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Thermodynamics of Mixtures Containing a Strongly Polar Compound. 9. Liquid−Liquid Equilibria for ε-Caprolactam + Selected Alkanes

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The coexistence curves of the liquid−liquid equilibria (LLE) for (ε-caprolactam + heptane), (ε-caprolactam + octane), (ε-caprolactam + nonane), (ε-caprolactam + decane), and (ε-caprolactam + 2,2,4-trimethylpentane) have been determined by critical opalescence with a laser scattering technique. All the curves show an upper critical solution temperature (UCST) and have a rather horizontal top, and their symmetry depends on the size of the alkane. The UCST increases almost linearly with the chain length of the alkane. For the octane mixture, the UCST is lower than for the solution including 2,2,4-trimethylpentane.

1. Introduction

We are engaged in a systematic investigation on the thermodynamic properties of mixtures containing a compound with a very high dipolar moment in the gas phase (μ), such as thiophene 1,1-dioxide[1,2] ($\mu = 16.04 \cdot 10^{-30}$ C·m[3]), dimethyl sulfoxide[4] ($\mu = 13.54 \cdot 10^{-30}$ C·m[3]), 1-methyl-2-pyrrolidinone[5,6] (NMP; $\mu = 13.64 \cdot 10^{-30}$ C·m[3]), *N*,*N*-dialkylamides[6,7] (*N*,*N*-dimethylmethanamide (DMF), $\mu = 12.28 \cdot 10^{-30}$ C·m;[8] *N*,*N*-dimethyltacetamide (DMA), $\mu = 12.37 \cdot 10^{-30}$ C·m[8]), *N*-alkylamides,[9] or propylene carbonate ($\mu = 16.49 \cdot 10^{-30}$ C·m[3]).

Amides, amino acids, peptides, and their derivatives are of interest because they are simple models in biochemistry. *N*-Methylmethanamide 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 that 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. On the other hand, DMF and NMP are used as highly selective extractants for the recovery of aromatic and saturated hydrocarbons from petroleum feedstocks,[12] and ε-caprolactam is used for the production of nylon 6, which is a polycaprolactam formed by a ring-opening polymerization.

From a theoretical point of view, amides are also a very interesting class of compounds. In the 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] 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 also be taken into account.[13,16] This is the case of ε-caprolactam, a cyclic secondary amide with a high dipole moment ($12.97 \cdot 10^{-30}$ C·m[8]).

As a continuation of our investigations on mixtures involving amides,[5−7,9,17] we report here LLE curves for (ε-caprolactam + heptane), (ε-caprolactam + octane), (ε-caprolactam + nonane), (ε-caprolactam + decane), and (ε-caprolactam + 2,2,4-trimethylpentane). As far as we know, no LLE data for these systems are available in the literature.

2. Experimental Section

2.1. Materials. Heptane (142-82-5, puriss p.a. ≥ 0.995); octane (11-65-9, puriss p.a. ≥ 0.99); nonane (111-84-2, puriss p.a. 0.99); decane (124-18-5, puriss p.a. ≥ 0.99); and 2,2,4-trimethylpentane (540-84-1, puriss p.a. ≥ 0.995) were from Fluka (purities expressed in mass fraction). ε-Caprolactam (106-60-2, puriss p.a. ≥ 0.99) was from Aldrich. Prior to the measurements, the chemicals were stored over molecular sieves (Union Carbide Type 4 Å 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 experimental values.[3] The fusion point of ε-caprolactam (342.21 K) measured in our laboratory is in excellent agreement with the value reported in the literature (342.3 K).[18] The water contents, determined by the Karl Fischer method, were as follows (in mass fraction): $2 \cdot 10^{-5}$ for heptane, octane, and ε-caprolactam; 10^{-5} for nonane and decane; and $5 \cdot 10^{-5}$ for 2,2,4-trimethylpentane.

2.2. Apparatus and Procedure. Mixtures were prepared by mass, with an uncertainty of ± 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.[19]

The coexistence curves of the binary mixtures were determined by the method of the critical opalescence. The samples in the sealed Pyrex tubes are placed in a thermostat bath a few hundredths of a degree above the expected temperature. A He−Ne laser is placed on one side of the equilibrium cell so that the light beam passing through the solution is focused on a light sensor. When decreasing the temperature slowly (1.2 K·h^{-1}), the growth of small drops of the dispersed liquid phase causes a diffusion of light during the transition. This results in

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a voltage variation, measured by a digital multimeter model Agilent 34410A connected to a PC, which allows simultaneous accurate measurements of the transition temperatures. The temperature was measured with a precision of ± 0.001 K and estimated uncertainty of ± 0.05 K by a Pt-1000 resistance connected to a multimeter model Philips PM2353, in such a way that the resistance variations upon cooling are also registered in a PC. The thermometer was 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 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 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 ($\approx$1.17 cm^3).

