Excess Molar Enthalpies of 1-Octanol with Ethylbenzene, Ethyl Benzoate, Acetophenone, Anisole, or Methanol at 298.15 K

Pei-Jung Lien, Pannuru Venkatesu, Ho-Mu Lin,* and Ming-Jer Lee

Department of Chemical Engineering, National Taiwan University of Science and Technology,
43 Keelung Road, Section 4, Taipei 106-07, Taiwan

Excess molar enthalpies, H^E, of binary mixtures of 1-octanol with ethylbenzene, ethyl benzoate, acetophenone, anisole, or methanol have been measured at 298.15 K under atmospheric pressure using an isothermal microcalorimeter. The experimental H^E values are positive for all the binary mixtures over the entire range of compositions. The experimental data have been correlated with the modified Redlich−Kister polynomial equation. The results were qualitatively interpreted in terms of thermodynamic molecular interactions between the mixing components.

Introduction

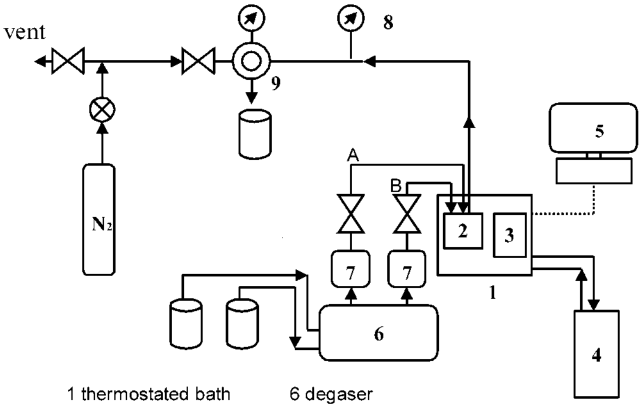
Knowledge of mixing properties such as excess molar enthalpies, H^E, is fundamental to better understanding of molecular interactions and to design and development of industrial processes. Enthalpy data have proven imperative in elucidating the structural interactions among the components and in verifying predictive methods for thermodynamic properties of mixtures originating from theories of intermolecular forces.[1−5]

The need for accurate data of enthalpies of mixtures has led to development of more and more sophisticated calorimeters. Of these, the isothermal flow calorimeter has widely been applied by several investigators.[6−12] The principle of flow calorimetry is based on mixing of two fluids under isothermal conditions and, after establishing the equilibrium state, measuring the energy absorbed or released with the help of an electronically controlled cooling−heating combination. As an inherent advantage of isothermal microcalorimetry, the heat capacity of the calorimeter is not involved once steady-state operation has been achieved.

The present study is undertaken to determine experimentally excess molar enthalpies for binary mixtures of 1-octanol with ethylbenzene, ethyl benzoate, acetophenone, anisole, or methanol at 298.15 K with an isothermal microcalorimeter. Alcohols are strongly associated by hydrogen bonding, while ethylbenzene, ethyl benzoate, acetophenone, and anisole are technically important classes of solvents. The results of this work will supplement the database useful for investigation of hydrogen bonding and its interactions with the functional groups of the benzene ring.

Experimental Section

Chemicals. 1-Octanol (>99 mass %), 1-methanol (>99.9 mass %), and acetophenone (>99 mass %) were supplied by Acros, USA. Ethylbenzene (>99 mass %) was purchased from Merck-Schuchardt, Germany, and ethyl benzoate (>99 mass %) and anisole (>99.7 mass %) were from Aldrich, USA. All chemicals were used without further purification. The purities of the samples were verified by measuring their densities with a densimeter (DMA 4500, Anton Paar, accuracy ±5 × 10^{-5} g·cm^{-3}). The results are reported in Table 1 in comparison with literature values.



1 thermostated bath
2 mixing cell
3 reference cell
4 refrigerated bath
5 PC
6 degaser
7 liquid pump
8 pressure transducer
9 back pressure regulator

Figure 1. Schematic diagram of the flow-type isothermal microcalorimeter.

