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Excess Molar Volumes, Viscosity Deviations, and Isentropic Compressibility Changes in Binary Mixtures of *N*-Methylacetamide + 2-Methoxyethanol and *N*-Methylacetamide + Water at (308.15, 313.15, and 318.15) K

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Densities, viscosities, and ultrasonic velocities of the binary mixtures of *N*-methylacetamide + 2-methoxyethanol and + water have been measured at (308.15, 313.15, and 318.15) K. The excess molar volumes, viscosity deviations, and isentropic compressibility changes of the mixture from the ideal mole fraction rule have been calculated from these data. The computed results have been fitted to the Redlich−Kister polynomial.

Introduction

In recent years, there has been a considerable upsurge in the theoretical and experimental investigations of the excess thermodynamic properties of binary liquid mixtures.[1,2] The importance of *N*-methylacetamide as a strongly hydrogen-bonded, highly structured, protic and basic solvent lead us to investigate its excess properties with the familiar solvents 2-methoxyethanol and water. The amide group in *N*-methylacetamide is a good model of a peptide bond. We believe that a systematic study of the structural and energetic consequences of the interactions between *N*-methylacetamide and water and between *N*-methylacetamide and an organic solvent will enable us to understand how water exercises thermodynamic and kinetic control over the chemical activities of polypeptides in aqueous media.

We have measured densities, viscosities, and ultrasonic velocities for the liquid mixtures of *N*-methylacetamide + 2-methoxyethanol and *N*-methylacetamide + water over the entire range of their compositions at (308.15, 313.15, and 318.15) K. The excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and isentropic compressibility changes ($\Delta\kappa_s$) of these systems have been calculated at these temperatures.

Experimental Section

N-Methylacetamide (G.R., E. Merck, Germany) was purified by fractional distillation over nitrogen. Its density (0.942 24 g cm^{-3} at 313.15 K) and viscosity (3.004 mPa s at 313.15 K) compared well with the literature values,[3] which are 0.9420 g cm^{-3} and 3.02 mPa s at 313.15 K, respectively.

2-Methoxyethanol (G.R., E. Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use, and the middle fraction was collected. The purified solvent had a density of 0.960 02 g cm^{-3} and a coefficient of viscosity of 1.541 mPa s at 298.15 K. These values are in good agreement with the literature values,[4] which are 0.960 28 g cm^{-3} and 1.543 mPa s, respectively.

Densities were measured with an Ostwald−Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at (308.15, 313.15, and 318.15) K with triply distilled water and benzene. The reproducibility of the density measurements was $\pm 3 \times 10^{-5}$ g cm^{-3}. The temperature of the thermostatic water bath was controlled to ±0.01 K of the desired temperature.

The kinematic viscosities were measured by means of a suspended-level Ubbelohde viscometer with a flow time of about 539 s for distilled water at 298.15 K. The time of efflux was measured with a stopwatch capable of recording ±0.1 s. The viscometer was always kept in a vertical position in a water thermostat controlled to ±0.01 K. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = ct - k/t \tag{1}$$

$$\eta = \nu\rho \tag{2}$$

where t is the efflux time, ρ is the density, and c and k are the characteristic constants of the viscometer. The values of the constants c and k, determined by using water and benzene, were found to be 1.648×10^{-5} cm^2 s^2 and −0.023 31 cm^2, respectively. The estimated error of the viscosity measurements was ±0.2%.

Sound velocities were measured, with an uncertainty of ±0.3%, using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at 4 MHz, which was calibrated with water, methanol, and benzene at each temperature. The temperature stability was maintained within ±0.01 K by circulating thermostated water around the cell with a circulating pump. The thermostatic bath was controlled to ±0.01 K.

Isentropic compressibility (κ_s) can then be calculated by the following formula:

$$\kappa_s = 1/(u^2\rho) \tag{3}$$

where u is the sound velocity and ρ is the density of the experimental liquid.

In all cases, the experiments were performed at least in five replicates for each composition and at each temperature, and the results were averaged.

