Excess Molar Enthalpies for Binary Mixtures of Ethanol + Acetone, + Octane, + Cyclohexane and 1-Propanol + Acetone, + Octane, + Heptane at 323.15 K

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A flow-type isothermal microcalorimeter was used to measure excess enthalpies, H^E, of the binary mixtures of ethanol + acetone, + octane, + cyclohexane and 1-propanol + acetone, + octane, + heptane at 323.15 K at atmospheric pressure. The experimental results show that the excess enthalpies of these systems are all endothermic over the entire composition range, and their maximum values of H^E are in a range of 946.9 J·mol^{-1} to 1549.4 J·mol^{-1}. The data were correlated with a modified Redlich−Kister equation to within experimental uncertainty, except for 1-propanol + acetone.

Introduction

Enthalpy calculations are required in many engineering applications, such as heat exchanger design and process simulation. The reliability of the calculations needs to be tested by data. In addition, the excess molar enthalpies are fundamental for the understanding of intermolecular interactions between dissimilar molecules and to development of thermodynamic models. Although plentiful excess enthalpy (H^E) data at 298.15 K are available in the literature, the data at other temperatures are rather limited.[1,2] In the present study, a flow-type isothermal microcalorimeter was employed to measure the excess enthalpies at 323.15 K for the binary systems of ethanol + acetone, + octane, + cyclohexane and 1-propanol + acetone, + octane, and + heptane. These H^E data were well correlated with a modified Redlich−Kister equation over the entire composition range.

Experimental Section

Chemicals. 1-Propanol (99+ mass %), acetone (99.5 mass %), octane (99 mass %), cyclohexane (99.5 mass %), and heptane (99+ mass %) were purchased from Arcos (USA). Ethanol (99.5 mass %) was supplied by Shimakyu (Japan). The densities of these chemicals at 298.15 K were measured by an Anton Paar densimeter, DMA 4500, with an accuracy of ±5 × 10^{-5} g·cm^{-3}. The results are consistent with literature values as given in Table 1. All chemicals were used without further purification.

Table 1. Densities of Pure Components at 293.15 K and the Data Sources of H^E Used for Determination of Calibration Constants at 323.15 K

component	ρ/g·cm^{-3} this work	ρ/g·cm^{-3} literature	data sources of H^E used for determination of calibration coefficients
ethanol	0.78929	0.78937[3]	ref 7[a]
1-propanol	0.80363	0.80375[3]	ref 8[b]
acetone	0.79031	0.7905[4]	ref 9[c]
octane	0.70287	0.7022[4]	ref 10[d]
cyclohexane	0.77856	0.77836[5]	ref 8[b]
heptane	0.68391	0.6836[5]	ref 7[a]

[a] Ethanol + heptane at 323.15 K. [b] 1-Propanol + cyclohexane at 323.15 K. [c] Methanol + acetone at 323.15 K. [d] Benzene + octane at 323.15 K.

Apparatus and Procedure. A flow-type isothermal microcalorimeter (model: 4400 IMC, Calorimeter Science Corporation, USA) was used in this study to measure the enthalpy changes of mixing. The schematic diagram and the procedure of the operations have been detailed in elsewhere.[6] The apparatus consists of a flow-mixing cell, a reference cell, a thermostatic water bath, a data acquisition system, and two liquid pumps (model: PU-1580, JASCO, Japan) with an on-line degasser (model: DG-1580−50, JASCO). The degasser was used to remove the trace amount of noncondensable gas from the chemicals continuously, before entering the liquid pumps and then the mixing cell. The temperature of the bath was controlled to within ±0.05 K. The heat of mixing can be measured to within a sensitivity of ±0.1 μW.

The molar ratio of the two mixing-streams was calculated from the molecular weights, densities, and the volumetric flow rates of components 1 and 2. In general, the total flow rates were kept at about 0.4 cm^3 min^{-1}, which is a preferable condition as a result of test runs. However, the total flow rates may vary to as high as 0.8 cm^3 min^{-1} in the region of dilute ethanol or 1-propanol. The accuracy of reported composition of each run was estimated to within ±0.001 in mole fraction.

