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Refractive Indices, Molar Refractions, Surface Tension and Polarizability for Binary Mixtures of Benzyl Alcohol with Glycols and Their Deviations

Sahar M. Tawfik and Farid M. Farag

Refining Division, Egyptian Petroleum Research Institute Nasr City, Cairo, 11727 Egypt.

DENSITIES (ρ), refractive indices (n_D) and surface tension (σ) of the binary mixtures of benzyl alcohol (BA) + ethylene glycol (EG), BA+ diethylene glycol (DEG) and BA + triethylene glycol(TEG)] were determined over the entire range of mole fractions at temperature 20^0c and atmospheric pressure. Excess molar volume (V^E), excess refractive indices (n_D^E), molar refraction deviation (ΔR), excess surface tension ($\Delta\sigma$) also the polarizability (α) were calculated. The excess refractive indices n_D^E of BA with DEG and TEG are negative but with EG are positive. Excess molar volume (V^E) and molar refraction deviations (ΔR) are negative for all. Surface tension for both binary mixtures of BA+EG and BA+DEG have negative deviation, but in case of binary mixture of BA+TEG the deviation are negative till $x_1 \approx 0.6$ after that it is positive. The experimental and calculated quantities are used to study the effect of mixing between mixed components. All the results show that we can use 0.3 mole fraction of TEG as anti-solvent with BA

Keywords: Refractive indices; Densities; Benzyl alcohol; Glycols; Surface tension.

Introduction

Solvent properties such as, density ρ, refractive index n_D and surface tension σ are required to understand the interaction between the different molecules in liquid mixtures. The excess thermodynamic quantities (excess molar volume V^E, excess refractive index n_D^E and excess surface tension $\Delta\sigma$) have been derived to provide information on the extent of the specific inter molecular interaction between the components in binary system [1, 2].

The data on excess thermodynamic properties will provide useful information on the intermolecular and structural that is prevailing between the components of the mixture with different shapes, size and chemical nature [3]. In the field of refining lubricating oils, solvent extraction represents one of the possible routes. To obtain high quality lube oil from a crude oil fraction, separation of aromatics from isoparaffins and naphthenes is required. The selection of the best solvent for a given separation is the first problem to be met in the design of the process. Several criteria are to be considered in this selection such as selectivity, solvent power and other properties. The more promising method of combining solvent is based on the mutual relation between selectivity and solvent power. By mixing a basic solvent of high selectivity and low solvent power such as glycols [4] as anti -solvent with a solvent of high solvent power and low selectivity, the mixture can be adjusted to optimum values.

Nowadays, most lube oils extraction processes use N-methyl pyrrolidone (NMP)[5] andfurfural[6]. Few works appeared dealing with use of benzyl alcohol (BA)as an extracting solvent for refining lubricating oils [7]. The efficiency of benzyl alcohol can be modified by the addition of selective anti-solvents. Glycols are well known for their high selectivity and inertness to chemical reaction with respect to solvent extraction of oils, the problem is how to select the best anti solvent from the glycols used (EG, DEG and TEG). More studies using the excess thermodynamic function was done to select the best one.

Benzyl alcohol and glycols are a very interesting class of the solvents, due to the simultaneous presence of the hydroxyl groups

in the same molecule, which allows their self-association via intra- and/or intermolecular hydrogen bonds [8-9]. The excess properties of binary liquid mixtures containing BA have been studied previously [10, 11]. We use a variety of glycols which represents different types and degrees of association between unlike molecules to study more systematically the benzyl alcohol with glycols interaction.

In field of moderate strength, the induced dipole moment U is proportional to the field strength E that is: $U = \alpha E$

In which the proportional factor α is a fundamental property of the substance, it is called polarization, which means the ease with which the molecule's electrons can be displaced by an electric field[12].

Maxwell equations, which describe the properties of electromagnetic radiation led to the conclusion that the refractive index of non-magnetic medium is related to the relative permittivity at the frequency by: $n = \varepsilon^{1/2}$. The molar polarizability, and hence the molecular polarizability, can therefore be measured at optical frequencies simply by measuring the sample's refractive index using a refractometer and using the clausius-mosscotti equation. This is normally expressed in terms of the molar refractivity Rm [12].

Surface tension (σ) is the fundamental parameter of surface chemistry that characterizes the free energy per unit area required for the formation of a liquid-air interface at constant temperature, pressure and composition. It is an important characteristic of two-phase systems because it influences many physicochemical processes such as distillation, condensation, gas adsorption and liquid-liquid extraction.

Surface tension is the single most accessible experimental parameter that describes the thermodynamic state and contains at least implicit information on the internal structure of a liquid interface[6], it is also a property that represents changes in molecular interaction and could thus be used as means of interpreting behavior of binary mixtures. The literature dealing with surface tension of binary mixture is extensive[13-16].

