

Volumetric, viscometric and refractive index behaviour of amino acids in aqueous glycerol at different temperatures

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Abstract: Densities, ρ , viscosities, η , and refractive indices, n_D , of solutions of some amino acids (glycine, DL-alanine, DL- α -amino-*n*-butyric acid, L-valine and L-leucine) in the concentration range 0.02 to 0.10 *m* in 5 % (v/v) aqueous glycerol were determined at 298.15, 303.15, 308.15 and 313.15 K. These experimental data were used to calculate the apparent molar volumes, ϕ_v , the infinite dilution apparent molar volumes, ϕ_v^0 , the partial molar volumes of transfer, $\phi_v^0(\text{tr})$, of the amino acids from aqueous to aqueous glycerol solution, as well as the viscosity *A* and *B* coefficients of the Jones–Dole equation of the amino acids. The free energies of activation of viscous flow, $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ per mole of solvent and solute, respectively, were obtained by application of the transition–state theory to the *B* coefficient data and the corresponding activation enthalpy, ΔH^* , and entropy, ΔS^* , were also determined. The ϕ_v^0 , *B* coefficients and $\Delta\mu_2^{0\#}$ were found to vary linearly with increasing number of carbon atoms in the alkyl chain of the amino acids, and they were split into contributions from the zwitterionic end groups (NH_3^+ , COO^-) and methylene (CH_2) groups of the amino acids. The experimental values of the refractive indices, n_D , were used to calculate the molar refractive indices, R_D , of the amino acids + aqueous glycerol ternary mixtures. The results were interpreted in the light of the solute–solvent and solute–solute interactions in the mixed solvents.

Keywords: apparent molar volumes, transfer volumes, viscosity *B*-coefficient, activation parameters, side-chain contributions.

INTRODUCTION

Hydration of proteins is an important factor responsible for maintaining their native structures in aqueous solutions. The specific interactions of water with various functional groups on the protein, as well as other solvent–related effects, contribute to the formation of the stable folded structure of proteins in solutions.¹ As proteins are complex macromolecules, the direct study of these important protein–water interactions is difficult. The small amino acid molecules incorporate some of the structural

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features found in proteins and have been used as model compounds for specific aspects of proteins in aqueous solution.^{2,3} Amino acids are basic component of proteins and are considered to be one of the important model compounds of protein molecules, which participate in all the physiological processes of living cells.

The properties of amino acids in aqueous alcohol solutions have been studied by some workers⁴⁻⁶ in order to obtain a better understanding of solute-solvent interactions and the role of alcohol on the conformational stability of proteins.

It has been reported^{7,8} that polyhydric alcohols increase the thermal stability of proteins or reduce the extent of their denaturation by other reagents. The properties of solutions of polyols in aqueous and mixed solutions are important in many areas of applied chemistry and are essential for understanding the chemistry of biological systems^{9,10} and act as a vehicles for pharmaceuticals or cosmetics when introduced into living organisms. Glycerol is found as a primary biomolecule in the intestines, as a product of lipids, and also in the liver, where it participates in the metabolism of glucose.⁶ These considerations led us to investigate the interactions of amino acids in aqueous glycerol solution at different temperatures.

As a part of ongoing studies^{4,11,12} on the thermodynamic and transport properties of amino acids in various aqueous mixed solvents, the densities, ρ , viscosities, η and refractive indices, n_D of 5 % v/v aqueous glycerol (mixed solvent) and of 0.02, 0.04, 0.06, 0.08, and 0.10 *m* (mol kg⁻¹) amino acids (glycine (Gly), DL-alanine (Ala), DL- α -amino-*n*-butyric acid (Abu), L-valine (Val), and L-leucine (Leu)) in aqueous glycerol at 298.15, 303.14, 308.15, and 313.15 K are reported here. The experimental values of ρ and η were used to estimate the apparent molar volume, ϕ_v , the partial molar volume at infinite dilution, ϕ_v^0 , the partial molar volume of transfer, $\phi_v^0(\text{tr})$, and the viscosity *A* and *B* coefficients of the Jones-Dole¹³ equation. Free energies of activation of viscous flow, $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ per mole of solvent (mixed) and solute (amino acid), respectively, were obtained by employing the transition-state theory¹⁴ to the *B* coefficient data and the corresponding activation enthalpy, ΔH^* , and entropy, ΔS^* , were also estimated. The experimental values of n_D were used to compute the molar refractivity, R_D , of the ternary mixtures under study. The contributions of the charged end groups (NH₃⁺, COO⁻) and CH₂ groups of the side-chain of the amino acids to ϕ_v^0 , the *B* coefficients and $\Delta\mu_2^{0\#}$ were also estimated. All these parameters were used to interpret the solute-solute and solute-solvent/cosolvent (glycerol) interactions in the present ternary mixtures.

EXPERIMENTAL

Glycine and DL-alanine were the same as used in previous work¹² and were used without further purification, except drying over P₂O₅ for 72 h. DL- α -amino-*n*-butyric acid (CDH, 99 %), L-valine (Loba Chemicals, 99 %), and L-leucine (Thomas Baker, 99 %) were recrystallized from ethanol + water mixtures and dried over P₂O₅ in a desiccator for 72 h before use. Glycerol (Merck, 98 %) was purified as described in the literature.¹⁵ Aqueous glycerol (5 % v/v) mixed solvent was used to prepare 0.02, 0.04, 0.06, 0.08, and 0.10 *m* amino acid solutions. Deionized and doubly dis-

tilled water was used for the preparation of the solutions. All solutions of the ternary mixtures were freshly prepared and kept in airtight bottles to minimize the absorption of atmospheric moisture and carbon dioxide. To prevent the formation of air bubbles, all solutions were preheated to 5 °C above the measuring temperatures before taking the reading. A Precisa XB-220A (Swiss make) electronic balance with an accuracy of ± 0.0001 g was used for the weighings. Densities of aqueous glycerol and those of the five amino acids in this mixed solvent were measured at 298.15, 303.15, 308.15 and 313.15 K, using a single capillary pycnometer of bulb capacity 8×10^{-3} dm³. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated using double distilled water. The pycnometer was kept for about 30 min in an electronically controlled thermostated water bath in order to minimize thermal fluctuations and the position of the liquid level on the capillary was noted. For the viscosity measurements, a suspended-level Ubbelohde type¹⁶ viscometer with a flow time of 300 s for water at 298.15 K was employed. The viscometer was calibrated with pure water and the viscosities were averaged from three readings for each solution. The accuracy in the density and viscosity measurements were found to be ± 0.01 kg m⁻³ and 3×10^{-6} N m⁻² s, respectively. The refractive indices were measured with the aid of an Abbe-refractometer to an accuracy of ± 0.0001 . The calibration of the refractometer was done by measuring the refractive indices of pure water and benzene at a known temperature. All necessary precautions were taken during the measurements of ρ , η and n_D . The desired temperatures of the solutions for the measurements of ρ , η and n_D were maintained in an electronically controlled thermostated water bath (Julabo, Germany) to an accuracy of ± 0.02 K.

