Densities and Isothermal Compressibilities at Pressures up to 20 MPa of the Systems 1-Methyl-2-pyrrolidone + 1-Chloroalkane or + α,ω-Dichloroalkane

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Densities of pure 1-methyl-2-pyrrolidone were measured at (288.15, 298.15, 308.15, and 318.15) K at pressures up to 20 MPa, and from them isothermal compressibilities were obtained. Densities for 1-methyl-2-pyrrolidone + 1-chlorobutane, or + 1-chlorohexane, or + 1-chlorooctane, or + 1,2-dichloroethane, or + 1,4-dichlorobutane, or + 1,6-dichlorohexane at 298.15 K and at pressures up to 20 MPa were measured, and isothermal compressibilities were obtained.

Introduction

To continue with the systematic study of thermodynamic properties of mixtures containing amides and chloroalkanes,[1,2] we present here the densities, ρ, at 298.15 K and at pressures up to 20 MPa of 1-methyl-2-pyrrolidone + 1-chlorobutane, or + 1-chlorohexane, or + 1-chlorooctane, or + 1,2-dichloroethane, or + 1,4-dichlorobutane, or + 1,6-dichlorohexane. This work is part of research to study the intermolecular interactions present in mixtures such as amide + 1-chloroalkane, or + α,ω-dichloroalkane; these interactions could be dipolar as those in the pure 1-chloroalkanes and amides and also acceptor−donor interactions present in the mixtures of these compounds.

Densities, ρ, of the pure liquids (1-methyl-2-pyrrolidone, 1-chlorobutane,[1] 1-chlorohexane,[1] 1-chlorooctane,[1] 1,2-dichloroethane,[2] 1,4-dichlorobutane,[2] and 1,6-dichlorohexane[2]) were measured at (288.15, 298.15, 308.15, and 318.15) K at pressures up to 20 MPa, and from them thermal expansion coefficients, α, were derived.

Isothermal compressibilities, κ_T, of the pure liquids and their mixtures were calculated, and the excess isothermal compressibilities, κ_T^E, of the mixtures were derived. As far as we know, there are no previous densities, ρ, and isothermal compressibilities, κ_T, on these mixtures in the literature, but other properties are published.[3,4]

Experimental section

Materials. 1-Methyl-2-pyrrolidone (mole fraction purity > 99.5 %) and 1-chlorobutane (mole fraction purity ≥ 99.8 %) were obtained from Riedel-de Häen; 1-chlorohexane (mole fraction purity of 99 %) and 1,6-dichlorohexane (mole fraction purity of 98 %) were obtained from Aldrich Chem. Co.; 1-chlorooctane (mole fraction purity > 98 %), 1,2-dichloroethane (mole fraction purity > 99.5 %), and 1,4-dichlorobutane (mole fraction purity > 97 %) were obtained from Fluka AG Buchs. All the purities are given by the supplier, and the liquids were used without further purification.

In Table 1, the measured densities, ρ, and isothermal compressibilities, κ_T, are compared with literature values. As can be seen, there is a good agreement between our values and those from the literature, even though the differences found are higher for isothermal compressibilities, κ_T, than for densities, ρ.

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Apparatus and Procedure. The mixtures were prepared by mass, and the mole fraction uncertainty was estimated to be less than ± 10^{-4}. The densities, ρ, of the pure components were measured at (288.15, 298.15, 308.15, and 318.15) K at pressures up to 20 MPa. For binary mixtures, experimental densities were measured at 298.15 K at pressures up to 20 MPa. The measured densities were determined with a vibrating-tube densimeter with a DMA 512 high-pressure cell. High pressures were generated by a liquid pump (model LC-10 AT of Shimadzu).

The vibrating-tube temperature, T, measured using an Anton-Paar CKT 100 digital thermometer, was stable to better than ± 0.01 K using a Grant LT D6G thermostat. Pressures, p, were measured with a pressure gauge from Druck (model DPI 145 (0 to 20) MPa, uncertainty 0.005 % full scale).

The forced path mechanical calibration model[15] was used to calibrate the densimeter. 1,2-Dichloroethane[13] was used as a reference liquid for calibration purposes. This liquid was chosen because it is widely studied in the literature and because its density, ρ, is higher than the values of density, ρ, studied in our research. The uncertainty of the reported densities was estimated to be 10^{-4} g·cm^{-3}.

Results and Discussion

Some of the measured densities, ρ, for 1-methyl-2-pyrrolidone at (288.15, 298.15, 308.15, and 318.15) K and at pressures, p, up to 20 MPa are reported in Table 2. Some of the isothermal compressibilities, κ_T

$$\kappa_T = \rho^{-1}(\delta\rho/\delta P)_T \quad (1)$$

obtained at (288.15, 298.15, 308.15, and 318.15) K for the cyclic amide are given in Table 2. The complete set of densities, ρ, and isothermal compressibilities, κ_T, is given as Supporting Information. Density data were fitted to second-order equations, and analytical differentiation was done to obtain the isothermal compressibilities. The uncertainty of the reported isothermal compressibilities was estimated to be ± 10^{-6} MPa^{-1}. The isothermal compressibility values, κ_T, obtained for the cyclic amide at (288.15, 298.15, 308.15, and 318.15) K are represented against pressure in Figure 1. The isothermal compressibilities, κ_T, obtained for 1-chloroalkanes and α,ω-dichloroalkanes at 298.15 K are represented against pressure in previous works.[1,2] For given values of p and T, for example, 20 MPa and 298.15 K, the density, ρ, of 1-methyl-2-pyrrolidone, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, 1-chloroalkanes, and

10.1021/je7003758 CCC: $40.75
Published on Web 12/04/2007

Table 1. Densities, ρ, and Calculated Isothermal Compressibility Values, κ_T, for the Pure Components and Those from the Literature

