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Measurement of Activity Coefficients of Solutes at Infinite Dilution in (Dimethyl Sulfoxide + Acetamide, or Formamide, or Urea) Using Gas Liquid Chromatography at the Temperature 298.15 K

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Using gas liquid chromatography, activity coefficients of 12 solutes at infinite dilution (γ_1^∞) in the stationary solvent dimethyl sulfoxide + additives (acetamide, or formamide, or urea) at the temperature 298.15 K have been measured. The effect of composition of the mixed solvents on γ_1^∞ and on selectivity $S(i/j)$ has been discussed.

1. Introduction

In the separation process of aromatics from aliphatic hydrocarbons, dimethyl sulfoxide (DMSO) is an important selective solvent for extraction separation. It is reported that the selectivity parameters and partition coefficients of aromatic compounds between aliphatic solvents, such as dodecane and hexadecane, and DMSO are high.[1] It is also reported that the activity coefficients of aliphatic solutes differ greatly from those of aromatics in DMSO.[2,3] It is well-known that the additives will influence the activity coefficients and selectivity markedly. But there are few studies with DMSO solvent. Liu had reported the influence of water on the extraction of aromatics from aliphatic solvents.[1]

The activity coefficient of solute at infinite dilution (γ_1^∞) represents an important property, which is used in particular for the selection of solvents (e.g. for extraction and extractive distillation) and for the reliable design of thermal separation processes. The γ_1^∞ value provides an insight into solute−solvent interactions. The measurement of γ_1^∞ by gas−liquid chromatography (GLC) is an adequate technique.[4] Most measurements use nonpolar or moderate polar solvents as stationary solvents.[2,3,5−7] However, there are few data of γ_1^∞ in mixed solvents.

To obtain more information on the effect of a third component on the activity coefficient, the activity coefficients at infinite dilution for some organic solutes in {dimethyl sulfoxide (DMSO) + acetamide, or formamide, or urea} mixed solvents have been measured by GLC at T = 298.15 K. Heptane, cyclohexane, benzene, tetrachloromethane, chloroform, dichloromethane, ethyl acetate, methyl formate, acetone, butanone, diethyl ether, and tetrahydrofuran were used as solutes. Acetamide, formamide, and urea were selected as additives to mix with DMSO. These species may be considered as a series of compounds with a common formula $R{-}CONH_2$, in which the group R changes from $-CH_3$, $-H$, to $-NH_2$, that is, from a nonpolar group to a polar group. Our interest is to find how the substituting of R causes the change in γ_1^∞ for different types of solute, such as aliphatics, aromatics, ketones, esters, and carbon chlorides.

2. Experimental Section

The infinite dilution activity coefficients γ_1^∞ were measured by gas−liquid chromatography. The calculation of γ_1^∞ requires the measurement of the following variables: (a) net retention time ($t_1 - t_0$) of solute, that is, the difference between the retention times of solute (1) and inert gas (0); (b) column temperature T; (c) column inlet pressure P_i and outlet pressure P_o; (d) carrier gas flow rate F measured at temperature T_f and pressure P_f; (e) mass w_s of solvent contained within the column.

From these experimental data, the retention volume V_g and infinite dilution activity coefficient γ_1^∞ can be calculated. The James−Martin correction factor j_3^2 for the pressure gradient and gas compressibility inside the column was applied in the calculation of V_g.[4] The gas-phase nonidealities were taken into account by means of the virial equation of state.

$$V_g = F(273.15/T_f)(t_1 - t_0)((P_f - P_w^s)/P_0)j_3^2/w_s \quad (1)$$

$$\ln \gamma_1^\infty = \ln(273.15R/M_sP_1^sV_g) - (B_{11} - V_1)P_1^s/RT + (2B_{10} - V_1^\infty)j_3^2P_0/RT \quad (2)$$

In these equations, P_w^s and P_1^s are, respectively, the vapor pressure of water at temperature T_f and that of the organic solute 1 at column temperature T; M_s is the molecular weight of the stationary solvent; R is the universal gas constant; B_{11} and B_{10} are the second virial coefficient of solute 1 and the cross second virial coefficient of solute with carrier gas 0; V_1 is the liquid molar volume of solute 1 at temperature T; and the values of B_{11} and B_{10} were calculated by Pitzer's[8] method.

A Shimadzu GC-9A gas chromatograph with a thermal conductivity detector was used in the measurements. The carrier gas was hydrogen flowing at about 30 cm^3/min. The flow rates were measured with a soap-film meter, and

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Table 1. Solvent (Formamide) Percent (wt %) on Solid Support, Retention Volume (V_g) of Solute, Solvent Loss (Δw_s) at 298.15 K, and the Statistic Parameters

	V_g/cm^3.g^{-1}						
wt %	ethyl acetate	acetone	butanone	dichloromethane	chloroform	tetrachloromethane	Δw_s/g
23.34	344.9	528.0	674.1	56.28	74.34	19.94	0.15
20.40	388.6	498.5	714.8	74.31	108.5	31.34	0.005
18.87	391.8	502.2	719.8	73.93	108.4	31.21	0.001
17.33	395.3	504.6	725.5	76.42	111.2	31.97	0.002
statistic parameters[a]							
$M(V_g)$	391.9	501.8	720.0	74.89	109.4	31.51	
σ	2.7	2.5	4.4	1.1	1.3	0.33	
rsd	0.69	0.50	0.61	1.5	1.2	1.0	
M(rsd)			0.91				
RD(V_g)	12.0	5.2	6.4	25	32	37	

[a] $M(V_g) = \sum_{i=1}^{n} V_g(i)/n$, $\sigma = [\sum_{i=1}^{n}(x_i - \bar{x})^2/n]^{1/2}$, rsd $= \sigma/\bar{x} \times 100\%$, and $M(\text{rsd}) = (1/n)\sum_{i=1}^{n}(\sigma/\bar{x})_i \times 100\%$. $M(V_g)$, σ, rsd, and M(rsd) were calculated for columns with solvent percent 20.40, 18.87, and 17.33%. For the column with solvent percent 23.34%, only RD(V_g) has been calculated, where RD(V_g) $= [V_g(23.34\%) - M(V_g)]/M(V_g) \times 100\%$.

temperatures with a mercury thermometer. The column outlet pressure was determined with a barometer. The pressure drop inside the column was read with a cathetometer from a U tube mercury manometer. The column was taken out of the column box, and its temperature was controlled by a water bath, with an accuracy of ±0.05 K.

The mixed solvents of DMSO (3) + acetamide (2) (or formamide, urea) are prepared by mass and used as stationary solvents. Silanized 101 white solid support, 60/80 meshes, was used as the solid support. The stationary phase for each column was prepared by mixing acetone with known masses of solvents and inert solid support. The relative loading of the stationary phase (mass of the solvents/mass of the solid support) in the column is about 1/4. Acetone was then slowly evaporated from the mixture, in a rotary evaporator at temperature 308.15 K and under reduced pressure. A stainless steel column (length, 2 m; inner diameter, 4.1 mm) was carefully filled with the coated solid support.

