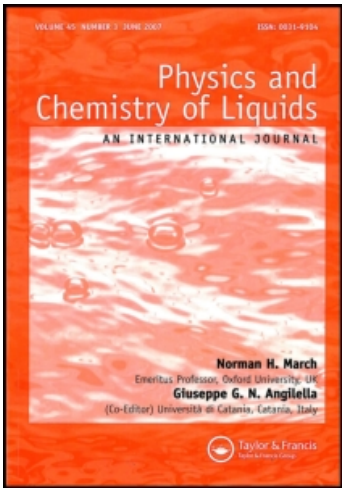

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Temperature Dependence of Changes of Refractive Index in Methyl Acetate, Ethanol and 2-Propanol Mixtures

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TEMPERATURE DEPENDENCE OF CHANGES OF REFRACTIVE INDEX IN METHYL ACETATE, ETHANOL AND 2-PROPANOL MIXTURES

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The refractive indices of the mixtures methyl acetate+ethanol+2-propanol, methyl acetate+ethanol and methyl acetate+2-propanol have been determined experimentally as a function of composition at the temperature range 288.15–308.15 K and atmosphere. Parameters of polynomial equations which represent the composition and temperature dependence of the corresponding derived magnitude are gathered. The applicability of semiempirical equations is analyzed in order to estimate the ternary changes of refractive indices on mixing at these temperatures by means of only binary derived values.

Keywords: Refractive index; derived magnitude; methyl acetate; ethanol; 2-propanol; temperature dependence; estimation

1. INTRODUCTION

Physical properties of liquid mixtures that may have hydroxyl groups and polarizable electron pairs like alkanols, ketones, acetates or amines, depend to a large extent on the interactions by hydrogen bonding and polar interactions. The structure of the molecular chain

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influences the intensity of the interactions in mixture, there being high non-ideality in mixtures with relatively small and non-branching molecules. The studied mixtures forms part of a program to determine thermodynamic, derived and excess properties, as well as phase equilibria data of a series of systems containing common homogeneous azeotropes in chemical industry and alternative entrainers/coentrainers for solvent recovery processes [1–3]. In this paper, we report experimental values of refractive indices of the ternary mixture methyl acetate + ethanol + 2-propanol and the binary mixtures methyl acetate + ethanol and methyl acetate + 2-propanol at the temperature range 288.15–308.15 K and atmosphere. The fitting parameters of polynomial equations which represent the composition/temperature dependence of the corresponding derived property are gathered. The validity of predicting the ternary derived magnitude was examined by different binary contribution equations which consider such contribution to the ternary values in different graphical trends.

2. EXPERIMENTAL

The substances employed were supplied by Merck (Lichrosolv quality). Their molefraction purities were better than 0.995 for methyl acetate and better than 0.998 for the alkanols used, by means of gas-liquid chromatographic test, in accordance with vendor specifications. Values of measured properties were in accordance with which published in open literature as is observed in Table I. Usual purification procedure for chemicals were applied using molecular sieves (4 Å) in order to dehydrate, ultrasonic treatment for degassing solvents and injection of argon in solvents bottles (argon N-55, better than 2 ppmv in water). Manipulation procedure of chemicals, applied techniques and calibration in our laboratory are commented on a previous paper [1]. The refractive indices were measured by an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of ± 0.00001. Thermostation of refractometer was realized by a controller bath PolyScience model 9510, with a temperature stability of $\pm 10^{-2}$ K. Samples preparation was made by weight using a Mettler AE-240 balance with a precision of $\pm 10^{-4}$ g, covering the composition range of the mixtures. The accuracy for both, changes of refractive

TABLE I Comparison of experimental data with literature

	$n_D(298.15\,K)$	
Component	*exptl.*	*lit.*[a]
Methyl acetate	1.35850	1.3589[a] 1.3614[b]
Ethanol	1.35903	1.35941[a] 1.35941[b]
2-Propanol	1.37474	1.3752[a] 1.3752[b]

[a] Ref. [4],
[b] Ref. [5].

indices on mixing and mole fractions, was estimated as better than 10^{-4}.

