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Thermodynamic Properties of the Binary and Ternary Systems Containing *N*-Formylmorpholine, Methanol, Benzene and Toluene at 298.15 K

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Abstract

Excess molar volumes and the deviations in molar refraction of the *N*-formylmorpholine (NFM) + methanol, methanol+benzene, NFM +benzene, NFM +toluene, methanol + toluene binary systems and also for the ternary systems of NFM + methanol + benzene and NFM + methanol + toluene have been determined at 298.15 K and at atmospheric pressure, by measuring densities and refractive indices over the entire range of composition. These derived data of binary and ternary mixtures were fitted to Redlich–Kister and Cibulka equations for the binary and ternary systems. The ternary data were also compared with the predicted values using the binary contribution models of Tsao-Smith, Kohler and Radojkovicˇ.

Introduction

The studies of liquid mixture behaviour of industrially important chemicals have generated considerable interest in recent years. Studies of the phase equilibrium behaviour and excess properties of liquid mixtures are of great importance for the design of separation processes and for theoretical understanding of the nature of molecular interactions [1]. While large numbers of phase equilibria and other mixture properties are available for binary mixtures, the excess properties of ternary mixtures, required to obtain insight into the nature and degree of interactions, are relatively unexplored. It is important to test methods of estimating excess properties of ternary mixtures from binary data [2].

N-Formylmorpholine (NFM) is a highly polar and dense solvent with good stability as an extractive agent and has been successfully used in industry for the extraction and extractive distillation of pure monocyclic aromatic hydrocarbons from petroleum feedstock's [3].

This paper reports the measured densities and refractive indices as well as excess and derived properties of the ternary mixture for the ternary systems of NFM + methanol + benzene and NFM + methanol + toluene at 298.15 K and atmospheric pressure. The experimental results are used to calculate excess molar volumes, and refractive index deviations from the volume fraction average. The excess quantities of binary mixtures have been fitted to the Redlich-Kister equation to determine the coefficients. For correlating the ternary data, the Cibulka and Redlich-Kister equation were used. As far as we know, no ternary data are available for the mixtures investigated in the open literature.

Experimental

Materials:

NFM, (Fluka AG,Puriss.P.a), benzene, toluene and methanol were supplied from (Merck, mole fraction purity > 0.995). All chemicals were used without further purification but were kept over freshly activated molecular sieves of type 4A for several days before use. The purity of solvents was further ascertained by comparing their densities and refractive indices at a temperature of 298.15 K, and the results are generally in agreement with the corresponding values reported in the literature values [4-11] as shown in Table 1. All the mixtures were prepared by mass using an electronic balance (model GR-202R, AND, Japan) with a precision of ± 0.01 mg. The accuracy of the mole fraction was estimated to be $\pm(2\times10^{-4})$.

Table (1)

Density (r) and refractive index (n_D) of pure liquids with the corresponding literature values at a temperature of 298.15 K.

Substance	***r /g . cm^{-3}***		***n_D***	
	Exptl.	***Lit.***	***Exptl.***	***Lit.***
NFM	1.14637	1.14628(4)	1.4839	1.4837 (5)
Benzene	0.87391	0.87360(6) 0.87362(7)	1.4980	1.4979(8)
Toluene	0.86201	0.86219(6) 0.86231(9)	1.4942	1.4941(8)
Methanol	0.78660	0.7864(10) 0.7867(11)	1.3266	1.3264(5)

Measurements:

The density measurements of the pure solvents and the mixtures were performed by means of an Anton Paar, model DMA 48, Graz, Austria with a precision of ±0.00005 g cm^{-3}at 298.15. The DMA cell was calibrated with dry air and deionized pure water at atmospheric pressure. The sample size was 0.70 cm^3 and the sample thermostat was controlled to ±0.01 K. The accuracy in density measurements was better than ±(1×10^{-2}) kg.m^{-3}.

Refractive indices values for the D-line were measured with a thermostated Abbe refractometer (Tefsa) with a precision of ±0.0001. The refractometer was calibrated using deionized water and toluene. A minimum of three independent readings were recorded for each composition. The refractive index values were ±(2×10^{-4}). All measurements were performed in a thermostat maintained at ±0.05 K using a HAKKE-D1-G thermostat water bath.