The amount of stationary phase (solid + solvent) inside the column, W(s+l), was measured gravimetrically before V_g measuring. An analytical balance (accuracy ±0.0001 g) was used. After V_g measurements, the column was reweighed. The estimated mean error of W(s+l) was 0.02 g (its relative deviation is 1.2%). The average value of W(s+l) was calculated and used for the calculation of solvent mass (w_s) in the column.

The solvent percent was determined by an extraction method. The coated solid was filled into a 20 cm^3 bottle. Acetone was used as an extraction solvent. The sample weight of solid is about 2 g; its accurate value was measured by an analytical balance. More than three samples were extracted. To monitor the solvent loss, samples collected before V_g measuring were extracted as comparison. With the aim of eliminating the operation error, a parallel measure for pure solid support was carried out. After extraction, all samples were dried at 423 K and then weighed. The average value of solvent percent was used to calculated solvent mass w_s in the column. The mean deviation of solvent percent by extraction is 0.02%. The estimated relative error of solvent mass (w_s) is 0.2%.

Solvent loss control was improved by some operations: (1) a presaturation column was used; (2) the solvent percent on the solid support was controlled (In our experience, the solvent percent should be 20% for 60/80 meshes solid support. More solvent would reduce the adsorption effect, but it would cause liquid dispersion un-uniformly and cause solvent loss.); (3) to eliminate the temperature disturbance from the sample injection block, the length of the gas inlet pipe was prolonged, possibly, and the temperature was controlled under 298 K for more of the gas inlet pipe. By these operations, the solvent loss was less than 0.2%. The experimental conditions (gas flow, solvent loss, etc.) were monitored by measuring the retention volume V_g of a reference substance (for instance, ethyl acetate) in regular time intervals. The estimated mean relative standard deviation on V_g was 0.91%.

The adsorption on a polar solute is mainly caused by polar–polar and hydrogen-bond interactions between solute and solid. To weaken the adsorption effect, covering the polar group on the solid is an effective treatment. In our work, the solid was treated by a silanization method, and then it was coated with a high extent of solvent percent (about 20% for solid with particle size of 60/80 meshes).

To test the effect of adsorption on solute, and to test the quantities of solvent loss during measurement, the retention volumes of some sample solutes were measured with four columns of different solvent percent, ranging from 17 to 23%. Formamide is chosen as a sample solvent. The particle size of the solid support is 60/80 meshes. Experimental data of V_g, solvent loss Δw_s, and the statistic data are listed in Table 1. Some conclusions can be drawn from these data. First, the solvent loss (Δw_s) is neglectable while solvent percent is lower than 20%. In the column of solvent percent being 23.34, solvent loss is not neglectable. Second, the value of V_g is decreased with the increase in solvent percent until the ratio is 20%. This is an indication that, within this range, the effect of adsorption is weakened while more solvent is covering the surface of the solid. In this range, the mean relative standard deviation of V_g (mean rsd in Table 1) is 0.91%. But in the column of 23.34%, the retention volumes for all solutes change greatly and exceed the experimental error. This is another indication that a saturation ratio for solvent loading has been reached. An optimum value for solvent loading should be lower than the ratio. In our experience, solid with a different particle size shows a different saturation ratio. The optimum value is 20% for solid support with particle size of 60/80 meshes.

Hamilton gastight syringes, 1 μL capacity, were used to inject the solutes into the carrier gas stream. Air was used as the inert gas to obtain the reference retention time t_0. For most solutes, good peaks were obtained by injecting 0.2 μLof liquid solute together with a similar amount of air.

In our experience, the skew peak is related to an intense adsorption of solute on solid and solvent; to a loose particle density in the column; to an overinjected amount of solute

Table 2. Vapor Pressures (P_i^s),[a] Virial Coefficients (B_{ii} and B_{ij}), and Liquid Molar Volumes (V_i) at 298.15 K

solute	P_i^s kPa	V_i^b $cm^3 \cdot mol^{-1}$	B_{ii} $cm^3 \cdot mol^{-1}$	B_{ij} $cm^3 \cdot mol^{-1}$
heptane	6.117	147.4	−1918	−0.8187
cyclohexane	13.02	97.69	−1732	−9.890
benzene	12.68	89.41	−1537	−17.13
tetrachloromethane	14.76	97.08	−1532	−17.29
chloroform	26.22	80.67	−1166	−14.18
dichloromethane	57.26	63.90	−844.3	−4.201
diethyl ether	48.25	104.7	−1129	−9.018
ethyl acetate	12.52	98.55	−1800	−14.59
butanone	12.05	90.17	−1759	−15.09
terahydrofurane	23.46	81.76	−1554	−14.04
methyl formate	77.71	62.35	−777.4	−8.203
acetone	32.07	73.99	−1231	−10.98
DMSO		71.33		
formamide		39.89		
urea		41.28[c]		
acetamide		55.78[c]		

[a] P_i^s is calculated by the Antoine equation; the Antoine constants are obtained from the literature.[11] [b] The values of V_i from the literature.[9] [c] The value is the partial molar volume at infinite dilution in DMSO, obtained from the literature.[10]

in the carrier gas stream; and to a poor sensitivity of the detector. Moreover, to get a symmetrical peak, the important thing in operation is to ensure the detector of the apparatus runs in a linear response range. Some operations have been carried out to reduce the skew peak: first, injecting a minimum amount of solute into the carrier gas stream, so as to ensure the amount of solute is not over the extent of gas−liquid equilibrium (this is important especially for nonpolar solutes) and to keep the detector sensitivity in a linear response range; second, to increase the solvent percent in the column possibly, so as to reduce the adsorption effect on the solid, to keep the solute at infinite dilution, and to ensure there is enough efflux time for solute contact to solvent; third, using silanized nonpolar solid support to reduce the adsorption effect; fourth, loading solid into the column in high density possibly, so as to keep gas flowing through the column uniformly and not disturbed by the packing state; fifth, setting the sensitivity of the detector at a high level but in the linear response range, so that a minimum amount of solute is detectable.

DMSO, analytical grade, was dried over molecule sieves and then purified by vacuum distillation. Formamide, chemical reagent grade, was dried with freshly ignited calcium oxide and then purified by vacuum distillation. Acetamide and urea, analytical grade, were purified by recrystallization and then dried at $T = 333$ K for 10 h under vacuum. Silanized 101 white solid support was washed with ethanol and then dried at $T = 393$ K. All other chemicals were of reagent grade and were used without further purification. Since GLC is itself a separation technique, the experimental results are not influenced by small amounts of impurities. All chemicals were from Shanghai Chemical Co.

