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Intermolecular Interaction for Ternary Mixture of N-Methylmoprphline with Aromatic Hydrocarbons with Determined Densities to Measure Excess Molar Volume

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ABSTRACT

The determination of excess molar volume, which is dependent on the nature of liquid mixtures as well as intermolecular interactions, is the main emphasis of the presented study. For the mixture of N-methylmorpholine + o-xylene, benzene + N-methylmorpholine (NMM) + toluene+ benzene, and N-methylmorpholine + benzene+ mesitylene, as well as constituent binary mixes of benzene, N-methylmorpholine + N-methylmorpholine + N-methylmorpholine + o-xylene+ toluene, and N-methylmorpholine + mesitylene at 298.15K under atmospheric pressure, excess molar volume was computed from measured data of density over the entire range of mole fraction.

INTRODUCTION

Understanding the behavior of various liquids as well as functional groups is aided by the study of thermo-dynamic characteristics of the ternary and binary mixes. The development of the theories for liquid state as well as predictive techniques, and design of industrial processes, greatly benefit from this information (1,2). To better understand the intermolecular interactions and for developing models for their description and simulation processes, a great deal of experimental and theoretical research was done on the thermodynamic as well as transport properties of the binary mixture of N-methylmorpholine (NMM) with aromatic hydrocarbons (3). The behavior of cyclic compounds as well as their open-chain homologues, and between branching and linear isomers, differed in previous research on ketones, ethers, and amines in various solvents (4,5). This discrepancy could be attributed to one or both of the next causes: (i) a different strength of the polar functional group's interaction with the solvent, depending on the different shape of the molecule; that is, a group's lower or easier accessibility when it is part of a ring or branch; (ii) a different packing into the solvent (and possibly a different interaction with it) as a result of the

different shapes of linear and ring/branched molecules. This study on the accumulation of binary and ternary mixtures is being continued. The ternary systems N-methylmorpholine + o-xylene+ benzene, N-methylmorpholine (NMM) + toluene+ benzene, and N-methylmorpholine + mesitylene+ benzene, as well as component binary mixes of N-methylmorpholine + toluene, N-methylmorpholine + benzene, N-methylmorpholine + mesitylene, and N-methylmorpholine + o-xylene, were measured at 298.15K under the atmospheric pressure.

EXPERIMENTAL

Materials: Every chemical used was of AnalaR grade and was obtained from Sigma-Aldrich and Fluka. Materials supplied by E. Merck have been used exactly as supplied. GLC and a comparison of experimental density values with those published in the public domain were used to determine the liquids' purity (7.8), as shown in Table 1.

Table 1. Densities, ρ of pure components at 298.15 K

Components	ρ/g.cm^{-3}	
	Experimental	Literature
NMM	0.91169	0.91168
Benzene	0.71232	0.71233
Toluene	0.88201	0.88211
o-Xylene	0.86231	0.86219
Mesitylene	0.86218	0.86209

MEASUREMENTS

A high precision vibrating-tube digital densimeter (DMA 60/602 model) was used for the purpose of measuring density values of pure component liquids as well as their binary mixes when the temperature of the cell has been regulated automatically to within ± 0.01K of chosen value. Prior to every measurement, the series has been calibrated at atmospheric pressure by using dry air and double-distilled water. For dry air and water, at the variety of the working temperature degrees, densities have been provided by manufacturer in instruction manual, for the measurements of uncertainty density within ± 3x10^{-5}g/cm^3.

RESULTS AND DISCUSSION

Tables 2, and 3 represent experimental density values (ρ), and calculated excess molar volume values (V^E) for ternary and binary mixes that have been studied at 298.15K under the atmospheric pressure.

