254 J. Chem. Eng. Data **2002,** *47,* 254−257

Molar Excess Enthalpies of Binary Liquid Mixtures of γ-Valerolactone or δ-Valerolactone + Benzene, + Toluene, or + Ethylbenzene at 293.15 K and Atmospheric Pressure

B. S. Bjola,[†] M. A. Siddiqi,[‡] and P. Svejda*

Institut für Thermo- und Fluiddynamik, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Molar excess enthalpies of binary liquid mixtures of γ-valerolactone or δ-valerolactone + benzene, + toluene, or + ethylbenzene were measured by means of a flow microcalorimeter of Picker type at 293.15 K and atmospheric pressure.

Introduction

Recent measurements[1] of the excess enthalpies of binary systems of γ-butyrolactone + an aromatic solvent at 293.15 K and atmospheric pressure showed very interesting results: The mixture of γ-butyrolactone + benzene behaved almost athermally, and its H^E versus mole fraction curve exhibited a pronounced M shape, while the lactone systems with toluene or with ethylbenzene showed normal endothermal excess enthalpies and slightly asymmetrical curves. A strong dipole−induced dipole interaction between the polar lactone molecule and the polarizable benzene ring was offered as an explanation for the uncommon behavior of the mixture with benzene.[1]

To follow up the suggested relationship between the molecular structure of the lactone and the peculiar H^E curves of the mixtures, the molar excess enthalpies of binary liquid mixtures of the two related lactones, γ-valerolactone or δ-valerolactone, + benzene, + toluene, or + ethylbenzene, were measured at 293.15 K and atmospheric pressure, and the results are presented here.

Like γ-butyrolactone, γ-valerolactone also contains a five-membered ring but with an additional methyl group attached (Figure 1), which keeps the molecules further apart in the pure liquid and in mixtures. δ-Valerolactone is an isomer of γ-valerolactone but with a six-membered ring, which exhibits less strain.

Experimental Section

γ-Valerolactone (5-methyloxolan-2-one, $C_5H_8O_2$; Fluka A.G., Buchs, Switzerland), δ-valerolactone (oxan-2-one, $C_5H_8O_2$; Lancaster Synthesis, Newgate, England), benzene (J. T. Baker Chemicals B.V., Deventer, The Netherlands), toluene (J. T. Baker Chemicals B.V., Deventer, The Netherlands), ethylbenzene (Fluka A.G., Buchs, Switzerland), and carbon tetrachloride (J. T. Baker Chemicals B.V., Deventer, The Netherlands) with stated purities of better than (99, 99, 99.5, 99, and 99) mol %, respectively, were stored over a molecular sieve (0.4 nm, J. T. Baker Chemicals B.V., Deventer, The Netherlands). The purity of the chemicals was checked also by gas chromatography and was found to be in very good agreement with the original specification, as described in a previous work.[2] The drying by zeolites, degassing prior to use, molecular mass, and density were the same as those given in recently published papers.[1,2]

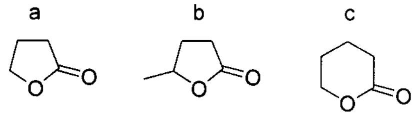

Figure 1. Chemical structure of the lactones (a) γ-butyrolactone, (b) γ-valerolactone, and (c) δ-valerolactone.

The molar excess enthalpies H^E were measured with a dynamic flow calorimeter of Picker type (Setaram, France) at 293.15 K and at atmospheric pressure as described in detail elsewhere.[3] The composition of each mixture was determined by its density,[1] which was measured in a thermostatically controlled flow densimeter (DMA 602, Chempro Paar, Germany) connected in series immediately behind the calorimeter. With the help of the densities and of the previously measured excess volumes of these systems,[4,5] the mole fraction of the mixture could be calculated to an estimated uncertainty of ±0.0001. The calorimeter was thermostated to ±0.03 K or better and controlled by calibrated Pt-100 thermoresistors. It was checked routinely by measurements on the system benzene + cyclohexane, and the agreement with these literature data[6] was found to be within less than 1% over the central range of the concentration. The reproducibility of the H^E data, even at low concentration ranges, appeared to be better by about 1 order of magnitude, as can be noticed in the figures. All points were taken at several different days and still show only little scatter about the fitting curve.

Results

The experimental values of the molar excess enthalpies H^E are summarized in Table 1 at various mole fractions x_i of the mixtures and have been fitted to “square-root”-type polynomials:[7]

$$H^E_{calc}/\mathrm{J \cdot mol^{-1}} = x_1 x_2 \sum_{i=0}^{k} A_i x_1^{\,i/2} \qquad (1)$$

---

* Corresponding author. Fax: +49-234 32 14280. E-mail: peter.svejda@ruhr-uni-bochum.de.