Table 1. Densities of Pure Components at 298.15 K and the Data Sources of H^E Used for Determination of Calibration Constants

	ρ/g·cm^{-3}		data sources of H^E used for determination of calibration constants
component	this work	lit.	
1-octanol	0.8219	0.8225[13]	18
ethylbenzene	0.8625	0.8626[14]	19
ethyl benzoate	1.0413	1.0414[15]	20
acetophenone	1.0225	1.0225[16]	21
anisole	0.9891	0.9884[16]	22
methanol	0.7875	0.7865[17]	19

Apparatus and Procedure. The excess molar enthalpies have been measured using the isothermal microcalorimeter (model 4400 IMC) available commercially from Calorimeter Science Corporation, USA. A schematic diagram of the microcalorimeter is shown in Figure 1. The calorimeter consists of a mixing cell, a reference cell, a thermostatic water bath, a data acquisition system, and

---

* Corresponding author. Telephone: +886+2-2737-6643. Fax: +886-2-2737-6644. E-mail: hml@ch.ntust.edu.tw.

10.1021/je0102154 CCC: $22.00

two liquid pumps (model PU-1580, JASCO, Japan) together with an on-line degasser. The water bath controls the temperature of the heat sink where the mixing cell, reference cell, and thermoelectric sensors are located. The temperature of the bath is controlled to within ±0.05 K.

The components, partially degassed by agitation under reduced pressure, were loaded into the pumps at selected flow rates. The molar ratio of the two mixing streams was calculated from the molecular weights, densities, and volumetric flow rates of components 1 and 2. In general, the total flow rates are kept at about 0.4 $\mathrm{cm^3 \cdot min^{-1}}$. In both dilute regions, the total flow rates, however, may increase to as high as 0.8 $\mathrm{cm^3 \cdot min^{-1}}$.

The excess molar enthalpy was obtained from the following equation:

$$H^{\mathrm{E}} = \frac{\epsilon_{\mathrm{m}}(V_{\mathrm{m}} - V_{\mathrm{m}}^{\circ})}{\dfrac{f_1\rho_1}{\mathrm{MW}_1} + \dfrac{f_2\rho_2}{\mathrm{MW}_2}} \qquad (1)$$

where f_i, ρ_i, and MW_i are the volumetric flow rate, density, and molecular weight of constituent i, respectively. The voltage of mixing, V_{m}, is one of the measurable variables which is accessible from the data acquisition system. Meanwhile, the voltage of the baseline, V_{m}°, was calculated from

$$V_{\mathrm{m}}^{\circ} = \frac{f_1 V_1^{\circ} + f_2 V_2^{\circ}}{f_1 + f_2} \qquad (2)$$

where V_i° is the baseline voltage for component i. The baseline voltages were determined by charging with a pure compound at several different flow rates. In general, the value of V_{m}° is much smaller than that of V_{m} (<0.1%). The variable ϵ_{m} in eq 1 is the calibration coefficient for mixing runs. Its value was estimated from the following equation:

$$\epsilon_{\mathrm{m}} = \Phi_1\epsilon_1 + \Phi_2\epsilon_2 = \left(\frac{f_1}{f_1 + f_2}\right)\epsilon_1 + \left(\frac{f_2}{f_1 + f_2}\right)\epsilon_2 \qquad (3)$$

where Φ_i and ϵ_i are the volumetric fraction and calibration coefficient for constituent i, respectively. It should be noted that the values of the calibration coefficients, ϵ_i, vary with several factors, including temperature, volumetric flow rate, and the path of streams. For a specific stream at a given operating temperature, the relationship between ϵ_i and the flow rate f_i was found to be linear for all the experimental conditions of this study. Equation 3 can thus be expressed as

$$\epsilon_{\mathrm{m}} = \left(\frac{f_1}{f_1 + f_2}\right)(a_{01} + a_{11}f_1) + \left(\frac{f_2}{f_1 + f_2}\right)(a_{02} + a_{12}f_2) \qquad (4)$$

where (a_{01}, a_{11}) and (a_{02}, a_{12}) are the calibration constants for streams A and B, respectively. These constants have to be determined for each constituent compound by fitting experimental results to reliable literature H^{E} data of the related mixtures, prior to measuring a new system. The sources of the literature data used in this work for determination of the calibration constants are listed in Table 1.

