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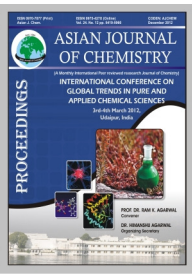

Study of Refractive Index, Density, Molar Volume and Their Excess Properties of Binary Systems†

S.P. KAMBLE[1,*], P.B. UNDRE[2], Y.S. SUDAKE[2], A.P. MAHAROLKAR[2] and P.W. KHIRADE[2]

[1]Department of Physics, C.T. Bora College, Shirur (Ghodnadi), Dist. Pune-412 210, India
[2]Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431 004, India

*Corresponding author: E-mail: siddharth_kamble82@yahoo.co.in

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Refractive index and density have been measured over the whole composition range for (dimethyl sulphoxide, dimethyl acetamide, 2-propanol(2-P), glycerol (GL), 2-methoxymethanol(2-ME) and 2-ethoxyethanol(2-EE)) at 293 K along with the properties of the pure component. Excess density, excess refractive index and molar volume for the binary system at above mentioned temperature were calculated and fitted to Redlich-Kister equation to determine a_j coefficient. And the deviation of the excess properties from the ideal values suggests that there may be the hydrogen bonding and dispersion intermolecular interactions in the system under study.

Key Words: Refractive index, Excess molar volume, Molar refraction, Molecular interactions.

INTRODUCTION

Several binary liquids system parameters are extensively used to investigate and interpret the medium effects in chemical reactions and molecular interactions[1-6]. It is well known that physical properties of binary liquid such as refractive index of a mixture provides a simple, rapid determination of the composition and density are strictly related to the molecular interactions present in the different binary liquid system. The variation of these properties with concentrations gives us important data about intermolecular interactions. Many investigations on molecular structure including internal molecular motion[7] using optical, electrical and spectroscopic method have been done but the changes occurring during the process of mixing is difficult to access. In optical method measurement of refractive index have been extensively made with the aim of explaining its dependence on structural details[8-11]. Refractive index is the ratio of light in material medium[12] this optical property is very sensitive to changes in molecular associations of pure liquid solutions and mixtures. Light passes more slowly through a substance than through a vacuum as light enters a denser substance the advancing wave at the interface are modified by being closer together owing to their slower speed and shorter wavelength. If the light enters the denser substance at an angle one part of the wave slows down more quickly as it passes the interface and it produces a bending of the wave towards the interface is the refraction. If the light enters the less denser substance it is refracted away from the interface rather than towards it and the relative value of this effect is the refractive index.

The refractive index and Lorentz-Lorentz function[8] (η_D^2 -1/η_D^2 +2) are intensive properties of homogeneous mixture. Molar refraction is defined as:

$$R_m = (\eta_D^2 - 1/\eta_D^2 + 2) \times V_m$$

where, V_m is the molar volume and molar refractions also expressed in the same units as molar volumes .The molar refractions of pure liquid has found to be an additive property of structural elements. Excess molar volume also gives the information regarding the interactions of binary mixtures[13-17].

Dimethyl sulphoxide, dimethyl acetamide, glycerol, 2-methoxymethanol, 2-ethoxyethanol, and 2-propanol play an important role in many chemical reactions and they have many applications in the industrial field and medical field.

In the present work, refractive index and densities of dimethyl sulphoxide + dimethylacetamide, dimethyl sulphoxide + glycerol, dimethyl acetamide + glycerol, 2-methoxymethanol + 2-propanol, 2-ethoxyethanol + 2-propanol, 2-methoxymethanol + 2-ethoxyethanol binary liquid mixtures have been measured at 294K.

EXPERIMENTAL

The chemicals dimethyl sulphoxide, dimethyl acetamide, 2-propanol, glycerol, 2-methoxymethanol and 2-ethoxyethanol are obtained from Qualigens Fine Chemicals and Kemphasol, Mumbai. These chemicals were used without further purification.

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The mixtures were prepared by mixing appropriate volume of liquids.

Density of pure liquids and their mixtures were determined by vibrating tube densimeter (Anton DMA 602 Paar/mpD5400 system) with an accuracy of 0.005 kg/m^3. The accuracy in the temperature during the measurements however is ± 0.1 ºC because Pt 100 measuring sensors were used.