3. DATA CORRELATION

The refractive indices of binary and ternary mixtures are given in Tables II and III, the Eq. (1) being applied to compute the corresponding derived magnitude:

$$\delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{1}$$

In these equation, n_D is the refractive index in the mixture, n_{Di} is the property of pure components, x_i the molar fraction of component i in the mixture, N is the number of components and δ means the variation of a magnitude. The changes of refractive index on mixing at measurement temperature are enclosed in the same tables. A Redlich-Kister type equation [6] was used to correlate the changes of refractive indices on mixing as a function of temperature for the corresponding binary mixtures, a generalized set of parameters being computed. Some of these data were obtained from literature [7–9], specifically, methyl acetate + ethanol and methyl acetate + 2-propanol data at 298.15 K and ethanol + 2-propanol at the temperature range. The parameters of these binary mixtures are those corresponding to

TABLE II Refractive indices and changes of refractive indices on mixing of the binary mixtures methyl acetate + (ethanol or 2-propanol) at 288.15 and 308.15 K

x_1	n_D (288.15 K)	δn_D (288.15 K)	n_D (308.15 K)	δn_D (308.15 K)
		Methyl acetate(1) + Ethanol(2)		
0.8910	1.36370	−0.00020	1.35306	−0.00034
0.7460	1.36348	−0.00033	1.35280	−0.00082
0.5980	1.36336	−0.00037	1.35282	−0.00101
0.5201	1.36322	−0.00046	1.35292	−0.00103
0.4017	1.36311	−0.00050	1.35320	−0.00093
0.3314	1.36309	−0.00048	1.35336	−0.00087
0.2107	1.36331	−0.00019	1.35370	−0.00071
0.1606	1.36339	−0.00008	1.35385	−0.00063
		Methyl acetate(1) + 2-Propanol(3)		
0.9002	1.36499	−0.00050	1.35424	−0.00070
0.7960	1.36595	−0.00113	1.35506	−0.00165
0.7114	1.36680	−0.00158	1.35591	−0.00224
0.5997	1.36814	−0.00195	1.35745	−0.00260
0.5123	1.36936	−0.00207	1.35896	−0.00258
0.3952	1.37120	−0.00202	1.36122	−0.00231
0.2011	1.37467	−0.00152	1.36511	−0.00173
0.0808	1.37721	−0.00082	1.36806	−0.00082

the fitting equation which is expressed as:

$$\delta Q_{ij} = x_i x_j \sum_{p=0}^{m} A_p (x_i - x_j)^p \tag{2}$$

$$A_p = \sum_{q=0}^{3} B_{pq} T^q \tag{3}$$

where m is the limit of the expansion (Bevington test [10]), B_{pq} are the fitting parameters and T is the temperature expressed by Kelvin degrees. The ternary correlation was realized by means of a modified Cibulka type equation [11] as follows:

$$\delta Q_{123} = \delta Q_{12} + \delta Q_{13} + \delta Q_{23} + x_1 x_2 x_3 (C_0 + C_1 x_1 + C_2 x_2) \tag{4}$$

$$C_i = \sum_{j=0}^{3} D_{ij} T^j \tag{5}$$

where δQ_{12}, δQ_{13} and δQ_{23} are the contributions by the modified Redlich-Kister expression explained above for each binary mixture and D_{ij} are the composition/temperature dependent ternary derived

TABLE III Refractive indices and changes of refractive indices on mixing of methyl acetate(1) + ethanol(2) + 2-propanol(3) at the range 288.15 – 308.15 K

