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Liquid-liquid equilibria in binary mixtures of some normal alkanes (C7 - C17) + .alpha.,.omega.-diiodoalkanes (C3, C4, C5)

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The liquid-liquid miscibility curves are presented for 1,3-diiodopropane with heptane or heptadecane, for 1,4-diiodobutane with heptane, undecane, or heptadecane, and for 1,5-diiodopentane with pentadecane. The DISQUAC group-contribution model leads to qualitatively correct predictions of the miscibility curves of α,ω-diiodoalkanes with n-alkanes using the interaction parameters derived previously from vapor-liquid equilibria and excess enthalpies of 1-iodoalkane + n-alkane mixtures.

1. INTRODUCTION

1-Iodoalkane + n-alkane mixtures are miscible at room temperature. The thermodynamic excess properties, molar excess Gibbs energies, G^E, and molar excess enthalpies, H^E, have been investigated experimentally and compared with DISQUAC group-contribution model predictions [MUNJ0871]. For α,ω-diiodoalkane + n-alkane mixtures, of appropriate chain-lengths, DISQUAC predicts partial miscibility. No solubility data have been reported in the literature to test this prediction. The aim of the present work was to experimentally investigate the effect of the chain length of each of the two linear molecules on the liquid-liquid equilibrium in this class of systems.

2. EXPERIMENTAL SECTION

2.1. Apparatus and Procedure

The measurements were carried out in an all-glass cell filled with mixtures of known composition prepared by mass. The temperature T was measured with an ASL digital thermometer model F25. The contents of the cell was continuously stirred with a magnetic stirrer. The phase change was observed visually as the mixture was cooled. The reproducibility of the temperatures was within $\sigma(T)$ = 0.01 K. The estimated uncertainty in the mole fraction composition $\sigma(x_i)$ is estimated to be less than 0.0001 for the whole temperature range studied.

2.2. Materials

$C_3H_6I_2$, 1,3-Diiodopropane. Aldrich Chem. Co., Inc. (Milwaukee, WI, USA) material of stated purity 99 mole %, dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification. n(D,298.15 K) = 1.6391; ρ(298.15 K)/kg m^{-3} = 2561.21.

$C_4H_8I_2$, 1,4-Diiodobutane. Aldrich Chem. Co., Inc. (Milwaukee, WI, USA) material of stated purity 99 mole %, purified as above and used without further purification. n(D,298.15 K) = 1.6184; ρ(298.15 K)/kg m^{-3} = 2349.38.

$C_5H_{10}I_2$, 1,5-Diiodopentane. Aldrich Chem. Co., Inc. (Milwaukee, WI, USA) material of stated purity > 97 mole %, purified as above and used without further purification. n(D,298.15 K) = 1.5987; ρ(298.15 K)/kg m^{-3} = 2169.16.

C_7H_{16}, Heptane. Fluka AG (Buchs, Switzerland) "puriss" grade material of stated purity > 99.5 mole %, purified as above and used without further purification. n(D,298.15 K) = 1.3815; ρ(298.15 K)/kg m^{-3} = 679.46.

$C_{11}H_{24}$, Undecane. Fluka AG (Buchs, Switzerland) "purum" grade material of stated purity 97 mole %, purified as above and used without further purification. n(D,298.15 K) = 1.4154; ρ(298.15 K)/kg m^{-3} = 736.80.

$C_{15}H_{32}$, Pentadecane. Fluka AG (Buchs, Switzerland) "puriss" grade material of stated purity 98 mole %, purified as above and used without further purification. n(D,298.15 K) = 1.4298; ρ(298.15 K)/kg m^{-3} = 764.80.

$C_{17}H_{36}$, Heptadecane. Fluka AG (Buchs, Switzerland) "purum" grade material of stated purity > 99 mole %, purified as above and used without further purification. n(D,298.15 K) = 1.4347; ρ(298.15 K)/kg m^{-3} = 774.33.

3. RESULTS

The direct experimental x_1 - T values of the 6 systems are tabulated and graphed in the Appendix and all are saved on disk as Standard ELDATA Files **ORTJ0955.001** through **ORTJ0955.006**.

4. DISCUSSION AND CONCLUSIONS

α,ω-Diiodoalkane + n-alkane mixtures are regarded in DISQUAC as possessing two types of contact surfaces: (1) type a, aliphatic (CH_3 or CH_2 groups, which are assumed to exert the same force field); and type (d), iodine (I).