3. Results and Discussion

3.1. Activity Coefficients at Infinite Dilution in Pure DMSO. The ancillary data of vapor pressures (P_i^s), virial coefficients (B_{11} and B_{10}), and liquid molar volume (V_1) at 298.15 K are presented in Table 2, in which some data are taken from the literature.[9−11]

Experimental data of the retention volume (V_g) and the activity coefficients at infinite dilution of solutes (1) in acetamide (2) (or formamide, urea) + DMSO (3) are presented in Tables 3−5. In the solvents formamide (2) + DMSO (3), γ_1^∞ was measured in the range $x_2 = 0$ to 1.

Letcher[2] had published data on infinite activity coefficients of several alkanes and cycloalkanes in DMSO at 298 K. The data of heptane and cyclohexane have been included in Table 6 for comparison. Topphoff et al.[3] published data for several solutes in DMSO at 303, 318, and 333 K. The graphs of ln γ_1^∞ against $1/T$ show a straight

Table 3. Data of V_g and γ_1^∞ for Solutes (1) in Acetamide (2) + DMSO (3) Mixed Solvents at 298.15 K[a]

x_2	hep	c-hex	ben.	DEE	TCM	CF	DCM	AC	MEK	THF	MF	EA
$V_g/cm^3 \cdot g^{-1}$												
0	32.6	52.1	755	51.5	418	2429	924	450	938	378	218	583
0.0397	31.3	47.8	672	47.6	373	2157	784	422	867	356	201	537
0.0777	26.0	41.8	590	44.5	315	1803	671	408	816	345	190	495
0.1161	25.6	41.2	557	43.3	296	1701	621	404	808	344	186	481
0.1519	25.0	40.7	544	42.8	293	1640	608	390	778	335	178	471
0.1894	24.2	39.2	514	41.3	272	1478	557	384	759	333	173	468
0.2251	24.2	39.1	498	41.3	266	1453	534	387	766	335	171	461
0.2748	24.0	38.6	468	40.4	252	1299	488	384	741	338	165	456
0.3188	23.8	38.5	449	40.6	243	1249	475	379	741	341	164	454
0.3604	24.2	37.9	435	40.3	239	1184	453	378	735	344	160	452
0.3888	24.3	37.5	422	40.4	234	1143	437	377	736	347	158	450
0.4246	23.5	36.4	405	39.7	223	1068	408	374	728	347	154	444
0.4640	20.3	33.6	374	39.1	196	902	357	377	710	351	149	436
γ_1^∞												
0	146	43.1	3.05	11.9	4.73	0.460	0.559	2.04	2.58	3.32	1.76	4.00
0.0397	154	47.4	3.45	13.0	5.35	0.518	0.665	2.19	2.82	3.55	1.92	4.38
0.0777	187	54.7	3.97	14.1	6.39	0.632	0.785	2.29	3.00	3.70	2.06	4.80
0.1161	196	56.7	4.25	14.6	6.88	0.676	0.855	2.34	3.08	3.75	2.12	4.99
0.1519	193	56.6	4.39	14.9	7.02	0.708	0.883	2.44	3.23	3.88	2.23	5.14
0.1894	207	60.0	4.69	15.6	7.62	0.793	0.972	2.50	3.34	3.94	2.32	5.22
0.2251	208	60.8	4.88	15.7	7.86	0.814	1.02	2.51	3.34	3.95	2.36	5.35
0.2748	213	62.5	5.27	16.3	8.41	0.922	1.14	2.56	3.50	3.97	2.49	5.48
0.3188	217	63.1	5.55	16.4	8.81	0.970	1.18	2.63	3.54	3.98	2.53	5.56
0.3604	216	64.9	5.79	16.7	9.05	1.04	1.25	2.66	3.61	3.99	2.63	5.65
0.3888	217	66.2	6.01	16.8	9.32	1.08	1.31	2.69	3.64	3.99	2.68	5.72
0.4246	227	68.8	6.34	17.3	9.88	1.17	1.41	2.74	3.71	4.03	2.77	5.85
0.4640	265	75.3	6.94	17.7	11.4	1.40	1.63	2.74	3.84	4.03	2.90	6.04

[a] hep, heptane; *c*-hex, cyclohexane; ben., benzene; DEE, diethyl ether; TCM, tetrachloromethane; CF, chloroform; DCM, dichloromethane; AC, acetone; MEK, butanone; THF, tetrahydrofuran; MF, methyl formate; EA, ethyl acetate.

Table 4. Data of V_g and γ_1^∞ for Solutes (1) in Formamide (2) + DMSO (3) Mixed Solvents at 298.15 K[a]

x_2	hep	*c*-hex	ben.	DEE	TCM	CF	DCM	AC	MEK	THF	MeF	EA
						V_g/cm^3·g^{-1}						
0.0416	30.6	48.9	697	49.6	375	2119	858	441	914	372	212	558
0.0697	29.9	48.0	667	47.7	360	2093	759	422	872	361	201	536
0.1052	28.1	45.2	628	45.9	332	1901	705	412	842	354	194	518
0.1315	23.6	42.3	554	44.8	285	1637	672	404	822	350	190	501
0.1616	22.3	40.7	536	43.6	276	1493	609	401	803	347	185	489
0.2965	19.7	33.4	453	39.2	219	1107	471	388	749	338	169	439
0.4209	17.6	30.3	384	37.6	179	836	366	383	716	338	158	419
0.5349	13.2	24.0	280	34.3	122	540	264	380	684	341	149	398
0.6333	11.5	21.4	248	33.3	108	451	226	392	688	349	146	405
0.7237	9.87	18.2	199	32.1	85.6	337	179	404	679	358	142	398
0.8061	7.49	14.2	152	30.2	63.3	240	137	424	679	368	141	388
0.8728	6.38	11.8	122	28.9	50.1	183	111	447	690	381	143	393
0.9414	5.64	9.76	94.9	27.8	39.9	139	89.3	471	705	394	144	387
0.9492	5.55	9.69	93.5	27.8	38.6	136	88.0	475	704	394	145	386
0.9604	5.50	9.37	89.9	27.3	37.2	130	84.5	480	706	395	146	386
0.9735	5.30	9.11	85.9	27.3	35.4	124	81.2	485	709	397	146	389
0.9838	5.30	8.59	80.7	27.3	33.3	116	77.3	492	710	400	146	389
1	5.36	8.23	76.7	26.8	31.4	109	74.4	499	715	401	147	389
						γ_1^∞						
0.0416	159	46.7	3.36	12.6	5.37	0.537	0.613	2.12	2.70	3.42	1.84	4.25
0.0697	164	48.1	3.55	13.3	5.66	0.550	0.702	2.24	2.86	3.57	1.96	4.48
0.1052	178	52.0	3.83	14.0	6.23	0.615	0.767	2.33	3.01	3.71	2.07	4.71
0.1315	214	56.1	4.39	14.5	7.34	0.723	0.814	2.41	3.12	3.79	2.13	4.93
0.1616	229	59.2	4.60	15.1	7.66	0.803	0.914	2.45	3.22	3.86	2.22	5.12
0.2965	277	76.9	5.80	17.9	10.3	1.15	1.25	2.71	3.70	4.24	2.60	6.07
0.4209	329	90.0	7.30	19.9	13.5	1.63	1.72	2.92	4.11	4.50	2.95	6.77
0.5349	467	121	10.6	23.1	20.9	2.68	2.53	3.12	4.58	4.75	3.32	7.57
0.6333	565	143	12.7	25.2	25.0	3.39	3.12	3.20	4.81	4.90	3.59	7.86
0.7237	696	178	16.6	27.5	33.3	4.78	4.15	3.28	5.14	5.04	3.87	8.45
0.8061	966	240	23.0	30.9	47.4	7.07	5.74	3.29	5.41	5.17	4.11	9.13
0.8728	1185	302	29.9	33.7	62.7	9.67	7.39	3.26	5.56	5.21	4.25	9.40
0.9414	1405	382	40.3	36.7	82.5	13.4	9.62	3.24	5.71	5.29	4.41	10.0
0.9492	1437	387	41.1	36.9	85.7	13.7	9.82	3.23	5.75	5.31	4.42	10.1
0.9604	1460	404	43.1	37.9	89.5	14.5	10.3	3.22	5.78	5.34	4.43	10.2
0.9735	1529	419	45.5	38.3	95.1	15.4	10.8	3.22	5.81	5.36	4.45	10.2
0.9838	1541	448	48.8	38.6	102	16.5	11.5	3.19	5.84	5.37	4.49	10.3
1	1542	473	52.0	39.7	110.	17.8	12.1	3.19	5.87	5.41	4.51	10.4

