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ALKALI HALIDE-ACID AMIDE INTERACTION IN GAS CHROMATOGRAPHIC STATIONARY PHASES

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SUMMARY

Specific interaction occurring between an alkali-metal halide and an acid amide in a gas chromatographic stationary phase has been investigated by using nine alkali-metal-halide-containing polyethylene glycol stationary phases and nine aliphatic acid amides as sample solutes. The magnitude of the interaction is evaluated in terms of excess free energy of transfer ($\Delta\overline{G}_t^\circ$) for each combination of halide and amide used. A discussion is presented of the dependence of $\Delta\overline{G}_t^\circ$ on the change in (i) the polarity of the stationary phase, (ii) the concentration of the halide in the stationary phase, (iii) the ionic radii of the cations and anions of the alkali-metal halides, and (iv) the chemical structure of the amide molecule. It is suggested that the solubility of an alkali-metal halide in the stationary phase and the dipole moment of the amide molecule contribute to the change in solute retention in alkali-metal-halide-containing columns. The utility of the findings is demonstrated by the fact that diacetamide and butyramide are eluted from a column of polyethylene glycol 20,000 containing lithium chloride in the reverse order of their elution from an analogous, but salt-free, column.

INTRODUCTION

Mixed stationary phases are widely used in the gas chromatographic separation of particular components of mixtures; the first example was the use of a polyethylene glycol (PEG) column containing silver nitrate¹, on which an olefinic compound was selectively retarded because of its specific interaction with silver cations in the stationary phase. The addition of an inorganic salt to the stationary phase generally gives rise to either retardation or acceleration of the elution of interacting species, depending on whether there is a salting-in or a salting-out effect. Sometimes, however, particularly strong interaction may result in chemical reaction to yield a non-volatile product that does not emerge from the column.

It is known that some aliphatic amides react with alkali-metal halides to form stable complexes. Some such complexes have been isolated², and studies have been made of their electrical conductivity³⁻⁶, heat of solution⁷⁻¹³ and IR spectra¹⁴; they have also been subjected to X-ray analysis^{15,16}. Uno *et al.*¹⁴ found that mixing diacetamide with alkali-metal halide in the solid state produced a change in the IR spectrum

and suggested that ion-dipole interaction gave rise to a configurational change in the diacetamide molecule from *cis-trans* to *trans-trans*. It was also found from X-ray analysis that sodium bromide could react with acetamide¹⁵ or diacetamide¹⁶ to form a 1:2 complex; in the latter complex, the diacetamide moiety has *trans-trans* configuration, which facilitates interaction between Br⁻ and -NH- and between Na⁺ and >C=O. Prompted by these findings, we have attempted to ascertain whether interactions of this type occur in gas chromatographic stationary phases and to consider the thermodynamics and analytical applications of such interactions.

The partition coefficient of a solute between mobile and stationary phases in gas chromatography is given by

$$K = V'_r/V_L \quad (1)$$

where V'_r and V_L are the adjusted retention volume and the volume of stationary phase, respectively. The partial molar free energy of transfer ($\Delta\overline{G}_t^\circ$) is defined as the difference in partial molar free energy of excess ($\Delta\overline{G}_e^\circ$) between a binary system (solute and stationary phase) and a ternary system (solute, salt and stationary phase). Thus,

$$\Delta\overline{G}_t^\circ = \Delta\overline{G}_{e,1+2}^\circ - \Delta\overline{G}_{e,1}^\circ = RT_c \ln (\gamma_{1+2}^\circ/\gamma_1^\circ) \quad (2)$$

where the subscripts 1 and 2 refer to solute and salt, respectively, R is the gas constant, T_c is the column temperature (in Kelvins) and γ° is the activity coefficient of the solute at infinite dilution. Thus, by definition, $\Delta\overline{G}_t^\circ$ is a parameter that represents the magnitude of the interaction between solute and salt in the stationary phase. If retention of a solute is measured on both salt-containing and salt-free stationary phases at the same temperature, $\Delta\overline{G}_t^\circ$ can be calculated from the expression

