

Density, Refractive Index, Permittivity, and Related Properties for *N*-Formylmorpholine + Ethyl Acetate and + Butanone at 298.15 K

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Density (ρ), refractive index (n_D), and permittivity (ϵ) were measured for *N*-formylmorpholine + ethyl acetate and + butanone over the entire composition range at 298.15 K. Excess molar volumes (V^E) were calculated and fitted to the Redlich–Kister equation.

1. Introduction

As a part of our experimental program on the physico-chemical properties of binary liquid mixtures containing *N*-formylmorpholine (NFM) as a common solvent (Awwad et al., 1985; Awwad, 1988), we report here measurements on the density, refractive index, and permittivity for *N*-formylmorpholine + ethyl acetate and + butanone at 298.15 K over the whole mole-fraction range. From these data we calculated the excess molar volumes (V^E) and the Kirkwood correlation factor (g_K). The V^E values were fitted to the Redlich–Kister polynomial equation (Redlich–Kister, 1948) to estimate the required number of adjustable parameters A_i and standard errors σ .

2. Experimental Section

2.1. Materials. Ethyl acetate (stated purity 99.5 mol %), butanone (stated purity 99.5 mol %), and *N*-formylmorpholine (stated purity >99.5 mol %) were obtained from Fluka AG. *N*-Formylmorpholine was further purified as previously described (Awwad, 1988). All liquids were kept over freshly activated molecular sieves of type 4A (Union Carbide) and filtered before use. The purity of liquids was confirmed by gas liquid chromatographic analysis. The liquid purity was ascertained by comparing their density, refractive index, and permittivity values with the literature data (Table 1). Binary mixtures were prepared on a weight basis. The uncertainty in the mole fraction was $<2 \times 10^{-4}$.

2.2. Measurements. Densities were measured with a digital precision densimeter DMA 60/602 (Anton Paar). The reproducibility of the density measurement was $\pm 2 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$.

Refractive indices for the sodium D line were measured with a thermostated Abbe refractometer (Tefsa, Germany), and the values presented here are the mean values from at least three independent readings for each solvent composition. The precision of the refractive index values was $\pm 2 \times 10^{-4}$.

Permittivity measurements were carried out at 1 MHz with a Wissenschaftlich–Technischen Werkstaten GMBH NF-Dekameter model 'DK-05'. The measuring cell was NFL-2 and calibrated with standard pure liquids, such as cyclohexane, dichloromethane, and acetone. All these solvents were spectrograde quality. Permittivities for the

Table 1. Experimental Density, Refractive Index, and Permittivity of Pure Liquids with Literature Values at 298.15 K

liquid	$\rho/\text{g}\cdot\text{cm}^{-3}$		n_D		ϵ	
	expt	lit.	expt	lit.	expt	lit.
ethyl acetate	0.894 50	0.894 55 ^a	1.3706	1.36979 ^a	6.05	6.02 ^a
butanone	0.798 61	0.799 7 ^a	1.3760	1.3764 ^a	17.37	
NFM	1.146 37	1.146 28 ^b	1.4850	1.4837 ^b	14.95	

^a Riddick and Bunger, 1970. ^b Awwad, 1988.

standards were taken from the literature (Riddick and Bunger, 1970). The reproducibility of permittivity data was within ± 0.05 .

In all measurements a Schott-Gerate CT1150 thermostat was used at a constant digital temperature control of ± 0.01 K.

3. Results and Discussion

The experimental results of densities, ρ , refractive indices, n_D , and permittivities, ϵ , over the whole mole fraction range at 298.15 K are reported in Table 2. The variation of these properties with mole fraction could be performed by using the following equation

$$Y = \sum_{i=0}^n A_i x_1^i \quad (1)$$

where Y represents n_D or ϵ of the mixtures and A_i are the parameters which could be estimated from a nonlinear least-squares method. Equation 1 fits the experimental values well and calculates the property Y within the limits of experimental error at each composition. The coefficients of eq 1 and standard errors are listed in Table 3.

The excess molar volumes have been calculated by the following equation:

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1 M_1 (\rho^{-1} - \rho_1^{-1}) + x_2 M_2 (\rho^{-1} - \rho_1^{-1}) \quad (2)$$

where x_1 and x_2 are the mole fractions of *N*-formylmorpholine and ethyl acetate or butanone, respectively. ρ , ρ_1 , and ρ_2 are the densities of the mixture, *N*-formylmorpholine, and ethyl acetate or butanone, respectively. M_1 and M_2 are the molecular weights of the pure fluids. The determined

