

Key words: Excess Molar Enthalpy (H^E), DIPE (*di*-isopropyl ether), DBE (*di*-butyl ether), PVE (propyl vinyl ether), Ethanol, Isooctane

INTRODUTION

The carbon-oxygen bond of ethers is not easily cleaved and these characteristics make ethers behave as inert solvents in many organic syntheses. Ethers are used by the lubricating oil, agricultural pesticides, food, and flavors industries. Recently, some ether compounds have seen increasing use as gasoline additives. Studies on the behavior of the mixing process are of great importance for developing separation processes and theoretical understanding of the nature of molecular interaction [1]. However, despite their increasing usage, the mixing properties for ether compounds are still not readily available.

We have studied the phase equilibria and mixture properties systematically for several ether compounds, because accurate data for such properties are strongly related to the processing of these compounds and application of the group contribution method. Previously, we reported vapor-liquid and liquid-liquid phase equilibria, as well as excess properties, for various binary and ternary systems involving methyl *tert* butyl ether (MTBE), ethyl *tert* butyl ether (ETBE), *tert* amyl methyl ether (TAME), *di*-methyl ether (DME), *di*-butyl ether (DBE) and propyl vinyl ether (PVE) [2-8].

In this work, we report the molar excess enthalpies (H^E) data at 298.15 K under atmospheric pressure for the binary systems *di*-isopropyl ether (DIPE, 1)+ethanol (2), DIPE (1)+isooctane (2), ethanol (1)+isooctane (2), DBE (1)+ethanol (2), DBE (1)+isooctane (2), PVE (1)+ethanol (2) and PVE (1)+isooctane (2). Isooctane is a major component of gasoline, and ethanol is a good substitute for MTBE as an octane booster as like another ether compound, such as DIPE, TAME, ETBE, etc. And as far as we know, there are no H^E data

for systems containing PVE. The measured H^E data were correlated well with Redlich-Kister polynomial. Additionally, infinitely dilute partial molar excess enthalpies ($H^{E,\infty}$) for each binary are calculated with fitted parameters and isoclines of H^E for ternary systems, DIPE (1)+ethanol (2)+isooctane (3), DBE (1)+ethanol (2)+isooctane (3) and PVE (1)+ethanol (2)+isooctane (3) calculated by using the Radojkovič equation. Since the ternary H^E data are still very rare, it is therefore usually necessary to estimate ternary H^E from binary H^E data.

EXPERIMENTAL

1. Materials

The analytical commercial grade chemicals from Aldrich were used in this investigation. All the chemicals were dried by using molecular sieves with a pore diameter of 0.4 nm. After that, the purity of each chemical was examined by gas chromatography and by comparing the experimentally measured density with the reported literature values. It is shown by gas chromatographic analysis that the purity of each chemical was better than 99.6 wt%. The water con-

Table 1. The purity of chemicals used in these experiments

Chemicals	GC analysis (wt%)	ρ/g·cm^{-3} at 298.15 K	
		Present study	Literature value[a]
DIPE	99.8	0.71877	0.7182
DBE	99.7	0.76425	0.7641
PVE	99.6	0.76296	-
Ethanol	99.9	0.78531	0.7850
Isooctane	99.9	0.68816	0.6878

[a]Reference 8.

†To whom correspondence should be addressed.
E-mail: sjpark@cnu.ac.kr

tent of each chemical, determined by Karl-Fischer titration (Metrohm 684 KF-Coulometer), was less than 8×10^{-5} g/g. The density of PVE is not available in the literature [9]. The measured densities of the pure substances, along with literature values, are summarized in Table 1.

2. Methods and Equipment

H^E was determined with an isothermal micro-calorimeter (Calorimetry Sciences Corporation, CSC-4400, Utah, U.S.A) with a flow-mixing cell (part number 4442, CSC, UT). The measuring unit of the calorimeter is a large aluminum heat sink (ca. 66 liters) in which sample and reference test wells are incorporated. The water bath of the calorimeter provided temperature control of ±0.0005 K. The 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. The thermoelectric sensors located between the sample and the aluminum block will generate a voltage that is proportional to the temperature gradient across the sensors, which is caused by the flow of heat into or out of a sample. The calorimeter was calibrated electrically at 298.15 K by an auto calibration mode and the pressure in the calorimeter was fixed by a backpressure regulator (Grove Valves & Regulator Co., Stafford, TX, U.S.A) [10]. A block diagram showing the main components of the calorimeter is shown in Fig. 1.