$$\Delta\overline{G}_t^\circ = RT_c \ln \frac{K_1}{K_{1+2}} \cdot \frac{W_2/M_2 + W_L/M_L}{W_2/d_2 + W_L/d_L} \cdot \frac{M_L}{d_L} \quad (3)$$

where the subscript L refers to the stationary phase, and M , d and W are, respectively, the molecular weight, the density and the weight of the component specified by the subscript. With regard to the stationary phase, the increasing number of oxyethylene units in PEG reduces the contribution of the terminal hydroxyl group to partition of the solute in contrast with that of the oxyethylene units. The PEG 20M used in this work has, on average, more than 450 oxyethylene units and only two hydroxyl groups; we assumed, therefore, that each oxyethylene unit acts as a stationary phase molecule and thus M_L in eqn. 3 has the value 44.05.

EXPERIMENTAL

Gas chromatography

The Shimadzu GC-5A instrument used was equipped with a thermal-conductivity detector and a U-shaped glass column (1 m × 3 mm I.D.). The column packings were prepared by mixing the appropriate halide (LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr or KI) with PEG 20 M (5, 10 or 20%, w/w, of halide) and coating

Chromosorb W (60–80 mesh; AW; DMCS-treated) with 20%, by weight, of the mixture.

Columns so prepared were operated at 165, 185 or 205°, with the injector and detector each at 210°, and helium as carrier gas; the flow-rate was measured with a soap-film meter and was corrected with respect to temperature and pressure.

Materials

Formamide (FA), N-methylacetamide (MAA) and dimethylacetamide (DMA) were obtained from Nakarai Chemicals (Kyoto, Japan), acetamide (AA) from Wako (Osaka, Japan), *n*-propionamide (PA) from BDH (Poole, Dorset, Great Britain) and butyramide (BA) from Tokyo Kasei Kogyo (Tokyo, Japan). Diacetamide (DAA), dipropionamide (DPA) and *n*-valeramide (VA) were synthesized by established methods; no impurity was found on the chromatogram within full-scale recorder response of

TABLE I

PARTITION COEFFICIENTS (*K*) OF AMIDES ON COLUMNS CONTAINING LITHIUM HALIDES

The molality is expressed by *m*.

Amide	Temp. (°C)	PEG (<i>m</i> =0.00)	LiCl (20%) (<i>m</i> =5.90)	LiBr (20%) (<i>m</i> =2.88)	LiI (5%) (<i>m</i> =0.385)	LiI (10%) (<i>m</i> =0.812)	LiI (20%) (<i>m</i> =1.83)
Formamide	205	4.634	5.022	5.347	5.420	5.710	7.135
	185	5.233	5.601	5.909	5.949	6.266	7.735
	165	5.922	6.281	6.560	6.613	6.914	8.372
Acetamide	205	4.534	4.908	5.367	5.334	5.696	7.200
	185	5.132	5.584	5.931	5.884	6.295	7.809
	165	5.795	6.212	6.632	6.527	6.932	8.476
Propionamide	205	4.673	5.013	5.437	5.396	5.700	7.081
	185	5.263	5.595	5.986	5.963	6.291	7.715
	165	5.917	6.259	6.709	6.610	6.957	8.389
Butyramide	205	4.952	5.261	5.650		6.612	7.184
	185	5.544	5.848	6.229		7.104	7.841
	165	6.241	6.516	6.944		7.789	8.541
Valeramide	205	5.314	5.637	5.864		6.904	7.417
	185	5.978	6.255	6.581		7.432	8.105
	165	6.681	6.910	7.224		8.142	8.831
Diacetamide	205	4.962	4.924	5.382	5.606	5.931	7.208
	185	5.585	5.530	5.912	6.193	6.549	7.835
	165	6.278	6.198	6.706	6.896	7.264	8.501
Dipropionamide	205	5.177	5.061	5.487		6.517	7.129
	185	5.825	5.590	6.020		7.004	7.741
	165	6.527	6.229	6.829		8.144	8.411
Methylacetamide	205	4.165	4.449	4.846	5.054*	5.410**	5.914***
	185	4.720	5.057	5.688	5.590*	5.964**	6.514***
	165	5.337	5.602	5.996	6.202*	6.595**	7.156***
Dimethylacetamide	205	3.593	3.828	4.108	4.191*	4.369**	4.609***
	185	4.059	4.345	4.808	4.605*	4.788**	5.064***
	165	4.554	4.758	5.960	5.051*	5.262**	5.510***