[†] Permanent address: Department Applied Physical Chemistry, Politehnica University of Bucharest, Str. Polizu nr. 1, Ro-78126 Bucharest, Romania.

[‡] Fakultät Ingenieurwissenschaften, Thermodynamik, Gerhard Mercator Universität Duisburg, Lotharstrasse 1, D-47057 Duisburg, Germany.

10.1021/je010244e CCC: $22.00

Table 1. Molar Excess Enthalpies H^E of Binary Liquid Mixtures of γ-Valerolactone or δ-Valerolactone + Benzene, + Toluene, or + Ethylbenzene at 293.15 K and Atmospheric Pressure

x_1	H^E/ J·mol^{-1}	x_1	H^E/ J·mol^{-1}	x_1	H^E/ J·mol^{-1}	x_1	H^E/ J·mol^{-1}
γ-Valerolactone (1) + Benzene (2)							
0.0047	5.7	0.1568	−13.1	0.4531	−65.0	0.7729	−30.3
0.0076	7.3	0.1982	−29.6	0.4848	−63.8	0.8036	−23.7
0.0135	11.2	0.2299	−37.2	0.5279	−62.1	0.8362	−18.1
0.0249	15.7	0.2579	−45.5	0.5536	−59.4	0.8628	−14.6
0.0415	16.6	0.2866	−51.0	0.5972	−55.2	0.8943	−10.0
0.0583	16.6	0.3339	−59.3	0.6217	−52.1	0.9349	−5.5
0.0815	11.6	0.3550	−61.0	0.6729	−45.2	0.9671	−2.5
0.1122	2.7	0.3889	−63.8	0.7019	−40.1	0.9832	−1.2
0.1399	−6.9	0.4183	−64.7	0.7348	−36.0		
γ-Valerolactone (1) + Toluene (2)							
0.0102	16.3	0.1041	90.5	0.3845	100.7	0.6917	65.8
0.0145	24.6	0.1279	97.3	0.4132	98.2	0.7288	59.1
0.0216	34.7	0.1736	104.1	0.4437	96.0	0.7830	51.2
0.0310	44.7	0.1982	105.9	0.4823	91.6	0.8266	41.5
0.0383	51.6	0.2408	107.6	0.5141	89.0	0.8731	33.0
0.0568	66.1	0.2697	107.3	0.5381	86.3	0.9120	24.1
0.0655	72.3	0.3158	105.9	0.6003	78.1	0.9686	8.9
0.0838	82.3	0.3441	104.5	0.6395	73.1		
γ-Valerolactone (1) + Ethylbenzene (2)							
0.0054	11.7	0.2661	241.0	0.5682	260.3	0.8464	137.5
0.0260	54.1	0.2977	251.7	0.5951	252.3	0.8651	124.9
0.0385	73.4	0.3341	258.1	0.6324	244.2	0.8997	97.4
0.0619	106.2	0.3739	266.4	0.6599	233.7	0.9224	78.1
0.0832	129.4	0.4060	266.9	0.6915	224.3	0.9495	52.7
0.1026	146.9	0.4449	271.1	0.7176	211.7	0.9797	21.9
0.1496	185.4	0.4685	268.2	0.7505	196.8		
0.1850	204.9	0.5078	268.3	0.7928	172.9		
0.2215	224.6	0.5358	263.4	0.8142	160.3		
δ-Valerolactone (1) + Benzene (2)							
0.0021	1.1	0.0867	−34.7	0.3958	−162.5	0.7641	−89.0
0.0064	2.6	0.1213	−58.7	0.4367	−163.1	0.8207	−67.8
0.0113	3.5	0.1510	−77.7	0.4699	−162.8	0.8628	−51.6
0.0125	3.5	0.1828	−98.9	0.5040	−159.7	0.9177	−30.1
0.0220	2.4	0.2149	−114.4	0.5686	−149.5	0.9523	−17.2
0.0286	−0.1	0.2436	−129.0	0.6357	−132.2	0.9825	−6.1
0.0370	−2.8	0.2913	−144.8	0.6704	−121.2	0.9903	−3.4
0.0621	−18.3	0.3442	−157.7	0.7215	−103.9		
δ-Valerolactone (1) + Toluene (2)							
0.0068	12.1	0.0698	67.0	0.3220	91.4	0.6907	59.5
0.0118	19.3	0.0879	75.6	0.3524	89.3	0.7360	52.4
0.0182	29.1	0.1045	79.8	0.4029	86.2	0.7926	44.5
0.0205	30.7	0.1417	86.1	0.4502	83.0	0.8551	34.9
0.0274	39.0	0.1751	90.7	0.4945	79.4	0.8839	29.1
0.0360	46.5	0.2131	92.2	0.5428	75.2	0.9165	21.2
0.0400	50.4	0.2490	92.6	0.5871	71.6	0.9445	15.4
0.0501	56.8	0.2759	92.3	0.6392	65.3	0.9741	7.3
δ-Valerolactone (1) + Ethylbenzene (2)							
0.0147	32.8	0.2152	222.1	0.5550	268.6	0.8620	135.6
0.0250	52.3	0.2735	247.2	0.5992	262.6	0.9003	102.4
0.0461	86.9	0.3111	259.2	0.6448	249.0	0.9383	65.7
0.0792	124.8	0.3683	271.4	0.6907	236.2	0.9751	27.0
0.1160	160.3	0.4169	276.2	0.7316	217.5		
0.1586	189.0	0.4521	277.4	0.7764	195.4		
0.1940	210.6	0.5071	275.7	0.8138	171.4		

