ments is adequate in regions common to both data sets. The new data present a more thorough analysis of the near-critical region; within 10% of the critical pressure, the data follow asymptotic forms of the scaling relations (eq 2 and 3).

Acknowledgment

Glossary

A_1, A_2	parameters in eq 5 and 6
P	pressure
P_c	critical pressure
x	liquid-phase mole fraction
y	vapor-phase mole fraction
β, ν	scaling-law parameters (critical indices)
γ	interfacial tension
ϵ_γ	uncertainty in measured interfacial tension
ρ^L	liquid-phase density
ρ^V	vapor-phase density
$\Delta\rho$	liquid-phase density minus vapor-phase density

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Enthalpies of Mixing of Tetrahydrofuran + γ-Butyrolactone and Water + γ-Butyrolactone Systems at 299.15 K

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Enthalpies of mixing have been reported for the systems tetrahydrofuran (THF) + γ-butyrolactone and water + γ-butyrolactone at 299.15 K and 1.013 bar. Data have been fitted to the Redlich–Kister type equation.

Introduction

Enthalpies of mixing ΔH^m are necessary for the treatment of isobaric vapor–liquid equilibrium data as well as in distillation column design calculations. In our present thermodynamic studies of tetrahydrofuran (THF) + water + γ-butyrolactone system, ΔH^m data are available only for the tetrahydrofuran (THF) + water system (1–3). Hence, it was decided to measure ΔH^m data for the binary mixtures (i) THF + γ-butyrolactone and (ii) water + γ-butyrolactone.

Experimental Section

Materials. Tetrahydrofuran (THF), supplied by Sarabhai Chemicals, India, was found to be 99.68 mol % pure by GC on a column packed with Carbowax 20M using thermal conductivity detector.

Double distilled deionized water with 2 μmho cm⁻¹ electrical conductivity was used for the measurements.

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Table I. Enthalpies of Mixing, ΔH^m, of the THF + Water System at 299.15 K

	ΔH^m/J mol⁻¹		
	at 299.15 K,	at 298.15 K	
x_{THF}	present values[a]	ref 1[b]	ref 2[c]
0.0476	−504	−534[d]	−527[e]
0.1572	−743	−730	−740
0.2572	−625	−650	−657
0.5123	−215	−200	−213

[a] ±14 J mol⁻¹. [b] ±4 to ±8 J mol⁻¹. [c] ±8 J mol⁻¹. [d] At x_{THF} = 0.049. [e] At x_{THF} = 0.05.

Table II. Enthalpies of Mixing ΔH^m of the Two Binaries at 299.15 K

x	ΔH^m/J mol⁻¹	x	ΔH^m/J mol⁻¹
x(Water) + (1 − x)(γ-Butyrolactone)		x(THF) + (1 − x)(γ-Butyrolactone)	
0.1237	237	0.0957	48
0.1971	619	0.1977	91
0.3909	915	0.2944	138
0.4934	774	0.3926	203
0.7163	96	0.4891	197
0.8524	14	0.5953	113
0.8932	5	0.6953	98
0.9645	−23	0.9084	46
0.9703	−26		

Fluka AG Switzerland make γ-butyrolactone of 99.02 mol % purity, as determined chromatographically on a column packed with 12% EGS (ethylene glycol succinate) on Anakrom using thermal conductivity detector, was used.

Table III. Values of the Adjustable Parameters of Eq 1 and Standard Deviation $\sigma(\Delta H^m)$

system	C_0	C_1	C_2	C_3	C_4	$\sigma(\Delta H^m)/$ J mol^{-1}
x(THF) + $(1 - x)\cdot$ (γ-butyrolactone)	740.9	−542.8	−1495.0	827.9	1823.1	14
x(water) + $(1 - x)\cdot$ (γ-butyrolactone)	2741.5	−5962.7	790.3	7960.7	−6674.8	33

Calorimetry. Enthalpies of mixing were measured at 299.15 K and 1.013 bar with a Tian Calvet conduction calorimeter constructed by Deshpande and Prabhu (4), and has been described in detail elsewhere (5, 6).

