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EXCESS MOLAR VOLUMES, EXCESS VISCOSITIES AND REFRACTIVE INDICES OF A QUATERNARY LIQUID MIXTURE AT 298.15 K

CANZONIERI, S.H.[1]; POSTIGO, M.A.[1]; SALAS, J.A.[2]; KATZ, M.[2*]

[1]Cátedra de Fisicoquímica, Depto de Química, Facultad de Ingeniería, U.N. del Comahue, Buenos Aires 1400, Neuquén (8300), Argentina. Investigador del CONICET. Fax: (54)(99)-48-8306 e-mail: postigo@uncoma.edu.ar.

[2]Cátedra de Fisicoquímica, Departamento de Química (Ingeniería Química), U.N. de Tucumán, Avda. Independencia 1800, Tucumán (4000). e-mail: mkatz@herrera.unt.edu.ar.

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ABSTRACT

Excesss molar volumes, excess viscosities and refractive indices for the quaternary system n-hexanol + ethanenitrile + dichloromethane + tetrahydrofuran at 298.15 K are reported along with corresponding data for the two constituent binary mixtures. Flory's statistical theory has been applied to predict excess molar volumes and compare them to experimental data. We have also applied Grunberg and Nissan's equation for calculating viscosities and Lorenz-Lorentz's equation for predicting refractive indices, by knowing the values of the pure components.

RESUMEN

Se dan datos del volumen molar de exceso, viscosidad de exceso e índices de refracción para el sistema cuaternario n-hexanol + etanonitrilo + diclorometano + tetrahidrofurano a 298.15 K, así como los de los sistemas binarios correspondientes. Se aplica la teoría de Flory para los volúmenes de exceso y se compara con valores experimentales. Se aplica también la ecuación de Grunberg y Nissan para al cálculo de las viscosidades y la de Lorentz-Lorenz para la predicción de índices de refracción, conociendo la de los componentes puros.

INTRODUCTION

In recent paper [1] from our laboratory, we have described measurements of excess properties of one quaternary system.

Theoretical predictions of excess molar volumes and excess viscosities of non-ideal binary mixtures have been satisfactory in explaining their sign and magnitudes in terms of interaction between the pure components. For ternary systems the predictions are more complex, and thus empirical methods based on experimental data have to be used [2-6]. For quaternary liquid mixtures, there are less data of excess properties [7-9].

In this work, we have determined the molar excess volumes (V^E), excess viscosities (η^E) and the excess refractive indices (n_D^E) for a quaternary liquid mixture formed by n-hexanol (HE) (component1) + ethanenitrile (EN) (component 2) + dichloromethane (DCM) (component 3) + tetrahydrofuran (THF) (component 4) at 298.15 K and some correlations were found.

Flory's statistical theory was extended to a quaternary mixture [7]. Viscosity data have been analyzed in terms of Grunberg and Nissan [10] method and compared with experimental data.

The knowledge of refractive indices of a quaternary liquid mixture is often desirable and in this work the Lorenz-Lorentz's equation was used to calculate the refractive indices of a quaternary mixture, by knowing the refractive indices of the pure components [9].

EXPERIMENTAL

The methods used in our laboratory have been described previously [6]. Densities were determined in a digital densimeter Mettler model DA 310, thermostatically controlled at 0.01 K. Calibration was done with air and doubly distilled water with a precision of $\pm 10^{-2}$ $kg.m^{-3}$. Viscosities of the pure liquids and of the mixture were determined with a thermostat CT 1450 using Ubbelhode viscosimeters. The estimated error was ± 0.005 mPa.s. The dynamic viscosity η was determined from the following relationship

$$\eta = \rho k(t-c) \qquad [I]$$

where t, k, c and ρ are respectively the flow time, the viscosity constant, the Hagenbach correction and density. Refraction indices were measured using a Jena dipping refractometer, with an estimated error of $\pm 2x10^{-5}$. All weightings were made on a H315 Mettler balance, with an error $\pm 10^{-7}$ kg. The substances have been purified as previously described [11]. Mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

RESULTS AND DISCUSSION

The experimental results for the pure components are reported in Table 1, together with literature values for comparison purposes. Densities and refraction indices of some binary mixtures [12] have been published as follows: HE(1) + EN(2) ; HE(1) + DCM(3) and EN(2) + DCM(3) . With these data and experimental results of the other systems we can calculate V^E, η^E and n_D^E as follows:

$$V^E = \sum_{i=1}^{2} x_i M_i (\rho^{-1} - \rho_i^{-1}) \qquad [II]$$

$$\eta^E = \eta - \exp\left(\sum_{i=1}^{2} x_i \ln \eta_i\right) \qquad [III]$$

$$n_D^E = n_D - \sum_{i=1}^{2} x_i n_{Di} \qquad [IV]$$

where are the molar fraction, molecular weight, density, viscosity and refractive index of component i, and, the density, viscosity and refraction index of the solution. Each set of results of the binary systems have been fitted with a Redlich-Kister equation of the type:

$$X^E = x_i x_j \sum_{k=0}^{n} a_k (x_i - x_j)^k \qquad [V]$$

TABLE 1. Properties characterizing the pure components at 298.15 k.

Substance	$\rho \times 10^3$ (kg m^{-3}) Exp.	Lit.	η (mPa s) Exp.	Lit.	n_D Exp.	Lit.
HE	0.81515	0.81534[a]	4.566	4.4592[a]	1.41582	1.4157[a]
EN	0.77677	0.77649[a]	0.343	0.341[a]	1.43157	1.43163[a]
DCM	1.31616	1.31678[a]	0.406	0.404[a]	1.42116	1.42115[a]
THF	0.88249	0.88190[a]	0.474	0.460[a]	1.40533	1.40496[a]

[a]Ref.[19]

where X^E represents V^E or η^E or n_D^E ; x_i and x_j the mole fractions of the components i and j, and a_k the polynomial coefficients. The method of least squares has been used to determine the values of the coefficients.