1-Methyl-2-pyrrolidone					
	ρ/(g·cm^{-3})			$10^4\kappa_T$/MPa^{-1}	
P/MPa	exptl	lit.		exptl	lit.
		T = 288.15 K			
0.1	1.0367	1.0370[5]		4.98	4.96[5]
1	1.0372	1.0375[5]		4.95	4.94[5]
5	1.0392	1.0386[6]	1.0396[7]	4.83	4.84[5]
10	1.0417	1.0411[6]	1.0420[7]	4.67	4.72[5]
15	1.0441	1.0436[6]	1.0445[7]	4.52	4.61[5]
20	1.0464	1.0461[6]	1.0469[7]	4.37	4.51[5]
		T = 298.15 K			
0.1	1.0280	1.0282[7]		5.23	5.22[5]
1	1.0284	1.0287[7]		5.20	5.19[5]
5	1.0305	1.0309[5]	1.0297[6]	5.05	5.08[5]
10	1.0331	1.0335[5]	1.0324[6]	4.87	4.96[5]
15	1.0355	1.0361[5]	1.0350[6]	4.69	4.84[5]
20	1.0379	1.0386[5]	1.0375[6]	4.51	4.72[5]
		T = 308.15 K			
0.1	1.0193	1.0193[5]		5.33	5.50[5]
1	1.0198	1.0198[5]		5.30	5.48[5]
5	1.0218	1.0220[5]	1.0209[6]	5.16	5.36[5]
10	1.0246	1.0247[5]	1.0237[6]	4.99	5.22[5]
15	1.0270	1.0275[5]	1.0264[6]	4.82	5.08[5]
20	1.0294	1.0301[5]	1.0291[6]	4.66	4.96[5]
		T = 318.15 K			
0.1	1.0110	1.0106[5]		5.88	5.83[5]
1	1.0114	1.0111[5]		5.84	5.80[5]
5	1.0138	1.0135[5]	1.0121[6]	5.68	5.67[5]
10	1.0166	1.0164[5]	1.0150[6]	5.48	5.51[5]
15	1.0194	1.0192[5]	1.0179[6]	5.28	5.36[5]
20	1.0220	1.0219[5]	1.0206[6]	5.09	5.22[5]
		1-Chlorobutane			
		T = 298.15 K			
0.1	0.8806	0.88075[8]		12.05	12.13[9]
		1-Chlorohexane			
		T = 298.15 K			
0.1	0.8731	0.87333[8]		10.16	10.07[10]
		1-Chlorooctane			
		T = 298.15 K			
0.1	0.8688	0.86883[11]		8.98	
		1,2-Dichloroethane			
		T = 288.15 K			
0.1				7.32	7.63[7]
10				6.88	7.09[7]
20				6.46	6.63[7]
		T = 298.15 K			
0.1	1.2455	1.24598[7]	1.2456[13]	7.97	8.12[7]
10	1.2551	1.2555[12]		7.53	7.57[7]
20				7.09	7.09[7]
		1,4-Dichlorobutane			
		T = 298.15 K			
0.1	1.1337	1.1333[14]		6.90	
		1,6-Dichlorohexane			
		T = 298.15 K			
0.1	1.0638	1.0637[14]		6.44	

α,ω-dichloroalkanes studied in previous works[1,2] decreases following the sequence 1,2-dichloroethane[2] > 1,4-dichlorobutane[2] > 1,6-dichlorohexane[2] > 1-methyl-2-pyrrolidone > *N*,*N*-dimethylformamide[1] > *N*,*N*-dimethylacetamide[1] > 1-chlorobutane[1] > 1-chlorohexane[1] > 1-chlorooctane,[1] and the isothermal compressibility, κ_T, decreases following the sequence 1-chlorobutane[1] > 1-chlorohexane[1] > 1-chlorooctane[1] > 1,2-dichloroethane[2] > 1,4-dichlorobutane[2] > 1,6-dichlorohexane[2] > *N*,*N*-dimethylformamide[1] > *N*,*N*-dimethylacetamide[1] > 1-methyl-2-pyrrolidone. From the experimental values, it can be observed that the isothermal compressibility, κ_T, decreases as the length of the aliphatic chain of the linear amides, 1-chloroalkanes, and α,ω-dichloroalkanes increases.

Table 2. Experimental Values of Density, ρ, and Calculated Isothermal Compressibility, κ_T, for the Pure 1-Methyl-2-pyrrolidone Studied at Pressure, p, and Temperature, T

1-Methyl-2-pyrrolidone					
T = 288.15 K			T = 298.15 K		
p/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}	p/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}
0.1	1.0368	4.98	0.1	1.0280	5.23
2.0	1.0377	4.92	2.0	1.0289	5.16
4.0	1.0387	4.86	4.0	1.0300	5.09
6.0	1.0396	4.80	5.9	1.0310	5.02
8.0	1.0407	4.74	8.0	1.0320	4.94
10.0	1.0417	4.67	10.0	1.0331	4.87
12.1	1.0427	4.61	12.0	1.0341	4.80
14.0	1.0436	4.55	14.0	1.0351	4.72
16.0	1.0445	4.49	16.0	1.0360	4.65
18.0	1.0454	4.43	17.9	1.0370	4.59
20.0	1.0464	4.37	20.0	1.0379	4.51
T = 308.15 K			T = 318.15 K		
p/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}	p/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}
0.1	1.0193	5.33	0.1	1.0110	5.88
2.0	1.0203	5.26	2.0	1.0121	5.80
4.0	1.0214	5.20	4.0	1.0132	5.72
6.0	1.0224	5.13	6.0	1.0144	5.64
8.1	1.0235	5.06	8.0	1.0155	5.56
10.0	1.0246	4.99	10.0	1.0166	5.48
12.0	1.0255	4.92	12.0	1.0178	5.40
14.0	1.0265	4.86	14.0	1.0188	5.32
16.0	1.0275	4.79	16.0	1.0199	5.25
18.0	1.0285	4.73	18.0	1.0210	5.17
20.0	1.0294	4.66	20.0	1.0220	5.09

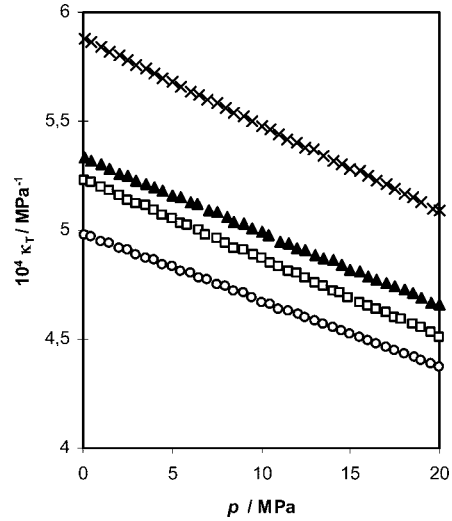

Figure 1. Isothermal compressibility, κ_T, of 1-methyl-2-pyrrolidone plotted against pressure at: ○, T = 288.15 K; □, T = 298.15 K; △, T = 308.15 K; ×, T = 318.15 K.

