1187. *Optical Studies of the Soret Effect. Part II.*[1] *Entropies and Heat Capacities of Transfer of Glycine,* DL-α-*Alanine,* β-*Alanine, Glycolamide, and Lactamide in Aqueous Solution.*

By H. J. V. Tyrrell and M. Zaman.

Soret coefficients for aqueous solutions of isoelectric glycine, DL-α-alanine, and β-alanine, together with those for glycolamide and lactamide solutions, have been measured over concentration ranges from 0·1 molal upwards, by the optical beam-displacement method described in Part I. Mean cell temperatures of 25°, 35°, and, for glycine and glycolamide, of 30° also, were used. Entropies and heat capacities of transfer have been calculated from the results. The amino-acids examined have, in general, smaller entropies of transfer than have the isomeric hydroxy-amides at comparable concentrations. The heat capacities of transfer for the former are positive, and quite large; those for the latter are small and negative. These findings suggest that the dipolar ions have a larger net structure-breaking effect on the solvent than their non-polar isomers, which appear to be net structure-forming solutes.

Soret coefficients (σ) have been studied chiefly in aqueous solutions of electrolytes, and it is probably only for these that reliable experimental values exist. If activity-coefficient measurements are also available, heats and entropies of transfer can be calculated. From the change of the heat of transfer, Q^*, with temperature, the "heat capacity of transfer"[2] can be obtained. For most electrolytes, the Soret coefficient has a sign such that the solute concentrates in the colder parts of the cell, this behaviour corresponding to a positive value of the heat of transfer. In dilute solutions, this increases with temperature for most cases so far examined,[2] though this is not always so for concentrated electrolytes.[1] The variation of Q^* with concentration for very dilute electrolytes can be understood reasonably well in terms

[1] Part I, H. J. V. Tyrrell, J. G. Firth, and M. Kennedy, *J.*, 1961, 3432.
[2] J. N. Agar, Adv. Electrochem. Electrochem. Eng., 1963, 3, 31.

of the Debye–Hückel theory,[2,3] but, as might be expected, this theory is not satisfactory for more concentrated solutions. This paper describes an attempt to isolate the effect of purely electrostatic forces on the size of Q^* by comparing a dipolar ion, such as isoelectric glycine, with its relatively non-polar isomer, glycolamide. Other compounds studied here are lactamide and its isomers, DL-α- and β-alanine. Since the physical properties of solutions of this class have been studied extensively, the data for the calculation of heats and entropies of transfer from Soret coefficient measurements are available, and the results can be discussed within the wider context of what is already known about these systems.

Experimental

Soret coefficients were measured by the optical beam-displacement method described in Part I.[1] The cell with a 2 mm. separation between the plates was almost invariably used, and the experimental techniques were unchanged, with one important exception: the displacement of the interference pattern in the image plane, as recorded photographically, was measured with a photoelectric microscope similar to that described by Bennett and Koehler;[4] with this, the position of the rather broad fringes could be located relative to the graticule image with an accuracy of ± 2 microns, compared with ± 10 microns with the visual microscope used earlier. The temperature interval across the cell was approximately 3° (~ 15° cm.$^{-1}$), and was applied symmetrically, the median plane remaining at the mean working temperature in both the isothermal and non-isothermal states. The Soret coefficient was calculated from the steady-state deflection only, since it was shown in Part I that satisfactory results could be obtained in this way for silver nitrate solutions. This was confirmed for a 1·99-molal glycine solution in a similar, 4 mm. cell, by following the rate at which the Soret equilibrium was obtained; from these measurements, a Soret coefficient was calculated, which was identical with that obtained from the steady-state concentration gradient in the same experiment.

The accuracy of the Soret coefficients depends on the concentration range being studied. In dilute solutions, the change in refractive-index gradient due to concentration changes is small compared with that due to the temperature effect itself, and, at 0·1 molal, the practical limit for this method, the reproducibility of the successive experiments was around 5—6%. At higher concentrations, successive measurements did not differ by more than 1—2%. Most values quoted are the mean of at least two measurements.

The absolute accuracy of the measured coefficients depends to a considerable extent upon the accuracy with which the variation of the refractive index (n) with temperature and concentration of the solution is known. For all the systems studied here, rather accurate values of refractive indexes at 25° are available, at any rate over part of the concentration range required. These have been derived from Rayleigh interferograms obtained in diffusion cells, and are normally expressed as power series in molarity. Together with density data, which are usually available from the same literature source, $(\partial n/\partial m)_{25}$ can be calculated (m = molality). These published measurements were confirmed, and extended where necessary, by using a Hilger Rayleigh refractometer. In principle, this is an admirable instrument for measuring the small refractive index difference (Δn) between two solutions differing slightly in molality by Δm; the ratio $\Delta n/\Delta m$ provides a good estimate of $(\partial n/\partial m)_T$ at the mean concentration. However, the well known difficulty of identifying the zero-order fringe unequivocally cannot always be overcome[5,6] easily. Horne and Bearman[5] have described a simple reversal method for cyclohexane–benzene mixtures, which we have applied successfully to aqueous glycolamide solutions, but it does not seem to be universally applicable. The same seems to be true of the technique of using several monochromatic sources in addition to the white light source.[6] In the present work, we have found it best first to obtain an approximate value of $(\partial n/\partial m)_T$, (either by making measurements with a Pulfrich refractometer or by using published data in a neighbouring concentration range) and to use the value to calculate the nearest whole number fringe shift in the Rayleigh refractometer. The exact value, including the fractional part, was then obtained unequivocally by direct observation of the appropriate monochromatic fringes.