x_1	x_2	n_D (288.15 K)	δn_D (288.15 K)	n_D (298.15 K)	δn_D (298.15 K)	n_D (308.15 K)	δn_D (308.15 K)
0.1092	0.5795	1.36867	0.00028	1.36423	0.00037	1.35949	0.00009
0.6023	0.2375	1.36551	−0.00076	1.36012	−0.00111	1.35506	−0.00126
0.1095	0.2981	1.37290	0.00004	1.36823	−0.00005	1.36365	−0.00011
0.3077	0.3843	1.36804	−0.00041	1.36300	−0.00071	1.35833	−0.00072
0.6361	0.1887	1.36567	−0.00086	1.36037	−0.00108	1.35528	−0.00122
0.1360	0.7252	1.36583	0.00017	1.36115	0.00001	1.35684	0.00016
0.1502	0.2096	1.37343	−0.00021	1.36855	−0.00046	1.36384	−0.00061
0.0474	0.0742	1.37692	−0.00045	1.37262	−0.00018	1.36804	−0.00026
0.2464	0.0748	1.37290	−0.00141	1.36821	−0.00135	1.36323	−0.00167
0.4473	0.0741	1.36924	−0.00200	1.36448	−0.00183	1.35924	−0.00226
0.6636	0.0875	1.36626	−0.00146	1.36099	−0.00160	1.35560	−0.00201
0.8539	0.0558	1.36455	−0.00076	1.35905	−0.00095	1.35400	−0.00086
0.0659	0.2063	1.37496	−0.00002	1.37045	0.00002	1.36602	0.00009
0.2172	0.2137	1.37204	−0.00051	1.36704	−0.00081	1.36225	−0.00099
0.4812	0.2187	1.36724	−0.00119	1.36204	−0.00145	1.35688	−0.00179
0.7407	0.2124	1.36402	−0.00053	1.35859	−0.00078	1.35344	−0.00091
0.0586	0.3423	1.37356	0.00063	1.36876	0.00035	1.36431	0.00037
0.2332	0.3414	1.36995	−0.00032	1.36492	−0.00067	1.36051	−0.00048
0.4123	0.3361	1.36695	−0.00067	1.36176	−0.00100	1.35688	−0.00114
0.6086	0.3116	1.36458	−0.00042	1.35898	−0.00098	1.35384	−0.00122
0.0617	0.4763	1.37123	0.00047	1.36672	0.00046	1.36232	0.00051
0.2422	0.4676	1.36787	−0.00026	1.36293	−0.00053	1.35825	−0.00062
0.4550	0.4684	1.36436	−0.00050	1.35916	−0.00083	1.35414	−0.00110
0.5649	0.2596	1.36600	−0.00050	1.36026	−0.00123	1.35517	−0.00144
0.3921	0.5657	1.36394	−0.00034	1.35872	−0.00077	1.35380	−0.00100
0.0680	0.6827	1.36779	0.00041	1.36340	0.00049	1.35890	0.00041
0.2294	0.6860	1.36454	−0.00032	1.35972	−0.00052	1.35505	−0.00065
0.0654	0.8506	1.36509	0.00034	1.36057	0.00026	1.35594	0.00001
0.1467	0.8097	1.36412	−0.00004	1.35929	−0.00035	1.35479	−0.00039
0.0399	0.9091	1.36431	0.00010	1.35988	0.00007	1.35567	0.00022

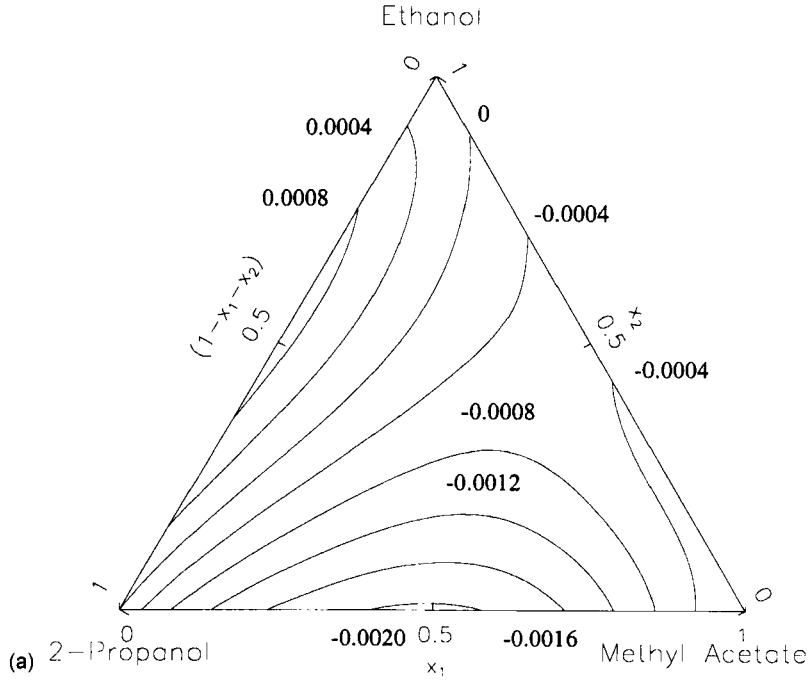
magnitude parameters which are enclosed in Table IV. The correlation was realized taking into account the binary contributions, by the method of least squares with all points weighting equally using a routine developed in accordance with Marquard algorithm [12]. The root square deviation at each correlation is enclosed as a measurement of the validity of the fitting parameters and equations applied, which is expressed by Eq. (6). In this equation the value of the property and the number of experimental data are represented by z and n, respectively.