The relative molecular volumes r_i, the surfaces q_i, and

the surface fractions α_{si} (s = a, d; i = 1, 2) of all the molecular species have been calculated as described in [MUNJ0871]. The calculated r_i, q_i, α_{ai}, and α_{di} values are, respectively:

4.0333, 3.1069, 0.4495, and 0.5505 (1,3-diiodopropane)
4.6309, 3.5724, 0.5212, and 0.4788 (1,4-diiodobutane)
5.2284, 4.0379, 0.5764, and 0.4236 (1,5-diiodopentane)

The same dispersive and quasi-chemical parameters have been used as for 1-iodoethane or higher 1-iodoalkanes:

$$C^{dis}_{ad,1} = 0.309, C^{quac}_{ad,1} = 1.743,$$

$$C^{dis}_{ad,2} = 0.428, C^{quac}_{ad,2} = 2.760.$$

The calculated coordinates of the upper critical solution points, temperature T^c and mole fraction of α,ω-diiodoalkane, x_1^c, change with the chain length n of the normal alkane in qualitative agreement with experiment: both T^c and x_1^c, increase with increasing n. The differencies between the experimental T^c's and the calculated values range irregularly from −33 to +25 K (less than 10 %).

Comparison of the model with the available experimental H^E data on 1,5-diiodopentane or 1,6-diiodohexane + n-alkane mixtures [ORTJ0933], using always the same interaction parameters as for 1-iodoethane or higher 1-iodoalkanes, results in calculated equimolar H^E values smaller by ca. 250 J mol^{-1} (ca. 20 %) in the average than the experimental data. This may be attributed to some degree of orientational order existing in α,ω-diiodoalkanes, as found previously in α,ω-dibromoalkanes [ARTM0914]. However, in order to optimize the iodine/alkane interaction parameters, accurate vapor-liquid equilibrium data should be measured for selected α,ω-diiodoalkane + n-alkane mixtures.

REFERENCES

[ARTM0914] – Artal, M.; Munoz Embid, J.; Otin, S.; Velasco, I.; Kehiaian, H. V. Excess enthalpies of binary mixtures containing alpha,omega-dibromoalkanes. Measurement and analysis in terms of group contributions (DISQUAC). *Fluid Phase Equilib.* **1991,** *70,* 267-274.

[MUNJ0871] – Munoz Embid, J.; Otin, S.; Velasco, I.; Gutierrez Losa, C.; Kehiaian, H. V. Excess enthalpies of 1-iodoalkane + n-alkane mixtures. Measurement and analysis in terms of group contributions (DISQUAC). *Fluid Phase Equilib.* **1987,** *38,* 1-17.

[ORTJ0933] – Ortega, J.; Placido, J. Excess enthalpies of 1,5-diiodopentane or 1,6-diiodohexane + some normal alkane (C5-C17) mixtures. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1993,** *21,* 232-245.

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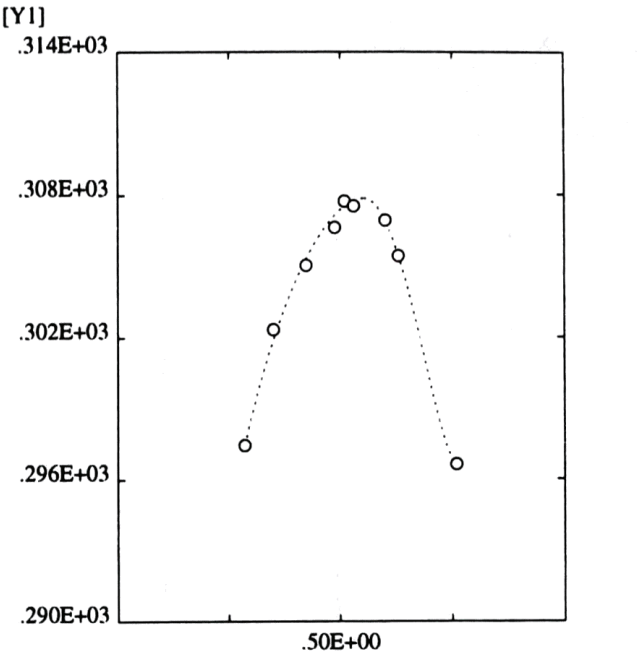
Property Code: [ELLM1000] LIQUID-LIQUID EQUILIBRIUM IN MIXTURES AND SOLUTIONS **PLAJ0951.001**
State: Two-component two-phase liquid-liquid system
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] T/K, Temperature
Method: Direct low-pressure measurement of T at variable x_1

Components: **1. $C_3H_6I_2$, 1,3-Diiodopropane**
2. C_7H_{16}, Heptane

[X1]	[Y1]		
.286900E+00	.297450E+03		
.350300E+00	.302350E+03		
.424900E+00	.305050E+03		
.487500E+00	.306650E+03		
.510300E+00	.307750E+03		
.530000E+00	.307550E+03		
.600000E+00	.306950E+03		
.630000E+00	.305450E+03		
.760000E+00	.296650E+03		



