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MEASURED DENSITIES, REFRACTIVE INDICES, EXCESS MOLAR VOLUMES AND DEVIATIONS CALCULATED FROM MOLAR REFRACTION OF THE BINARY MIXTURE OF ETHANOL + 1-NONANOL AND TERNARY MIXTURE ETHANOL + 1-NONANOL + WATER AT 293.15 K

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ABSTRACT

Densities, and refractive indices were measured for the binary system ethanol + 1-nonanol and ternary system ethanol + 1-nonanol + water at 293.15 K. The excess molar volumes, and the deviations molar refraction were calculated for binary and ternary system. Redlich-Kister type equation was fitted to the excess molar volumes and, the deviations from a mole fraction average of the molar refraction, and the values of coefficients were calculated.

Key Words: 1-nonanol, Ethanol, Density, Refractive indices, Binary mixture

ETANOL + 1-NONANOL İKİLİ SİSTEMİ VE ETANOL + 1-NONANOL + SU ÜÇLÜ SİSTEMİNİN 293.15 K SICAKLIKTAKİ YOĞUNLUKLARININ, REFRAKTİF İNDİSLERİN ÖLÇÜLMESİ VE AŞIRI MOLAR HACİMLERİNİN VE MOLAR REFRAKSİYONLARININ HESAPLANMASI

ÖZET

Etanol+1-nonanol ikili sistemi ve etanol+1-nonanol+su üçlü sistemi için çeşitli karışımlarda yoğunluklar ve kırılma indisleri 293.15 K de ölçülmüştür. İkili ve üçlü sistemler için aşırı molar hacim ve molar refraksiyon sapmaları hesaplanmıştır. Aşırı molar hacim ve molar refraksiyon sapmaları için Redlich–Kister eşitliği uygulanarak eşitlik katsayıları hesaplanmıştır.

Anahtar Kelimeler : 1-nonanol, Etanol, Yoğunluk, Refraktif indis, İkili karışım

1. INTRODUCTION

Ethanol is an important solvent with extensive use. Ethyl alcohol is produced by the direct hydration of acetaldhyd or by fermentation of molasses. The literature reports several studies concerning density, refractive indices and derived properties, such as deviation from a mole fraction average of the molar refraction, excess molar volumes for the mixture of ethanol and several solvents. (Arce et all., 1993; Jayalakshmi and Reddy, 1985a; Reddy, 1985b; Arce at all., 1994). Many experiments have been carried out on the selective recovery of ethanol and various alcohols. 1-nonanol can be considered as a suitable solvent for the selective recovery of alcohols. To our knowledge, there is no data concerning experimental values of density, refractive indices and deviation from a mole fraction average of the molar refraction, excess molar volumes of its binary mixture with 1-nonanol and its ternary mixture with water + 1-nonanol present in the literature.

The aim of this study is to present experimental values of the density, refractive indices, excess molar volume and the deviations from a mole fraction average of the molar refraction, for the binary mixture of ethanol+1-nonanol and ternary mixture of ethanol+1-nonanol+water and to calculate the Redlich-Kister parameters excess molar volume and the deviations from a mole fraction average of the molar refraction, for the binary mixture of ethanol+1-nonanol at 293.15 K.

2. MATERIAL AND METHOD

Ethanol, and 1-nonanol were supplied from Merck Co. The purifies of ethanol, and 1-nonanol were 99.5 %, and 96 %, respectively. Ethanol and 1-nonanol were used without any purification. The stated , density, viscosity and refractive index of each solvent are reported in Table 1 and all of the solvents are compared with literature(Weast, 1990). It is seen that the values obtained in our experiments for pure solvents are in agreement with literature values.

Mixture Preparations: The binary mixture in our study were prepared by mass. In order to reduce the evaporation losses , the residence time of the sample in the all equipments and bottles are kept at minimal time and volume. Therefore, fresh compositions of liquid mixtures have been performed and the mixtures were prepared either freshly or stored in air tight bottles.

