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THERMODYNAMICS OF MIXTURES CONTAINING A VERY STRONGLY POLAR COMPOUND. 10. LIQUID-LIQUID EQUILIBRIA FOR N,N-DIMETHYLACETAMIDE + SELECTED ALKANES

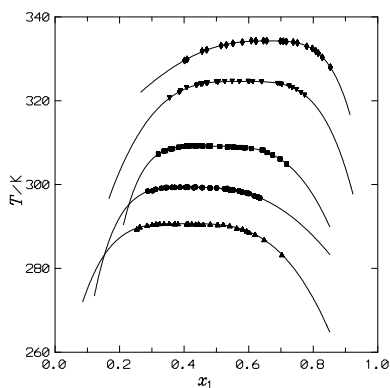
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Thermodynamics of mixtures containing a very strongly polar compound. 10. Liquid-liquid equilibria for *N,N*-dimethylacetamide + selected alkanes

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ABSTRACT

Liquid-liquid equilibrium (LLE) temperatures vs. composition for *N,N*-dimethylacetamide (DMA) + decane, or + dodecane, or + tetradecane, or + 2,2,4-trimethylpentane or + methylcyclohexane, or + cyclooctane mixtures have been measured by means of the critical opalescence method using a laser scattering technique. All the systems show an upper critical solution temperature (UCST). In the case of *n*-alkane mixtures, UCST increases almost linearly with the chain length of the *n*-alkane. Moreover, these solutions show higher UCST values than those with isomeric cyclic alkanes. Branching leads to a strong decrease of UCST. The symmetry of the LLE curves depends on the size and shape of the alkane. DISQUAC correctly represents the coordinates of the critical points using interaction parameters available in the literature.

Keywords DMA, alkanes, cyclization; branching; DISQUAC

1. INTRODUCTION

Amides have a large number of applications. For example, 1-Methyl-2-pyrrolidinone (NMP), or *N,N*-dimethylacetamide (DMA) are used as selective extractants for the recovery, from petroleum feedstocks, of aromatic or saturated hydrocarbons.¹ Amides are substances of basic importance in biochemistry, where peptide bond plays as essential role.^{2,3} It is well known that proteins are polymers of amino acids linked by peptide bonds. For this reason, we are engaged in a systematic research of mixtures containing amides. Thus, we have investigated using different models, DISQUAC,⁴ ERAS,⁵ the Kirkwood-Buff integrals formalism⁶ or the concentration-concentration structure factor,⁷ mixtures of secondary or tertiary amides with different solvents.⁸⁻¹¹ The theoretical interest of amide solutions is related, in large extent, to the large dipole moments of these compounds¹² ($12.37 \cdot 10^{-30}$ C·m for DMA), and consequently of their effective dipole moments,¹⁰ which lead to a significant local order in the pure liquid state.¹³ In fact, for *N,N*-dialkylamides, this has been ascribed to the existence of strong dipole-dipole interactions.¹³ On the other hand, we have provided LLE data on *N,N*-dimethylmethanamide (DMF), or DMA or ϵ -caprolactam with selected alkanes.^{14,15} As continuation, we report now liquid-liquid equilibrium temperatures for the systems DMA + decane, or + dodecane, or + tetradecane, or + 2,2,4-trimethylpentane, or + methylcyclohexane, or + cyclooctane. Data for mixtures containing DMA and other *n*-alkanes are available in the literature.¹⁶⁻²⁰ This data collection allows examine effects such as alkane size, cyclization or branching on the corresponding coexistence curves. Finally, we also show DISQUAC predictions on LLE for the present solutions and on H_m^E for systems with miscibility gaps, which were not considered in our previous studies.

2. EXPERIMENTAL

2.1 Materials

Information on source, purity, water content, determined by the Karl-Fisher method, and density of the chemical used is shown in Table 1. Densities were measured with an Anton Paar DMA 602 vibrating-tube densimeter automatically thermostated within ± 0.01 K. Details on its calibration can be found elsewhere.²¹ The resolution in density is $|\Delta\rho / \rho| = 6 \cdot 10^{-6}$, while the corresponding accuracy is estimated to be $\pm 2 \cdot 10^{-2}$ kg·m⁻³.