In a general way, $\Delta\sigma$ values should be negative for any mixture, because the compound which is more surface active should be displaced to the surface while the other compound should stay in the bulk. The more difference between surface tension of the pure components, the more negative surface tension deviations should be [17].

In this paper, we have decided to carry out the measurements of density ρ, refractive index n_D and surface tension σ for the binary mixtures of benzyl alcohol (BA) with ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol(TEG) over the entire composition range using the excess thermodynamic function to select the best antisolvents.

Experiments

Materials

The chemicals used were of analytical grade and were used without further purification. The sources and mass fraction purities of the chemicals employed are as follows:

Benzyl alcohol (p.a. > 99.8 mass %) was supplied by Riedel-de Haën, ethylene glycol, diethylene glycol and triethylene glycol (p.a. > 97 mass %) were supplied by Merck and were used as received. Binary mixtures were prepared by mixing measured volumes of the components in airtight stopper bottles to obtain mixtures of different compositions.

The structure of pure components:
BA: $C_6H_5CH_2OH$
EG: $HO-CH_2-CH_2-OH$
DEG: $HO-CH_2-CH_2-O- CH_2-CH_2OH$
TEG: $HO-CH_2-CH_2-O- CH_2-CH_2O- CH_2-CH_2-OH$

All the experiments were done at 20^0c.

The densities and refractive index of the pure compounds are given in Table 1 and compared with the literature value.

TABLE 1. Physical properties of the pure component at 20^0c.

substance	ρ/g.cm3		nD	
	expt	Lit*	expt	Lit*
BA	1.0451	1.05	1.54	1.538
EG	1.113	1.115	1.431	1.434
DEG	1.118	1.119	1.447	1.445
TEG	1.125	1.126	1.455	1.457

*Thermodynamic research center, Texas A&M University System: College Station, TX,1998.

Measurements

Densities of the pure liquids and their mixtures were measured with an oscillating body method using Mettler Toledo DE 40 density meter (Mettler Toledo, Inc., Columbus, OH) with an accuracy of ± 0.0001g/cm². The apparatus used was calibrated periodically with double distilled water and dry air.

Refractive indices were measured using a thermostat Abbe refractometer (Carl Zeiss, model G, Jena, Germany) with uncertainty less than ± 0.0001 units, using sodium D-line (wavelength 589.3 nm). Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostatic water path. Calibration was performed by measuring the refractive indices of doubly-distilled water and toluene, an average of four measurements was taken for each mixture.

The surface tension of the sample was measured by the ring detachment method using K.9 tensiometer kruss torsion balance (Germany). The platinum ring was thoroughly cleaned and flame-dried before each measurement. Each measurement was repeated up to 10 times to check for reproducibility. The system was not isolated from ambient moisture. The measured was done at ambient temperature. The accuracy of the surface tension measurement is ±0.5% of the final value of surface tension and the corresponding reproducibility is ±0.01 mN m⁻¹.

Results and Discussion

It is often advantageous to treat mixture data in terms of excess properties of solution because this is the smallest and most sensitive measure of mixture properties. The experimental values of density (ρ) of pure benzyl alcohol (BA), ethyleneglycol (EG), diethyleneglycol (DEG) triethyleneglycol (TEG), and binary mixtures of BA+EG, BA+DEG and BA+TEG at20⁰c are listed in Table 2.

The excess molar volume V^E and the relative change in volume ΔV were computed by the following equations:

$$V^E = V - (X_1 V_1^o + X_2 V_2^o) \qquad (1)$$
$$\Delta V = V^E / (X_1 V_1^o + X_2 V_2^o) \qquad (2)$$
$$V = M / \rho \qquad (3)$$

Where V is the molar volume of the mixtures, V_1^o and V_2^o are those of pure components, ρ is the density, x_1 and x_2 are the mole fractions of the pure components, ΔV is the relative change in volume and M is the mean molecular weight, the

data are represented in Table 2 and Fig. 1. In Fig. 1 the excess molar volume V^E is negative over the entire composition range display a minimum at $x_1 \approx 0.65$ for all glycols (EG, DEG and TEG), the negativity coming in the sequence EG > TEG > DEG. The chemical effects in the excess molar volume take into account a compromise between the positive contribution, due to net destruction of order during the mixing (e.g. the disruption of H-bonds), and the negative contribution, due to net creation of order during the mixing (e.g. the decrease in free volume by new H-bonds formed between the component molecules in solution) [18-19], Thus the negative VE values suggest that there is a reduction in the free volume as a result of the formation of new H-bonds between molecules in solution and the difference in molar value. In general, the excess volume data of liquid mixtures may be explained in terms of various factors [19]:

- Chemical or specific interaction, which includes charge transfer complexes, formation of hydrogen bonding, dipole – dipole interaction and other complex forming between dissimilar molecules.
- Loss of dipolar association and difference in size and shape.
- Physical interaction consisting dispersion forces or weak dipole – dipole interaction.