Table 2. Coefficients A_i and Standard (σ) and Maximum (δ) Deviations (Eqs 1−3) for the Experimental Excess Enthalpies at 293.15 K and Atmospheric Pressure

A_0	A_1	A_2	A_3	A_4	σ/ J·mol^{-1}	δ/ J·mol^{-1}
γ-Valerolactone (1) + Benzene (2)						
1746.2	−8829.9	13727.3	−9122.4	2412.5	0.8	1.9
γ-Valerolactone (1) + Toluene (2)						
2394.4	−6212.4	6198.0	−2095.4	-	0.7	2.1
γ-Valerolactone (1) + Ethylbenzene (2)						
2797.8	−5017.2	4432,0	−1117.3	-	1.0	1.8
δ-Valerolactone (1) + Benzene (2)						
1162.5	−9263.9	16204.1	−11990.3	3541.5	0.6	1.2
δ-Valerolactone (1) + Toluene (2)						
2552.2	−8506,0	12774.8	−9439.9	2913.7	0.6	1.3
δ-Valerolactone (1) + Ethylbenzene (2)						
2829.9	−5228.6	4846.4	−1272.6	-	1.6	2.6

The coefficients A_i are summarized in Table 2 together with the standard deviation σ, defined as

$$\sigma^2 = \sum_N [H^E - H^E_{calc}]^2/(N - m) \tag{2}$$

where N is the number of data points and m is the number of coefficients A_i, and the maximum deviation δ is

$$\delta = \max |H^E - H^E_{calc}| \tag{3}$$

As may be observed from Table 2, the experimental results (even of the S-shaped curves) could be fitted quite well using the square-root polynomials. A Redlich−Kister fit of the same quality would have required between two and four additional parameters for each of the investigated systems.

Discussion

The molar excess enthalpies of the investigated binary systems represented in Figure 2 show significant differences in shape and range. Again the mixtures containing benzene exhibit the most interesting results: Whereas the system γ-butyrolactone + benzene showed an almost symmetrical M-shaped H^E versus x curve at 293.15 K,[1] in the present work the curve for γ-valerolactone has a clear S shape, with a small endothermal part at *low* lactone concentrations (Figure 2a). This endothermal part with a maximum of about 17 J·mol^{-1} is well reproducible, as has been checked carefully. Additionally, an inflection in the H^E curve is left at *high* mole fractions of γ-valerolactone, where the system γ-butyrolactone + benzene showed endothermal behavior before.[1]

For the mixture of δ-valerolactone + benzene, the H^E versus x_1 curve is exothermal and parabolic in shape (Figure 2b), except for a small, reproducible endothermal part with a maximum of ≃4 J·mol^{-1} at very low lactone concentrations ($x_1 < 0.03$). This gives an S-shaped curve to this system too. There are only a few other examples in the literature concerning H^E curves of M or S shape for binary mixtures of aromatics + polar components.[8,9]

As discussed previously,[1] the exothermal effect in the binary mixtures of the three lactones + benzene depends strongly on steric factors, because their dipole moments are almost equal.[2] The shape and size of the molecules appear most favorable for attractive interactions between benzene and lactone molecules. Thus, even stronger exothermal effects were observed in the present work for the binary mixtures of benzene + γ-valerolactone or + δ-valerolactone than for the mixture with γ-butyrolactone,[1] with minimum values of about −65 and −165 J·mol^{-1}, respectively.

