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Thermodynamics of Mixtures Containing a Strongly Polar Compound. 8. Liquid−Liquid Equilibria for *N*,*N*-Dialkylamide + Selected *N*-Alkanes

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The coexistence curves of the liquid−liquid equilibria (LLE) for systems of dimethylformamide (DMF) with hexane, heptane, octane, or nonane and of dimethylacetamide (DMA) with heptane have been determined visually. All the curves show an upper critical solution temperature (UCST) and have a rather horizontal top. The measured LLE curves for DMF mixtures show that their symmetry depends on the size of the alkane. For a given alkane, the UCST is higher for systems with DMF. This reveals that dipole−dipole interactions between amide molecules are stronger in such solutions. The DISQUAC model represents fairly well the LLE curves.

Introduction

We are engaged in a systematic investigation on the thermodynamic properties of mixtures containing a compound with a very high dipolar moment in gas phase (μ), such as sulfolane[1,2] ($\mu = 16.04 \cdot 10^{-30}$ C·m^3); dimethyl sulfoxide[4] ($\mu = 13.54\ 10^{-30}$ C·m^3); 1-methylpyrrolidin-2-one[5,6] (NMP; $\mu = 13.64 \cdot 10^{-30}$ C·m·D^3); *N*,*N*-dialkylamides[6,7] (DMF, $\mu = 12.28 \cdot 10^{-30}$ C·m;[8] DMA, $\mu = 12.37 \cdot 10^{-30}$ C·m[8]); *N*-alkylamides[8] or propylene carbonate ($\mu = 16.49 \cdot 10^{-30}$ C·m·D^3).

Amides, amino acids, peptides, and their derivatives are of interest because they are simple models in biochemistry. *N*-Methylformamide (NMF) possesses the basic (-CO) and acidic (-NH) groups of the very common, in nature, peptide bond.[10] So, proteins are polymers of amino acids linked to each other by peptide bonds. Cyclic amides are also of importance due to they are related to structural problems in biochemistry. Consequently, the understanding of liquid mixtures involving the amide functional group is necessary as a first step to a better knowledge of complex molecules of biological interest.[11] For example, the aqueous solution of DMF is a model solvent representing the environment of the interior of proteins. Moreover, DMF and NMP are used as highly selective extractants for the recovery of aromatic and saturated hydrocarbons from petroleum feedstocks.[12]

From a theoretical point of view, amides are also a very interesting class of compounds. In pure liquid state, they present a significant local order[13] as their quite high heats of vaporization indicate.[14] In the case of *N*,*N*-dialkylamides, this is due to the dominance of the general dipole−dipole interactions,[13] which can be ascribed to their very high effective dipole moments[7] ($\bar{\mu}$), a useful magnitude to examine the impact of polarity on bulk properties.[7,15] For primary and secondary amides, their self-association via H-bonds must be also taken into account.[13,16]

As a continuation of our investigations on mixtures involving amides,[5−7,9] we report here LLE curves for DMF with hexane, heptane, octane, or nonane and for DMA with heptane. LLE data for DMF with decane,[17] hexadecane,[18] methylcyclohexane,[19] or 2-methylpentane[20] and for DMA with *n*-alkanes[21−26] (from pentane to nonane) are available in the literature. Results for the DMA + heptane system from different laboratories[23,26] differ substantially.

Table 1. Density, ρ, of Pure Compounds at 298.15 K and Atmospheric Pressure

compound	ρ/g·m^{-3} this work	ρ/g·m^{-3} literature
dimethylformamide	0.943875	0.94387[3]
dimethylacetamide	0.936214	0.936337[3]
hexane	0.655248	0.65484[3]
heptane	0.679627	0.67946[3]
octane	0.698636	0.69862[3]
nonane	0.714064	0.71375[3]

Experimental Section

Materials. DMF (puriss ≥ 99.5 %), DMA (puriss ≥ 99 %), hexane (puriss p.a. ≥ 99.5 %), heptane (puriss. p.a. ≥ 99.5 %), octane (purum ≥ 99 %), and nonane (purum ≥ 99 %) were from Fluka (purities expressed in mass fraction). Prior to the measurements, the chemicals were stored over molecular sieves (Union Carbide Type 4Å from Fluka). All these chemicals were used without other further treatment. The densities ρ at 298.15 K and atmospheric pressure were in good agreement with literature values (Table 1). The water contents, determined by the Karl Fischer method, were as follows (in mol %): 0.01, 0.02, 0.01, 0.02, 0.02, and 0.004 for DMF, DMA, hexane, heptane, octane, and nonane, respectively.