The total volumetric flow rate of this study was 0.5 cm³ min⁻¹, depending on the magnitude of the measured heat signal. The pumps for introducing samples to the calorimeter (not depicted in Fig. 1) were calibrated by determining the volumetric flow rates from (0.01 to 0.5) cm³ min⁻¹ of bi-distilled water. Empirical correction equations were provided for each pump with an accuracy of ±1%. To eliminate the uncertainties in the volumetric flow rate, liquid components were kept in double glass-lined jacketed bottles controlled by circulating coolant from a thermostat. These components were pumped into the mixing cell of the calorimeter by a digital HPLC pump (Acuflow Series II, Fisher Scientific, U.S.A) operated at steady-state mode, at atmospheric pressure. For optimum calorimeter performance, the temperature of the room was kept constant at (298.15 ±1) K and relative humidity was maintained below 30% by a glove box, which was equipped with an air pump, desiccant cartridge, and hydrometer.

H^E was experimentally obtained by subtracting heat effects from baseline values. The baseline values were determined by running pump I at maximum (total) flow rate while pump II was turned off, then repeating with pump I off and pump II at the maximum flow rate. Baseline values, Φ of each composition can be calculated according to the following relation:

$$\Phi = \dot{q}_1 \cdot \frac{\dot{v}_1}{\dot{v}_T} + \dot{q}_2 \cdot \frac{\dot{v}_2}{\dot{v}_T} \tag{1}$$

where $\dot{q}_i$ is heat flux of component i and $\dot{v}_i$ and $\dot{v}_T$ are the volumetric flow rate of components (i=1, 2), and the total flow rate, respectively. From volumetric flow rates, the molar masses (M_1 and M_2), 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 by:

$$x_1 = \left(\dot{v}_1 \cdot \frac{\rho_1}{M_1} \right) \bigg/ \left\{ \left(\dot{v}_1 \cdot \frac{\rho_1}{M_1} \right) + \left(\dot{v}_2 \cdot \frac{\rho_2}{M_2} \right) \right\} \tag{2}$$

$$H_m^E = \Phi - \dot{q} \bigg/ \left\{ \left(\dot{v}_1 \cdot \frac{\rho_1}{M_1} \right) + \left(\dot{v}_2 \cdot \frac{\rho_2}{M_2} \right) \right\} \tag{3}$$

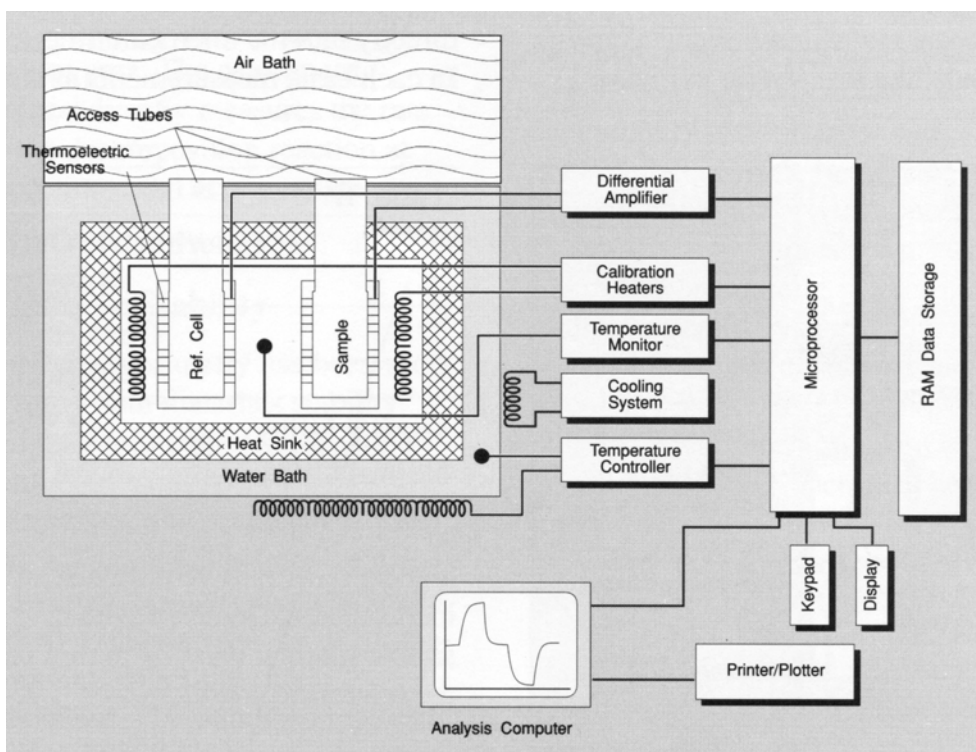where $\dot{q}$ is the heat flux upon mixing.