The molar excess enthalpies are positive for the other four investigated systems (Figure 2a,b), suggesting that the heteromolecular interactions are weaker, mainly because of steric factors, and only an endothermal effect is observed. However, the influence of the attractive forces is still evident in the mixtures containing toluene. The measured H^E curves of these systems are asymmetric, with maxima of about +100 J·mol^{-1} displaced toward the low mole fraction of lactone (about 0.25) but with an almost straight

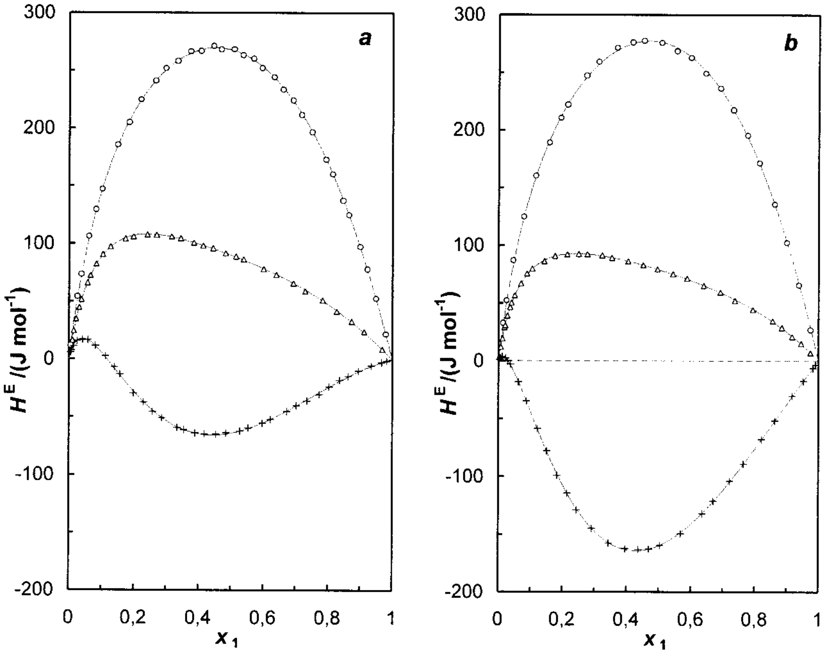

Figure 2. Molar excess enthalpy H^E versus mole fraction x_1 of the binary liquid mixtures of (a) γ-valerolactone (1) (+) + benzene (2), (△) + toluene (2), or (○) + ethylbenzene (2) and of (b) δ-valerolactone (1) (+) + benzene (2), (△) + toluene (2), or (○) + ethylbenzene (2) at 293.15 K and atmospheric pressure.

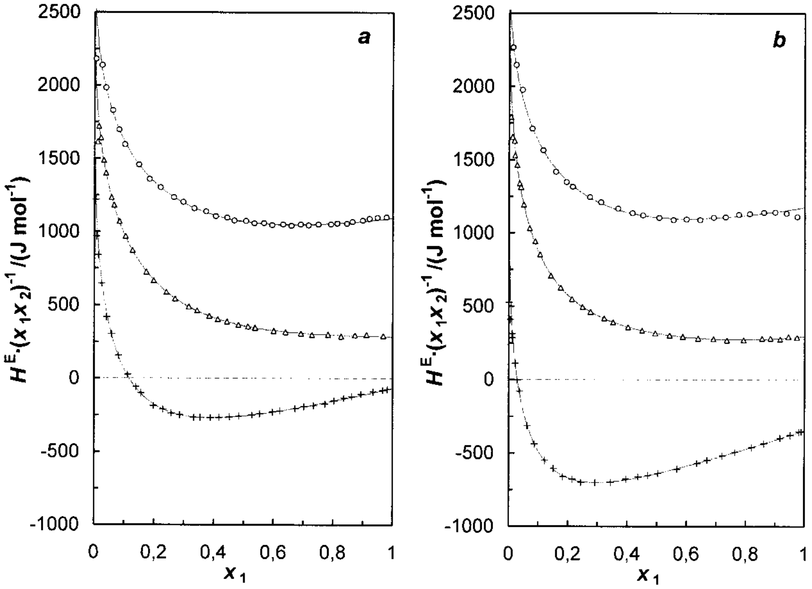

Figure 3. Reduced molar excess enthalpy (H^E/x_1x_2) versus mole fraction x_1 of the binary liquid mixtures of (a) γ-valerolactone (1) (+) + benzene (2), (△) + toluene (2), or (○) + ethylbenzene (2), and of (b) δ-valerolactone (1) (+) + benzene (2), (△) + toluene (2), or (○) + ethylbenzene (2) at 293.15 K and atmospheric pressure.

part of the H^E curve at $x_1 \simeq 0.75$. Perhaps there is a weak exothermal effect superimposed.