Table2. Values of Density, and estimated Excess Molar Volumes for N-Methylmorpholine (1) +Aromatic Hydrocarbon (2) Systems at 298.15K

x_1	ρ/g.cm^{-3}	V^E/cm^3.mol^{-1}	x_1	ρ/g.cm^{-3}	V^E/cm^3.mol^{-1}
N-Methylmorpholine (1) + Benzene (2)					
0.0562	0.66078	-0.0263	0.5217	0.71037	0.1648
0.0891	0.66441	-0.0296	0.6061	0.72048	0.1683
0.1244	0.66767	-0.0238	0.6923	0.73003	0.1521
0.1826	0.67361	-0.0044	0.7449	0.73816	0.1269
0.2467	0.68021	0.0304	0.8022	0.74584	0.0972
0.3211	0.68801	0.0766	0.8565	0.75331	0.0661
0.4001	0.69273	0.1217	0.9301	0.76366	0.0263
0.4829	0.70587	0.1555	0.9844	0.77147	0.0043
N-Methylmorpholine (1) + Toluene(2)					

x_1	ρ g.cm^{-3}	V^E/cm^3.mol^{-1}	x_1	ρ g.cm^{-3}	V^E/cm^3.mol^{-1}
N-Methylmorpholine (1) + Benzene (2)					
0.0501	0.70101	0.0312	0.4889	0.72567	0.4037
0.1249	0.70468	0.0947	0.5961	0.73345	0.4208
0.1688	0.70689	0.1377	0.6781	0.74011	0.3977
0.2001	0.70852	0.1696	0.7024	0.74221	0.3845
0.2549	0.71145	0.2255	0.7556	0.74704	0.3455
0.3011	0.71401	0.2708	0.8111	0.75242	0.2899
0.3767	0.71845	0.3367	0.8604	0.75761	0.2283
0.4221	0.72126	0.3689	0.9447	0.76697	0.0993
N-Methylmorpholine (1) + o-Xylene (2)					
0.0412	0.72683	0.0484	0.4578	0.73915	0.4256
0.0925	0.72801	0.1175	0.5012	0.74091	0.4352
0.1601	0.72973	0.1862	0.5622	0.74355	0.4454
0.2241	0.73132	0.2863	0.6022	0.74541	0.4509
0.2643	0.73248	0.3232	0.6911	0.74986	0.4582
0.3101	0.73389	0.3595	0.7711	0.75444	0.4476
0.3567	0.73543	0.3878	0.5867	0.76022	0.3879
0.4001	0.73696	0.4073	0.9766	0.77104	0.1022
N-Methylmorpholine (1) + mestylene (2)					
0.0511	0.74566	0.0813	0.5679	0.75336	0.6032
0.1241	0.74638	0.1843	0.6098	0.75439	0.6156
0.1898	0.74711	0.2674	0.7098	0.75737	0.6045
0.2501	0.74785	0.3376	0.7634	0.75934	0.5678
0.3244	0.74888	0.4171	0.8069	0.76121	0.5182
0.4001	0.75006	0.4897	0.8573	0.76371	0.4342
0.4889	0.75166	0.5602	0.9245	0.76779	0.2701
0.5207	0.75231	0.5802	0.9827	0.77222	0.0705

Table 3. Values of the Density, and the estimated Excess Molar Volume values for Ternary Mixes at 298.15K.

x_1	x_2	ρ	V^E	x_1	x_2	ρ	V^E
		g.cm^{-3}	cm^3.mol^{-1}			g.cm^{-3}	cm^3.mol^{-1}
N-Methylmorpholine (1) + Benzene (2) + Toluene (3)							
0.0619	0.2469	0.76266	0.6179	0.5559	0.1168	0.71262	-0.0453
0.1316	0.2277	0.75623	0.4946	0.5829	0.1085	0.70915	-0.0646
0.1896	0.2132	0.75079	0.4355	0.6707	0.0764	0.69776	-0.0833
0.2344	0.1974	0.74645	0.2972	0.7211	0.0663	0.69177	-0.0933
0.2751	0.1868	0.74245	0.2277	0.7513	0.0577	0.68816	-0.1569
0.3197	0.1772	0.73811	0.1448	0.7909	0.0441	0.68268	-0.1599