RESULTS AND DISCUSSION

The densities, ρ , viscosities, η and refractive indices, n_D data measured for aqueous glycerol and for the 0.02, 0.04, 0.06, 0.08 and 0.10 molal solutions of the five amino acids in aqueous glycerol at 298.15, 303.15, 308.15, and 313.15 K are listed in Table I. The apparent molar volumes, ϕ_v , of the amino acids in the ternary solutions can be calculated from the solutions densities, ρ , by the relation:

$$\phi_v = (M/\rho) - 1000 (\rho - \rho_0)/(m\rho\rho_0) \quad (1)$$

where M and m are, respectively, the molar mass and molality of the amino acids, and ρ_0 is the density of the solvent (aqueous glycerol). The ϕ_v values of the amino acids as functions of molality and temperature are given in Table II. The apparent molar volumes of the amino acids were found to be a linear function of molality over the studied concentration range. Hence, the apparent molar volumes at infinite dilution, ϕ_v^0 (also known as the partial molar volume at infinite dilution) of the amino acids were obtained from the linear least-squares fit of the ϕ_v data to the equation:

$$\phi_v = \phi_v^0 + S_v^* m \quad (2)$$

ϕ_v^0 provides information regarding solute-solvent interactions; S_v^* is the experimental slope, which is some times considered to be the volumetric pairwise interaction coefficient¹⁷ and is a measure of solute-solute interactions and m is the molality of the solute (amino acid). The regression coefficients ϕ_v^0 and S_v^* of Eq. (2) for the amino acids in aqueous glycerol at different temperatures are presented in Table III. The transfer volumes, $\phi_{v(tr)}^0$ of the amino acids from water to aqueous

glycerol solution, also included in Table III, were calculated from the relation:

$$\phi_{\nu}^0(\text{tr}) = \phi_{\nu}^0(\text{aqueous glycerol}) - \phi_{\nu}^0(\text{aqueous}) \quad (3)$$

where ϕ_{ν}^0 (aqueous) values at 298.15, 308.15 and 313.15 K were taken from the literature.¹⁸

TABLE I. Values of density, ρ , viscosity, η , and refractive index, n_D , of the amino acids in aqueous glycerol at 298.15, 303.15, 308.15 and 313.15 K

$m/\text{mol kg}^{-1}$	298.15 K	303.15 K	308.15 K	313.15 K
Gly + aqueous glycerol				
$\rho/\text{kg m}^{-3}$				
0.00	1012.3	1010.8	1009.3	1007.8
0.02	1009.4	1007.8	1005.9	1004.0
0.04	1010.3	1008.6	1006.6	1004.8
0.06	1011.0	1009.3	1007.3	1005.4
0.08	1011.7	1009.9	1007.8	1005.9
0.10	1012.4	1010.6	1008.4	1006.3
$10^{-3} \eta/\text{N m}^{-2} \text{ s}$				
0.00	0.9040	0.8096	0.7304	0.6631
0.02	0.8052	0.8126	0.7353	0.6689
0.04	0.9076	0.8150	0.7376	0.6717
0.06	0.9099	0.8171	0.7391	0.6734
0.08	0.9127	0.8195	0.7408	0.6754
0.10	0.9154	0.8218	0.7417	0.6770
n_D				
0.00	1.3397	1.3304	1.3392	1.3388
0.02	1.3398	1.3395	1.3393	1.3389
0.04	1.3399	1.3397	1.3395	1.3391
0.06	1.3404	1.3400	1.3398	1.3394
0.08	1.3409	1.3405	1.3402	1.3398
0.10	1.3414	1.3410	1.3407	1.3402
Ala + aqueous glycerol				
$\rho/\text{kg m}^{-3}$				
0.00	1012.3	1010.8	1009.3	1007.8
0.02	1009.4	1007.7	1005.9	1004.1
0.04	1010.0	1008.1	1006.3	1004.3
0.06	1010.8	1008.7	1006.8	1004.7
0.08	1011.3	1009.1	1007.3	1005.0
0.10	1012.0	1009.6	1007.8	1006.0

TABLE I. Continued

$m/\text{mol kg}^{-1}$	298.15 K	303.15 K	308.15 K	313.15 K
	$10^{-3} \eta/\text{N m}^{-2} \text{ s}$			
0.00	0.9040	0.8096	0.7304	0.6631
0.02	0.9016	0.8108	0.7338	0.6683
0.04	0.9044	0.8137	0.7366	0.6708
0.06	0.9086	0.8173	0.7402	0.6743
0.08	0.9130	0.8215	0.7437	0.6771
0.10	0.9182	0.8265	0.7486	0.6819
	n_D			
0.00	1.3397	1.3394	1.3392	1.3388
0.02	1.3392	1.3388	1.3384	1.3379
0.04	1.3398	1.3393	1.3389	1.3384
0.06	1.3404	1.3398	1.3394	1.3388
0.08	1.3409	1.3403	1.3399	1.3391
0.10	1.3414	1.3407	1.3402	1.3394
	Abu + aqueous glycerol			
	$\rho/\text{kg m}^{-3}$			
0.00	1012.3	1010.8	1009.3	1007.8
0.02	1009.4	1007.7	1005.9	1004.1
0.04	1009.8	1008.3	1006.7	1005.2
0.06	1010.4	1008.9	1007.4	1005.8
0.08	1011.0	1009.4	1007.8	1006.2
0.10	1011.4	1009.7	1008.1	1006.4
	$10^{-3} \eta/\text{N m}^{-2} \text{ s}$			
0.00	0.9040	0.8096	0.7304	0.6631
0.02	0.8996	0.8092	0.7329	0.6678
0.04	0.9025	0.8131	0.7379	0.6730
0.06	0.9092	0.8193	0.7439	0.6779
0.08	0.9145	0.8249	0.7485	0.6822
0.10	0.9213	0.8293	0.7526	0.6874
	n_D			
0.00	1.3397	1.3394	1.3392	1.3388
0.02	1.3393	1.3389	1.3385	1.3380
0.04	1.3399	1.3395	1.3392	1.3388
0.06	1.3404	1.3401	1.3397	1.3393
0.08	1.3409	1.3405	1.3401	1.3397
0.10	1.3413	1.3408	1.3405	1.3400