[a] hep, heptane; *c*-hex, cyclohexane; ben., benzene; DEE, diethyl ether; TCM, tetrachloromethane; CF, chloroform; DCM, dichloromethane; AC, acetone; MEK, butanone; THF, tetrahydrofuran; MF, methyl formate; EA, ethyl acetate.

Table 5. Data of V_g/cm^3·g^{-1} and γ_1^∞ for Solutes (1) in Urea (2) + DMSO (3) Mixed Solvents at 298.15 K[a]

x_2	hep	c-hex	ben.	DEE	TCM	CF	DCM	AC	MEK	THF	MF	EA
						V_g/cm^3·g^{-1}						
0.0261	27.6	44.4	651	45.1	353	2066	775	423	873	357	205	519
0.0512	24.7	40.4	610	42.2	324	1894	713	398	802	324	184	487
0.0760	22.9	38.0	563	39.0	300	1736	642	368	734	306	176	453
0.0953	20.6	37.6	525	37.1	272	1559	594	366	713	303	173	434
0.1119	19.4	32.6	507	35.3	261	1488	570	355	690	294	163	418
0.1507	16.9	29.9	470	32.5	236	1321	512	336	640	278	157	389
0.1678	16.2	29.4	455	31.2	227	1247	495	326	618	271	153	380
0.1869	14.6	25.3	416	28.8	203	1098	444	310	578	255	143	354
0.2039	13.4	22.3	374	26.6	178	954	391	295	541	244	135	324
0.2297	12.2	19.9	343	24.4	160	862	353	281	507	232	128	300
0.2462	11.5	18.7	321	22.9	148	778	328	271	482	223	122	285
						γ^∞						
0.0261	174	50.8	3.55	13.7	5.64	0.544	0.671	2.18	2.79	3.53	1.88	4.52
0.0512	196	56.2	3.84	14.7	6.19	0.597	0.734	2.33	3.05	3.91	2.10	4.84
0.0760	210	60.0	4.13	16.0	6.71	0.655	0.819	2.54	3.36	4.16	2.22	5.22
0.0953	237	66.7	4.48	16.9	7.42	0.733	0.889	2.56	3.47	4.23	2.27	5.49
0.1119	252	70.7	4.65	17.8	7.78	0.771	0.930	2.66	3.60	4.37	2.41	5.72
0.1507	292	77.7	5.07	19.5	8.67	0.877	1.05	2.83	3.90	4.67	2.52	6.21
0.1678	305	82.9	5.26	20.5	9.05	0.932	1.09	2.93	4.07	4.81	2.61	6.38
0.1869	342	92.8	5.78	22.3	10.2	1.06	1.22	3.10	4.38	5.13	2.80	6.88
0.2039	374	106	6.45	24.3	11.7	1.23	1.39	3.26	4.70	5.39	2.98	7.54
0.2297	413	119	7.07	26.6	13.1	1.37	1.55	3.45	5.04	5.70	3.17	8.21
0.2462	441	127	7.59	28.4	14.2	1.52	1.67	3.60	5.32	5.95	3.34	8.66

[a] hep, heptane; *c*-hex, cyclohexane; ben., benzene; DEE, diethyl ether; TCM, tetrachloromethane; CF, chloroform; DCM, dichloromethane; AC, acetone; MEK, butanone; THF, tetrahydrofuran; MF, methyl formate; EA, ethyl acetate.

line. Using their results, a value of γ_1^∞ at 298.15 K was extrapolated by the linear relationship. In Table 6, the linear fitting parameters and the extrapolated values of γ_1^∞ at 298.15 K are listed. By comparing the data in this

Table 6. Comparison of the Data of γ_1^∞ from This Work with Literature and the Extrapolated Values: Linear Fitting Parameters (A, B), Correlation Coefficients (R), and Standard Deviations (s)

solute	γ^∞ in this work	lit.[2] [a]	γ^∞ extrapolated[b]	A	B	R	s[c]
heptane	146	150, 121.1					
cyclohexane	43.1	46.0, 40.6					
benzene	3.05		3.37	0.141 99	0.319 83	0.9931	0.007
chloroform	0.460		0.428	2.322 89	−0.945 36	0.9945	0.02
dichloromethane	0.559		0.574	1.919 18	−0.737 73	0.9936	0.01
diethyl ether	11.9		10.0	0.755 55	0.461 34	0.9969	0.007
butanone	2.59		2.58	0.262 83	0.204 09	0.9999	0.0001
tetrahydrofuran	3.32		3.38	0.036 77	0.352 53	0.9999	0.0007
acetone	2.04		1.98	0.271 58	0.122 02	0.9934	0.0025