2.2 Apparatus and Procedure

Mixtures were prepared by mass (weighing accuracy to ± 0.00001 g), in small tubes made of Pyrex (0.9 cm i.d. and about 4 cm length). These equilibrium cells were immediately sealed by capping at atmospheric pressure and room temperature. Conversion to molar quantities was based on the relative atomic mass Table of 2006 issued by IUPAC.²² The liquid-liquid equilibrium temperatures of the binary systems were determined by the method of the

critical opalescence. Shortly, the method is as follows. A He-Ne laser beam is sent through the sample, placed in an equilibrium cell at a few hundredths of degree above the expected temperature, to a light sensor. When the transition takes place, the light is dispersed and a voltage variation arises. This voltage variation is measured by a digital multimeter (model Agilent 34410A) connected to a PC, which allows simultaneous accurate measurements of the transition temperatures. The method has been explained in detail elsewhere.¹⁵ Temperature measurements were carried out using a Pt-1000 resistance, calibrated on the basis of the ITS-90 scale of temperature using the triple point of the water, and the fusion point of Ga. The thermometer precision is ± 0.001 K and its accuracy is ± 0.05 K. The equilibrium temperatures were reproducible to ± 0.02 K at temperatures near the UCST. Regarding the precision of the equilibrium composition is expected is 0.0005 in mole fraction.¹⁵

3. RESULTS

Table 2 lists the direct experimental results obtained in this work of the liquid-liquid equilibrium temperatures T vs. x_1 , the mole fraction of DMA. We note that all the systems show an UCST. Data were reduced using the equation:

$$T / K = T_c / K + k|y - y_c|^m \quad (1)$$

with

$$y = \frac{\alpha x_1}{1 + x_1(\alpha - 1)} \quad (2)$$

$$y_c = \frac{\alpha x_{1c}}{1 + x_{1c}(\alpha - 1)} \quad (3)$$

The parameters m , k , α , T_c and x_{1c} (the two latter parameters are the coordinates of the critical points) are obtained from the fitting of the experimental data by means of eq (1), which is similar to:

$$\Delta\lambda = B\tau^\beta \quad (4)$$

when $\alpha = 1$.²²⁻²⁴ In eq 4, $\Delta\lambda_1 = \lambda_1' - \lambda_2''$ stands for any density variable in the conjugate phase (the so-called order parameter; here, $\lambda_1 = x_1$), τ is the reduced temperature $(T_c - T)/T_c$ and β a critical exponent corresponding to the selected order parameter. The β value depends on the theory applied to its determination.²⁴⁻²⁶

The fitting was conducted on the basis of a Marquardt algorithm²⁷ with all the points weighted equally. Results are listed in Table 3, which also contains the standard deviation defined by:

$$(\sigma(T)/K) = \left[\sum (T_i^{\text{exp}} - T_i^{\text{cal}})^2 / (N - n) \right]^{1/2} \quad (5)$$

where N and n are the number of data points and the number of fitted parameters, respectively.

4. DISCUSSION

From inspection of the LLE data for mixtures with DMA, some features can be stated.

(i) UCST increases almost linearly with the chain length of the n -alkane, and the LLE curves are progressively skewed towards higher mole fractions of DMA. This may be ascribed to size effects.²⁸ (ii) UCST of the system with methylcyclohexane is very similar to that of the heptane solution. (iii) Mixtures with cyclic alkanes are characterized by UCST values lower than systems with isomeric n -alkanes. (iv) UCST also increases with the size of the cyclic alkane. (v) Branching effect leads to a sharp decrease of UCST. (vi) The symmetry of LLE curves containing linear alkanes are opposite to that of solutions with cyclic or branched isomeric alkanes. Thus, for mixtures including alkanes of similar molar volume, octane ($163.50 \text{ cm}^3 \cdot \text{mol}^{-1}$)¹⁴ or 2,2,4-trimethylpentane ($166.08 \text{ cm}^3 \cdot \text{mol}^{-1}$; this work), $x_{1c} = 0.536$ and 0.403 , respectively.

This clearly shows the shape effect on the symmetry of the LLE curves.