Apparatus and Procedure. Mixtures were prepared by mass, with weighing accurate to ± 0.00001 g, in Pyrex tubes of 0.9 cm i.d. and about 4 cm length, which then were immediately sealed by capping at atmospheric pressure and room temperature. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC in 1986.[27]

The coexistence curves of the binary mixtures were determined visually.[28−30] The samples in the sealed Pyrex tubes were placed in a thermostat bath a few hundredths of degree above the expected temperature, and the appearance of a second phase upon slow cooling (1.2 K·h^{-1}) was noted. The separation temperatures were reproducible to ± 0.02 K for temperatures near the upper critical solution temperature. The precision of the equilibrium composition is expected to be better than 0.0005 in mole fraction. The weighing technique gives a precision better

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Table 2. Experimental Liquid−Liquid Equilibrium Temperatures for *N*,*N*-Dialkylamide (1) + *n*-Alkane (2) Mixtures

x_1	T/K	x_1	T/K	x_1	T/K
Dimethylformamide (1) + *n*-Hexane (2)					
0.2958	335.24	0.4827	337.78	0.5754	337.52
0.3607	336.91	0.4852	337.60	0.5843	337.21
0.3818	337.24	0.5038	337.59	0.6173	336.71
0.4106	337.53	0.5268	337.83	0.6336	336.43
0.4503	337.73	0.5285	337.59	0.6547	335.64
0.4626	337.76	0.5342	337.78	0.6999	333.32
0.4745	337.58	0.5430	337.61		
Dimethylformamide (1) + *n*-Heptane (2)					
0.2648	336.67	0.4472	342.33	0.6181	342.22
0.3056	338.74	0.4880	342.48	0.6457	341.55
0.3529	340.56	0.5092	342.63	0.6915	340.28
0.3693	341.15	0.5446	342.56	0.6916	340.42
0.4034	341.76	0.5775	342.37	0.7489	337.31
0.4243	342.08	0.5984	342.30		
Dimethylformamide (1) + *n*-Octane (2)					
0.3619	344.71	0.4822	347.31	0.6045	347.34
0.3840	345.68	0.5062	347.18	0.6244	347.18
0.4016	346.12	0.5188	347.35	0.6748	346.78
0.4394	346.92	0.5502	347.26	0.7099	345.93
0.4581	346.91	0.5839	347.31	0.7132	345.99
0.4618	347.01	0.6012	347.35	0.7425	344.66
0.4803	347.11	0.6019	347.34		
Dimethylformamide (1) + *n*-Nonane (2)					
0.4144	350.31	0.5702	352.71	0.6788	352.41
0.4235	350.58	0.5720	352.66	0.6952	352.22
0.4555	351.44	0.5829	352.63	0.7081	351.98
0.4961	352.20	0.5974	352.71	0.7417	351.31
0.5138	352.39	0.5979	352.61	0.7471	351.12
0.5239	352.54	0.6276	352.58	0.7731	350.06
0.5516	352.66	0.6559	352.56	0.7967	348.67
0.5550	352.77	0.6687	352.55		
Dimethylacetamide (1) + *n*-Heptane (2)					
0.2235	305.20	0.4505	309.58	0.5949	309.08
0.2804	307.77	0.4988	309.69	0.6210	308.89
0.2970	308.07	0.5000	309.75	0.6517	308.17
0.3304	309.12	0.5327	309.48	0.6769	307.20
0.3578	309.40	0.5610	309.59	0.6913	306.52
0.3633	309.33	0.5741	309.43	0.7547	301.82
0.3974	309.46	0.5786	309.47		