In case of EG the molar volumes (55.76 cm.³mol⁻¹) differ considerably than BA (103.47cm.³mol⁻¹) but DEG (94.92cm³.mol⁻¹) and TEG (133.48 cm3.mol⁻¹) are approximately near to BA. Hence smaller EG molecules are interstitially accommodated into aggregates of BA yielding negative V^E than the other DEG and TEG as shown in Fig.1.

From the measured refractive indices (n_D), the excess refractive indices (n_D^E) were calculated using the following equation:

$$n_D^E = n_m - (x_1 n_1 + x_2 n_2) \qquad (4)$$

In which x_1, x_2, n_1, and n_2 are the mole fractions and refractive indices of the first and the second solvents in their mixtures, respectively, and n_m is the refractive index of the solvent mixtures. The molar refraction deviations ΔR were calculated from Lorentz-Lorenz equation[20]

$$\Delta R = R_m - \Sigma R_i Q_i \qquad (5)$$

In which R_i and R_m are the molar refractions of the pure components and of the mixture, respectively, and Q_i, is the volume fraction of the ith component, given as

TABLE 2. Mole fractions (x1, x2), densities (ρ), mean molecular weight (M), molar volume (Vm) and molar excess volume (VE) of benzyl alcohol with glycols.

Conc. cm³/mol		ρ	$\overline{M}$	V^{mes}	V^E
x_1	x_2	g.cm-3		cm³/mol	cm³/mol
EG+BA					
1.0000	0.0000	1.1130	62.07	55.76	0.000
0.9435	0.0565	1.1024	64.67	58.66	-3.083
0.8813	0.1187	1.0951	67.53	61.67	-5.726
0.8124	0.1877	1.0887	70.71	64.95	-7.799
0.7357	0.2643	1.0758	78.20	72.69	-9.948
0.6498	0.3502	1.0758	78.20	72.69	-9.948
0.5530	0.4470	1.0693	82.66	77.30	-9.912
0.4429	0.5570	1.0630	87.73	82.53	-9.044
0.3169	0.6831	1.0569	93.54	88.50	-7.224
0.1709	0.8291	1.0506	100.26	95.43	-4.254
0.0000	1.0000	1.0451	108.14	103.47	0.000
DEG+BA					
1.0000	0.0000	1.1180	106.12	94.92	0.000
0.9071	0.0929	1.1110	106.31	95.69	0.027
0.8128	0.1872	1.1040	106.50	96.47	0.055
0.7169	0.2831	1.0971	106.69	97.25	0.092
0.6195	0.3805	1.0905	106.89	98.02	0.156
0.5205	0.4795	1.0835	106.89	98.84	0.186
0.4198	0.5802	1.0755	107.09	99.76	0.122
0.3175	0.6825	1.0675	107.29	100.70	0.056
0.2090	0.7910	1.0595	107.50	101.66	0.025
0.1076	0.8924	1.0525	107.71	102.54	0.014
0.0000	1.0000	1.0451	108.10	103.47	0.000
TEG+BA					
1.0000	0.0000	1.1250	150.17	133.48	0.000
0.8746	0.1254	1.1185	144.90	129..55	-0.168
0.7562	0.2438	1.1123	139.92	125.79	-0.363
0.6440	0.3560	1.1056	135.21	122.29	-0.494
0.5377	0.4623	1.0988	130.74	118.98	-0.609
0.4367	0.5633	1.0914	126.49	115.90	-0.657
0.3407	0.6593	1.0832	122.46	113.05	-0.619
0.2494	0.7506	1.0742	118.62	110.43	-0.501
0.1640	0.8360	1.0644	114.96	108.01	-0.355
0.0180	0.9190	1.0550	111.47	105.66	-0.207
0.0000	1.0000	1.0451	108.10	103.44	0.000

