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Refractive Indices and Their Related Properties for Adipic Acid in Mixed Aqueous Methanol Solvents at Different Temperatures

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Keywords

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Experimental refractive index data for binary aqueous methanol systems of adipic acid, at T = 298.15 K, 303.15 K, 308.15 K, and 313.15 K, over the entire mole fraction range are reported. The excess refractive index, n_D^E, molar refraction, R, and excess molar refraction, R_E, were calculated from the experimental data. The experimental density data of the studied mixtures, previously measured, were used to calculate the partial and apparent volumetric properties at in finite dilution. Moreover, the excess molar quantities have evidenced intermolecular interactions between the components of mixtures. Refraction properties are determined here are important parameters of lenses manufacturing.

Introduction

Knowledge of thermo physical properties of organic binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in the design process (flow, mass transfer, or heat transfer calculations) of many chemical and industrial processes. The information about thermodynamic characters of liquid mixtures containing adipic acid, and their dependence on both compositions and temperature are important data for their applications in the separation fields. Adipic acid is an important substance in chemical industries. It is ranked in the top ten by the term of volume used [1]. It is used as a raw material in the productions of polyamide [2, 3], polyurethane, polyester resins, plasticizers, lubricants [4], carpet fibers, specialty foams, reinforcements, and several items of clothing [5]. Oxidation of cyclohexanone-cyclohexanol mixture with nitric acid is the conventional route for preparing adipic acid [1]. In the industry, it is mainly produced by oxidation of cyclohexane with air and nitric acid [6]. After oxidization process, crude adipic acid has to be purified to obtain pure adipic acid [7]. Refractive index and density measurements are expected to enlighten both solvent –solvent and solute –solvent interactions. The excess properties of binary liquid mixtures are of considerable importance in the fundamental understanding and interpreting of nature of the interactions between unlike molecules. The refractive index of a liquid at the sodium line light, n_D, being a property comfortable to measure with good accuracy, it has been often associated with other electrical and thermo physical properties, as dielectric permittivity, surface tension and density. For most practical purposes, the refraction index of light through air can be used to calculate refractive index of unknown materials [7, 8].

Experimental

Materials

The substances were commercial products from Aldrich and Merck, of the first grade purity. The quality of the compounds was verified by gas chromatography and it was better than declared. The liquids were stored over 4A molecular sieves, therefore dried by water traces and used without other further purification procedure.

Apparatus and Procedure

The binary mixtures were prepared by mixing the known masses of the pure liquids in airtight narrow-mouth grounded glass stopped bottle, taking the precaution to minimize the evaporation losses, and weighed using a GH-252 (A&D Japan) electronic balance with a precision of $\pm 10^{-7}$ kg. The experimental uncertainty in mole fractions was estimated to be less than ±0.0002. The refractive indices of the pure compounds and their mixtures were carried out at the 589.3 nm wavelength of the sodium D line, using a digital automatic refractometer Abbi RXA 170 (Anton Paar-Austria) with uncertainty of ±0.00001 for refractive index. The temperature of the prism was controlled within ±0.01 K. The apparatus was calibrated with dry air and deionized ultra-pure water at atmospheric pressure, according to the instrument operating instructions. For each measurement of refractive index, we made at least three independent readings for the same sample at working temperature, to obtain the reproducibility of the measurements; hence, its averaged value as one experimental point is reported in the paper.