TABLE I. Continued

$m/\text{mol kg}^{-1}$	298.15 K	303.15 K	308.15 K	313.15 K
Val + aqueous glycerol				
$\rho/\text{kg m}^{-3}$				
0.00	1012.3	1010.8	1009.3	1007.8
0.02	1009.4	1007.7	1006.0	1004.2
0.04	1009.8	1008.2	1006.5	1004.9
0.06	1010.3	1008.7	1007.1	1005.5
0.08	1010.9	1009.2	1007.6	1006.0
0.10	1011.3	1009.5	1008.1	1006.6
$10^{-3} \eta/\text{N m}^{-2} \text{ s}$				
0.00	0.9040	0.8096	0.7304	0.6631
0.02	0.9117	0.8154	0.7349	0.6660
0.04	0.9217	0.8236	0.7413	0.6716
0.06	0.9331	0.8333	0.7494	0.6767
0.08	0.9473	0.8432	0.7568	0.6827
0.10	0.9573	0.8519	0.7644	0.6881
n_D				
0.00	1.3397	1.3394	1.3392	1.3388
0.02	1.3394	1.3390	1.3396	1.3381
0.04	1.3400	1.3396	1.3391	1.3387
0.06	1.3405	1.3400	1.3396	1.3392
0.08	1.3410	1.3405	1.3401	1.3396
0.10	1.3414	1.3408	1.3405	1.3400
Leu + aqueous glycerol				
$\rho/\text{kg m}^{-3}$				
0.00	1012.3	1010.8	1009.3	1007.8
0.02	1009.5	1007.8	1006.2	1004.4
0.04	1009.9	1008.4	1006.2	1004.7
0.06	1010.2	1008.9	1006.5	1005.1
0.08	1010.6	1009.1	1006.9	1005.6
0.10	1010.9	1009.4	1007.2	1006.0
$10^{-3} \eta/\text{N m}^{-2} \text{ s}$				
0.00	0.9040	0.8096	0.7304	0.6631
0.02	0.8959	0.9054	0.7304	0.6655
0.04	0.9041	0.8132	0.7375	0.6722
0.06	0.9129	0.8203	0.7447	0.6796
0.08	0.9214	0.8301	0.7541	0.6877
0.10	0.9361	0.8432	0.7652	0.6975

TABLE I. Continued

$m/\text{mol kg}^{-1}$	298.15 K	303.15 K	308.15 K	313.15 K
	n_D			
0.00	1.3397	1.3394	1.3392	1.3388
0.02	1.3396	1.3391	1.3388	1.3382
0.04	1.3402	1.3398	1.3392	1.3388
0.06	1.3406	1.3402	1.3396	1.3393
0.08	1.3410	1.3406	1.3400	1.3397
0.10	1.3413	1.3409	1.3403	1.3400

TABLE II. Values of the apparent molar volume, ϕ_v , for the amino acids in aqueous glycerol at 298.15, 303.15, 308.15 and 313.15 K

$m/\text{mol kg}^{-1}$	$10^{-4} \phi_v/\text{m}^3 \text{mol}^{-1}$			
	298.15 K	303.15 K	308.15 K	313.15 K
	Gly + aqueous glycerol			
0.02	2.1599	2.2144	2.4174	2.6068
0.04	1.2315	1.2907	1.4047	1.4921
0.06	0.95416	0.98776	1.0813	1.1496
0.08	0.81760	0.85586	0.92650	0.98646
0.10	0.73176	0.76633	0.83675	0.89377
	Ala + aqueous glycerol			
0.02	2.259	2.4050	2.5493	2.7045
0.04	1.4432	1.5496	1.6221	1.7496
0.06	1.1250	1.2255	1.2970	1.3955
0.08	1.0025	1.0903	1.1293	1.2305
0.10	0.90951	0.99958	1.0309	1.0605
	Abu + aqueous glycerol			
0.02	2.4354	2.5345	2.6787	2.8534
0.04	1.6289	1.6323	1.6602	1.6636
0.06	1.3281	1.3305	1.3411	1.3518
0.08	1.1781	1.1924	1.2130	1.2213
0.10	1.1072	1.1297	1.1405	1.1672
	Val + aqueous glycerol			
0.02	2.5666	2.6660	2.7859	2.9412
0.04	1.7699	1.7981	1.8512	1.8798
0.06	1.4845	1.5036	1.5229	1.5422
0.08	1.3292	1.3561	1.3708	1.3856
0.10	1.2558	1.2875	1.2797	1.2817

TABLE II. Continued

$m/\text{mol kg}^{-1}$	$10^{-4} \phi_v^0/\text{m}^3 \text{mol}^{-1}$			
	298.15 K	303.15 K	308.15 K	313.15 K
Leu + aqueous glycerol				
0.02	2.6664	2.7561	2.8266	3.0066
0.04	1.8850	1.8887	2.0658	2.0700
0.06	1.6402	1.6102	1.7619	1.7486
0.08	1.5053	1.5078	1.5973	1.572
0.10	1.4340	1.4363	1.5083	1.4809

TABLE III. Values of the limiting apparent molar volume, ϕ_v^0 , experimental slope, S_v^* , ϕ_v^0 (water), and volume transfer, $\phi_{v(\text{tr})}^0$, for the amino acids in aqueous glycerol at 298.15, 303.15, 308.15 and 313.15 K