The instrument was calibrated with air, four times distilled and freshly degassed water at each measuring temperature using inbuilt software driven special adjustment procedure. Two independent density measurements were performed with each solution. The refractive index of pure liquids and their mixtures were measured by using Abbe's refractometer with an accuracy of ± 0.001.

Data analysis: The literature values of density (ρ) and refractive index (η_D) of dimethylsulphoxide, dimethyl acetamide, 2-propanol glycerol, 2-methoxymethanol and 2-ethoxyethanol at 293 K are listed in Table-1.

TABLE-1
DENSITY (ρ) (kg/ m^3) AND REFRACTIVE INDEX (ηD) OF DIMETHYLSULPHOXIDE, DIMETHYL ACETAMIDE, 2-PROPANOL GLYCEROL, 2-METHOXYMETHANOL AND 2-ETHOXYETHANOL AT 293 K

Liquid property	DMSO	DMA	GL	2-ME	2-EE	2-Propanol
(ρ) (kg/ m^3)	1.101	0.9370	1.2613	0.965	0.93	0.7855
ηD	1.4790	1.4380	1.47	1.4021	1.3796	1.39

The excess properties of the mixtures were calculated using the following equation.

$$A^E = A_{mix}-(A_1 X_1 + A_2X_2) \quad (1)$$

where, A^E represents the excess refractive index, excess densities or excess molar volume. A_1, A_2 and A_{mix} represent the refractive index or density or molar volume of pure liquids 1, 2 and mixture respectively. The X_1 and X_2 represents the mole fraction of component 1 and 2 of the mixtures. The molar volume of the mixture was calculated as:

$$V = (X_1M_1+X_2M_2)/\rho \quad (2)$$

where, M_1 and M_2 represents molecular weight of components 1 and 2 respectively and is the experimental density.

The values of excess parameters were fitted to the Redlich-Kister equation.

$$Y^E = X_1(1-X_1)\sum_{i=0}^{3} a_j(2X_1-1)^1 \quad (3)$$

The values of the interaction coefficient (a_j) were evaluated by the method of least squares fit and are listed in Table-2, along with standard deviation (σ)[15,16], between the experimental and calculated values were calculated with:

$$\sigma = [\Sigma(X_{expt}-X_{caled})^2/(n-p)]^{(1/2)} \quad (4)$$

where, n-number of experimental points,

p-Number of interaction coefficient parameters and X_{expt}, X_{caled} - are the experimental and calculated properties, respectively.

RESULTS AND DISCUSSION

The experimental and estimated values of various parameters are given in Table-2a and 2b of all binary mixtures.

The solid line through the data points indicates the Redlich-Kister model.

TABLE-2a
EXPERIMENTAL DENSITY (kg/ m^3), REFRACTIVE INDEX AT T = 294 K

Mole fraction of DMSO in DMA+ DMSO	ρ(kg/m^3) *10^3	η_D	Mole fraction of DMSO in GL+ DMSO	ρ(kg/m^3) *10^3	η_D	Mole fraction of DMA in GL + DMA	ρ(kg/m^3) *10^3	η_D
0.0000	0.9592	1.435	1.2614	1.261	1.471	0.0000	1.2614	1.471
0.1244	0.9651	1.436	1.2501	1.250	1.473	0.0891	1.2231	1.467
0.2423	0.9781	1.436	1.2394	1.239	1.473	0.1803	1.1887	1.463
0.3541	0.9910	1.437	1.2269	1.227	1.474	0.2739	1.1558	1.459
0.4603	1.0054	1.439	1.2147	1.215	1.474	0.3698	1.1233	1.456
0.5612	1.0203	1.440	1.2008	1.201	1.475	0.4681	1.0910	1.452
0.6574	1.0363	1.443	1.1848	1.185	1.4753	0.569	1.0590	1.448
0.749	1.0517	1.449	1.1664	1.166	1.4755	0.6725	1.0284	1.444
0.8365	1.0675	1.457	1.1450	1.145	1.4756	0.7788	0.9980	1.442
0.9201	1.0836	1.465	1.1230	1.123	1.4757	0.8879	0.9690	1.439
1.0000	1.1003	1.474	1.1020	1.102	1.475	1.0000	0.9417	1.435

