Relative Permittivities, Refractive Indices, and Densities for the Binary Mixtures *N*,*N*′-Dimethylacetamide with Methanol, Ethanol, 1-Butanol, and 2-Propanol at 298.15 K

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Densities, refractive indices, and relative permittivities have been measured over the entire range of composition for binary mixtures of *N*,*N*′- dimethylacetamide with methanol, ethanol, 1-butanol, and 2-propanol at 298.15 K. From these experimental data, excess volume and deviations in refractive index Δn_D, relative permittivity $\Delta\epsilon$, and molar polarization ΔP_m, have been calculated. The results have been fitted to the Redlich−Kister equation, and the resulting coefficients have been calculated.

Introduction

This paper is part of our general work concerning the study of some physical and physicochemical properties of binary liquid mixtures in order to gain information about molecular interactions between the molecules in these systems (Ritzoulis, 1989; Moumouzias et al., 1991; Konti et al., 1997).

In the present study the density *d*, relative permittivity ϵ, and refractive index n_D of the binary mixtures *N*,*N*′-dimethylacetamide (DMA) with methanol (MeOH), ethanol (EtOH), 1-butanol (BuOH), and 2-propanol (2-PrOH) over the entire range of composition at 298.15 K are measured. From the above experimental values the excess molar volume V^E and the deviations in refractive indices Δn_D, relative permittivity $\Delta\epsilon$, and molar polarization, ΔP_m are also calculated.

Experimental Section

All chemicals were purchased from Merck Co. Their purities were 99.5% or better, and no further purification has been done. The chemicals were stored over molecular sieves.

Liquid solutions of various compositions were prepared by mass using a Shimadzu AEG-220 analytical balance of four decimal places and were degassed by ultrasonic treatment.

Density measurements of pure liquids and binary liquid solutions were carried out using an Anton-Paar DMA (measuring cell 602 and processing unit 60) vibrating tube densimeter. The densimeter was calibrated with degassed water and dehumidized air at atmospheric pressure. The temperature was regulated with a Haake F3-K digital thermostat with a stability of ±0.02 °C and measured with a DT 100-30 Anton−Paar digital thermometer. The accuracy in the density measurement was better than $\pm 5 \times 10^{-5}$ g/cm^3.

Relative permittivities were measured with a Wissenschaftlich Technische Werkstatten GmbH, model WTW DM-01, dipolemeter. Cell MFL 2 has been used with a permittivity range of 7 to 21, and cell MFL 3, with a permittivity range of 20 to 50. The cells were previously calibrated with standard pure liquids (water, nitrobenzene, ethylene chloride, and benzyl alcohol in accordance with National Bureau of Standards Circular 514 (Weast 1987−1988). The temperature of the dipolemeter's cell was held constant using a YSI (model 72) thermostat with a stability of ±0.005 K.

The refractive indices were measured with an Abbe refractometer (aus Jenna, model G). The accuracy of the refractive index measurement was better than ±0.0002, and all values were obtained for Na (D) light. The temperature was held constant by using the same thermostat mentioned for the relative permittivity.

Table 1. Experimental and Literature Values of Pure Liquids at 298.15 K

liquid	n_D exptl	n_D lit.	ϵ exptl	ϵ lit.	d/g cm^{-3} (exptl)	d/g cm^{-3} (lit.)
N,*N*′-dimethyl-acetamide	1.4356	1.4363[i] 1.4356[a]	37.756		0.9366	0.9363[a]
methanol	1.3266	1.3265[g] 1.3264[c]	32.64	32.70[j]	0.7866	0.7868[h] 0.7866[d] 0.7865[c]
ethanol	1.3597	1.3594[l] 1.35931[c]	24.55	24.55[a]	0.7852	0.7852[c] 0.7854[e] 0.78493[a] 0.7853[f]
1-butanol	1.3973	1.39741[a] 1.3978[i] 1.3973[g]	17.10	17.43[k] 17.50[j]	0.8060	0.8056[b] 0.8058[a]
2-propanol	1.3752	1.3751[c] 1.3752[g]	18.20		0.7810	0.78102[a] 0.78096[c]