The thermal expansion coefficient, α, for 1-methyl-2-pyrrolidone is obtained by using the following equation

$$\alpha = -\rho^{-1}(\delta\rho/\delta T)_P \quad (2)$$

Density data were fitted to a second-order equation, and analytical differentiation was done to obtain the thermal expansion

Table 3. Experimental Values of Density, ρ, and Calculated Isothermal Compressibility, κ_T, for the Studied Mixtures at Pressure, p, and 298.15 K

p/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}	p/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}	p/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}
1-Methyl-2-pyrrolidone (x) + 1-Chlorobutane ($1-x$)								
	$x = 0.1004$			$x = 0.2002$			$x = 0.2974$	
0.1	0.8966	10.85	0.1	0.9120	10.07	0.1	0.9268	8.96
2.0	0.8984	10.67	2.0	0.9136	9.90	2.0	0.9284	8.85
4.0	0.9003	10.48	4.0	0.9154	9.71	4.0	0.9300	8.72
6.0	0.9021	10.29	5.9	0.9171	9.54	6.0	0.9317	8.60
7.9	0.9039	10.11	8.0	0.9189	9.35	8.0	0.9333	8.48
10.0	0.9058	9.90	10.0	0.9207	9.15	9.9	0.9348	8.37
12.0	0.9076	9.72	12.0	0.9224	8.97	11.9	0.9363	8.25
14.1	0.9095	9.52	14.1	0.9241	8.79	14.0	0.9378	8.13
16.0	0.9111	9.35	16.0	0.9256	8.62	16.0	0.9394	8.01
18.0	0.9127	9.17	18.0	0.9271	8.44	18.0	0.9408	7.89
20.0	0.9145	8.98	20.0	0.9287	8.26	20.0	0.9426	7.77
	$x = 0.4000$			$x = 0.5052$			$x = 0.6019$	
0.1	0.9422	8.38	0.1	0.9575	7.66	0.1	0.9717	7.00
2.0	0.9436	8.28	2.0	0.9589	7.57	2.0	0.9730	6.93
4.0	0.9451	8.17	4.0	0.9603	7.48	3.9	0.9742	6.86
6.0	0.9467	8.06	6.0	0.9618	7.38	6.0	0.9756	6.78
8.0	0.9483	7.95	8.0	0.9632	7.29	8.0	0.9769	6.71
10.0	0.9498	7.84	10.0	0.9647	7.19	10.0	0.9783	6.64
12.0	0.9512	7.73	12.0	0.9660	7.10	12.0	0.9796	6.57
13.9	0.9527	7.63	14.0	0.9674	7.01	14.1	0.9810	6.49
16.0	0.9541	7.52	16.0	0.9687	6.91	16.0	0.9821	6.43
18.1	0.9556	7.40	18.0	0.9700	6.82	18.1	0.9834	6.35
20.0	0.9570	7.30	20.0	0.9714	6.73	20.0	0.9846	6.28
	$x = 0.7039$			$x = 0.8011$			$x = 0.9002$	
0.1	0.9862	6.48	0.1	1.0001	6.05	0.1	1.0143	5.62
2.0	0.9874	6.41	2.0	1.0012	5.98	2.0	1.0153	5.56
4.0	0.9887	6.34	4.0	1.0024	5.92	4.0	1.0165	5.49
6.0	0.9900	6.28	6.0	1.0036	5.85	6.0	1.0176	5.43
7.9	0.9911	6.21	8.0	1.0048	5.79	8.0	1.0187	5.36
10.0	0.9924	6.14	10.1	1.0061	5.72	10.0	1.0198	5.29
12.0	0.9936	6.08	12.0	1.0071	5.66	12.0	1.0209	5.23
14.0	0.9948	6.01	14.0	1.0082	5.60	14.0	1.0220	5.16
16.0	0.9960	5.94	16.0	1.0093	5.53	16.0	1.0230	5.10
18.0	0.9972	5.88	18.0	1.0105	5.47	18.0	1.0240	5.03
20.0	0.9984	5.81	20.0	1.0116	5.41	20.0	1.0251	4.96
1-Methyl-2-pyrrolidone (x) + 1-Chlorohexane ($1-x$)								
	$x = 0.1003$			$x = 0.1988$			$x = 0.3050$	
0.1	0.8849	9.45	0.1	0.8970	8.95	0.1	0.9110	8.67
2.0	0.8864	9.29	2.0	0.8984	8.83	1.9	0.9123	8.53
4.0	0.8880	9.13	4.0	0.9000	8.71	4.1	0.9140	8.36
5.9	0.8896	8.97	6.0	0.9016	8.58	6.0	0.9154	8.22
8.0	0.8912	8.81	8.0	0.9031	8.46	8.0	0.9170	8.06
10.0	0.8929	8.64	10.0	0.9047	8.33	10.0	0.9186	7.91
12.0	0.8943	8.48	12.0	0.9062	8.21	12.0	0.9199	7.76
14.0	0.8959	8.33	14.0	0.9077	8.09	14.0	0.9213	7.61
16.0	0.8974	8.17	16.0	0.9090	7.97	16.0	0.9227	7.46
18.0	0.8988	8.02	18.0	0.9105	7.85	18.0	0.9240	7.32
20.0	0.9003	7.86	20.0	0.9120	7.72	20.0	0.9254	7.16
	$x = 0.4005$			$x = 0.5007$			$x = 0.5974$	
0.1	0.9242	8.03	0.1	0.9389	7.50	0.1	0.9541	7.02
2.0	0.9256	7.92	2.0	0.9402	7.40	2.0	0.9553	6.94
4.0	0.9271	7.80	4.0	0.9416	7.31	4.0	0.9566	6.85
6.0	0.9286	7.68	6.0	0.9430	7.21	6.0	0.9580	6.76
8.0	0.9299	7.57	8.0	0.9443	7.12	8.0	0.9592	6.67
10.0	0.9314	7.45	10.0	0.9457	7.02	10.0	0.9605	6.58
12.0	0.9328	7.33	11.9	0.9470	6.93	12.0	0.9618	6.49
14.0	0.9341	7.22	13.9	0.9483	6.84	14.0	0.9631	6.41
16.0	0.9354	7.11	16.0	0.9496	6.74	15.9	0.9642	6.33
18.0	0.9367	7.00	18.0	0.9508	6.65	18.0	0.9654	6.24
20.0	0.9382	6.88	20.0	0.9522	6.55	20.0	0.9667	6.15
	$x = 0.7016$			$x = 0.8002$			$x = 0.8995$	
0.1	0.9715	6.52	0.1	0.9887	6.14	0.1	1.0074	5.67
2.0	0.9727	6.45	2.0	0.9898	6.08	2.0	1.0084	5.61
4.0	0.9740	6.39	4.0	0.9910	6.01	4.0	1.0096	5.56
6.0	0.9752	6.32	6.0	0.9922	5.94	6.0	1.0107	5.50
8.0	0.9764	6.26	8.0	0.9933	5.87	8.0	1.0118	5.45
9.9	0.9777	6.19	10.0	0.9945	5.80	10.0	1.0129	5.39