$$\sigma = \sqrt{\frac{\sum_i^n (z_{\text{exp}} - z_{\text{pred}})^2}{n}} \tag{6}$$

TABLE IV Parameters of Eqs. (3) and (5) and root mean square deviations (σ)

		Methyl acetate + Ethanol		
δn_D	$B_{01} = 0.227534$	$B_{02} = -0.001443$	$B_{03} = 2.242\,10^{-6}$	
	$B_{11} = -0.570455$	$B_{12} = 0.003951$	$B_{13} = -6.825\,10^{-6}$	
	$B_{21} = 1.505623$	$B_{22} = -0.010008$	$B_{23} = 1.661\,10^{-5}$	
	$B_{31} = -1.031366$	$B_{32} = 0.006502$	$B_{33} = -1.020\,10^{-5}$	$\sigma = 0.000015$
		Methyl acetate + 2-Propanol		
δn_D	$B_{01} = 0.323416$	$B_{02} = -0.002136$	$B_{03} = 3.418\,10^{-6}$	
	$B_{11} = -1.294200$	$B_{12} = 0.008878$	$B_{13} = -1.522\,10^{-5}$	
	$B_{21} = 1.435960$	$B_{22} = -0.009607$	$B_{23} = 1.605\,10^{-5}$	
	$B_{31} = 6.306190$	$B_{32} = -0.042627$	$B_{33} = 7.203\,10^{-5}$	$\sigma = 0.000017$
		Ethanol + 2-Propanol		
δn_D	$B_{01} = 0.143441$	$B_{02} = -0.000974$	$B_{03} = 1.698\,10^{-6}$	
	$B_{11} = 0.432698$	$B_{12} = -0.002889$	$B_{13} = 4.823\,10^{-6}$	
	$B_{21} = -0.613629$	$B_{22} = 0.004067$	$B_{23} = -6.723\,10^{-6}$	
	$B_{31} = -1.444533$	$B_{32} = 0.009772$	$B_{33} = -1.651\,10^{-5}$	$\sigma = 0.000019$
		Methyl acetate + Ethanol + 2-Propanol		
δn_D	$D_{01} = -4.551178$	$D_{02} = 0.031543$	$D_{03} = -5.459\,10^{-5}$	
	$D_{11} = 4.320839$	$D_{12} = -0.030557$	$D_{13} = 5.393\,10^{-5}$	
	$D_{21} = 5.348721$	$D_{22} = -0.036976$	$D_{23} = 6.387\,10^{-5}$	$\sigma = 0.000113$

No values of the derived magnitud for these systems has been published in currently available literature at the studied conditions. Figures 1a, 1b and 1c show the derived property in the ternary mixture against molar fraction as well as the curves fitted for each temperature (288.15, 298.15 and 308.15 K, respectively). As it could be observed, higher temperatures yield more intense values in binary systems, increasing the positive changes of refractive indices of alkanols mixture and decreasing the negative values in the mixtures where methyl acetate is enclosed. The sigmoid behaviour observed at low acetate compositions in methyl acetate + ethanol mixture disappears at high temperatures. Then, the contractive tendence by hydrogen bonds rises slightly by increasing temperature. On the other hand, the expansive behaviour in methyl acetate mixtures due to the alkanol structure breakage is higher when temperature increases, this effect being supported when alkanol shows branched chains (2-propanol in this case) by steric hindrance among aliphatic residues. The effect is analogous for the ternary mixture, the methyl acetate contributes as a structure breaker in alkanol environment, the most intensive effect being observed at approximately acetate + alcohols equimolar compositions. Low temperatures moderate the methyl acetate activity. An