Results and Discussion

Binary Systems:

The excess molar volumes (V^E) for the multicomponent mixtures and deviations in the refraction (ΔR_m) of the mixtures were calculated using the following relations:

$$V^E = V - \sum_{i=1}^{2} V_i x_i \quad \text{.....................................(1)}$$

$$\Delta R_m = R_m - \sum_{i=1}^{2} R_i \emptyset_i \quad \text{..............................(2)}$$

$$\emptyset_i = \frac{V_i x_i}{\sum_{i=1}^{m} V_i x_i} \quad \text{..(3)}$$

Where x_i and $\emptyset i$ represent the mole fraction and volume fraction of the pure component *i*, respectively; *V* and R_m are the molar volume and molar refraction of the mixtures, respectively, and V_i and R_i the corresponding properties of the pure components. The molar refraction was calculated from the Lorentz–Lorentz equation [12].

The values of the excess molar volumes and the changes of refractive indexes on mixing, were fitted by the Redlich–Kister equation for every binary mixture, according to the equation [13]:

$$Y = x_i x_j \sum_{K=0}^{p} A_k \ (x_i - x_j)^K \quad \text{...........................(4)}$$

Where Y is V^E, ΔR_m and p is the degree of polynomial expansion. The adjustable parameters A_k obtained by fitting the equations to the experimental values with a least-squares algorithm.

The root mean square deviations presented in this paper were computed using [14]:

$$\sigma = \left[\frac{\sum_{i=1}^{n}(Y^{exp} - Y^{calc})^2}{n-m}\right]^{0.5} \quad \text{.......................(5)}$$

Where n is the number of experimental data and m is the number of parameters.

In Table (5), the fitting parameters corresponding to Eq.(4) and the corresponding standard deviations are shown.

Table (2)

Experimental Densities, refractive indices, excess molar volumes and deviations in molar refraction for the Binary Systems at 298.15 K.

x_1	r / g. cm^{-3}	n_D	V^E / cm^{3}mol^{-1}	ΔR_m / cm^3 mol^{-1}
NFM (1)+ methanol(2)				
0.0000	0.78660	1.3266	0.000	0.000
0.1698	0.91557	1.3853	-0.465	-3.282
0.2041	0.93554	1.3990	-0.542	-3.502
0.2973	0.98141	1.4132	-0.663	-4.273
0.3977	1.02069	1.4313	-0.709	-4.413
0.4965	1.05197	1.4444	-0.699	-4.232
0.6155	1.08240	1.4569	-0.632	-3.658
0.6783	1.09588	1.4611	-0.560	-3.282
0.7819	1.11545	1.4681	-0.443	-2.464
0.8845	1.13144	1.4736	-0.262	-1.502
1.0000	1.14637	1.4839	0.000	0.000
Methanol (1) + Benzene (2)				
0.0000	0.87391	1.4980	0.000	0.000
0.0917	0.87028	1.4898	-0.021	-0.871
0.2078	0.86487	1.4814	-0.026	-1.712
0.3028	0.85977	1.4715	-0.024	-2.353
0.4014	0.85376	1.4575	-0.024	-2.957
0.5370	0.84411	1.4409	-0.030	-3.293
0.5866	0.84018	1.4318	-0.041	-3.378
0.6634	0.83337	1.4173	-0.053	-3.340
0.8195	0.81605	1.3829	-0.061	-2.553
0.9106	0.80289	1.3581	-0.046	-1.524
1.0000	0.78660	1.3266	0.000	0.000
NFM (1)+ Benzene (2)				
0.0000	0.87391	1.4980	0.000	0.000
0.1128	0.91138	1.4963	-0.340	-0.127
0.2011	0.93937	1.4951	-0.526	-0.192
0.2818	0.96444	1.4939	-0.687	-0.250
0.3212	0.97649	1.4934	-0.762	-0.273
0.4337	1.00969	1.4918	-0.911	-0.321
0.5033	1.02905	1.4908	-0.931	-0.328
0.6483	1.06724	1.4887	-0.867	-0.306
0.7233	1.08554	1.4877	-0.751	-0.263
0.8551	1.11589	1.4859	-0.463	-0.161
1.0000	1.14637	1.4839	0.000	0.000