Density: A digital densiometer was used to measure density (Anton Par DMA-48). All the density experiments were carried out at 20±0.01°C. Double distilled water was used for the densiometer calibration. Gas Chromatography (HP, 6890 Series) was used to check the variation mixture after the density measurements and it was found that variation of mixture was minimal. The mixture densities were obtained by averaging the results from three measurements.

Refractive indices: Refractive indices were determined with respect to do sodium D line. An Abbe refractometer was used for this purpose. It was connected with the constant temperature water bath (±0.01 ^{o}C). An average of triplicate measurement was considered for the calculation of refractive indices values.

Table 1. Densities d and Refractive Indices n_D of the Pure Components at 293.15 K

Component	Density ($g.cm^{-3}$)		Refractive index	
	Exptl.	Lit.(Weast, 1990)	Exptl.	Lit.(Weast, 1990)
Ethanol	0.78925	0.78504	1.3592	1.3594
1-nonanol	0.82728	0.8273	1.4333	1.4332
Water	0.99818	0.99823	1.3324	1.3325

3. RESULT AND DISCUSSION

Excess volumes, V^E was calculated from the Equation (1).

$$V^E = \frac{x_1M_1 + x_2M_2}{d_m} - \frac{x_1M_1}{d_1} - \frac{x_2M_2}{d_2} \qquad (1)$$

Where M_1 and M_2 are the molecular weights of components 1 and 2, x_1 and x_2 the mole fractions of components 1 and 2, d_1 and d_2 are the densities of pure components 1 and 2, d_m is the measured density of the mixture.

The molar refraction, *R*, was calculated using the Lorentz-Lorenz equation;

$$R = \frac{n_D^2 - 1}{n_D^2 + 2} V \qquad (2)$$

where n_D is the refractive index of the mixture and *V* molar volume of the mixture. The deviation from a mole fraction average of the molar refraction was computed according to the Equation (3)

$$\delta R = R - \sum_i x_i R_i \qquad (3)$$

Where R_i is the refractive indices of the component *i* in the mixture.

The experimental values of density, refractive indices, excess molar volume, and the deviations of molar refraction for binary mixture of ethanol and 1-nonanol at different concentrations and at 293.15 K are listed in Table 2. It is seen from Table 2 that the binary mixture ethanol+1-nonanol is positive δR values with a maximum of 0.027 $cm^3.mol^{-1}$ and the binary mixture ethanol+1-nonanol is also positive V^E values with a maximum of 0.085 $cm^3.mol^{-1}$.

Table 2. Densities, d, Refractive Indices n_D, Excess Volumes, V^E, and δR Values of 1-Nonanol + Ethanol at 293.15 K

$X_{1\text{-nonanol}}$	n_D	δR/($cm^3.mol^{-1}$)	d/(g cm^{-3})	V^E/ ($cm^3.mol^{-1}$)
0.070	1.3689	0.012	0.79577	0.042
0.120	1.3770	0.016	0.79963	0.057
0.191	1.3866	0.022	0.80418	0.074
0.245	1.3975	0.025	0.80719	0.083
0.351	1.4029	0.027	0.81205	0.085
0.394	1.4063	0.022	0.81380	0.071
0.445	1.4075	0.019	0.81562	0.062
0.508	1.4137	0.017	0.81759	0.055
0.557	1.4165	0.015	0.81896	0.049
0.602	1.4188	0.014	0.82012	0.043
0.649	1.4211	0.013	0.82125	0.033
0.692	1.4226	0.012	0.82168	0.031
0.743	1.4249	0.011	0.82310	0.030
0.802	1.4262	0.010	0.82343	0.027
0.849	1.4288	0.008	0.82502	0.024
0.895	1.4303	0.005	0.82615	0.017
0.952	1.4324	0.004	0.82654	0.012

The excess volume and *δR* were correlated using Redlich-Kister expression (Redlich and Kister; 1948; Fermeglia at all., 1999):

$$Y^E = (x_i)(x_j)\sum_{p=0}^{p} A_k (x_1 - x_2)^p \quad p= 0,1,2,3.. \qquad (4)$$

where Y^E is V^E or *δR*, x_i and x_j are the mole fractions of components 1 and 2, p is the degree of the polynomial and A_k are the adjustment parameters. The values of the coefficients for binary mixture are presented in Table 3.

