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^{1}H NMR studies of aqueous solutions of some *n*-alkoxyethanols (C_1E_m, *m*=1,2,3) or polyethers ($C_1E_mC_1$, *m*=1,2,3,4) at 298.15 K

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Abstract

^{1}H NMR spectra in binary mixtures of water and ethylene glycol monomethyl ether (2-methoxyethanol, $C_3H_7O_2$; C_1E_1), diethylene glycol monomethyl ether (2-(2-methoxyethoxy)ethanol, $C_5H_{12}O_3$; C_1E_2), triethylene glycol monomethyl ether [2-{2-(2-methoxyethoxy)ethoxy}ethanol, $C_7H_{16}O_4$; C_1E_3), ethylene glycol dimethyl ether (1,2-dimethoxyethane, $C_4H_{10}O_2$; $C_1E_1C_1$), diethylene glycol dimethyl ether (bis(2-methoxyethyl)ether, $C_6H_{14}O_3$; $C_1E_2C_1$), triethylene glycol dimethyl ether (1,2-bis(2-methoxyethoxy)ethane, $C_8H_{18}O_4$; $C_1E_3C_1$), and tetraethylene glycol dimethyl ether (2,5,8,11,14-pentaoxapentadecane, $C_{10}H_{22}O_5$; $C_1E_4C_1$) are recorded over the whole composition range at 298.15 K under atmospheric pressure. The experimental data have been used to calculate the deviations in chemical shift from the additive properties, viz. $\Delta\delta$ as a function of mole fractions, and values obtained are fitted to the Redlich–Kister polynomial equation to obtain the binary coefficients and the standard errors. An attempt has also been made to correlate the values of the spectral parameter $\Delta\delta$ calculated from ^{1}H NMR data with various physicochemical properties.

Keywords: ^{1}H NMR; Binary mixtures, alkoxyethanols; Polyethers

1. Introduction

Physicochemical properties such as density, excess volume, viscosity, surface tension and speed of sound of aqueous mixtures of alkoxyethanols or polyethers have been extensively reported [1–14]. The interest in such studies develops owing to peculiar mixing behavior of alkoxyethanols or polyethers in the presence of a water molecule. Such mixtures are known to exhibit interesting thermodynamic functions which are commonly discussed in terms of molecular interactions. Previously reported values of excess volumes are found to be negative for all the systems which suggest the association through intermolecular hydrogen bonding between the water and the ether molecules. Also, the results show the decrease in excess volume with the introduction of an oxyethylene group in the alkoxyethanol or polyether molecule indicating increased interactions between unlike molecules. This behavior might be related to enhanced hydrophilic characteristics of the organic component of the binary mixtures.

Alkoxyethanols, like alcohols, are highly self-associated molecules in neat [15–17]. Theoretically, the self-association may take place by means of O–H bridging or due to dipole–dipole interactions among $-OC_2H_4$ groups or both. Mixing of water to these solvents disturbs this association giving rise to important effects, i.e. physical, chemical and structural, which are expected to contribute to the value of excess functions and spectral properties. NMR has appeared to be a powerful tool, not only for analytical purposes, but also for gaining insight into the structure of molecules [18]. The chemical shifts which are solvent-dependent provide valuable information about solute–solvent interactions and accompanying electronic displace-

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Table 1
Chemical shift: $\delta(H_2O)$, $\delta(-CH_3)$, $\delta(H_2O-CH_3)$ and deviations in chemical shift $\Delta\delta$, as a function of mole fraction for various binary mixtures at 298.15 K