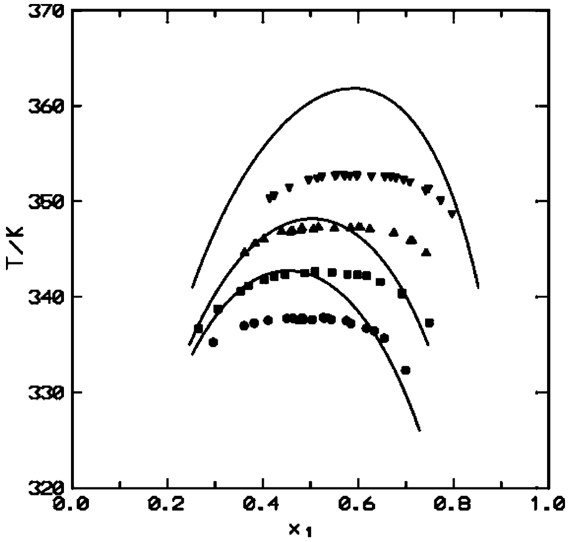

Figure 1. LLE of DMF (1) + *n*-alkanes (2) mixtures. Points, experimental results (this work): ●, *n*-hexane; ■, *n*-heptane; ▲, *n*-octane; ▼, *n*-nonane. Solid lines, DISQUAC calculations with interaction parameters from the literature[7] for systems with hexane, heptane, or nonane.

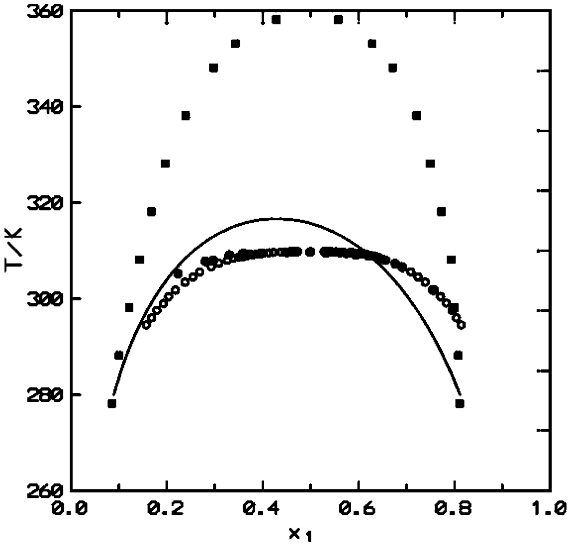

Figure 2. LLE of DMA (1) + *n*-heptane (2) mixture. Points, experimental results: ●, this work; ○, ref 23; ■, ref 26. Solid lines, DISQUAC calculations with interaction parameters from the literature.[7]

than 0.0001 in mole fraction, but this is reduced slightly due to partial evaporation of the more volatile component to the free volume of the ampule (≈1.17 cm^3).

The temperature was measured with a precision of ± 0.01 K and estimated accuracy of ± 0.1 K by a Hewlett-Packard model 2804A quartz thermometer calibrated on the basis of the ITS-90 scale of temperature using the triple point of the water.

Results

Table 2 lists the direct experimental results of the liquid−liquid equilibrium temperatures, T, versus the mole fraction of the amide, x_1, for the investigated mixtures (see also Figures 1 and 2). All the systems show an UCST. LLE coexistence curves have a rather horizontal top, and their symmetry depends on the size of the alkane (Figure 1).

The coordinates of the critical points, x_{1c} and T_c (Table 3), were obtained by reducing the experimental data with[31,32]

$$T/\mathrm{K} = T_c/\mathrm{K} + k|y - y_c|^m \tag{1}$$

where

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

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

In eqs 1 to 3, m, k, α, T_c, and x_{1c} are the coefficients to be fitted to the experimental results. When α = 1, eq 1 is similar to the well-known equation:[15,33,34]

$$\Delta\lambda = B\tau^{\beta} \tag{4}$$

where $\Delta\lambda_1 = \lambda_1' - \lambda_1''$ is the so-called order parameter, which can be any density variable in the conjugate phase (in our case $\lambda_1 = x_1$), τ is the reduced temperature $(T_c - T)/T_c$, and β is a critical exponent corresponding to this order parameter. The β value depends on the theory applied to its determination.[33,34] More details are given elsewhere.[35]