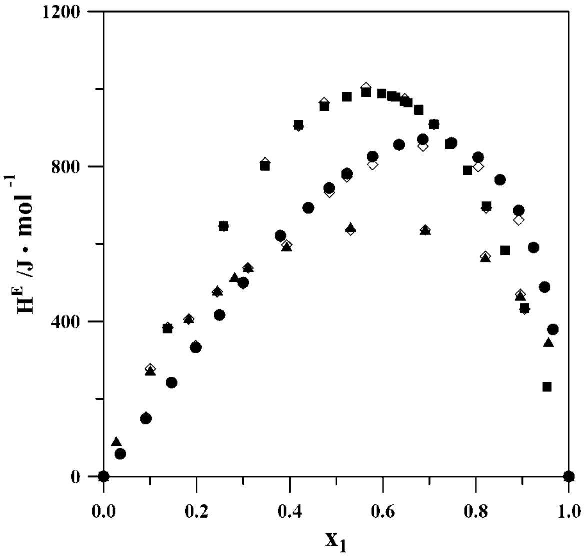


Figure 2. Molar excess enthalpies, H^{E}, for the test systems of benzene (1) + *n*-octane (2) [(■) experimental values; (◇) literature data[23]], *n*-octane (1) + ethanol (2) [(▲) experimental values; (◇) literature data[24]], and benzene (1) + ethanol (2) [(●) experimental values; (◇) literature data[25]] at 298.15 K.

Table 2. Experimental Excess Enthalpies, H^{E}, of 1-Octanol (1) + Solvents (2) as a Function of Mole Fraction, x_1, of 1-Octanol at 298.15 K

x_1	H^{E}/J·mol^{-1}	x_1	H^{E}/J·mol^{-1}
	1-Octanol (1) + Ethylbenzene (2)		
0.0495	534.9	0.4987	895.7
0.1004	743.0	0.5996	777.2
0.2001	907.8	0.6978	625.7
0.2985	971.1	0.7979	421.0
0.3492	976.0	0.8997	202.2
0.3997	961.8		
	1-Octanol (1) + Ethyl Benzoate (2)		
0.0500	378.5	0.5022	1494
0.0989	689.7	0.5500	1453
0.2095	1239	0.6008	1388
0.3005	1432	0.6984	1138
0.3514	1493	0.8006	775.0
0.4004	1528	0.8999	405.9
0.4498	1530		
	1-Octanol (1) + Acetophenone (2)		
0.1018	713.6	0.5503	1624
0.2004	1240	0.6011	1553
0.3013	1527	0.7015	1265
0.4017	1658	0.7981	926.2
0.4506	1682	0.9015	483.6
0.5010	1665		
	1-Octanol (1) + Anisole (2)		
0.0500	634.9	0.4506	1632
0.1000	964.1	0.5007	1560
0.1999	1437	0.5998	1311
0.3002	1623	0.6991	984.2
0.3499	1660	0.7993	651.1
0.4001	1644	0.8999	281.7
	1-Octanol (1) + Methanol (2)		
0.0521	159.5	0.4505	342.9
0.0999	250.1	0.5010	315.2
0.1515	313.4	0.5497	289.9
0.1992	344.5	0.6042	258.5
0.2497	364.7	0.7056	191.7
0.2992	371.9	0.8022	121.4
0.3497	368.9	0.9015	57.3
0.3997	356.1		

Results and Discussion

To verify the reliability of measurements, three standard systems, benzene + *n*-octane, *n*-octane + ethanol, and benzene + ethanol were measured at 298.15 K. The calibration constants for benzene and ethanol were determined from literature H^{E} values of benzene + *n*-octane[23] and *n*-octane + ethanol.[24] These determined calibration constants were then introduced into eqs 1 and 4 to obtain