Some of the features state above, namely (i), (iii) and (iv) are still valid for mixtures with DMF, NMP, or ϵ -caprolactam. However, there are also differences. In the case of DMF solutions, the UCST value is practically independent of the solute, hexane or 2-methylpentane (337.69).^{14,29} For NMP + isomeric hexane mixtures, UCST changes rather erratically with the alkane: 322.92 K (hexane)³⁰; 325.49 K (2-methylpentane)³⁰; 319.04 K (3-methylpentane)³⁰; 322.32 K (2,2-dimethylbutane)³⁰; 315.88 K (2,3-dimethylbutane).³⁰ When replacing octane by 2,2,4-trimethylpentane, UCST slightly decreases (Table 4). The opposite trend is observed in solutions with ϵ -caprolactam. One can conclude that UCST values of systems formed by a given solute and linear or branched isomeric alkanes depend on the solute nature and of the branching of the alkanes.

On the other hand, for mixtures including a given alkane, $\text{UCST}(\text{DMF}) > \text{UCST}(\text{DMA})$ (Tables 3,4), which indicates that amide-amide interactions are stronger in DMF systems. This is supported by the corresponding effective dipole moments of these amides;¹⁰ $\bar{\mu}$ (DMF) = 1.60 ; $\bar{\mu}$ (DMA) = 1.49 . Interestingly, although $\bar{\mu}$ (NMP) = 1.59 is similar to the value of DMF, the UCSTs are higher for NMP mixtures (Table 4). This can be ascribed to the polar groups are

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3 less sterically hindered in cyclic molecules. Solutions including ϵ -caprolactam also show
4 higher UCST values (Table 4), as this is a secondary amide and self-association via H-bonds
5 must be also taken into account.
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8 Finally, we have applied DISQUAC to the present systems. The interaction parameters
9 for the amide/aliphatic (n,a) and amide/cyclic (n,c) contacts are equal to those previously
10 determined.¹⁴ Only the $C_{nc,l}^{DIS}$ coefficient has been slightly modified. Actually, its value is 4.95
11 (previous value 4.85). The coordinates of the critical points are described by the model in the
12 correct range of composition and temperature (Table 3), as in many other applications.^{8,10,14,31,32}
13 Of course, LLE curves are more rounded than the experimental ones (Figure 1). This is a typical
14 result given by mean field theories, which assume that the excess Gibbs energy in an analytical
15 function close to the critical point.^{23,24} Nevertheless, the increase of x_{1c} with the chain length of
16 the n -alkane is well represented by DISQUAC (Table 3). On the other hand, Figures 2 and 3
17 show DISQUAC H_m^E calculations for systems not considered in previous works. We note that
18 there is an excellent agreement with the experimental values. This is an important result as both
19 LLE and H_m^E are calculated using the same interaction parameters and remarks that the
20 temperature dependence of the thermodynamic properties are well represented by the model.
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31 5. CONCLUSIONS

32 LLE coexistence curves have been obtained for DMA + alkane mixtures. It has been
33 found that UCST increases almost linearly with the chain length of the n -alkane and that
34 mixtures with cyclic alkanes show lower UCST values than systems with isomeric n -alkanes.
35 Branching effect leads to a strong decrease of UCST. DISQUAC describes the coordinates of
36 the critical points in the correct range of temperature and composition.
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Table 1 Properties of Pure Compounds at 0.1 MPa

Compound	CAS	Source	Initial mole fraction	$\rho^a(298.15\text{K})/$		Water ^b content
				$\text{kg}\cdot\text{m}^{-3}$		
				Exp.	Lit.	
<i>N,N</i> -dimethylacetamide	127-19-5	Fluka	≥ 0.99	936.88	936.337 ³³	$46\cdot 10^{-6}$
Decane	24-18-5	Fluka	≥ 0.99	726.43	726.35 ³³	$12\cdot 10^{-6}$
Dodecane	112-40-3	Fluka	≥ 0.98	741.54	745.56 ³⁴	$11\cdot 10^{-6}$
Tetradecane	629-59-4	Fluka	≥ 0.99	759.27	759.29 ³⁵	$25\cdot 10^{-6}$
2,2,4-trimethylpentane	540-84-1	Fluka	≥ 0.995	687.77	687.81 ³³	$6\cdot 10^{-6}$
methyl-cyclohexane	108-87-2	Fluka	≥ 0.98	764.86	765.06 ³³	$6\cdot 10^{-6}$
Cyclooctane	292-64-8	Fluka	≥ 0.99	831.87	831.51 ³⁶	$7\cdot 10^{-6}$