The excess molar enthalpy was determined from the following equation:

$$H^E = \frac{\epsilon_m(V_m - V_m^\circ)}{\dfrac{f_1\rho_1}{MW_1} + \dfrac{f_2\rho_2}{MW_2}} \tag{1}$$

where f_i, ρ_i, and MW_i are the volumetric flow rate, density, and molecular weight of constituent i, respectively. The variables V_m° and V_m are the voltage of the baseline and the voltage during mixing, respectively, which are indicated from the data acquisition system. As noted by Lien et al.,[6] ϵ_m, the calibration coefficient for mixture runs, is given as

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Table 2. Excess Molar Enthalpies H^E of Binary Mixtures Containing Ethanol at 323.15 K

	H^E		H^E		H^E		H^E
x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}
Ethanol (1) + Acetone (2)							
0.050	255	0.300	1018	0.551	1109	0.800	701
0.102	483	0.352	1085	0.600	1066	0.850	560
0.150	652	0.400	1124	0.650	1005	0.901	392
0.200	805	0.452	1144	0.702	919	0.950	211
0.252	928	0.501	1139	0.752	818		
Ethanol (1) + Octane (2)							
0.028	861	0.252	1484	0.502	1352	0.752	906
0.054	1075	0.304	1492	0.551	1283	0.801	798
0.104	1268	0.352	1486	0.601	1206	0.850	668
0.151	1366	0.404	1454	0.651	1119	0.901	505
0.201	1437	0.452	1412	0.700	1026	0.950	340
Ethanol (1) + Cyclohexane (2)							
0.032	445	0.251	907	0.500	910	0.750	628
0.054	554	0.300	935	0.551	874	0.802	531
0.102	707	0.351	947	0.601	829	0.851	424
0.151	805	0.401	946	0.650	774	0.901	302
0.202	868	0.452	933	0.707	690	0.951	159

Table 3. Excess Molar Enthalpies H^E of Binary Mixtures Containing 1-Propanol at 323.15 K

	H^E		H^E		H^E		H^E
x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}
1-Propanol (1) + Acetone (2)							
0.025	253	0.302	1303	0.601	1483	0.901	705
0.052	405	0.351	1396	0.651	1424	0.952	467
0.101	645	0.401	1462	0.702	1337	0.975	336
0.151	844	0.451	1504	0.752	1235		
0.200	1024	0.501	1518	0.800	1108		
0.252	1180	0.551	1512	0.851	931		
1-Propanol (1) + Octane (2)							
0.027	845	0.254	1536	0.500	1411	0.752	895
0.053	1063	0.301	1550	0.550	1339	0.802	756
0.103	1295	0.352	1537	0.602	1244	0.852	619
0.150	1411	0.401	1520	0.652	1123	0.901	443
0.208	1501	0.452	1470	0.702	1013	0.950	328
1-Propanol (1) + Heptane (2)							
0.010	403	0.203	1127	0.503	1087	0.801	613
0.024	593	0.254	1166	0.551	1035	0.851	517
0.034	675	0.301	1182	0.602	969	0.901	413
0.053	788	0.353	1180	0.651	895	0.951	300
0.103	959	0.402	1159	0.702	814		
0.154	1064	0.451	1130	0.750	729		

$$\epsilon_m = \left(\frac{f_1}{f_1 + f_2}\right)(a_{01} + a_{11}f_1) + \left(\frac{f_2}{f_1 + f_2}\right)(a_{02} + a_{12}f_2) \quad (2)$$

where (a_{01}, a_{11}) and (a_{02}, a_{12}) are the calibration constants for the streams 1 and 2, respectively. Because these calibration constants are dependent on temperature for a specific constituent compound, their values were determined by fitting the voltages of mixing to eq 1 with reliable literature H^E data of related mixtures at the temperature of interest, 323.15 K in this work, prior to measuring a system. Table 1 lists the sources of the literature data used for determination the calibration constants. The uncertainty of the reported H^E is estimated to be better than ±2%.