3. Results

Table 1 lists the direct experimental results of the liquid−liquid equilibrium temperatures T vs the mole fraction of the amide, x_1, for the investigated mixtures, and they are shown in Figure 1.

All the systems show an UCST. The LLE coexistence curves have a flat maximum, and their symmetry depends on the size of the alkane as shown in Figure 1.

The coordinates of the critical points, x_{1c} and T_c (Table 2), were obtained by reducing the experimental data with the equation[20,21]

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

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 $\alpha = 1$, eq 1 is similar to the well-known equation[15,22,23]

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

where $\Delta\lambda_1 = \lambda_1' - \lambda_2''$ 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.[22,23] More details are given elsewhere.[24]

The fitting was performed using the Marquardt algorithm[25] with all the points weighted equally. Results are collected in Table 2. Also listed is the standard deviation defined by

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

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.

Table 1. Experimental Liquid−Liquid Equilibrium Temperatures for ε-Caprolactam (1) + Alkane (2) Mixtures

x_1	T/K	x_1	T/K
	ε-Caprolactam (1) + Heptane (2)		
0.2691	346.47	0.4991	352.17
0.2952	348.31	0.5217	352.08
0.3188	349.57	0.5464	351.92
0.3459	350.69	0.5709	351.62
0.3690	351.29	0.5962	351.10
0.3968	351.72	0.6204	350.34
0.4207	352.00	0.6310	349.83
0.4452	352.14	0.6488	348.84
0.4700	352.21	0.6702	347.44
0.4977	352.18	0.6955	344.80
0.4978	352.11		
	ε-Caprolactam (1) + Octane (2)		
0.3058	349.77	0.4994	354.57
0.3260	350.88	0.5240	354.63
0.3479	351.98	0.5377	354.58
0.3614	352.57	0.5552	354.55
0.3777	353.17	0.5751	354.48
0.4007	353.72	0.5986	354.29
0.4139	354.02	0.6303	353.69
0.4264	354.30	0.6503	353.18
0.4457	354.36	0.6666	352.48
0.4618	354.55	0.6766	352.06
0.4772	354.58	0.6930	351.01
0.4788	354.56		
	ε-Caprolactam (1) + Nonane (2)		
0.3442	354.21	0.5715	358.60
0.3732	355.78	0.5865	358.56
0.3957	356.75	0.5963	358.57
0.4188	357.45	0.6221	358.45
0.4477	358.01	0.6455	358.14
0.4699	358.31	0.6551	357.99
0.5007	358.49	0.6725	357.62
0.5059	358.53	0.6820	357.30
0.5209	358.60	0.7062	356.20
0.5449	358.62	0.7207	355.41
0.5488	358.70		
	ε-Caprolactam (1) + Decane (2)		
0.3936	360.15	0.5565	363.41
0.4175	361.23	0.5756	363.43
0.4430	362.01	0.5957	363.45
0.4707	362.65	0.6042	363.45
0.4769	362.78	0.6160	363.39
0.4945	363.09	0.6459	363.32
0.4969	363.06	0.6711	363.06
0.4980	363.09	0.6971	362.59
0.5159	363.24	0.7207	361.65
0.5449	363.40	0.7421	360.76
	ε-Caprolactam (1) + 2,2,4-Trimethylpentane (2)		
0.3206	358.94	0.4999	362.34
0.3476	360.11	0.5052	362.35
0.3681	360.84	0.5213	362.35
0.3947	361.59	0.5315	362.31
0.3971	361.60	0.5460	362.27
0.4198	361.94	0.5765	362.06
0.4486	362.19	0.5951	361.80
0.4733	362.30	0.6222	361.21
0.4766	362.34	0.6472	360.26
0.4865	362.39	0.6717	358.93
0.4879	362.34		