X1:mole fraction of BA

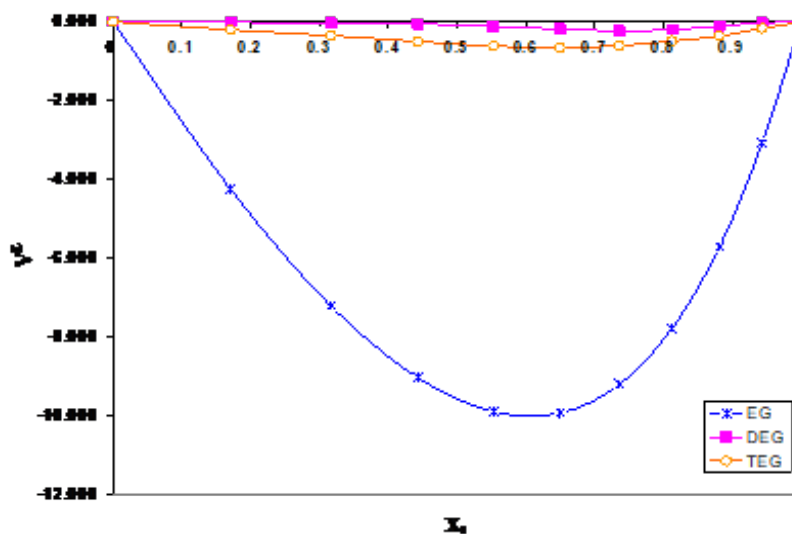X2:mole fraction of Glycols

Fig. 1. Relation between excess molar volume VE versus mole fraction of benzyl alcohol with glycols.

$$Q_i = X_i V_i / \Sigma X_i V_i \qquad (6)$$

In which: $V_i = M_i / P_i$

The molar refraction, R_i, was obtained from the formula

$$R_i = \{[n_i^2 - 1] / [n_i^2 + 2]\} V_i = P_a + P_E = P_t = P_D \qquad (7)$$

in which: n_i is the refractive index for the pure i^{th} component. Thus, the equation for binary mixtures becomes

$$R_m = \{[n_{D(m)}^2 - 1] / [n_{D(m)}^2 + 2]\} V_m \qquad (8)$$

In which R_m is the molar refraction deviation, $nD_{(m)}$ is the refractive index of the mixture, and V_m is the molar volume. Table 3 shows volume fraction Q_1 and Q_2, measured refractive indices n_D, molar volume V_i, molar refraction R_m and molar refraction deviation ΔR. Figure 2 shows the deviation in the excess refractive indices (n_D^E) of BA +TEGwhich is more negative than the deviation of BA+DEG, in case of BA+EG the deviation is positive.

In general, the magnitude of n_D^E increases with decrease in the strength of interaction between the component molecules in the mixtures [21], as in the present case it means that the strength of interaction coming in the following order TEG > DEG > EG and the maximum strength for TEG at $x_1 \approx 0.3$.

During their recent study Brocos et. al.[22] have suggested that the ΔR deviation from ideality is physically more interpretable when defined on a volume fraction basis instead of mole fraction basis. However, in the work reported by others[23], the mole fraction basis has been used to calculate ΔR values. Figure 3 shows the relation between molar refraction deviation ΔR and Q_1, which demonstrate a negative deviation for the all composition range which coming in the order EG > DEG > TEG. Since the molar refraction is a measure of volume occupied with an atom or molecule and depends on the wave length of the light used for measurement[24].

It is noted that the molar refraction of the studied solvent mixtures increases as the molar volume and refractive index increase, and vice versa.

From Maxwell equations [25], which describe the properties of electromagnetic radiation lead to the conclusion that the refractive index of non-magnetic medium is related to the relative permittivity at the frequency by: $n = e^{1/2}$. The molar polarizability, and hence the molecular polarizability, can therefore be measured at optical frequencies simply by measuring the sample's refractive index using a refractometer and using the clausius-mosscotti equation. This is normally expressed in terms of the molar refractivity Rm. The right-hand side of the equation (7) is equal to the summation of both the atomic polarization (Pa)and electronic polarization (PE), which is the total molar (PT) or distortion polarization (PD). The Pa was calculated from the equation [26]

TABLE 3. Volume fraction (Q1,Q2), refractive indices (nD), molar volume (Vi), molar refraction (Rm) and molar refraction deviation (ΔR) of benzyl alcohol with glycols.