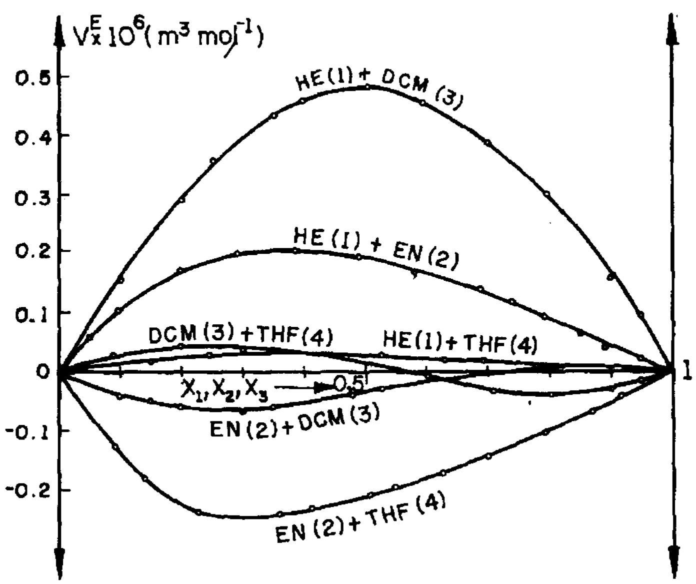

FIGURE 1. Experimental values of V^E at 298.15 K. Continuous curves are calculated with equation 5 using the coefficients of Table 2.

In each case, the optimum number of coefficients has been ascertained from an examination of the variation of the standard error of estimate

$$\sigma = \left[\sum (X_{obs}^E - X_{cal}^E)^2 / (n_{obs} - n)\right]^{1/2} \qquad [VI]$$

where n_{obs} is the observed experimental results and n the number of parameters necessary to calculate x_{cal}^E. The values adopted for the coefficients and standard error of estimate associated with the use of equation VI are summarized in Table 2. Figures 1, 2 and 3 show the experimental values for the six binary systems.

TABLE 2. Coefficients a_k from equation [V] and standard deviations for the binary systems at 298.15 K

Systems	a_0	a_1	a_2	a_3	a_4	σ
			$V^E \times 10^3$(kg m^{-3} mol^{-1})			
HE(1)+EN(2)	0.77419	-0.39025	0.15884	-0.08105	0.22976	3×10^{-3}
HE(1)+DCM(3)	1.93148	-0.10038	-0.58252	0.30740	0.53022	3×10^{-3}
HE(1)+THF(4)	0.11280	-0.09130	0.00338	0.04194	-0.02595	1×10^{-3}
EN(2)+DCM(3)	-0.13828	0.32532	-0.14651	0.00268	0.02211	2×10^{-3}
EN(2)+THF(4)	-0.84025	0.63122	-0.74114	-0.07811	0.57113	2×10^{-3}
DCM(3)+THF(4)	0.05575	-0.40898	-0.21286	0.04548	0.14401	2×10^{-3}
			η^E (mPa s)			
HE(1)+EN(2)	-0.24033	-0.48761	-0.90864	-1.05580	-0.50175	6×10^{-3}
HE(1)+DCM(3)	-0.07170	0.50310	0.99346	0.16525	-0.98669	2×10^{-3}
HE(1)+THF(4)	0.11280	-0.09130	0.00338	0.04194	-0.02595	2×10^{-3}
EN(2)+DCM(3)	0.09880	-0.01636	0.00136	—	—	4×10^{-4}
EN(2)+THF(4)	-0.04517	0.01086	-0.01550	—	—	8×10^{-4}
DCM(3)+THF(4)	0.10822	0.00240	-0.08415	0.06722	0.21281	3×10^{-4}
			n_D^E			
HE(1)+EN(2)	0.06369	-0.00434	-0.02650	0.04585	0.04492	2×10^{-3}
HE(1)+DCM(3)	-0.01091	0.00710	-0.00300	0.00425	—	6×10^{-5}
HE(1)+THF(4)	0.00560	-0.00073	0.00046	0.00090	0.00194	3×10^{-5}
EN(2)+DCM(3)	0.01596	-3.6×10^{-6}	-0.00307	—	—	1×10^{-4}
EN(2)+THF(4)	0.03001	0.00530	0.00191	-0.00208	0.01522	1×10^{-4}
DCM(3)+THF(4)	-0.00456	-0.00258	0.00129	0.00233	—	4×10^{-5}

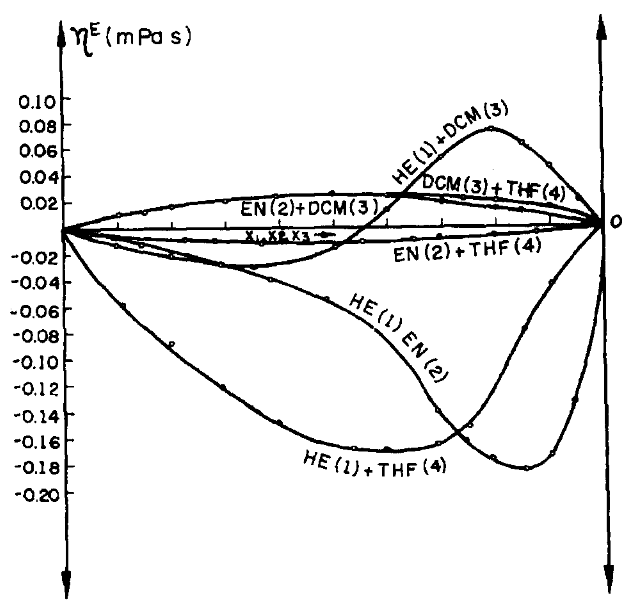

FIGURE 2. Experimental values of η^E at 298.15 K. Continuous curves are calculated with equation [V] using coefficients of Table 2.

Excess molar volumes excess viscosities and excess refraction indices with equations II, III and IV are extended to the four components of the mixture. The experimental values of the quaternary system are obtained by adding the second binary mixture to the first, in such a way that the relation between mole fractions is maintained constant. These values are showed in Table 3, Table 4 and Table 5 with the excess properties defined by equations II, III, and IV extended to a mixture of four components.

