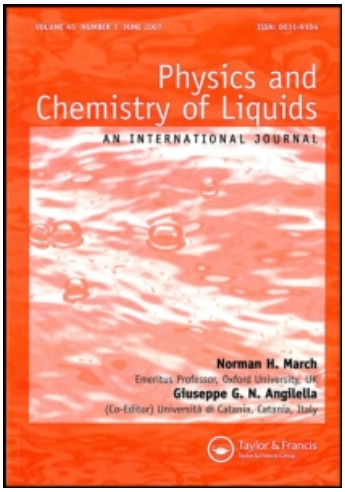

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Excess Enthalpies of Binary Solvent Mixtures of γ-Butyrolactone with Hexan-1-ol, Heptan-1-ol, Octan-1-ol and Decan-1-ol

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To cite this Article Rambabu, K. , Raman, G. K. and Ramakrishna, M.(1990) 'Excess Enthalpies of Binary Solvent Mixtures of γ-Butyrolactone with Hexan-1-ol, Heptan-1-ol, Octan-1-ol and Decan-1-ol', Physics and Chemistry of Liquids, 22: 1, 61 — 64
To link to this Article: DOI: 10.1080/00319109008036411
URL: http://dx.doi.org/10.1080/00319109008036411

Phys. Chem. Liq., 1990, Vol. 22, pp. 61–64
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EXCESS ENTHALPIES OF BINARY SOLVENT MIXTURES OF γ-BUTYROLACTONE WITH HEXAN-1-OL, HEPTAN-1-OL, OCTAN-1-OL AND DECAN-1-OL

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(Received 14 December 1989)

The excess enthalpies of four alcohols with γ-butyrolactone were determined at 25°C, by a Parr 1451 solution Calorimeter. All the four systems showed endothermic behaviour. The results are explained on the basis of a steric effect on interaction. Enthalpies of mixing of binary mixtures do provide valuable insight into molecular interactions.

KEY WORDS: Calorimetry, Lactone-alcohol complexes, Steric effect.

INTRODUCTION

In the chemical industry there exists a continuing need for reliable thermodynamic data of binary systems. This is particularly true for systems involved in industrial processes. A survey of the literature reveals that γ-butyrolactone is used in separation processes, yet there have been relatively few measurements on binary mixtures containing γ-butyrolactone. For this reason, we have determined the excess enthalpies (H^E) of γ-butyro lactone + hexan-1-ol, heptan-1-ol, octan-1-ol and decan-1-ol at 298.15 K.

EXPERIMENTAL SECTION

The excess enthalpies were determined by a Parr 1451 solution Calorimeter. The Calorimeter and the experimentation were standardised by measuring excess enthalpies of a standard systems cyclohexane + *n*-hexane, throughout the concentration range at 298.15 K. The results were in agreement with those obtained by the standard equation.[1]

All the chemicals were purified by the methods described by Riddick and Bunger.[2] Hexan-1-ol (BDH), heptan-1-ol (Koch- light), octan-1-ol (Aldrich Gold Label) and decan-1-ol (Aldrich Gold label) were dried by refluxing with fused Calcium oxide and fractionally distilled. γ-Butyro lactone (Fluka AG, puriess) was used without further purification and kept over freshly activated molecular sieve type 4A (Union Carbide). The purity of the samples was checked by comparing the measured densities and boiling points with those reported in the literature.[3]

RESULTS AND DISCUSSION

The excess enthalpies of γ-butyro lactone with hexan-1-ol, heptan-1-ol, octan-1-ol and decan-1-ol at 25°C have been given in Table 1. The data are fitted by means of

Table 1 Excess enthalpies of γ-butyro lactone-alcohols systems at 25°C.

X_1 *Mole fraction of γ-butyro lactone*	H^E / $J\,mol^{-1}$	X_1 *mole fraction of γ-butyro-lactone*	H^E / $J\,mol^{-1}$
γ-butyrolactone + hexan-1-ol.			
0.1156	1061.3	0.6995	1884.3
0.2275	1674.6	0.7413	1755.0
0.3155	1954.0	0.7896	1565.5
0.4019	2102.5	0.8439	1289.5
0.4698	2148.0	0.8907	987.6
0.5241	2145.5	0.9419	579.0
γ-butyro lactone + heptan-1-ol.			
0.1524	1238.6	0.7258	1964.1
0.2715	1806.7	0.7662	1811.2
0.3631	2078.7	0.8102	1602.5
0.4474	2217.4	0.8586	1310.6
0.5217	2256.9	0.9013	993.9
0.5658	2250.5	0.9483	569.2
γ-butyro lactone + octan-1-ol.			
0.1743	1529.7	0.7497	1982.5
0.2987	2067.9	0.7869	1821.0
0.3922	2281.9	0.8281	1599.5
0.4771	2370.3	0.8728	1296.0
0.5432	2376.5	0.9117	978.2
0.5943	2343.9	0.9538	557.9
γ-butyro lactone + decan-1-ol.			
0.2065	1749.3	0.8043	1862.5
0.3445	2168.3	0.8321	1712.0
0.4420	2300.5	0.8597	1532.5
0.5151	2344.8	0.8920	1282.5
0.5722	2346.5	0.9254	960.2
0.6186	2324.2	0.9610	548.5

Table 2 Coefficients and percentage of standard deviation $\%\sigma(H^E)$ for least squares representation of H^E.