[a] Riddick et al., 1986. [b] Aminabhavi et al., 1998. [c] Francesconi and Comeli, 1998. [d] Martin and Mato, 1995. [e] Hiaki et al., 1995. [f] El-Banna and Radaman, 1995. [g] Wingetors, 1981. [h] Nikam et al., 1995. [i] Aminabhavi et al., 1995. [j] Sastry and Valand, 1998. [k] D'Aprano et al., 1979. [l] Oehme, 1962.

Results and Discussion

The results of the experimental measurements for the pure components are reported in Table 1 and are compared to the values taken from the existing literature.

Measured values of density, relative permittivity, and refractive index together with those of the molar polariza-

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Table 2. Density *d*, Relative Permittivity ϵ, Refractive Index n_D, and Molar Polarization P_m for *N*,*N*′-Dimethylacetamide (1) + Alcohols at $T = 298.15$ K

x_1	d/g cm^{-3}	ϵ	n_D	P_m/cm^3 mol^{-1}
N,*N*′-Dimethylacetamide (1) + Methanol (2)				
0.0000	0.7866	32.64	1.3266	285.1
0.1000	0.8221	33.80	1.3506	333.2
0.1998	0.8504	35.10	1.3699	382.5
0.2999	0.8724	35.68	1.3857	427.5
0.4000	0.8899	36.26	1.3989	474.2
0.4997	0.9030	36.60	1.4094	519.5
0.5997	0.9122	36.86	1.4177	565.7
0.7000	0.9202	37.10	1.4248	612.2
0.7998	0.9262	37.35	1.4289	660.2
0.9000	0.9315	37.59	1.4325	708.6
1.0000	0.9366	37.75	1.4356	755.4
N,*N*′-Dimethylacetamide (1) + Ethanol (2)				
0.0000	0.7852	24.55	1.3597	305.7
0.1000	0.8111	26.22	1.3763	348.7
0.1999	0.8328	27.93	1.3883	392.0
0.3000	0.8518	29.51	1.3972	432.0
0.4000	0.8688	30.97	1.4065	476.4
0.4998	0.8835	32.42	1.4140	523.4
0.5999	0.8972	33.54	1.4211	566.3
0.7002	0.9089	34.82	1.4265	615.1
0.8001	0.9198	36.01	1.4302	663.9
0.9000	0.9287	36.94	1.4335	708.8
1.0000	0.9366	37.75	1.4356	755.4
N,*N*′-Dimethylacetamide (1) + 1-Butanol (2)				
0.0000	0.8060	17.10	1.3973	325.5
0.1000	0.8203	18.48	1.4013	352.9
0.2000	0.8343	20.23	1.4052	388.8
0.2998	0.8468	22.16	1.4091	429.1
0.3999	0.8592	24.23	1.4130	472.6
0.5001	0.8720	26.33	1.4168	516.3
0.6000	0.8843	28.31	1.4207	558.1
0.7000	0.8970	30.57	1.4245	605.6
0.8002	0.9097	33.12	1.4283	659.0
0.9000	0.9230	35.76	1.4219	714.1
1.0000	0.9366	37.75	1.4356	755.4
N,*N*′- Dimethylacetamide (1) + 2-Propanol (2)				
0.0000	0.7810	18.20	1.4356	293.5
0.1000	0.7997	20.00	1.3839	332.0
0.1994	0.8174	21.53	1.3910	364.6
0.2993	0.8344	23.19	1.3976	402.0
0.4000	0.8508	25.03	1.4036	443.9
0.4998	0.8664	27.02	1.4091	490.0
0.6000	0.8814	29.14	1.4140	450.1
0.7000	0.8960	31.37	1.4183	593.8
0.8001	0.9106	33.69	1.4220	650.9
0.9000	0.9236	36.07	1.4276	710.8
1.0000	0.9366	37.75	1.4356	755.4

tion P_m for the binary mixtures at 298.15 K are listed in Table 2.

