Solubility of polymorphic glycine in mixed solutions with molecular dynamic simulation and thermodynamic analysis.

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1. Details of the Chemicals

Table S1 Details of the Chemicals used in this study.

Chemicals	CAS number	Chemical formula	Source	Purity
Glycine	56-40-6	$C_2H_5NO_2$	Shanghai Aladdin Biochemical	≥0.990
Ammonium Chloride	12125-02-9	NH_4Cl	Shanghai Aladdin Biochemical	≥0.995
Hexamethylenetetramine	100-97-0	$C_6H_{12}N_4$	Shanghai Aladdin Biochemical	≥0.995
Sodium Chloride	67-56-1	CH_4O	Shanghai Macklin Biochemical	≥0.995

2. Infrared spectra and PLS calibration

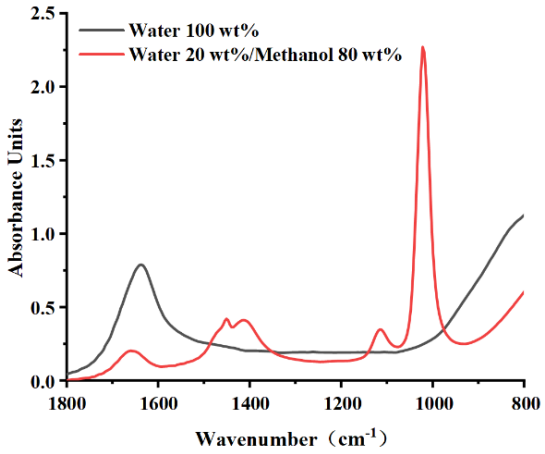


Fig. S1 Infrared spectra of the water and ethanol.

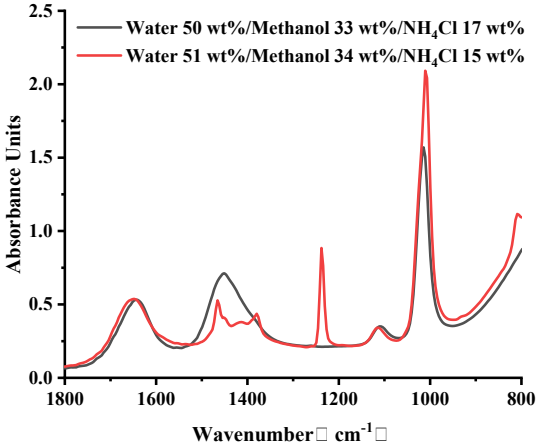


Fig. S2 Infrared spectra of the water-methanol-NH_4Cl and water-methanol-HMTA.

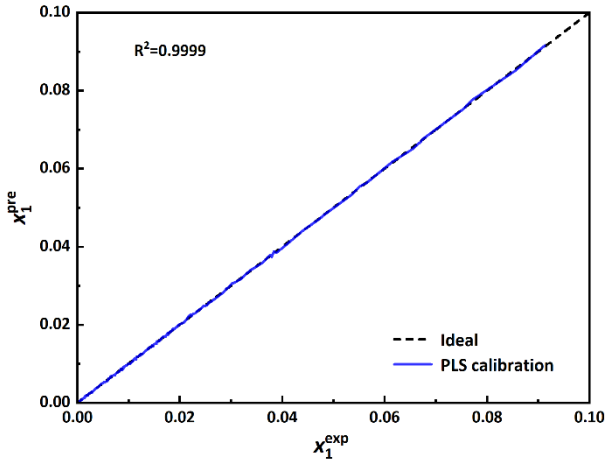


Fig. S3 Predicted versus experimental value of glycine for the training set (x_1 represents the mole fraction of glycine in the mixture).