Methanol (1) + Toluene (2)				
0.0000	0.86201	1.4942	0.000	0.000
0.0993	0.85910	1.4889	-0.016	-1.261
0.2073	0.85542	1.4799	-0.027	-2.596
0.2872	0.85234	1.4734	-0.038	-3.418
0.3541	0.84943	1.4671	-0.045	-4.021
0.4860	0.84271	1.4522	-0.060	-4.910
0.5926	0.83594	1.4359	-0.067	-5.286
0.7067	0.82687	1.4149	-0.070	-5.130
0.8106	0.81621	1.3926	-0.062	-4.249
0.8999	0.80430	1.3667	-0.039	-2.788
1.0000	0.78660	1.3266	0.000	0.000
NFM (1) + Toluene (2)				
0.0000	0.86201	1.4942	0.000	0.000
0.1078	0.89396	1.4931	-0.352	-0.118
0.2054	0.92289	1.4921	-0.608	-0.204
0.2611	0.93914	1.4915	-0.701	-0.238
0.3453	0.96358	1.4907	-0.799	-0.269
0.501	1.00859	1.4891	-0.879	-0.296
0.5726	1.02905	1.4883	-0.860	-0.293
0.6896	1.06206	1.4871	-0.752	-0.256
0.786	1.08870	1.4860	-0.582	-0.204
0.8666	1.11042	1.4851	-0.373	-0.138
1.0000	1.14637	1.4839	0.000	0.000

Table (3)

Densities, refractive indices, excess molar volumes, and deviations in molar refraction for NFM (1) + methanol (2) + benzene (3) ternary system at 298.15 K.

x_1	x_2	$r\ /g\ .\ cm^{-3}$	n_D	$V^E/cm^3\ mol^{-1}$	$\Delta R_m/cm^3\ mol^{-1}$
0.1445	0.8117	0.90053	1.4322	-0.338	-2.099
0.1852	0.7619	0.92439	1.4459	-0.419	-2.421
0.2087	0.7250	0.93703	1.4496	-0.459	-2.706
0.2143	0.6808	0.94017	1.4529	-0.472	-2.909
0.2336	0.7303	0.94923	1.4513	-0.482	-2.703
0.3143	0.3562	0.98017	1.4539	-0.709	-3.543
0.3271	0.6013	0.99031	1.4516	-0.615	-3.578
0.3993	0.5005	1.01565	1.4508	-0.689	-3.877
0.4091	0.4028	1.01603	1.4520	-0.789	-3.799
0.4720	0.2729	1.03187	1.4534	-0.876	-3.456
0.5009	0.3868	1.04634	1.4582	-0.759	-4.055
0.5806	0.2786	1.06501	1.4682	-0.774	-3.745
0.7654	0.1234	1.10436	1.4580	-0.601	-2.435
0.8113	0.0924	1.11297	1.4630	-0.513	-1.962
0.8145	0.1215	1.11622	1.4563	-0.499	-2.457
0.8631	0.0101	1.11693	1.4819	-0.309	-0.377
0.9264	0.0111	1.13272	1.4814	-0.298	-0.656

Table (4)

Densities, refractive indices, excess molar volumes, and deviations in molar refraction for NFM (1) + methanol (2) + toluene (3) ternary system at 298.15 K.