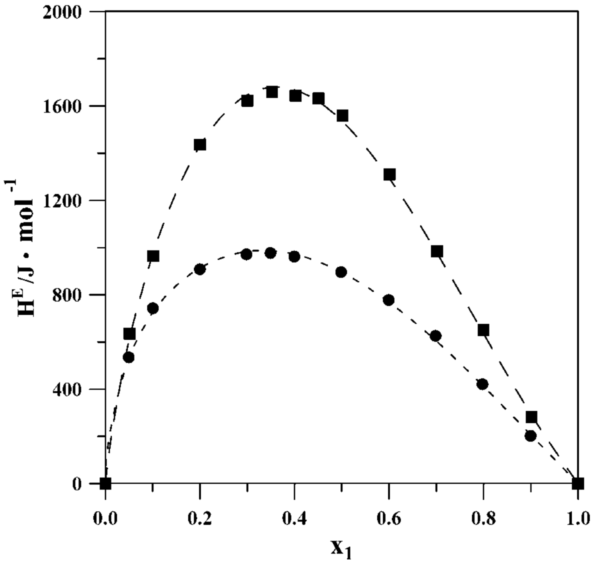


Figure 3. Molar excess enthalpies, H^E, for the mixtures 1-octanol (1) + ethylbenzene (2) (●) and 1-octanol (1) + anisole (2) (■) at 298.15 K: (points) experimental values; (- - -) calculated from the modified R−K equation.

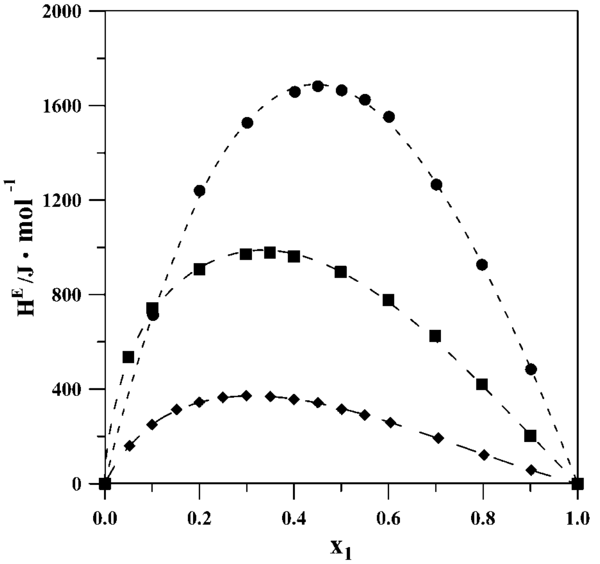


Figure 4. Molar excess enthalpies, H^E, for the mixtures 1-octanol (1) + ethyl benzoate (2) (■), 1-octanol (1) + acetophenone (2) (●), and 1-octanol (1) + methanol (2) (◆) at 298.15 K: (points) experimental values; (- - -) calculated from the modified R−K equation.

the experimental H^E values of benzene + ethanol. Figure 2 compares the experimental H^E values with the literature values for these three test systems, indicating that the agreement is satisfactory. The accuracy of the reported H^E values in this study is estimated approximately to be within ±2%.

Table 2 lists the experimental excess enthalpies, H^E, for the five binary systems of 1-octanol with ethylbenzene, ethyl benzoate, acetophenone, anisole, or methanol at 298.15 K. Figures 3 and 4 present the variations of the experimental H^E values with x_1, the mole fraction of 1-octanol. The maximum values of H^E for these five binary systems follow the order acetophenone (1682 J·mol^{-1} at x_1 = 0.4506) > anisole (1660 J·mol^{-1} at x_1 = 0.3499) > ethyl benzoate (1530 J·mol^{-1} at x_1 = 0.4498) > ethylbenzene (976.0 J·mol^{-1} at x_1 = 0.3492) > methanol (371.9 J·mol^{-1} at x_1 = 0.2992). All the H^E values are positive (endothermic) over the entire composition range, revealing that the physical forces between the dissimilar molecules are dominant in these investigated mixtures. Although the relatively small values of H^E for 1-octanol + methanol are partly attributed to the formation of hydrogen bonds between 1-octanol and methanol, the hydrogen bonding effect is rather weak, such that the excess enthalpies are still positive.