3. Solubility data of polymorphic glycine

Table S2 Mole fraction solubility of α-form glycine (x_1) in water (x_2)-methanol (x_3) binary solvent mixtures at temperatures from 293.15 K to 333.15 K (p = 0.1 MPa).

x_3	$10^3 x_1^{exp}$	Apelbat $10^3 x_1^{cal}$	λh $10^3 x_1^{cal}$	NRTL $10^3 x_1^{cal}$
T=293.15 K				
0.00	50.08	50.13	50.41	51.01
0.058	32.59	32.61	33.05	33.51
0.13	20.63	20.66	20.75	20.63
0.27	7.34	7.33	7.34	7.52
0.46	2.21	2.22	2.23	2.27
0.69	0.64	0.63	0.62	0.54
T=303.15 K				
0.00	61.80	61.62	61.09	61.52
0.058	43.00	42.91	42.57	43.02
0.13	28.46	28.37	27.98	27.83
0.27	10.20	10.29	10.26	10.13
0.46	3.22	3.21	3.15	3.11
0.69	0.75	0.80	0.82	0.75
T=313.15 K				
0.00	73.55	73.73	72.97	72.88
0.058	54.21	54.35	53.81	53.78
0.13	37.47	37.45	36.93	36.75
0.27	14.28	14.07	14.02	13.89
0.46	4.44	4.43	4.36	4.23
0.69	1.08	1.04	1.06	1.04
T=323.15 K				
0.00	86.17	86.14	86.03	85.59
0.058	66.59	66.50	66.86	65.99
0.13	47.51	47.70	47.79	47.39
0.27	18.54	18.75	18.77	18.53
0.46	5.83	5.86	5.90	5.67
0.69	1.37	1.36	1.35	1.40
T=333.15 K				
0.00	98.53	98.51	100.19	99.38
0.058	78.91	78.93	81.74	79.03
0.13	58.99	58.87	60.71	60.08
0.27	24.52	24.45	24.65	25.13
0.46	7.46	7.44	7.83	7.53
0.69	1.78	1.80	1.69	1.87

x_3 is the initial mole fraction of methanol in the (water-methanol) binary solvent mixtures; x_1^{exp} is the experimentally determined solubility of α-form Glycine; x_1^{cal} is the calculated solubility by the

modified Apelblat model (Eq. (5)), the λh (Eq. (6)) and the NRTL model (Eq. (7)), respectively.

Table S3 Mole fraction solubility of γ-form glycine (x_1) in water (x_2)-methanol (x_3) binary solvent mixtures at temperatures from 293.15 K to 333.15 K (p = 0.1 MPa).

x_3	$10^3 x_1^{exp}$	Apelbat $10^3 x_1^{cal}$	λh $10^3 x_1^{cal}$	NRTL $10^3 x_1^{cal}$
T=293.15 K				
0.00	47.63	47.60	47.91	48.17
0.058	31.33	31.33	31.57	32.30
0.13	20.22	20.27	20.41	20.31
0.27	7.29	7.19	7.21	7.53
0.46	2.13	2.12	2.12	2.21
0.69	0.50	0.51	0.50	0.44
T=303.15 K				
0.00	58.53	58.66	58.20	58.20
0.058	41.10	41.16	40.70	41.29
0.13	28.07	27.88	27.49	27.37
0.27	9.59	9.94	9.97	9.91
0.46	2.92	2.97	2.98	2.95
0.69	0.70	0.66	0.68	0.60
T=313.15 K				
0.00	70.61	70.36	69.69	69.60
0.058	52.36	52.14	51.48	51.88
0.13	36.70	36.77	36.26	35.87
0.27	13.82	13.48	13.48	13.64
0.46	4.15	4.09	4.09	3.99
0.69	0.85	0.87	0.90	0.80
T=323.15 K				
0.00	82.19	82.39	82.33	81.87
0.058	63.65	63.93	64.02	63.37
0.13	46.50	46.70	46.88	46.10
0.27	18.04	17.97	17.88	18.13
0.46	5.55	5.54	5.52	5.32
0.69	1.16	1.18	1.18	1.06
T=333.15 K				
0.00	94.49	94.43	96.09	95.61
0.058	76.27	76.16	78.34	76.41
0.13	57.51	57.36	59.51	58.15
0.27	23.43	23.59	23.28	24.14
0.46	7.38	7.40	7.30	7.10
0.69	1.66	1.64	1.52	1.42

x_3 is the initial mole fraction of methanol in the (water-methanol) binary solvent mixtures; x_1^{exp} is the experimentally determined solubility of γ-form glycine; x_1^{cal} is the calculated solubility by the

modified Apelblat model (Eq. (5)), the λh (Eq. (6)) and the NRTL model (Eq. (7)), respectively.