Results

Enthalpies of mixing were measured for the system THF + water in our calorimeter at 299.15 K in order to check the performance of the calorimeter. The data are reported in Table I together with the literature values. If the temperature effect is neglected, the agreement between our values and those of ref 1 and 2 is satisfactory. The uncertainty in our values is estimated to be ±14 J mol^{-1}.

The experimental enthalpies of mixing for the two binaries, water + γ-butyrolactone and THF + γ-butyrolactone, at 299.15 K are given in Table II and are graphically represented in Figure 1. The dependence of ΔH^m on composition was represented by the Redlich–Kister type equation of the form:

$$\Delta H^m (\text{J mol}^{-1}) = x(1 - x)[C_0 + C_1(2x - 1) + C_2(2x - 1)^2 + C_3(2x - 1)^3 + C_4(2x - 1)^4] \quad (1)$$

The adjustable parameters $C_0 - C_4$ were computed by the least-squares regression analysis and are given in Table III along with the standard deviation $\sigma(\Delta H^m)$. The values of $\sigma(\Delta H^m)$ were obtained by using eq 2.

$$\sigma(\Delta H^m) = \left[\frac{\sum(\Delta H^m_{calcd} - \Delta H^m_{exptl})^2}{n - 1} \right]^{1/2} \quad (2)$$

where n is the number of experimental data points.

Discussion

The enthalpy of mixing for water + γ-butyrolactone is comparatively higher than for the THF + γ-butyrolactone and THF + water systems at equimolar concentrations.

For the THF + γ-butyrolactone system, the fitting of the experimental data to the Redlich–Kister type equation was satisfactory. For the water + γ-butyrolactone system, the standard deviation is 31 J mol^{-1}, which is twice the experimental uncertainty. We have also fitted the data of Nakayama et al. (1) for THF + water system to eq 1. Their data also showed a standard deviation of 32 J mol^{-1} which indicates that for the
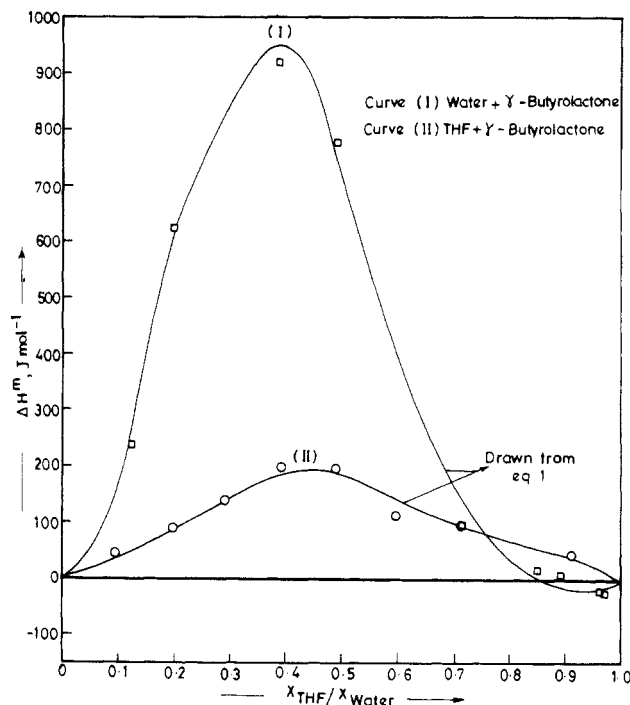

Figure 1. Enthalpies of mixing of the water + γ-butyrolactone and THF + γ-butyrolactone systems at 299.15 K.

THF + water and water + γ-butyrolactone systems which are polar in nature, the Redlich–Kister type of equation does not represent the data well. However, it is reported here for interpolation purposes for engineering applications.

For the water + γ-butyrolactone system, the negative enthalpy of mixing at lower concentrations of γ-butyrolactone may be due to the enhancement of water–water hydrogen bonding ("iceberg" effect), which is due to the structural influence of γ-butyrolactone on water. This type of behavior in ΔH^m is in agreement with the characteristic behavior of V^E, and excess adiabatic compressibilities for this system, measured by Werblan and Lesinski (7). Similar observation for aqueous alcohol systems has also been reported by Franks (8).

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