	298.15 K	303.15 K	308.15 K	313.15 K
Gly + aqueous glycerol				
$10^{-4} \phi_v^0/\text{m}^3 \text{mol}^{-1}$	2.1599 ± 0.31	2.2222 ± 0.31	2.4250 ± 0.34	2.6051 ± 0.38
$10^{-3} S_v^*/\text{m}^3 \text{mol}^{-2} \text{kg}$	-1.633 ± 0.48	-1.663 ± 0.48	-1.8177 ± 0.52	$\pm 1.9637 \pm 0.58$
$10^{-5} \phi_v^0(\text{water})/\text{m}^3 \text{mol}^{-1}$	4.3200 ^a		4.3790 ^a	4.4170 ^a
$10^{-4} \phi_{v(\text{tr})}^0/\text{m}^3 \text{mol}^{-1}$	1.7279		1.9871	2.1634
Ala + aqueous glycerol				
$10^{-4} \phi_v^0/\text{m}^3 \text{mol}^{-1}$	2.3178 ± 0.29	2.4334 ± 0.29	2.5829 ± 0.31	2.7684 ± 0.30
$10^{-3} S_v^*/\text{m}^3 \text{mol}^{-2} \text{kg}$	-1.5989 ± 0.44	-1.6270 ± 0.44	-1.7561 ± 0.46	-1.8942 ± 0.46
$10^{-5} \phi_v^0(\text{water})/\text{m}^3 \text{mol}^{-1}$	6.0490 ^a		6.1010 ^a	6.1200 ^a
$10^{-4} \phi_{v(\text{tr})}^0/\text{m}^3 \text{mol}^{-1}$	1.7120		1.9728	2.1564
Abu + aqueous glycerol				
$10^{-4} \phi_v^0/\text{m}^3 \text{mol}^{-1}$	2.4707 ± 0.27	2.5418 ± 0.31	2.6672 ± 0.35	2.7997 ± 0.42
$10^{-3} S_v^*/\text{m}^3 \text{mol}^{-2} \text{kg}$	-1.5514 ± 0.41	-1.6225 ± 0.47	-1.7595 ± 0.53	-1.9051 ± 0.64
$10^{-5} \phi_v^0(\text{water})/\text{cm}^3 \text{mol}^{-1}$	7.6350 ^a		7.6610 ^a	7.6340 ^a
$10^{-4} \phi_{v(\text{tr})}^0/(\text{m}^3 \cdot \text{mol}^{-1})$	1.7071		1.9011	2.0363
Val + aqueous glycerol				
$10^{-4} \phi_v^0/\text{m}^3 \cdot \text{mol}^{-1}$	2.5996 ± 0.26	2.6816 ± 0.29	2.8095 ± 0.31	2.9496 ± 0.36
$10^{-3} S_v^*/\text{m}^3 \cdot \text{mol}^{-2} \text{kg}$	-1.5257 ± 0.40	-1.5939 ± 0.44	-1.7402 ± 0.48	$\pm 1.8997 \pm 0.54$
$10^{-5} \phi_v^0(\text{water})/\text{m}^3 \text{mol}^{-1}$	9.0980 ^a		9.1550 ^a	9.1670 ^a
$10^{-4} \phi_{v(\text{tr})}^0/\text{mol}^{-1}$	1.6898		1.8940	2.0329
Leu + aqueous glycerol				
$10^{-4} \phi_v^0/\text{cm}^3 \text{mol}^{-1}$	2.6781 ± 0.26	2.7444 ± 0.30	2.8820 ± 0.25	3.0384 ± 0.31
$10^{-3} S_v^*/\text{m}^3 \text{mol}^{-2} \text{kg}$	-1.4165 ± 0.39	-1.5040 ± 0.46	-1.5463 ± 0.37	-1.7659 ± 0.47
$10^{-5} \phi_v^0(\text{water})/\text{m}^3 \text{mol}^{-1}$	1.0777 ^a		1.0841 ^a	1.0900 ^a
$10^{-4} \phi_{v(\text{tr})}^0/\text{m}^3 \text{mol}^{-1}$	1.6004		1.7979	1.9484

^aData taken from Reference 18

The alkyl chain of the homologous series of amino acids investigated in this work are as follows: CH₂- (Gly), CH₃CH- (Ala), CH₃CH₂CH- (Abu), CH₃CH₂CHCH- (Val) and CH₃CH₂CHCH₂CH- (Leu). It was observed that the values of ϕ_v^0 of the present amino acids in aqueous glycerol vary linearly with the number of carbon atoms, n_C , in their alkyl chains at a given temperature. Similar linear correlation for the homologous series of α -amino acids has also been reported in aqueous¹⁹ and aqueous glucose¹² solutions. Thus, a linear regression analysis of the ϕ_v^0 values as a function of n_C is represented by

$$\phi_v^0 = \phi_v^0(\text{NH}_3^+, \text{COO}^-) + n_C \phi_v^0(\text{CH}_2) \quad (4)$$

where $\phi_v^0(\text{NH}_3^+, \text{COO}^-)$ and $\phi_v^0(\text{CH}_2)$ are the zwitterionic end groups and the methylene side group contributions to ϕ_v^0 , respectively. These values are included in Table IV. The values of $\phi_v^0(\text{CH}_2)$ obtained by this procedure characterize the mean contribution of CH and CH₃ groups to the ϕ_v^0 of the amino acids. As suggested by Hakin *et al.*,^{20,21} the contribution of the other alkyl chains of the amino acids, reported in Table IV, were calculated as follows:

TABLE IV. Contribution of (NH₃⁺, COO⁻) and (CH₂) groups to the limiting apparent molar volume, ϕ_v^0 , volume transfer, $\phi_{v(\text{tr})}^0$, B coefficient and $\Delta\mu_2^{0\#}$, of the amino acids in aqueous glycerol at 298.15, 303.15, 308.15 and 313.15 K