Results and Discussion

The measurements of refractive indices provide precious information on the interactions determined only by dispersive forces [9, 10] as the refractive index values are closer associated to the mean polarizability, P, of the liquid, by the molar refraction, R:

$$R = V_M({n_D}^2 - 1)/({n_D}^2 - 2) \tag{1}$$

$$R = P_A + P_E = P_D = P_T \tag{2}$$

Where V_M is the molar volume of saturated adipic acid solutions which equal $(\frac{M}{d})$, where M and d are the molecular weight and the measure density of saturated adipic acid solutions at different used temperatures The polarizability represents the relative tendency of a system of electric charges to become polarized in the presence of an external electric field (such as the field generated by sodium D line light in optical region). Polarizability allows understanding better the interactions between non-polar atoms or molecules and other electrically charged species, such as ions or polar molecules with dipole moments. From the measured data of refractive index, the excess refractive indices, n_D^E, were estimated.

$$n_D^E = n_{D\,mix} - (x_{s1}.n_{D1} + x_{s2}.n_{D2}) \tag{3}$$

Where, X_{S1}, $X_{S,}$ n_1 and n_2 are the mole fractions by weight and the refractive indexes of the organic solvent MeOH and water, respectively.

The values of X_{S1} and X_{S2} were calculated by applying equation (4):

$$X_{s1} = \frac{\frac{vol\%(1)xd1}{M1}}{\frac{vol\%(1)xd1}{M1} + \frac{vol\%(2)xd2}{M2}} \tag{4}$$

where d_1, d_2, M_1, M_2, vol. % (1) and vol. % (2) are the densities, the molecular weights and the volume percentages of the organic solvents methanol (MeOH) and water, respectively. The X_{s2} values in equation 2 are equal to $(1\text{-}X_{s1})$. [11-21]

The right hand side of equation (2) is equal to total polarization or distortion polarization which equal to the summation of the electronic polarization (P_E) and atomic polarization (P_A). The atomic polarization (P_A) was calculated [22-31] using equation 5.

$$P_A = 1.05\ n^2 \tag{5}$$

The molecular polarizability (α) can be calculated from optical refractive index (n_D) of the saturated phthalic acid solutions containing N molecules per unit volume. The refractive index is related to the polarizability of saturated molecules by Lorenz-Lorenz formula [31-40] as explained in equation (6).

$$\frac{n^2-1}{n^2+2} = \frac{4\ \bar{n}\ \alpha\ \pi}{3} \quad (6)$$

Where $\bar{n} = \frac{N}{V}$, N is Avogadro's number and V is the molar volume of saturated adipic acid solutions. Applying equation (6), the polarizabilities of saturated adipic acid solutions were calculated at different temperatures and presented in Tables 1, 2, 3, and 4.

The solvated diameters of the saturated adipic acid solutions in mixed (MeOH-H_2O) solvents were calculated using equation (7) considering spherical form of the solvated adipic acid solutions [32-51].

$$V = \frac{1}{6} N\ \pi\ \sigma^3 \quad (7)$$

Where σ the solvated diameters and N is Avogadro's number

The measured values of refractive indices (n), the excess refractive indices (n_E), the molar refraction (R), the atomic polarization (P_A), electronic polarization (P_E), polarizabilities (α) molar volumes (V), and the solvated diameters (*σ)* are listed in Tables 1-4, at different temperatures. The relation between mole fraction (X_s), (α) and (μ) for adipic acid in mixed methanol-water solvents at different temperatures are shown i n Fig. 1 and 2 at 298.15 K and 303.15K as chosen temperatures at the three dimensions. The parameters given here explain reflection, refraction, absorption and passing through materials determine the color and transparency of the substances.

Table (1). *Refraction parameters for saturated adipic acid in mixed methanol-water solvents at 298.15K.*

$\sigma x10^8$	$\mu x10^{22}$	ε	$\alpha x10^{23}$	P_E	P_T	P_A	R	$n_d^{(E)}10^3$	V_M	X_S
7.7183	2.188	78.3	1.206	-1.6769	0.2098	1.8867	30.429	0	144.98	0
7.7569	2.118	73.744	1.234	-1.6837	0.2115	1.8952	31.135	2.152	147.17	0.0999
7.8779	2.02	67.884	1.318	-1.7007	0.2157	1.9164	33.256	8.56	154.16	0.2284
7.9685	1.89	60.169	1.383	-1.7122	0.2184	1.9306	34.858	12.098	159.54	0.3976
8.0095	1.702	49.129	1.421	-1.7237	0.2212	1.9449	35.846	15.059	162.02	0.6397
8.0696	1.393	32.7	1.411	-1.6961	0.2146	1.9107	35.56	0	165.69	1