Results and Discussion

Tables 2 and 3 are the experimental H^E at 323.15 K for the binary systems containing ethanol and 1-propanol, respectively. Figures 1 and 2 illustrate the excess molar enthalpies varying with the mole fraction of the alkanols, indicating that the excess molar enthalpies are all positive (endothermic) over the entire composition range for each binary system. This can be interpreted as the proposition that the physical forces are the dominant interactions between dissimilar molecules. Althoug the excess molar enthalpies vary almost symmetrically with composition for alkanols (1) + acetone (2), asymmetric behavior was exhibited from the mixtures of alkanols (1) + hydrocarbons (2). Among these studied systems, their maximum H^E follow the order of octane (1492 J·mol^{-1} at x_1 = 0.304) > acetone (1144 J·mol^{-1} at x_1 = 0.452) > cyclohexane (947 J·mol^{-1} at x_1 = 0.351) for ethanol-containing systems and octane (1550 J·mol^{-1} at x_1 = 0.301) > acetone (1518 J·mol^{-1} at x_1 = 0.501) > heptane (1182 J·mol^{-1} at x_1 = 0.301) for 1-propanol-containing systems. Comparing with the H^E value at 298.15 K,[11] the excess molar enthalpies increase at higher temperature (323.15 K). The behavior is consistent with the discussions in Ott and Sipowska.[12]

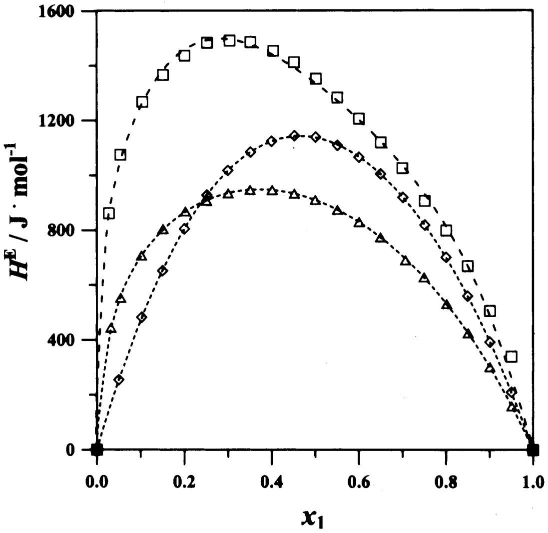

Figure 1. Excess molar enthalpies, H^E, for ethanol + acetone (◇), + octane (□), + cyclohexane (△) at 323.15 K; calculated results (−).

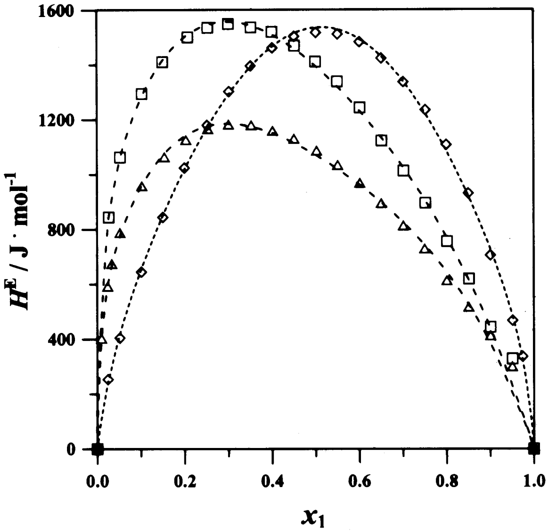

Figure 2. Excess molar enthalpies, H^E, for 1-propanol + acetone (◇), + octane (□), + *n*-heptane (△) at 323.15 K; calculated results (−).

Data Correlation

The Redlich−Kister (R−K) type equation has been used to correlate H^E data. However, it fails to represent accurately systems asymmetric H^E with respect to composi-

Table 4. Correlation Results of H^E Data

mixture[a]	a_0	a_1	a_2	a_3	a_4	k	AAD H^E [b] (%)	σ (H^E)[c] (J·mol^{-1})
M1	4576	−2203	29.7			0.575	0.8	8
M2	5349	−2862	1561.0	−2233		0.988	1.1	17
M3	3651	−2402	406.2			0.935	1.0	8
M4	6075	−4935	695.6	−4178	3980	0.883	1.9	25
M5	5697	−3104	31.1			0.966	1.9	24
M6	4282	−2307	1074	−1702		0.984	1.5	16

[a] M1, ethanol + acetone; M2, ethanol + octane; M3, ethanol + cyclohexane; M4, 1-propanol + acetone; M5, 1-propanol + octane; M6, 1-propanol + heptane. [b] Defined as in eq 4. [c] Defined as in eq 5.