[a] Data of γ_1^∞ at 303.15, 318.15, and 333.15 K were obtained from the literature[3], and used to fit the equation in footnote *b*. [b] The values of γ_1^∞ at 298.15 K were extrapolated from the equation $\ln(\gamma_1^\infty) = A + 1000B/T$. [c] Standard deviation: $s = \{Q\}^{1/2}$. Correlation coefficients: $R = (1 - Q/D_{yy})^{1/2}$, where $Q = \sum_{i=1}^{m} \{[\ln \gamma_1^\infty(i) - \ln \gamma_1^{\infty,\mathrm{cal}}(i)]\}^2$, $D_{yy} = \sum_{i=1}^{m} (\ln \gamma_1^\infty(i) - \overline{\ln\gamma_1^\infty})^2$, $\overline{\ln\gamma_1^\infty} = \sum_{i=1}^{m} \ln \gamma_1^\infty(i)/m$, and m is the number of data points.

work and literature values, good agreement was found for the solutes acetone, butanone, THF, dichloromethane, and heptane. The relative deviations, $[\gamma_1^\infty(\text{this work}) - \gamma_1^\infty(\text{lit.})]/\gamma_1^\infty(\text{lit.})$, are less than 3%. For cyclohexane and chloroform, the relative deviations are between (6 and 8)%. Diethyl ether has a high relative deviation of 19%.

For the convenience of analysis, solutes are divided into three groups according to their molecular structure and chemical characteristics. The first group includes the nonpolar heptane, cylcohexane, and benzene. The second group includes tetrachloromethane, chloroform, and dichloromethane. Solutes containing the oxygen atom belong to the third group.

In the first group, the values of γ_1^∞ in pure DMSO increase greatly in the following sequence: benzene (3.05) < cyclohexane (43.1) < heptane (146). The ratio of the activity coefficients is denoted as the selectivity $S(i/j)$

$$S(i/j) = \gamma_1^\infty(i)/\gamma_1^\infty(j) \tag{3}$$

For separation applications, selectivities greater than 1 are desired. The value of S(cyclohxane/ benzene) is 14.1, and S(heptane/benzene) is 47.9. This is coincides with the fact that DMSO is known as a good selectivity solvent for the extractive separation of aromatics from aliphatic hydrocarbons.

In the second group, the values of γ_1^∞ increase in the following sequence: chloroform (0.460) < dichloromethane (0.559) < tetrachloromethane (4.73). Tetrachloromethane is nonpolar. Its value of γ_1^∞ is much higher than that of another two solutes in DMSO. The γ_1^∞ value of chloroform is the minimum. The dipole moment and H-bond interaction between solute and DMSO play an important role in the contributions to γ_1^∞. Similar phenomena were also found in the case of solutes in *N*-ethylformamide, *N*-methylacetamide, *N*,*N*-dimethylacetamide, and *N*,*N*-dibutylformamide.[3,5]

For solutes in the third group, the values of γ_1^∞ increase in the following sequence: methyl formate (1.76) < acetone (2.04) < butanone (2.58) < tetrahydrofuran (3.32) < ethyl acetate (4.00) < diethyl ether (11.9). The values of γ_1^∞ are less than 10 except for that for diethyl ether. This is a reflection that γ_1^∞ was mainly contributed by dipole−dipole interaction between solute and DMSO. For homogeneous solutes, γ_1^∞ increases with the number of nonpolar groups. For example, the γ_1^∞ value for methyl formate < ethyl acetate and acetone < butanone.

3.2. Activity Coefficients in Mixed Solvents. In Figures 1−3, the changes of $\ln \gamma_1^\infty$ for three groups of solutes against the mole fraction x_2 in acetamide (2) + DMSO (3) solution are presented. All the curves show a common trend, that $\ln \gamma_i^\infty$ becomes greater with x_2 increase. A similar trend exists in the cases of solutes in formamide + DMSO and urea + DMSO.

The infinite dilution activity coefficients of a nonelectrolyte solute in a mixed solvent can be calculated by the addition of two terms, combinatorial (comb) and residual (res)

$$\ln \gamma_1^\infty = \ln \gamma_1^{\infty,\mathrm{comb}} + \ln \gamma_1^{\infty,\mathrm{res}} \tag{4}$$

where the Flory−Huggins's expression can be applied in the combinatorial contribution and Scachard−Hildebrand's solution theory can be applied in the residual term[12]

$$\ln \gamma_1^{\infty,\mathrm{comb}} = \ln(V_1/V_{2+3}) + 1 - V_1/V_{2+3} \tag{5}$$

$$\begin{aligned}\ln \gamma_1^{\infty,\mathrm{res}} &= (V_1/RT)[\chi_{12}\phi_2 + \chi_{13}\phi_3 - \chi_{23}\phi_2\phi_3] \\ &= (V_1/RT)[A_1 + A_2\phi_2 + A_3\phi_2^2] \qquad (6)\end{aligned}$$

where χ_{ij} is the interaction parameter between species i and j, and ϕ_i is the volume fraction. $A_1 = \chi_{13}$, $A_2 = \chi_{12} - \chi_{13} - \chi_{23}$, and $A_3 = \chi_{23}$. The parameters A_i can be obtained by fitting the experimental data of γ_1^∞ using a least-squares method. In Table 7, the values of relative standard deviation s and correlation coefficients R are presented. The agreement between calculation and experimental data is not satisfactory. By carefully inspecting the curve shape, inserting a cubic term in eq 6 is necessary. That is

$$\ln \gamma_1^{\infty,\mathrm{res}} = (V_1/RT)[A_1 + A_2\phi_2 + A_3\phi_2^2 + A_4\phi_2^3] \tag{7}$$

Fitting the experimental data of γ_1^∞ by eqs 7 and 5, the agreement between calculation and experiment is satisfactory. The fitting results are listed in Table 7 and shown in Figures 1−3 graphically for examples.

To get more information on the effect of a third component on the activity coefficient, acetamide, formamide, and urea were used to mix with DMSO. These species may be considered as a series of compounds with the common formula R−CONH$_2$, in which the group R changes from −CH$_3$ to −H to −NH$_2$, that is from a nonpolar group to a polar group. Our interest is to find how the substituting of R causes the change in γ_1^∞ for different types of solute. In Figures 4−7, curves of $\ln \gamma_1^\infty$ against x_2 are shown for some solutes. It can be observed from these figures that they have similar curve shape. From acetamide to urea, their curves become much steeper. But urea causes $\ln \gamma_1^\infty$ to increase much faster than those of formamide and acetamide did. By comparing the curves of formamide and acetamide, it can be found that, in the range of lower x_2,