x_1	x_2	ρ	V^E	x_1	x_2	ρ	V^E
		g.cm^{-3}	cm^3.mol^{-1}			g.cm^{-3}	cm^3.mol^{-1}
0.3784	0.1528	0.73138	0.1176	0.8383	0.0389	0.67722	-0.1247
0.4401	0.1432	0.72503	0.0569	0.8669	0.0278	0.67296	-0.1194
0.4857	0.1314	0.72008	-0.0016	0.9512	0.0096	0.66146	-0.0214
N-Methylmorpholine (1) + Benzene (2) + o-Xylene (3)							
0.0308	0.4018	0.73021	0.4169	0.4516	0.2207	0.69872	0.1099
0.0955	0.3651	0.72655	0.2773	0.5207	0.1803	0.69382	0.1242
0.1509	0.3435	0.72188	0.2995	0.5531	0.1774	0.69119	0.0102
0.1993	0.3232	0.71827	0.2547	0.6217	0.1406	0.68587	0.0672
0.2287	0.3207	0.71569	0.1745	0.6689	0.1201	0.68209	0.0754
0.2767	0.2778	0.71316	0.2236	0.7187	0.1005	0.67803	0.0741
0.3007	0.2815	0.71078	0.1359	0.7559	0.0985	0.67494	-0.0433
0.3509	0.2623	0.70672	0.1213	0.8669	0.0391	0.66654	-0.0089
0.4213	0.2208	0.70199	0.1004	0.9552	0.0199	0.65922	-0.1242
N-Methylmorpholine (1) + Benzene (2) + Mesitylene (3)							
0.0559	0.3071	0.76203	0.4159	0.5169	0.1051	0.70787	-0.0217
0.1358	0.2859	0.74484	0.3205	0.5998	0.0882	0.69889	-0.0242
0.2016	0.2657	0.73887	0.2483	0.6284	0.0822	0.69583	-0.0163
0.2521	0.2453	0.73436	0.1798	0.7115	0.0737	0.68721	-0.0129
0.3326	0.1999	0.72694	0.0969	0.7872	0.0603	0.67911	-0.0118
0.3784	0.1718	0.72189	0.1737	0.8349	0.0463	0.67388	-0.0296
0.4297	0.1344	0.71669	0.1369	0.8809	0.0298	0.66876	-0.0695
0.4579	0.1238	0.71398	0.0744	0.9534	0.0119	0.66042	-0.0168

Excess molar volume values (V^E) for binary mixes have been estimated from density data by the equation below:

$$V^E / cm^3.mol^{-1} = \frac{(x_1M_1 + x_2M_2)}{\rho} - x_1\frac{M_1}{\rho_1} - x_2\frac{M_2}{\rho_2}$$

Where

x_i = mole fraction

M_i = molecular weights

ρ_i = densities of pure component liquids

ρ = mixture density.

Excess molar volume values that were estimated from eq. (1) for the binary mixes have been fitted to Redlich-Kister polynomial eq. (9):

$$V^E / cm^3.mol^{-1} = x_1x_2\sum_{i=0}^{k} A_j(x_1 - x_2)^i$$

Table4 lists A_j coefficients together with standard deviation, characterized by:

Where (1)

N = No. of experimental points.

m = No. of parameters in corresponding analytical equation.

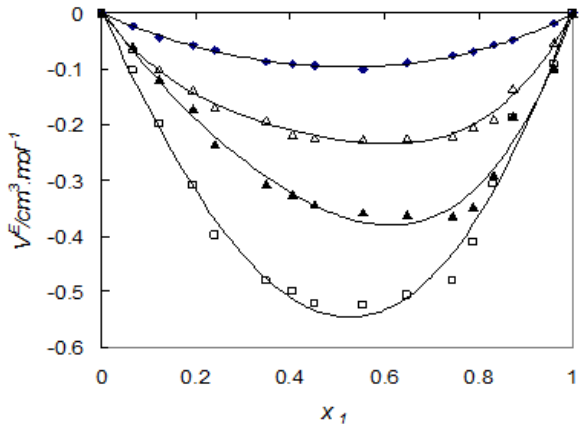

Figure 1. Excess molar volumes at 298.15K for binary mixes: ♦, NMM (1) + Benzene (2);; Δ, NMM (1) + Toluene (2); ▲, NMM (1) + o-Xylene (2); □, NMM (1) + Mestylene