Table 3. Coefficients a_i (J·mol^{-1}), k (J·mol^{-1}), and AAD H^E (%) for the Representation of Excess Enthalpies, H^E, by Eq 5

mixture[a]	a_0	a_1	a_2	k	AAD H^E [b] (%)
M1	3581.8	−1331.0	−938.1	0.953	1.36
M2	6062.3	−2245.8	−1294.0	0.696	1.48
M3	6674.0	1423.6	−7.3	0.015	0.78
M4	6153.2	−2010.2	−3095.6	0.953	1.43
M5	1272.4	−3.1	−358.0	0.781	0.62

[a] M1: 1-octanol + ethylbenzene. M2: 1-octanol + ethyl benzoate. M3: 1-octanol + acetophenone. M4: 1-octanol + anisole. M5: 1-octanol + methanol. [b] Defined as in eq 6.

The new H^E data are fitted to the modified Redlich−Kister (R−K) equation:

$$H^E = x_1(1 - x_1)\sum_{i=0}^{m} a_i(1 - 2x_1)^i/[1 - k(1 - 2x)] \qquad (-1 < k < 1) \quad (5)$$

The coefficients a_i and k are adjustable parameters obtained by the least-squares regression. Table 3 gives the optimized values of the parameters along with the percentage average absolute deviation (AAD), which is defined as

$$\text{AAD } H^E (\%) = \frac{100}{n}\left(\sum_{i=1}^{n} |(H^E_{\text{calc}(i)} - H^E_{\text{expt}(i)})/H^E_{\text{expt}(i)}|\right) \quad (6)$$

where n is the number of data points. The correlated results are shown as dash curves in Figures 3 and 4. In general, the modified R−K equation correlates the excess enthalpy data to within an acceptable accuracy.

Literature Cited

(1) Francesconi, R.; Comelli, F. Excess Molar Enthalpies of Binary Mixtures Containing Dimethyl Carbonate or Diethyl Carbonate and one of six Methyl *n*-Alkyl Ketones. Application of an Extended Cell Model. *Thermochim. Acta* **1995**, *264*, 95−104.
(2) Hofman, T.; Casanova, C. Thermodynamics of Alkanol- Alkane Systems, New Modifications of ERAS Model. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1175−1185.
(3) Ott, J. B.; Sipowska, J. T. Applications of Calorimetry to Nonelectrolyte Solutions. *J. Chem. Eng. Data* **1996**, *41*, 987−1004.
(4) Peng, D.-Y.; Horikawa, Y.; Wang, Z.; Benson, G. C.; Lu, B. C.-Y. Excess Enthalpies of 2,2,4-Trimethylpentane + *n*-Alkane Binary Mixtures at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 237−238.
(5) Sastry, N. V.; Patel, S. R.; Prasad, D. H. L. Measurements and Theoretical Analysis of Excess Enthalpies and Excess Volumes of Methyl Methacrylate + *n*-Alkanes (*n*-Pentane, *n*-Hexane, *n*-Heptane, *n*-Decane and n-Dodecane). *Thermochim. Acta* **2000**, *359*, 169−180.
(6) Siddiqi, M. A.; Lucas, K. An Isothermal High-Pressure Flow Calorimeter. The Excess Enthalpy of (Cyclohexane +*n*-Hexane) at Different Pressures at 288.15, 298.15 and 313.15 K. *J. Chem. Thermodyn.* **1982**, *14*, 1183−1190.
(7) Heintz, A.; Lichtenthaler, R. N. An Isothermal Flow Calorimeter for Pressures to 600 bar. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 853−856.
(8) Christensen, J. J.; Izatt, R. M. An Isothermal Flow Calorimeter Designed for High Temperature, High-Pressure Operation. *Thermochim. Acta* **1984**, *73*, 117−129.
(9) Wormald, C. J.; Lewis, K. L.; Mosedale, S. The Excess Enthalpies of Hydrogen + Methane, Hydrogen + Nitrogen, Methane + Nitrogen, Methane + Argon and Nitrogen + Argon at 298 and 301 K at Pressures up to 10.2 MPa. *J. Chem. Thermodyn.* **1977**, *9*, 27−42.