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Table 1. Density, ρ, Viscosity, η, and Ultrasonic Velocity, u, for N-Methylacetamide (1) + 2-Methoxyethanol (2) at (308.15, 313.15, and 318.15) K

	ρ/(g·cm^{-3})			η/(mPa·s)			u/(m·s^{-1})		
x_1	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0000	0.946 80	0.942 33	0.937 62	1.315	1.200	1.098	1309.67	1294.26	1276.94
0.0301	0.947 28	0.942 96	0.938 38	1.362	1.242	1.136	1314.35	1298.93	1281.53
0.0501	0.947 61	0.943 37	0.938 88	1.393	1.270	1.160	1316.87	1301.33	1283.92
0.0752	0.948 00	0.943 88	0.939 49	1.431	1.304	1.191	1319.66	1304.17	1286.93
0.1036	0.948 49	0.944 36	0.940 13	1.476	1.343	1.227	1322.33	1307.00	1289.90
0.1301	0.948 90	0.944 85	0.940 67	1.515	1.378	1.259	1324.68	1309.35	1292.39
0.1700	0.949 48	0.945 42	0.941 25	1.574	1.432	1.307	1327.85	1312.65	1296.00
0.2032	0.949 83	0.945 77	0.941 61	1.624	1.477	1.348	1330.39	1315.22	1298.92
0.2501	0.950 24	0.946 20	0.942 05	1.696	1.541	1.404	1333.86	1318.55	1302.77
0.3020	0.950 57	0.946 53	0.942 35	1.776	1.613	1.468	1337.09	1322.03	1306.24
0.4032	0.950 83	0.946 80	0.942 63	1.940	1.758	1.596	1342.25	1327.13	1311.81
0.5037	0.950 73	0.946 69	0.942 65	2.114	1.910	1.730	1346.32	1331.45	1316.26
0.6033	0.950 25	0.946 23	0.942 33	2.308	2.074	1.876	1349.49	1334.34	1319.46
0.6500	0.949 90	0.945 90	0.942 07	2.409	2.160	1.950	1350.66	1335.46	1320.39
0.7021	0.949 47	0.945 47	0.941 70	2.526	2.259	2.038	1351.61	1336.55	1321.41
0.7503	0.949 06	0.945 07	0.941 33	2.641	2.357	2.124	1352.27	1337.41	1322.31
0.8032	0.948 57	0.944 58	0.940 89	2.775	2.477	2.227	1352.78	1338.15	1323.11
0.8524	0.948 01	0.944 05	0.940 41	2.908	2.594	2.328	1353.36	1338.77	1323.70
0.9035	0.947 43	0.943 44	0.939 85	3.061	2.724	2.439	1353.94	1339.41	1324.31
0.9301	0.947 09	0.943 11	0.939 54	3.145	2.795	2.500	1354.06	1339.43	1324.46
0.9702	0.946 60	0.942 62	0.939 08	3.277	2.913	2.597	1354.35	1339.51	1324.75
1.0000	0.946 24	0.942 24	0.938 72	3.380	3.004	2.673	1354.28	1339.48	1324.80

Table 2. Density, ρ, Viscosity, η, and Ultrasonic Velocity, u, for N-Methylacetamide (1) + Water (2) at (308.15, 313.15, and 318.15) K