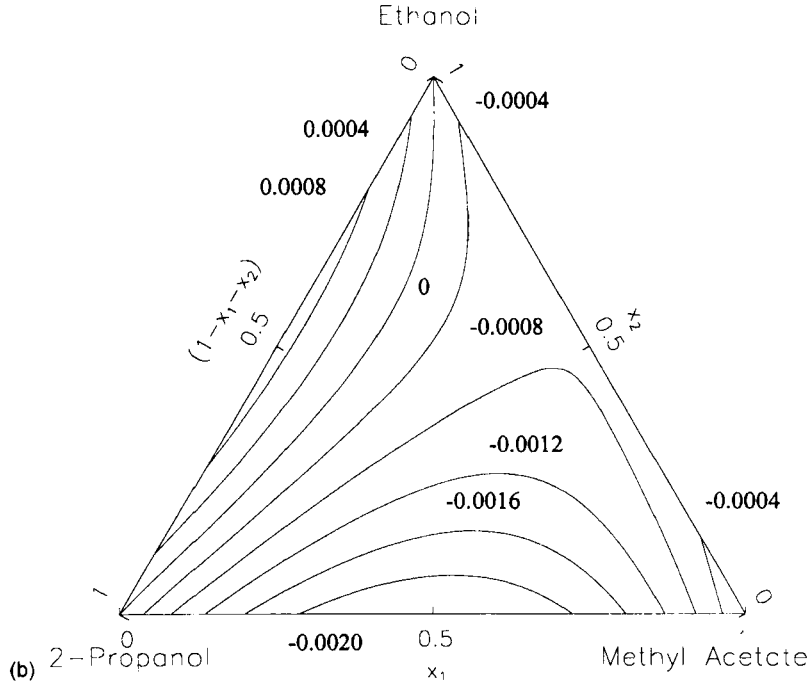


FIGURE 1 Curves of constant changes of refractive indices in accordance with Eqs. (4) and (5) for methyl acetate + ethanol + 2-propanol at the temperatures (a) 288.15, (b) 298.15 K and (c) 308.15 K.

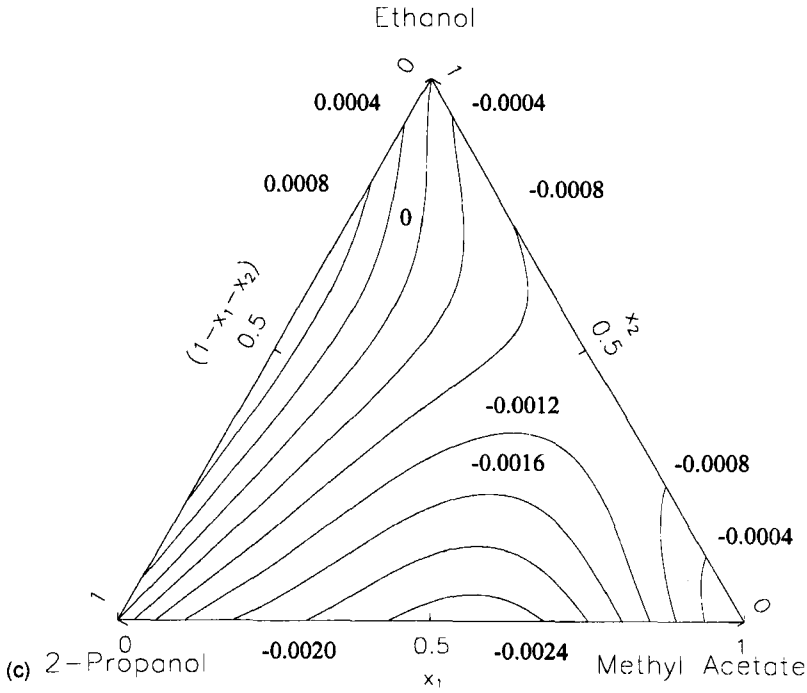


FIGURE 1 (Continued).

interesting tendence of this magnitude is the evolution of the null isoline of change of refractive index from pure ethanol towards binary methyl acetate + ethanol mixture at the lowest temperature. At this small range of composition, the abundance of short alcohol molecules and low temperature allows ethanol to establish hydrogen bonds and alter the expansive effect at poorer alcohol molar fractions.