The fitting was developed using the Marquardt algorithm[36] with all the points weighted equally. Results are collected in Table 3. Also listed is the standard deviation defined by

$$(\sigma(T)/\mathrm{K}) = [\textstyle\sum(T_i^{\mathrm{exp}} - T_i^{\mathrm{cal}})^2/(N - n)]^{1/2} \tag{5}$$

where N and n stand for the number of data points and the number of fitted parameters, respectively. We note that eq 1 fits well the experimental data. For the DMA + heptane system,

Table 3. Coefficients in Equation 1 for the Fitting of the (x_1, T) Pairs Given in Table 2 for *N*,*N*-Dialkylamide (1) + *n*-Alkane (2) Mixtures[a]

N[b]	m	K	α	T_c/K	x_{1c}	σ/K
Dimethylformamide (1) + *n*-Hexane (2)						
20	3.30	−862	0.608	337.69	0.494	0.10
				(342.7)	(0.453)	
Dimethylformamide (1) + *n*-Heptane (2)						
17	2.78	−289	0.813	342.55	0.524	0.07
				(348.2)	(0.504)	
Dimethylformamide (1) + *n*-Octane (2)						
20	3.52	−849	0.820	347.30	0.558	0.08
				(355.6)	(0.556)	
Dimethylformamide (1) + *n*-Nonane (2)						
23	2.97	−370.	0.744	352.67	0.600	0.06
				(361.8)	(0.595)	
Dimethylacetamide (1) + *n*-Heptane (2)						
20	3.46	−598	0.889	309.64	0.476	0.10
				(315.7)	(0.431)	

[a] σ is the standard deviation defined by eq 5. DISQUAC values for the coordinates of the critical points, T_c and x_{1c}, calculated using the interaction parameters from the literature[7] and from Table 4 are given in parentheses. [b] Number of experimental data points.

we obtain $x_{1c} = 0.476$ and $T_c = 309.64$ K in good agreement with the values reported by Xuequin et al.[23] ($x_{1c} = 0.473$ and $T_c = 309.827$ K) and very different from those given by Marongiu[26] ($x_{1c} = 0.49$ and $T_c = 358.6$ K) (see Figure 2).

Discussion

For DMF systems, the UCST of the studied systems increases with the length chain of the *n*-alkane (Figure 3). The same behavior is observed in mixtures formed by *n*-alkane with, DMA,[21−25] NMP[5] (Figure 3), linear alkanone,[37] linear organic carbonate,[38] acetic anhydride;[39] alkoxyethanol,[35,40,41] or polyether.[42,43] Figure 1 shows that the LLE curves are progressively skewed to high x_1 values when the chain length of the alkane increases. A similar trend is encountered for many other mixtures.[21−25,35,37,38,40−43]

For a fixed *n*-alkane, we note that UCST (DMA) < UCST (DMF). That is, dipole−dipole interactions between amide molecules are stronger in the case of the DMF. This is supported by the fact that $\bar{\mu}(\mathrm{DMF}) = 1.60 > \bar{\mu}(\mathrm{DMA}) = 1.49$.[7] For the same reason, dipolar interactions are also stronger in NMP mixtures ($\bar{\mu}(\mathrm{NMP}) = 1.59$). Here, it should be also taken into account that in cyclic molecules the polar groups are less sterically hindered and dipole−dipole interactions between such molecules become stronger.

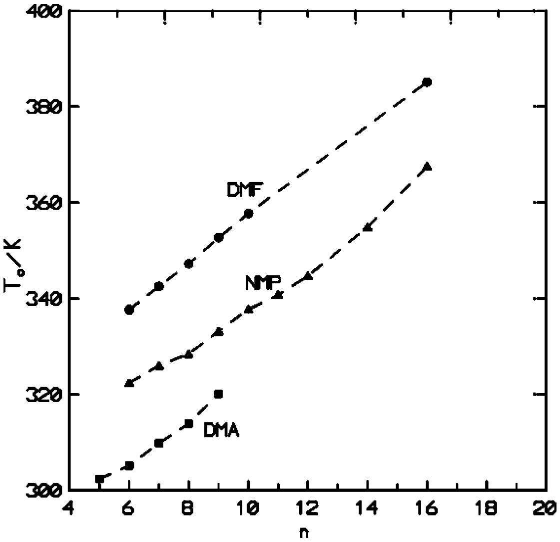

Figure 3. Upper critical solution temperatures (T_c) vs n, the number of carbon atoms in the *n*-alkane, for some amide + *n*-alkane mixtures. Values for systems with DMA were taken from refs 21 to 25. For NMP mixtures, see ref 5. Values for DMF + *n*-decane or + *n*-hexadecane were taken from refs 17 and 18, respectively.