Q_1	Q_2	n_D	V_i, $cm^3 mol^{-1}$	R_m	ΔR
EG + BA					
1.0000	0.0000	1.4310	55.77	14.4356	0.0000
0.7899	0.2101	1.4384	58.71	15.4236	-2.7978
0.6257	0.3743	1.4477	61.70	16.5070	-4.6731
0.4937	0.5063	1.4580	65.98	18.0041	-5.5545
0.3853	0.6147	1.4707	68.60	19.1643	-6.3476
0.2947	0.7053	1.4825	72.69	20.7425	-6.4018
0.2179	0.7821	1.4938	77.34	22.5063	-6.0219
0.1519	0.8481	1.5054	82.53	24.4959	-5.2216
0.0946	0.9054	1.5171	88.50	26.7801	-3.9698
0.0444	0.9556	1.5290	95.44	29.4336	-2.2209
0.0000	1.0000	1.54000	103.44	32.4545	0.0000
DEG +BA					
1.0000	0.0000	1.4470	94.92	25.3612	0.0000
0.8995	0.1005	1.4501	95.12	25.5675	-0.5066
0.7993	0.2007	1.4548	95.48	25.8953	-0.8895
0.6991	0.3009	1.4600	95.82	26.2427	-1.2529
0.5989	0.4011	1.4660	96.19	26.6410	-1.5654
0.4989	0.5011	1.4732	96.76	27.1543	-1.7613
0.3989	0.6011	1.4812	97.36	27.7167	-1.9083
0.2991	0.7009	1.4908	98.10	28.4014	-1.9315
0.1951	0.8049	1.5023	99.21	29.2917	-1.7789
0.0996	0.9004	1.5161	100.76	30.4381	-1.3099
0.0000	1.0000	1.5400	103.44	32.4545	0.0000
TEG+ BA					
1.0000	0.0000	1.4550	133.48	36.2156	0.0000
0.8649	0.1351	1.4568	129.55	35.2693	-0.4381
0.7399	0.2601	1.4600	125.79	34.4525	-0.7848
0.6240	0.3760	1.4631	122.29	33.6882	-1.1132
0.5161	0.4839	1.4680	118.98	33.0744	-1.3213
0.4156	0.5844	1.4732	115.9000	32.5251	-1.4926
0.3216	0.6784	1.4792	113.0500	32.0693	-1.5948
0.2336	0.7664	1.4870	110.4300	31.7606	-1.5725
0.1525	0.8475	1.5010	108.0100	31.8214	-1.2067
0.0748	0.9252	1.5207	105.6600	32.1579	-0.5780
0.0000	1.0000	1.5400	103.4400	32.4545	0.0000

Q1: volume fraction of BA
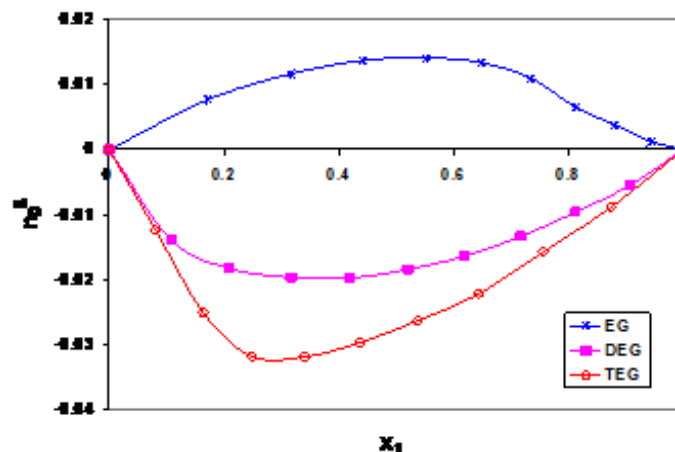Q2: volume fraction of Glycols

Fig.2. Relation between excess refractive indices nDE versus mole fraction of benzyl alcohol with glycols.
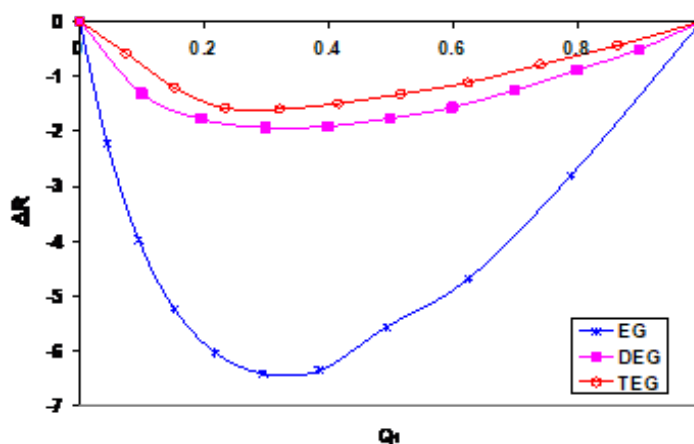

Fig.3. Relation between molar refraction deviation ΔR versus volume fraction of benzyl alcohol with glycols.

$P_a = 1.05 \, n^2$ (9)

The refractive indices are related to the polarizability of the molecules by the Lorentz_Lorenz formula as follows [27]:

$\{[n^2 - 1] / [n^2 + 2]\} = (4/3) \, \pi \, n' \, \alpha$ (10)

Where, $n' = N / V$, N is Avogadro's constant, V is the molar volume and α is the polarization. From the equation (10), the polarizabilities of the solvent mixtures under investigation were calculated. Considering spherical forms of the solvated molecules [28], the solvated radii r of the solvents were calculated using the equation:

$V = (4/3) \, \pi \, r^3$ (11)

Table 4 shows the mole fraction x_1, excess refractive indices n_D^E, solvated radii r,

polarizability α and atomic polarization P_a for the binary mixture solutions BA + EG, BA + DEG and BA + TEG. It's observed that the polarizability and the solvated radii (r) coming in the following order TEG > DEG > EG.