Table 3. (continued)

p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}	p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}	p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}
				1-Methyl-2-pyrrolidone (x) + 1-Chlorohexane ($1-x$)				
11.9	0.9789	6.13	12.0	0.9957	5.73	12.0	1.0140	5.33
14.0	0.9801	6.06	14.0	0.9968	5.66	14.0	1.0151	5.28
16.0	0.9813	6.00	16.1	0.9980	5.59	16.0	1.0161	5.22
18.0	0.9823	5.94	18.0	0.9990	5.53	18.0	1.0171	5.17
20.0	0.9838	5.87	20.0	1.0002	5.46	20.0	1.0183	5.11
				1-Methyl-2-pyrrolidone (x) + 1-Chlorooctane ($1-x$)				
	$x = 0.0969$			$x = 0.2014$			$x = 0.3097$	
0.1	0.8780	8.59	0.1	0.8888	8.19	0.1	0.9012	7.80
2.0	0.8794	8.48	2.0	0.8902	8.09	2.0	0.9025	7.73
4.0	0.8808	8.36	4.0	0.8916	7.99	4.0	0.9040	7.65
6.0	0.8823	8.24	6.0	0.8931	7.89	6.0	0.9054	7.58
7.9	0.8837	8.13	8.0	0.8944	7.80	8.0	0.9067	7.50
10.0	0.8853	8.00	10.0	0.8959	7.69	10.0	0.9081	7.43
11.9	0.8866	7.88	12.0	0.8973	7.60	12.0	0.9095	7.35
14.0	0.8881	7.76	13.9	0.8985	7.50	14.0	0.9108	7.28
16.0	0.8894	7.64	16.0	0.8999	7.40	16.0	0.9121	7.21
18.0	0.8907	7.53	18.0	0.9012	7.31	18.0	0.9134	7.13
20.0	0.8921	7.41	20.0	0.9026	7.21	20.0	0.9147	7.06
	$x = 0.4076$			$x = 0.5021$			$x = 0.6022$	
0.1	0.9136	7.54	0.1	0.9269	7.40	0.1	0.9425	6.89
2.0	0.9149	7.46	2.0	0.9282	7.30	2.0	0.9437	6.81
4.0	0.9163	7.38	4.0	0.9295	7.19	4.0	0.9450	6.72
6.0	0.9176	7.30	5.9	0.9308	7.10	6.0	0.9463	6.63
8.0	0.9189	7.22	8.0	0.9321	6.99	8.0	0.9475	6.55
10.0	0.9204	7.14	10.0	0.9335	6.88	10.0	0.9488	6.46
12.0	0.9216	7.06	12.0	0.9348	6.78	12.0	0.9501	6.37
14.0	0.9229	6.98	14.0	0.9360	6.68	14.0	0.9512	6.29
16.0	0.9242	6.91	15.9	0.9372	6.59	16.0	0.9524	6.20
18.0	0.9255	6.83	18.0	0.9384	6.48	18.0	0.9535	6.12
20.1	0.9268	6.74	20.0	0.9398	6.38	20.0	0.9548	6.03
	$x = 0.7005$			$x = 0.8007$			$x = 0.9008$	
0.1	0.9598	6.55	0.1	0.9796	6.16	0.1	1.0022	5.81
2.0	0.9609	6.48	2.0	0.9807	6.09	2.0	1.0032	5.73
4.0	0.9622	6.41	4.0	0.9819	6.01	4.0	1.0044	5.66
6.0	0.9634	6.34	6.0	0.9831	5.93	6.0	1.0055	5.58
8.0	0.9646	6.27	8.0	0.9842	5.85	8.0	1.0066	5.51
10.0	0.9659	6.19	9.9	0.9854	5.77	10.0	1.0078	5.43
12.0	0.9670	6.12	12.0	0.9865	5.69	12.0	1.0088	5.36
14.0	0.9682	6.05	14.0	0.9877	5.61	14.0	1.0099	5.28
15.9	0.9693	5.99	16.0	0.9887	5.53	16.0	1.0110	5.21
18.0	0.9704	5.91	18.0	0.9897	5.45	18.0	1.0120	5.13
20.0	0.9717	5.84	20.1	0.9910	5.37	20.0	1.0132	5.06
				1-Methyl-2-pyrrolidone (x) + 1,2-Dichloroethane ($1-x$)				
	$x = 0.0993$			$x = 0.2025$			$x = 0.3012$	
0.1	1.2204	7.41	0.1	1.1953	7.05	0.1	1.1723	6.80
2.0	1.2221	7.32	2.0	1.1969	6.98	2.0	1.1737	6.73
4.0	1.2239	7.23	4.0	1.1985	6.91	4.0	1.1753	6.64
6.0	1.2257	7.13	6.0	1.2002	6.84	6.0	1.1769	6.56
8.0	1.2274	7.04	8.0	1.2018	6.77	8.0	1.1784	6.48
10.0	1.2292	6.94	10.0	1.2036	6.69	9.9	1.1800	6.39
12.0	1.2308	6.85	12.0	1.2051	6.62	12.0	1.1815	6.31
14.0	1.2325	6.76	14.0	1.2066	6.55	14.0	1.1830	6.23
16.0	1.2342	6.66	15.9	1.2082	6.49	16.0	1.1844	6.15
18.0	1.2358	6.57	18.0	1.2098	6.41	18.0	1.1858	6.07
20.0	1.2375	6.48	20.0	1.2114	6.34	20.0	1.1874	5.98
	$x = 0.4029$			$x = 0.4975$			$x = 0.5832$	
0.1	1.1492	6.43	0.1	1.1283	6.18	0.1	1.1100	5.97
2.0	1.1506	6.37	2.0	1.1296	6.13	2.0	1.1112	5.91
4.0	1.1520	6.31	4.0	1.1310	6.08	4.0	1.1125	5.84
6.0	1.1535	6.25	6.0	1.1324	6.02	6.0	1.1138	5.78
8.0	1.1549	6.18	7.9	1.1337	5.97	8.0	1.1150	5.71
10.0	1.1564	6.12	9.9	1.1350	5.91	10.0	1.1164	5.64
12.0	1.1578	6.06	11.9	1.1364	5.86	12.0	1.1177	5.58
14.0	1.1592	6.00	14.0	1.1377	5.81	14.0	1.1189	5.51
16.0	1.1605	5.94	16.0	1.1390	5.75	15.9	1.1200	5.45
17.9	1.1618	5.89	18.0	1.1403	5.70	18.0	1.1212	5.38
20.0	1.1634	5.82	20.0	1.1419	5.64	20.0	1.1226	5.32