[3] E. Helfand and J. G. Kirkwood, *J. Chem. Phys.*, 1960, **32**, 857.
[4] J. M. Bennett and W. F. Koehler, *J. Opt. Soc. Amer.*, 1959, **49**, 466.
[5] F. H. Horne and R. J. Bearman, *J. Chem. Phys.*, 1962, **37**, 2842.
[6] E. Grunwald and E. J. Berkowitz, *Analyt. Chem.*, 1957, **29**, 124.

The change in refractive index with temperature can be conveniently obtained from measurements on a Rayleigh refractometer without the necessity for locating a zero-order fringe with a white-light source.[7] However, this method requires a cell of long path-length or observations over a rather large temperature interval if the required accuracy is to be attained. The correct type of cell was not available, and the method was therefore only applicable to systems for which the quantity $[(\partial n/\partial T)_{\text{soln.}} - (\partial n/\partial T)_{\text{solvent}}]$ was independent of temperature over the range 25—35°. This was true for aqueous solutions of glycolamide with respect to water as solvent, and a satisfactory value of the above difference was obtained in this case over this temperature range. Absolute values of $(\partial n/\partial T)_{\text{soln.}}$ were then obtained from these differences and the values of $(\partial n/\partial T)_{\text{water}}$ obtained by Tilton and Taylor.[8] However, for solutions of glycine and β-alanine, the measured difference in $(\partial n/\partial T)$ between solution and solvent decreased rapidly as the temperature rose, and it was necessary to revert to the method described in Part I for measuring $(\partial n/\partial T)_{\text{soln.}}$. The solution was placed in a Soret cell 10 mm. high, the temperature coefficient applied, and the refractive index gradient measured at the median plane of the cell at a time immediately after the full establishment of the temperature gradient and before concentration changes had begun to occur at this plane. The values of $(\partial n/\partial T)$ obtained are characteristic of the local temperature in the median plane. Changes in the above difference for lactamide and for α-alanine solutions are with temperature very small, but it was convenient to use this method for these systems also.

Activity coefficients for all the solutes studied have been measured at 25° by the isopiestic method. In addition to the derived activity coefficients, either the isopiestic ratio, or the molal osmotic coefficient, ϕ, is usually tabulated as a function of concentration. The most convenient and accurate way of obtaining the required function $(1+\partial \ln \gamma/\partial \ln m)$ is then through the exact equation

$$(1+\partial \ln \gamma/\partial \ln m) = \phi(1+\partial \ln \phi/\partial \ln m) \quad (1)$$

the derivative $\partial \ln \phi/\partial \ln m$ being obtained graphically. In some cases, ϕ was given as a power series in concentration, and the required function could be obtained analytically. The temperature coefficient of this function is given by:

$$\frac{\partial}{\partial T}\left[1+\frac{\partial \ln \gamma}{\partial \ln m}\right] = -\frac{1}{RT^2}\frac{\partial \bar{L}_2}{\partial \ln m}. \quad (2)$$

Relative partial molar heats of dilution, $\bar{L}_2$, can be obtained for glycine and DL-α-alanine from the data of Zittle and Schmidt[9] for their heats of dilution. Strictly, it is necessary to know the temperature coefficient of this, but the contribution of the integrated term derived from equation (2) to the thermodynamic correction factor valid at 35° is small, and the further correction would be quite negligible. For β-alanine, and for glycolamide, the activity-coefficient term calculated for 25° was applied unchanged to the Soret coefficients obtained at 35°.

Glycine (Hopkin and Williams analytical) was dried in a desiccator before use, as was α-alanine (Light's). β-Alanine (B.D.H.) was dissolved in hot water and precipitated with alcohol. After three precipitations, the product was dried at 105°.

Commercial glycolamide is not pure and is very expensive. The cheapest starting material is t-butyl glycolate (Fluka purum). This was distilled at reduced pressure, and dry ammonia passed into it for some hours. The glycolamide crystallised out and was periodically removed. The final product was crystallised thrice from alcohol and dried. The purified sample melted sharply at 115·4° (uncorrected) (Found: C, 32·0; H, 6·7; N, 18·7. Calc. for $C_2H_5NO_2$: C, 32·2; H, 6·85; N, 18·4%).