TABLE-2b
EXPERIMENTAL DENSITY (kg/ m^3), REFRACTIVE INDEX AT T = 294 K

Mole fraction of 2-ME in 2-EE+2-	ρ(kg/m^3) *10^3	η_D	Mole fraction of 2-ME in 2-P + 2-ME	ρ(kg/m^3) *10^3	η_D	Mole fraction 2-EE in 2-P+2-EE	ρ(kg/m^3) *10^3	η_D
0.0000	0.9288	1.406	0.0000	0.7884	1.377	0.0000	0.788	1.377
0.1202	0.9323	1.406	0.0969	0.8051	1.379	0.0804	0.803	1.380
0.2351	0.9357	1.4063	0.1945	0.8221	1.382	0.1643	0.8201	1.383
0.3451	0.9391	1.4062	0.2927	0.8385	1.383	0.2521	0.838	1.386
0.4504	0.9425	1.4057	0.3917	0.8550	1.385	0.344	0.854	1.389
0.5515	0.9460	1.4049	0.4913	0.8711	1.387	0.4403	0.869	1.392
0.6484	0.9496	1.404	0.5916	0.8874	1.389	0.5413	0.882	1.395
0.7415	0.9533	1.4035	0.6926	0.9051	1.391	0.6473	0.894	1.398
0.831	0.9570	1.403	0.7944	0.9245	1.394	0.7588	0.906	1.401
0.9171	0.9607	1.402	0.8968	0.9450	1.397	0.8762	0.917	1.404
1.0000	0.9643	1.401	1.0000	0.9641	1.401	1.0000	0.929	1.406

Fig. 1(a), 3(a), 4(a), and 5(a) shows that excess molar volume for the system appears to be positive over the entire range of concentrations. It may be due to contribution of:

ˆ Hetero-cooperative interactions of DMSO + DMA, DMA + GL, 2-ME + 2-EE, 2-ME + 2-P molecules, this would correspond to volume expansion.

TABLE-3
INTERACTION COEFFICIENT a_i AND STANDARD DEVIATION (σ) FOR DENSITY (kg/m^3), REFRACTIVE INDEX AND EXCESS MOLAR VOLUME (cc.mol^{-1}) FOR BINARY MIXTURES AT T = 294 K

System	#	a_0	a_1	a_2	a_3	σ
DMSO+DMA	ρ^E	-0.07309	0.01102	-0.00746	-0.00748	0.0139
	η_D^E	-0.06319	-0.04902	0.00895	0.04585	0.01806
	V^E	3.08603	-1.81624	0.71603	0.49747	0.12317
DMSO+GL	ρ^E	0.08098	0.02535	-0.03178	-0.03574	0.0164
	η_D^E	0.00581	-0.00225	0.00158	-0.00385	0.005392
	V^E	-4.57239	-1.7377	1.80189	2.2059	0.126596
DMA+GL	ρ^E	-0.11654	0.01156	-0.02765	0.03133	0.0171
	η_D^E	-0.01504	-0.0031	0.00352	0.00816	0.007743
	V^E	3.19744	0.56732	1.73351	-1.6951	0.135864
2ME+2-P	ρ^E	-0.01591	-0.02813	0.0116	0.03743	0.0002
	η_D^E	-0.00966	-0.00915	0.00038	-0.00063	0.00004
	V^E	1.952181	2.331935	-1.08535	-3.23227	0.015521
2EE+2-P	ρ^E	0.071664	-0.02933	-0.0319	0.04169	0.0137
	η_D^E	1.85453	1.6493	4.27333	4.85943	0.00614
	V^E	-3.73925	2.33063	3.1761	-3.9436	0.124584
2-ME+2-EE	ρ^E	-0.00943	-0.00175	0.00233	0.00117	0.0034
	η_D^E	0.00732	-0.0046	0.000228	0.011132	0.000002076
	V^E	0.19713	0.06973	-0.23024	-0.08084	0.030267