4. Discussion

The UCST of the studied systems increases with the chain length of the n-alkane (Figure 2). The same behavior is observed in mixtures formed by n-alkane with DMF,[17] DMA,[26−30] and NMP[5] (Figure 2), linear alkanone,[31] linear organic carbonate,[32] acetic anhydride,[33] alkoxyethanol,[24,34,35] or polyether.[36,37] 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.[24,26−37] On the other hand, we note that UCST(2,2,4-trimethylpentane) > UCST(octane) (Table 2, Figure 1). UCST values of systems with the same solute and different isomeric alkanes strongly depend on the solute nature and size and shape of the alkanes. So, when methanol is mixed with isomeric hexanes, we have the following UCST values:[38] T = 313.42 K for hexane; T =

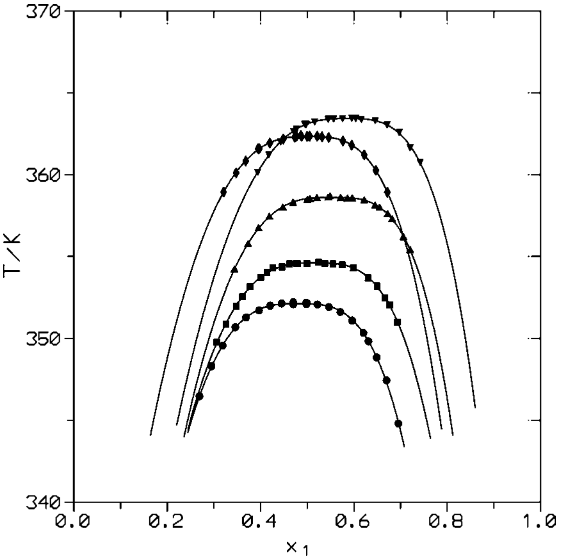

Figure 1. LLE of ε-caprolactam (1) + alkane (2) mixtures. Points, experimental results: ●, heptane; ■, octane; ▲, nonane; ▼, decane; ◆, 2,2,4-trimethylpentane. Solid lines, results from the fitting of eq 1.

Table 2. Coefficients in Equation 1 for the Fitting of the (x_1, T) Pairs Given in Table 1 for ε-Caprolactam (1) + Alkane (2) Mixtures[a]

N^b	m	K	α	T_c/K	x_{1c}	σ/K
		ε-Caprolactam (1) + Heptane (2)				
21	3.10	−811	0.830	352.13	0.482	0.06
		ε-Caprolactam (1) + Octane (2)				
23	3.05	−653	0.781	354.51	0.519	0.05
		ε-Caprolactam (1) + Nonane (2)				
21	3.18	−774	0.696	358.61	0.554	0.04
		ε-Caprolactam (1) + Decane (2)				
20	3.03	−560	0.657	363.43	0.586	0.04
		ε-Caprolactam (1) + 2,2,4-Trimethylpentane (2)				
21	2.93	−593	0.746	362.34	0.505	0.03

[a] σ is the standard deviation defined by eq 5. [b] Number of experimental data points.

304.05 K for 2-methylpentane; T = 293.02 K for 2,2-dimethylbutane; and T = 299.20 K for 2,3-dimethylbutane. In the case of 2-methoxyethanol solutions,[39] the UCST is T = 327.94 K and T = 322.41 K for the mixtures including octane and 2,2,4-trimethylpentane, respectively. In systems with polystyrene1241,[40] the UCST is T = 285.2 K for the octane mixture and T = 262.2 K for that including 2,2,4-trimethylpentane. For the same solute and isomeric hexanes, we have T = 274.9 K for hexane, T = 278.2 K for 2,2,dimethylbutane, and T = 310.4 K for 2,3-dimethylbutane. The UCST values are T = 322.41 K, T = 327.60 K, and T = 319.22 K when NMP is mixed with hexane,[41] 2,2-dimethylbutane,[42] or 2,3-dimethylbutane,[42] respectively.

Finally, it is interesting to note that interactions between amide molecules are stronger in ε-caprolactam systems than in those mixtures including tertiary *N*,*N*-dialkylamides (DMF, DMA, NMP), as is indicated by the higher UCSTs of the former solutions shown in Figure 2. This may be due to the existence of H-bonds between ε-caprolactam molecules.

5. Conclusions

LLE coexistence curves were determined for mixtures of ε-caprolactam with hexane, heptane, octane, nonane, decane, or 2,2,4-trimethylpentane. The UCST increases almost linearly with the chain length of the *n*-alkane and is higher for the solution including 2,2,4-trimethylpentane than for the octane system.