The molar volume of the binary mixture is defined by

$$V = (x_1M_1 + x_2M_2)/d \tag{1}$$

where M_1 and M_2 are the molecular weights of the components and d is the density of the solution.

The excess volume was calculated from the equation

$$V^E = V - (x_1V_1 + x_2V_2) \tag{2}$$

and the deviations of refractive index and relative permittivity were calculated from the following expressions:

$$\Delta n_D = n_D - (n_{D,1}x_1 + n_{D,2}x_2) \tag{3}$$

$$\Delta\epsilon = \epsilon - (\epsilon_1x_1 + \epsilon_2x_2) \tag{4}$$

The V^E, Δn_D, and $\Delta\epsilon$ values have been fitted using least squares to a Redlich−Kister type equation (Redlich and Kister, 1948):

$$X = x_1x_2\sum b_j(x_1 - x_2)^j \tag{5}$$

where X represents the excess volume or deviations, b_j is the polynomial coefficient, and j is the polynomial degree. In each case, the number of coefficients b_j is determined by examining the alteration of the relation

$$\sigma(x) = [\sum(x_{obs} - x_{cale})^2/(n - p)]^{1/2} \tag{6}$$

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

The resulting parameters b_j are given along with the standard deviation $\sigma(x)$ in Table 3.

The experimentally obtained values of the relative permittivity of mixtures are used to calculate the molar polarization of the mixture P_m from the Kirkwood−Frohlich equation:

$$P_m = (\epsilon - n_D^2)(2\epsilon + n_D^2)V/9\epsilon \tag{7}$$

and the deviation of the molar polarization, ΔP_m was calculated using the following equation:

$$\Delta P_m = P_m - (x_1P_{m1} + x_2P_{m2}) \tag{8}$$

where $P_{m,i}$ refers to the pure component.

The calculated values of P_m are given in Table 2. The obtained ΔP_m values were fitted to the equation

$$\Delta P_m = x_1x_2\sum b_i(x_1 - x_2)^i \tag{9}$$

The values of the coefficients b_i and the standard deviations are listed in Table 3.

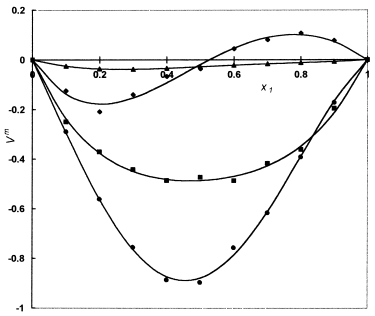

Figure 1. Plot of V^E against mole fraction of *N*,*N*′-dimethylacetamide x_1: (●) methanol; (■) ethanol; (▲) 2-propanol; (◆) 1-butanol.

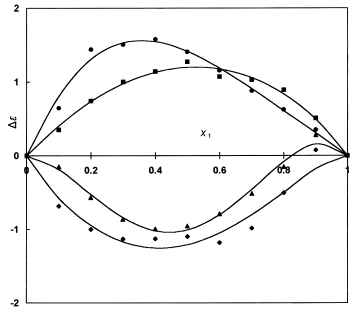

Figure 2. Plot of $\Delta\epsilon$ against mole fraction of *N*,*N*′-dimethylacetamide x_1: (●) methanol; (■) ethanol; (▲) 2-propanol; (◆) 1-butanol.

