Apparent Molar Volumes of Sodium Chlorobenzoates in *N*,*N*-Dimethylformamide−Water Mixtures at 298.15 K

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Densities of sodium chlorobenzoates (o-, m-, p-) have been measured in dimethylformamide (DMF)−water mixtures at 298.15 K with an oscillating-tube densimeter. From these densities, apparent molar volumes of sodium chlorobenzoates in DMF−water mixtures have been calculated, and partial molar volumes at infinite dilution have been evaluated. Transfer volumes of each isomer from water to DMF−water mixed solvents have also been calculated from partial molar volumes at infinite dilution.

Introduction

There is an increased interest in the thermodynamic behavior in ternary mixtures (water + nonaqueous solvent + electrolyte) (Peña et al., 1995). However, there is a shortage of investigations of such mixtures, especially of aromatic solutes, which contain a substituted group. Systematic studies of aromatic solutes have usually been limited to their aqueous solutions (Desnoyers et al., 1973; Perron and Desnoyers, 1979; Strong et al., 1994; Gianni and Lepori, 1996). Little is known about the effect of substituents on the thermodynamic properties in mixed solvents. With this aim in mind, we report the densities of three geometrical isomers of sodium chlorobenzoates in dimethylformamide (DMF)−water mixtures.

Mixtures of aliphatic amides and water have been the subject of many studies (Assarsson and Eirich, 1968; Saphon and Bittrich, 1973). Since these amides cover a very wide range of dielectric constants and are usually miscible with water, they are used in studies of the interactions between the solubility of drugs and the dielectric constants of the pure compounds and of their aqueous mixtures (Rohdewald and Möldner, 1973). In addition, the amides can serve as model compounds for the investigation of the properties in aqueous solutions (de Visser et al., 1977).

Among these amides, DMF is of particular interest in view of the lack of hydrogen bonding in the pure solvent. Therefore, we have used its aqueous mixtures to study the influence of solvent structure on the solvation of a third compound.

Experimental Section

o-Chlorobenzoic acid (chemical grade, 99.0?100.0 mass%), *m*-chlorobenzoic acid (fluca, >98 mass %), *p*-chlorobenzoic acid (chemical grade, >99.5 mass%), and DMF (analytical grade, >99.5 mass %) were used without further purification. Water was deionized and redistilled. Each acid was purified from an ethanol−water mixture. A stock solution of each salt was prepared by weight by dissolving the purified acid in the appropriate amount of NaOH solution in neutralization ratio, and the final solution has 1% excess of NaOH. The working solutions were obtained by weight dilution. All solutions were prepared by weight using a Mettler AE200 analytical balance with a precision of ±0.0001 g.

The densities of solutions were determined by a vibrating-tube digital densimeter (model DMA 55, Anton Paar). The densimeter was calibrated with water (ρ = 0.997 071 g cm^{-3}) and air (ρ = 0.001 185 g cm^{-3}). The U-tube of the densimer was washed with water and acetone repeatedly and then dried with air before the measurement. The temperature of the measuring cell was controlled at (298.15 ± 0.01) K by circulating water from a thermostat (HAAKE C). An average of triplicate measurements was taken into account. The accuracy of the density values was ±1 × 10^{-5} g cm^{-3}.

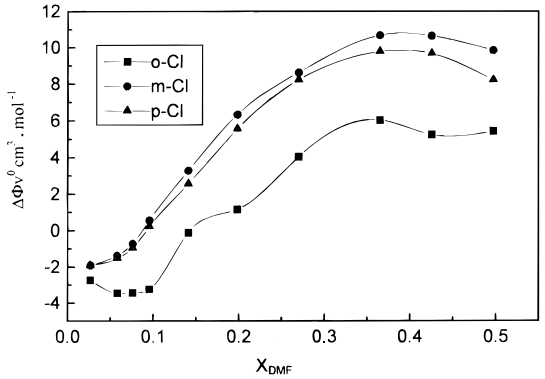

Figure 1. Transfer volumes of sodium chlorobenzoates from water to DMF−H_2O mixtures at 298.15 K.

Results and Discussion

The apparent molar volumes Φ_v are calculated from solution densities using eq 1

$$\Phi_v = M_S/\rho - 1000(\rho - \rho_0)/m_S\rho\rho_0 \qquad (1)$$

where M_S, m_S, ρ, and ρ_0 are the solute molar mass, solute molality, and densities of the solution and solvent, respectively.