x_1	x_2	r/g. cm^{-3}	n_D	V^E/cm^3 mol^{-1}	ΔR_m/cm^{3}mol^{-1}
0.1312	0.6217	0.89519	1.4270	-0.355	-3.880
0.2122	0.5619	0.93254	1.4352	-0.523	-4.106
0.2198	0.5325	0.93516	1.4395	-0.533	-4.223
0.2841	0.5022	0.96176	1.4426	-0.620	-4.190
0.3070	0.6103	0.97790	1.4250	-0.601	-3.699
0.4955	0.3582	1.03533	1.4574	-0.789	-4.321
0.5110	0.3913	1.04459	1.4532	-0.765	-4.331
0.5800	0.4106	1.07358	1.4496	-0.723	-4.421
0.5916	0.3338	1.06814	1.4587	-0.775	-4.243
0.6588	0.2729	1.08375	1.4642	-0.732	-4.012
0.6866	0.2286	1.08739	1.4683	-0.719	-3.702
0.6985	0.1586	1.08237	1.4746	-0.732	-3.011
0.7306	0.1134	1.08672	1.4781	-0.701	-2.356
0.7631	0.0924	1.09372	1.4794	-0.645	-2.023
0.8567	0.0865	1.12017	1.4788	-0.442	-2.004
0.8834	0.0234	1.11888	1.4834	-0.396	-0.671
0.9076	0.0156	1.12424	1.4837	-0.317	-0.460

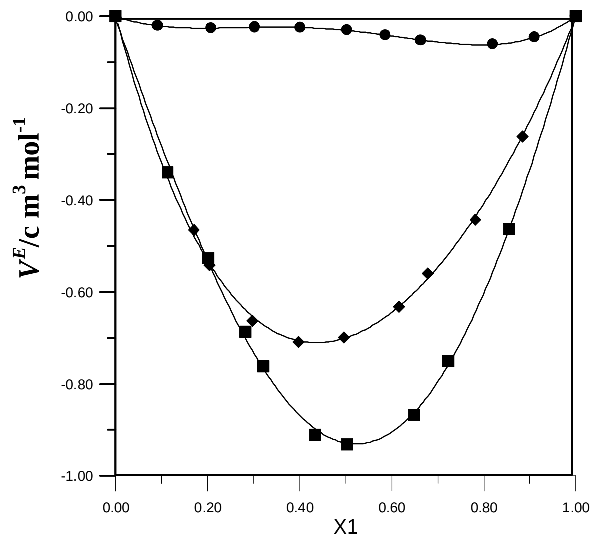

Fig. (1) Excess molar volumes (V^E) for the three binary systems of NFM, methanol, and benzene at 298.15 K: ♦ , NFM (1) + methanol (2); ● , methanol (1) + benzene (2); ■, NFM (1) + benzene (2).

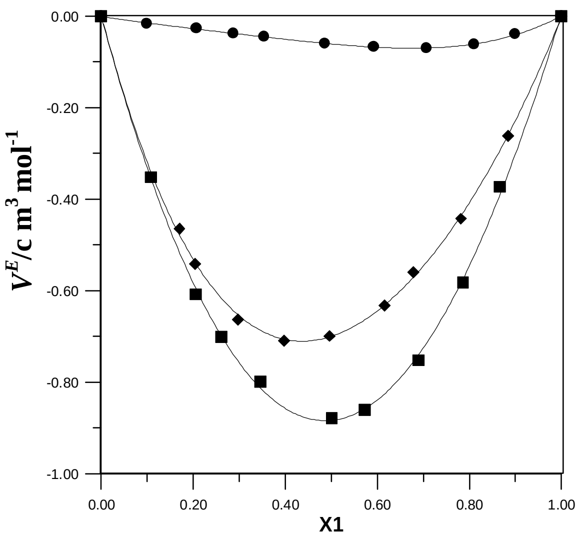

Fig.(2) Excess molar volumes (V^E) for the three binary systems of NFM, methanol, and toluene at 298.15 K: ♦ , NFM (1) + methanol (2); ● , methanol (1) + toluene (2); ■, NFM (1) + toluene (2).

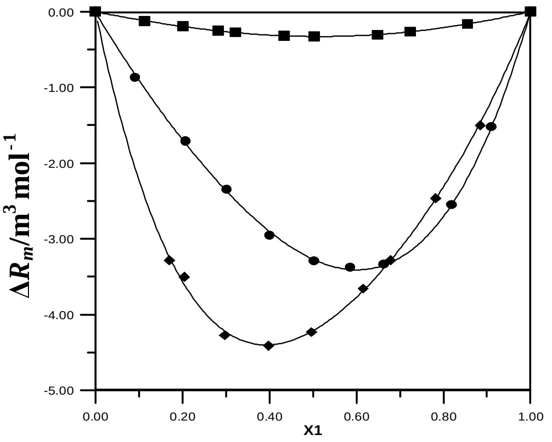

Fig.(3) Deviations in molar refraction (ΔR_m) for the three binary systems of NFM, methanol, and benzene at 298.15 K: ♦ , NFM (1) + methanol (2); ● , methanol (1) + benzene (2); ■, NFM (1) + benzene (2).