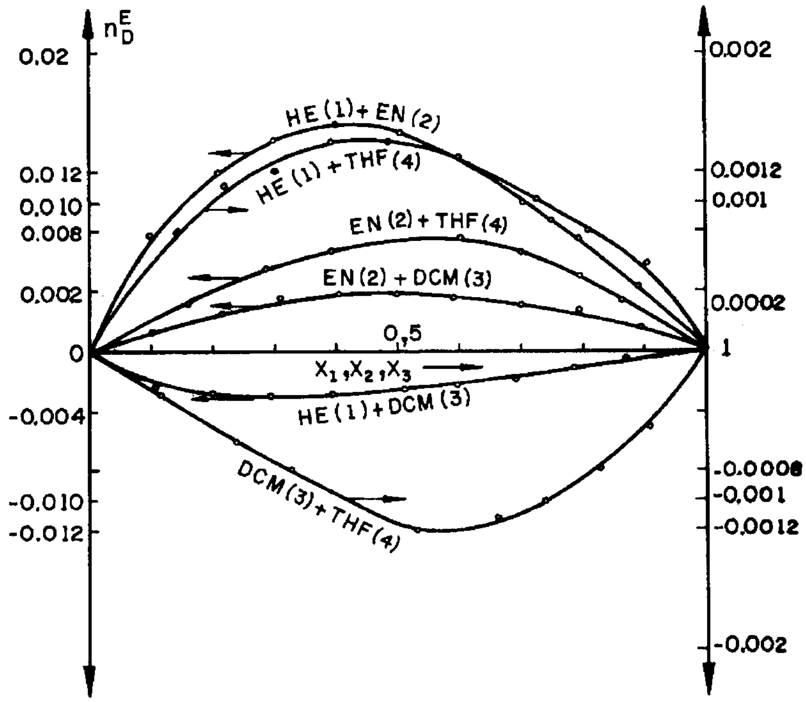

FIGURE 3. Experimental values of n_D^E at 298.15 K. Continuous curves are calculated with equation 5 using the coefficients of Table 2.

If interactions in a quaternary system i+j+k+l are assumed to be closely dependent on the interaction of the constituents i+j, i+k, i+l, j+k, j+l and k+l mixtures, it should be possible to evaluate thermodynamic excess properties for quaternary systems of non-electrolytes, by knowing the corresponding functions for the six binary mixtures.

From the different expressions existing in the literature for predicting the excess molar volumes or viscosities for a ternary system, we have taken[3] the following expression applied to a quaternary one.

$$V_{1234}^{E} = V_{12*}^{E} + V_{13*}^{E} + V_{14*}^{E} + V_{23*}^{E} + V_{24*}^{E} + V_{34*}^{E} \quad \text{[VII]}$$

where V_{12*}^{E}, V_{13*}^{E}, V_{14*}^{E}, V_{23*}^{E}, V_{24*}^{E} and V_{34*}^{E} represent the excess molar volumes calculated with equation II where x_1, x_2, x_3 and x_4 are the mole fractions of the quaternary system by using the coefficients of Table 2. Kohler[13] proposed an equation for a ternary system, which extended to a quaternary system, results:

$$V_{1234}^{E} = (x_1 + x_2)^2 V_{12}^{E} + (x_1 + x_3)^2 V_{13}^{E} + (x_1 + x_4)^2 V_{14}^{E} + (x_2 + x_3)^2 V_{23}^{E} + (x_2 + x_4)^2 V_{24}^{E} + (x_3 + x_4) V_{34}^{E} \quad \text{[VIII]}$$

TABLE 3. Densities ρ and excess molar volumes V^E_{1234} for n-hexanol (1) + ethanenitrile (2) + dichloromethane (3)+tetrahydrofurane(4) system at 298.15 K.

x_1	x_2	x_3	$\rho x10^3 (kg\ m^{-3})$	V^E_{1234} x103(kg m^{-3})
$x_1 / x_2 = 0.0947$; $x_3 / x_4 = 0.1010$				
0.0000	0.0000	0.0917	0.91423	0.025
0.0082	0.0862	0.0831	0.90580	-0.052
0.0174	0.1837	0.0733	0.89554	-0.126
0.0266	0.2808	0.0635	0.88388	-0.130
0.0443	0.4676	0.0448	0.85873	-0.100
0.0608	0.6424	0.0272	0.83188	-0.041
0.0733	0.7745	0.0140	0.80929	0.009
0.0865	0.9135	0.0000	0.78258	0.093
$x_1 / x_2 = 0.2538$; $x_3 / x_4 = 0.2968$				
0.0000	0.0000	0.2289	0.96429	0.045
0.0215	0.0845	0.2046	0.95108	-0.198
0.0427	0.1681	0.1806	0.93467	-0.205
0.0621	0.2448	0.1586	0.91859	-0.161
0.0840	0.3312	0.1338	0.90018	-0.128
0.1034	0.4074	0.1120	0.88341	-0.092
0.1243	0.4899	0.0883	0.86457	-0.040
0.1633	0.6434	0.0422	0.82734	-0.052
0.1834	0.7225	0.0215	0.80838	0.114
0.2024	0.7976	0.0000	0.78920	0.170
$x_1 / x_2 = 0.9736$; $x_3 / x_4 = 0.9996$				
0.0000	0.0000	0.4999	1.73444	0.125
0.0442	0.0454	0.4551	1.04524	-0.016
0.1028	0.1056	0.3957	1.00796	0.036
0.1514	0.1555	0.3465	0.97862	0.065
0.2015	0.2069	0.2957	0.94947	0.102
0.2483	0.2551	0.2482	0.92330	0.133
0.3029	0.3112	0.1929	0.89413	0.158
0.3527	0.3623	0.1425	0.86861	0.179
0.4418	0.4538	0.0522	0.82539	0.198
0.4933	0.5067	0.0000	0.80174	0.200
$x_1 / x_2 = 3.0000$; $x_3 / x_4 = 2.8835$				
0.0000	0.0000	0.7425	1.18435	-0.030
0.0752	0.0251	0.6680	1.12671	0.126
0.1477	0.0492	0.5963	1.07783	0.208
0.2315	0.0772	0.5133	1.02737	0.271
0.2683	0.0895	0.4768	1.00710	0.278
0.3826	0.1275	0.3637	0.95015	0.263
0.4625	0.1542	0.2846	0.91469	0.239
0.5243	0.1748	0.2234	0.88936	0.216
0.5915	0.1972	0.1569	0.86362	0.193
0.6444	0.2148	0.1045	0.84458	0.172
0.7500	0.2500	0.0000	0.80959	0.110