Fig. 1. The block diagram of the isothermal micro calorimeter.

The performance of the calorimeter was examined by means of comparing the experimental values of model compound with the reported values [11].

RESULTS AND DISCUSSION

The excess enthalpy, H^E between the enthalpy of pure substances and mixtures can be calculated by using Eq. (4).

$$H^E = H_m - (x_1 H_1 + x_2 H_2) \tag{4}$$

where x_i, H_1 and H_m are the mole fraction, molar enthalpy of com-

Table 2. Experimental H^E data for the binary systems DIPE (1)+ ethanol (2), DIPE (1)+isooctane (2), ethanol (1)+isooctane (2), DBE (1)+ethanol (2), DBE (1)+isooctane (2), PVE (1)+ ethanol (2) and PVE (1)+isooctane (2) at 298.15 K

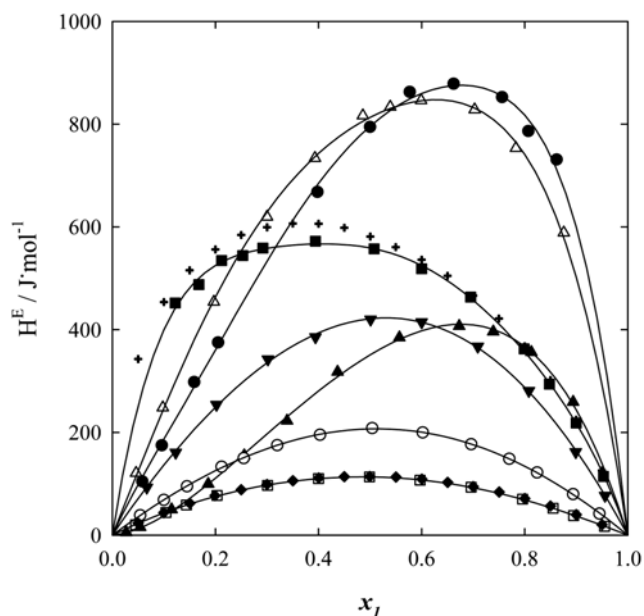| x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
DIPE (1)+ethanol (2)					
0.0270	5.50	0.2560	155.10	0.6730	407.10
0.0540	15.60	0.3390	222.60	0.7390	396.10
0.1150	50.10	0.4370	317.90	0.8130	356.20
0.1860	99.70	0.5570	384.60	0.8940	259.20
DIPE (1)+isooctane (2)					
0.9450	42.00	0.6020	199.80	0.2120	133.20
0.8940	79.80	0.5040	208.30	0.1450	95.00
0.8240	122.00	0.4030	195.50	0.1000	68.70
0.7700	148.80	0.3200	175.10	0.0540	38.70
0.6960	176.80	0.2550	150.10		
Ethanol (1)+isooctane (2)					
0.9530	114.40	0.6000	518.60	0.2530	544.30
0.9000	218.30	0.5080	557.50	0.2120	534.60
0.8480	294.00	0.3940	572.10	0.1680	487.70
0.7990	362.50	0.2920	558.90	0.1220	452.00
0.6950	463.30				
DBE (1)+ethanol (2)					
0.0460	121.00	0.3930	734.00	0.7030	828.30
0.0980	248.50	0.4860	816.70	0.7830	753.40
0.1970	454.20	0.5390	833.70	0.8760	588.90
0.3000	619.70	0.5990	846.50		
DBE (1)+isooctane (2)					
0.9550	17.19	0.5970	107.17	0.2030	77.35
0.8950	38.25	0.4990	113.41	0.1440	58.72
0.8550	52.33	0.4000	110.18	0.1040	44.09
0.7960	70.21	0.3010	96.86	0.0450	20.23
0.6960	93.41				
PVE (1)+ethanol (2)					
0.0580	104.40	0.3980	668.20	0.7560	852.60
0.0960	174.80	0.5000	794.60	0.8070	786.50
0.1590	298.00	0.5770	862.70	0.8620	731.20
0.2050	375.10	0.6620	878.70		
PVE (1)+isooctane (2)					
0.9560	77.20	0.6000	414.60	0.2020	253.90
0.8990	161.90	0.5010	420.10	0.1230	160.80
0.8080	281.00	0.3940	385.60	0.0670	92.90
0.7090	367.10	0.3020	342.40		