Parameter

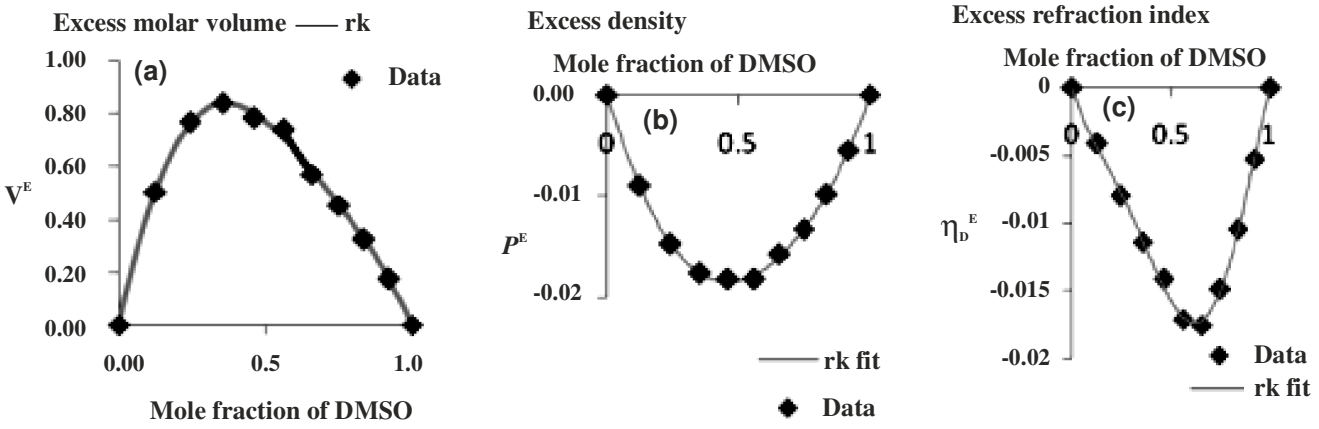

Fig. 1. Excess (a) molar volume (b) density (c) Refractive Index against mole fraction of DMSO+DMA

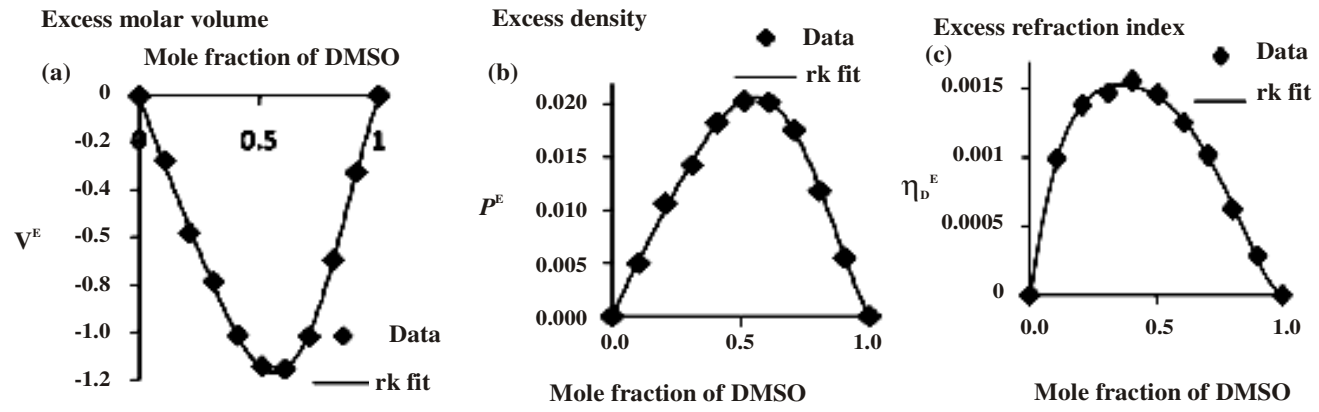

Fig. 2. Excess (a) molar volume (b) density (c) refractive index against mole fraction of DMSO+GL