Table S4 Mole fraction solubility of α-form glycine (x_1) in water (x_2)-methanol (x_3)-NH_4Cl (x_4) ternary solvent mixtures at temperatures from 293.15 K to 333.15 K (p = 0.1 MPa).

x_4	$10^3x_1^{exp}$	Apelbat $10^3x_1^{cal}$	λh $10^3x_1^{cal}$	NRTL $10^3x_1^{cal}$
T=293.15 K				
0.020	11.50	11.38	11.43	11.95
0.030	12.75	12.72	12.74	13.48
0.039	13.79	13.94	13.98	14.72
0.049	15.36	15.36	15.41	16.15
0.058	16.46	16.48	16.56	17.27
0.067	18.22	18.24	18.28	18.56
T=303.15 K				
0.020	14.74	15.23	15.18	15.26
0.030	16.98	17.08	17.06	17.40
0.039	19.26	18.80	18.57	19.32
0.049	20.43	20.43	20.32	20.76
0.058	22.07	22.04	21.85	22.21
0.067	23.79	23.73	23.65	23.60
T=313.15 K				
0.020	20.59	19.87	19.78	20.50
0.030	22.46	22.43	22.39	22.71
0.039	24.22	24.44	24.19	24.59
0.049	26.44	26.43	26.28	26.66
0.058	28.62	28.53	28.27	28.46
0.067	30.15	30.15	30.05	29.87
T=323.15 K				
0.020	25.00	25.35	25.32	26.07
0.030	29.00	28.86	28.85	29.63
0.039	30.36	30.81	30.95	31.45
0.049	33.33	33.36	33.40	34.05
0.058	35.65	35.87	35.95	36.04
0.067	37.43	37.53	37.56	37.62
T=333.15 K				
0.020	31.73	31.70	31.89	34.11
0.030	36.37	36.47	36.55	38.33
0.039	38.11	37.75	38.95	40.43
0.049	41.19	41.18	41.76	43.22
0.058	44.04	43.93	44.96	45.55
0.067	45.89	45.82	46.25	47.18

x_4 is the initial mole fraction of NH_4Cl in the (water-methanol-NH_4Cl) ternary solvent mixtures;

x_1^{exp} is the experimentally determined solubility of α-form glycine; x_1^{cal} is the calculated solubility by the modified Apelblat model (Eq. (5)), the λh (Eq. (6)) and the NRTL model (Eq. (7)), respectively.

Table S5 Mole fraction solubility of γ-form glycine (x_1) in water (x_2)-methanol (x_3)-NH_4Cl (x_4) ternary solvent mixtures at temperatures from 293.15 K to 333.15 K (p = 0.1 MPa).

x_4	$10^3x_1^{exp}$	Apelbat $10^3x_1^{cal}$	λh $10^3x_1^{cal}$	NRTL $10^3x_1^{cal}$
T=293.15 K				
0.020	10.43	10.43	10.47	10.85
0.030	11.69	11.71	11.79	12.32
0.039	13.46	13.45	13.49	13.88
0.049	15.14	15.15	15.15	15.48
0.058	15.72	15.75	15.82	16.56
0.067	17.50	17.49	17.51	18.03
T=303.15 K				
0.020	14.27	14.30	14.21	14.42
0.030	16.43	16.37	16.14	16.44
0.039	17.87	17.91	17.83	18.02
0.049	19.90	19.87	19.85	19.91
0.058	21.18	21.08	20.90	21.33
0.067	22.73	22.76	22.73	22.81
T=313.15 K				
0.020	19.09	19.00	18.88	19.20
0.030	21.95	21.92	21.62	21.76
0.039	23.35	23.24	23.13	23.46
0.049	25.54	25.56	25.54	25.55
0.058	27.28	27.32	27.08	27.26
0.067	29.04	29.03	28.98	28.89
T=323.15 K				
0.020	24.43	24.55	24.61	25.18
0.030	28.09	28.26	28.39	28.41
0.039	29.35	29.47	29.49	30.13
0.049	32.30	32.30	32.30	32.72
0.058	34.28	34.40	34.47	34.61
0.067	36.37	36.34	36.34	36.43
T=333.15 K				
0.020	30.99	30.94	31.53	32.98
0.030	35.33	35.23	36.60	36.84
0.039	36.62	36.58	36.98	38.64
0.049	40.19	40.18	40.21	41.67
0.058	42.32	42.23	43.17	43.66
0.067	44.73	44.75	44.88	45.65