* *m* = 0.273.

** *m* = 0.575.

*** *m* = 1.30.

the main peak. All alkali-metal halides from commercial sources were of reagent grade and were used without further purification.

The density of PEG 20M was measured with a pycnometer; the values were 0.988 at 165°, 1.005 at 185° and 1.020 at 205°. Retention times were repeatedly measured with a stop-watch, and the average was taken for calculation of the partition coefficient.

RESULTS AND DISCUSSION

When a gas chromatographic stationary phase is used as a solvent in which solute-salt interaction takes place, it must be polar enough to dissolve both solute and salt, as well as being heat resistant. The dielectric constant is one parameter that represents the polarity of a stationary phase, and PEG was used as stationary phase because it had modest resistance to heat and a relatively high dielectric constant. The dielectric constant of PEG 20 M (which was not found in the literature) was estimated by extrapolation of available data^{17,18} for low-degree PEG; the value obtained was *ca.* 8 at 60°. Considering the temperature dependence of the dielectric constant, this value was higher than those for methyl acetate (7.3 at 20°) and aniline (7.21 at 20°) (see ref.

TABLE II
PARTITION COEFFICIENTS (*K*) OF AMIDES ON COLUMNS CONTAINING SODIUM HALIDES

The molality is expressed by *m*. Values for PEG are as in Table I.

<i>Amide</i>	<i>Temp.</i> (°C)	<i>NaCl</i> (20%) (<i>m</i> =4.28)	<i>NaBr</i> (20%) (<i>m</i> =2.43)	<i>NaI</i> (5%) (<i>m</i> =0.351)	<i>NaI</i> (10%) (<i>m</i> =0.741)	<i>NaI</i> (20%) (<i>m</i> =1.67)
Formamide	205			5.193	5.526	6.264
	185			5.827	6.091	6.862
	165			6.419	6.781	7.490
Acetamide	205	4.667	4.766	5.108	5.480	6.227
	185	5.246	5.322	5.704	5.963	6.825
	165	5.880	5.968	6.335	6.728	7.456
Propionamide	205			5.200	5.511	6.188
	185			5.788	6.116	6.782
	165			6.471	6.775	7.431
Butyramide	205			5.421	5.700	6.315
	185			6.045	6.309	6.948
	165			6.744	7.019	7.617
Valeramide	205			5.764	6.001	6.573
	185			6.387	6.643	7.232
	165			7.131	7.392	7.835
Diacetamide	205	5.141	5.219	5.435	5.722	6.373
	185	5.745	5.827	6.033	6.334	7.013
	165	6.438	6.523	6.753	7.057	7.684
Dipropionamide	205			5.624	5.895	6.373
	185			6.276	6.557	7.036
	165			6.753	7.332	7.899
Methylacetamide	205	4.304	4.401	4.718	5.074	5.770
	185	4.839	4.907	5.288	5.537	6.349
	165	5.421	5.490	5.886	6.272	6.956
Dimethylacetamide	205	3.723	3.813	3.817	3.973	4.459
	185	4.177	4.228	4.256	4.298	4.877
	165	4.653	4.707	4.692	4.857	5.272

19), which suggested that PEG 20 M was adequate for our purposes. In fact, preliminary experiments showed that PEG 20M dissolved 20% (by weight) of LiI at the column temperatures used (165–205°).