x_1	x_2	x_3	$\rho x10^3 (kg\ m^{-3})$	$V^E_{1234}\ x103 (kg\ m^{-3})$
$x_1 / x_2 = 8.7943$; $x_3 / x_4 = 9.0806$				
0.0000	0.0000	0.9008	1.26404	-0.130
0.0915	0.0104	0.8090	1.18348	-0.131
0.1800	0.0205	0.7202	1.11875	-0.108
0.2645	0.0301	0.6355	1.06548	-0.101
0.3537	0.0402	0.5459	1.01665	-0.020
0.4520	0.0514	0.4473	0.96952	0.049
0.5238	0.0596	0.3753	0.93896	0.130
0.6227	0.0708	0.2760	0.90040	0.250
0.7066	0.0804	0.1919	0.87110	0.356
0.7923	0.0901	0.1060	0.84374	0.528
0.8979	0.1021	0.0000	0.81305	0.160
$x_1/x_3 = 0.1077$; $x_2 /x_4 = 0.1131$				
0.0000	0.1016	0.0000	0.87673	-0.130
0.0095	0.0917	0.0880	0.90800	-0.131
0.0178	0.0829	0.1657	0.93589	-0.108
0.0273	0.0730	0.2538	0.96835	-0.101
0.0381	0.0618	0.3534	1.00465	-0.020
0.0479	0.0515	0.4452	1.03941	0.049
0.0569	0.0421	0.5289	1.07123	0.130
0.0673	0.0312	0.6253	1.10822	0.250
0.0779	0.0202	0.7273	1.14706	0.356
0.0879	0.0098	0.8159	1.18320	0.528
0.0972	0.0000	0.9028	1.22675	0.160
$x_1 / x_3 = 0.3296$; $x_2 / x_4 = 0.3346$				
0.0000	0.2507	0.0000	0.86653	-0.245
0.0236	0.2268	0.0716	0.89085	-0.100
0.0461	0.2041	0.1398	0.91376	0.026
0.0700	0.1799	0.2124	0.93793	0.148
0.0944	0.1553	0.2863	0.96219	0.266
0.1208	0.1285	0.3665	0.98875	0.343
0.1441	0.1049	0.4373	1.01198	0.401
0.1705	0.0783	0.5172	1.03811	0.441
0.1961	0.0524	0.5494	1.06326	0.474
0.2219	0.0263	0.6733	1.08914	0.444
0.2479	0.0000	0.7521	1.11569	0.350
$x_1 / x_3 = 0.9968$; $x_2 / x_4 = 1.0152$				
0.0000	0.5038	0.0000	0.84322	-0.210
0.0361	0.4673	0.0362	0.85637	-0.112
0.0905	0.4125	0.0908	0.87457	0.050
0.1467	0.3557	0.1472	0.89234	0.170
0.1908	0.3113	0.1914	0.90529	0.258
0.2388	0.2628	0.2396	0.91879	0.328
0.2924	0.2087	0.2953	0.93319	0.370
0.3452	0.1554	0.3463	0.94632	0.421
0.3749	0.1255	0.3761	0.95342	0.439
0.4516	0.0480	0.4531	0.97064	0.483
0.4992	0.0000	0.5008	0.98083	0.479

(Cont.)

(Table 3, cont.)

x_1	x_2	x_3	$\rho x10^3 (kg\ m^{-3})$	$V^E_{1234}\ x103(kg\ m^{-3})$
$x_1 / x_3 = 2.9562$; $x_3 / x_4 = 2.97796$				
0.0000	0.7487	0.0000	0.81458	-0.125
0.0632	0.6834	0.0214	0.82269	0.100
0.1400	0.6084	0.0474	0.83291	0.226
0.2100	0.5283	0.0710	0.84081	0.352
0.2748	0.4734	0.0930	0.84794	0.411
0.3457	0.4023	0.1169	0.85522	0.427
0.4282	0.3196	0.1449	0.86311	0.433
0.5097	0.2380	0.1724	0.86994	0.430
0.5965	0.1510	0.2018	0.87653	0.416
0.6801	0.0673	0.2301	0.88230	0.388
0.7472	0.0000	0.2528	0.88665	0.350
$x_1 / x_3 = 8.6712$; $x_2 / x_4 = 9.1523$				
0.0000	0.9015	0.0000	0.79276	-0.050
0.0674	0.8338	0.0078	0.79899	0.048
0.1512	0.7495	0.0174	0.80545	0.170
0.2294	0.6708	0.0265	0.81069	0.272
0.3035	0.5964	0.0350	0.81549	0.311
0.3864	0.5130	0.0446	0.82031	0.343
0.4855	0.4134	0.0560	0.82539	0.362
0.5861	0.3122	0.0676	0.83004	0.354
0.6965	0.2012	0.0804	0.83466	0.317
0.8061	0.0909	0.0930	0.83887	0.244
0.9866	0.0000	0.1034	0.84210	0.016
$x_1 / x_4 = 0.1086$; $x_2 / x_3 = 0.1158$				
0.0000	0.1038	0.8962	1.27023	-0.060
0.0078	0.0956	0.8248	1.22735	0.020
0.0140	0.0890	0.7679	1.19548	0.035
0.0212	0.0813	0.7019	1.16059	0.030
0.0291	0.0730	0.6300	1.12478	0.004
0.0383	0.0633	0.5462	1.08547	-0.038
0.0480	0.0530	0.4572	1.04687	-0.133
0.0583	0.0421	0.3633	1.00867	-0.248
0.0703	0.0294	0.2535	0.96596	-0.316
0.0839	0.0149	0.1287	0.91946	-0.270
0.0980	0.0000	0.0000	0.87272	0.015
$x_1 / x_4 = 0.3383$; $x_2 / x_3 = 0.3308$				
0.0000	0.2486	0.0000	1.20234	-0.060
0.0176	0.2312	0.0522	1.16605	0.027
0.0320	0.2171	0.0945	1.13918	0.050
0.0489	0.2005	0.1446	1.10968	0.052
0.0678	0.1819	0.2003	1.07936	0.026
0.0903	0.1598	0.2669	1.04664	-0.075
0.1149	0.1356	0.3395	1.01293	-0.135
0.1415	0.1094	0.4183	0.97912	-0.190
0.1738	0.0777	0.5136	0.94116	-0.210
0.2119	0.0403	0.6260	0.90009	-0.165
0.2528	0.0000	0.7472	0.85925	0.025