All values of n_D^E (except EG), V^E and ΔR have negative deviation. This effect can be attributed to the hetero association which exceeds the positive contribution to the breaking of the self-associated like molecules of EG.

Surface tension values (σ) and surface tension deviation (Δσ) for the binary mixtures BA with EG, DEG and TEG are given in Table 5.

The surface tension of pure glycols is higher than that of benzyl alcohol in all systems, (σ) increased with increasing glycol mole fraction and decreased rapidly with decreasing glycol

concentration. This behavior is explained by difference in distribution of molecules between the surface and bulk of the liquid. In a characteristic case, the compound having a lower surface tension is expelled from the bulk to the liquid-air interface due to the attractive forces between solvent molecules.

The deviation from ideal behavior can be quantified by the surface tension deviation $\Delta\sigma$. It is defined as the difference between the surface tension of the mixture σ and that expected based on an average mole fraction [29].

$$\Delta\sigma = \sigma - (x_1\sigma_1 + x_2\sigma_2) \qquad (12)$$

Where σ, σ_1 and σ_2 are the surface tension of the mixture and the pure components respectively

Figure 4 shows that surface tension deviation $\Delta\sigma$ are negative for the binary mixtures of BA with

TABLE 4. Mole fraction (x1, x2), excess refractive indices (nDE), plarizability(α), solvated radii (r) and atomic polarization(Pa) of benzyl alcohol withglycols.

x_1	x_2	n_D^E	$\alpha \times 10^{-23}$	r^3	r	P_a
EG + BA						
1.0000	0.0000	0.0000	1.13	13.3083	2.3698	2.1501
0.9435	0.0565	0.0012	1.20	14.0099	2.4107	2.1724
0.8813	0.1187	0.0038	1.28	14.7232	2.4509	2.2006
0.8124	0.1876	0.0066	1.38	15.7458	2.5064	2.2321
0.7357	0.2643	0.0109	1.46	16.3707	2.5392	2.2711
0.6498	0.3502	0.0133	1.57	17.3474	2.5887	2.3077
0.5530	0.4470	0.0141	1.69	18.4551	2.6426	2.3430
0.4430	0.5570	0.0137	1.83	19.6953	2.7006	2.3795
0.3169	0.6831	0.0116	1.98	21.1205	2.7642	2.4167
0.1709	0.8291	0.0076	2.16	22.7745	2.8345	2.4547
0.0000	1.0000	0.0000	2.37	24.6845	2.9117	2.4902
DEG + BA						
1.0000	0.0000	0.0000	1.96	22.6512	2.8294	2.1985
0.9071	0.0929	-0.0055	1.98	22.6992	2.8314	2.2079
0.8128	0.1872	-0.0096	2.00	22.7847	2.8350	2.2223
0.7169	0.2831	-0.0133	2.0100	22.8649	2.8383	2.2382
0.6195	0.3805	-0.0164	2.04	22.9545	2.8420	2.2566
0.5205	0.4795	-0.0184	2.07	23.0909	2.8476	2.2788
0.4198	0.5802	-0.0198	2.10	23.2334	2.8535	2.3037
0.3175	0.6825	-0.0197	2.14	23.4100	2.8607	2.3336
0.2090	0.7910	-0.0183	2.19	23.6740	2.8714	2.3698
0.1076	0.8924	-0.0139	2.25	24.0445	2.8863	2.4135
0.0000	1.0000	0.0000	2.37	24.6845	2.9117	2.4902
TEG + BA						
1.0000	0.0000	0.0000	2.79	31.8532	3.1699	2.2229
0.8746	0.1254	-0.0089	2.71	30.9153	3.1385	2.2284
0.7562	0.2438	-0.0157	2.65	30.0181	3.1079	2.2382
0.6440	0.3560	-0.0222	2.58	29.1828	3.0788	2.2477
0.5377	0.4623	-0.0263	2.53	28.3930	3.0507	2.2628
0.4367	0.5633	-0.0297	2.48	27.6580	3.0242	2.2788
0.3407	0.6593	-0.0318	2.43	26.9778	2.9992	2.2974
0.2494	0.7506	-0.0318	2.40	26.3526	2.9758	2.3217
0.1640	0.8360	-0.0251	2.38	25.7751	2.9539	2.3657
0.0810	0.9190	-0.0124	2.38	25.2143	2.9323	2.4282
0.0000	1.0000	0.0000	2.37	24.6845	2.9117	2.4902

EG and DEG in almost the whole composition range.