	298.15 K	303.15	308.15	313.15 K
	$10^{-5} \phi_v^0/\text{m}^3 \text{mol}^{-1}$			
(NH ₃ ⁺ ,COO ⁻)	20.4973	21.3691	23.3114	25.1797
(CH)	0.6591	0.6463	0.5702	0.5237
Gly(CH ₂)	1.3182	1.2926	1.1406	1.0476
(CH ₃)	1.9773	1.9389	1.7109	1.5714
Ala (CH ₃ CH-)	2.6364	2.5852	2.2812	2.0951
Abu (CH ₃ CH ₂ CH-)	3.9546	3.8778	3.4217	3.1427
Val (CH ₃ CH ₂ CHCH-)	5.2728	5.1705	4.5623	4.1903
Leu (CH ₃ CH ₂ CHCH ₂ CH-)	6.5910	6.4631	5.7029	5.2379
	$10^{-5} \phi_{v(\text{tr})}^0/\text{m}^3 \text{mol}^{-1}$			
(NH ₃ ⁺ ,COO ⁻)	17.104		20.4774	22.3360
(CH ₂)	-0.2781		-0.4572	-0.5537
	$10^{-1} B/\text{dm}^3 \text{mol}^{-1}$			
(NH ₃ ⁺ ,COO ⁻)	-0.1927	-0.8658	-1.7145	-1.7019
(CH ₂)	1.9448	1.9609	2.0008	1.8144
	$\Delta\mu_2^{0\#}/\text{kJ mol}^{-1}$			
(NH ₃ ⁺ ,COO ⁻)	31.6484	23.9017	98.7700	16.7477
(CH ₂)	27.8079	28.4165	31.5662	27.0737

$$\phi_v^0(\text{CH}_3) = 1.5 \phi_v^0(\text{CH}_2) \quad (5)$$

$$\phi_v^0(\text{CH}) = 0.5 \phi_v^0(\text{CH}_2) \quad (6)$$

To pursue the analysis of the interactions of amino acids in aqueous glycerol through a viscometric study, the viscosity data, Table I, obtained for both solvent and solutions as a function of amino acid concentration and temperature were used to calculate the B coefficient of the viscosity for all five amino acids in aqueous glycerol solution using the Jones–Dole equation:¹³

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (7)$$

where c is the molarity (calculated from molality) of the amino acid in solution, η_r is the relative viscosity, η and η_0 are the viscosities of the solution and solvent (aqueous glycerol), respectively. A , the Falkenhagen coefficient, is a measure of solute–solute interactions theoretically and B , the Jones–Dole coefficient, is empirical and is a function of the solute–solvent interactions. The viscosity A and B coefficients were obtained from the intercepts and slopes of the plots of $(\eta_r - 1)/c^{1/2}$ versus $c^{1/2}$ and are given in Table V. According to Eyring and co-workers,²² the free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{0\#}$, can be calculated using the Equation:

TABLE V. Values of the A and B coefficients of the Jones–Dole Equation, free energy of activation for the solvent, $\Delta\mu_1^{0\#}$, and solute, $\Delta\mu_2^{0\#}$, for the amino acids in aqueous glycerol at 298.15, 303.15, 308.15 and 313.15 K

	298.15 K	303.15 K	308.15 K	313.15 K
Gly + aqueous glycerol				
$10^{-2} A/\text{dm}^{3/2} \text{ mol}^{-1/2}$	-1.4992	-0.81535	4.4859	5.7317
$10^{-1} B/\text{dm}^3 \text{ mol}^{-1}$	1.7208	1.2314	1.5332	2.6890
$\Delta\mu_1^{0\#}/\text{kJ mol}^{-1}$	9.2610	9.1421	9.0330	8.9318
$10^1 \Delta\mu_2^{0\#}/\text{kJ mol}^{-1}$	5.8748	5.3575	4.2049	4.6570
Ala + aqueous glycerol				
$10^{-2} A/\text{dm}^{3/2} \text{ mol}^{-1/2}$	-7.4921	-3.6603	-0.7728	2.2946
$10^{-1} B/\text{dm}^3 \text{ mol}^{-1}$	3.8926	3.1440	2.5978	1.9226
$\Delta\mu_1^{0\#}/(\text{kJ mol}^{-1})$	9.2610	9.1421	9.0330	8.9318
$10^1 \Delta\mu_2^{0\#}/\text{kJ mol}^{-1}$	8.9943	8.2448	7.6841	6.9998
Abu + aqueous glycerol				
$10^{-2} A/\text{dm}^{3/2} \text{ mol}^{-1/2}$	-11.4130	-7.1796	-3.4424	-1.9810
$10^{-1} B/\text{dm}^3 \text{ mol}^{-1}$	5.4750	4.7675	4.2271	3.6935
$\Delta\mu_1^{0\#}/\text{kJ mol}^{-1}$	9.2610	9.1421	9.0330	8.9318
$10^1 \Delta\mu_2^{0\#}/\text{kJ mol}^{-1}$	11.3179	10.5992	10.1605	9.72463
Val + aqueous glycerol				
$10^{-2} A/\text{dm}^{3/2} \text{ mol}^{-1/2}$	-4.9291	-4.5600	-4.3811	-4.0107

TABLE V. Continued

	298.15 K	303.15 K	308.15 K	313.15 K
$10^{-1} B/\text{dm}^3 \text{ mol}^{-1}$	7.4580	6.6671	6.0097	5.0390
$\Delta\mu_1^{0\#}/\text{kJ mol}^{-1}$	9.2610	9.1421	9.0330	8.9318
$10^1 \Delta\mu_2^{0\#}/\text{kJ mol}^{-1}$	14.1461	13.3720	12.8166	11.8184
Leu + aqueous glycerol				
$10^{-2} A/\text{dm}^{3/2} \text{ mol}^{-1/2}$	-1.9861	-1.6905	-1.2297	-8.7473
$10^{-1} B/\text{dm}^3 \text{ mol}^{-1}$	9.6622	9.2745	8.4513	7.7828
$\Delta\mu_1^{0\#}/\text{kJ mol}^{-1}$	9.2610	9.1421	9.0330	8.9318
$\Delta\mu_2^{0\#}/\text{kJ mol}^{-1}$	17.2029	17.0021	17.4218	15.7846

$$\eta_0 = (h N_A / \bar{V}_1^0) \exp(\Delta\mu_1^{0\#} / RT) \quad (8)$$

where h , N_A , and \bar{V}_1^0 are the Planck constant, Avogadro number and partial molar volumes of the solvent, respectively.