	ρ/(g·cm^{-3})			η/(mPa·s)			u/(m·s^{-1})		
x_1	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0000	0.994 11	0.992 21	0.990 27	0.721	0.656	0.600	1519.36	1528.58	1535.48
0.0301	0.995 32	0.992 95	0.990 74	0.997	0.893	0.812	1575.71	1563.16	1564.53
0.0600	0.996 62	0.993 86	0.991 13	1.293	1.137	1.026	1609.87	1602.90	1598.87
0.1002	0.997 15	0.994 03	0.991 30	1.693	1.465	1.301	1645.22	1639.95	1633.16
0.1500	0.997 62	0.994 36	0.991 09	2.240	1.902	1.651	1658.71	1652.29	1645.58
0.1999	0.997 54	0.993 70	0.989 92	2.766	2.326	2.001	1654.34	1645.42	1636.10
0.2450	0.995 95	0.992 09	0.988 30	3.108	2.626	2.257	1644.46	1632.75	1621.49
0.3006	0.992 74	0.988 96	0.985 09	3.402	2.882	2.483	1626.26	1611.60	1599.04
0.3502	0.989 10	0.985 18	0.981 63	3.597	3.063	2.646	1604.04	1588.82	1575.75
0.4012	0.985 26	0.981 58	0.977 80	3.748	3.198	2.769	1576.24	1561.27	1548.32
0.4501	0.981 50	0.977 79	0.974 08	3.852	3.300	2.859	1548.65	1533.78	1520.12
0.5000	0.977 75	0.974 08	0.970 34	3.921	3.370	2.914	1521.75	1506.54	1492.51
0.5502	0.974 07	0.970 30	0.966 67	3.942	3.398	2.938	1497.54	1481.64	1467.37
0.6018	0.970 28	0.966 39	0.962 83	3.906	3.382	2.928	1475.24	1459.56	1444.48
0.6550	0.966 48	0.962 56	0.958 95	3.825	3.327	2.894	1454.41	1438.53	1423.55
0.7019	0.963 35	0.959 40	0.955 78	3.765	3.281	2.869	1436.93	1421.58	1406.30
0.7551	0.959 87	0.955 86	0.952 28	3.688	3.226	2.832	1419.04	1403.08	1388.62
0.8070	0.956 69	0.952 67	0.949 11	3.606	3.167	2.797	1403.33	1387.46	1372.97
0.8450	0.954 39	0.950 40	0.946 77	3.554	3.130	2.768	1392.64	1376.62	1362.60
0.9015	0.951 17	0.947 18	0.943 61	3.495	3.077	2.733	1378.36	1362.50	1348.20
0.9500	0.948 62	0.944 62	0.941 07	3.440	3.044	2.703	1366.24	1350.74	1336.34
1.0000	0.946 24	0.942 24	0.938 72	3.380	3.004	2.673	1354.28	1339.48	1324.80

Results

Solvent Parameters of the Mixtures. The densities, viscosities, and ultrasonic velocities of the N-methylacetamide + 2-methoxyethanol mixture and the N-methylacetamide + water mixture as a function of mole fraction of N-methylacetamide, at (308.15, 313.15, and 318.15) K, are presented in Tables 1 and 2.

Excess Properties of the Mixtures. The excess functions have been evaluated using the following equations:

$$V^{E} = V - (V_1x_1 + V_2x_2) \tag{4}$$

$$\Delta\eta = \eta - (\eta_1x_1 + \eta_2x_2) \tag{5}$$

$$\Delta\kappa_s = \kappa_s - (\kappa_{s1}x_1 + \kappa_{s2}x_2) \tag{6}$$

where V, η, and κ_s are the respective solution properties and V_1 and V_2, η_1 and η_2, and κ_{s1} and κ_{s2} are the molar volumes, the viscosities, and the isentropic compressibilities of the pure components.

The molar volume V is defined by the relation $V = (M_1x_1 + M_2x_2)/\rho$, where M_1 and M_2 are the molecular masses of pure substances and ρ is the density of the mixture.

Graphical representations of V^E, $\Delta\eta$, and $\Delta\kappa_s$ as functions of mole fraction of N-methylacetamide are given in Figures 1−3.

The excess properties Y^E were fitted to the Redlich−Kister equation[5]

$$Y^E = x_1(1 - x_1)\sum A_j(1 - 2x_1)^j \tag{7}$$

where A_0, A_1, A_2, are adjustable parameters. These parameters were evaluated by fitting $Y^E/x_1(1 - x_1)$ to eq 7 by the method of least squares. The values of these parameters along with the standard deviation $\sigma(Y^E)$ of Y^E as defined by the equation

$$\sigma(Y^E) = [\sum(Y^E{}_{obs} - Y^E{}_{calc})^2/(N - M)]^{0.5} \tag{8}$$

are recorded in Tables 3 and 4 for N-methylacetamide + 2-methoxyethanol and N-methylacetamide + water sys-