Table (2). *Refraction parameters for saturated adipic acid in mixed methanol-water solvents at 303.15K.*

$\sigma x10^8$	$\mu x10^{22}$	ε	$\alpha x10^{23}$	P_E	P_T	P_A	R	$n_d^{(E)}10^3$	V_M	X_s
7.7517	2.177	76.305	1.225	-1.679	0.2104	1.889	30.908	0	146.87	0
7.7884	2.106	71.75	1.251	-1.684	0.2118	1.8966	31.557	1.552	148.97	0.0999
7.9057	2	65.89	1.334	-1.701	0.216	1.9178	33.653	7.828	155.8	0.2284
8.0066	1.87	58.17	1.403	-1.713	0.21876	1.9932	35.405	11.198	161.84	0.3976
8.0513	1.679	47.13	1.446	-1.726	0.2217	1.9477	36.5014	14.428	164.57	0.6397
8.1252	1.35	30.71	1.446	-1.7	0.2157	1.9164	36.488	0	169.14	1

Table (3). *Refraction parameters for saturated adipic acid in mixed methanol-water solvents at 308.15K.*

$\sigma x10^8$	$X10^{22}\mu$	ε	$\alpha x10^{23}$	P_E	P_T	P_A	R	$n_d^{(E)}10^3$	V_M	X_S
7.7806	2.131	74.55	1.2437	-1.682	0.2112	1.8938	31.379	0	148.52	0
7.8017	2.09	70.079	1.2595	-1.685	0.2121	1.898	31.7605	0.652	149.73	0.0999
7.9369	2	64.329	1.353	-1.704	0.21655	1.9207	34.1403	7.556	157.65	0.2284
8.0214	1.86	56.757	1.4149	-1.715	0.2193	1.9349	35.6922	11.098	162.74	0.3976
8.0726	1.67	45.92	1.46	-1.727	0.222	1.9492	36.837	14.059	165.88	0.6397
8.0972	1.344	29.8	1.4363	-1.701	0.216	1.9178	34.1591	0	167.4	1

Table (4). *Refraction parameters for saturated adipic acid in mixed methanol-water solvents at 313.15K.*

$\sigma x10^8$	$X10^{22}\mu$	ε	$\alpha x10^{23}$	P_E	P_T	P_A	R	$n_d^{(E)}10^3$	V_M	X_s
0.8098	2.15	73.0091	1.263	-1.685	0.2121	1.898	31.8602	0	150.2	0
7.9001	2.05	68.603	1.311	-1.688	0.2126	1.9008	33.0645	0.152	155.47	0.0999
7.9426	1.98	62.93	1.359	-1.706	0.2171	1.9235	34.3014	7.056	157.99	0.2284
8.0424	1.85	55.47	1.429	-1.717	0.2198	1.9377	36.063	10.598	164.02	0.3976
8.1824	1.66	44.79	1.524	-1.729	0.2226	1.952	38.455	13.559	172.74	0.6397
8.436	1.33	28.9112	1.627	-1.705	0.2168	1.9221	41.0468	0	189.3	1