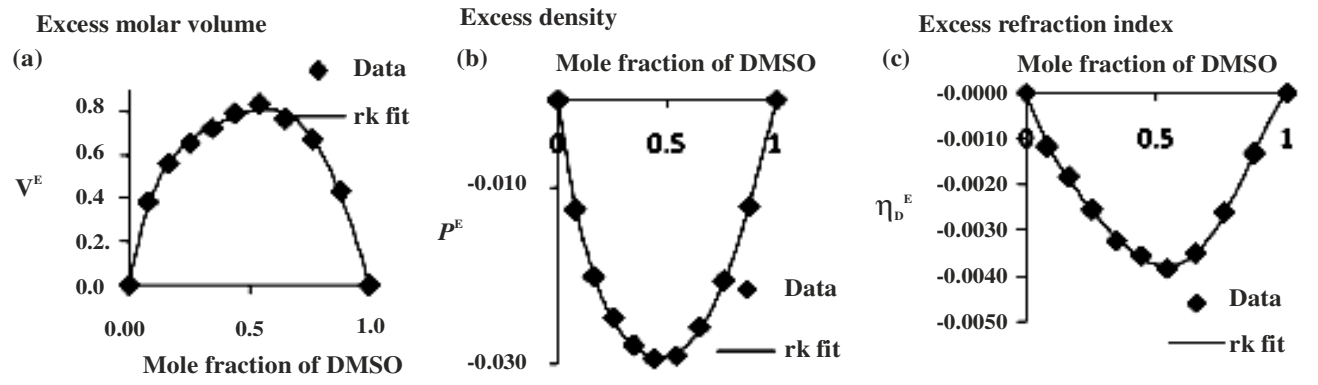

Fig. 3. Excess (a) molar volume (b) density (c) refractive index against mole fraction of DMA+GL

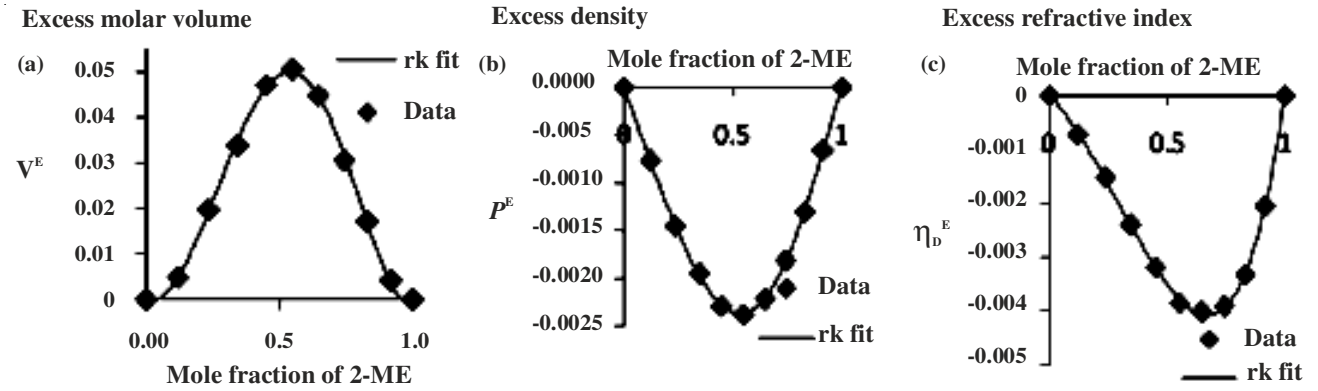

Fig. 4. Excess (a) molar volume (b) density (c) refractive index against mole fraction of 2-ME+2-EE

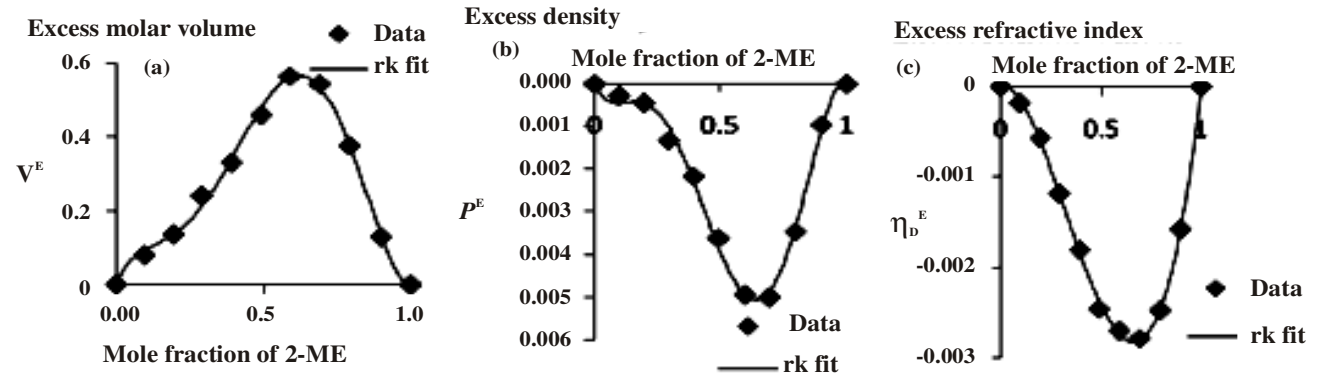

Fig. 5. Excess (a) molar volume (b) density (c) refractive index against mole fraction of 2-ME+2-P