The molal concentration (m), densities(ρ), and apparent molar volumes (Φ_v) of the sodium chlorobenzoate (o-, m-,

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Table 1. Molar Concentration (m), Densities (ρ), and Apparent Molar volumes (Φ_v) of the Sodium *o*-Chlorobenzoate in DMF−H_2O Mixtures at 298.15 K

m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}	m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}	m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}
	$x_{DMF} = 0.0000$			$x_{DMF} = 0.0956$			$x_{DMF} = 0.3650$	
0.0000	0.99707		0.0000	0.99683		0.0000	0.98663	
0.0750	1.00308	97.87	0.0750	1.00301	95.59	0.0750	0.99215	104.77
0.1000	1.00505	98.01	0.1000	1.00504	95.70	0.1000	0.99396	104.88
0.1250	1.00700	98.18	0.1250	1.00702	96.09	0.1250	0.99575	105.04
0.2500	1.01656	98.72	0.2500	1.01678	96.84	0.2500	1.00442	105.95
0.3750	1.02587	98.96	0.3750	1.02614	97.58	0.3750	1.01271	106.70
0.5000	1.03491	99.18	0.5000	1.03513	98.25	0.5000	1.02076	107.13
	$x_{DMF} = 0.0267$			$x_{DMF} = 0.1410$			$x_{DMF} = 0.4250$	
0.0000	0.99626		0.0000	0.99698		0.0000	0.98200	
0.0750	1.00244	95.60	0.0750	1.00294	98.55	0.0750	0.98755	104.49
0.1000	1.00447	95.71	0.1000	1.00489	98.72	0.1000	0.98936	104.60
0.1250	1.00648	95.85	0.1250	1.00681	98.99	0.1250	0.99115	104.93
0.2500	1.01629	96.55	0.2500	1.01619	99.85	0.2500	0.99977	106.18
0.3750	1.02578	97.03	0.3750	1.02521	100.50	0.3750	1.00802	107.03
0.5000	1.03496	97.45	0.5000	1.03394	100.97	0.5000	1.01600	107.57
	$x_{DMF} = 0.0581$			$x_{DMF} = 0.1980$			$x_{DMF} = 0.4970$	
0.0000	0.99639		0.0000	0.99598		0.0000	0.97651	
0.0750	1.00261	95.06	0.0750	1.00184	99.91	0.0750	0.98208	104.36
0.1000	1.00464	95.30	0.1000	1.00376	100.05	0.1000	0.98388	104.76
0.1250	1.00665	95.53	0.1250	1.00565	100.30	0.1250	0.98563	105.34
0.2500	1.01649	96.26	0.2500	1.01487	101.17	0.2500	0.99427	106.40
0.3750	1.02596	96.89	0.3750	1.02371	101.88	0.3750	1.00260	107.02
0.5000	1.03511	97.40	0.5000	1.03226	102.39	0.5000	1.01058	107.64
	$x_{DMF} = 0.0759$			$x_{DMF} = 0.2700$				
0.0000	0.99687		0.0000	0.99288				
0.0750	1.00308	95.19	0.0750	0.99845	102.65			
0.1000	1.00511	95.40	0.1000	1.00037	103.07			
0.1250	1.00710	95.77	0.1250	1.00220	103.22			
0.2500	1.01687	96.66	0.2500	1.01106	104.15			
0.3750	1.02630	97.26	0.3750	1.01957	104.81			
0.5000	1.03545	97.68	0.5000	1.02782	105.23			

Table 2. Molar Concentration (m), Densities (ρ), and Apparent Molar Volumes (Φ_v) of the Sodium *m*-Chlorobenzoate in DMF−Water Mixtures at 298.15 K