x_4 is the initial mole fraction of NH_4Cl in the (water–methanol–NH_4Cl) ternary solvent mixtures; x_1^{exp} is the experimentally determined solubility of α-form glycine； x_1^{cal} is the calculated solubility by the modified Apelblat model (Eq. (5)), the λh (Eq. (6)) and the NRTL model (Eq. (7)), respectively.

Table S6 Mole fraction solubility of α-form Glycine (x_1) in water (x_2)-methanol (x_3)-HMTA (x_4) ternary solvent mixtures at temperatures from 293.15 K to 333.15 K (p = 0.1 MPa).

x_4	$10^3x_1^{exp}$	Apelbat $10^3x_1^{cal}$	λh $10^3x_1^{cal}$	NRTL $10^3x_1^{cal}$
T=293.15 K				
0.005	7.03	7.05	7.03	7.27
0.010	6.51	6.53	6.51	6.72
0.015	5.81	5.84	5.84	6.14
0.020	5.52	5.54	5.51	5.71
0.025	5.12	5.11	5.10	5.27
0.030	4.51	4.53	4.51	4.80
T=303.15 K				
0.005	9.91	9.85	9.89	9.93
0.010	9.26	9.17	9.20	9.20
0.015	8.37	8.29	8.31	8.42
0.020	7.79	7.73	7.82	7.79
0.025	7.16	7.22	7.26	7.17
0.030	6.48	6.42	6.47	6.57
T=313.15 K				
0.005	13.52	13.52	13.59	13.56
0.010	12.57	12.64	12.70	12.53
0.015	11.49	11.51	11.56	11.49
0.020	10.68	10.72	10.86	10.62
0.025	10.20	10.04	10.10	9.93
0.030	8.98	8.99	9.07	8.98
T=323.15 K				
0.005	18.17	18.28	18.28	18.58
0.010	17.10	17.16	17.16	17.26
0.015	15.56	15.68	15.73	15.76
0.020	14.74	14.80	14.75	14.69
0.025	13.60	13.77	13.74	13.52
0.030	12.32	12.44	12.43	12.34
T=333.15 K				
0.005	24.44	24.36	24.14	25.73
0.010	23.03	22.96	22.75	23.92
0.015	21.05	20.96	20.99	21.83
0.020	20.42	20.36	19.66	20.65
0.025	18.68	18.62	18.33	18.87

0.030	17.13	17.04	16.71	17.28

x_4 is the initial mole fraction of HMTA in the (water-methanol-HMTA ternary solvent mixtures; x_1^{exp} is the experimentally determined solubility of α-form Glycine; x_1^{cal} is the calculated solubility by the modified Apelblat model (Eq. (5)), the λh (Eq. (6)) and the NRTL model (Eq. (7)), respectively.