Lactamide was prepared similarly from ethyl lactate (B.D.H.). In this case, the lactamide is so soluble in the ethyl alcohol formed at the same time, that crystals do not appear until the reaction flask is cooled. An increased yield can be obtained by evaporating off the alcohol under reduced pressure. The crude product was recrystallised thrice from a saturated solution of water in ethyl acetate,[10] and dried (Found: C, 40·4; H, 7·65; N, 15·9. Calc. for $C_3HN_7O_2$: C, 40·45; H, 7·9; N, 15·7%).

[7] H. J. V. Tyrrell and L. Guczi, unpublished work.
[8] L. W. Tilton and J. K. Taylor, *J. Res. Nat. Bur. Stand.*, 1938, **20**, 419.
[9] C. A. Zittle and C. L. A. Schmidt, *J. Biol. Chem.*, 1935, **108**, 161.
[10] F. T. Gucker and T. W. Allen, *J. Amer. Chem. Soc.*, 1942, **64**, 191.

Results

Soret coefficients, σ, and entropies of transfer, S^*, are summarised in Tables 1—5 together with values of $(\partial n/\partial T_m)$, and $(\partial n/\partial m)_T$ used in the calculations. Activity-coefficient terms at 25° were calculated from data derived from the following sources:

(*a*) Glycine; Smith and Smith,[11] isopiestic ratio with sucrose.
(*b*) Glycolamide; Stokes,[12] isopiestic ratio with potassium chloride.
(*c*) DL-α-Alanine; Smith and Smith,[13] isopiestic ratio with sucrose.
(*d*) β-Alanine; Smith and Smith,[14] as α-alanine.
(*e*) Lactamide; Dunlop and his co-workers,[15] isopiestic ratio with potassium chloride.

Figure 1 shows the calculated values of $(1+[\partial \ln \gamma/\partial \ln m])$ for the first four solutes; those for lactamide are almost indistinguishable from those for glycolamide.

Table 1.

Soret coefficients and entropies of transfer for aqueous glycine solutions (T_m = mean temperature of cell, τ = temperature interval across cell, a = cell height).

Molality (m)	$10^4\left(\frac{\partial n}{\partial T}\right)_m$	$\left(\frac{\partial n}{\partial m}\right)_T$	τ/a (deg. cm.$^{-1}$)	Soret coefficient $10^3\sigma$ (deg.$^{-1}$)	S^* (cal. mole^{-1} deg.$^{-1}$)
		(*a*) $T_m = 25°$			
0·102	1·074	0·01333	15·10	2·18	1·25
0·205	1·090	0·01313	12·75	1·48	0·96
0·260	1·100	0·01302	14·41	1·29	0·72
0·299	1·106	0·01295	14·17	1·24	0·69
0·416	1·124	0·01273	15·20	0·98	0·54
0·503	1·138	0·01256	15·20	0·90	0·49
0·625	1·157	0·01233	14·51	1·02	0·55
0·683	1·166	0·01222	14·31	1·17	0·62
0·705	1·170	0·01212	15·20	1·20	0·64
0·803	1·186	0·01200	14·41	1·28	0·67
1·004	1·216	0·01168	15·14	1·29	0·68
1·467	1·286	0·01104	14·31	1·40	0·72
2·004	1·340	0·01050	14·31	1·54	0·79
2·060	1·346	0·01045	15·10	1·51	0·77
		(*b*) $T_m = 30°$			
0·098	1·221	0·01324	13·67	2·79	1·64
0·255	1·245	0·01295	13·57	2·17	1·24
0·295	1·251	0·01286	13·83	2·07	1·18
0·489	1·279	0·01254	13·64	1·50	0·83
0·766	1·319	0·01198	13·76	1·61	0·86
1·008	1·345	0·01162	13·62	1·62	0·86
1·498	1·409	0·01098	13·67	1·80	0·94
1·990†	1·455	0·01045	12·63	1·75	0·90
		(*c*) $T_m = 35°$			
0·112	1·360	0·01314	14·78	2·48	1·52
0·318	1·390	0·01276	14·80	2·41	1·38
0·503	1·416	0·01242	14·80	2·19	1·22
0·803	1·454	0·01186	14·71	1·93	1·04
1·020	1·478	0·01152	14·85	1·84	0·99
1·110	1·486	0·01141	13·17	1·77	0·94
1·270	1·504	0·01118	14·64	1·96	1·04
1·363	1·512	0·01107	13·21	1·94	1·03
1·467	1·520	0·01094	14·78	2·06	1·09
1·682	1·538	0·01072	13·07	2·07	1·09
2·011	1·566	0·01048	14·86	2·16	1·13

† Experiment in cell 4·10 mm. high.

[11] E. R. B. Smith and P. K. Smith, *J. Biol. Chem.*, 1937, **117**, 210.
[12] R. H. Stokes, *Trans. Faraday Soc.*, 1954, **50**, 565.
[13] E. R. B. Smith and P. K. Smith, *J. Biol. Chem.*, 1937, **121**, 606.
[14] E. R. B. Smith and P. K. Smith, *J. Biol. Chem.*, 1940, **132**, 47.
[15] H. D. Ellerton, G. Reinfelds, D. E. Mulcahy, and P. J. Dunlop, *J. Phys. Chem.*, 1964, **68**, 398.