Table4. Redlich-Kister Coffecients and Standard Deviations of Binary Mixes at 298.15K

A_0	A_1	A_2	A_3	σ
N-Methylmorpholine (1) + Benzene (2)				
0.6402	0.4803	-0.8849	0.0693	0.0011
N-Methylmorpholine (1) + Toluene(2)				
1.6253	0.6522	-0.4118	0.0773	0.0033
N-Methylmorpholine (1) + o-Xylene (2)				
1.7429	0.3891	1.0974	0.0784	0.0018
N-Methylmorpholine (1) + mestylene (2)				
0.9571	0.5677	1.1356	1.5447	0.0028

Negative values of V^E for binary mixes of N-methylmorpholine + toluene, N-methylmorpholine +benzene, N-methylmorpholine+ mesitylene, and N-methylmorpholine+ o-xylene, exhibit negative deviation over the entire range of mole fractions, as in Figure 1. V^E value is proportional directly with methyl substitutants of the benzene ring.

excess molar volume values for binary mixes that have been obtained were found in a good agreement with the results that have been published in literature.(1,2) when x_1 = 0.5 NMM (1) + benzene (2), + toluene (2), + o-xylene (2), and + mesitylene (2) 0.1603, 0.4079, 0.5676, agree with the obtained results are 0.1601, 0.4006, 0.5675, 0.6256, respectively.

For ternary mixtures of NMM) + toluene+ benzene, NMM + benzene + o-xylene, and NMM + mesitylene+benzene at 298.15K, excess molar volume values have been determined by the equation:

$$V^E / cm^3 mol^{-1} = \left(\frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho}\right) - \left(x_1\frac{M_1}{\rho_1} + x_2\frac{M_2}{\rho_2} + x_3\frac{M_3}{\rho_3}\right)$$

ternary systems obtained excess molar volumes agreed with Cibuulka's equation(10,11):

$$V^E = V^E{}_{binary} = x_1x_2(1-x_1-x_2)(B_1 - B_2x_1 - B_3x_2)$$

Coefficient values, B_i and standard deviation, σ, are shown in Table5 which were obtained by least-squares approach

Table5. Cibulka Coefficient values and Standard Deviation values for Excess Molar Volumes of Ternary Mixes at 298.15K

B_0	B_1	B_2	σ
N-Methylmorpholine (1) + Benzene (2) + Toluene (3)			
56.94	-61.76	-144.61	0.005
N-Methylmorpholine (1) + Benzene (2) + o-Xylene (3)			
8.689	-43.918	-9.119	0.004
N-Methylmorpholine (1) + Benzene (2) + Mesitylene (3)			
-9.59	17.55	2.93	0.002

Ternary mixtures N-methylmorpholine (NMM) + toluene+ benzene, N-methylmorpholine + benzene + mesitylene, N-methylmorpholine + o-xylene+ benzene, excess molar volumes illustrated in table 2, were plotted as a function of the mole fraction x_1, x_2 and x_3 at 298.15K, as shown in fig. (2-4).

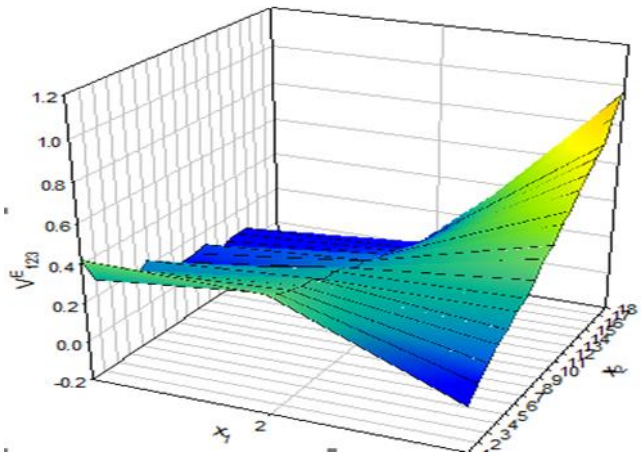

Figure2. Excess molar volume values, V^E_{123} for ternary system x1 NMM + x2 Benzene + x3 Toluene at 298.15K.