Feakins and co-workers¹⁴ applied the transition state treatment of relative viscosity to solutions and showed that the B coefficient is given as:

$$B = (\bar{V}_1^0 - \bar{V}_2^0) / 1000 + \bar{V}_1^0 [(\Delta\mu_2^{0\#} - \Delta\mu_1) / RT] / 1000 \quad (9)$$

where $\bar{V}_2^0 (= \phi_v^0)$ is the partial molar volume of the solute (amino acid) and $\Delta\mu_2^{0\#}$ is the contribution per mole of the solute to the free energy of activation of viscous flow of the solution. On rearranging Eqs. (8) and (9), the values of $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ are obtained as:

$$\Delta\mu_1^{0\#} = RT \ln(\eta_0 \bar{V}_1^0 / h N_A) \quad (10)$$

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + (RT / \bar{V}_1^0) [1000 B - (\bar{V}_1^0 - \bar{V}_2^0)] \quad (11)$$

The values of $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ for the amino acids in aqueous glycerol at 298.15, 303.15, 308.15 and 313.15 K are listed in Table V. The total free energy of activation of viscous flow of the solution, $\Delta\mu^{0*}$, was calculated from the relation:

$$\Delta\mu^{0*} = n_1 \Delta\mu_1^{0\#} + n_2 \Delta\mu_2^{0\#} \quad (12)$$

where n_1 and n_2 are the number of moles of mixed solvent and solute, respectively. The values of $\Delta\mu^{0*}$ are presented in Table VI. The thermodynamic data, ΔH^* and ΔS^* of all the amino acids in aqueous glycerol were calculated using the following Equation and are listed in Table VI:

$$\Delta\mu^{0*} = \Delta H^* - T\Delta S^* \quad (13)$$

The ΔH^* and ΔS^* values were obtained from the intercepts and slopes of the plots of $\Delta\mu^{0*}$ versus T . ΔH^* and ΔS^* values have proved useful in yielding structural information about solute species and about solute-solvent interactions.

TABLE VI. Values of the energy of activation of the solution, $\Delta\mu^{0*}$, enthalpy, ΔH^* , and entropy, ΔS^* , for the amino acids in aqueous glycerol at 298.15, 303.15, 308.15 and 313.15 K

$m/\text{mol kg}^{-1}$	$\Delta\mu^{0*}/\text{kJ mol}^{-1}$				ΔH^* kJ mol^{-1}	$10^{-2} \Delta S^*$ kJ mol^{-1}
	298.15K	303.15 K	308.15 K	313.15 K		
Gly + aqueous glycerol						
0.00	5.0277	4.9631	4.9039	4.8490	8.58	1.19
0.02	5.0864	5.0167	4.9460	4.8955	8.92	1.29
0.04	5.1452	5.0703	4.9800	4.9421	9.26	1.38
0.06	5.2039	4.1239	5.0301	4.9887	9.61	1.48
0.08	5.2627	5.1774	5.0721	5.0353	9.95	1.56
0.10	5.3214	5.2310	5.1142	5.0818	10.30	1.67
Ala + aqueous glycerol						
0.00	5.0277	4.9631	4.9039	4.8490	8.58	1.19
0.02	5.1176	5.0456	4.9807	4.9190	9.06	1.32
0.04	5.2076	5.1280	5.0576	4.9890	9.53	1.45
0.06	5.2975	5.2105	5.1344	5.0590	10.01	1.58
0.08	5.3874	5.2929	5.2113	5.1290	10.49	1.71
0.10	5.4774	5.3754	5.2881	5.1990	10.97	1.85
Abu + aqueous glycerol						
0.00	5.0277	4.9631	4.9039	4.8490	8.58	1.19
0.02	5.1409	5.0691	5.0055	4.9462	9.00	1.30
0.04	5.2540	5.1751	5.1071	5.0435	9.42	1.40
0.06	5.3672	5.2811	5.2087	5.1407	9.85	1.50
0.08	5.4804	5.3871	5.3103	5.2380	10.27	1.61
0.10	5.5936	5.4931	5.4119	5.3352	10.69	1.71
Val + aqueous glycerol						
0.00	5.0277	4.9631	4.9039	4.8490	8.58	1.19
0.02	5.1691	5.0968	5.0321	4.9672	9.17	1.34
0.04	5.3106	5.2306	5.1602	5.0853	9.76	1.49
0.06	5.4521	5.3643	5.2884	5.2035	10.35	1.64
0.08	5.5935	5.4980	5.4166	5.3217	10.94	1.79
0.10	5.7350	5.6317	5.5447	5.4399	11.53	1.94
Leu + aqueous glycerol						
0.00	5.0277	4.9631	4.9039	4.8490	8.58	1.19
0.02	5.1997	5.1332	6.0781	5.0068	8.98	1.27
0.04	5.3717	5.3032	5.2523	5.1647	9.38	1.34
0.06	5.5438	5.4732	5.4266	5.3225	9.78	1.42
0.08	5.7158	5.6432	5.6008	5.4804	10.10	1.50
0.10	5.8878	5.8132	5.7750	5.6382	10.59	1.57

The molar refractivity, R_D , of the mixtures under study can be calculated from the refractive indices, n_D , data using the Lorentz–Lorenz Equation:

$$R_D = [(n_D^2 - 1) / (n_D^2 + 2)] \left(\sum_{i=1}^3 x_i M_i / \rho \right) \quad (14)$$

Volumetric properties, such as ϕ_v , ϕ_v^0 and $\phi_{v(tr)}^0$, are regarded as sensitive tools for the understanding of interactions in solutions. The apparent molar volume can be considered to be the sum of the geometric volume of the solute molecule and changes in the solvent volume due to its interaction with the solute. Table II shows that the values of ϕ_v are large and positive for all five systems, suggesting strong solute–solvent interactions. The apparent molar volumes were found to decrease with increasing concentration of amino acid in aqueous glycerol and increase with increasing temperature for all the amino acids under study. Table III shows that the values of ϕ_v^0 are large and positive for all the amino acids at all the investigated temperatures, suggesting the presence of strong solute–solvent interaction.²³ Furthermore, at each temperature, the values of ϕ_v^0 increase with increasing number of carbon atoms (or size of alkyl group) from Gly to Leu. A similar increase in ϕ_v^0 with increasing number of carbon atoms for amino acids in aqueous glycerol, at 298.15 K, was also reported by Banipal *et al.*⁶ The behavior of ϕ_v^0 for the present systems can be explained employing the cosphere model, proposed by Friedman and Krishnan,²⁴ according to which the effect of overlap of hydration cospheres is destructive. Mishra *et al.*²⁵ using this model observed that an overlap of cospheres of two ionic species causes an increase in volume, whereas an overlap of hydrophobic–hydrophobic groups and ion–hydrophobic groups results in a net decrease in volume. Thus, the observed positive ϕ_v^0 values, Table III, is due to the effect of ion–hydrophilic interactions (between zwitterionic centres of the amino acids and the –OH groups of glycerol) which predominate over ion–hydrophobic interactions (between zwitterionic centres and non-polar parts of glycerol) and hydrophobic–hydrophobic interactions (between non-polar parts of the amino acids and glycerol) and increase in the order Gly < Ala < Abu < Val < Leu at each investigated temperature. This indicates the trend of the strength of the solute–solvent interactions in the ternary mixtures. The values of ϕ_v^0 were found to increase with increasing temperature. This may be attributed to the release of some solvation molecules from the loose solvation layers of the solutes in solution. Furthermore, the S_v^* values, Table III, are negative for all five amino acids, suggesting weak solute–solvent interactions.