TABLE 2.

Soret coefficients and entropies of transfer for aqueous glycolamide solutions.

Molality (m)	$10^4\left(\frac{\partial n}{\partial T}\right)_m$	$\left(\frac{\partial n}{\partial m}\right)_T$	τ/a (deg. cm.$^{-1}$)	Soret coefficient $10^3\sigma$ (deg.$^{-1}$)	S^* (cal. mole^{-1} de.g^{-1})
		(a) $T_m = 25°$			
0·199	1·090	0·00909	13·13	2·07	1·21
0·384	1·120	0·00887	15·59	2·18	1·26
0·404	1·126	0·00885	13·17	2·22	1·27
0·566	1·152	0·00866	15·59	2·18	1·24
0·913	1·212	0·00834	15·59	2·15	1·21
1·529	1·315	0·00780	15·59	2·20	1·21
2·087	1·408	0·00734	15·59	2·18	1·17
		(b) $T_m = 30°$			
0·319	1·258	0·00884	13·44	2·05	1·22
0·476	1·282	0·00868	13·48	2·07	1·21
0·640	1·311	0·00852	13·57	2·12	1·22
1·020	1·374	0·00819	13·50	2·11	1·20
1·411	1·438	0·00783	13·39	2·12	1·19
2·060	1·545	0·00730	13·34	2·14	1·17
		(c) $T_m = 35°$			
0·319	1·394	0·00876	13·44	1·88	1·13
0·476	1·420	0·00860	13·48	1·94	1·15
0·640	1·447	0·00845	13·37	1·93	1·13
1·020	1·510	0·00811	13·35	1·95	1·13
1·411	1·574	0·00776	13·39	1·98	1·13
2·06	1·681	0·00722	13·44	2·07	1·15

TABLE 3.

Soret coefficients and entropies of transfer for aqueous α-alanine solutions.

Molality (m)	$10^4\left(\frac{\partial n}{\partial T}\right)_m$	$\left(\frac{\partial n}{\partial m}\right)_T$	τ/a (deg. cm.$^{-1}$)	Soret coefficient $10^3\sigma$ (deg.$^{-1}$)	S^* (cal. mole^{-1} deg.$^{-1}$)
		(a) $T_m = 25°$			
0·104	1·078	0·01510	12·97	3·93	2·33
0·199	1·096	0·01488	12·86	3·83	2·27
0·303	1·112	0·01466	12·99	3·40	2·21
0·389	1·126	0·01446	13·01	3·75	2·22
0·493	1·141	0·01424	12·95	3·70	2·20
0·523	1·146	0·01418	13·03	3·68	2·18
0·715	1·173	0·01376	12·99	3·69	2·20
0·784	1·183	0·01357	13·39	3·78	2·25
0·981	1·203	0·01317	12·99	3·76	2·25
1·230	1·225	0·01274	12·97	3·73	2·26
1·405	1·239	0·01249	12·91	3·76	2·30
1·628	1·250	0·01217	12·92	3·73	2·31
		(b) $T_m = 35°$			
0·110	1·361	0·01491	14·06	4·15	2·54
0·213	1·381	0·01468	14·15	4·15	2·55
0·301	1·397	0·01448	14·29	4·10	2·51
0·496	1·425	0·01402	14·17	4·06	2·50
0·700	1·455	0·01364	14·24	3·92	2·42
0·881	1·475	0·01325	14·24	3·99	2·47
0·919	1·480	0·01318	13·21	3·92	2·44
0·961	1·484	0·01312	14·24	(4·02)	(2·50)
1·151	1·503	0·01277	14·19	3·91	2·45
1·371	1·520	0·01246	14·24	3·91	2·48
1·691	1·542	0·01202	14·24	3·87	2·49

The experimental value of the mean temperature gradient, τ/a, is also given. This was assumed to be equal to the temperature gradient encountered by the light beam in its passage through the central part of the cell (see Discussion in Part I for a justification of this). In all these experiments

TABLE 4.

Soret coefficients and entropies of transfer for aqueous β-alanine solutions.