Table 3. (continued)

p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}	p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}	p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}
1-Methyl-2-pyrrolidone (x) + 1,2-Dichloroethane ($1-x$)								
	$x = 0.7037$			$x = 0.7984$			$x = 0.9029$	
0.1	1.0851	5.59	0.1	1.0663	5.39	0.1	1.0462	5.25
2.0	1.0863	5.55	2.0	1.0674	5.36	2.0	1.0473	5.22
4.0	1.0876	5.51	4.0	1.0686	5.33	4.0	1.0483	5.19
6.0	1.0887	5.46	6.0	1.0697	5.31	6.0	1.0494	5.16
8.0	1.0900	5.42	8.0	1.0709	5.28	8.0	1.0506	5.13
10.0	1.0911	5.38	10.0	1.0720	5.25	10.0	1.0517	5.10
12.0	1.0923	5.34	12.0	1.0730	5.22	12.0	1.0527	5.07
14.0	1.0934	5.29	14.0	1.0742	5.19	14.0	1.0538	5.04
16.0	1.0946	5.25	16.0	1.0753	5.16	16.0	1.0548	5.01
18.0	1.0957	5.21	18.0	1.0764	5.13	18.0	1.0558	4.98
20.0	1.0969	5.17	20.0	1.0775	5.11	20.0	1.0571	4.95
1-Methyl-2-pyrrolidone (x) + 1,4-Dichlorobutane ($1-x$)								
	$x = 0.1039$			$x = 0.2034$			$x = 0.3036$	
0.1	1.1238	6.59	0.1	1.1142	6.50	0.1	1.1043	6.32
2.0	1.1252	6.53	2.0	1.1156	6.44	2.0	1.1057	6.26
4.0	1.1267	6.46	4.0	1.1170	6.37	4.0	1.1070	6.20
5.9	1.1281	6.41	6.0	1.1184	6.30	6.0	1.1083	6.14
8.0	1.1295	6.34	8.0	1.1198	6.23	8.0	1.1097	6.08
10.0	1.1310	6.28	10.0	1.1213	6.15	10.0	1.1111	6.01
12.0	1.1325	6.22	12.0	1.1226	6.08	12.0	1.1124	5.95
14.0	1.1338	6.15	14.0	1.1240	6.01	13.9	1.1137	5.89
16.0	1.1352	6.09	16.0	1.1253	5.95	16.0	1.1151	5.83
18.0	1.1365	6.03	18.0	1.1266	5.88	18.0	1.1163	5.77
20.0	1.1380	5.97	20.0	1.1280	5.81	20.0	1.1177	5.71
	$x = 0.4020$			$x = 0.5025$			$x = 0.5968$	
0.1	1.0944	6.16	0.1	1.0840	6.08	0.1	1.0739	5.83
2.0	1.0957	6.10	2.0	1.0852	6.01	2.0	1.0751	5.77
4.0	1.0970	6.05	4.0	1.0864	5.94	4.0	1.0764	5.72
6.0	1.0983	5.99	5.9	1.0877	5.87	6.0	1.0776	5.66
8.0	1.0996	5.93	7.9	1.0890	5.79	8.0	1.0788	5.61
10.0	1.1010	5.88	10.0	1.0903	5.71	10.0	1.0800	5.55
12.0	1.1022	5.82	12.0	1.0916	5.64	12.0	1.0812	5.50
14.0	1.1035	5.76	14.0	1.0928	5.57	14.0	1.0824	5.44
16.0	1.1048	5.71	16.0	1.0940	5.50	16.0	1.0835	5.39
18.0	1.1060	5.65	18.0	1.0951	5.42	18.0	1.0847	5.33
20.0	1.1074	5.60	20.0	1.0965	5.35	20.0	1.0860	5.28
	$x = 0.7003$			$x = 0.8008$			$x = 0.8971$	
0.1	1.0627	5.62	0.1	1.0514	5.53	0.1	1.0402	5.31
2.0	1.0638	5.58	2.0	1.0525	5.47	2.0	1.0413	5.27
4.0	1.0650	5.55	4.0	1.0536	5.42	4.0	1.0423	5.23
6.0	1.0662	5.51	6.0	1.0548	5.36	6.0	1.0435	5.18
8.0	1.0674	5.47	8.0	1.0559	5.30	8.0	1.0445	5.14
10.0	1.0686	5.43	10.0	1.0571	5.24	10.0	1.0456	5.10
12.0	1.0697	5.39	12.0	1.0582	5.19	11.9	1.0466	5.06
14.0	1.0709	5.35	14.0	1.0592	5.13	14.0	1.0477	5.01
16.0	1.0720	5.31	16.0	1.0603	5.07	15.9	1.0488	4.97
18.0	1.0731	5.28	18.0	1.0613	5.02	18.0	1.0498	4.93
20.0	1.0745	5.24	20.0	1.0624	4.96	20.0	1.0509	4.89
1-Methyl-2-pyrrolidone (x) + 1,6-Dichlorohexane ($1-x$)								
	$x = 0.1182$			$x = 0.2016$			$x = 0.3079$	
0.1	1.0607	6.58	0.1	1.0584	6.52	0.1	1.0554	6.31
2.0	1.0620	6.52	2.0	1.0597	6.44	2.0	1.0566	6.25
4.0	1.0633	6.45	4.0	1.0611	6.36	4.0	1.0579	6.19
6.0	1.0647	6.37	6.0	1.0624	6.28	6.0	1.0594	6.13
8.0	1.0661	6.30	8.0	1.0637	6.20	8.0	1.0605	6.07
10.0	1.0674	6.23	10.0	1.0652	6.12	10.0	1.0619	6.00
12.0	1.0688	6.16	12.0	1.0664	6.04	12.0	1.0631	5.94
14.0	1.0700	6.09	14.0	1.0676	5.96	14.0	1.0644	5.88
16.0	1.0714	6.02	16.0	1.0690	5.88	16.0	1.0656	5.81
17.9	1.0726	5.96	18.0	1.0702	5.80	18.0	1.0667	5.75
20.0	1.0739	5.89	20.0	1.0714	5.72	20.0	1.0682	5.69
	$x = 0.4114$			$x = 0.5049$			$x = 0.6008$	
0.1	1.0520	6.20	0.1	1.0490	6.18	0.1	1.0456	5.85
2.0	1.0533	6.14	2.0	1.0501	6.11	2.0	1.0467	5.81
4.0	1.0546	6.08	4.0	1.0514	6.03	4.0	1.0479	5.77

