Refractive Indices, Densities, and Excess Properties of 4-(2-Hydroxyethyl)morpholine + Water at (298.15, 308.15, and 318.15) K

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Refractive index and density have been measured at (298.15, 308.15, and 318.15) K for the binary mixtures of 4-(2-hydroxyethyl)morpholine + water over the whole mole fraction range. From these data, the excess molar volume and the deviations in molar refractivity were calculated and fitted to the Redlich−Kister polynomial equation to estimate the adjustable parameters and the standard errors.

1. Introduction

In our preceding papers (Awwad and Kanbour, 1980; Awwad et al., 1983, 1985, 1988; Awwad, 1988) the experimental values of density, sound velocity, and viscosity have been reported for the binary mixtures containing morpholine, *N*-methylmorpholine, and *N*-formylmorpholine as one component. As a part of our experimental program on the physiochemical properties of binary mixtures of morpholines, we present here the experimental results of the density, ρ, and the refractive index, n_D, for the binary mixtures of 4-(2-hydroxyethyl)morpholine + water at (298.15, 308.15, and 318.15) K over the whole mole fraction range. From these results, the excess molar volumes and the deviation in molar refractivity, ΔR, have been calculated over the whole mole fraction range.

2. Experimental Section

2.1. Materials. The water was deionized and doubly distilled. Its specific conductivity was $<1 \times 10^{-6}$ S cm^{-1}. 4-(2-Hydroxyethyl)morpholine (Aldrich, 99% purity) was purified as previously described (Awwad et al., 1983) and dried over freshly activated 4A molecular sieves (Fluka AG). The water content, as determined by gas−liquid chromatography, was $<0.1 \pm 0.01$%. The uncertainty in the mole fractions was $<2 \times 10^{-4}$.

2.2. Measurements. Densities were measured with a digital precision system DMA 60/602 (Anton Paar). Details of the system and the calibration procedure were adequately covered in previous work (Al-Azzawi and Awwad, 1990). The overall precision of the density measured is estimated to be better than $\pm 2 \times 10^{-5}$ g·cm^{-3}.

Refractive indices for the sodium D-line were measured with an Abbe refractometer. A minimum of three independent readings were taken for each composition. The refractive index values are accurate to $\pm 2 \times 10^{-4}$.

For all measurements, a Schott-Gerate CT 1150 thermostat was used at a constant digital temperature control of ±0.01 K at the desired temperature.

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3. Results and Discussion

The experimental data of densities, ρ, and refractive indices, n_D, at various mole fractions and three temperatures are presented in Table 1. The excess molar volumes have been calculated from the relation

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - x_1\frac{M_1}{\rho_1} - x_2\frac{M_2}{\rho_2} \quad (1)$$

Deviations in molar refractivity, ΔR, were calculated from (Aminabhavi and Golalakrishina, 1995)

$$\Delta R/\text{cm}^3\cdot\text{mol}^{-1} = R_m - \phi_1R_1 - \phi_2R_2 \quad (2)$$

$$R_m = \left(\frac{n_D^2 - 1}{n_D^2 + 1}\right)\left(\frac{x_1M_1 + x_2M_2}{\rho}\right) \quad (3)$$

$$R_i = \left(\frac{n_D^2 - 1}{n_D^2 + 1}\right)\left(\frac{M_i}{\rho_i}\right) \quad (4)$$

and

$$\phi_i = \frac{x_iV_i}{\sum_{i=1}^{2} x_iV_i} \quad (5)$$

where x_1 and x_2 are the mole fractions of 4-(2-hydroxyethyl)morpholine and water, respectively; ρ, ρ_1, and ρ_2 are the densities; and n_D and n_{Di} are the measured refractive indices of the mixture and the pure component liquids, respectively. M_1 and M_2 are the molecular weights of liquids 1 and 2, V_i is the molar volume of the ith component liquid. ϕ_1 and ϕ_2 are the volume fractions of component liquids 1 and 2.