Molality (m)	$10^4\left(\frac{\partial n}{\partial T}\right)_m$	$\left(\frac{\partial n}{\partial m}\right)_T$	τ/a (deg. cm.$^{-1}$)	Soret coefficient $10^3\sigma$ (deg.$^{-1}$)	S^* (cal. mole^{-1} deg.$^{-1}$)
		(a) $T_m = 25°$			
0·145	1·079	0·01572	13·39	3·59	2·07
0·243	1·093	0·01548	12·64	3·56	2·09
0·319	1·106	0·01530	13·33	3·35	1·97
0·477	1·128	0·01492	12·64	3·26	1·92
0·616	1·148	0·01460	12·82	3·16	1·86
0·645	1·153	0·01453	13·30	3·06	1·81
0·766	1·171	0·01427	12·73	3·04	1·81
0·952	1·198	0·01387	12·82	2·92	1·75
1·295	1·248	0·01316	12·82	2·82	1·72
1·478	1·274	0·01277	12·77	2·84	1·76
2·068	1·340	0·01160	12·75	2·69	1·75
		(b) $T_m = 35°$			
0·093	1·353	0·01571	13·05	3·82	2·34
0·192	1·364	0·01546	13·12	3·76	2·28
0·282	1·375	0·01526	13·07	3·58	2·17
0·498	1·407	0·01474	13·03	3·47	2·11
0·588	1·413	0·01452	13·30	3·51	2·14
0·816	1·441	0·01043	13·26	3·42	2·10
0·996	1·463	0·01366	13·21	3·41	2·11
1·191	1·479	0·01326	13·11	3·35	2·10
1·541	1·504	0·01256	13·26	3·24	2·08
2·187	1·539	0·01124	13·30	3·15	2·13

TABLE 5.

Soret coefficients and entropies of transfer for aqueous lactamide solutions.

Molality (m)	$10^4\left(\frac{\partial n}{\partial T}\right)_m$	$\left(\frac{\partial n}{\partial m}\right)_T$	τ/a (deg. cm.$^{-1}$)	Soret coefficient $10^3\sigma$ (deg.$^{-1}$)	S^* (cal. mole^{-1} deg.$^{-1}$)
		(a) $T_m = 25°$			
0·099	1·076	0·01089	12·73	5·54	3·25
0·177	1·092	0·01080	12·77	5·49	3·20
0·255	1·103	0·01064	12·73	5·41	3·15
0·393	1·130	0·01044	12·54	5·24	3·02
0·518	1·154	0·01026	12·54	5·13	2·93
0·692	1·186	0·01001	12·77	4·97	2·82
0·903	1·224	0·00975	12·73	4·91	2·76
1·026	1·248	0·00960	12·82	4·82	2·69
1·262	1·292	0·00934	12·77	4·68	2·59
1·413	1·320	0·00916	12·77	4·61	2·54
1·924	1·414	0·00860	12·77	4·38	2·37
		(b) $T_m = 35°$			
0·097	1·358	0·01070	14·29	5·18	3·14
0·197	1·375	0·01055	14·38	5·08	3·06
0·292	1·391	0·01042	14·29	5·01	2·99
0·384	1·407	0·01027	14·17	4·96	2·96
0·499	1·427	0·01009	14·11	4·88	2·89
0·613	1·447	0·00992	14·20	4·74	2·79
0·775	1·475	0·00970	14·11	4·68	2·73
0·960	1·507	0·00949	14·11	4·62	2·68
1·359	1·577	0·00905	14·15	4·47	2·55
1·754	1·644	0·00860	14·11	4·28	2·41

the cell height was close to 2·24 mm. The single experiment on 1·99-molal glycine in a 4·10 mm. cell at a mean temperature of 30°, temperature interval 5·18°, gave the following results from an analysis of the rate of attainment of the Soret equilibrium: $\sigma = 1{\cdot}75 \times 10^{-3}$ deg.$^{-1}$, $D = 9{\cdot}3 \times 10^{-6}$ cm.^{2} sec.$^{-1}$. In the same experiment, the steady-state concentration gradient corresponded to an

identical value of σ. Diffusion coefficients for concentrated glycine solutions [16] have been measured accurately at 25°; interpolation gave a value for a 1·99-molal solution, which, on correction to 30° by use of the Stokes–Einstein equation and published viscosity data, gave $D = 9{\cdot}45 \times 10^{-6}$ cm.^{2} sec.$^{-1}$.

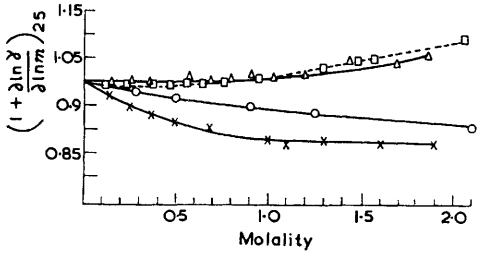

FIG. 1.

The thermodynamic factors $(1+\partial \ln \gamma/\partial \ln m)$ at 25° for aqueous glycine, glycolamide, DL-α-alanine and β-alanine solutions. Sources shown in text.

× glycine; ○ glycolamide;
△ DL-α-alanine; □ β-alanine.

These S^* values have been plotted on large scale graphs, and values of the difference between the entropy of transfer for the non-polar and polar isomer interpolated at arbitrary concentrations. The results are shown in Figure 2. Heat capacities of transfer defined [2] as,

$$C^* = T\,\mathrm{d}S^*/\mathrm{d}T$$

have been calculated from the entropies of transfer at 25° and 35°. Those average values are shown as functions of concentration in Figure 3. They are not, of course, of high accuracy.