Fig. 2. H^E for the seven binary systems at 298.15 K: DIPE (1)+ethanol (2), (▲); DIPE (1)+isooctane (2), (○); ethanol (1)+ isooctane (2), (■); DBE (1)+ethanol (2), (△); DBE (1)+ isooctane (2), (□); DBE (1)+isooctane (2) by Pang et al. [11], (◆); PVE (1)+ethanol (2), (●); PVE (1)+isooctane (2), (▼); ethanol (1)+isooctane (2) by Wang et al. [12], (+). Solid curves were calculated from the Redlich-Kister polynomial.

ponent i (i=1, 2) and mixture enthalpy, respectively.

The experimental H^E for the 7 binary systems DIPE (1)+ethanol (2), DIPE (1)+isooctane (2), ethanol (1)+isooctane (2), DBE (1)+ ethanol (2), DBE (1)+isooctane (2), PVE (1)+ethanol (2) and PVE (1)+isooctane (2) at 298.15 K are listed in Table 2 and plotted in Fig. 2. The measured H^E value for the DBE (1)+isooctane (2) system agreed very well with data reported by Peng and his group [12]. However, for the case of the ethanol (1)+isooctane (2) system, our data showed slightly lower values than those of Wang et al. in the ethanol-rich regions [13]. We did not find any H^E data for other systems.

The binary H^E data were correlated with Redlich-Kister polynomial, Eq. (5) [14].

$$H^E_{12}/\text{J}\cdot\text{mol}^{-1} = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{5}$$

The standard deviation of the fits, σ_{st}, was then calculated from the experimental data and recalculated values with Redlich-Kister parameters, defined as

$$\sigma_{st}/\text{J}\cdot\text{mol}^{-1} = \left[\frac{\sum_i ((H^E)_{cal} - (H^E)_{exp})^2_i}{(N-n)}\right]^{1/2} \tag{6}$$

where N is the number of experimental data points and n is the number of fitted parameters.

All of the measured binary H^E data, even though some data are highly skewed (as shown in Fig. 2), were correlated well with the Redlich-Kister polynomial. The solid lines were calculated values

Table 3. Fitted parameters for the Redlich-Kister equation and standard deviations for binary systems of DIPE, DBE, PVE, ethanol and isooctane at 298.15 K

System	A_1	A_2	A_3	A_4	A_5	σ_{st}	$\overline{H}_1^{E,\infty}$	$\overline{H}_2^{E,\infty}$
DIPE (1)+ethanol (2)	1403.43	1208.77	249.62	350.33	-	5.49	93.96	3212.16
DIPE (1)+isooctane (2)	827.46	47.88	−44.04	−6.46	-	1.01	742.01	824.84
Ethanol (1)+isooctane (2)	2236.26	−381.71	898.35	−1373.17	1507.99	7.09	6397.46	2887.72
DBE (1)+ethanol (2)	3253.16	1023.48	1421.09	1176.63	-	8.98	2474.14	6874.36
DBE (1)+isooctane (2)	453.43	−26.77	−10.67	−22.77	-	0.67	492.30	393.22
PVE (1)+ethanol (2)	3183.43	1753.95	777.48	1745.31	1687.29	15.79	2148.95	9147.48
PVE (1)+isooctane (2)	1684.94	216.29	−23.78	−39.24	-	3.95	1484.10	1838.21

using fitted Redlich-Kister parameters. These adjusted Redlich-Kister parameters of each system are given in Table 3 along with standard deviations between calculated and experimental data. The number of parameters used to represent the experimental data depends on the molecular complexity of the H^E behavior, the quality of the data, and the number of data points available. The reliable and extensive data justify the use of five parameters. For all systems studied, the obtained standard deviations are within the estimated experimental error of few %.

The H^E of all measured binary systems show positive deviation (i.e., endothermic mixing) from ideality. The maximum binary H^E values calculated were 410.70 J·mol^{-1} at x_1=0.6766 for DIPE (1)+ethanol (2) system, 847.57 J·mol^{-1} at x_1=0.6275 for DBE (1)+ethanol (2) system, 875.93 J·mol^{-1} at x_1=0.6783 for PVE (1)+ethanol (2) system, 207.03 J·mol^{-1} at x_1=0.5150 for DIPE (1)+isooctane (2) system, 113.45 J·mol^{-1} at x_1=0.4856 for DBE (1)+isooctane (2) system, 422.93 J·mol^{-1} at x_1=0.5312 for PVE (1)+isooctane (2) system and 566.93 J·mol^{-1} at x_1=0.4100 for ethanol (1)+isooctane (2) system, respectively.