x_1	x_2	x_3	$\rho x10^3 (kg\ m^{-3})$	$V^E_{1234}\ x103 (kg\ m^{-3})$
$x_1 / x_4 = 1.0255$; $x_2 / x_3 = 1.0284$				
0.0000	0.5070	0.4930	1.07011	-0.030
0.0277	0.4793	0.4659	1.04865	-0.022
0.0509	0.4560	0.4433	1.03195	-0.010
0.0792	0.4277	0.4158	1.01324	-0.009
0.1117	0.3952	0.3842	0.99347	-0.010
0.1521	0.3547	0.3449	0.97118	-0.016
0.1982	0.3085	0.2999	0.94826	-0.024
0.2510	0.2557	0.2486	0.92493	-0.031
0.3187	0.1878	0.1826	0.89862	-0.037
0.4049	0.1015	0.0987	0.86996	-0.041
0.5063	0.0000	0.0000	0.84112	0.025
$x_1 / x_4 = 2.9936$; $x_2 / x_3 = 2.9620$				
0.0000	0.7476	0.2524	0.93422	0.000
0.0752	0.6726	0.2271	0.91429	0.001
0.1559	0.5921	0.1999	0.89677	-0.001
0.2295	0.5187	0.1752	0.88346	-0.004
0.2994	0.4490	0.1516	0.87258	-0.009
0.3785	0.3721	0.1256	0.86220	-0.032
0.4526	0.2962	0.1000	0.85346	-0.034
0.5207	0.2283	0.0771	0.84637	-0.032
0.5938	0.1554	0.0525	0.83957	-0.028
0.6709	0.0784	0.0265	0.83313	-0.018
0.7496	0.0000	0.0000	0.82708	-0.015

TABLE 4. Molar fractions x_i, viscosities coefficients and excess viscosities for n-hexanol(1) + ethanenitrile(2) + dichloromethane(3)+tyetrahydrofurane(4) system at 298.15 K.

x_1	x_2	x_3	η (mPa s)	η^E_{1234} (mPa s)
$x_1/x_2 = 0.1096$; $x_3 /x_4 = 0.1376$				
0.0000	0.0000	0.1210	0.475	0.010
0.0076	0.0690	0.1117	0.470	-0.007
0.0335	0.3059	0.0799	0.442	-0.015
0.0537	0.4898	0.0552	0.437	-0.016
0.0762	0.6950	0.0277	0.432	-0.016
0.0945	0.8627	0.0052	0.431	-0.013
0.0988	0.9012	0.0000	0.431	-0.012
$x_1 /x_2 = 0.1794$; $x_3 / x_4 = 0.3350$				
0.0000	0.0000	0.2509	0.475	0.019
0.0105	0.0585	0.2336	0.477	0.018
0.0425	0.2368	0.1809	0.468	-0.002
0.0835	0.4657	0.1131	0.469	-0.015

(Cont.)

(Table 4, cont.)

x_1	x_2	x_3	η (mPa s)	η^E_{1234} (mPa s)
0.1162	0.6479	0.0592	0.477	-0.019
0.1451	0.8088	0.0116	0.487	-0.019
0.1521	0.8479	0.0000	0.493	-0.018
$x_1 / x_2 = 0.4214$; $x_3 / x_4 = 0.8625$				
0.0000	0.0000	0.4631	0.469	0.028
0.0147	0.0349	0.4401	0.485	0.032
0.0815	0.1933	0.3358	0.522	0.014
0.1474	0.3498	0.2328	0.568	-0.002
0.2137	0.5071	0.1293	0.626	-0.014
0.2813	0.6676	0.0237	0.694	-0.026
0.2965	0.7035	0.0000	0.710	-0.028
$x_1 / x_2 = 0.9917$; $x_3 / x_4 = 1.8798$				
0.0000	0.0000	0.6528	0.450	0.022
0.0239	0.0241	0.6205	0.476	0.025
0.1179	0.1188	0.4975	0.570	0.018
0.2263	0.2282	0.3555	0.695	-0.001
0.3406	0.3435	0.2059	0.872	-0.017
0.4630	0.4669	0.0457	1.097	-0.058
0.4979	0.5021	0.0000	1.189	-0.056
$x_1 / x_2 = 2.4747$; $x_3 / x_4 = 4.9325$				
0.0000	0.0000	0.8314	0.435	0.018
0.0350	0.0141	0.7906	0.471	0.019
0.1407	0.0569	0.6672	0.587	0.010
0.2791	0.1128	0.5056	0.790	-0.005
0.4442	0.1795	0.3129	1.114	-0.051
0.6523	0.2636	0.0699	1.760	-0.127
0.7122	0.2878	0.0000	2.018	-0.150
$x_1 / x_2 = 4.9123$; $x_3 / x_4 = 6.1381$				
0.0000	0.0000	0.8599	0.431	0.016
0.0258	0.0053	0.8332	0.461	0.020
0.1639	0.0334	0.6903	0.623	0.012
0.2985	0.0608	0.5509	0.835	-0.004
0.4766	0.0970	0.3667	1.309	-0.029
0.7099	0.1445	0.1252	2.115	-0.100
0.8309	0.1691	0.0000	2.761	-0.186
$x_1 / x_3 = 0.1360$; $x_2 / x_4 = 0.4167$				
0.0000	0.2941	0.0000	0.420	-0.010
0.0071	0.2768	0.0520	0.445	0.008
0.0332	0.2126	0.2441	0.475	0.015
0.0604	0.1457	0.4442	0.513	0.028
0.0867	0.0812	0.6374	0.495	-0.014
0.1112	0.0208	0.8181	0.469	-0.050
0.1197	0.0000	0.8803	0.538	-0.014

x_1	x_2	x_3	η (mPa s)	η^E_{1234} (mPa s)
$x_1 / x_3 = 0.2421$; $x_2 / x_4 = 0.7759$				
0.0000	0.4369	0.0000	0.401	-0.011
0.0103	0.4138	0.0426	0.415	-0.007
0.0499	0.3250	0.2063	0.470	0.007
0.0932	0.2280	0.3849	0.525	0.013
0.1357	0.1328	0.5604	0.573	0.007
0.1805	0.0323	0.5604	0.621	-0.008
0.1949	0.0000	0.7456	0.631	-0.020
$x_1 / x_3 = 0.5010$; $x_2 / x_4 = 1.5226$				
0.0000	0.6036	0.0000	0.378	-0.011
0.0169	0.5731	0.0336	0.402	-0.005
0.0776	0.4633	0.1549	0.471	-0.004
0.1447	0.3419	0.2889	0.560	-0.003
0.2239	0.1987	0.4469	0.686	-0.003
0.3040	0.6538	0.6069	0.840	-0.004
0.3338	0.0000	0.6662	0.880	-0.030
$x_1 / x_3 = 0.9607$; $x_2 / x_4 = 3.0257$				
0.0000	0.7516	0.0000	0.364	-0.008
0.0219	0.7180	0.0228	0.387	-0.006
0.1008	0.5970	0.1049	0.460	-0.023
0.1869	0.6469	0.1946	0.592	-0.012
0.2957	0.2981	0.3077	0.801	-0.001
0.4368	0.0815	0.4547	1.112	0.015
0.4899	0.0000	0.5100	1.313	-0.016
$x_1 / x_3 = 2.5435$; $x_3 / x_4 = 7.8298$				
0.0000	0.8867	0.0000	0.352	-0.004
0.0174	0.8653	0.0068	0.367	-0.005
0.1176	0.7415	0.0462	0.453	-0.030
0.2447	0.5845	0.0962	0.615	-0.058
0.4032	0.3887	0.1585	0.892	-0.090
0.6157	0.1269	0.2418	1.893	0.127
0.7178	0.0000	0.2822	2.431	0.060
$x_1 / x_3 = 6.1670$; $x_2 / x_4 = 19.3974$				
0.0000	0.9510	0.0000	0.346	-0.002
0.0210	0.9278	0.0034	0.364	-0.004
0.1238	0.8141	0.0201	0.456	-0.025
0.2715	0.6509	0.0440	0.667	-0.038
0.4864	0.4134	0.0789	1.177	-0.056
0.7318	0.1422	0.1187	2.272	-0.060
0.8605	0.0000	0.1395	3.328	-0.070