The calculated values of V^E and ΔR were fitted to the Redlich−Kister polynomial equation (Redlich and Kister, 1948):

$$V^E \text{ (or } \Delta R) = x_1x_2\sum_{j=0}^{n} A_j(x_2 - x_1)^j \quad (6)$$

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Table 1. Experimental Values of the Refractive Index (n_D) and Density (ρ), Deviation of the Molar Refractivity (ΔR) and Excess Molar Volumes (V^E) for 4-(2-Hydroxyethyl)morpholine at (298.15, 308.15, and 318.15) K

x_1	n_D	ΔR/cm^3·mol^{-1}	ρ/g·cm^3	V^E/cm^3·mol^{-1}
		$T = 298.12$ K		
0.0000	1.3329	0.0000	0.99707	0.0000
0.0224	1.3329	−3.4528	1.01696	−0.1989
0.0423	1.3736	−5.7459	1.03023	−0.3504
0.0636	1.3826	−7.7675	1.04165	−0.5023
0.0859	1.3959	−9.3511	1.05098	−0.6436
0.0993	1.4020	−10.1352	1.05587	−0.7284
0.1401	1.4241	−11.5911	1.06615	−0.9234
0.1974	1.4303	−13.2515	1.07468	−1.1228
0.2976	1.4470	−13.7804	1.08145	−1.3314
0.4008	1.4574	−12.7804	1.08191	−1.3292
0.4992	1.4636	−11.5234	1.08031	−1.2057
0.5945	1.4673	−9.7397	1.07851	−1.0384
0.6884	1.4704	−7.6401	1.07634	−0.8077
0.7859	1.4717	−5.4649	1.07471	−0.5829
0.8802	1.4734	−3.1426	1.07324	−0.3515
0.9500	1.4747	−1.2501	1.07210	−0.1476
1.0000	1.4756	0.0000	1.07132	0.0000
		$T = 308.15$ K		
0.0000	1.3316	0.0000	0.99406	0.0000
0.0224	1.3520	−3.4792	1.01087	−0.1541
0.0423	1.3720	−5.7855	1.02413	−0.3152
0.0636	1.3824	−7.7955	1.03518	−0.4688
0.0859	1.3934	−9.4092	1.04499	−0.6322
0.0993	1.4001	−10.1842	1.04992	−0.7245
0.1401	1.4125	−11.6033	1.05971	−0.8755
0.1974	1.4276	−13.3057	1.06738	−1.1163
0.2976	1.4435	−13.8353	1.07321	−1.3140
0.4008	1.4540	−13.0157	1.07341	−1.3172
0.4992	1.45997	−11.5675	1.07177	−1.2055
0.5945	1.4643	−9.7160	1.06885	−0.9674
0.6884	1.4664	−7.7134	1.06695	−0.7602
0.7859	1.4688	−5.4179	1.06532	−0.5391
0.8802	1.4704	−3.0894	1.06413	−0.3379
0.9500	1.4709	−1.2413	1.06309	−0.1387
1.0000	1.4716	0.0000	1.06225	0.0000
		$T = 318.15$ K		
0.0000	1.3301	0.0000	0.99025	0.0000
0.0224	1.3509	−3.4720	1.00656	−0.1525
0.0423	1.3701	−5.7906	1.01889	−0.2999
0.0636	1.3813	−7.7871	1.02933	−0.4444
0.0859	1.3905	−9.4241	1.03843	−0.5941
0.0993	1.3974	−10.2021	1.04435	−0.7147
0.1401	1.4152	−11.5001	1.05422	−0.8700
0.1974	1.4253	−13.3009	1.06063	−1.0826
0.2976	1.4406	−13.8005	1.06382	−1.1653
0.4008	1.4514	−12.9636	1.06448	−1.1699
0.4992	1.4573	−11.4986	1.06314	−1.0575
0.5945	1.4604	−9.7212	1.06144	−0.8928
0.6884	1.4641	−7.6540	1.06001	−0.7192
0.7859	1.4652	−5.4116	1.05838	−0.4962
0.8802	1.4667	−3.1011	1.05746	−0.3185
0.9500	1.4672	−1.2411	1.05641	−0.1366
1.0000	1.4682	0.0000	1.05572	0.0000

where n is the number of adjustable parameters A_j. In each case, the optimum number of adjustable parameters is ascertained from an examination of the variation in standard errors, σ, as given by

$$\sigma(V^E \text{ or } \Delta R) = \left[\frac{((V^E \text{ or } \Delta R)_{obs}) - ((V^E \text{ or } \Delta R)_{cal})^2}{(N - P)}\right]^{1/2} \quad (7)$$