^adensity, uncertainty, $u(\rho) = \pm 0.02 \text{ kg}\cdot\text{m}^{-3}$; $u(T) = \pm 0.01 \text{ K}$; $u(p) = \pm 0.1 \text{ kPa}$; ^bin mass fraction

Table 2 Experimental Liquid-Liquid Equilibrium Temperatures for DMA(1) + Alkane(2) Mixtures^a at 0.1 MPa

x_1	T/K	x_1	T/K
DMA(1) + decane(2)			
0.3549	320.66	0.5260	324.59
0.3699	320.99	0.5486	324.64
0.3854	321.97	0.5710	324.60
0.3886	322.35	0.5987	324.64
0.3912	322.09	0.6011	324.56
0.4077	323.10	0.6126	324.54
0.4380	323.63	0.6404	324.51
0.4403	323.79	0.6895	324.14
0.4522	324.02	0.6970	324.08
0.4567	324.04	0.7025	323.92
0.4689	324.22	0.7252	323.54
0.4721	324.22	0.7348	323.13
0.4999	324.55	0.7481	322.70
0.5038	324.46	0.7618	321.99
0.5057	324.57	0.7735	321.35
DMA(1) + dodecane(2)			
0.4013	329.63	0.6559	334.32
0.4091	329.87	0.6986	334.21
0.4323	331.11	0.7072	334.20
0.4556	331.86	0.7166	334.11
0.4699	332.17	0.7382	334.00
0.5147	333.15	0.7509	333.81
0.5305	333.31	0.7799	332.97
0.5511	333.69	0.7974	332.48
0.5805	334.00	0.8079	331.85
0.6083	334.34	0.8157	331.36
0.6218	334.32	0.8282	330.33
0.6229	334.19	0.8532	327.98
0.6460	334.33		
DMA(1) + tetradecane(2)			
0.5170	339.78	0.7340	342.81
0.5359	340.39	0.7480	342.67
0.5724	341.84	0.7687	342.30

Table 2 (continued)

0.5841	342.03	0.7934	341.81
0.6220	342.77	0.8111	341.35
0.6598	342.87	0.8245	340.55
0.6773	342.91	0.8459	339.83
0.7197	342.82		
DMA(1) + methylcyclohexane(2)			
0.3195	307.27	0.4820	309.20
0.3376	307.99	0.5108	309.11
0.3432	308.06	0.5335	308.93
0.3571	308.58	0.5365	309.00
0.3606	308.50	0.5526	308.96
0.3650	308.60	0.5552	308.90
0.3829	308.90	0.5708	308.87
0.3949	309.09	0.5748	308.88
0.3971	309.07	0.5869	308.76
0.4077	309.22	0.5909	308.78
0.4157	309.20	0.6084	308.59
0.4208	309.24	0.6415	308.26
0.4345	309.19	0.6449	308.18
0.4471	309.24	0.6571	307.62
0.4580	309.17	0.6742	307.06
0.4761	309.18	0.6973	306.10
0.4776	309.28	0.7176	304.88
DMA(1) + 2,2,4-trimethylpentane(2)			
0.2533	289.38	0.4357	290.54
0.2627	289.91	0.4447	290.56
0.2853	290.26	0.4456	290.52
0.3011	290.46	0.4596	290.51
0.3123	290.56	0.4810	290.56
0.3143	290.54	0.5034	290.51
0.3241	290.67	0.5046	290.39
0.3376	290.69	0.5214	290.47
0.3539	290.72	0.5414	290.16
0.3710	290.75	0.5631	289.61
0.3717	290.61	0.5813	289.38

Table 2 (continued)