In previous papers,[6,7] we have determined, in the framework of DISQUAC,[44] the interaction parameters for mixtures including DMF, DMA, diethylformamide (DEF), or dimethylpropanamide (DMPA) and different organic solvents (alkanes, benzene, toluene, alcohols). Here, we have used our LLE data, and those available in the literature that are consistent with them,[21−25] in order to re-adjust the first dispersive interaction parameters of systems containing DMA, DMPA, or DEF (Table 4). The remainder interaction parameters are the same to those reported in previous works.[6,7] Details of the fitting procedure have been elsewhere and will not be repeated here.[6] DISQUAC predictions on the coordinates of the critical points for the studied systems are shown in Table 3 (see also Figures 1 and 2). It should be noted that the theoretical calculations on the LLE are developed under the basic and wrong assumption that the molar excess

Table 4. Dispersive (DIS) and Quasichemical (QUAC) Interchange Coefficients (l = 1, Gibbs energy; l = 2, enthalpy, l = 3, heat capacity) for (s,n) Contacts in Tertiary Amide + Organic Solvent Mixtures

system[a]	contact (s,n)[b]	$C_{\mathrm{sn},1}^{\mathrm{DIS}}$	$C_{\mathrm{sn},2}^{\mathrm{DIS}}$	$C_{\mathrm{sn},3}^{\mathrm{DIS}}$	$C_{\mathrm{sn},1}^{\mathrm{QUAC}}$	$C_{\mathrm{sn},2}^{\mathrm{QUAC}}$	$C_{\mathrm{sn},3}^{\mathrm{QUAC}}$
DMA, DMPA, or DEF + *n*-C_n ($n \le 6$)	(a,n)	4.75	12.0	2	8	6	2
DMA, DMPA, or DEF + *n*-C_n ($n \ge 7$)	(a,n)	4.4	12.0	2	8	6	2
DEA + *n*-C_n ($n \le 6$)	(a,n)	4.75	10.3	2	8	6	2
DEA + *n*-C_n ($n \ge 7$)	(a,n)	4.4	10.3	2	8	6	2
DMA, DMPA, or DEF + c-C_n	(c,n)	4.85[c]	12.75	2	8	6	2
DMA + C_6H_6	(b,n)	2.4[c]	7.55	3.55	5	0.8	2
DMPA + C_6H_6	(b,n)	2.55[c]	7.12	3.55	5	0.8	2
DEF + C_6H_6	(b,n)	2.55	7.4	3.55	5	0.8	2
DMA + C_7 H_8	(p,n)	2.2[c]	7.33	3.55	5	0.8	2
DMPA + C_7H_8	(p,n)	2.4[c]	6.70	3.55	5	0.8	2
DEF + C_7H_8	(p,n)	2.4[c]	7.15	3.55	5	0.8	2
DMA + methanol	(h,n)	−3.2	5	7	−0.75	−2.2	−3
DMA + ethanol	(h,n)	−1.7	8.6	7	−0.75	−1.52	−3
DMA + 1-propanol	(h,n)	−1.7[c]	10	7	−0.75	−1.52	−3
DMA + 1-butanol	(h,n)	−1.7[c]	11	7	−0.75	−1.52	−3
DMA + 2-propanol	(h,n)	1.5[c]	10	7	−0.75	−1.52	−3
DMA + 2-butanol	(h,n)	1.5[c]	11	7	−0.75	−1.52	−3

[a] DMA, dimethylacetamide; DMPA, dimethylpropanamide; DEF, diethylformamide. [b] s = a, H, CH_3, or CH_2 in *n*-alkanes, methylcyclohexane, toluene, alkanols, or amides; s = b, C_6H_6; s = c, c-CH_2 in cyclohexane; s = h, OH in alkanols; s = p, C_6H_5 in toluene; n, N−CO in linear tertiary amides. [c] Estimated values.