The contribution of the stationary phase to the interaction was examined by using columns containing (1) 5% of LiI alone, (2) 20% of diethylene glycol succinate polymer (DEGS), and (3) a mixture of 5% of LiI and 20% of DEGS. There was no difference between the retention time of acetamide and the gas hold-up time on column 1. We also found, by comparison of the partition coefficients for acetamide on columns 2 and 3, that the addition of LiI to DEGS has little effect on the retention of the solute. These results suggested that the interaction was enhanced by a polar stationary phase (which tends to dissolve the alkali-metal halide).

The results obtained for partition coefficients and partial molar free energies of transfer are shown in Tables I to VI, in which the degree of scatter of the values is less than $\pm 2\%$ of the average for K and ± 0.05 kcal/mole for ΔG_r° . These values show that addition of KCl to PEG 20 M decreases the partition coefficient of AA, DAA, MAA and DMA, thereby making ΔG_r° a positive quantity; this means that these amide molecules undergo a salting-out effect in this system. The addition of other salts, how-

TABLE III

PARTITION COEFFICIENTS (K) OF AMIDES ON COLUMNS CONTAINING POTASSIUM HALIDES

The molality is expressed by m . Values for PEG are as in Table I.

Amide	Temp. (°C)	KCl (20%) ($m=3.35$)	KBr (20%) ($m=2.19$)	KI (5%) ($m=0.317$)	KI (10%) ($m=0.669$)	KI (20%) ($m=1.51$)
Formamide	205			5.202	5.483	5.747
	185			5.795	6.099	6.393
	165			6.449	6.751	7.121
Acetamide	205	4.542	4.723	5.109	5.436	5.671
	185	5.078	5.256	5.693	6.038	6.309
	165	5.707	5.893	6.347	6.678	7.079
Propionamide	205			5.214	5.466	5.675
	185			5.768	6.084	6.315
	165			6.418	6.732	7.074
Butyramide	205			5.410	5.675	5.856
	185			6.021	6.301	6.513
	165			6.699	6.978	7.293
Valeramide	205			5.741	5.984	6.163
	185			6.429	6.632	6.851
	165			7.175	7.362	7.638
Diacetamide	205	4.988	5.170	5.568	5.693	5.894
	185	5.580	5.759	6.038	6.334	6.566
	165	6.269	6.451	6.696	7.013	7.371
Dipropionamide	205			5.604	5.873	6.051
	185			6.254	6.547	6.760
	165			6.980	7.287	7.595
Methylacetamide	205	4.170	4.353	4.724	5.040	5.136
	185	4.668	4.847	5.277	5.623	5.808
	165	5.243	5.429	5.872	5.873	6.115
Dimethylacetamide	205	3.592	3.768	3.858	3.990	4.139
	185	3.998	4.171	4.264	4.418	4.594
	165	4.470	4.644	4.729	4.857	5.063

TABLE IV
PARTIAL MOLAR FREE ENERGY OF TRANSFER (ΔG_i°) OF AMIDES ON COLUMNS
CONTAINING LITHIUM HALIDES

The molality is expressed by *m*.