The minimum values of these properties are located at mole fraction $x_1 \approx 0.73$, but the deviation for the binary mixture containing BA with TEG show negative deviation with maximum negativity at $x_1 \approx 0.3$, after that the deviation in surface tension become positive with maximum value at mole fraction $x_1 \approx 0.73$

The negative deviation from ideality means that the surface concentration of the component with higher surface tension (glycols in this system) is lower than its bulk concentration[30]. Therefore, the surface tension of the mixture is lower than the expected ideal values. For the

binary mixture of BA with TEG it is different, it has positive deviation with maximum at the same concentration $x_1 \approx 0.73$ mole fractions of TEG.

From our previous work [31] we found in Figure 5 the relation between excess free energy ΔG^E and x_1 show positive deviation with the sequence TEG >DEG >EG. According to Reed[32] and Meyer et al. [33], positive ΔG^E value indicates specific interaction, the large positive ΔG^E value for BA with TEG and DEG mixtures speak in a favor of strong specific interactions through complex formation in the systems. The value of ΔG^E for BA + EG mixtures is less positive, suggesting weaker interaction in the system.

The maximum deviation at $x_1 \approx 0.3$ mole

TABLE 5. Surface tension (σ) and excess surface tension (Δσ) of benzyl alcohol with glycols.

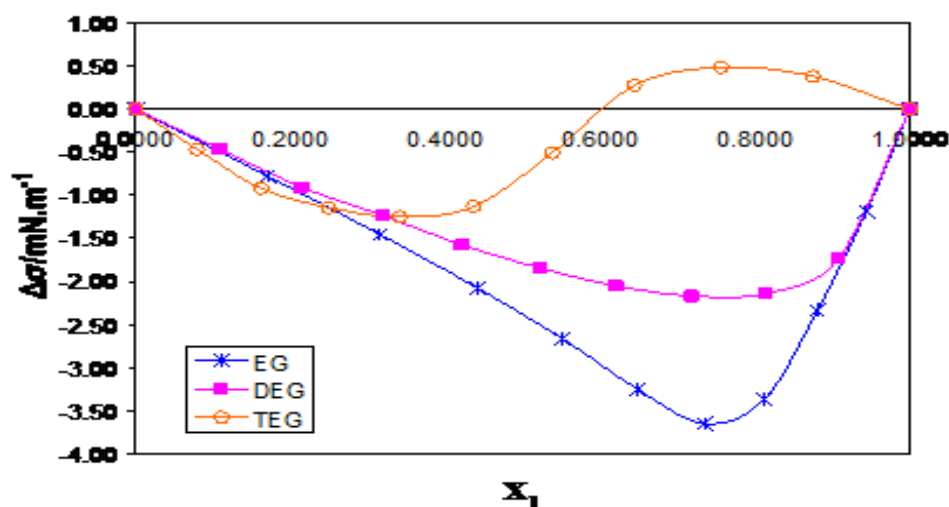| X_1	σ /mN. m^{-1}	$\Delta\sigma$ /mN. m^{-1}
EG+ BA		
1.0000	44.00	0.00
0.9432	42.35	-1.19
0.8807	40.70	-2.33
0.8115	39.10	-3.37
0.7346	38.20	-3.65
0.6486	37.90	-3.25
0.5516	37.70	-2.67
0.4416	37.40	-2.08
0.3157	37.00	-1.46
0.1702	36.50	-0.78
0.0000	35.90	0.00
DEG+ BA		
1.0000	44.80	0.00
0.9075	42.24	-1.74
0.8134	41.00	-2.14
0.7178	40.12	-2.17
0.6205	39.37	-2.05
0.5216	38.70	-1.84
0.4209	38.07	-1.58
0.3184	37.50	-1.23
0.2142	36.90	-0.91
0.1080	36.40	-0.46
0.0000	35.90	0.00
TEG+ BA		
1.0000	46.50	0.00
0.8746	45.55	0.38
0.7561	44.40	0.48
0.6440	43.00	0.27
0.5376	41.09	-0.51
0.4367	39.40	-1.13
0.3407	38.26	-1.25
0.2494	37.40	-1.14
0.1623	36.70	-0.92
0.0793	36.27	-0.47
0.0000	35.90	0.00