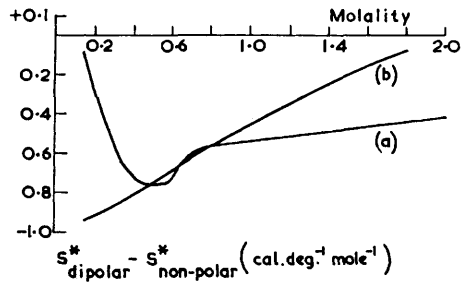

FIG. 2.

Differences in the entropy of transfer of non-polar and dipolar pairs at 25°. (A negative value shows that the entropy of transfer for the non-polar isomer is greater than that for the polar isomer.)

(a) glycine–glycolamide at 25°;
(b) DL-α-alanine–lactamide at 25°.

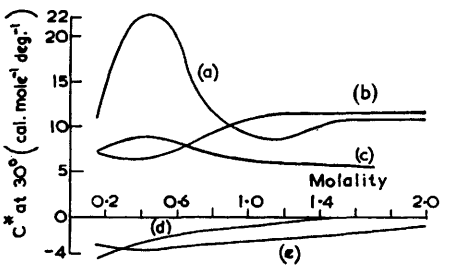

FIG. 3.

Mean heat capacities of transfer (C^*) at 30°.

(a) glycine; (b) β-alanine (c) DL-α-alanine; (d) lactamide; (e) glycolamide.

The results may be briefly summarised as follows:

(i) The entropy of transfer of lactamide is very much greater than that of glycolamide. For non-polar solutes in non-aqueous solvents, there is some connexion between the molecular-weight difference of the two components and the ease with which separation occurs in a thermal gradient.[17] Whether a similar connexion exists for non-polar solutes in water remains to be seen, but the present observation is consistent with the belief that non-polar solutes in water exert on the solvent a structure-forming influence that increases with molecular weight.[18] The functional dependence of S^* upon concentration is quite different for these two systems, but the heat capacities of transfer are small and negative in both cases.

[16] H. D. Ellerton, G. Reinfelds, D. E. Mulcahy, and P. J. Dunlop, *J. Phys. Chem.*, 1964, **68**, 403.
[17] H. J. V. Tyrrell, "Diffusion and Heat Flow in Liquids," Butterworths, London, 1961.
[18] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 1945, **13**, 492, 507. H. S. Frank and Wen-Yang, Wen *Discuss. Faraday Soc.*, 1957, **24**, 133.

(ii) The heat capacities of transfer for all three amino-acids examined are comparatively large and positive. Again, the dependence on concentration varies considerably from one compound to another but, at high concentrations, the heat capacity of transfer is approximately the same for glycine and β-alanine ($\sim$ **10** cal. mole^{-1} deg.$^{-1}$) and approximately twice that for α-alanine.

(iii) In general, the entropy of transfer at 25° for the amino-acids is less than that for the corresponding non-polar isomers. The difference between the entropies of transfer for α-alanine and for lactamide is less than that between β-alanine and lactamide. At 35°, these differences are somewhat smaller.

(iv) Some preliminary measurements on glycine solutions to which an equivalent amount of (a) hydrochloric acid and (ii) sodium hydroxide had been added showed that the magnitude of σ had changed to a remarkable extent. The solutions of $Cl^-NH_3^+{\cdot}CH_2{\cdot}CO_2H$ showed a small negative Soret coefficient at 25°, which could not be measured because of the onset of convection in the cell. At 40°, a barely measurable positive value of σ was found at all concentrations. This behaviour is similar to that of ammonium chloride. Solutions of $NH_2{\cdot}CH_2{\cdot}CO_2^-Na^+$ had a considerably larger Soret coefficient than glycine itself, which decreased slightly with temperature. In the absence of activity data, S^* values could not be calculated, and these results are not therefore discussed further at present.

Discussion

The heat and entropy of transfer can be given a physical significance in terms of the thermodynamics of the steady state and of Onsager's reciprocity principle. If, in an isothermal system, a particle diffuses from one side of a reference plane to another, heat will be transferred with it, in the sense that heat will be absorbed on one side of the plane and liberated on the other. Part of this heat is the partial molal enthalpy of the particle and the rest is the "reduced heat flow," or the heat of transfer per particle. This quantity is the amount of heat that must be supplied to that side of the plane from which the particle diffuses in order to keep the local temperature identical with that of the rest of the system. A similar amount of heat has to be removed from the other side of the plane in consequence of the arrival of the particle there. Thus, a positive value of Q^* and of S^* corresponds to an increase of entropy in the region from which the particle has migrated. A quantitative treatment of heats and entropies of transfer in terms of this model has been attempted for dilute electrolyte solutions by Agar[2] and, among other things, he concluded that, ignoring electrophoretic corrections, the variation of $S^*_\pm$ with concentration is approximately the change in the excess entropy of the salt, that is,

$$S^*_\pm = (S^*_\pm)^\circ + R(\ln \gamma_\pm + T\partial \ln \gamma_\pm/\partial T) \quad (3)$$

where $(S^*_\pm)^\circ$ is the mean entropy of transfer in an infinitely dilute solution. A more sophisticated treatment in, terms of the Debye–Hückel theory, by Helfand and Kirkwood[3] gave an equation, which at a corresponding level of accuracy can be written,

$$S^*_\pm = (S^*_\pm)^\circ + R(4/3 \ln \gamma_\pm + T\partial \ln \gamma_\pm/\partial T) \quad (4)$$