Table 3. Redlich-Kister Parameters of the Excess Volume and the Deviations of Molar Refraction for the Binary Mixtures of Ethanol +1-Nonanol

Parameters	A_0	A_1	A_2	A_3	A_4
The values of coefficients for excess molar volumes	0.23099	-0.33135	0.21909	0.11368	0.06746
The values of coefficients for the deviations of molar refraction	0.06470	-0.06749	0.10536	0.01367	-0.02273

The values of density and refractive indices of water+ethanol+1-nonanol mixture were measured and these values were used to calculate for excess molar volumes and the deviations of molar refraction within the miscible region of the ternary mixture (Table 4). The boundaries of the region was established in our laboratory. It is seen from the Table 4 that V^E values for the ternary mixture ethanol+1-nonanol+water are positive with a maximum of 0.011 $cm^3.mol^{-1}$ for the low water content and *δR* values are positive and negative with a maximum of 0.022 $cm^3.mol^{-1}$ and minimum of -0.018 $cm^3.mol^{-1}$.

Table 4. Excess volumes, V^E, and *δR* values of 1-nonanol+ethanol+water at 293.15 K.

x_{water}	$x_{ethanol}$	V^E ($cm^3.mol^{-1}$)	*δR* ($cm^3.mol^{-1}$)	x_{water}	$x_{ethanol}$	V^E ($cm^3.mol^{-1}$)	*δR* ($cm^3.mol^{-1}$)
0.098	0.902	-0.345	-0.011	0.251	0.715	-0.520	-0.011
0.087	0.801	-0.197	-0.004	0.210	0.502	-0.230	0.007
0.075	0.681	-0.107	0.004	0.157	0.403	-0.135	0.019
0.067	0.650	-0.065	0.009	0.101	0.296	-0.055	0.015
0.059	0.590	-0.041	0.014	0.052	0.172	-0.015	0.011
0.045	0.451	-0.019	0.018	0.361	0.612	-0.912	-0.025
0.035	0.352	-0.003	0.022	0.340	0.550	-0.602	-0.012
0.025	0.253	0.009	0.019	0.312	0.452	-0.370	0.004
0.017	0.172	0.011	0.015	0.223	0.383	-0.197	0.017
0.007	0.070	0.001	0.006	0.171	0.302	-0.085	0.014
0.152	0.802	-0.545	-0.018	0.131	0.294	-0.042	0.011
0.140	0.675	-0.245	-0.009	0.421	0.423	-0.592	-0.011
0.125	0.552	-0.185	-0.003	0.205	0.212	-0.095	0.008
0.060	0.201	-0.010	0.012	0.101	0.200	-0.022	0.003

4. CONCLUSION

The V^E and δR values for the binary mixture ethanol+1-nonanol was found to be positive. The binary mixture ethanol+1-nonanol was positive δR values with a maximum of 0.027 cm ^{3}.mol^{-1} and the binary mixture ethanol+1-nonanol was also positive V^E values with a maximum of 0.085 cm^3.mol^{-1}. It was shown that these deviations slightly greater than the mixtures of octanol+ethanol at 293.15 K (Arce, at all., 1993). V^E values for the ternary mixture ethanol+1-nonanol +water was found to be positive for the low water content. The V^E values for the ternary mixture ethanol+1-nonanol +water were positive with a maximum of 0.011 cm ^{3}.mol^{-1} for the low water content and δR values were positive and negative with a maximum of 0.022 cm^3.mol^{-1} and minimum of -0.018 cm^3.mol^{-1}.

In order for the study of a chemical or a physical changes in chemical process, it is necessary that there should be strict parameter control of the system. Systems can be monitored by some parameters such as density, refractive index. Although the deviations in densities and refractive indices of mixtures are small in our study and some other studies, careful measurements and calculations are done to use them for monitoring the resulting changes of the composition, since the deviations were not changed proportionally.

Therefore the authors think that the results obtained in this study are important since they represent the first published data for the binary mixture studied and will receive considerable interest and be will useful for engineers who will work in this field.

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