Table S7 Mole fraction solubility of γ-form Glycine (x_1) in water (x_2)-methanol (x_3)-HMTA (x_4) ternary solvent mixtures at temperatures from 293.15 K to 333.15 K (p = 0.1 MPa).

x_4	$10^3x_1^{exp}$	Apelbat $10^3x_1^{cal}$	λh $10^3x_1^{cal}$	NRTL $10^3x_1^{cal}$
T=293.15 K				
0.005	6.43	6.48	6.46	6.92
0.010	5.95	5.96	5.94	6.27
0.015	5.47	5.49	5.47	5.67
0.020	4.89	4.91	4.88	5.10
0.025	4.64	4.66	4.60	4.65
0.030	4.23	4.25	4.23	4.20
T=303.15 K				
0.005	9.42	9.26	9.26	9.57
0.010	8.52	8.46	8.54	8.66
0.015	7.88	7.84	7.87	7.90
0.020	7.11	7.04	7.08	7.16
0.025	6.48	6.41	6.58	6.52
0.030	6.20	6.14	6.15	6.02
T=313.15 K				
0.005	12.92	12.93	12.97	13.06
0.010	11.75	11.88	11.98	11.88
0.015	11.01	11.00	11.06	10.96
0.020	9.91	9.95	10.03	9.95
0.025	8.93	8.95	9.18	9.07
0.030	8.71	8.71	8.73	8.49
T=323.15 K				
0.005	17.37	17.70	17.76	17.82
0.010	16.62	16.50	16.45	16.65
0.015	15.08	15.19	15.19	15.17
0.020	13.83	13.91	13.87	13.91
0.025	12.54	12.66	12.54	12.72
0.030	11.96	12.10	12.11	11.89
T=333.15 K				
0.005	23.35	23.81	23.83	24.91
0.010	22.64	22.68	22.12	23.15
0.015	20.76	20.68	20.44	21.20
0.020	19.31	19.23	18.80	19.60

0.025	18.18	18.09	16.80	18.26
0.030	16.62	16.53	16.44	16.77

x_4 is the initial mole fraction of HMTA in the (methanol-water-HMTA ternary solvent mixtures; x_1^{exp} is the experimentally determined solubility of γ-form Glycine; x_1^{cal} is the calculated solubility by the modified Apelblat model (Eq. (5)), the λh (Eq. (6)) and the NRTL model (Eq. (7)), respectively.

4. Molecular dynamics simulation under different simulation times

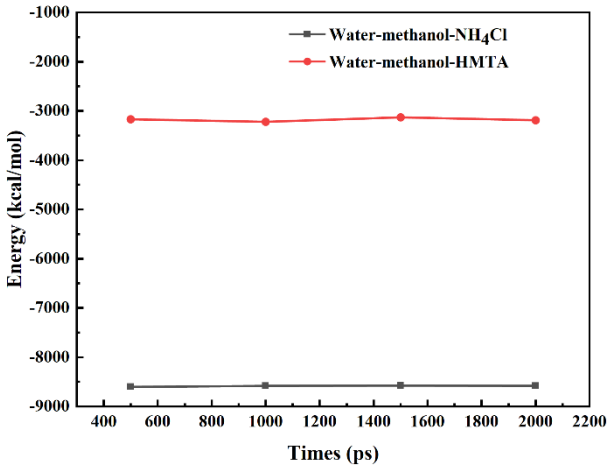
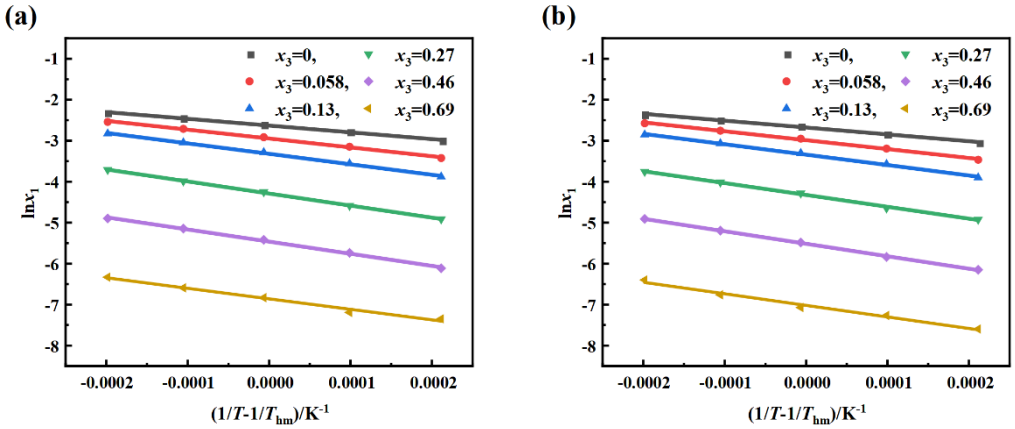