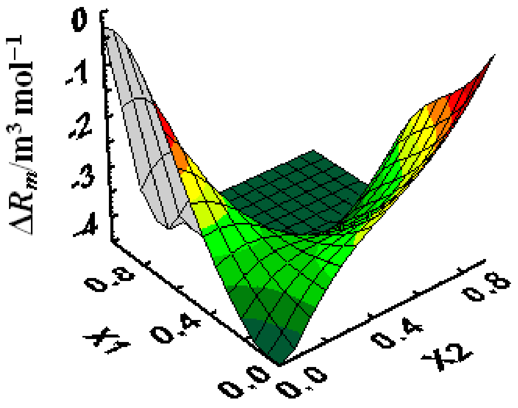

Fig.(6) Deviations in molar refraction for ternary system NFM (1)+methanol (2)+ benzene (3) at 298.15 K.

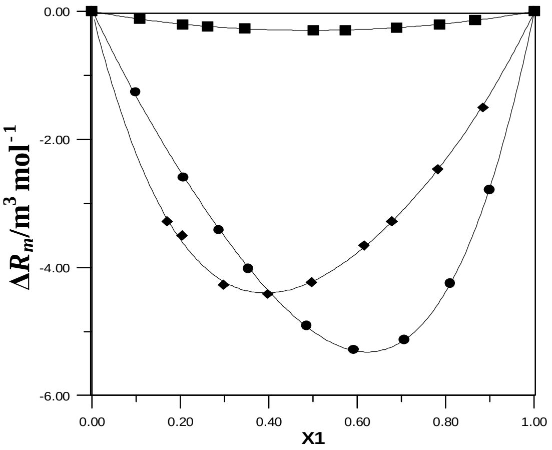

Fig.(4) Deviations in molar refraction (ΔR_m) for the three binary systems of NFM, methanol, and toluene at 298.15 K: ♦ , NFM (1) + methanol (2); ● , methanol (1) + toluene (2); ■, NFM (1) + toluene (2).

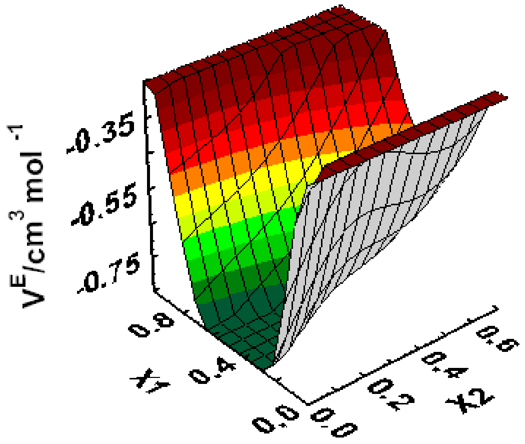

Fig.(7) Excess molar volume for ternary system NFM (1) + methanol (2) + toluene (3) at 298.15 K.

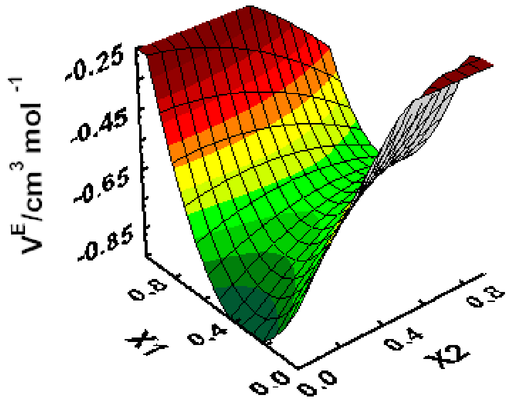

Fig.(5) Excess molar volume for ternary system NFM (1) + methanol (2) + benzene(3) at 298.15 K.