Table 7. Relative Standard Deviations *s* and the Correlation Coefficients *R* of the Fit by Eqs 6 and 7, and the Fitting Parameters A_i of Eq 7[a]

	eq 6		eq 7					
solute	*s*	*R*	*s*	*R*	A_1	A_2	A_3	A_4
				Acetamide + DMSO				
heptane	0.065	0.9506	0.034	0.9884	89.1	89.77	−371.9	555.7
cyclohexane	0.046	0.9661	0.018	0.9951	96.92	107.9	−425.4	624
benzene	0.034	0.9921	0.015	0.9986	31.86	124.3	−364.9	499.7
tetrachloromethane	0.052	0.9828	0.022	0.9973	40.92	142.1	−493.9	706.4
chloroform	0.051	0.9898	0.027	0.9974	−23.88	173.1	−533	782.3
dichloromethane	0.051	0.9882	0.021	0.9982	−21.95	226.1	−732.4	1045
diethyl ether	0.022	0.9879	0.0083	0.9985	60.81	70.91	−226.4	288.4
ethyl acetate	0.027	0.9820	0.0097	0.9980	36.52	81.9	−282.3	372.3
terahydrofurane	0.016	0.9739	0.0063	0.9964	36.83	60.4	−213.8	257.8
butanone	0.019	0.98974	0.0086	0.9983	27.05	74.57	−228.4	286.7
acetone	0.014	0.9907	0.0089	0.9966	24.21	65.1	−184.6	213.3
methyl formate	0.018	0.9931	0.0072	0.9991	23.00	105.3	−302.4	397.7
				Formamide + DMSO				
heptane	0.054	0.9992	0.056	0.9992	90.27	66.07	−6.677	−1.973
cyclohexane	0.031	0.9996	0.028	0.9997	97.34	81.41	−24.44	16.42
benzene	0.039	0.9995	0.036	0.9996	32.61	101.4	−35.80	23.96
tetrachloromethane	0.046	0.9995	0.041	0.9996	41.96	117.2	−55.07	30.07
chloroform	0.043	0.9996	0.038	0.9997	−23.02	161.3	−72.81	33.38
dichloromethane	0.036	0.9996	0.029	0.9998	−21.28	173.8	−92.99	43.02
diethyl ether	0.023	0.9995	0.014	0.9998	61.04	63.35	−42.64	21.29
ethyl acetate	0.019	0.9989	0.014	0.9997	36.72	71.29	−67.95	33.52
terahydrofurane	0.020	0.9979	0.0087	0.9996	37.01	50.31	−51.99	26.07
butanone	0.022	0.9989	0.011	0.9997	27.25	66.64	−58.41	25.63
acetone	0.021	0.9968	0.011	0.9992	24.45	61.78	−68.19	28.94
methyl formate	0.031	0.9985	0.0096	0.9998	23.18	90.86	−80.86	31.54
				Urea + DMSO				
heptane	0.023	0.9985	0.020	0.9991	89.78	177.2	−631.1	2117
cyclohexane	0.037	0.9956	0.028	0.9976	97.26	241.1	−1267	5640
benzene	0.035	0.9941	0.023	0.9977	32.00	247.7	−1594	6805
tetrachloromethane	0.041	0.9947	0.028	0.9976	41.44	258.0	−1529	6734
chloroform	0.035	0.9965	0.028	0.9980	−23.20	290.4	−1351	6342
dichloromethane	0.040	0.9943	0.026	0.9977	−21.77	403.6	−2544	10619
diethyl ether	0.025	0.9969	0.015	0.9990	60.91	193.6	−1033	4326
ethyl acetate	0.027	0.9954	0.016	0.9984	36.54	191.6	−1161	4921
terahydrofurane	0.021	0.9951	0.015	0.9977	36.54	184.8	−1073	4114
butanone	0.021	0.9969	0.015	0.9986	26.75	191.0	−969.1	3836
acetone	0.017	0.9962	0.012	0.9981	23.87	181.3	−961.2	3761
methyl formate	0.025	0.9932	0.018	0.9969	22.59	258.4	−1665	6654

[a] $s = Q^{1/2}/(m - n)$, $R = (1 - Q/D_{yy})^{1/2}$, where *m* is the number of experimental data and *n* is the number of fitting parameters, and $Q = \sum_{i=1}^{m}[\gamma_1{}^{\infty,\mathrm{exp}}(i) - \gamma_1{}^{\infty,\mathrm{cal}}(i)]^2$, $D_{yy} = \sum_{i=1}{}^{m}(\gamma_1{}^{\infty,\mathrm{exp}}(i) - \bar{\gamma}_1)^2$, $\bar{\gamma}_1 = \sum_{i=1}{}^{m}\gamma_1{}^{\infty,\mathrm{exp}}(i)/m$.

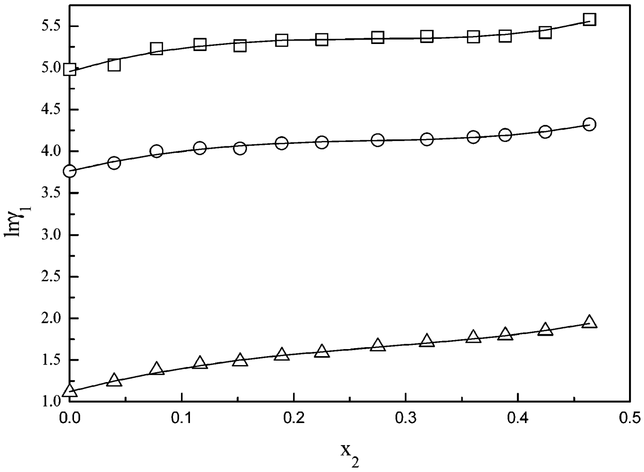

Figure 1. Values of ln $\gamma_1{}^{\infty}$ for solutes in acetamide (2) + DMSO (3) solution as a function of x_2: □, heptane; ○, cyclohexane; △, benzene; —, calculated by eq 7.

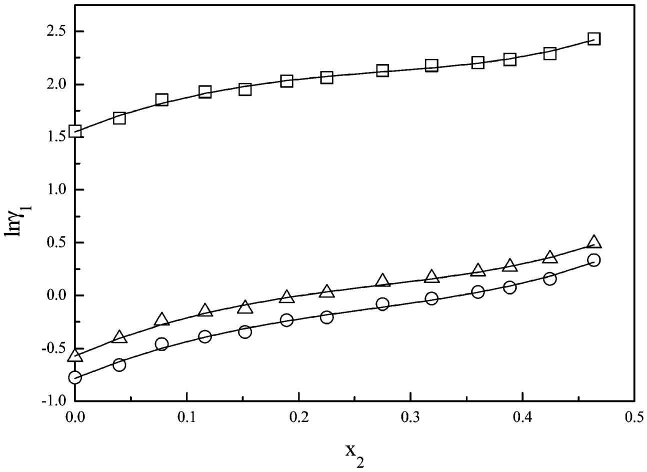

Figure 2. Values of ln $\gamma_1{}^{\infty}$ for solutes in acetamide (2) + DMSO (3) solution as a function of x_2: □, tetrachloromethane; ○, chloroform; △, dichloromethane; —, calculated by eq 7.

there is not a noticeable difference between them. But with the increase in x_2, their difference becomes observable.