N represents the number of experimental points and P the number of adjustable parameters. The values of these parameters, A_j, along with the standard errors, σ, are listed in Table 2.

Excess molar volumes (V^E) and deviations in molar refractivity (ΔR) are negative for the system studied over the entire range of mole fraction at (298.15, 308.15, and 318.15) K. V^E and ΔR show a negligible temperature dependence. However, this dependence is not shown graphically to avoid overcrowding of graphs. Figures 1 and 2 show that there is a minimum in V^E and ΔR in the water-rich region, which is related to the composition of 4-(2-hydroxyethyl)morpholine + water at a ratio of 2 mol of water to 1 mol of 4-(2-hydroxyethyl)morpholine. Such behavior is similar to that obtained by Al-Azzawi et al. (1990) for the system of 2-pyrrolidone + water. Such behavior may be attributed mainly to the association through intermolecular hydrogen bonding between the water and hydroxy groups

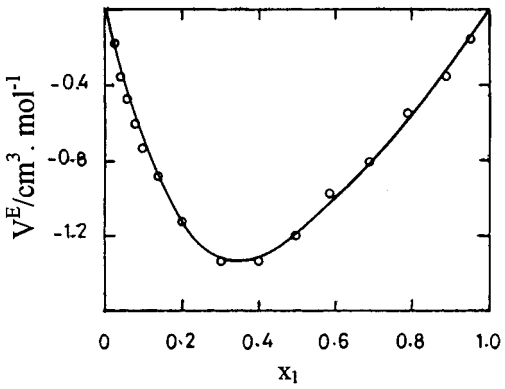

Figure 1. Excess molar volume V^E versus x_1, mole fraction of 4-(2-hydroxyethyl)morpholine at 298.15 K.

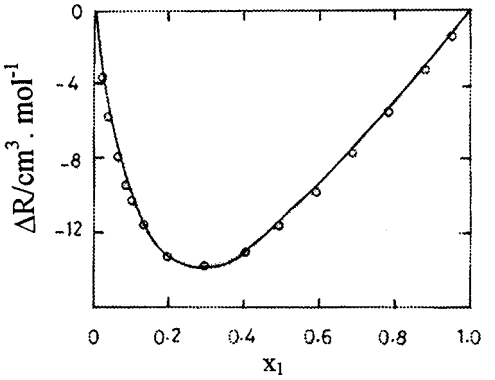

Figure 2. Deviations in molar refractivity ΔR versus x_1, mole fraction of 4-(2-hydroxyethyl)morpholine at 298.15 K.

Table 2. Parametric (A_i) and Standard Errors (σ) of the Redlich−Kister Equation

function	T/K	A_0	A_1	A_2	A_3	σ
V^E/cm^3·mol	298.15	−4.5309	−6.0414	−3.5193		0.011
	308.15	−4.4799	−3.1816	−2.7731	−3.5995	0.012
	318.15	−4.1267	−2.8834	−2.9503	−3.7305	0.011
ΔR/cm^3·mol^{-1}	298.15	36.4354	−5.3778	−91.7138	−135.9570	0.45
	308.15	36.5827	−5.5621	−92.1290	−136.7065	0.50
	318.15	36.3940	−5.3762	−92.2967	−136.8291	0.47

and the lone pair electrons on the nitrogen atom of 4-(2-hydroxyethyl)morpholine. These interactions lead to higher negative V^E and ΔR values.

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