Amide	Temp., °C	LiCl (20%) (<i>m</i> =5.90)	LiBr (20%) (<i>m</i> =2.88)	LiI (5%) (<i>m</i> =0.385)	LiI (10%) (<i>m</i> =0.812)	LiI (20%) (<i>m</i> =1.83)
Formamide	205	-0.256	-0.629	-0.742	-1.338	-2.356
	185	-0.230	-0.570	-0.647	-1.151	-2.258
	165	-0.213	-0.513	-0.598	-1.066	-2.116
Acetamide	205	-0.243	-0.743	-0.756	-1.425	-2.512
	185	-0.305	-0.682	-0.680	-1.227	-2.418
	165	-0.263	-0.686	-0.633	-1.181	-2.317
Propionamide	205	-0.210	-0.678	-0.683	-1.284	-2.267
	185	-0.196	-0.613	-0.633	-1.115	-2.213
	165	-0.198	-0.647	-0.599	-1.077	-2.135
Butyramide	205	-0.181	-0.614		-1.194	-2.100
	185	-0.171	-0.579		-1.034	-2.073
	165	-0.139	-0.569		-1.000	-1.985
Valeramide	205	-0.195	-0.474		-1.129	-1.978
	185	-0.146	-0.504		-0.937	-1.917
	165	-0.100	-0.431		-0.925	-1.857
Diacetamide	205	0.149	-0.350	-0.607	-1.062	-2.113
	185	0.156	-0.253	-0.549	-0.856	-2.030
	165	0.169	-0.330	-0.535	-0.845	-1.919
Dipropionamide	205	0.223	-0.246		-0.890	-1.833
	185	0.320	-0.132		-0.456	-1.725
	165	0.358	-0.221		-0.106	-1.623
Methylacetamide	205	-0.149	-0.592	-0.835*	-1.169**	-1.640***
	185	-0.043	-0.749	-0.701*	-1.039**	-1.532***
	165	-0.137	-0.538	-0.756*	-1.095**	-1.578***
Dimethylacetamide	205	-0.108	-0.439	-0.565*	-0.731**	-0.951***
	185	-0.085	-0.636	-0.494*	-0.658**	-0.902***
	165	-0.078	-0.340	-0.429*	-0.610**	-0.819***

* *m* = 0.273.

** *m* = 0.575.

*** *m* = 1.30.

ever, causes an increase in partition coefficient and consequently ΔG_i° becomes negative, *i.e.*, the amide undergoes a salting-in effect. Fig. 1 shows the relationship between ΔG_i° and concentration of iodide in the stationary phase for several systems. All the alkali-metal iodides tested exert a relatively strong salting-in effect on AA, MAA, DAA and DMA, and ΔG_i° decreases with increase in iodide concentration, *i.e.*, the salting-in effect is almost proportional to the iodide concentration within the measured range. Bigli and co-workers²⁰⁻²² investigated the interaction between LiCl and some alcohols, esters and ketones in an LiCl-PEG 400 column and obtained ΔG_i° values of -0.24 kcal/mole for ethanol, 0.21 kcal/mole for diethyl ketone and 0.25 kcal/mole for ethyl acetate. Compared with those values, our results, *e.g.*, -1.18 kcal/mole for AA in LiI-PEG 20M suggest relatively strong interaction in the stationary phase. Among the amides tested, AA and MAA showed lower ΔG_i° values than did DMA in most of the iodide concentration ranges, indicating that the hydrogen

TABLE V

PARTIAL MOLAR FREE ENERGY OF TRANSFER ($\Delta\overline{G}_i^\circ$) OF AMIDES ON COLUMNS CONTAINING SODIUM HALIDESThe molality is expressed by *m*.