System	a_0	a_1	a_2	$\%\sigma(H^E)$
γ-butyro lactone hexan-1-ol.	8603.925	−189.512	2758.965	0.1
γ-butyro lactone + heptan-1-ol.	9022.757	804.753	2327.007	0.1
γ-butyro lactone + octan-1-ol.	9516.189	476.305	3288.694	0.1
γ-butyro lactone +	9354.266	855.784	5295.574	0.1

the least squares method to the Redlich–Kister equation.

$$H = X_1X_2[a_0 + a_1(X_1 - X_2) + a_2(X_1 - X_2)^2] \quad (1)$$

The parameters (a_0, a_1 and a_2) of the equation along with the percentage of standard deviations $\%\sigma(H^E)$ for these systems are given in Table 2. $\%\sigma(H^E)$ is calculated using the equation

$$\%\sigma(H^E) = \left[\sum\left(\frac{H^E_{obs} - H^E_{Cal}}{H^E_{obs}} \times 100\right)^2 \Big/ (n^{-m}_{obs})\right]^{1/2}$$

The enthalpies of mixing as a function of the mole fraction of lactone (X_1) have been represented in Figure 1.

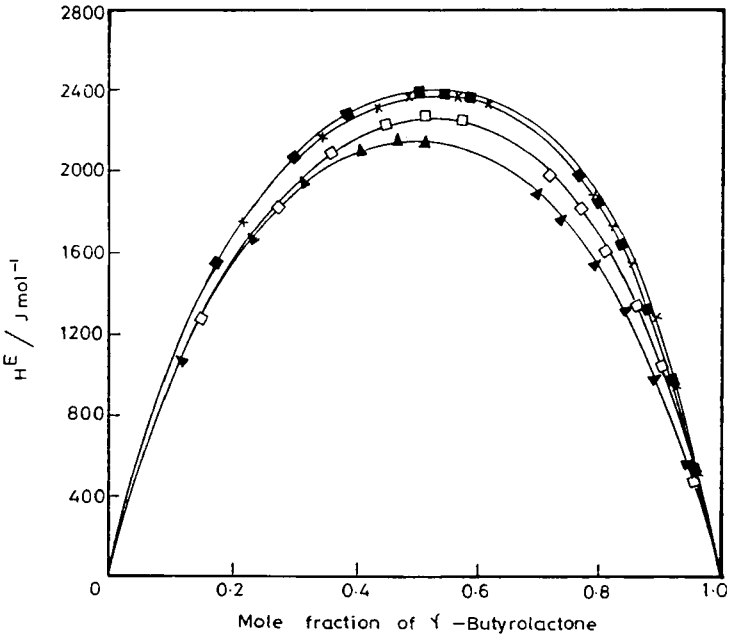

Figure 1 Excess enthalpies (H^E) for γ-butyrolactone + hexan-1-ol (▲), + heptan-1-ol (□), + octan-1-ol (■) and + decan-1-ol (×) at 298.15 K.

All the four systems show endothermic behaviour. It has been established that the lactone and alcohol pair acts as a electron acceptor and—donor pair and a hydrogen bond is formed between the hydroxyl H and ethenal O. The observed enthalpy of mixing is therefore the net effect of two opposite heat effects, viz., an endothermic effect due to the dissociation of self-associated alcohol polymers by lactone molecules, and an exothermic due to hydrogen bond formation between lactone and alcohol molecules. The enthalpy of hydrogen bonding of self-associated alcohol molecular is greater than that between alcohol and lactone molecules. The enthalpies of mixing for these systems are therefore positive inspite of the formation of hydrogen-bonded complexes in the solution. Due to the electron acceptor ability of the γ-butyrolactone, a weak charge-transfer complex would be formed.

Recent vapour pressure measurements by Grant *et al.*[4] on γ-butyrolactone + iso octane mixtures do suggest very weak specific interactions between γ-butyro lactone molecules. Although the vapor pressure data could be described by a monomer/pentamer association model, the authors cautioned that their results did not definitely prove the existence of pentameric species in solution. As in all cases, the presence of molecular complexes should be supported by independent measurements involving spectroscopy, calorimetry etc.,

The high endothermic enthalpy of mixing may be attributed to the breaking of hydrogen bonds and the enthalpy of hydrogen bonds breaking (in the low concentration range) is in the order

$$\text{hexan-1-ol} > \text{heptan-1-ol} > \text{decan-1-ol} > \text{octan-1-ol}.$$

The above order is due to the steric hindrance of the alcohol.

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