0.3807	290.64	0.5936	288.93
0.4076	290.62	0.6018	288.58
0.4107	290.53	0.6198	288.15
0.4127	290.61	0.6481	286.86
0.4236	290.62	0.7030	283.25
DMA(1) + cyclooctane(2)			
0.2870	298.41	0.4809	299.16
0.3025	298.53	0.5009	299.16
0.3115	298.86	0.5245	298.98
0.3295	299.11	0.5327	298.95
0.3427	299.27	0.5337	299.07
0.3466	299.29	0.5413	298.72
0.3626	299.33	0.5456	298.73
0.3706	299.33	0.5528	298.69
0.3874	299.35	0.5695	298.51
0.4044	299.32	0.5793	298.23
0.4086	299.35	0.5947	297.98
0.4116	299.36	0.5982	297.87
0.4298	299.27	0.6008	297.88
0.4354	299.38	0.6173	297.31
0.4558	299.30	0.6283	297.03
0.4559	299.24	0.6348	296.79
0.4801	299.18		

^auncertainties, u are; $u(x_1) = 0.0005$; $u(T) = 0.05$ K; $u(p) = \pm 0.1$ kPa

Table 3 Coefficients in Eq. (1) for the Fitting of the (x_1, T) Pairs given in Table 2 for DMA(1) + Alkane(2) Mixtures; σ is the Standard Deviation defined by eq 5.

N^a	m	k	α	T_c/K	x_{1c}	σ/K
DMA(1) + decane(2)						
28	3.46	-752	0.792	324.60 (329.9) ^b	0.580 (0.549) ^b	0.07
DMA(1) + dodecane(2)						
25	2.98	-356	0.433	334.27 (339.8) ^b	0.661 (0.613) ^b	0.09
DMA(1) + tetradecane(2)						
15	2.55	-304	0.95	342.94 (347.8) ^b	0.684 (0.667) ^b	0.10
DMA(1) + methylcyclohexane(2)						
27	3.95	-2297	1.68	309.13 (296.8) ^b	0.479 (0.342) ^b	0.03
DMA (1) + 2,2,4-trimethylpentane(2)						
32	3.51	-623	1.39	290.65 (313.2) ^b	0.403 (0.451) ^b	0.11
DMA (1) + cyclooctane(2)						
33	3.55	-698	2.11	299.32 (295) ^b	0.416 (0.316) ^b	0.07

^a number of experimental data points; ^bDISQUAC value

Table 4 Critical Coordinates, Composition and Temperature, of Amide(1) + Hydrocarbon (2) Mixtures.

System	x_{1c}	T_c /K	Ref.
DMF + hexane	0.494	337.69	14
DMF + 2-methylpentane	0.487	337.69	29
DMF + heptane	0.524	342.55	14
DMF + octane	0.558	347.30	14
DMF + nonane	0.600	352.67	14
DMF + decane	0.6686	357.76	37
DMF + hexadecane	0.7977	385.15	38
DMF + cyclohexane	0.4027	320.04	39
DMF + methylcyclohexane	0.4853	322.82	40
DMA + pentane	0.407	302.4	18
DMA + hexane	0.455	305.3	16
DMA + heptane	0.499	309.8	20
DMA + octane	0.536	314	17
DMA + nonane	0.574	320.1	19
NMP + butane		338.73	41
NMP + pentane	0.348	324.35	42
NMP + hexane	0.443	324.65	43
	0.446	322.92	30
NMP + 2-methylpentane	0.422	325.49	30
NMP + 3-methylpentane	0.412	319.04	30
NMP + 2,2-dimethylbutane	0.354	327.6	44
	0.405	322.32	30
NMP + 2,3-dimethylbutane	0.384	319.22	44
	0.432	315.88	30
NMP + heptane	0.455	326.05	43
NMP + octane	0.488	328.5	43
	0.529	328.99	30
NMP + 2,2,4-trimethylpentane	0.508	326.93	30
NMP + nonane	0.544	333.19	42
NMP + decane	0.511	336.72	45
NMP + undecane	0.523	340.8	45
NMP + tridecane	0.630	348.9	45

Table 4 (continued)