m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}	m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}	m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}
	$x_{DMF} = 0.0000$			$x_{DMF} = 0.0956$			$x_{DMF} = 0.3650$	
0.0000	0.99707		0.0000	0.99715		0.0000	0.98664	
0.0250	0.99910	97.19	0.0750	1.00310	98.68	0.0250	0.98841	108.04
0.0500	1.00111	97.40	0.1000	1.00504	98.92	0.0500	0.99016	108.25
0.0750	1.00310	97.60	0.1250	1.00696	99.15	0.0750	0.99190	108.34
0.1000	1.00508	97.71	0.2500	1.01633	99.97	0.1000	0.99362	108.49
0.1250	1.00703	97.94	0.3750	1.02532	100.66	0.1250	0.99533	108.59
0.2000	1.01283	98.25	0.5000	1.03405	101.09	0.2500	1.00358	109.47
	$x_{DMF} = 0.0267$			$x_{DMF} = 0.1410$			$x_{DMF} = 0.4250$	
0.0000	0.99644		0.0000	0.99703		0.0000	0.98208	
0.0750	1.00259	96.00	0.0750	1.00277	101.50	0.0250	0.98385	108.20
0.1000	1.00461	96.11	0.1000	1.00465	101.64	0.0500	0.98560	108.42
0.1250	1.00662	96.17	0.1250	1.00650	101.89	0.0750	0.98732	108.78
0.2500	1.01635	97.03	0.2500	1.01551	102.81	0.1000	0.98904	108.87
0.3750	1.02577	97.54	0.3750	1.02417	103.45	0.1250	0.99072	109.17
0.5000	1.03493	97.87	0.5000	1.03255	103.91	0.2500	0.99892	110.07
	$x_{DMF} = 0.0581$			$x_{DMF} = 0.1980$			$x_{DMF} = 0.4970$	
0.0000	0.99643		0.0000	0.99622		0.0000	0.97637	
0.0750	1.00254	96.54	0.0750	1.00177	104.08	0.0250	0.97816	107.56
0.1000	1.00450	97.12	0.1000	1.00359	104.19	0.0500	0.97994	107.57
0.1250	1.00646	97.39	0.1250	1.00540	104.26	0.0750	0.98167	108.15
0.2500	1.01608	98.08	0.2500	1.01421	104.82	0.1000	0.98341	108.23
0.3750	1.02533	98.70	0.3750	1.02268	105.33	0.1250	0.98509	108.72
0.5000	1.03426	99.21	0.5000	1.03084	105.78	0.2500	0.99340	109.50
	$x_{DMF} = 0.0759$			$x_{DMF} = 0.2700$				
0.0000	0.99663		0.0000	0.99290				
0.0750	1.00267	97.48	0.0750	0.99828	106.48			
0.1000	1.00464	97.72	0.1000	1.00005	106.53			
0.1250	1.00658	98.03	0.1250	1.00179	106.72			
0.2500	1.01609	98.85	0.2500	1.01034	107.18			
0.3750	1.02521	99.56	0.3750	1.01848	107.85			
0.5000	1.03405	100.04	0.5000	1.02636	108.29			

p-) in DMF−water mixtures at 298.15 K are reported in Tables 1−3.

Since the data concerning the pressure dependence of the dielectric constant of the DMF−water system are not

Table 3. Molar Concentration (m), Densities (ρ), and Apparent Molar Volumes (Φ_v) of the Sodium *p*-Chlorobenzoate in DMF−H_2O Mixtures at 298.15 K

m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}	m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}	m/mol kg^{-1}	ρ/g cm^{-3}	Φ_v/cm mol^{-1}
	$x_{DMF} = 0.0000$			$x_{DMF} = 0.0956$			$x_{DMF} = 0.3650$	
0.0000	0.99707		0.0000	0.99700		0.0000	0.98661	
0.0750	1.00314	97.07	0.0750	1.00299	98.14	0.0750	0.99192	107.65
0.1000	1.00514	97.11	0.1000	1.00491	98.72	0.1000	0.99365	107.97
0.1250	1.00708	97.54	0.1250	1.00683	98.99	0.1250	0.99535	108.18
0.2500	1.01672	98.07	0.2500	1.01616	100.06	0.2500	1.00363	109.22
0.3750	1.02608	98.39	0.3750	1.02511	100.83	0.3750	1.01148	110.01
0.5000	1.03522	98.55	0.5000	1.03376	101.38	0.5000	1.01919	110.38
	x_{DMF} =0.0267			$x_{DMF} = 0.1410$			$x_{DMF} = 0.4250$	
0.0000	0.99620		0.0000	0.99696		0.0000	0.98200	
0.0750	1.00237	95.74	0.0750	1.00278	100.43	0.0750	0.98732	107.40
0.1000	1.00439	95.91	0.1000	1.00464	101.04	0.1000	0.98905	107.93
0.1250	1.00640	96.02	0.1250	1.00650	101.33	0.1250	0.99076	108.18
0.2500	1.01614	96.91	0.2500	1.01555	102.36	0.2500	0.99905	109.20
0.3750	1.02554	97.51	0.3750	1.02426	103.02	0.3750	1.00702	109.83
0.5000	1.03462	98.02	0.5000	1.03259	103.69	0.5000	1.01472	110.28
	$x_{DMF} = 0.0581$			x_{DMF} =0.1980			$x_{DMF} = 0.4970$	
0.0000	0.99638		0.0000	0.99599		0.0000	0.97632	
0.0750	1.00252	96.14	0.0750	1.00157	103.28	0.0500	0.97995	106.31
0.1000	1.00451	96.51	0.1000	1.00337	103.79	0.0750	0.98169	107.17
0.1250	1.00646	96.98	0.1250	1.00514	104.27	0.1000	0.98346	107.18
0.2500	1.01610	97.80	0.2500	1.01384	105.28	0.1250	0.98515	107.79
0.3750	1.02536	98.48	0.3750	1.02224	105.82	0.2500	0.99340	109.29
0.5000	1.03440	98.83	0.5000	1.03034	106.28	0.3750	1.00135	110.03
	$x_{DMF} = 0.0759$			$x_{DMF} = 0.2700$				
0.0000	0.99660		0.0000	0.99284				
0.0750	1.00268	96.94	0.0750	0.99827	105.80			
0.1000	1.00463	97.52	0.1000	1.00002	106.22			
0.1250	1.00658	97.79	0.1250	1.00173	106.724			
0.2500	1.01607	98.81	0.2500	1.01019	107.55			
0.3750	1.02520	99.51	0.3750	1.01833	108.10			
0.5000	1.03397	100.15	0.5000	1.02621	108.48			