Gibbs energy is an analytical function close to the critical point. This is an important shortcoming of any mean field theory, such as DISQUAC. In accord with the mentioned assumption, the model provides LLE curves, which are too high at the UCST and too low at the LCST (lower critical solution temperature).[15,45] So, the calculated UCSTs are higher than the experimental values.[1,5,7,39] Nevertheless, the coordinates of the critical points are represented in the correct range of temperature and composition (Table 3). The more rounded shape of the theoretical LLE curves (Figures 1 and 2) can be explained in similar terms as above.[7]

Conclusions

LLE coexistence curves were determined for mixtures of DMF with hexane, heptane, octane, or nonane and for DMA with heptane. For a given alkane, the UCST is higher for mixtures containing DMF. Dipolar interactions decrease in the sequence: DMF > NMP > DMA.

Literature Cited

(1) González, J. A.; Domanska, U. Thermodynamics of mixtures containing a very strongly polar compound. Part 1. Experimental phase equilibria (solid−liquid and liquid−liquid) for sulfolane + alkan-1-ols systems. Analysis of some mixtures including sulfolane in terms of DISQUAC. *Phys. Chem. Chem Phys.* **2001**, *3*, 1034−1042.

(2) Domanska, U.; González, J. A. Thermodynamics of mixtures containing a very strongly polar compound. Part II. Solid−liquid equilibria for sulfolane + nitrile systems and characterization of the sulfolane-nitrile and sulfolane-1-alkyne interactions in terms of DISQUAC. *Can. J. Chem.* **2002**, *80*, 476−482.

(3) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Techniques of Chemistry*, Vol. II; Weissberger, A., Ed.; Wiley: NewYork, 1986.

(4) González, J. A.; Villa, S.; Riesco, N.; García de la Fuente, I.; Cobos, J. C. Thermodynamics of mixtures containing a very strongly polar compound. IV. Application of the DISQUAC; UNIFAC and ERAS models to DMSO + organic solvent systems. *Phys. Chem. Liq.* **2003**, *41*, 583−597.

(5) González, J. A.; Domanska, U.; Lachwa, J. Thermodynamics of mixtures containing a very strongly polar compound. Part 3. DISQUAC characterization of NMP + organic solvent mixtures. *Can. J. Chem.* **2003**, *81*, 1451−1461.

(6) González, J. A.; Domanska, U.; Lachwa, J. Thermodynamics of mixtures containing a very strongly polar compound. 7. Isothermal VLE measurements for NMP + 2-propanol or + 2-butanol systems. DISQUAC and ERAS characterization of NMP or *N,N*-dialkylamide + 2-alkanol mixtures. Comparison with results from Dortmund UNIFAC. *Ind. Eng. Chem. Res.* **2005**, *44*, 5795−5804.

(7) González, J. A.; Cobos, J. C.; García de la Fuente, I. Thermodynamics of mixtures containing a very strongly polar compound. Part 6. DISQUAC characterization of *N,N*-dialkylamides. *Fluid Phase Equilib.* **2004**, *234*, 169−181.

(8) McClellan, A. L. *Tables of Experimental Dipole Moments*, Vols. 1−3; Rahara Enterprises: El Cerrito, US, 1974.

(9) González, J. A. Thermodynamics of mixtures containing a very strongly polar compound. V. Application of the extended real associated solution model to 1-alkanol + secondary amide mixtures. *Phys. Chem. Liq.* **2004**, *42*, 159−172.

(10) Bour, P.; Tam, C. N.; Sopková, J.; Trouw, F. R. Measurement and ab initio modelling of the inelastic neutron scattering of solid *N*-methylformamide. *J. Chem. Phys.* **1998**, *108*, 351−359.

(11) Eberhardt, E. S.; Raines, R. T. Amide−amide interactions and amide−water hydrogen bonds: implication for proteins folding and stability. *J. Am. Chem. Soc.* **1994**, *116*, 2149−2150.