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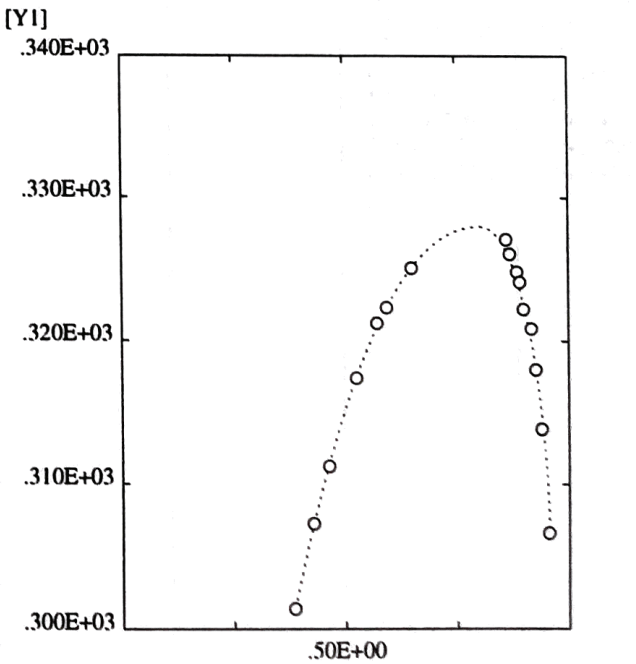
State: Two-component two-phase liquid-liquid system
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] T/K, Temperature
Method: Direct low-pressure measurement of T at variable x_1

Components: **1. $C_3H_6I_2$, 1,3-Diiodopropane**
2. $C_{17}H_{36}$, Heptadecane

[X1]	[Y1]		
.386200E+00	.301450E+03		
.428900E+00	.307250E+03		
.465300E+00	.311250E+03		
.526900E+00	.317450E+03		
.574700E+00	.321250E+03		
.596000E+00	.322350E+03		
.651600E+00	.325150E+03		
.863100E+00	.327150E+03		
.870500E+00	.326150E+03		
.886000E+00	.324880E+03		
.893600E+00	.324180E+03		
.901300E+00	.322250E+03		
.917300E+00	.320950E+03		
.927500E+00	.318050E+03		
.939200E+00	.313850E+03		
.956200E+00	.306600E+03		



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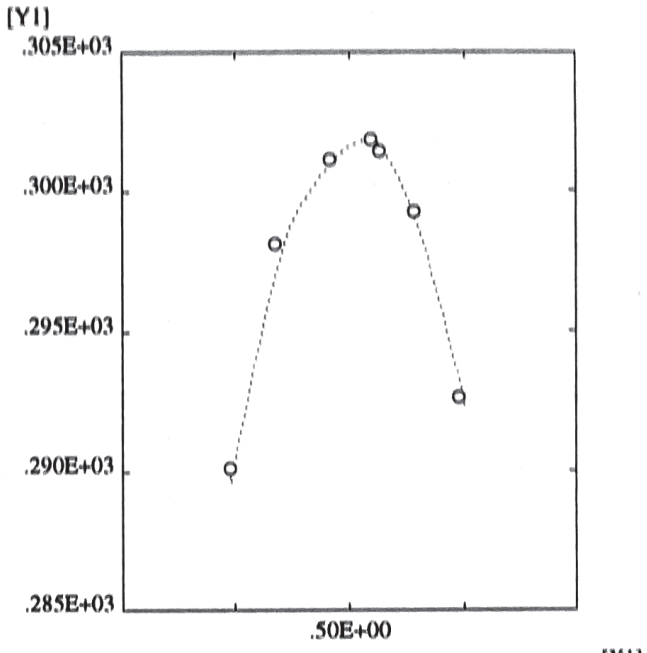
State: Two-component two-phase liquid-liquid system
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] T/K, Temperature
Method: Direct low-pressure measurement of T at variable x_1