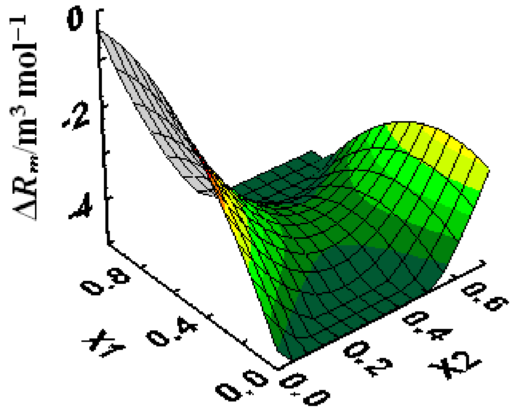

Fig.(8) Deviations in molar refraction for ternary system NFM (1)+methanol (2)+ toluene (3) at 298.15 K.

Table (5)

Binary Interaction Coefficients of the Redlich-Kister Equation and Standard Deviations σ for V^E, ΔR_m of five Binary Systems at T = 298.15 K.

Function	***A_0***	***A_1***	***A_2***	***A_3***	***σ***
NFM (1)+ methanol(2)					
V^E / cm^{3}mol^{-1}	-2.8036	-0.7726	-0.3610	0.4134	0.006
ΔR_m / cm^3 mol^{-1}	-16.8723	-6.9864	-4.1039	1.5674	0.045
Methanol (1) + Benzene (2)					
V^E / cm^{3}mol^{-1}	-0.1234	0.1951	-0.4240	-0.0151	0.007
ΔR_m / cm^3 mol^{-1}	-13.0743	5.2718	-1.8473	0.0427	0.013
NFM (1)+ Benzene (2)					
V^E / cm^{3}mol^{-1}	-3.7183	0.4938	0.4852	-0.4284	0.001
ΔR_m / cm^3 mol^{-1}	-1.31204	0.1452	0.1248	-0.2042	0.003
Methanol (1) + Toluene (2)					
V^E / cm^{3}mol^{-1}	-0.2430	0.1936	-0.1027	-0.0355	0.001
ΔR_m / cm^3 mol^{-1}	-19.9952	9.2671	-4.1608	1.7162	0.017
NFM (1) + Toluene (2)					
V^E / cm^{3}mol^{-1}	-3.5330	-0.0442	0.0089	-0.4787	0.008
ΔR_m / cm^3 mol^{-1}	-1.1912	-0.0124	-0.0764	-0.0341	0.002

Table (6)

Fitted Redlich-Kister and Cibulka Parameters with the Standard Deviations for V^E, ΔR_m of NFM + methanol + benzene and NFM + methanol + toluene at 298.15 K.

Function	***B_0***	***B_1***	***B_2***	***B_3***	***B_4***	***B_5***	***B_6***	***σ***
NFM (1) + methanol (2) + benzene (3)								
Cibulka Eq(6)								
V^E / cm^{3}mol^{-1}	1.4618	-8.6650	-0.6101	9.3748				0.033
ΔR_m / cm^3 mol^{-1}	7.2248	-22.9665	-7.6587	16.5079				0.005
Redlich-Kister Eq.(7)								
V^E / cm^{3}mol^{-1}	-0.1301	-2.2907	-5.0712	-7.4510	-11.262	11.070	26.4184	0.003
ΔR_m / cm^3 mol^{-1}	-1.1735	0.3361	-3.3733	-3.1354	4.7125	1.5479	-1.1999	0.004
NFM (1) + methanol (2) + toluene (3)								
Cibulka Eq(6)								
V^E / cm^{3}mol^{-1}	1.2470	1.2302	-3.1269	-3.6622				0.006
ΔR_m / cm^3 mol^{-1}	-1.0118	-2.7414	-0.1903	0.0687				0.010
Redlich-Kister Eq.(7)								
V^E / cm^{3}mol^{-1}	-0.7998	-0.4437	3.0572	2.6855	1.9327	-8.4994	-4.1844	0.004
ΔR_m / cm^3 mol^{-1}	2.9277	4.3454	-20.1889	-15.7698	-13.3006	43.509	16.240	0.009

Table (7)

Standard Deviations for the Estimation Results of V^E, ΔR_m of NFM + methanol + benzene and NFM + methanol + toluene at 298.15 K.