(12) Blanco, B.; Sanz, M. T.; Beltrán, S.; Cabezas, J. L.; Coca, J. Vapor−liquid equilibria for the ternary system benzene + *n*-heptane + *N,N*-dimethylformamide at 101.33 kPa. *Fluid Phase Equilib.* **2000**, *175*, 117−124.

(13) Jorgensen, W. L.; Swenson, C. L. Optimized intermolecular potential functions for amides and peptides. Structure and properties of liquid amides. *J. Am. Chem. Soc.* **1985**, *107*, 569−578.

(14) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; Blackwell: Oxford, 1985.

(15) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworths: London, 1982.

(16) Ludwig, R. Cooperative hydrogen bonding in amides and peptides. *J. Mol. Liq.* **2000**, *84*, 65−75.

(17) Antosik, M.; Stafiej, A.; Stryjek, R. Mutual solubility of binary *trans*-decalin +, and *n*-decane + polar component mixtures. *Fluid Phase Equilib.* **1990**, *58*, 325−333.

(18) Rogalski, M.; Stryjek, R. Mutual solubility of *n*-hexadecane and polar compound systems. *Bull. Acad. Pol. Sci., Ser. Sci. Chim*. **1980**, *XXVIII*, 139−145.

(19) Bendová, M.; Rehák, K.; Matous, J.; Novák; J. P. Liquid−liquid equilibrium and excess enthalpies in the binary systems methylcyclohexane + methanol and methylcyclohexane + *N,N*-dimethylformamide. *J. Chem. Eng. Data* **2003**, *48*, 152−157.

(20) Bendová, M.; Rehák, K.; Matous, J.; Novák; J. P. Liquid−liquid equilibrium and excess enthalpies in the binary system 2-methylpentane + *N,N*-dimethylformamide. *J. Chem. Eng. Data* **2004**, *49*, 1318−1322.

(21) Xuequin, A.; Haihong, Z.; Fuguo, J.; Weiguo, S. The (liquid + liquid) critical phenomena of (a polar liquid + an *n*-alkane). III. Coexistence curves of *N,N*-dimethylacetamide + pentane). *J. Chem. Thermodyn.* **1995**, *27*, 1241−1247.

(22) Xuequin, A.; Weiguo, S.; Haijun, W.; Guokang, Z. J.; The (liquid + liquid) critical phenomena of (a polar liquid + an *n*-alkane). I. Coexistence curves of *N,N*-dimethylacetamide + hexane). *J. Chem. Thermodyn.* **1993**, *25*, 1373−1383.

(23) Xuequin, A.; Haihong, Z.; Fuguo, J.; Weiguo, S. The (liquid + liquid) critical phenomena of (a polar liquid + an *n*-alkane). V. Coexistence curves of *N,N*-dimethylacetamide + heptane). *J. Chem. Thermodyn.* **1996**, *28*, 1221−1232.

(24) Xuequin, A.; Weiguo, S. The (liquid + liquid) critical phenomena of (a polar liquid + an *n*-alkane). II. Coexistence curves of *N,N*-dimethylacetamide + octane). *J. Chem. Thermodyn.* **1994**, *26*, 461−468.

(25) Xuequin, A.; Haihong, Z.; Weiguo, S. The (liquid + liquid) critical phenomena of (a polar liquid + an *n*-alkane). IV. Coexistence curves of *N,N*-dimethylacetamide + nonane). *J. Chem. Thermodyn.* **1996**, *28*, 1165−1172.

(26) Marongiu, B. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1985**, *3*, 148−149.

(27) IUPAC Commission on Atomic Weights and Isotopic Abundances 1985. *Pure Appl. Chem.* **1986**, *58*, 1677.

(28) Loven, A. W.; Rice, O. K. Coexistence curve of the 2,6-lutidene + water system in the critical region. *Trans. Faraday Soc*. **1963**, *59*, 2723−2727.

(29) Young, C. L. Upper critical solution temperature of perfluoro-*n*-alkane and *n*-alkane mixtures. *Trans. Faraday Soc*. **1969**, *65*, 2639−2644.