Fig. 4. Relation between Surface tension deviation Δσ versus mole fraction of benzyl alcohol with glycols.
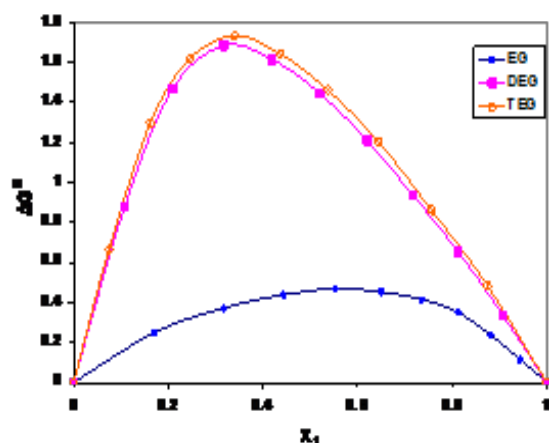

Fig. 5. Relation between excess free energy ΔGE versus mole fraction of benzyl alcohol with glycols.

fraction means more strength interaction for TEG than the other glycols.

Conclusion

From the measured data presented in this paper about densities, surface tension and refractive indexes of the binary system (BA with EG, DEG and TEG) at ambient temperature and atmospheric pressure, the excess refractive indices, molar refraction, excess molar refraction, excess surface tension and polarizability have been calculated.

As the molecules possess hydrogen bond

donors on the OH-group and acceptors on the oxygen atom[33], they are showing a strong ability for hydrogen bond formation,

- The data proved that the strength of interaction between TEG and BA is more than the other two solvents EG and DEG due to its high polarizability and high negativity of n_D^E at the concentration of ≈ 0.3 mole fraction, also it has a structure of large size than the others (solvated radii r is large).

- A negative deviation of the molar refraction coming in the order EG >DEG >TEG but the plorizability coming in the reverse sequence

TEG >DEG >EG which confirm the strength of interaction of TEG

- The excess surface tension show a negative deviation from ideality for the binary mixtures of BA with EG and DEG, while the binary mixture of BA with TEG change from negative to positive deviation at $x_1 \approx 0.6$ mole fraction of TEG with maximum negativity at $x_1 \approx 0.3$.

- The negative values of $\Delta\sigma$ indicate a different distribution of the solvent and hydrocarbon molecule between the surface and the bulk region. Probably, the surface concentration of benzyl alcohol, which is the component with lower surface tension, is higher than its bulk concentration [34]. According to reports of other researches [35,36], the $\Delta\sigma$ tend to be positive for binary mixtures in which the molecular interactions in the bulk are significant.

- From the previous work [31], the relation between excess free energy ΔG^E and x_1 show positive deviation with the sequence TEG >DEG >EG with a maximum deviation at $x_1 \approx 0.3$ mole fraction which means more strength interaction for TEG than the other.

- The results from this study and our previous work are identical. So, TEG can be used as anti-solvent with BA at $x_1 \approx 0.3$ mole fraction of TEG to increase the efficiency of BA.

- By measuring refractive index, density and surface tension of solution, we can understand its behavior without going to extraction method to select the best anti-solvent from the glycols used.

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دراسة معامل الإنكسار، الإنعكاس الجزيئي، التوتر السطحي والإستقطاب للمحاليل الثنائية
من الكحول البنزيلي مع الجليكول وحيودها

سحر محمود توفيق- فريد محمد فرج

قسم التكرير- معهد بحوث البترول-مدينة نصر القاهرة - مصر.

تم قياس الكثافة ومعامل الإنكسار والتوتر السطحي للمحاليل الثنائية للكحول البنزيلي مع أحادي وثنائي وثلاثي أثيلين جليكول لكل التركيزات عند درجة حرارة ٢٠°م درجة مئوية و عند الضغط الجوي.

ولقد تم حساب الزيادة في الحجم وكذلك الزيادة في معامل الإنكسار والحيود في الإنعكاس الجزيئي وأيضاً الزيادة في التوتر السطحي والإستقطاب.

ولقد وجد أن الزيادة في معامل الإنكسار للكحول البنزيلي مع ثنائي وثلاثي أثيلين جليكول سالب، ولكن مع أحادي أثيلين جليكول كان موجب. ووجد أيضاً أن الزيادة في الحجم والحيود في الإنعكاس سالب لكل المحاليل.

أما بالنسبة للتوتر السطحي وجد سالب مع أحادي وثنائي أثيلين جليكول، ولكن بالنسبة إلى ثلاثي الأثيلين جليكول وجد أنه سالب حتى تركيز 0.6 وبعد ذلك كان موجب.

تمت التجارب وحساباتها لدراسة الروابط بين مكونات المحاليل لإختيار الجليكول المناسب للإضافة.

ولقد وجد أن جميع النتائج تظهر أنه يمكن إستخدام ثلاثي أثيلين جليكول مع الكحول البنزيني بتركيز 0.3 لتحسين مواصفات الكحول كمذيب لإستخلاص المواد الأروماتية.