NMP + tetradecane	0.645	354.9	45
NMP + hexadecane	0.678	367.65	38
NMP + cyclopentane	0.219	277.07	44
NMP + cyclohexane	0.278	283.10	44
NMP + cycloheptane	0.341	289.07	44
NMP + cyclooctane	0.351	291.87	44
NMP + methylcyclohexane	0.419	291.2	44
ϵ -caprolactam + heptane	0.482	352.13	15
ϵ -caprolactam + octane	0.519	354.51	15
ϵ -caprolactam + 2,2,4-trimethylpentane	0.505	362.34	15
ϵ -caprolactam + nonane	0.554	358.61	15
ϵ -caprolactam + decane	0.586	363.43	15

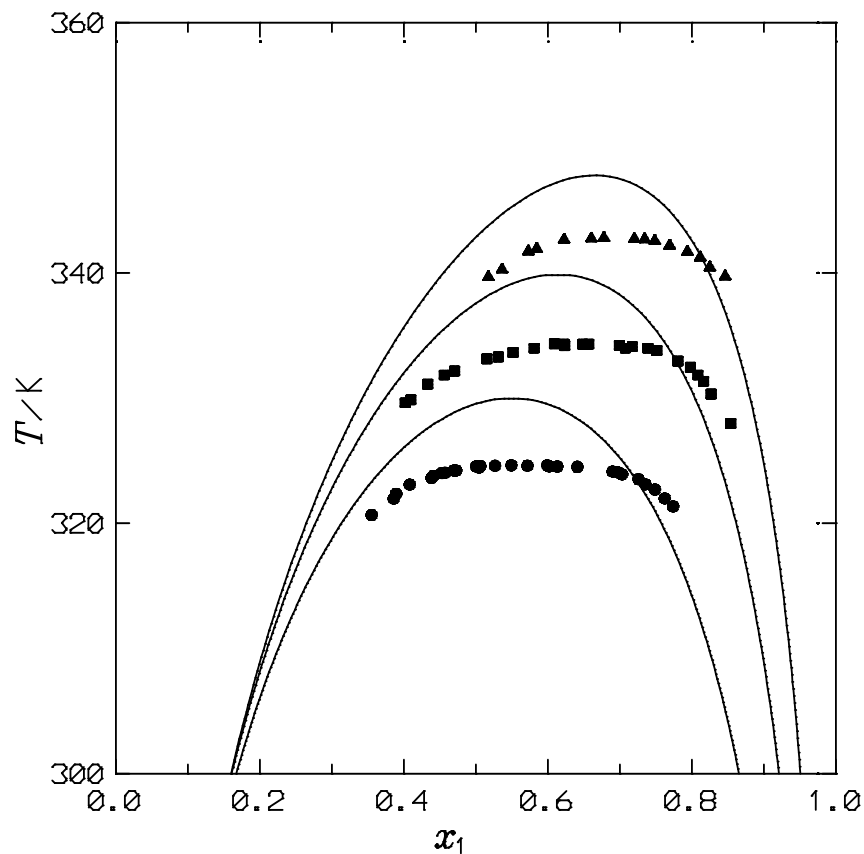


Figure 1 LLE for N,N-dimethylacetamide(1) + alkane(2) mixtures. Points, experimental results (this work): (●), decane; (■), dodecane; (▲), tetradecane; Solid lines, DISQUAC calculations.