Table 4. Volumetric Parameters for Eq 2 of Sodium *o*-Chlorobenzoate

x_{DMF}	Φ_v^0/cm^3 mol^{-1}	r	S_v*	SD
0.0000	97.07	0.99307	3.07	0.071
0.0267	94.35	0.99904	4.38	0.037
0.0581	93.61	0.99966	5.36	0.021
0.0759	93.63	0.99678	5.86	0.092
0.0956	93.84	0.99765	6.15	0.082
0.1410	96.96	0.99936	5.72	0.040
0.198	98.24	0.99925	5.89	0.045
0.2700	101.13	0.99730	5.91	0.085
0.3650	103.10	0.99731	5.75	0.083
0.4250	102.33	0.99724	7.53	0.109
0.4970	102.51	0.99222	7.41	0.182

Table 5. Volumetric Parameters for Eq 2 of Sodium *m*-Chlorobenzoate

x_{DMF}	Φ_v^0/cm^3 mol^{-1}	r	S_v	SD
0.0000	96.58	0.99669	3.73	0.034
0.0267	94.67	0.9953	44.60	0.087
0.0581	95.21	0.99079	5.72	0.153
0.0759	95.87	0.99926	5.95	0.045
0.0956	97.15	0.99940	5.64	0.038
0.1410	99.88	0.99878	5.77	0.056
0.1980	102.92	0.99587	3.95	0.070
0.2700	105.21	0.99240	4.26	0.103
0.3650	107.28	0.97316	4.11	0.128
0.4250	107.23	0.99308	5.55	0.086
0.4970	106.43	0.97873	6.12	0.169

available, we cannot calculate the Debye−Hückel limiting slope. So we were forced to use the Masson equation

$$\Phi_v = \Phi_v^0 + S_v^* m^{1/2} \quad (2)$$

where Φ_v^0 is the limiting apparent molar volumes and S_v* is the experimental slope.

Table 6. Volumetric Parameters for Eq 2 of Sodium *p*-Chlorobenzoate

x_{DMF}	Φ_v^0/cm^3 mol^{-1}	r	S_V	SD
0.0000	96.13	0.97929	3.60	0.145
0.0267	94.20	0.99847	5.40	0.058
0.0581	94.62	0.99122	6.17	0.161
0.0759	95.19	0.99597	7.09	0.125
0.0956	96.34	0.99579	7.27	0.131
0.1410	98.69	0.99474	7.14	0.144
0.1980	101.69	0.98698	6.72	0.215
0.270	104.37	0.98658	6.03	0.195
0.3650	105.91	0.99720	6.50	0.095
0.4250	105.81	0.99364	6.49	0.144
0.4970	104.34	0.99168	9.52	0.204

Table 7. Transfer Volumes of Sodium Chlorobenzoate from Water to DMF−H_2O Mixtures at 298.15 K

	$\Delta\Phi_v^0$/cm^3 mol^{-1}		
x_{DMF}	o-	m-	p-
0.0267	−2.72	−1.91	−1.93
0.0581	−3.46	−1.37	−1.53
0.0759	−3.44	−0.71	−0.96
0.0956	−3.23	0.57	0.21
0.1410	−0.11	3.30	2.56
0.1980	1.17	6.34	5.56
0.2700	4.06	8.63	8.24
0.3650	6.03	10.70	9.78
0.4250	5.26	10.65	9.68
0.4970	5.44	9.85	8.21

The parameters of eq 2, correlation coefficients (r) and standard deviations (SD) of fitting, are listed in Tables 4−6.

Transfer volumes of each isomer from water to DMF−H_2O mixtures at 298.15 K are given in Table 7 by using eq 3:

$$(\Delta\Phi_v^0)_{tr} = \Phi_v^0(\mathrm{DMF}+\mathrm{H_2O}) - \Phi_v^0(\mathrm{H_2O}) \qquad (3)$$

The changes of transfer volumes of sodium *m*-chlorobenzoate and sodium *p*-chlorobenzoate with the molar fractions of DMF are similar (Figure 1), and both of them go through a maximum, but the amplitude of the maximum varies with the substituent position on aromatic ring. The changes of transfer volumes of sodium *o*-chlorobenzoate are different from those of the other two isomers. All of this can be assigned to the structural alteration of the mixed solvents and the different interactions between o-, m-, p-substituents and solvent.

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