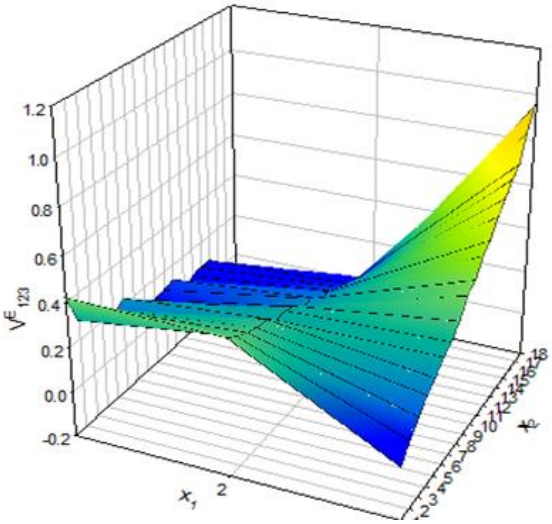

Figure3. Excess molar volume values, V^E_{123} for ternary system x1 NMM + x2 Benzene + x3 o-Xylene at 298.15K.

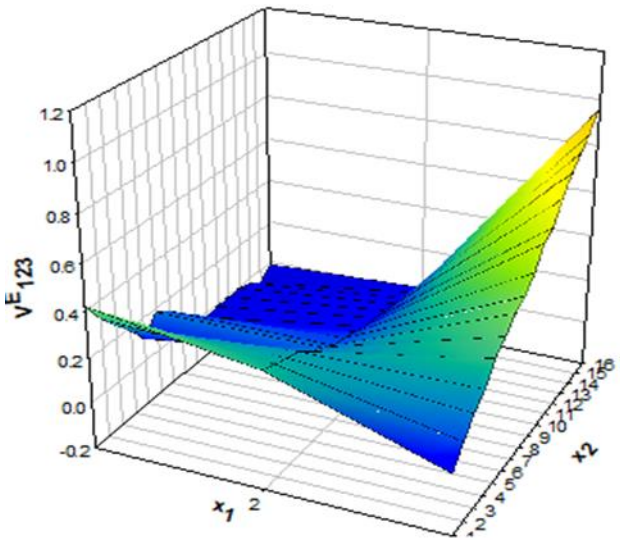

Figure4. Excess molar volume values, V^E_{123} for ternary system x1 NMM + x2 Benzene + x3 Mesitylene at 298.15K.

Shows positive deviation at low mole fraction x1 of NMM 0<x1<0.5 and a negative V^E_{123} deviation at high mole fraction 0.5<x1<1.0 for. This indicate that the third component liquid, toluene, o-xylene or mesitylene as a globular molecule modifies both the nature and degree of molecular interactions(12-14), the orientational order between the two other component liquids, the orientational order in these two liquids would be disturbed by a globular molecules of substituted benzene ring. The increase of positive excess molar volume values, as the number of the methyl group increases, reflect the increases positively as the mole fractions x3 of substituted benzene increase.

REFERENCES

[1]. Smiljanić, J. D., Kijevčanin, M. L., Djordjević, B. D., Grozdanić, D. K., & Šerbanović, S. P. (2008). Temperature dependence of densities and excess molar volumes of the ternary mixture (1-butanol+ chloroform+ benzene) and its binary constituents (1-butanol+ chloroform and 1-

butanol+ benzene). International Journal of Thermophysics, 29(2), 586-609. DOI 10.1007/s10765-008-0390-4

[2]. Goates, J. R., Ott, J. B., & Grigg, R. B. (1981). Excess volumes of n-hexane+ n-heptane,+ n-octane,+ n-nonane, and+ n-decane at 283.15, 298.15, and 313.15 K. The Journal of Chemical Thermodynamics, 13(10), 907-913. https://doi.org/10.1016/0021-9614(81)90071-9.