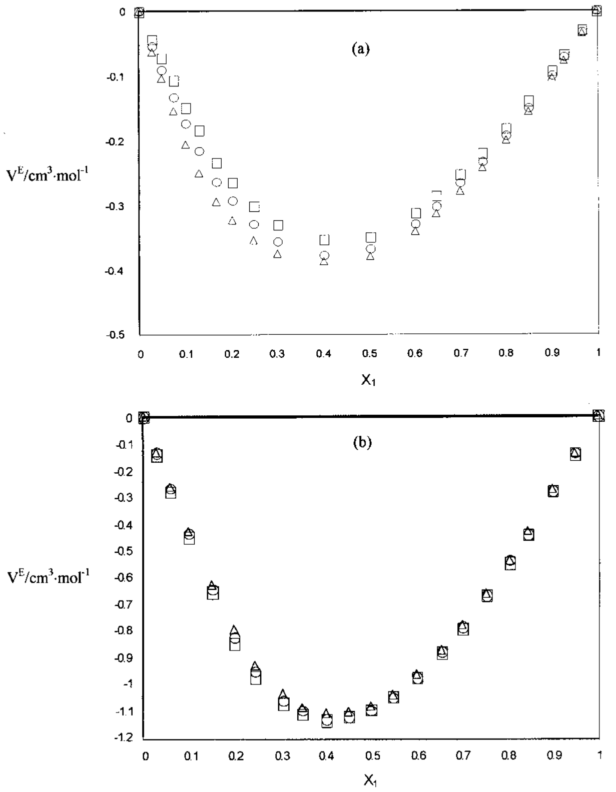

Figure 1. Variation of V^E of the binary mixtures of (a) *N*-methylacetamide (1) + 2-methoxyethanol (2) and (b) *N*-methylacetamide (1) + water (2) at 308.15 K (□), 313.15 K (○), and 318.15 K (△).

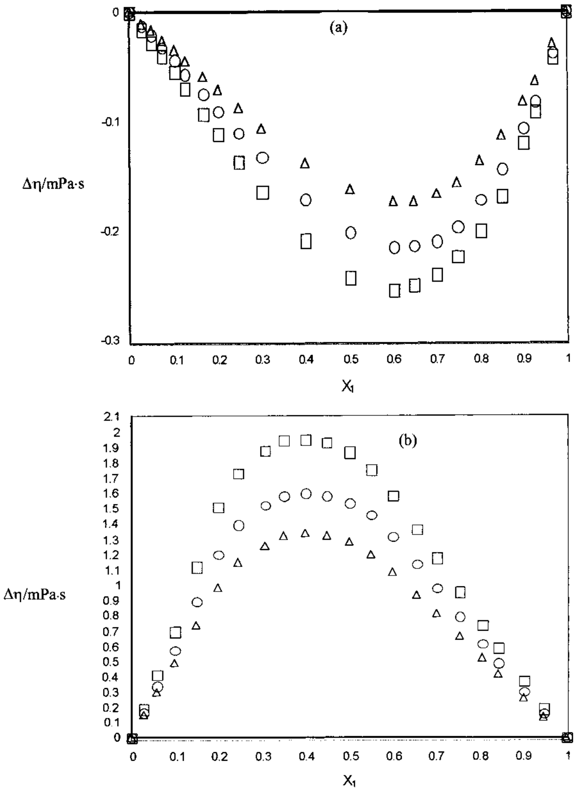

Figure 2. Variation of $\Delta\eta$ of the binary mixtures of (a) *N*-methylacetamide (1) + 2-methoxyethanol (2) and (b) *N*-methylacetamide (1) + water (2) at 308.15 K (□), 313.15 K (○), and 318.15 K (△).

tems, respectively. In eq 8, N is the total number of experimental points and M is the number of parameters.