Table III shows that the transfer volumes, $\phi_{v(tr)}^0$ of the amino acids from aqueous glycerol to aqueous solution at the three investigated temperatures (298.15, 308.15 and 313.15 K) are positive and decrease as the size of the alkyl chain of the amino acid increases from Gly to Leu. Banipal and co-workers⁶ also reported a decrease in the $\phi_{v(tr)}^0$ value with increasing size of the non-polar side chain of amino acids in aqueous glycerol. The introduction of a CH₃ group in Ala, a CH₃CH₂ group in Abu, a

(CH₃)₂CH group in Val and a (CH₃)₂CHCH₂ group in Leu provides an additional tendency of hydrophilic–hydrophobic and hydrophobic–hydrophobic interactions causing greater electrostriction of water molecules, resulting in a decrease of the $\phi_{v,0}^{0}(\text{tr})$ values from Gly to Leu. This is in good agreement with the conclusion drawn by Li *et al.*²⁶ in a study of Gly, Ala and Ser in aqueous glycerol at 298.15 K.

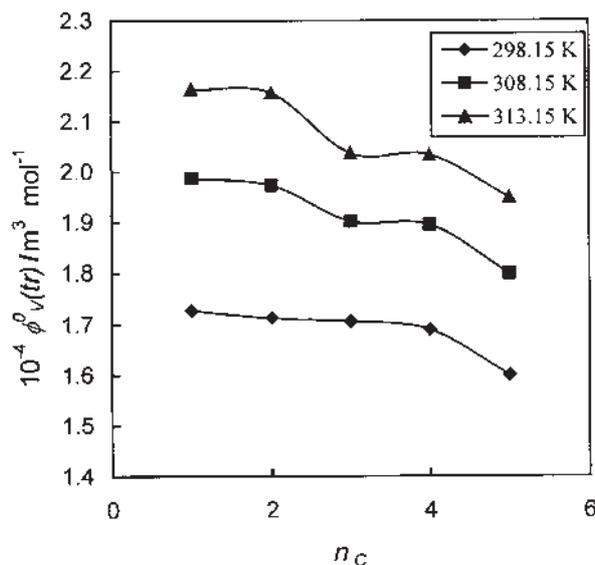


Fig. 1. Variation of $\phi_{v,0}^{0}(\text{tr})$ with the number of carbon atoms in the alkyl chain n_C , for all amino acids + aqueous glycerol at 298.15, 308.15 and 313.15 K.

Moreover, the contribution of the zwitterionic end group (NH_3^+ , COO^-) and a methylene group (CH_2), calculated using Eq. (4), and the contributions of other alkyl chains of the amino acids, calculated using Eqs. (5) and (6), to $\phi_{v,0}^0$ are included in Table IV. It should be noted that the $\phi_{v,0}^0(\text{CH}_2)$ value obtained here is the mean contribution of the $\phi_{v,0}^0(\text{CH})$ and $\phi_{v,0}^0(\text{CH}_3)$ values of the amino acids. It is clear, Table IV, that the $\phi_{v,0}^0(\text{NH}_3^+, \text{COO}^-)$ values are much larger than the $\phi_{v,0}^0(\text{CH}_2)$ values at all the investigated temperatures, suggesting that the interactions of the zwitterionic end group (NH_3^+ , COO^-) with glycerol and water are much stronger than those of the (CH_2) groups of the amino acids. Similar results were also reported²⁷ for some α -amino acids in aqueous sodium caprylate solutions.

The $\phi_{v,0}^{0}(\text{tr})$ values for the homologous series of amino acids against the number of carbon atoms, n_C , in their alkyl chains at three different temperatures are shown in Fig. 1. Good linear relations were observed, compared with previous results.⁴ It is evident that the intercepts and slopes of the straight lines represent the contributions of the (NH_3^+ , COO^-) and CH_2 groups to $\phi_{v,0}^{0}(\text{tr})$, respectively. The calculated values of the contribution of $\phi_{v,0}^{0}(\text{tr})(\text{NH}_3^+, \text{COO}^-)$, $\phi_{v,0}^{0}(\text{tr})(\text{CH}_2)$ and those of the alkyl chains of amino acids to $\phi_{v,0}^{0}(\text{tr})$, Table IV, show that $\phi_{v,0}^{0}(\text{tr})(\text{CH}_2)$ is negative and that of the zwitterionic group (NH_3^+ , COO^-) is positive at all the three investigated temperatures. The positive values of $\phi_{v,0}^{0}(\text{tr})$ observed in this work for the amino acids indicate that the effect of the zwitterionic portion of the amino acids

dominates over that of the alkyl chains. These conclusion support the results for the partial molar volume, ϕ_v^0 .

The values of the A and B coefficients of the Jones–Dole Equation are reported in Table V. It can be observed that the B coefficients are larger than the A coefficients, except for Gly at 308.15 and 313.15 K, supporting the behavior of ϕ_v^0 and S_v^* , respectively, both suggesting stronger solute–solvent interactions as compared to solute–solvent interactions. Table V shows that the values of the B coefficients of all five amino acids decrease with increasing temperature, *i.e.*, the dB/dT values are negative. The negative dB/dT values for the present amino acids in aqueous glycerol indicate that these amino acids behave as structure-makers. This is consistent with a previous study¹² of the B coefficient for amino acids in aqueous glucose solution.