[3]. Lepori, L., Gianni, P., & Matteoli, E. (2013). The effect of the molecular size and shape on the volume behavior of binary liquid mixtures. Branched and cyclic alkanes in heptane at 298.15 K. Journal of Solution Chemistry, 42(6), 1263-1304. DOI 10.1007/s10953-013-0023-9.

[4]. Khanlarzadeh, K., & Iloukhani, H. (2011). Application of ERAS-model and Prigogine–Flory–Patterson theory to excess molar volumes for ternary mixtures of (2-chlorobutane+ butylacetate+ isobutanol) at T= 298.15 K. The Journal of Chemical Thermodynamics, 43(11), 1583-1590. https://doi.org/10.1016/j.jct.2011.05.017.

[5]. Forghani, F., Iloukhani, H., & Khanlarzadeh, K. (2022). Experimental study and modeling using the PFP theory and the ERAS model of the excess molar volume and isentropic compressibility of dimethylbenzylamine with alkanol mixtures at different temperatures. Journal of Chemical & Engineering Data, 67(2), 297-304. https://doi.org/10.1021/acs.jced.1c00752.

[6]. Forghani, F., Iloukhani, H., & Khanlarzadeh, K. (2023). Volumetric and acoustic investigation on the binary mixtures of monoethanolamine+ 1-alcohols (C3–C6) at different temperatures from experimental and theoretical points of view. Journal of Solution Chemistry, 52(4), 385-412. https://doi.org/10.1007/s10953-022-01236-1.

[7]. Awwad, A. M., & Salman, M. A. (1986). Volume of mixtures of nonane isomers with normal nonane and normal hexadecane at 298.15 K; an interpretation in terms of the Flory—Patterson theory. Fluid phase equilibria, 31(1), 105-115. https://doi.org/10.1016/S0378-3812(86)87034-0.

[8]. Awwad, A. M., Hassan, F. A., & Salman, M. A. (1987). Volumes of mixing of decane isomers with normal hexadecane at 298.15 K. An interpretation in terms of the Van-Patterson theory. Fluid phase equilibria, 38(3), 291-298. https://doi.org/10.1016/0378-3812(87)85006-9.

[9]. Razzaq, L., Farooq, M., Mujtaba, M. A., Sher, F., Farhan, M., Hassan, M. T., ... & Imran, M. (2020). Modeling viscosity and density of ethanol-diesel-biodiesel ternary blends for sustainable environment. Sustainability, 12(12), 5186. https://doi.org/10.3390/su12125186.

[10]. Gómez-Ibáñez, J. D., & Wang, T. C. (1966). The excess volume of binary mixtures of trans-decalin with cyclohexane and with n-alkanes. The Journal of Physical Chemistry, 70(2), 391-395. https://doi.org/10.1021/j100874a012.

[11]. Li, D., Wu, Q., Liu, L., Guo, M., & Wang, H. (2018). Density, Viscosity and Volatility of Binary Mixtures of Isopropyl Ether and exo-Tetrahydrodicyclopentadiene. Journal of Solution Chemistry, 47(3), 544-559. https://doi.org/10.1007/s10953-018-0736-x.

[12]. Zhao, X., Mi, J., Dai, Y., He, G., Guo, Y., & Fang, W. (2020). Density and viscosity measurements on the ternary system of exo-tetrahydrodicyclopentadiene (1)+ n-decane (2)+ iso-butanol (3) and corresponding binary systems. Journal of Chemical & Engineering Data, 65(5), 2527-2539. https://doi.org/10.1021/acs.jced.9b01171.

[13]. Jabrou, S. N., Radhi, M. M., Al-Mulla, E. A. J., & Azooz, E. A. (2024). Rifampicin nanopatricles: thermodynamic properties in

KCl electrolyte using cyclic voltammetry. Nano Biomed. Eng., 16, 128. DOI: 10.26599/NBE.2024.9290046

[14]. Abdullah, W. R., & Jabrou, S. N. (2022). Improving Ionic Exchange Process of Potassium in Poor Soils by Bentonite. In IOP Conference Series: Earth and Environmental Science (Vol. 961, No. 1, p. 012098). IOP Publishing. DOI 10.1088/1755-1315/961/1/012098.