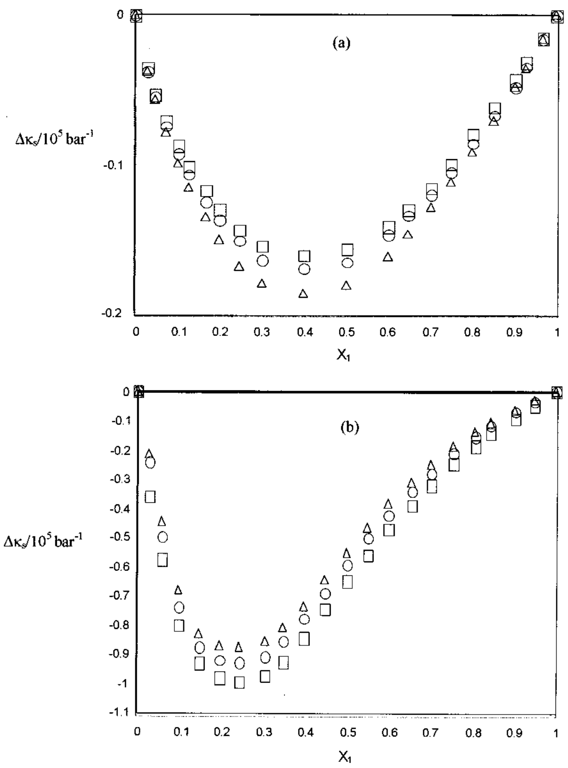

Figure 3. Variation of $\Delta\kappa_s$ of the binary mixtures of (a) *N*-methylacetamide (1) + 2-methoxyethanol (2) and (b) *N*-methylacetamide (1) + water (2) at 308.15 K (□), 313.15 K (○), and 318.15 K (△).

Discussion

Excess Molar Volume. The systems *N*-methylacetamide + 2-methoxyethanol and *N*-methylacetamide + water show negative V^E values over the entire range of mole fraction and over the range of temperatures studied (Figure 1). Both the systems show clear minima at a mole fraction of about 0.40 of *N*-methylacetamide.

N-Methylacetamide is a dipolar protic solvent with a very high dielectric constant ($\epsilon = 191.3$ at 305.15 K), which is attributed to the liquid being highly structured with polymeric chains linked by hydrogen bonding.

On the other hand, the molecules of *n*-alkoxyethanols, in general, are self-associated and form intermolecular as well as intramolecular hydrogen bonds. Moreover, the calculated values of the Kirkwood correlation factors, g_k, for pure 2-methoxyethanol in the temperature range studied are not much greater than unity (the g_k values of 2-methoxyethanol are 1.483, 1.478, and 1.463 at 298.15, 308.15, and 318.15 K, respectively). This indicates that 2-methoxyethanol is a relatively unstructured liquid and that there are strong but not specific dipole−dipole forces. It is also a quasi-aprotic solvent.

It is observed that the interaction between a highly structured *N*-methylacetamide, with many hydrogen bonding sites, and a relatively unstructured 2-methoxyethanol produces a negative V^E. The magnitude of V^E increases with an increase in temperature.

In the *N*-methylacetamide + water mixture, the excess molar volumes at the three temperatures investigated are negative over the whole range of compositions (Figure 1). However, the V^E values are three times bigger than those of the *N*-methylacetamide + 2-methoxyethanol mixture.

The negative V^E values at the three temperatures studied for this mixture and the minima in the curves seem to indicate association through multiple hydrogen bonding

Table 3. Coefficients of Least-Squares Fit by Eq 7 for Excess Molar Volumes, Viscosity Deviations, and Isentropic Compressibility Changes of *N*-Methylacetamide + 2-Methoxyethanol Mixtures at (308.15, 313.15, and 318.15) K

property	T/K	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
V^E/cm^3·mol^{-1}	308.15	−1.3817	0.5037	−0.1594	−0.2859	0.4126	0.002
	313.15	−1.4621	0.5591	−0.2733	−0.1552	0.3112	0.002
	318.15	−1.4928	0.6443	−0.6279	−0.0717	0.5042	0.006
$\Delta\eta$/mPa·s	308.15	−0.9521	−0.4792	−0.0435	−0.0037	0.0211	0.001
	313.15	−0.7940	−0.4502	−0.0791	−0.0123	0.0031	0.001
	318.15	−0.6482	−0.3582	0.0294	0.0048	−0.0773	0.001
$\Delta\kappa_s$/Pa^{-1}	308.15	−0.6378	0.1729	0.1128	0.2058	−0.3862	0.002
	313.15	−0.6631	0.1852	0.0324	0.2014	−0.3215	0.002
	318.15	−0.7296	0.2455	0.0440	0.1434	−0.2766	0.002