Components: **1. $C_4H_8I_2$, 1,4-Diiodobutane**
2. C_7H_{16}, Heptane

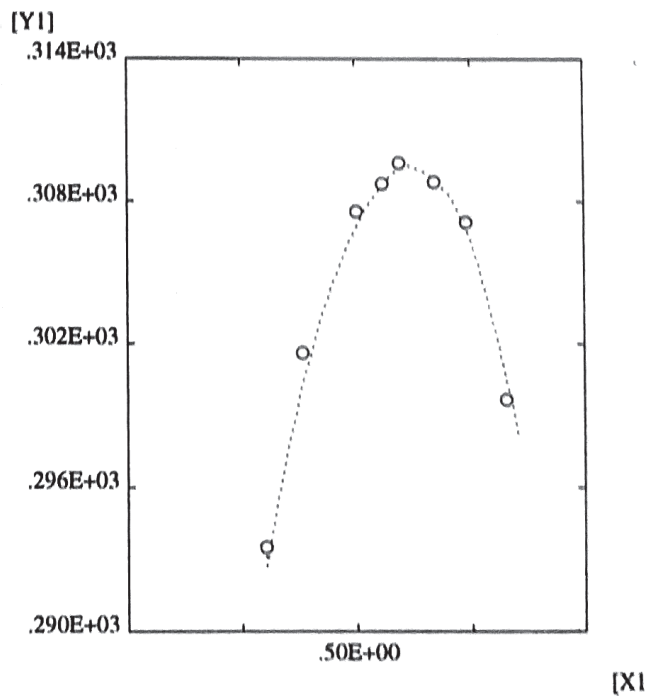
[X1]	[Y1]		
.239100E+00	.290150E+03		
.337600E+00	.298150E+03		
.456600E+00	.301150E+03		
.546800E+00	.301850E+03		
.564400E+00	.301450E+03		
.640000E+00	.299250E+03		
.737600E+00	.292650E+03		



Property Code: [ELLM1000] LIQUID-LIQUID EQUILIBRIUM IN MIXTURES AND SOLUTIONS **PLAJ0951.004**
State: Two-component two-phase liquid-liquid system
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] T/K, Temperature
Method: Direct low-pressure measurement of T at variable x_1

Components: **1. $C_4H_8I_2$, 1,4-Diiodobutane**
2. $C_{11}H_{24}$, Undecane

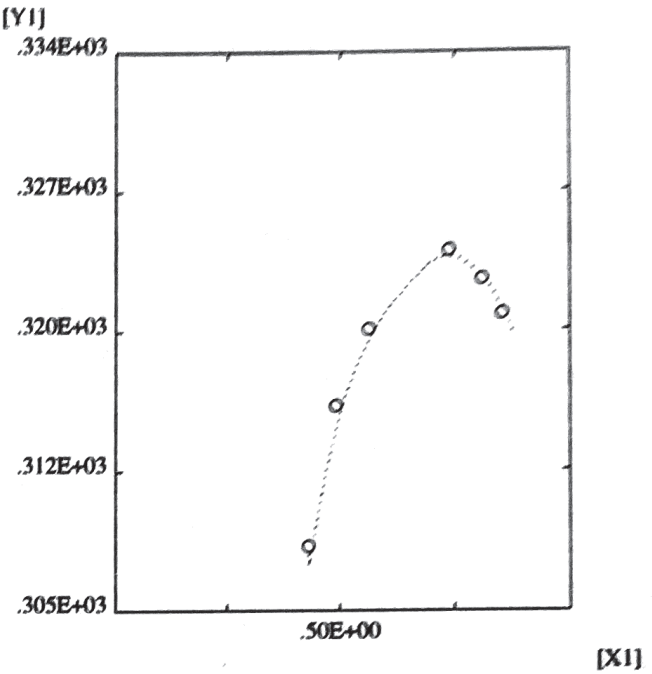
[X1]	[Y1]		
.302300E+00	.293550E+03		
.383100E+00	.301650E+03		
.502900E+00	.307600E+03		
.558000E+00	.308750E+03		
.596700E+00	.309650E+03		
.671400E+00	.308850E+03		
.740500E+00	.307150E+03		
.826200E+00	.299700E+03		



Property Code: [ELLM1000] LIQUID-LIQUID EQUILIBRIUM IN MIXTURES AND SOLUTIONS **PLAJ0951.005**
State: Two-component two-phase liquid-liquid system
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] T/K, Temperature
Method: Direct low-pressure measurement of T at variable x_1

Components: **1. $C_4H_8I_2$, 1,4-Diiodobutane**
2. $C_{17}H_{36}$, Heptadecane

[X1]	[Y1]
.432100E+00	.308350E+03
.490900E+00	.315650E+03
.563200E+00	.319600E+03
.737600E+00	.323650E+03
.810400E+00	.322150E+03
.854600E+00	.320350E+03



Property Code: [ELLM1000] LIQUID-LIQUID EQUILIBRIUM IN MIXTURES AND SOLUTIONS **PLAJ0951.006**
State: Two-component two-phase liquid-liquid system
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] T/K, Temperature
Method: Direct low-pressure measurement of T at variable x_1

Components: **1. $C_5H_{10}I_2$, 1,5-Diiodopentane**
2. $C_{15}H_{32}$, Pentadecane

[X1]	[Y1]
.387500E+00	.290550E+03
.466300E+00	.295450E+03
.540500E+00	.298650E+03
.586600E+00	.299650E+03
.623200E+00	.300650E+03
.660600E+00	.301150E+03
.690800E+00	.301550E+03
.737500E+00	.300450E+03
.761400E+00	.299650E+03
.764300E+00	.299650E+03