Table 3. (continued)

p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}	p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}	p / MPa	ρ / g·cm^{-3}	$10^4\kappa_T$ / MPa^{-1}
1-Methyl-2-pyrrolidone (x) + 1,6-Dichlorohexane ($1-x$)								
	$x = 0.4114$			$x = 0.5049$			$x = 0.6008$	
6.0	1.0558	6.02	6.0	1.0527	5.96	5.9	1.0492	5.73
8.0	1.0571	5.96	8.0	1.0540	5.88	8.0	1.0503	5.68
10.0	1.0584	5.90	10.0	1.0552	5.81	10.0	1.0516	5.64
12.0	1.0596	5.84	12.0	1.0564	5.73	12.0	1.0527	5.60
14.0	1.0609	5.78	13.9	1.0576	5.66	14.0	1.0539	5.56
16.0	1.0620	5.72	16.0	1.0588	5.58	16.0	1.0551	5.51
18.0	1.0633	5.66	18.0	1.0599	5.51	17.9	1.0562	5.48
20.1	1.0645	5.60	20.0	1.0612	5.43	20.0	1.0575	5.43
	$x = 0.7023$			$x = 0.8009$			$x = 0.8972$	
0.1	1.0416	5.76	0.1	1.0375	5.54	0.1	1.0331	5.34
2.0	1.0427	5.71	2.0	1.0386	5.50	2.0	1.0342	5.30
4.0	1.0439	5.65	4.0	1.0397	5.45	4.0	1.0353	5.26
6.0	1.0450	5.60	6.0	1.0408	5.41	6.0	1.0364	5.22
8.0	1.0462	5.54	8.0	1.0419	5.36	8.0	1.0374	5.17
10.0	1.0474	5.48	10.0	1.0431	5.31	10.0	1.0386	5.13
12.0	1.0485	5.43	12.0	1.0442	5.27	12.0	1.0396	5.09
14.0	1.0497	5.37	14.0	1.0453	5.23	14.0	1.0406	5.05
16.0	1.0508	5.32	16.0	1.0464	5.18	16.0	1.0417	5.01
18.0	1.0518	5.26	18.0	1.0475	5.14	18.0	1.0427	4.96
20.0	1.0530	5.21	20.0	1.0487	5.09	20.0	1.0438	4.92

Table 4. Parameters A_i and Standard Deviations σ for Least-Squares Representations of κ_T^E at 298.15 K and 0.10 MPa for {1-Methyl-2-pyrrolidone (x) + Chloroalkane ($1-x$)} Systems by Equation 4

system	A_0	A_1	A_2	σ/(10^{-4}·MPa^{-1})
1-methyl-2-pyrrolidone (x) + 1-chlorobutane ($1-x$)	−4.7263	−0.0933	−0.0292	3E−07
1-methyl-2-pyrrolidone (x) + 1-chlorohexane ($1-x$)	−2.3533	0.3083	−0.0350	2E−07
1-methyl-2-pyrrolidone (x) + 1-chlorooctane ($1-x$)	−1.3788	0.5718	−0.1647	3E−07
1-methyl-2-pyrrolidone (x) + 1,2-dichloroethane ($1-x$)	−1.1507	0.0416	0.0085	1E−07
1-methyl-2-pyrrolidone (x) + 1,4-dichlorobutane ($1-x$)	−0.3461	0.0248	−0.0005	1E−08
1-methyl-2-pyrrolidone (x) + 1,6-dichlorohexane ($1-x$)	0.4377	0.1235	−0.0250	2E−08

coefficient. The uncertainty of the reported thermal expansion coefficient was estimated to be ± 10^{-5} K^{-1}. We have obtained the value for α of 8.1·10^{-4} K^{-1} for 1-methyl-2-pyrrolidone at 298.15 K and 0.1 MPa. The value found in the literature for this amide is 8.4·10^{-4} K^{-1} [5] at the same conditions. As can be seen, there is a good agreement between the value of the thermal expansion coefficient, α, obtained by us and the literature value. In previous works, thermal expansion coefficients, α, of the pure liquids (1-chlorobutane,[1] 1-chlorohexane,[1] 1-chlorooctane,[1] 1,2-dichloroethane,[2] 1,4-dichlorobutane,[2] and 1,6-dichlorohexane[2]) at 298.15 K and 0.1 MPa are given, and a comparison with the literature is done.