4. BINARY CONTRIBUTION MODELS

Many different models exist to correlate and predict thermodynamic properties, equations based upon theories, methods of excess or derived magnitudes and equations of state. Most of them perform satisfactorely for binaries but the situation becomes complicated in the case of multicomponent mixtures. Moreover, accurate multicomponent thermodynamic data to evaluate models parameters are scarce

and testing models and parameters computation becomes difficult. Some empirical expressions for fitting excess functions require molar fraction dependent parameters and it may cause problems in their application to a multicomponent systems. Some simple procedures in the multicomponent derived magnitude estimation at standard or non-standard conditions is the application of semiempirical binary contribution models, which are useful due to its high simplicity and only enclosed binary systems data requirements at the same condition. These models perform with general accuracy when ternary contribution is reduced by similar structure in involved solvents. They have been proposed to determine excess functions as molar enthalpies or free energies but can also be applied to other derived magnitudes. In order to estimate the ternary values at different temperatures, we use different semitheoretical three-binary contributions models [13–18] which determine such magnitudes by means of different graphical rules. The ternary excess or derived properties of mixtures may be estimated from binary values applying the following equation:

$$\delta Q_{ijk} = \sum_{i<j} (x_i x_j / x'_i x'_j) \delta Q_{ij}(x'_i, x'_j) \tag{6}$$

For each ternary mixture the molar fractions x' may be obtained from a triangular diagram by projecting the point representing the ternary mixture onto the corresponding binary axis, using different symmetric or asymmetric criteria of binary contribution to the ternary value. In said rules asymmetry is understood to be the contribution of the three binaries to the ternary excess, all three of which contribute equally. Asymmetry is understood to indicate the individual contribution of one of the binaries, the latter being normally attributed to polar components. In Table V, the experimental and estimated derived values at different temperatures are compared showing σ deviations (Eq. (5)). In general, it could be observed as adequate deviations are obtained at the measurement temperatures, the symmetric (Kohler, Jacob-Fitzner and Colinet) as well as 2-propanol as asymmetric component in Scatchard and Toop methods showing the best results. In the Figure 2, the symmetric models are compared as a function of temperature attending to a z parameter which is related to molar composition. This parameter is the product of all molar fraction values

TABLE V Root mean square deviations of the experimental data from the estimation results for different empirical equations

	$\sigma(\delta n_D)$ *at* 288.15 *K*	$\sigma(\delta n_D)$ *at* 298.15 *K*	$\sigma(\delta n_D)$ *at* 308.15 *K*
Kohler	0.00015	0.00011	0.00014
Jacob-Fitzner	0.00015	0.00010	0.00015
Colinet	0.00014	0.00011	0.00014
Tsao-Smith[a]	0.00017	0.00012	0.00020
Tsao-Smith[b]	0.00035	0.00040	0.00039
Tsao-Smith[c]	0.00015	0.00018	0.00018
Scatchard[a]	0.00016	0.00013	0.00015
Scatchard[b]	0.00014	0.00010	0.00016
Scatchard[c]	0.00014	0.00009	0.00015
Toop[a]	0.00016	0.00013	0.00015
Toop[b]	0.00014	0.00010	0.00015
Toop[c]	0.00015	0.00010	0.00015

[a] Methyl acetate is the asymmetric component in the equation.
[b] Ethanol is the asymmetric component in the equation.
[c] 2-Propanol is the asymmetric component in the equation.