x_1	$\delta(H_2O)$/Hz	$\delta(-CH_3)$/Hz	$\delta(H_2O-CH_3)$/Hz	$\Delta\delta$/Hz
Ethylene glycol monomethyl ether (1)+water (2)				
0	942.7	677.3[a]	265.4	0
0.0104	963.5	680.0	283.5	19.7
0.0236	967.6	683.4	284.2	22.5
0.0484	969.8	687.3	282.5	24.6
0.0747	971.4	691.4	280.0	26.2
0.1663	964.3	703.2	261.1	21.5
0.2273	956.1	709.9	246.2	16.1
0.2867	947.5	717.6	229.9	9.1
0.3512	937.2	723.3	213.9	3.1
0.4932	923.7	738.2	185.5	−3.3
0.5681	911.7	739.9	171.8	−5.3
0.6090	906.7	741.1	165.6	−5.2
0.7389	892.1	746.4	145.7	−4.9
0.8365	883.5	752.6	130.9	−4.5
0.9545	872.5	756.9	115.6	−1.5
1	865.5[a]	755.5	110.0	0
Diethylene glycol monomethyl ether (1)+water (2)				
0	942.7	675.2[a]	267.5	0
0.0034	958.0	678.2	279.8	12.8
0.0068	961.7	681.2	280.5	14.0
0.0129	961.9	680.8	281.1	15.5
0.0287	967.0	685.2	281.8	18.5
0.0470	968.5	688.8	279.7	19.0
0.0902	962.8	693.6	269.2	14.8
0.1730	951.9	702.7	249.2	6.8
0.2693	932.2	711.6	220.6	−7.9
0.3438	914.5	716.5	198.0	−19.7
0.4050	908.2	721.7	186.5	−22.3
0.4511	902.1	723.1	179.0	−23.1
0.5172	896.1	726.2	169.9	−22.7
0.5662	893.0	729.2	163.8	−21.7
0.6795	883.2	733.2	150.0	−19.0
0.7362	878.1	734.2	143.9	−16.9
0.8402	871.6	737.3	134.3	−11.5
1	861.6[a]	739.0	122.6	0
Triethylene glycol monomethyl ether (1)+water (2)				
0	942.7	678.0[a]	264.7	0
0.0027	958.4	679.1	279.3	14.9
0.0056	960.6	680.3	280.3	16.2
0.0168	962.0	682.2	279.8	17.0
0.0410	960.8	685.6	275.2	15.1
0.0740	954.5	689.5	265.0	8.6
0.0787	953.4	689.9	263.5	7.6
0.1073	943.9	693.0	250.9	−1.8
0.1981	924.6	702.0	222.6	−19.9
0.3069	906.8	710.2	196.6	−33.6
0.4323	896.5	716.4	180.1	−36.1
0.5906	887.8	721.8	166.0	−32.4
0.7359	885.3	724.6	160.7	−21.4
1	880.8[a]	728.4	152.4	0
Ethylene glycol dimethyl ether (1)+water (2)				
0	942.7	676.6[a]	266.1	0
0.0048	964.3	678.2	286.1	21.4
0.0224	967.9	684.1	283.8	24.0
0.0312	968.1	686.2	281.9	24.6
0.0505	967.8	691.4	276.4	24.5
0.0881	964.5	700.2	264.3	23.0
Ethylene glycol dimethyl ether (1)+water (2)				
0	942.7	676.6[a]	266.1	0
0.1003	962.6	703.2	259.4	21.5
0.1964	944.4	723.6	220.8	10.0
0.3448	914.5	747.2	167.3	−1.7
0.5097	874.1	761.6	112.5	−10.1
0.6613	844.8	773.6	71.2	−8.7
0.7458	829.3	779.7	49.6	−6.5
0.8305	813.7	785.8	27.9	−4.3
0.8983	801.3	790.7	10.6	−2.5
1	782.6[a]	798.1	−15.5	0
Diethylene glycol dimethyl ether (1)+water (2)				
0	942.7	655.1[a]	287.6	0
0.0203	943.3	661.1	282.2	1.0
0.0348	943.3	665.4	277.9	1.2
0.0477	941.4	668.7	272.7	0.1
0.0746	933.4	674.5	258.9	−5.3
0.1356	910.4	686.1	224.3	−20.7
0.1597	901.3	690.7	210.6	−26.9
0.2373	877.1	700.9	176.2	−36.9
0.3179	851.9	711.4	140.5	−47.3
0.4506	816.9	722.4	94.5	−51.6
0.5085	804.4	725.6	78.8	−49.1
0.6441	779.9	731.9	48.0	−37.4
0.7288	764.4	735.2	29.2	−29.6
1	715.3[a]	741.7	−26.4	0
Triethylene glycol dimethyl ether (1)+water (2)				
0	942.7	654.6[a]	288.1	0
0.0067	940.2	656.5	283.7	−2.2
0.0344	931.5	664.4	267.1	−10.0
0.1238	896.3	681.5	214.8	−33.5
0.2115	858.4	694.3	164.1	−56.1
0.3011	826.3	703.5	122.8	−68.6
0.3884	797.1	709.4	87.7	−75.7
0.4576	781.8	712.2	69.6	−71.6
0.5393	769.4	716.9	52.5	−62.4
0.5932	760.6	717.8	42.8	−54.8
0.6610	749.5	720.6	28.9	−47.0
0.7458	735.6	722.9	12.7	−35.9
1	694.0[a]	727.0	−33.0	0
Tetraethylene glycol dimethyl ether (1)+water (2)				
0	942.7	653.0[a]	289.7	0
0.0027	939.8	654.0	285.8	−3.0
0.0075	938.0	655.8	282.2	−5.0
0.0144	934.8	657.8	277.0	−8.0
0.0325	926.9	661.7	265.2	−13.8
0.1354	871.3	680.9	190.4	−54.9
0.1960	841.8	689.2	152.6	−72.9
0.2496	819.5	694.7	124.8	−83.1
0.3893	770.0	703.5	66.5	−95.6
0.4407	755.8	705.8	50.0	−95.3
0.5399	737.3	710.2	27.1	−85.7
0.6610	716.0	712.3	3.7	−69.4
1	680.0[a]	718.0	−38.0	0

[a] Values extrapolated to 0 and 1.

ments [19,20]. The aim of the present work is to provide more specific information [21–23] using ^{1}H NMR spectral studies and to give an additional insight into the behavior