(10) Picker, P. New Concepts in Design and Applications of Flow Microcalorimetry. *Can. Res. Dev.* **1974**, Jan−Feb, 11−16.

(11) Tanaka, R.; D'Acry, P. J.; Benson, G. C. Application of a Flow Microcalorimeter to Determine the Excess Enthalpies of Binary Mixtures of Nonelectrolytes (Cyclohexane +*n*-Hexane) at Different Pressures at 288.15 K. *Thermochim. Acta* **1975**, *11*, 163−175.

(12) Kimura, F.; Benson, G. C.; Halpin, C. J. Excess Enthalpies of Binary Mixtures of *n*-Heptane with Hexane Isomers. *Fluid Phase Equilib.* **1983**, *11*, 245−250.

(13) *TRC Thermodynamic Tables, Non-Hydrocarbons*; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1993.

(14) Grolier, J.-P. E.; Faradjzadeh, A. *International Data Series, Selected Data on Mixtures, Ser. A*, Vol. 1980, No. 2; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1980; p 143.

(15) Grolier, J.-P. E. *International Data Series, Selected Data on Mixtures, Ser. A*, Vol. 1973, No. 2; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1973; p 109.

(16) Aminabhavi, V. A.; Aminabhavi, T. M.; Balundgi, R. H. Evaluation of Excess Parameters from Densities and Viscosities of Binary Mixtures Ethanol with Anisole, *N*,*N*-Dimethylformamide, Carbon Tetrachloride, and Acetophenone from 298.15 to 313.15 K. *Ind. Eng. Chem. Res.* **1990**, *29*, 2106−2111.

(17) Costas, M. *International Data Series, Selected Data on Mixtures, Ser. A*, Vol. 1992, No. 4; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1992; p 244.

(18) Featherstone, J. D. B.; Dickinson, N. A. Excess Enthalpy of *n*-Octane + *n*-Decane at 293.15, 298.15, 308.15 and 313.15 K. *J. Chem. Thermodyn.* **1977**, *9*, 75−77.

(19) Van Ness, H. C.; Abbott, M. M. *International Data Series, Selected Data on Mixtures, Ser. A*, Vol. 1976, No. 1; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1976; pp 9−10.

(20) Grolier, J.-P. E.; Ballet, D.; Viallard, A. Thermodynamics of Ester-Containing Ketones. Excess Enthalpies and Excess Volumes for Alkyl Acetates and Alkyl Benzoates + Alkanes, + Benzene, + Toluene, and Ethylbenzene. *J. Chem. Thermodyn.* **1974**, *6*, 895−908.

(21) Grolier, J.-P. E.; Kiyohara, O.; Benson, G. C. Thermodynamic Properties of Binary Mixtures Containing Ketones. II. Excess Enthalpies of some Aromatic Ketones + *n*-Hexane, + Benzene, and Tetrachloromethane. *J. Chem. Thermodyn.* **1977**, *9*, 697−703.

(22) Christensen, J. J.; Hanks, R. W.; Izatt, R. M. *Handbook of Heats of Mixing*;Wiley-Interscience: New York, 1982; p 86.

(23) Menduina, C.; Diaz Pena, M. *International Data Series, Selected Data on Mixtures, Ser. A*, Vol. 1976, No. 1; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1976; p 55.

(24) Christensen, J. J.; Hanks, R. W.; Izatt, R. M. *Handbook of Heats of Mixing*; Wiley-Interscience: New York, 1982; p 687.

(25) Van Ness, H. C.; Abbott, M. M. *International Data Series, Selected Data on Mixtures, Ser. A*, Vol.1976, No. 1; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1976; p 20.

Received for review July 31, 2001. Accepted March 18, 2002. Financial support from the National Science Council, ROC, through Grant No. NSC89-2214-E011-026 is gratefully acknowledged.

JE0102154