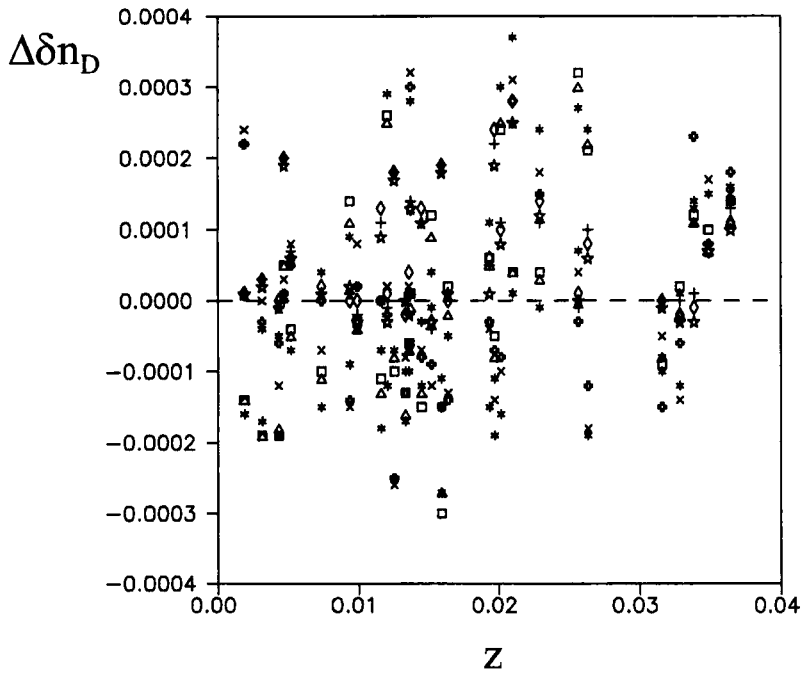


FIGURE 2 Deviations ($\Delta\delta n_D$) of experimental data from computed changes of refractive indices by application of the symmetric binary contribution models of Kohler (K), Jacob-Fitzner (JF) and Colinet (C) for the ternary mixture methyl acetate + ethanol + 2-propanol at the temperatures 288.15 (K, O; JF, □; C, Δ), 298.15 (K, ◊; JF, ☆; F, +) and 308.15 K (K, ×; JF, *; C,). The computed values from experimental data in mixture are shown through the dashed line of zero value. Parameter z is the adimensional product of molar fractions of multicomponent mixture.

at every experimental point in the mixture and is useful to depict into a two dimension figure, the multicomponent behaviour. Moreover, an equimolar analysis is possible due to the nature of the mathematical function. In this figure is shown as the lowest deviations are computed at 298.15 K, the diluted in one solvent mixtures (moderated values of z parameter) gathering the highest deviations in all cases due to the ternary molecular interaction contribution at these zones of composition (low methyl acetate molar fraction).

References

[1] Iglesias, M., Orge, B. and Tojo, J. (1996). *Fluid Phase Equilib.*, **126**, 203.
[2] Iglesias, M., Marino, G., Orge, B., Piñeiro, M. M. and Tojo, J. (1999). *Phys. Chem. Liq.*, **37**, 193.
[3] Iglesias, M., Orge, B. and Tojo, J. (1998). *Fluid Phase Equilib.*, **147**, 285.
[4] *TRC Thermodynamic Tables* (Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994).
[5] Riddick, J. A., Bunger, W. B. and Sakano, T. K. (1986). *Organic Solvents, Techniques of Chemistry* (4th ed., Vol. 2. Wiley-Interscience: New York).
[6] Redlich, O. and Kister, A. (1948). *Ind. Eng. Chem.*, **40**, 345.
[7] Rodriguez, A., Canosa, J., Orge, B., Iglesias, M. and Tojo, J. (1996). *J. Chem. Eng. Data*, **41**, 1446.
[8] Canosa, J., Rodriguez, A., Iglesias, M., Orge, B. and Tojo, J. (1997). *J. Chem. Thermodyn.*, **29**, 907.
[9] Orge, B., Iglesias, M., Marino, G., de Cominges, B. E., Piñeiro, M. M. and Vijande, J. (1999). *J. Thermal Anal. and Calorimetry.*, **56**, 381.
[10] Bevington, P., *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill: New York, 1969).
[11] Cibulka, I. (1982). *Coll. Czech. Comm.*, **47**, 1414.
[12] Marquardt, D. W. (1963). *J. Soc. Indust. Appl. Math.*, **2**, 431.
[13] Kohler, F. (1960). *Monatsh. Chem.*, **91**, 738.
[14] Jacob, K. T. and Fitzner, K. (1977). *Thermochim. Acta*, **18**, 197.
[15] Colinet, C. (1967). *Thesis*, University of Grenoble, France.
[16] Tsao, C. C. and Smith, J. M. (1953). *Chem. Eng. Prog. Symp. Series*, **49**, 107.
[17] Scatchard, G., Ticknor, L. B., Goates, J. R. and McCartney, E. R. (1952). *J. Am. Chem. Soc.*, **74**, 3721.
[18] Toop, G. W. (1965). *Trans. TMS–AIME*, **223**, 850.