By the way, the partial molar excess enthalpy at infinite dilution, $\overline{H}_i^{E,\infty}$ is of great importance because it relates thermodynamically with activity coefficients at infinite dilution (γ_i^∞). The temperature dependence of γ_i^∞ can be calculated from $\overline{H}_i^{E,\infty}$ and therefore $\overline{H}_i^{E,\infty}$ is used to test the quantity of γ_i^∞. We calculated $\overline{H}_i^{E,\infty}$ for each system from Redlich-Kister parameters using Eqs. (7) and (8). They are listed in Table 3.

$$\overline{H}_1^{E,\infty}/J\cdot mol^{-1}=A_1-A_2+A_3-A_4+A_5 \tag{7}$$

$$\overline{H}_2^{E,\infty}/J\cdot mol^{-1}=A_1+A_2+A_3+A_4+A_5 \tag{8}$$

Additionally, the isoclines of H^E for ternary systems DIPE (1)+ethanol (2)+isooctane (3), DBE (1)+ethanol (2)+isooctane (3) and PVE (1)+ethanol (2)+isooctane (3) at 298.15 K were calculated by using the Radojkovič equation [15] and plotted in Figs. 3 to 5. As shown in the figures, the ternary system shows only positive values of H^E at all the composition ranges. This can be easily expected from positive values of binary H^E data.

CONCLUSIONS

Excess molar enthalpies (H^E) were determined for seven binary systems at 298.15 K. The H^E values of all binary systems show endothermic mixing. The experimental H^E was correlated well with the Redlich-Kister polynomial even though for their highly skewed
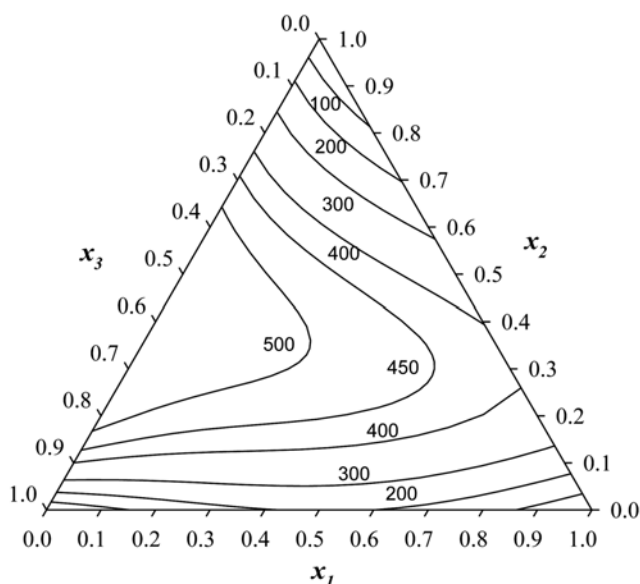

Fig. 3. Constant line of H^E at 298.15 K for the ternary system of DIPE (1)+ethanol (2)+isooctane (3), calculated by Radojkovič equation.
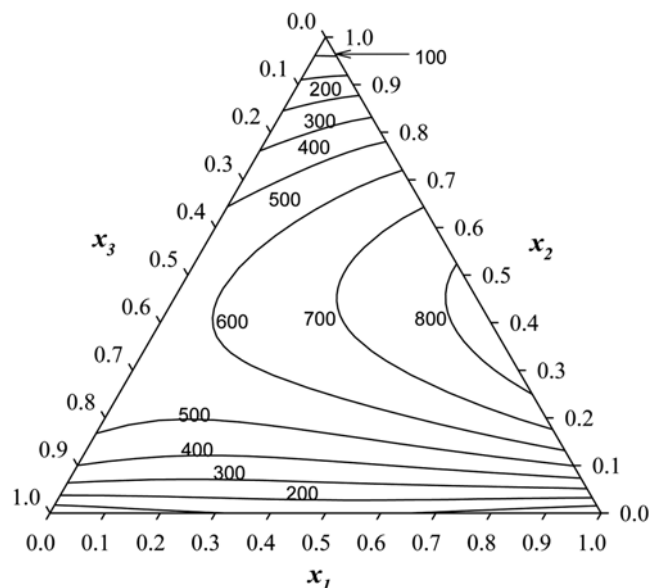