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Table 2. Experimental Density (ρ), Refractive Index (n_D), and Permittivity (ϵ) for *N*-Formylmorpholine + Ethyl Acetate and + Butanone at 298.15 K

x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	n_D	ϵ
(x ₁)NFM + (x ₂)Ethyl Acetate				
0.0000	0.894 50	0.0000	1.3706	6.05
0.0499	0.907 07	0.0221	1.3772	6.53
0.0914	0.917 51	0.0459	1.3827	6.94
0.1499	0.932 58	0.0648	1.3915	7.52
0.2026	0.945 50	0.0859	1.3990	8.06
0.2995	0.969 90	0.1086	1.4112	9.05
0.3914	0.993 18	0.1247	1.4220	10.00
0.4720	1.013 30	0.1276	1.4310	10.84
0.5911	1.043 30	0.1202	1.4442	12.05
0.6780	1.066 33	0.1153	1.4538	12.90
0.7919	1.094 76	0.0874	1.4650	13.95
0.8478	1.107 84	0.0747	1.4704	14.33
0.8899	1.118 40	0.0639	1.4745	14.60
0.9480	1.134 13	0.0308	1.4801	14.81
1.0000	1.146 37	0.0000	1.4850	14.95
(x ₁)NFM + (x ₂)Butanone				
0.0000	0.798 61	0.0000	1.3760	17.37
0.0479	0.815 52	0.1948	1.3835	17.45
0.0916	0.830 41	0.3594	1.3912	17.71
0.1836	0.862 41	0.6182	1.4039	17.86
0.2816	0.896 51	0.7989	1.4157	17.69
0.3865	0.932 91	0.9076	1.4273	17.62
0.4924	0.969 71	0.9227	1.4380	17.21
0.5943	1.005 29	0.8599	1.4489	16.87
0.6887	1.038 00	0.7384	1.4580	16.54
0.7900	1.073 21	0.5576	1.4678	16.13
0.8898	1.107 90	0.3250	1.4770	15.60
0.9555	1.130 93	0.1337	1.4821	15.22
1.0000	1.146 37	0.0000	1.4850	14.95

Table 3. Values of the Parameters (A_i) and Standard Errors (σ) of the Redlich–Kister Equation, at 298.15 K

	A_0	A_1	A_2	A_3	σ
(x ₁)NFM + (x ₂)Ethyl Acetate					
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.5076	-0.0321	0.0937	0.1526	0.0027
n_D	1.3706	0.1415	-0.0277		0.0005
ϵ	5.88	11.82	-2.44		0.03
(x ₁)NFM + (x ₂)Butanone					
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	3.6911	-0.6839	0.0751	0.1692	0.0035
n_D	1.3775	0.1416	-0.0341		0.0012
ϵ	17.50	1.71	4.32		0.01

V^E values from density measurements are accurate to within $\pm 3 \times 10^{-4} \text{ cm}^3\cdot\text{mol}^{-1}$.

The values of the excess quantities were fitted to the Redlich–Kister (Redlich and Kister, 1948) polynomial equation.

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1x_2 \sum_{i=0}^m A_i(x_1 - x_2)^i \quad (3)$$

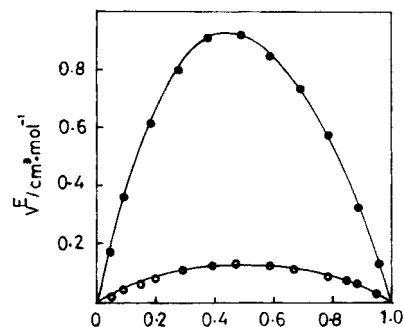
where A_0, A_1, A_2, \dots are adjustable parameters and evaluated by the method of least squares. The values of these parameters along with the standard errors

$$\sigma = \left[\frac{\sum (V_{\text{obs}}^E - V_{\text{cal}}^E)^2}{(n - p)} \right]^{1/2} \quad (4)$$

where n is the number of experimental points and p is the number of parameters A_i , are reported in Table 3.

The Kirkwood correlation factor (g_K) for pure components and binary mixtures was calculated from the following relation (Frohlich, 1958)

$$g_K = 9kT[(x_1M_1 + x_2M_2)/\rho] / [4\pi N(x_1\mu_1 + x_2\mu_2)^2][(\epsilon - \epsilon_\infty)(2\epsilon - \epsilon_\infty)/(\epsilon_\infty + 2)^2] \quad (5)$$

**Figure 1.** Excess molar volumes of (○) (x₁)NFM + (x₂)ethyl acetate and (●) (x₁)NFM + (x₂)butanone at 298.15 K.**Table 4. Values of the Kirkwood Correlation Factor g_K**

x_1	g_K	x_1	g_K
(x ₁)NFM + (x ₂)Ethyl Acetate			
0.0000	0.85	0.5911	0.57
0.2026	0.71	0.8899	0.47
0.4720	0.60	1.0000	0.42
(x ₁)NFM + (x ₂)Butanone			
0.0000	0.86	0.7900	0.51
0.3865	0.78	0.8898	0.46
0.5943	0.63		

where μ_i is the gas-phase dipole moment; in the above equation we used the dipole moment in nonpolar solvent for NFM = 4.09, ethyl acetate = 1.88, and butanone = 2.76 (Riddick and Bunger, 1970). ϵ_∞ is the square of the refractive index, $1.1n_D^2$ (Dannhauser and Bahe, 1964). k is the Boltzmann constant, T is the temperature in Kelvin, and N is Avogadro's number. The values of g_K are listed in Table 4.

The dependence of excess molar volumes (V^E) on the mole fraction of NFM is shown in Figure 1. For mixtures of ethyl acetate or butanone with NFM, the results of V^E are positive throughout the mole-fraction range, suggesting the predominance of the dispersion forces and dipolar dissociation over specific interactions in these mixtures.

The values of the Kirkwood correlation factor, g_K , for pure *N*-formylmorpholine, ethyl acetate, butanone, and their binary mixtures (Table 4) are less than unity. This indicates that NFM, ethyl acetate, and butanone and their mixtures are relatively unstructured liquids.

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