These equations give a reasonable explanation of the variation of $S^*_\pm$ with concentration in dilute solutions of sodium and potassium chlorides, and, in more concentrated solutions, reproduce, in a qualitative way, the observed minima in the plot of $S^*_\pm$ against $m^{1/2}$. There is apparently nothing in the derivation of equation (3) that would confine its validity to salt solutions rather than to dipolar ions or to neutral substances. However, neither equation (3) nor equation (4) provide even a qualitative representation of the change in S^* with concentration for glycine or DL-α-alanine solutions, the two systems studied here for which the excess molal entropies of the solutes can be calculated.

It is well known that the interaction between a solute, either polar or non-polar, and a solvent such as water is not simple. It is generally agreed that, in the immediate vicinity of an ion in water, there is a relatively small number of water molecules held firmly by ion–dipole forces. At large distances from the ion there will be a normal dielectric polarisation of the solvent molecules; this long-range interaction produces a positive contribution to S^*

which falls off rapidly with increasing concentration, because of mutual screening of the ions.[19] In addition to these effects, there is a good deal of evidence that most ions exert a structure-breaking effect on the water molecules just outside the first hydration sheath. In very dilute solutions, the situation can be described in terms of a zone of water molecules, lying between the first hydration sheath and the region of dielectric polarisation, which is more disordered than pure water at the same temperature. This concept has been discussed in great detail by Frank and his associates,[18] who have used it to explain the unexpectedly high entropies of hydration of gaseous ions, the large negative partial molal heat capacities of electrolytes in water, the contraction in volume that occurs when they are dissolved in water, and other, similar, properties of aqueous electrolytes. Non-polar molecules and certain large organic ions have, on the other hand, a lower entropy in water than would be expected from entropy data on the same solutes in non-aqueous solutions; this entropy is markedly temperature-dependent, and the abnormal lowering of the entropy increases with the size of the solute molecules. This, together with other evidence, such as the large positive partial molal heat capacities of these solutes in water, is explained in terms of the induction by the solute of regions of greater structure than are characteristic of pure water at the same temperature. In concentrated solutions, it becomes impossible to talk of definite zones of solvent round the solute particles, apart from the solvent molecules in the first hydration sheath, but it is not unreasonable to regard the hydrated solute as having a net structure-breaking or structure-forming effect on the rest of the solvent and to attempt to explain the properties of the solutions in these terms.

These conclusions are based on measurements of properties of the system that depend both on the nature of the solute itself and on its effect upon the surrounding solvent. Thus, the standard entropy of a solute is determined by the size of the free-volume box in which the solute particles can be considered to move, by its internal degrees of freedom, and by the effect it produces on the solvent molecules. The entropy of transfer is, however, not directly dependent on the internal degrees of freedom of the solute; for example, the partial molal enthalpy of the solute is specifically excluded from Q^*. Since the solvent molecules in the first hydration sheath probably move with the diffusing solute, these should not contribute to S^* either. It would be expected, though, to include a contribution from the entropy change as the solvent molecules relax into the state characteristic of the pure solvent when the diffusing molecule moves away. With ions, some of this will arise from the disappearance of the dielectric polarisation of the distant solvent molecules, and some from the effects of structure-breaking or structure-forming at shorter distances. For dipolar ions and for non-polar solutes, this dielectric polarisation contribution is, of course, negligible or non-existent. A zero value for S^* may well arise from a chance cancellation of opposing effects, and hence consideration of *changes* in S^* with changing experimental conditions will be important. If the solute has a net structure-breaking effect, this will provide a negative contribution to S^*. As the temperature rises, the normal structure of water becomes more disordered, and this negative contribution to S^* will decrease. The heat capacity of transfer should therefore be positive if the other contributions to S^* are approximately independent of temperature. A net structure-forming effect will, on the other hand, provide a positive contribution to S^*. The formation of ordered regions in the solvent will be opposed by thermal motion and, at higher temperatures, they should form less readily. The local entropy-density round the structure-forming solute will thus be greater at high temperatures than at low, and the positive contribution to S^* of these "micro-crystalline" regions should therefore decrease as the temperature rises; this would correspond to a negative heat-capacity of transfer. However, the normal structure of water at the higher temperature will also be less ordered than at the lower, and the *difference* between the condition of the solvent in the presence in and the absence of the solute could, in fact, vary only to a small extent with temperature; C^* ought therefore to be small, and possibly negative.