Fig. 4. Constant line of H^E at 298.15 K for the ternary system of DBE (1)+ethanol (2)+isooctane (3), calculated by Radojkovič equation.
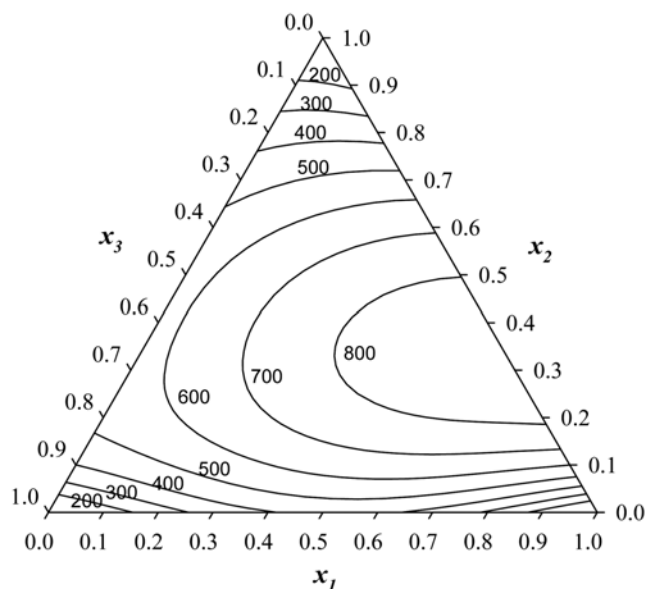
Fig. 5. Constant line of H^E at 298.15 K for the ternary system of PVE (1)+ethanol (2)+isooctane (3), calculated by Radojkovič equation.

tendency of some systems. Additionally, infinitely dilute partial molar enthalpies for each binary system and the isoclines of H^E for three ternary systems at 298.15 K were calculated by using the Radojkovič equation. The ternary systems also show positive values of H^E at all the composition ranges.

ACKNOWLEDGMENT

NOMENCLATURE

A$_i$: adjustable parameter for the Redlich-Kister equation
n   : number of parameters A$_i$
N   : number of experimental data points
H^E : excess molar enthalpy [J mol^{-1}]

H$_i$: molar enthalpy of the component i
H$_m$: enthalpy of the mixture
x$_i$: liquid phase mole fraction of the component i
q$_i$: heat flux of component i
v$_i$: volumetric flow rate of components (i=1, 2)
v$_T$: total flow rate
ρ : density [g/cm^3]

Greek Letters

σ_{st} : standard deviation
Φ : baseline values

REFERENCES

1. G. C. Pedrosa, J. A. Salas and M. Katz, *Thermochim. Acta*, **160**, 242 (1990).
2. S. J. Park and T. J. Lee, *Korean J. Chem. Eng.*, **12**, 110 (1995).
3. S. J. Park, K. J. Han and J. Gmehling, *Fluid Phase Equilib.*, **200**, 399 (2002).
4. J. H. Oh and S. J. Park, *J. Chem. Eng. Data*, **43**, 1000 (1998).
5. K. Fischer, S. J. Park and J. Gmehling, *J. Phys.-Chem. Data*, **2**, 135 (1996).
6. K. J. Han, S. J. Park and J. Gmehling, *J. Chem. Eng. Data*, **52**, 230 (2007).
7. K. J. Han, I. C. Hwang, S. J. Park and I. H. Park, *J. Chem. Eng. Data*, **52**, 1018 (2007).
8. I. C. Hwang, K. J. Han and S. J. Park, *J. Chem. Eng. Data*, **52**, 1118 (2007).
9. Dortmund Data Bank Software Package (DDBSP), version 2006 professional. (http://www.ddbst.de)
10. Isothermal Microcalorimeter Use's Manual Revision 3.0, Calorimetry Sciences Corp (1997).
11. Y. W. Kim and M. G. Kim, *Korean Chem. Eng. Res.*, **42**, 426 (2004).
12. D. Y. Peng, G. C. Benson and B. C.-Y. Lu, *J. Chem. Thermodynamics*, **34**, 413 (2002).
13. L. Wang, G. C. Benson and B. C.-Y. Lu, *J. Chem. Thermodyn.*, **24**, 1305 (1992).
14. O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).
15. N. Radojkovič, A. Tasič, B. Grozdanič and M. Malič, *J. Chem. Thermodyn.*, **9**, 349 (1977).