Only the systems of γ-valerolactone or δ-valerolactone + ethylbenzene exhibit nearly symmetrical H^E curves and much higher endothermal effects (up to 280 J·mol^{-1}).

Plots of the reduced molar excess enthalpy H^E/x_1x_2 versus x_1 (Figure 3), which are sensitive to the structure of the liquid mixtures,[10] show quite a well-defined minimum at a mole fraction x_1 of about 0.3 for both binary mixtures containing benzene. The minima of the systems with toluene and ethylbenzene are less pronounced and shifted toward higher x_1 values. A very similar behavior was observed also for the binary mixtures of these three aromatics with γ-butyrolactone.[1]

Literature Cited

(1) Bjola, B. S.; Siddiqi, M. A.; Svejda, P. Excess Enthalpies of Binary Liquid Mixtures of γ-Butyrolactone + Benzene, + Toluene, + Ethylbenzene, and + Carbon Tetrachloride, and Excess Volume of the γ-Butyrolactone + Carbon Tetrachloride Liquid Mixture. *J. Chem. Eng. Data* **2001**, *46*, 1167−1171.

(2) Fornefeld-Schwarz, U. M.; Svejda, P. Refractive Indices and Relative Permittivities of Liquid Mixtures of γ-Butyrolactone, γ-Valerolactone, δ-Valerolactone, or ε-Caprolactone + Benzene, + Toluene, or + Ethylbenzene at 293.15 K and 313.15 K and Atmospheric Pressure. *J. Chem. Eng. Data* **1999**, *44*, 597−604.

(3) Hahn, G.; Svejda, P.; Kehiaian, H. V. Excess Enthalpies of the Liquid Systems: 1,2-Dichloroethane + *n*-Alkanes or + 2,2,4-Trimethylpentane. *Fluid Phase Equilib.* **1986**, *28*, 309−323.

(4) Klein, A.; Svejda, P. Isothermal Vapor−Liquid Equilibria and Excess Volumes of Binary Mixtures of Benzene + γ-Butyrolactone, γ-Valerolactone, δ-Valerolactone, or ε-Caprolactone at 293.15 K and 313.15 K. *ELDATA Int. Electron. J. Phys. Chem. Data* **1995**, *1*, 87−94.

(5) Fornefeld-Schwarz, U.; Svejda, P. Excess Volumes of Liquid Mixtures of γ-Butyrolactone (Oxalan-2-one), γ-Valerolactone (5-Methyloxalan-2-one), δ-Valerolactone (Oxan-2-one), or ϵ-Caprolactone (Oxepan-2-one) + Toluene or + Ethylbenzene at 293.15 K and 313.15 K. *ELDATA Int. Electron. J. Phys. Chem. Data* **1997**, *3*, 17−24.
(6) Elliot, K.; Wormald, C. J. A Precision Differential Flow Calorimeter. The Excess Enthalpy of Benzene + Cyclohexane Between 280.15 K and 393.15 K. *J. Chem. Thermodyn.* **1976**, *8*, 881−893.
(7) Jones, D. E. G.; Weeks, I. A.; Anand, S. C.; Wetmore, R. W.; Benson, G. C. Thermodynamic Properties of Some Cycloalkane−Cycloalkanol Systems at 25 °C. *J. Chem. Eng. Data* **1972**, *17*, 501−506.
(8) Wilhelm, E.; Egger, W.; Vencour, M.; Roux, A. H.; Polednicek, M.; Grolier, J.-P. E. Thermodynamics of Liquid Mixtures Consisting of a Very Polar and a Non-Polar Aromatic: (Benzonitrile + Benzene, or Toluene). *J. Chem. Thermodyn.* **1998**, *30*, 1509−1532 and references cited therein.
(9) Letcher, T. M.; Deenadayalu, N. Excess Molar Enthalpies and Excess Molar Volumes of (1,3-Dimethyl-2-Imidazolidinone + an Aromatic Hydrocarbon) at T = 289.15 K. *J. Chem. Thermodyn.* **2001**, *33*, 441−450.
(10) Munn, R. J.; Svejda, P. Excess Enthalpy of Mixing of Propionic Acid + Triethylamine by Flow-Calorimetric Determination of Difference Enthalpies of Mixing. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 920−925.

Received for review September 3, 2001. Accepted December 6, 2001.

JE010244E