The present results show that, except in a restricted range of experimental conditions, the

[19] J. N. Agar, *Rev. Pure Appl. Chem.* (*Australia*), 1958, **8**, 1.

entropy of transfer for the dipolar isomer is less than that of the non-polar one. This is consistent with the belief that the structure-breaking effect of the former is greater than that of the latter. It is not surprising that S^* for β-alanine is consistently less than for α-alanine, since the former is the more polar compound. Also, the methyl group in α-alanine could have a structure-forming influence on the solvent. This is confirmed by the observed values of C^*; without exception, the heat capacities of transfer for the polar isomers are positive, glycine and β-alanine having generally larger values than α-alanine, and those for non-polar isomers are negative. These negative values are small, as would be expected from the discussion in the preceding paragraph.

The extensive data available on the comparative physical properties of isomeric pairs of this kind have mainly been interpreted in terms of "electrostriction," that is, the clustering and compression of water dipoles round the dipolar ion.[20] They could equally well be regarded as due to an increase in the structure-breaking power of the dipolar isomer in comparison with that of the non-polar isomer, this re-interpretation of the data being exactly parallel to that suggested by Frank for electrolyte solutions. The data for the entropy of transfer, on the other hand, can most simply be interpreted in terms of structure-breaking by the dipolar solutes. There is some independent evidence that glycine has a net structure-breaking influence on water. The energy of activation for viscous flow for glycine solutions is slightly less than that found for pure water,[21] whilst the relative partial molal entropy of water is positive at all glycine concentrations.[22] However, α- and β-alanine solutions have higher relative viscosities than those of glycine solutions, higher energies of activation for viscous flow than water, and the relative partial molal entropies of water are negative in these solutions, facts interpreted by suggesting that these amino-acids are net structure-formers in water, a conclusion that is not in agreement with our interpretation of the Soret-effect data. Comparisons of this type, between amino-acid solutions and solutions of their non-polar isomers, might resolve this apparent discrepancy, but the necessary experimental measurements on the latter compounds are not yet available.

Glycine, in dilute solution, was found to diffuse more rapidly than would be expected from the Stokes–Einstein equation, and this fact was originally interpreted in terms of net structure-breaking by the glycine.[23] Later, it was observed that glycolamide[24] behaved similarly, and, in fact, all the amino-acids and hydroxy-amides examined recently by Dunlop and his associates[16] behave in this way. There is no evidence that hydroxy-amides have any structure-breaking tendencies, and the earlier explanation of the observations on glycine is clearly inadequate. One interesting point does emerge from a study of the relationship between the frictional coefficients and viscosities of the substances examined by Dunlop *et al.* They found that a bi-logarithmic plot of relative frictional coefficient against relative viscosity was linear, with a slope of about 0·8 (1·0 for sucrose, as required by the Stokes–Einstein equation) for all substances examined except for glycine and glycylglycine. For low concentrations, the plots for these substances had a slope less than 0·8, which increased quite sharply at higher concentrations to give a slope roughly of 0·8, like the remaining compounds. The most rapid change in slope can be shown to be at $C \sim 0{\cdot}6$ molar (molality $\sim$ 0·65) for glycine. Below this concentration, the frictional coefficient was less than would be expected by comparison with any of the other solutes studied (urea, glycolamide, lactamide, DL-valine, α-aminobutyric acid, α-alanine, and β-alanine). This change in shape occurred, for glycine solutions, in the same concentration range as the sharp increase in S^* (cf. Fig. 2), an increase observed only for glycine but not for α- or β-alanine solutions, and is the only other case known to us where a sharp change in physical properties, characteristic of glycine but not of the alanines, has been observed in any concentration range. The

[20] *E.g.*, E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold, New York, 1943
[21] L. S. Mason, P. M. Kampmeyer, and A. L. Robinson, *J. Amer. Chem. Soc.*, 1952, **74**, 1287.
[22] A. L. Robinson, *J. Chem. Phys.*, 1946, **14**, 588; L. S. Mason, W. F. Offutt, and A. L. Robinson, *J. Amer. Chem. Soc.*, 1949, **71**, 1463.
[23] M. S. Lyons and J. V. Thomas, *J. Amer. Chem. Soc.*, 1950, **72**, 4506.
[24] P. J. Dunlop and L. J. Gosting, *J. Amer. Chem. Soc.*, 1953, **75**, 5073.

significance of this may become clearer from work in progress on the Soret coefficient of glycylglycine.

The present findings may be summarised as follows: the relatively non-polar hydroxyamides give entropies of transfer and heat capacities of transfer that are consistent with the belief that both these solutes exert a net structure-forming influence on the solvent. The amino-acids examined behave in a quite different manner, the simplest explanation for this being in terms of structure-breaking by these solutes, though only with glycine is there definite evidence supporting this conclusion. The data for the entropy of transfer for glycine show some remarkable changes with concentration, especially at 25°, quite unlike those observed with α- and β-alanine, but fuller comment on these changes is reserved until the results of further experimental work become available.

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