Moreover, it is interesting to note that the B coefficients of the studied amino acids show a linear correlation with the partial molar volumes ϕ_v^0 for the amino acids in aqueous glycerol solution. This means:

$$B = A_1 + A_2\phi_v^0 \quad (15)$$

The coefficients A_1 and A_2 are included in Table VII. This correlation is not unexpected, as both the viscosity B coefficient and the partial molar volume reflect the solute–solvent interactions in the solutions. A similar correlation was also used for amino acids in different solvents.^{28,29}

TABELA VII. Values of the A_1 and A_2 coefficients of the amino acids in aqueous glycerol

	A_1	$10^3 A_2$
Gly	0.8768±0.27	– 3.3677±1.15
Ala	1.3605±0.10	– 4.2428±0.41
Abu	1.8037±0.19	– 5.1517±0.74
Val	2.4675±0.13	– 6.6600±0.48
Leu	2.3698±0.08	– 5.2564±0.30

It is evidenced from the data in Table V that the $\Delta\mu_2^{0\#}$ values are positive and much larger than the $\Delta\mu_1^{0\#}$ values. This may be due to the fact that amino acid–solvent interactions in the ground state are stronger than in the transition state. In other words, the solvation of amino acids in the transition state is unfavourable in terms of free energy. Furthermore, as $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$, then according to the Feakins model,¹⁴ the solutes (amino acids) behave as structure-makers. This again supports the behavior of dB/dT for these solutes in aqueous glycerol. The $\Delta\mu_2^{0\#}$ values (Table V) of the amino acids were found to increase from Gly to Leu at a given temperature. This indicates that the solvation of the amino acids in the transition state becomes increasingly unfavorable as the hydrophobicity (number of carbon atoms) of the side chain increases from Gly to Leu.

The values of the activation enthalpy, ΔH^* and entropy, ΔS^* , calculated using Eqs. (12) and (13), of the amino acids + aqueous glycerol mixtures are listed in Ta-

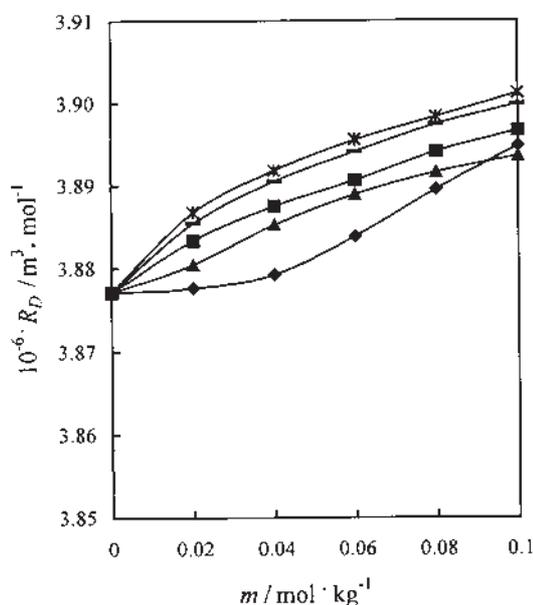


Fig. 2. Variation of R_D , versus C for the ternary mixtures of the amino acids {(\diamond) Gly, (\blacktriangle) Ala, (\blacksquare) Abu, - Val, (\star) Leu} + aqueous glycerol at 298.15 K.

ble VI. The data reveal that the ΔH^* values of the ternary mixtures are positive and increase regularly with increasing concentration of amino acid, thereby, suggesting that the formation of activated species for viscous flow becomes difficult as the amount of amino acid in the mixtures increases. The small values of ΔS^* , which increase with increasing concentration of amino acids, for all the studied mixtures, suggest that the net order of the system decreases as the concentration of amino acid in the mixture increases. Thus, the behavior of ΔS^* supports that of ΔH^* .

The observed values of the refractive index, Table I, increase with increasing concentration of the amino acids in the mixture. This reflects that the refractive index is directly related to the interactions in the mixture. However, a more useful parameter, the molar refractivity of the system, R_D , calculated using Eq. (14), and graphically shown in Fig. 2, increases almost linearly with increasing amount of amino acid in all the ternary mixtures. Since R_D is directly proportional to molecular polarizability, Fig. 2 reveals that the overall polarizability of the systems increases with increasing concentration of amino acid. The R_D values were plotted for a single temperature, as the variation in this parameter with temperature is not large.

ИЗВОД

ВОЛУМЕТРИЈСКО И ВИСКОЗНО КАРАКТЕРИСАЊЕ И ОДРЕЂИВАЊЕ
ИНДЕКСА ПРЕЛАМАЊА АМИНО КИСЕЛИНА У ВОДЕНОМ РАСТВОРУ
ГЛИЦЕРОЛА

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Гуштине, вискозност и индекси преламања раствора неких аминокиселина (глицин, DL-аланин, DL- α -амино-*n*-бутерна киселина, L-валин и L-леуцин) концентрација 0,02–0,10 *m* у 5 % *v/v* воденом раствору глицерола одређиване су на температурама 298,15, 303,15, 308,15 и 313,5 К. Из експерименталних података израчунате су привидне моларне запремине, привидне моларне запремине при бесконачном разблажењу, парцијалне моларне запремине прелаза аминокиселина из водених раствора у водени раствор глицерола, као и *A* и *B* коефицијенти Jones–Dole-ове једначине аминокиселина. Промене слободне енергије активације вискозног тока добијене су применом теорије прелазног стања на *B* коефицијент и одређене су одговарајуће промене енталпије и ентропије активације. Нађено је да се привидна моларна запремина при бесконачном разблажењу, *B* коефицијент и промена слободне енергије растворених аминокиселина линеарно мењају са повећањем броја угљеникових атома у алкилном ланцу аминокиселина и да се раздвајају доприноси цвтерјонског краја NH₃⁺ и COO⁻ група, као и метилenske (CH₂) групе аминокиселина. Из експерименталних вредности индекса преламања израчунате су моларне рефракције тернарних смеша аминокиселина и воденог раствора глицерола. Резултати су интерпретирани са аспекта интеракција растворена супстанца-растварач и растворена супстанца-растворена супстанца у мешаном растварачу.

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