tion, such as the systems of alkanols + hydrocarbons. A modified R−K model,[12] as defined below, was thus employed in the present study to correlate these new H^E data:

$$H^{E} = x_1(1 - x_1)\sum_{i=0}^{m} a_i(1 - 2x_1)^{i}/[1 - k(1 - 2x_1)] \qquad (3)$$

where k is a skewing factor ($-1 < k < 1$). The optimal values of k and a_i's were determined by the least-squares regression with the following objective function:

$$\text{AAD } H^{E}(\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{|H^{E}_{\text{calc,i}} - H^{E}_{\text{expt,i}}|}{H^{E}_{\text{expt,i}}} \qquad (4)$$

where AAD is the average absolute deviation and N is the number of data points. The correlated results are reported in Table 4, where $\sigma(H^E)$ is the root-mean-square deviation, defined as

$$\sigma(H^{E}) = \left[\frac{\sum_{j=1}^{N}(H^{E}_{\text{calc,j}} - H^{E}_{\text{expt,j}})}{N - n}\right]^{0.5} \qquad (5)$$

where n is the number of parameters. The dashed curves in Figures 1 and 2 are the correlated results. The modified R−K equation correlated the H^E data to within experimental uncertainty, an AAD of smaller than 2.0%, for each binary system.

Conculsions

The excess enthalpies were measured for the binary mixtures of ethanol + acetone, + octane, + cyclohexane and 1-propanol + acetone, + octane, and + heptane at 323.15 K at atmospheric pressure. It was found that the mixing process is endothermic for each binary system. The maximum H^E of these six binary systems followed the order of 1-propanol + octane > 1-propanol + acetone > ethanol + octane > ethanol + acetone > 1-propanol + heptane > ethanol + cyclohexane. In general, the experimental H^E data were well represented by the modified R−K equation.

Acknowledgment

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Literature Cited

(1) Löwen, B.; Schulz, S. Excess Molar Enthalpies of Cyclohexane + n-Alcohols at 283.15, 298.15, 323.15, 343.15 and 363.15 K and at a Pressure of 0.4 MPa. *Thermochim. Acta* **1995**, *265*, 63−71.

(2) Lietzmann, A.; Löwen, B.; Schulz, S. Excess Molar Enthalpies of Propanone + Heptane, Propanone + Ethanol, Ethanol + Heptane, and 2-Propanol + Water at 283.15, 298.15, 323.15, 343.15 and 363.15 K. *J. Chem. Eng. Data* **1994**, *39*, 785−788.

(3) *TRC Thermodynamic Tables, Non-Hydrocarbons*; Thermodynamics Research Center, The Texas A & M University System: College Station, TX, 1993; a-5030.

(4) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: NewYork, 1950.

(5) Papanastasiou, G. E.; Ziogas, I. Physical Behavior of Some Reaction Media. Density, Viscosity, Dielectric Constant, and Refractive Index Changes of Ethanol-Cyclohexane Mixtures at Several Temperatures. *J. Chem. Eng. Data* **1991**, *36*, 46−51.

(6) Lien, P. J.; Venkatesu, P.; Lin, H. M.; Lee, M. J. Excess Molar Enthalpies of 1-Octanol with Ethylbenzene, Ethyl Benzoate, Acetophenone, Anisole or Methanol at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 768−771.

(7) Shates, J. P., Jr.; Abbott, M. M.; Van Ness, H. C. Excess Thermodynamic Functions for Ternary Systems II. Chloroform-Ethanol-*n*-Heptane at 50 °C. *J. Chem. Eng. Data* **1975**, *20*, 406−409.

(8) Veselý, F.; Uchytil, P.; Zábransk×c6, M.; Pick, J. Heat of Mixing of Cyclohexane with 1-Propanol and 2-Propanol. *Collect. Czech. Chem. Commun.* **1979**, *44*, 2869−2881.

(9) Christensen, J. J.; Hanks, R. W.; Izatt, R. M. *Handbook of Heats of Mixing*; Wiley-InterScience Publication: New York, 1982; p 1024.

(10) Diaz Peña, M.; Menduiña, C. Excess Enthalpies at 323.15K of Binary Mixtures of Benzene with *n*-Alkanes. *J. Chem. Thermodyn.* **1974**, *6*, 1097−1102.

(11) Nagata, I.; Yamada, T. Correlation and Prediction of Excess Thermodynamic Functions of Strongly Nonideal Liquid Mixtures. *Ind. Eng. Chem. Process Des. Dev.* **1974**, *13*, 47−53.

(12) Ott, J. B.; Sipowska, J. T. Applications of Calorimetry to Nonelectrolyte Solution. *J. Chem. Eng. Data* **1996**, *41*, 987−1004.

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