TABLE 5. Molar fractions x_i, refractive indices n_D and excess refractive indices n^E_{D1234} for n-hexanol(1) + ethanenitrile (2) + dichloromethane (3) + tetrahydrofurane (4) system at 298.15 K.

x_1	x_2	x_3	n_D	n^E_{D1234}
$x_1 / x_2 = 0.0502$; $x_3 / x_4 = 0.15175$				
0.0000	0.0000	0.1361	1.40398	-0.0035
0.0122	0.2436	0.1013	1.39558	0.0040
0.0277	0.4528	0.0714	1.38414	0.0063
0.0281	0.5605	0.0560	1.37751	0.0067
0.0325	0.6484	0.0434	1.37157	0.0065
0.0405	0.8075	0.0207	1.36042	0.0058
0.0478	0.9522	0.0000	1.34912	0.0040
$x_1 / x_2 = 0.1073$; $x_3 / x_4 = 0.1362$				
0.0000	0.0000	0.1199	1.40688	-0.0003
0.0242	0.2257	0.0900	1.39745	0.0048
0.0454	0.4234	0.0637	1.38733	0.0075
0.0564	0.5255	0.0505	1.38119	0.0080
0.0648	0.6034	0.0398	1.37624	0.0078
0.0969	0.9031	0.0000	1.35576	0.0070
$x_1 / x_2 = 0.1529$; $x_3 / x_4 = 0.3211$				
0.0000	0.0000	0.2431	1.40858	-0,0006
0.0320	0.2092	0.1847	1.39803	0.0034
0.0566	0.3705	0.1393	1.38996	0.0055
0.0695	0.4545	0.1160	1.38552	0.0066
0.0946	0.6186	0.0697	1.37608	0.0085
0.1088	0.7117	0.0436	1.37019	0.0086
0.1326	0.8674	0.0000	1.36042	0.0090
$x_1 / x_2 = 0.2101$; $x_3 / x_4 = 0.3886$				
0.0000	0.0000	0.2799	1.40941	-0.0003
0.0391	0.1863	0.2168	1.39999	0.0027
0.0740	0.3522	0.1606	1.39161	0.0054
0.0972	0.4629	0.1231	1.38554	0.0068
0.1099	0.5229	0.1028	1.38220	0.0074
0.1432	0.6816	0.0490	1.37316	0.0089
0.8264	0.1736	0.0000	1.36515	0.0107
$x_1 / x_2 = 0.4181$; $x_3 / x_4 = 0.8615$				
0.0000	0.0000	0.4628	1.41156	-0.0011
0.0596	0.1426	0.3692	1.40467	0.0020
0.1163	0.2781	0.2803	1.39833	0.0051
0.1824	0.4364	0.1764	1.39045	0.0082
0.2343	0.5603	0.0951	1.38411	0.0105
0.2948	0.7052	0.0000	1.37746	0.0140

x_1	x_2	x_3	n_D	n^E_{D1234}
$x_1 / x_2 = 2.2086$; $x_3 / x_4 = 2.9578$				
0.0000	0.0000	0.7473	1.41616	-0.0010
0.1440	0.0652	0.5910	1.40954	-0.0025
0.2110	0.0956	0.5182	1.40643	-0.0032
0.2821	0.1277	0.4411	1.40403	-0.0031
0.3513	0.1590	0.3660	1.40217	-0.0025
0.5035	0.2280	0.2007	1.39826	-0.0010
0.6883	0.3117	0.0000	1.39268	0.0108
$x_1 / x_2 = 3.2509$; $x_3 / x_4 = 10.3058$				
0.0000	0.0000	0.9155	1.41928	-0.0048
0.1048	0.0322	0.7866	1.41537	-0.0015
0,2257	0.0694	0.6425	1.41282	-0.0006
0.2970	0.0913	0.5576	1.41204	0.0008
0.5056	0.1555	0.3089	1.40893	0.0033
0.6502	0.1999	0.1368	1.40785	0.0060
0.7648	0.2352	0.0000	1.40436	0.0083
$x_1 / x_2 = 14.6947$; $x_3 / x_4 = 0.1534$				
0.0000	0.0000	0.1330	1.40383	-0.0036
0.1318	0.0089	0.1143	1.40811	0.0001
0.2914	0.0198	0.0916	1.40957	0.0010
0.3711	0.0253	0.0803	1.40990	0.0016
0.4741	0.0323	0.0656	1.41108	0.0018
0.6746	0.0459	0.0372	1.41215	0.0021
0.9363	0.0637	0.0000	1.41349	0.0024
$x_1 /x_3 = 0.0191$; $x_2 / x_4 = 0.0522$				
0.0000	0.0496	0.0000	1.40317	0.0010
0.0047	0.0373	0.2430	1.40650	-0.0003
0.0086	0.0272	0.4435	1.40948	-0.0012
0.0098	0.0240	0.5065	1.41052	-0.0014
0.0129	0.0161	0.6629	1.41333	-0.0016
0.0153	0.0097	0.7898	1.41599	-0.0014
0.0187	0.0000	0.9813	1.42086	-0.0002
$x_1 / x_3 = 0.1306$; $x_2 / x_4 = 0.3898$				
0.0000	0.2805	0.0000	1.39324	0.0058
0.0266	0.2158	0.2040	1.39858	0.0035
0.0479	0.1642	0.3667	1.40340	0.0022
0.0616	0.1309	0.4718	1.40658	0.0015
0.0699	0.1108	0.5350	1.40833	0.0009
0.0877	0.0674	0.6720	1.41227	-0.0003
0.1155	0.0000	0.8845	1.41834	-0.0022

(Cont.)