Model eq.	*Kohler*	*Tsao-Smith*	*Radojkovicˇ*
NFM (1) + methanol (2) + benzene (3)			
V^E / cm^{3}mol^{-1}	0.073	0.185	0.090
ΔR_m/ cm^3 mol^{-1}	0.040	0.035	0.020
NFM (1) + methanol (2) + toluene (3)			
V^E / cm^{3}mol^{-1}	0.085	0.175	0.090
ΔR_m/ cm^3 mol^{-1}	0.009	0.013	0.008

The experimental densities, refractive indices, excess molar volumes, and the deviations in molar refraction at 298.15 K for the binary systems of the NFM + methanol, methanol + benzene, NFM +benzene, NFM + toluene, methanol + toluene are listed and plotted in Table (2) and Figs. (1 to 4) . It can be seen from Figs. (1, 2) that V^E values for all binary mixtures over the whole composition range are negative.

It can be summarized that [15] V^E values may be affected by two factors. The first factor is the physical intermolecular forces including electrostatic forces between charged particles and between permanent dipoles etc., induction forces between a permanent dipole and an induced dipole, and forces of attraction (dispersion forces) and repulsion between non polar molecules. Physical intermolecular forces are weak usually, and the sign of V^E values may be positive or negative. The second factor is the structural characteristics of the components, arising from geometrical fitting of one component into the other's structure due to the differences in shape and size of components and free volume.

The V^E values of methanol (1) + benzene (2) and methanol (1) + toluene (2) systems are very close to ideal behaviour. In contrast, the systems NFM (1) + benzene and NFM (1) + toluene (2) show relatively large negative deviations values. This suggest that the dipole-induced-dipole interaction between the formyl group (NCHO) of NFM is greater than the dispersive and dipole-dipole interaction and leads to a slight increase in the attraction, giving negative V^E values. The V^E of the NFM (1) + methanol (2) system show negative values in the whole composition range. This may be due to the destroying self association in methanol and new hydrogen bonds between the carbonyl group of NFM which have oxygen and the hydrogen of methanol was formed.

Figs.(3,4) show molar refraction deviations for the binary mixtures, plotted against the mole fraction together with the fitted curve, obtained from the Redlich-Kister equation. The ΔR_m data have negative deviations from the ideal solution for all binary system. That is because the molecular interactions between each component are not very strong in every binary and ternary system.

Ternary Systems:

The densities, refractive indices ,excess molar volumes, and the deviations in molar refraction at 298.15 K for the ternary systems of NFM (1) + methanol (2) + benzene (3) and NFM (1) + methanol (2) + toluene (3) are determined and listed in Tables (3) and 4 and Figs. (5 to 8). The measured ternary V^E and ΔR_m data have negative deviations from ideal behaviours over whole composition range. This suggest that the ternary mixtures are not ideal in terms of component binaries, indicating that the third component modifies the nature and degree of molecular interaction between NFM and methanol. The excess volume and the deviations in molar refraction data were correlated with Cibulka equation [16] as a modification of the Radojkovicˇ quation[17]:

$$\Delta Q_{123} = \Delta Q_{12}+\Delta Q_{13}+\Delta Q_{23}+x_1x_2x_3(B_0+B_1x_1+B_2x_2+B_3x_1^2) \ldots\ldots(6)$$

Where ΔQ_{12}, ΔQ_{13} and ΔQ_{23} represent the excess properties V^E and ΔR_m calculated from binary Redlich-Kister parameters and x_1, x_2 and x_3 are mole fractions in the ternary mixture.