3.3. Selectivity. There are three factors that influence *S*(*i*/*j*): the properties of the solute, the properties of additives in DMSO, and the mole fraction x_2. Figures 8−11 show some examples of *S*(*i*/*j*) affected by these factors.

Three characteristics can be observed from Figure 8. First, *S*(heptane/benzene) ≫ *S*(cyclohexane/benzene). Sec-

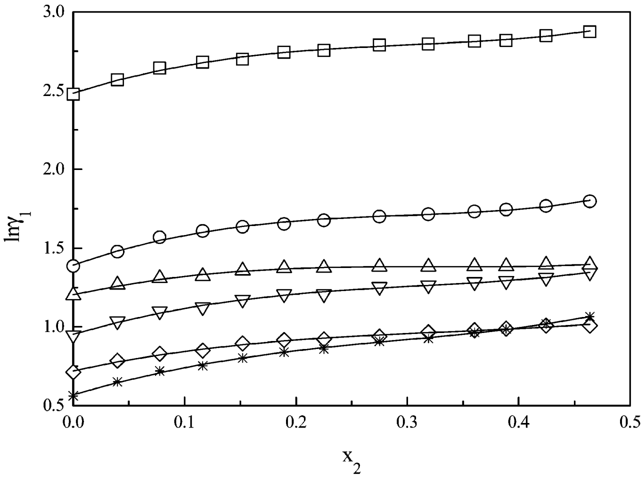

Figure 3. Values of ln γ_1^∞ for solutes in acetamide (2) + DMSO (3) solution as a function of x_2: □, diethyl ether; ○, ethyl acetate; △, terahydrofurane; ▽, butanone; ◇, acetone; ∗, methyl formate; —, calculated by eq 7.

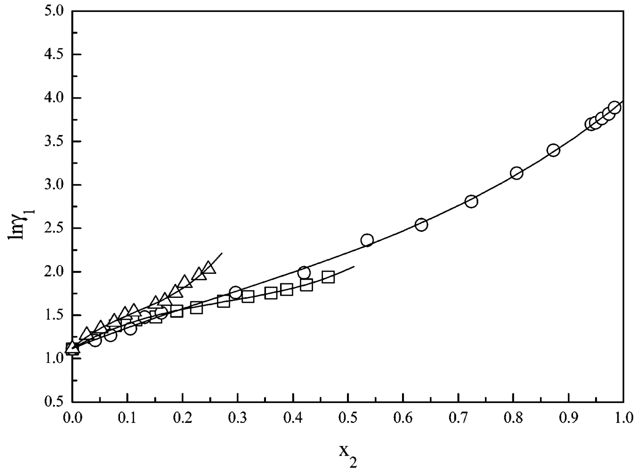

Figure 4. Changes of ln γ_i^∞ against x_2 for benzene in DMSO mixed with □, acetamide; ○, formamide; and △, urea.

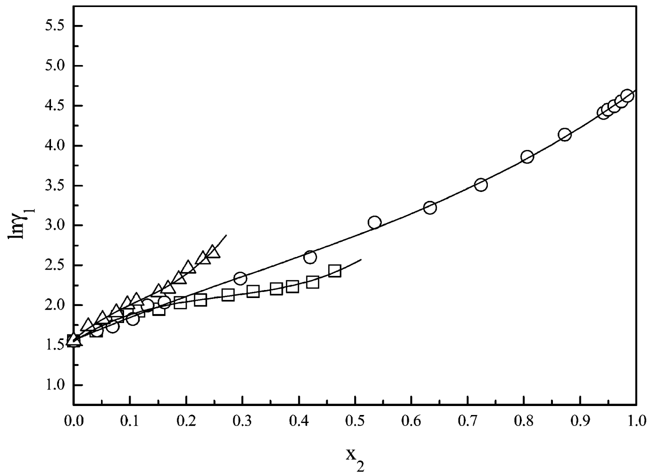

Figure 5. Changes of ln γ_i^∞ against x_2 for tetrachloromethane in DMSO mixed with □, acetamide; ○, formamide; and △, urea.

ond, acetamide causes $S(i/j)$ to decrease, and formamide causes $S(i/j)$ to decrease slightly. Urea causes $S(i/j)$ to increase in most regions of x_2. But in $x_2 > 0.2$, urea causes S(heptane/benzene) to decrease slightly with x_2 increase.

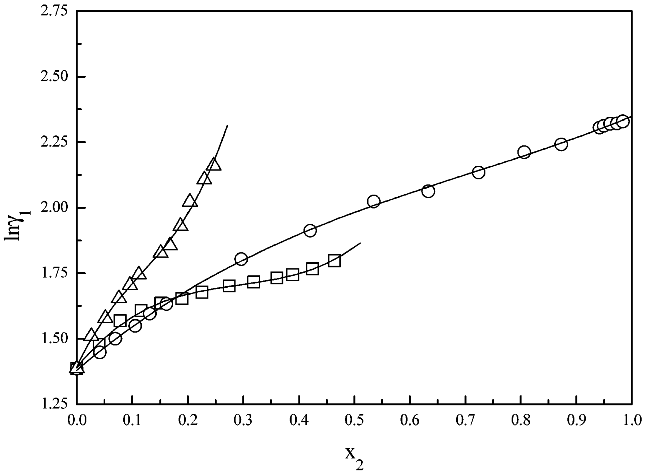

Figure 6. Changes of ln γ_i^∞ against x_2 for ethyl acetate in DMSO mixed with □, acetamide; ○, formamide; and △, urea.

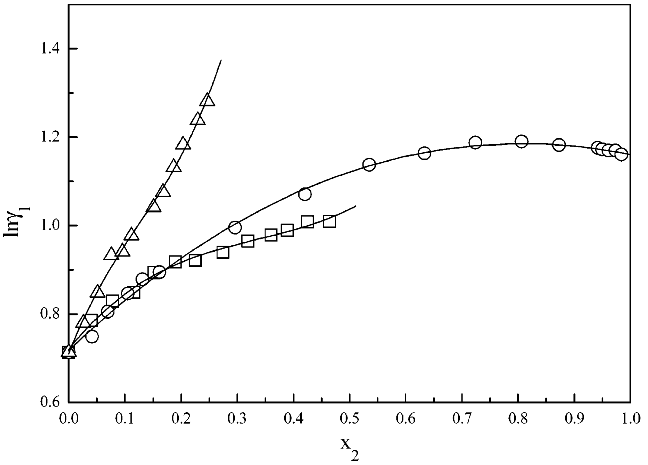

Figure 7. Changes of ln γ_i^∞ against x_2 for acetone in DMSO mixed with □, acetamide; ○, formamide; and △, urea.