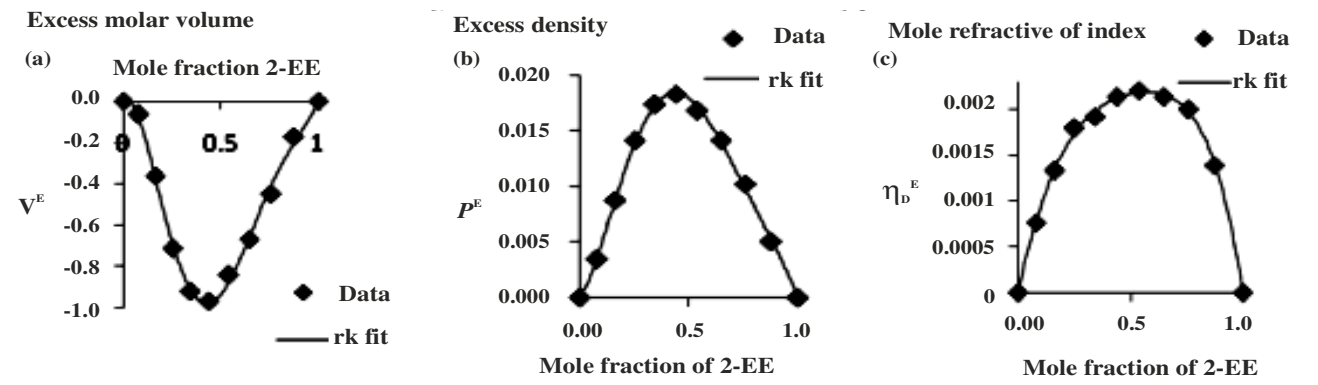

Fig. 6. Excess (a) molar volume (b) density (c) refractive index against mole fraction of 2-EE+2-P

ˆ The formation of weak DMSO+DMA, DMA+GL,2-ME+2-EE and 2-ME+2-P complex in this binary system.

ˆ The positive V^E values in the present case are indicative of[18] dispersion interaction between mixing components. This dispersion interaction may arise due to breaking of cohesive forces acting in like molecules with the subsequent increase[19] in V^E. Since normally dispersive interaction between unlike molecules is weaker than those between like molecules, it is reasonable that they contribute positively[19] to V^E.

From Fig. 2(a) and 6(a) it is observed that the excess molar volume for the system appears to be negative for entire concentration values indicating that there are dispersion forces between the different kind of molecules of the DMSO+GL and 2-EE+2-P liquid. This shows the existence of intermolecular interaction between the systems under study.

Excess molar volume: The negative values of excess molar volume (V^E) indicate that the packing degree in these mixed liquids is higher than in the pure species and in their idealized mixture suggesting that specific interactions such as hydrogen bonding and dipolar interactions of any are more effective among the chemical species. The attractive interactive interaction which are generally responsible for structure making effect[7]. Seem to be the driving forces able to sustain the liquid structure of these mixture even in presence of repulsive phenomenon due to steric hindrances and unfavourable interactions between polar and non-polar groups (structure breaking effects)[8].

Conclusion

The positive V^E values indicate there is dispersion interaction resulting in breaking of cohesive forces acting in like molecules. The negative V^E indicate charge transfer, formation of hydrogen bonds. The optical property molar refractions of mixing have been introduced for the components of liquid mixtures .The change in molar refractions of mixing is defined as the proper molar refraction deviation function. The profiles for their compositions dependence are discussed and compare with result previously obtained for different excess molar properties of organic component. From this comparison it is observed that optical properties to confirm the existence of aggregation of mixing in this binary system, which reflects to structural features of dimethyl sulphoxide + dimethyl acetamide, dimethyl sulphoxide + glycerol, dimethyl acetamide + glycerol, 2-methoxymethanol + 2-propanol, 2-ethoxyethanol + 2-propanol, 2-methoxymethanol + 2-ethoxyethanol.

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