On the other hand, the V^E and ΔR_m data were correlated by mean of Redlich-Kister equation:

$$\Delta Q_{123} = \Delta Q_{12}+\Delta Q_{13}+\Delta Q_{23}+x_1x_2x_3(B_0+B_1(x_1-x_2)+B_2(x_2-x_3)+B_3(x_1-x_3)+B_4(x_1-x_2)^2+B_5(x_2-x_3)^2+B_6(x_1-x_3)^2+\ldots) \ldots\ldots (7)$$

The unweighted least –squares method was used to fit the polynomial to the data. The parameters for fitting eqs. 6, 7 and the corresponding standard deviations obtained is given in Table (6).

Excess molar volumes and the deviations in molar refraction for the ternary system were calculated using three conventional prediction models of Tsao-Smith [18], Kohler [19] and Radojkovicˇ [17]. The expressions for these models are as follow:

Tsao-Smith equation:

$$\Delta Q_{123} = x_2(1-x_1)^{-1}\Delta Q_{12} + x_3(1-x_1)^{-1}\Delta Q_{3} + (1-x_1)\Delta Q_{23} \ldots\ldots(8)$$

Where ΔQ_{ij} is the binary contribution of the ternary property at x_i^o and x_j^o:

$x_i^o = 1 - x_j^o = x_i/(x_i + x_j)$

Kohler equation:

$$\Delta Q_{123} = (x_1+x_2)^2\Delta Q_{12} + (x_1+x_3)^2\Delta Q_{13} + (x_2+x_3)^2\Delta Q_{23} \ldots\ldots(9)$$

Radojkovicˇ equation:

$$\Delta Q_{123} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} \ldots\ldots(10)$$

In the Radojkovicˇ equation, the binary contribution ΔQ_{ij} is evaluated using directly the ternary mole fractions.

The standard deviations between our experimental ternary data and estimated values were determined from eq. 5, and the results are listed in Table (7). The Kohler equation gave the closest estimation results to the experimental data with the standard deviations of (0.073 and 0.085) $cm^{-3}mol^{-1}$ for the ternary V^E of NFM (1) + methanol (2) + benzene (3) and NFM (1) + methanol (2) + toluene (3). The Radojkovicˇ equation also provides good results in the estimation of ternary V^E ,and it gave the best results for the calculation of the ternary ΔR_m of NFM (1) + methanol (2) + benzene (3) and NFM (1) +methanol (2) + toluene (3) with the standard deviations of (0.020 and 0.008) $cm^{-3}mol^{-1}$, respectively.

Conclusions

Excess molar volumes and the deviations in molar refraction at 298.15 K were experimentally determined for the five binary systems of the NFM + methanol, methanol+benzene, NFM +benzene, NFM +toluene, methanol + toluene and also for the ternary systems of NFM + methanol + benzene and NFM + methanol + toluene. the binary and ternary V^E values show negative deviations from ideal behaviour over the whole composition range. The ΔR_m data have negative deviations from the ideal solution. That is because the molecular interactions between each component are not very strong in every binary and ternary system. The binary and ternary V^E and ΔR_m were correlated reliably with the Redlich-Kister equation, while the Cibulka equation was applied successfully for the ternary system. The experimental ternary V^E and ΔR_m results were compared with the predicted values using binary contribution models. The Kohler and Radojkovicˇ equations provided the best results.

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الخلاصة

تم في هذا البحث حساب الحجوم المولارلية الفائضة و انحراف الانكسارية المولارية عن المثالية للانظمة الثنائية N− فورمايل مورفلين + ميثانول, ميثانول + بنزين , N− فورمايل مورفلين + بنزين, N − فورمايل مورفلين + تلوين و ميثانول + تلوين والانظمة الثلاثية − فورمايل مورفلين + ميثانول + بنزين و N − فورمايل مورفلين + ميثانول + تلوين من قياس الكثافة ومعامل الانكسار على المدى الكامل من الكسور المولارية عند درجة 298.15 كلفن. وتم تعيبير القيم العملية لجميع الدوال الفائضة باستعمال معادلة ردلج−كستر متعددة الحدود ومعادلة كوبلكا للانظمة الثنائية و الثلاثية .وتم مقارنة القيم العملية للدوال الفائضة للانظمة الثلاثية مع القيم المحسوبة من معادلات تسو− سميث , كولير و رادوجكوفيك.