(Table 5, cont.)

x_1	x_2	x_3	n_D	n^E_{D1234}
$x_1 / x_3 = 0.6622$; $x_2 / x_4 = 1.2620$				
0.0000	0.5579	0.0000	1.37676	0.0076
0.0569	0.4783	0.0859	1.37561	-0.0012
0.1092	0.4050	0.1648	1.37480	-0.0085
0.1496	0.3485	0.2258	1.37437	-0.0138
0.1902	0.2915	0.2873	1.37397	-0.0193
0.2584	0.1960	0.3903	1.37332	-0.0284
0.3984	0.0000	0.6016	1.41613	-0.0029
$x_1 / x_3 = 1.0350$; $x_2 / x_4 = 3.1355$				
0.0000	0.7582	0.0000	1.36279	0.0058
0.0683	0.6564	0.0660	1.37273	0.0075
0.1514	0.5325	0.1463	1.38537	0.0101
0.1951	0.4674	0.1884	1.38907	0.0085
0.2307	0.4143	0.2229	1.39283	0.0080
0.3616	0.2191	0.3494	1.40530	0.0046
0.5086	0.0000	0.4914	1.41564	-0.0028
$x_1 / x_3 = 4.5969$; $x_2 / x_4 = 14.3601$				
0.0000	0.9349	0.0000	1.34752	0.0018
0.0890	0.8335	0.0194	1.36101	0.0076
0.2005	0.7067	0.0436	1.37508	0.0120
0.2667	0.6313	0.0580	1.38152	0.0127
0.3428	0.5447	0.0746	1.38831	0.0129
0.5349	0.3260	0.1164	1.40192	0.0099
0.8213	0.0000	0.1787	1.41557	-0.0010
$x_1 / x_4 = 0.5084$; $x_2 / x_3 = 1.0014$				
0.0000	0.5004	0.4996	1.38523	0.0039
0.0462	0.4317	0.4312	1.38992	0.0048
0.0963	0.3574	0.3569	1.39450	0.0053
0.1340	0.3014	0.3010	1.39763	0.0053
0.1569	0.2674	0.2671	1.39926	0.0051
0.2486	0.1313	0.1311	1.40505	0.0034
0.3371	0.0000	0.0000	1.41007	0.0012
$x_1 / x_4 = 1.2228$; $x_2 / x_3 = 2.4678$				
0.0000	0.7116	0.2884	1.36732	0.0028
0.0779	0.6109	0.2475	1.37758	0.0065
0.1482	0.5199	0.2107	1.38498	0.0079
0.1924	0.4627	0.1875	1.38919	0.0084
0.2467	0.3925	0.1591	1.39341	0.0080
0.3666	0.2374	0.0962	1.40284	0.0072
0.5501	0.0000	0.0000	1.41240	0.0013
$x_1 / x_4 = 5.7303$; $x_2 / x_3 = 10.9802$				
0.0000	0.9165	0.0835	1.34942	0.0012
0.0936	0.8158	0.0743	1.37047	0.0150
0.2530	0.6442	0.0587	1.38184	0.0140
0.2775	0.6178	0.0563	1.38274	0.0130
0.3342	0.5568	0.0507	1.38414	0.0100
0.5276	0.3485	0.0317	1.39301	0.0040
0.8514	0.0000	0.0000	1.41486	0.0006

in which V_{ij} represents the excess molar volumes of the binary mixtures at compositions x_i^0, x_j^0, such that:

$$x_i^0 = 1 - x_j^0 = x_i / (x_i + x_j) \qquad \text{[IX]}$$

for the six binary systems. Jacob and Fitzner [14] suggested an equation for estimating properties of ternary systems based on binary data. For a quaternary system, it takes the following form:

$$V_{1234}^E = \frac{x_1 x_2 V_{12}^E}{(x_1 + x_3/2)(x_2 + x_4/2)} + \frac{x_1 x_3 V_{13}^E}{(x_1 + x_2/2)(x_3 + x_4/2)} + \frac{x_1 x_4 V_{14}^E}{(x_1 + x_2/2)(x_4 + x_3/2)} + \frac{x_2 x_3 V_{23}^E}{(x_2 + x_1/2)(x_3 + x_4/2)} + \frac{x_2 x_4 V_{24}^E}{(x_2 + x_1/2)(x_4 + x_3/2)} + \frac{x_3 x_4 V_{34}^E}{(x_3 + x_1/2)(x_4 + x_2/2)} \qquad \text{[X]}$$

Cibulka [15] proposed an equation, for a ternary system, which can be extended to a quaternary system as follows:

$$V_{1234}^E = V_{12*}^E + V_{13*}^E + {}_{14*}^E + V_{23*}^E + V_{24*}^E + V_{34*}^E + x_1 x_2 x_3 x_4 (A + Bx_1 + Cx_2 + Dx_3) \qquad \text{[XI]}$$

where A, B, C and D are parameters calculated from experimental data.

Finally, Nagata and Tamura [16] proposed the following equation, which for a quaternary system, can be expressed as:

$$V_{1234}^E = V_{12*}^E + V_{13*}^E + V_{14*}^E + V_{23*}^E + V_{24*}^E + V_{34*}^E + x_1 x_2 x_3 x_4 \Delta_{1234} \qquad \text{[XII]}$$

where Δ_{1234} is a correction parameter used to satisfy equation XII. These two equations introduce corrected parameters and modifications of the Radojkovic's et al. equation. Table 6 shows the mean deviation calculated using the following expression:

$$MD = \left[\frac{\Sigma (V_{obs}^E - V_{cal}^E)^2}{n} \right]^{1/2} \qquad \text{[XIII]}$$

TABLE 6. Mean deviations for the n-hexanol (1) + ethanenitrile (2) + dichloromethane (3) + tetrahydrofurane (4) system at 298.15 K.