Table 4. Coefficients of Least-Squares Fit by Eq 7 for Excess Molar Volumes, Viscosity Deviations and Isentropic Compressibility Changes of *N*-Methylacetamide + Water Mixtures at (308.15, 313.15, and 318.15) K

property	T/K	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
V^E/cm^3·mol^{-1}	308.15	−4.3872	1.7434	−0.3593	−0.8871	1.2388	0.007
	313.15	−4.3929	1.6890	−0.1248	−0.9063	1.0421	0.006
	318.15	−4.3396	1.5804	0.0160	−0.7844	0.8828	0.004
$\Delta\eta$/mPa·s	308.15	7.4524	−4.9177	−0.4478	3.9205	−2.3466	0.032
	313.15	6.1492	−3.6705	−0.9434	2.7013	−1.2185	0.022
	318.15	5.1063	−2.9198	−0.9254	1.9479	−0.5084	0.012
$\Delta\kappa_s$/Pa^{-1}	308.15	−2.6676	3.2055	−1.5566	2.7700	−3.1008	0.022
	313.15	−2.2988	3.7868	−3.8487	0.7347	1.3313	0.024
	318.15	−2.1215	3.7966	−3.9381	0.1937	1.8652	0.027

between the polar group of *N*-methylacetamide and water, although the pure liquids are presumed to be highly structured. Although both are protic, *N*-methylacetamide is less protic than water. Hence, there is interaction among them, reducing the molar volume of the mixture considerably.

Viscosity Deviations. The *N*-methylacetamide + 2-methoxyethanol system displays a sharp negative deviation of $\Delta\eta$ from ideality over the entire mole fraction range and over the whole range of studied temperatures. The minima correspond to the mole fraction of about 0.60 in *N*-methylacetamide (Figure 2). As the temperature increases, the $\Delta\eta$ values become less and less negative and tend to approach ideality.

The highly associated *N*-methylacetamide seems to undergo a structure-breaking effect when mixed with 2-methoxyethanol, similar to *N*-methylacetamide's behavior with DMF. The change in the variation of density, viscosity, and ultrasonic velocity between mole fractions of 0.3 and 0.6 in *N*-methylacetamide supports this. Apart from this, dispersion and dipolar forces between these two weakly protic and unlike solvents may also give rise to negative $\Delta\eta$ values.

On the other hand, the *N*-methylacetamide + water system exhibits a sharp positive deviation of $\Delta\eta$ over the entire mole fraction range and over the three temperatures investigated (Figure 2). As the temperature increases, the $\Delta\eta$ values decrease. These positive $\Delta\eta$ values indicate specific hydrogen bond interactions between *N*-methylacetamide and water molecules. This is also supported by the excess molar volume studies as reported above. With the rise in temperature, these interactions decrease and the system approaches ideal behavior.

Isentropic Compressibility Changes. The results of deviations in isentropic compressibility versus mole fraction of *N*-methylacetamide are given in Figure 3 for *N*-methylacetamide + 2-methoxyethanol and *N*-methylacetamide + water systems, respectively. For both the systems, the values of $\Delta\kappa_s$ are negative over the entire composition range and at all the three temperatures studied. This indicates that the mixtures are more compressible than the corresponding ideal mixture. Due to these interactions, the ultrasonic velocity increases and the compressibility of these solutions decreases until the minima are reached and then these parameters follow the reverse trend.

In the case of *N*-methylacetamide + 2-methoxyethanol, all the three excess parameters are negative. Moreover, the V^E and $\Delta\kappa_s$ values become more negative as temperature increases. All these point to a possible structural effect in this system.

From the above considerations, it is clear that there is a strong association in the *N*-methylacetamide + water mixture, and this interaction may be accompanied by a minor disruption of water and/or *N*-methylacetamide structure. On the other hand, the interaction between *N*-methylacetamide and 2-methoxyethanol seems to be relatively weak. However, the sharp negative viscosity deviations also indicate that *N*-methylacetamide may undergo a structure-breaking effect when mixed with 2-methoxyethanol.

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