(30) Snyder, R. B.; Eckert, C. A. Effect of third component on liquid−liquid critical point. *J. Chem. Eng. Data* **1973**, *18*, 282−285.

(31) Ott, J. B.; Holscher, I. F.; Schneider, G. M. (Liquid−liquid) phase equilibria in (methanol + heptane) and (methanol + octane) at pressures from 0.1 to 150 MPa. *J. Chem. Thermodyn.* **1986**, *18*, 815−826.

(32) Haarhaus, U.; Schneider, G. M. (Liquid−liquid) phase equilibria in (methanol + butane) and (methanol + pentane) at pressures from 0.1 to 140 MPa. *J. Chem. Thermodyn.* **1988**, *20*, 1121−1129.

(33) Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Clarendon Press: Oxford, 1971.

(34) Novak, J. P.; Matous, J.; Pick, J. *Liquid−Liquid Equilibria*; Elsevier: Amsterdam, 1987.

(35) Rubio, M. A.; González, J. A.; García de la Fuente, I.; Cobos, J. C. Thermodynamic properties of *n*-alkoxyethanols + organic solvents mixtures. VIII. Liquid−liquid equilibria of systems containing 2-methoxyethanol and alkanes (C_6H_{12} and CH_3-$(CH_2)_u$-CH_3, $u = 3, 4, 6, 8$). *Fluid Phase Equilib.* **1998**, *143*, 111−123.

(36) Bevington, P. R. *Data Reductions and Error Analysis for the Physical Sciences*; McGraw-Hill Book Co.: London, 1969.

(37) Messow, U.; Doyé, U.; Kuntzsch, S. Liquid−liquid equilibrium, excess enthalpies and excess volumes of some alkanone (C_3, C_4) + normal alkane (C_{10}, C_{12}, C_{14}, C_{16}) mixtures. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1979**, *1*, 151−158.

(38) González, J. A.; García, I.; Cobos, J. C.; Casanova, C. Thermodynamics of binary mixtures containing organic carbonates. 4. Liquid−liquid equilibria of dimethyl carbonate + selected *n*-alkanes. *J. Chem. Eng. Data* **1991**, *36*, 162−164.

(39) Aboy, M.; Villa, S.; Riesco, N.; González, J. A.; García de la Fuente, I.; Cobos, J. C. Liquid−liquid equilibria for acetic anhydride + selected alkanes. *J. Chem. Eng. Data* **2002**, *47*, 950−953.

(40) Rubio, M. A.; González, J. A.; García de la Fuente, I., Cobos, J. C. Thermodynamic properties of *n*-alkoxyethanols + organic solvent mixtures. IX. Liquid−liquid equilibria of systems containing 2-methoxyethanol or 2-ethoxyethanol and selected *n*-alkanes. *J. Chem. Eng. Data* **1998**, *43*, 811−814.

(41) Martínez, R.; González, J. A.; García de la Fuente, I.; Cobos, J. C. Thermodynamic properties of *n*-alkoxyethanols + organic solvent mixtures. XIV. Liquid−liquid equilibria of systems containing 2-(2-ethoxyethoxy)ethanol and selected alkanes. *J. Chem. Eng. Data* **2000**, *45*, 1036−1039.

(42) Treszczanowicz, T.; Cieœlak, D. (Liquid + liquid) equilibria in (a dimethyl ether of a polyethene glycol + an *n*-alkane). *J. Chem. Thermodyn.* **1993**, *25*, 661−665.
(43) Mozo, I.; González, I.; García de La Fuente, I.; Cobos, J. C. Thermodynamics of mixtures containing ethers. Part III. Liquid−liquid equilibria for 2,5,8,11-tetraoxadodecane or 2,5,8,11,14-pentaoxapentadecane + selected *n*-alkanes. *J. Chem. Eng. Data* **2004**, *49*, 1091−1094.
(44) Kehiaian, H. V. Thermodynamics of binary liquid organic mixtures. *Pure Appl. Chem.* **1985**, *57*, 15−30.
(45) De Pablo, J. J.; Prausnitz, J. M. Thermodynamics of liquid−liquid equilibria including the critical region. *AIChE J.* **1988**, *34*, 1595−1606.

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