Fig. S4 The energy of impurity containing system under different molecular dynamics simulation time

5. van't Hoff plot of lnx_1 versus (1/T-1/T_{hm}) in mixed solutions



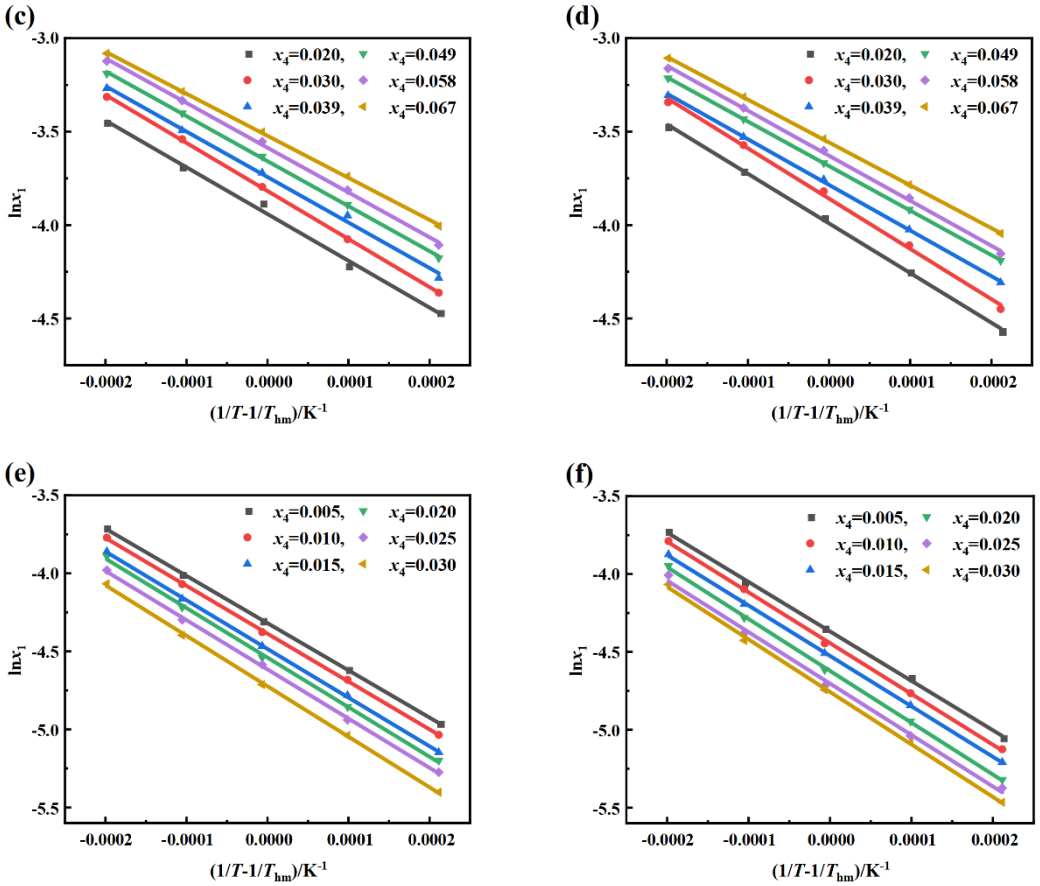


Fig. S5 van't Hoff plot of lnx_1 versus (1/T-1/T_{hm}) in mixed solvent: (a) α-form in water-methanol solution；(b) γ-form in methanol-water solution；(c) α-form in water-methanol-NH_4Cl solution；(d) γ-form in water-methanol-NH_4Cl solution；(e) α-form in water-methanol-HMTA solution；(f) γ-form in water-methanol-HMTA solution.