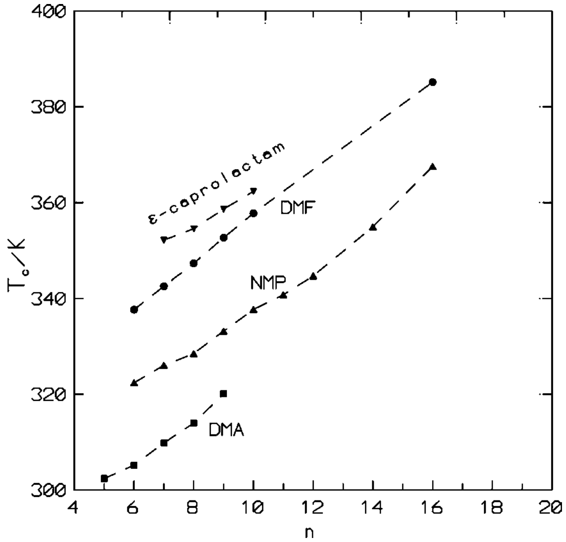

Figure 2. Upper critical solution temperatures T_c vs n, the number of carbon atoms in the n-alkane, for some amide + n-alkane mixtures. Values for systems with DMA were taken from refs 26 to 30. For NMP mixtures, see ref 5, and for DMF solutions, see refs 17, 43, and 44.

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*; Weissberger, A., Ed.; Wiley: NewYork, 1986; Vol. II.

(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*; Rahara Enterprises: El Cerrito, US, 1974; Vols. 1, 2, 3.

(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) Lobos, J.; Mozo, I.; Fernández Regúlez, M.; González, J. A.; García de la Fuente, I.; Cobos, J. C. Thermodynamics of mixtures containing a strongly polar compound. 8. Liquid-liquid equilibria for N, N-dialkylamide + selected N-alkanes. *J. Chem. Eng. Data* **2006**, *51*, 623–627.

(18) Kozyro, A. A.; Marachuk, L. I.; Krasulin, A. P.; Yursha, I. A.; Kabo, G. Ya. Thermodynamic properties of cyclohexanone oxime and ε-caprolactam. *J. Appl. Chem. USSR* **1989**, *62*, 547–550.

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

(20) 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.

(21) 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.

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

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

(24) 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.

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

(26) 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.

(27) 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.

(28) 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.

(29) 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.

(30) 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.

(31) 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.

(32) 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.

(33) 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.

(34) 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.

(35) 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.

(36) Treszczanowicz, T.; Cieślak, D. (Liquid + liquid) equilibria in (a dimethyl ether of a polyethene glycol + an n-alkane). *J. Chem. Thermodyn.* **1993**, *25*, 661–665.

(37) Mozo, I.; González, J. A.; 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.

(38) Trejo, A.; Yañez, P.; Eustaquio-Rincón, R. Liquid-liquid coexistence curves for binary systems: methanol + cyclohexane and + several isomers of hexane. *J. Chem. Eng. Data* **2006**, *51*, 1070–1075.

(39) Carmona, F. J.; González, J. A.; García de la Fuente, I.; Cobos, J. C. Thermodynamic properties of n-alkoxyethanols + organic solvent mixtures. X. Liquid-liquid equilibria of systems containing 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol or 2-(2-ethoxyethoxy)ethanol and selected alkanes. *J. Chem. Eng. Data* **1999**, *44*, 892–895.

(40) Imre, A. R.; Van Hook, W. A. The effect of branching of alkanes on the liquid-liquid equilibrium of oligostyrene/alkane systems. *Fluid Phase Equilib.* **2001**, *187*−*188*, 363–372.

(41) Eustaquio-Rincón, R.; Molnar, R.; Trejo, A. Liquid-liquid miscibility for binary systems: N-methylpyrrolidone + *n*-alkane and propanenitrile + n-alkane. *Fluid Phase Equilib.* **1991**, *68*, 187–195.

(42) Eustaquio-Rincón, R.; Romero-Martínez, A.; Trejo, A. Liquid-liquid miscibility curves for binary systems: N-methylpyrrolidone with several hydrocarbon isomers. *Fluid Phase Equilib.* **1993**, *91*, 187–201.

(43) 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.

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

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