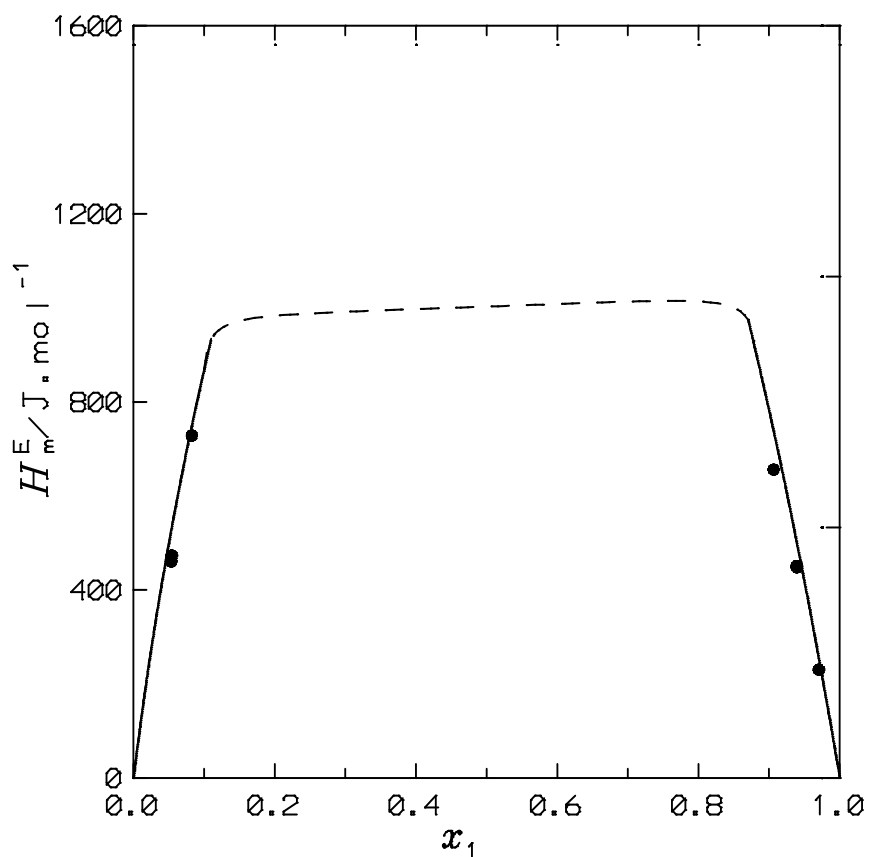


Figure 2 H_m^E for the *N,N*-dimethylformamide(1) + 2-methylpentane(2) system at 313.15

K. Points, experimental results.²⁸ Solid lines, DISQUAC calculations

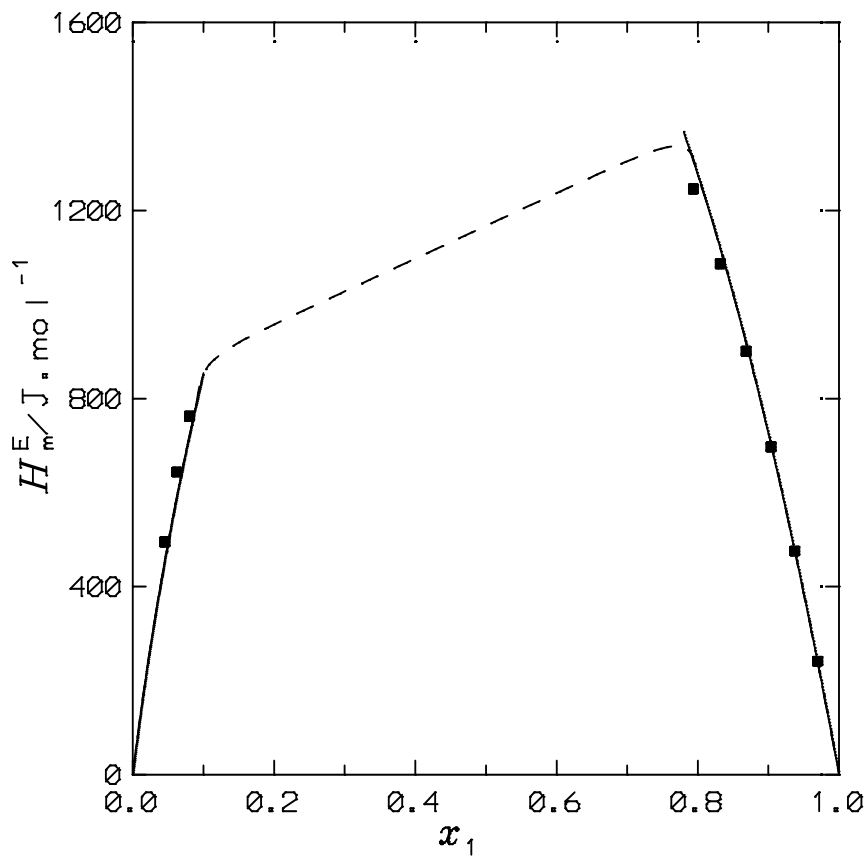


Figure 3 H_m^E for the N,N -dimethylformamide(1) + methylcyclohexane(2) system at 313.15 K. Points, experimental results.³⁹ Solid lines, DISQUAC calculations