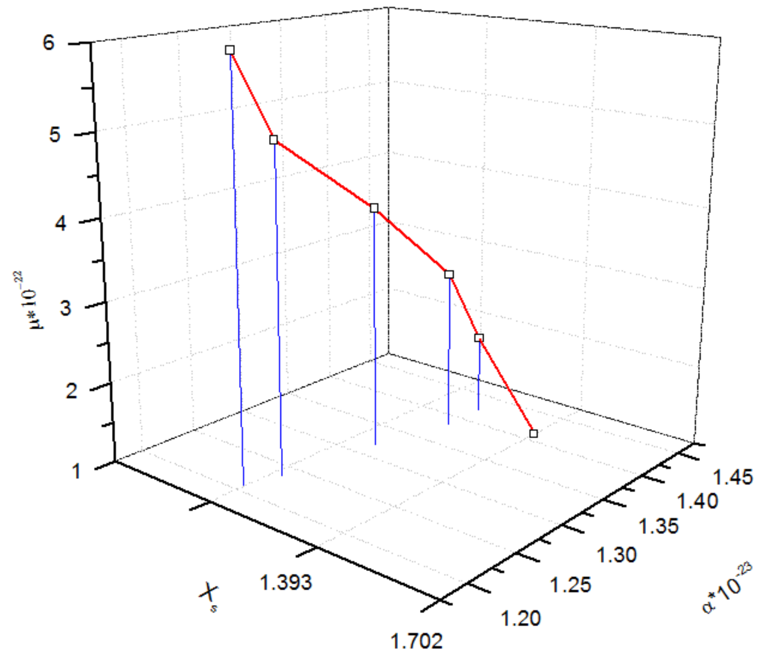

Fig. (1). *The relation between mole fraction (X_s), (μ) and (α) for adipic acid in mixed methanol-water solvents at 298.15 K.*

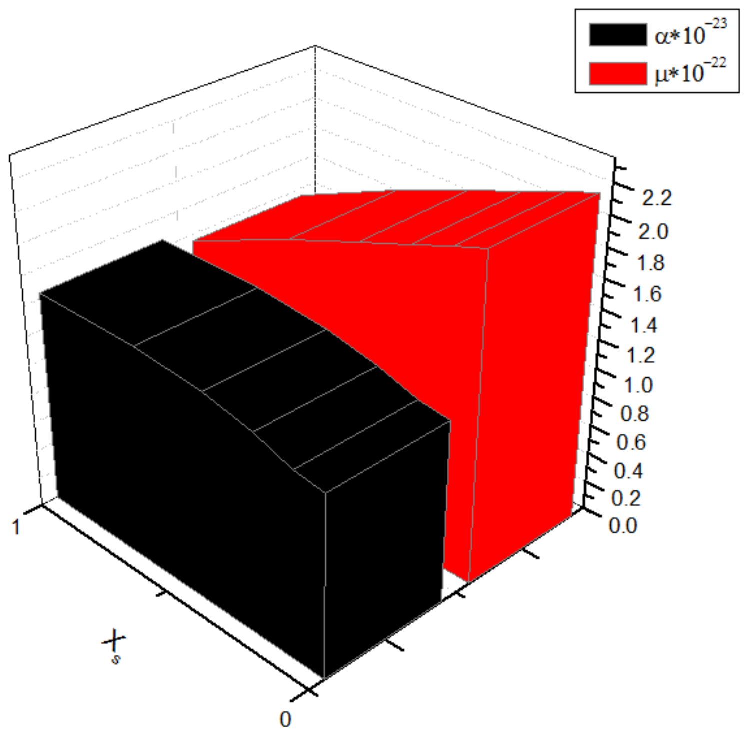

Fig. (2). *The relation between mole fraction (X_s), μ and (α) for adipic acid in mixed methanol-water solvents at 303.15 K.*

Conclusion

Maximum excess n_E refractive index for saturated adipic acid solutions were increased in mixed (MeOH-H_2O) solvents show maxima at Xs 0.6397 MeOH in mixed MeOH-water solvents indicating maximum interaction at this point. All polarization parameters for adipic acid solutions were increased by increasing both methanol and temperature due to more mobility and velocity of ionic species in the used solvents. All the data help to fabricate electrodynamics materials with negative electrodynamics properties with negative values of the dielectric permittivity and magnetic permeability needed in industry. ■

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