Table 3. Values of the Parameters b_i from Eqs 5 and 10 and the Standard Deviations $\sigma(V^E)$ and $\sigma(x)$

function	b_0	b_1	b_2	b_3	b_4	σ
298.15 K, *N*,*N*′- Dimethylacetamide + Methanol						
V^E/(cm^3 mol^{-1})	−0.87944	0.22693	1.26067	−0.23001	−0.38196	0.015
$\Delta\epsilon$	1.4113656	−0.93456	−1.17735	0.973672	−0.25149	0.093
Δn_D	0.028509	−0.00784	−0.02838	0.007962		0.0003
ΔP_m/(cm^3 mol^{-1})	−1.26386	−4.94268	6.232648	4.937069	−4.94669	0.48
298.15 K, *N*,*N*′-Dimethylacetamide + Ethanol						
V^E/(cm^3 mol^{-1})	−0.48649	0.032146	0.2704669	−0.02646	0.216365	0.015
$\Delta\epsilon$	1.198002	0.116456	−1.11315	−0.09546	−0.0896	0.064
Δn_D	0.017177	0.000806	−0.02468	−0.00034	0.007378	0.0010
ΔP_m/(cm^3 mol^{-1})	−8.60798	5.940333	9.94621	−5.57607	−1.39487	1.14
298.15 K, *N*,*N*′-Dimethylacetamide + 1-Butanol						
V^E/(cm^3 mol^{-1})	−0.01909	0.361313	−0.09596	−0.35985	0.117257	0.02
$\Delta\epsilon$	−1.20824	0.529348	1.416198	−0.43921	−0.1841	0.171
Δn_D	0.000498	0.00007	−0.00028	0.000095	−0.00012	0.00003
ΔP_m/(cm^3 mol^{-1})	−25.5662	12.64229	26.52639	−10.783		3.33
298.15 K, *N*,*N*′-Dimethylacetamide + 2-Propanol						
V^E/(cm^3 mol^{-1})	−0.02787	0.032862	0.000405	−0.03335	0.027251	0.001
$\Delta\epsilon$	−1.00751	0.567416	2.473503	−0.54971	−1.44228	0.0073
Δn_D	0.003713	−0.00636	−0.00856	0.00614	0.004871	0.00042
ΔP_m/(cm^3 mol^{-1})	−36.5865	10.05068	65.47576	−9.57959	−28.4296	1.51

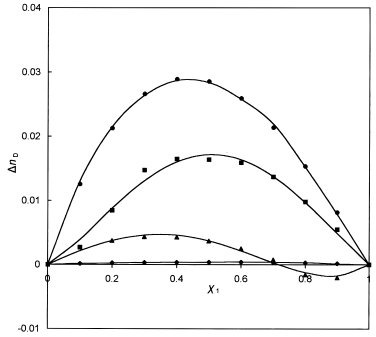

Figure 3. Plot of Δn_D against mole fraction of *N*,*N*′-dimethylacetamide x_1: (●) methanol; (■) ethanol; (▲) 2-propanol; (◆) 1-butanol.

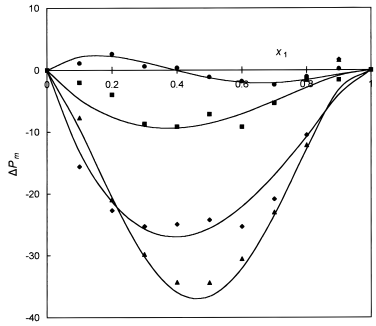

Figure 4. Plot of ΔP_m against mole fraction of *N*,*N*′-dimethylacetamide x_1: (●) methanol; (■) ethanol; (▲) 2-propanol; (◆) 1-butanol.

The variation of the excess volume with the mole fraction of *N*,*N*′-dimethylacetamide is shown in Figure 1. As can be seen in this figure, the values of V^E are negative for the binary mixture of *N*,*N*′-dimethylacetamide with methanol and ethanol. In the case of 1-butanol the values of V^E are close to zero. Finally, the excess volume of 2-propanol is almost zero through the entire range of mole fraction.

Figures 2 and 3 show the variation of $\Delta\epsilon$ versus x_1 and Δn_D vsersus x_1, respectively.

The variation of deviation in polar polarization of the four binary mixtures is shown in Figure 4.

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