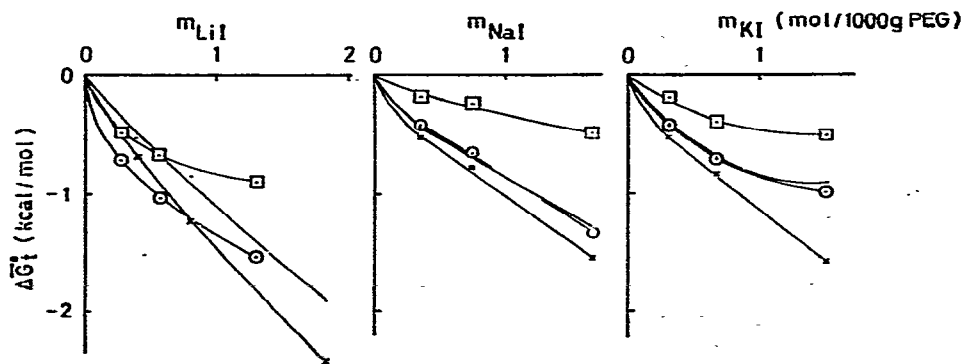
Amide	Temp., °C	NaCl (20%) (<i>m</i> =4.28)	NaBr (20%) (<i>m</i> =2.43)	NaI (5%) (<i>m</i> =0.351)	NaI (10%) (<i>m</i> =0.741)	NaI (20%) (<i>m</i> =1.67)
Formamide	205	-0.069		-0.530	-0.845	-1.542
	185	-0.028		-0.539	-0.779	-1.478
	165	-0.057		-0.432	-0.746	-1.361
Acetamide	205	-0.012	-0.195	-0.545	-0.896	-1.602
	185	0.014	-0.148	-0.519	-0.854	-1.535
	165	-0.100	-0.129	-0.469	-0.810	-1.441
Propionamide	205	-0.030		-0.499	-0.793	-1.433
	185	0.005		-0.477	-0.774	-1.378
	165	-0.016		-0.482	-0.745	-1.314
Butyramide	205			-0.443	-0.704	-1.288
	185			-0.455	-0.694	-1.274
	165			-0.437	-0.675	-1.193
Valeramide	205			-0.427	-0.650	-1.190
	185			-0.371	-0.603	-1.136
	165			-0.391	-0.618	-1.001
Diacetamide	205	-0.056	-0.218	-0.448	-0.719	-1.334
	185	-0.021	-0.195	-0.407	-0.680	-1.295
	165	-0.085	-0.192	-0.413	-0.674	-1.220
Dipropionamide	205			-0.423	-0.679	-1.130
	185			-0.409	-0.664	-1.097
	165			-0.196	-0.699	-1.191
Methylacetamide	205	-0.017	-0.197	-0.518	-0.856	-1.512
	185	0.011	-0.145	-0.428	-0.654	-1.333
	165	-0.112	-0.124	-0.484	-0.817	-1.132
Dimethylacetamide	205	-0.011	-0.191	-0.212	-0.358	-0.816
	185	0.016	-0.131	-0.179	-0.219	-0.682
	165	-0.112	-0.110	-0.119	-0.262	-0.620

atom of the amide function contributes greatly to the interaction; DAA, which has one NH group and two carbonyl groups, gave values of $\Delta\overline{G}_i^\circ$ in between those for MAA and DMA. The dependence of $\Delta\overline{G}_i^\circ$ of alkyl homologues on the concentration of LiI, NaI and KI is shown in Fig. 2, from which it can be seen that, in every combination of iodide and amide, higher concentration of iodide gave a larger negative value of $\Delta\overline{G}_i^\circ$ and that the magnitude of negativity increased in the order KI, NaI, LiI. Fig. 3 shows graphs of $\Delta\overline{G}_i^\circ$ plotted against carbon number for amide homologues on alkali-halide-containing PEG 20M columns, and shows that, except for FA, the salting-in effect becomes proportionately weaker as the alkyl-chain length increases, and that the combination of AA and LiI produces the strongest interaction of all the amide-salt systems studied. The deviation of the graph for FA from linearity may be related to the dipole moment of FA; the magnitude of this parameter measured in dioxane (3.86 Debye units) is smaller than that of AA (3.90 Debye units) and larger than that of *n*-propionamide (3.85 Debye units)²³. This suggests that ion-dipole interaction may be involved in amide-salt systems with PEG 20M as stationary phase. Fig. 4 shows graphs of $\Delta\overline{G}_i^\circ$ for AA, MAA and DAA vs. the reciprocal of the ionic radius of cation

TABLE VI

PARTIAL MOLAR FREE ENERGY OF TRANSFER (ΔG_i°) OF AMIDES ON COLUMNS CONTAINING POTASSIUM HALIDESThe molality is expressed by m .