For 1-methyl-2-pyrrolidone + 1-chlorobutane, or + 1-chlorohexane, or + 1-chlorooctane, or + 1,2-dichloroethane, or + 1,4-dichlorobutane, or + 1,6-dichlorohexane mixtures, some of the experimental densities, ρ, and isothermal compressibilities, κ_T, calculated with eq 1 are presented in Table 3. The complete set of the obtained values is given as Supporting Information. From the experimental values, it can be observed that the isothermal compressibility, κ_T, obtained for mixtures with 1-chloroalkane is higher than for mixtures with α,ω-dichloroalkane and decreases as the length of the aliphatic chain of the 1-chloroalkane or α,ω-dichloroalkane of the mixture increases. The same behavior is found in our previous works[1,2] and in the literature for series of nonsaturated hydrocarbons,[16] alcohols,[10,17] etc. However, a different behavior is found for series such as *n*-alkane,[18] for example. Thereby, we can conclude that even $(\delta V^E/\delta P)_T$ and the isothermal compressibility, κ_T, are related properties, and their behavior in function of the molecular structure related parameters such as, for example, the length of the aliphatic chain can be different. The reason may be that the isothermal compressibility, κ_T, depends on the molar volume of the studied systems which involves the structural effects in the systems, besides the molecular interactions.

The excess compressibility, κ_T^E, defined as

$$\kappa_T^E = -V^1(\delta V^E/\delta P)_T = \kappa_T - \varphi_1\kappa_1 - \varphi_2\kappa_2 \qquad (3)$$

where φ_1 and φ_2 are the volume fractions, is widely used. Values for κ_T^E were obtained with eq 3 using the volume fractions, φ_1 and φ_2, the isothermal compressibility, κ_1, of the

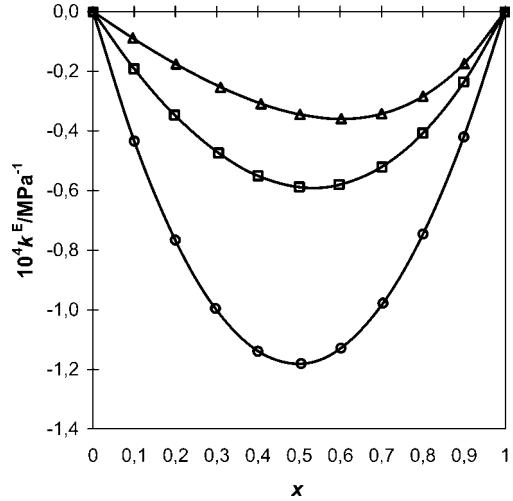

Figure 2. Excess isothermal compressibility, κ_T^E, represented against mole fraction of 1-methyl-2-pyrrolidone for the mixtures with ○, 1-chlorobutane; or □, 1-chlorohexane; or △, 1-chlorooctane at $T = 298.15$ K and 0.1 MPa. The solid lines are obtained from the Redlich–Kister equation using the parameters listed in Table 4.

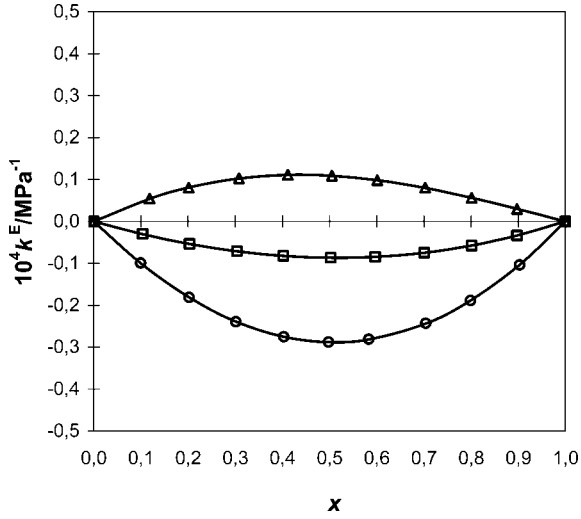

Figure 3. Excess isothermal compressibility, κ_T^E, represented against mole fraction of 1-methyl-2-pyrrolidone for the mixtures with ○, 1,2-dichloroethane; or □, 1,4-dichlorobutane; △, or 1,6-dichlorohexane at $T = 298.15$ K and 0.1 MPa. The solid lines are obtained from the Redlich–Kister equation using the parameters listed in Table 4.

amide at 298.15 K and 0.1 MPa (Table 2), the isothermal compressibility, κ_2, of the 1-cholroalkane[1] or α,ω-dichloroalkane[2] at 298.15 K and 0.1 MPa, and the isothermal compressibility, κ_T, obtained at 298.15 K and 0.1 MPa by fitting the experimental data against molar fraction of the amide. The κ_T^E results for each mixture were fitted with the Redlich–Kister equation

$$\kappa_T^E = x(1-x)\sum_{i=0}^{k} A_i(1-2x)^i \qquad (4)$$

where x is the mole fraction of 1-methyl-2-pyrrolidone. The parameters A_i in eq 4 determined by the unweighted least-squares method are tabulated in table 4, along with the standard deviation, σ, of the representations. The standard deviations were calculated from the equation of the form

$$\sigma = \left[\sum_{i=0}^{n} (\kappa_T^E(\text{calcd}) - \kappa_T^E(\text{exptl}))^2/(n-j)\right]^{1/2} \qquad (5)$$

where n is the number of experimental data and j is the number of parameters used in eq 4; $n = 9$ and $j = 3$ in this work. The σ values are within the experimental uncertainty in κ_T^E. The experimental values for κ_T^E at 298.15 K and 0.1 MPa and those calculated with eq 4 are represented against the mole fraction of the amide, x, in Figures 2 and 3.

The excess isothermal compressibility values, κ_T^E, increase in the following sequences: 1-methyl-2-pyrrolidone + 1-chlorobutane < 1-methyl-2-pyrrolidone + 1-chlorohexane < 1-methyl-2-pyrrolidone + 1-chlorooctane < 1-methyl-2-pyrrolidone + 1,2-dichloroethane < 1-methyl-2-pyrrolidone + 1,4-dichlorobutane < 1-methyl-2-pyrrolidone + 1,6-dichlorohexane.