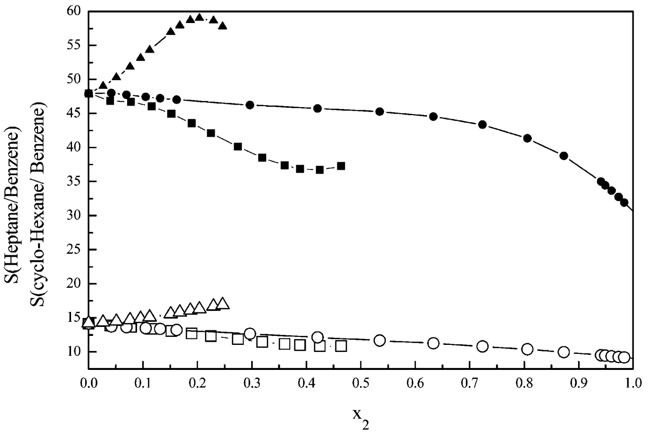

Figure 8. S(heptane/benzene) in DMSO mixed with ■, acetamide; ●, formamide; and ▲, urea. S(cyclohexane/benzene) in DMSO mixed with □, acetamide; ○, formamide; and △, urea.

Third, the change of S(heptane/benzene) with x_2 is more observable than the curves of S(cyclohexane/benzene) against x_2.

In Figure 9 are shown the curves of S(tetrachloromethane/chloroform) and S(dichloromethane/chloroform) against x_2. Two characteristics were observable. First, three curves of $S(i/j)$ overlap approximately into one for tetrachloromethane/

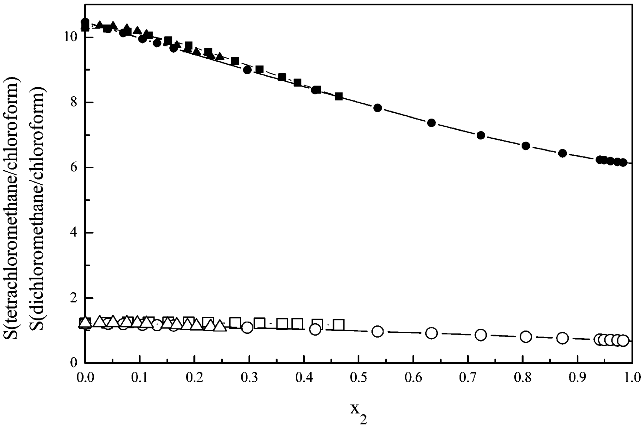

Figure 9. *S*(tetrachloromethane/chloroform) in DMSO mixed with ■, acetamide; ●, formamide; △, urea. *S*(dichloromethane/chloroform) in DMSO mixed with □, acetamide; ○, formamide; and △, urea.

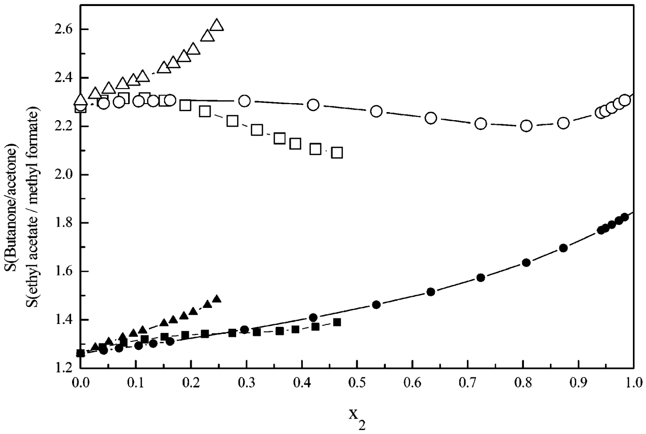

Figure 10. *S*(butanone/acetone) in DMSO mixed with ■, acetamide; ●, formamide; ▲, urea. *S*(ethyl acetate/methyl formate) in DMSO mixed with □, acetamide; ○, formamide; and △, urea.

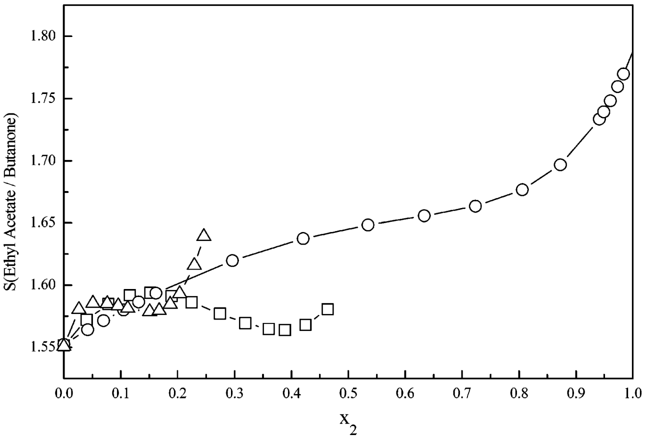

Figure 11. *S*(ethyl acetate/butanone) in DMSO mixed with □, acetamide; ○, formamide; and △, urea.

chloroform and dichloromethane/chloroform, respectively. Second, the value of *S*(tetrachloromethane/chloroform) decreased with x_2 increase. But the change of *S*(dichloromethane/chloroform) is slight.

In Figure 10, *S*(*i*/*j*) values for homogeneous polar solutes, butanone/acetone and ethyl acetate/methyl formate, are shown. There are three more CH_2 groups in a molecule of ethyl acetate than there are for methyl formate. However, there is only one more CH_2 group in butanone than in acetone. Two characteristics can be observed from Figure 10. First, in pure DMSO, *S*(ethyl acetate/methyl formate) > *S*(butanone/acetone). This is an indication that the bigger is the difference of a CH_2 group number for a pair of molecules *i* and *j*, the bigger their *S*(*i*/*j*) becomes in DMSO. Second, for systems of butanone and acetone, *S*(*i*/*j*) increasing caused by urea, formamide, and acetamide is of smaller difference. However, for the system of ethyl acetate and methyl formate, the composition effect on *S*(*i*/*j*) is observable. Urea caused *S*(*i*/*j*) to increase, acetamide caused *S*(*i*/*j*) to decrease, and formamide caused *S*(*i*/*j*) to change evenly.

Vapor pressure is an important property in distillation separation. The vapor pressures of ethyl acetate (12.52 kPa) and butanone (12.05 kPa) are close to each other at 298.15 K. Their CH_2 numbers are equal. In pure DMSO, *S*(ethyl acetate/butanone) is 1.55. In DMSO mixed solvents, urea, formamide, and acetamide all cause *S*(*i*/*j*) to increase slightly in the range $x_2 < 0.2$. But it is difficult to distinguish the effect between one and another. The effect caused by urea, formamide, and acetamide becomes distinguishable only when $x_2 > 0.2$. In this range, urea and formamide caused *S*(*i*/*j*) to increase, but urea's effect is much more steep. Acetamide caused *S*(*i*/*j*) to decrease first and then increase.

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