Equation	*MD in* V_{1234}^E *x*10^{-6}*(*m^3 *mol*$^{-1}$*)*	*MD in* η_{1234}^E *(mPa s)*
(VII)	0.152	0.027
(VIII)	0.153	0.032
(IX)	0.149	0.032
(X)	0.157	0.026
(XI)	0.180	0.027

The results obtained with these two equations, do not differ in a large extent from the other equations. The same calculation was made to evaluate η^E. The parameters from Cibulka's equation for V_{1234}^E are A = 82.44; B = 183.03; C = 28.85 and D = -75.80 and Δ_{1234} = 24.86 $cm^3.mol^{-1}$ from Nagata and Tamura equation. The parameters for η_{1234}^E are A = -2.65; B = -0.40; C = -14.80 and D = 20.26. The value for Δ_{1234} = -0.167 mPa.s.

Finally, following Shukla [7] we applied Flory's theory to a quaternary system. The values of reduced volumes, reduced temperatures and characteristic pressures for the pure components are obtained with the following equations:

$$\tilde{V}_i = \frac{V_i}{V_i^*} = \left[\frac{1+\frac{4}{3}\alpha_i T}{1+\alpha_i T}\right]^3 \qquad \text{[XIV]}$$

$$\tilde{T}_i = \frac{T_i}{T_i^*} = \frac{\tilde{V}_i^{1/3}}{\tilde{V}_i^{4/3}} \qquad \text{[XV]}$$

$$P_i^* = \frac{\alpha_i T \tilde{V}_i^2}{\kappa_i} \qquad \text{[XVI]}$$

where α_i is the thermal expansion, κ_i the isothermal compressibility for the pure components, V^* is the characteristic volume and T^*, the characteristic temperature. Considering every possibility of two-body interaction and the statistical mechanical concepts of Flory, we have:

$$\tilde{V}^E = \tilde{V} - \tilde{V}^0 = \frac{(\tilde{V}^0)^{7/3}}{\frac{4}{3} - (\tilde{V}^0)^{1/3}}(\tilde{T} - \tilde{T}^0) \qquad \text{[XVII]}$$

where $\tilde{T}^0$ is the ideal reduced temperature corresponding to the ideal reduced volume $\tilde{V}^0$:

$$\tilde{T}^0 = \frac{(\tilde{V}^0)^{1/3} - 1}{(\tilde{V}^0)^{4/3}} \qquad \text{[XVIII]}$$

$$\tilde{V}^0 = \sum \psi_i \tilde{V}_{ie} \qquad \text{[XIX]}$$

where ψ is the segment fraction defined as:

$$\psi_{i1-4} = \frac{x_{i1-4}}{x_i + \sum_{i=1}^{j=4} x_j (V_i^* / V_j^*)} \qquad \text{[XX]}$$

$\tilde{T}$ is the reduced temperature of the mixture, defined as:

$$\tilde{T} = \frac{T}{P^* / \sum_{i=1}^{4} (\psi_i P_i^*) / T_i^*} \qquad \text{[XXI]}$$

The characteristic pressure of the mixture, is given by:

$$P^* = \sum_{i=1}^{4} \psi_i P_i^* - (\psi_1\theta_2 X_{12} + \psi_2\theta_3 X_{23} + \psi_3\theta_4 X_{34} + \psi_4\theta_1 X_{41} + \psi_2\theta_4 X_{24} + \psi_3\theta_1 X_{31} \qquad \text{[XXII]}$$

θ_i is the site fraction given by :

$$\theta_{i1-4} = \frac{\psi_{i1-4}}{\psi_i + \sum_{j=1-4}^{j=4-1} \psi_j (V_i^* / V_j^*)^{1/3}} \qquad \text{[XXIII]}$$

where X_{12}, X_{23}, X_{34}, X_{41}, X_{24} and X_{31} are the interchange parameters assuming two body collisions. Here $X_{ij} = X_{ji}$ can be calculated by application of the Prigogine-Flory-Patterson theory [17] to the binary systems. They are X_{12} = -6.4065x10^6 J.m^{-3}; X_{13} = 2.9020x10^6 J.m^{-3} ; X_{14} = 7.9747x10^6 J.m^{-3} ;X_{23} = -5.2710x10^6 J m^{-3} ; X_{24} = -37.5760x10^6 J m^{-3} ; X_{34} = -19.7307x10^6 J m^{-3} . Table 7 gives the parameters employed in this theory for the pure components. The mean deviation is 0.18, which means that Flory's theory does not make good predictions for this system.

TABLE 7. Parameters for the pure components at 298.15 K.

Substance	*α/K^{-1}*	*κ_Tx10^6(kPa^{-1})*	$\tilde{V}$	*V^*x10^3(m^3 mol^{-1})*	*P^*(J cm^{-3})*	$\tilde{T}$	T^*
HE(1)	0.000878[a]	0.824[a]	1.2221	102.5663	474.5	0.05292	5633.98
EN(2)	0.001368[a]	1.070[a]	1.3186	40.0801	662.8	0.06679	4463.99
DCM(3)	0.001391[a]	1.026[a]	1.3227	48.7873	707.2	0.06730	4450.00
THF(4)	0.001138[a]	1.188[b]	1.2753	64.0701	464.5	0.06105	4883.70

[a]Ref.(19); [b]Ref.(20).

The empirical Grunberg and Nissan [10] equation has been found to be useful for viscosities of binary mixtures. Extended to a quaternary system, it takes the following expression:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3 + x_4 \ln \eta_4 + x_1 x_2 x_3 x_4 \delta \qquad \text{[XXIV]}$$

where δ are the parameters which reflect the non-ideality of the system. The parameter δ has usually been regarded as an appropiate measure of the strength of the interaction between components. Wakefield [8] also applied this equation to quaternary mixture at different temperatures. The value of δ obtained for this system is –2.80 with a mean deviation of 0.041. Besides, it is possible to predict refractive indices of quaternary liquid mixtures]18]. From the different expressions existing in the literature for predicting refractive indices for multicomponents system, we have taken the Lorentz-Lorenz relation, which has the following form:

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\rho}=\left(\frac{n_1^2-1}{n_1^2+2}\right)\frac{W_1}{\rho_1}+\left(\frac{n_2^2-1}{n_2^2+2}\right)\frac{W_2}{\rho_2}+\left(\frac{n_3^2-1}{n_3^2+2}\right)\frac{W_3}{\rho_3}+\left(\frac{n_4^2-1}{n_4^2+2}\right)\frac{W_4}{\rho_4} \qquad \text{[XXV]}$$

where $W_i = x_iM_i / \Sigma x_jM_j$ is the weight fraction. For our system at 298.15 K, the mean deviation defined by equation XXIII is 0.041, which means that the Lorentz-Lorenz equation predicts the refractive indices very well.

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