In any case, the explanation of the volumetric behavior of the studied mixtures is difficult from only this kind of measurement, given the variety and complexity of the interactional and geometric effects present in the pure 1-chloroalkane, α,ω-dichloroalkanes, and amides, for example, the dipole–dipole interactions, and the specific acceptor–donor interactions present in the mixtures and its variation with the length of the aliphatic chain of the 1-chloroalkane and α,ω-dichloroalkanes.

Supporting Information Available:

Experimental densities, ρ, and isothermal compressibilities, κ_T, calculated with eq 1, for 1-methyl-2-pyrrolidone and for 1-methyl-2-pyrrolidone + 1-chlorobutane, or + 1-chlorohexane, or + 1-chlorooctane, or + 1,2-dichloroethane, or + 1,4-dichlorobutane, or + 1,6-dichlorohexane mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) García-Giménez, P.; Martínez-López, J. F.; Blanco, S. T.; Velasco, I.; Otín, S. Densities and isothermal compressibilities at pressures up to 20 MPa of the systems N,N-dimethylformamide or N,N-dimethylacetamide + 1-chloroalkane. *J. Chem. Eng. Data* **2007**, *52*, 1693−1699.
(2) García-Giménez, P.; Martínez-López, J. F.; Blanco, S. T.; Velasco, I.; Otín, S. Densities and isothermal compressibilities at pressures up to 20 MPa of the systems N,N-dimethylformamide or N,N-dimethylacetamide + α,ω-dichloroalkane. *J. Chem. Eng. Data* **2007**, *52*, 1693−1699.
(3) Gnana Kumari, P.; Radhamma, M.; Sekhar, G. C.; Prabhakara; Rao, M. V. Excess Volumes and Speeds of Sound of *N*-Methyl-2-pyrrolidone with Chloroethanes and Chloroethenes at 303.15 K. *J. Chem. Eng. Data* **2002**, *47* (3), 425–427.
(4) Gnanakumari, P.; Prabhakara Rao, M. V.; Prasad, D. H. L.; Ravi Kumar, Y. V. L. Vapor-Liquid Equilibria and Excess Molar Enthalpies for *N*-Methyl-2-pyrrolidone with Chloroethanes and Chloroethenes. *J. Chem. Eng. Data* **2003**, *48* (3), 535–540.
(5) García, B.; Aparicio, S.; Alcalde, R.; Dávila, M. J.; Leal, J. M. Modeling the PVTx behavior of the N-methylpyrrolidinone/water mixed solvent. *Ind. Eng. Chem. Res.* **2004**, *43*, 3205–3215.
(6) Ihmels, E. C.; Gmehling, J. Liquid Densities of γ-Butyrolactone and *N*-Methyl-2-pyrrolidone form 273 to 473 K and Pressures up to 40 MPa. *J. Chem. Eng. Data* **2002**, *47*, 1547–1552.
(7) Malhotra, R.; Woolf, L. A. (p, V_m, T, x) measurements for liquid mixtures of 1,2-dichloroethane with 2,2,4-trimethylpentane. I. Experimental results, isothermal compressibilities, isobaric expansivities and heat capacities. *Fluid Phase Equilib.* **1994**, *94*, 227–251.
(8) Morávková, L.; Linek, J. Temperature dependence of the excess molar volume of (heptane+1-chloroalkane). *J. Chem. Thermodyn.* **2002**, *34*, 1387–1395.
(9) Matilla, A. D.; Tardajos, G.; Junquera, E.; Aicart, E. Thermodynamic properties for binary liquid mixtures of 1-chlorobutane + n-alkanes. *J. Solution Chem.* **1991**, *20*, 805–816.
(10) Tardajos, G.; Junquera, E.; Aicart, E. Isothermal compressibility and isobaric thermal expansivity of linear and branched hexanols at 298.15 K. *J. Chem. Eng. Data* **1994**, *39*, 349–350.
(11) Delitala, C.; Marongiu, B.; Porcedda, S.; Rosa, A. Thermodynamic properties of binary mixtures containing alkanenitriles II. Excess volumes of alkanenitriles + 1-chloroalkanes. *Fluid Phase Equilib.* **1996**, *126*, 195–202.
(12) Kumagai, A.; Takahashi, S. (Pressure, volume, temperature) behaviour of liquid 1,1-dichloroethane and 1,2-dichloroethane. *J. Chem. Thermodyn.* **1985**, *17*, 977–980.
(13) *TRC, Thermodynamics Tables Non-Hydrocarbons*; Thermodynamics Research Center, The TX A&M University System: College Station, TX, 1994.
(14) Ortega, J.; Marrero, E.; Toledo, F. J.; Espiau, F. Thermodynamic study of (alkyl esters + α,ω-alkyl dihalides) I: H_m^E and V_m^E for binary mixtures {x$C_{u-1}H_{2u-1}CO_2C_2H_5$ + (1-x) α,ω-$ClCH_2(CH_2)_{v-2}CH_2Cl$} where u=1 to 5, α=1 and v=w=2 to 6. *J. Chem. Thermodyn.* **2005**, *37*, 1332–1346.
(15) Bouchot, C.; Richon, D. An enhanced method to calibrate vibrating tube densimeters. *Fluid Phase Equilib.* **2001**, *191*, 189–208.
(16) Aicart, E.; Junquera, E.; Letcher, T. M. Isobaric thermal expansivity and isothermal compressibility of several nonsaturated hydrocarbons at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1225–1227.
(17) Díaz-Peña, M; Tardajos, G. Isothermal compressibilities of n-1-alcohols from methanol to 1-dodecanol at 298.15 K, 308.15 and 331.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 441–445.
(18) Matilla, A. D.; Aicart, E.; Díaz-Peña, M.; Tardajos, G. Isobaric thermal expansion and isothermal compressibility of ethylbenzene + n-hexane, and + n-octane at 25 and 45 °C. *J. Solution Chem.* **1989**, *18*, 143–150.

Received for review July 3, 2007. Accepted October 22, 2007. P. García-Giménez acknowledges the financial support received from DGA, Departamento de Educación y Ciencia, and the European Social Fund (B020/2003).

JE7003758