Amide	Temp., °C	KCl (20%) ($m=3.35$)	KBr (20%) ($m=2.19$)	KI (5%) ($m=0.317$)	KI (10%) ($m=0.669$)	KI (20%) ($m=1.51$)
Formamide	205			-0.542	-0.811	-1.067
	185			-0.514	-0.793	-1.067
	165			-0.462	-0.727	-1.056
Acetamide	205	0.011	-0.179	-0.548	-0.862	-1.091
	185	0.066	-0.110	-0.513	-0.830	-1.082
	165	0.092	-0.085	-0.483	-0.773	-1.130
Propionamide	205			-0.516	-0.758	-0.963
	185			-0.462	-0.752	-0.968
	165			-0.438	-0.715	-1.018
Butyramide	205			-0.437	-0.691	-0.869
	185			-0.437	-0.695	-0.894
	165			-0.401	-0.646	-0.927
Valeramide	205			-0.409	-0.641	-0.817
	185			-0.413	-0.600	-0.806
	165			-0.413	-0.598	-0.845
Diacetamide	205	-0.006	-0.197	-0.577	-0.699	-0.895
	185	0.021	-0.155	-0.414	-0.686	-0.905
	165	0.027	-0.150	-0.367	-0.645	-0.963
Dipropionamide	205			-0.408	-0.666	-0.841
	185			-0.393	-0.662	-0.862
	165			-0.397	-0.667	-0.941
Methylacetamide	205	0.010	-0.175	-0.538	-0.830	-1.056
	185	0.065	-0.166	-0.422	-0.703	-0.987
	165	0.091	-0.093	-0.255	-0.478	-0.732
Dimethylacetamide	205	0.021	-0.165	-0.254	-0.382	-0.574
	185	0.073	-0.101	-0.190	-0.296	-0.508
	165	0.088	-0.078	-0.155	-0.268	-0.507

Fig. 1. Relationship between ΔG_i° of amides and molality of iodides at 185°. \times , AA; \circ , MAA; \square , DMA; \bullet , DAA.

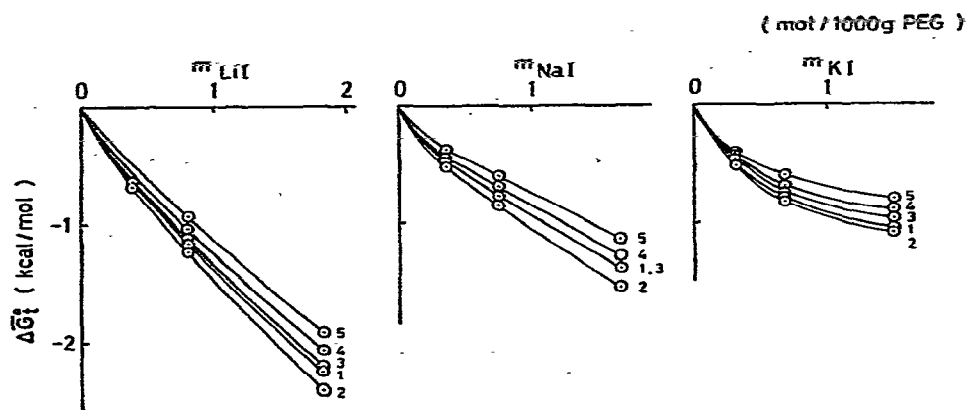


Fig. 2. Relationship between ΔG_i^0 of amide homologues and molality of iodides at 185°. 1 = FA; 2 = AA; 3 = PA; 4 = BA; 5 = VA.

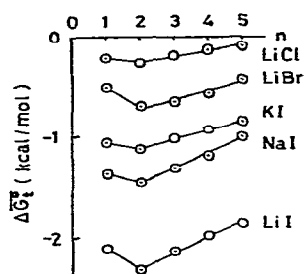


Fig. 3. Relationship between ΔG_i^0 and carbon number (n) in amide homologues at 165°.

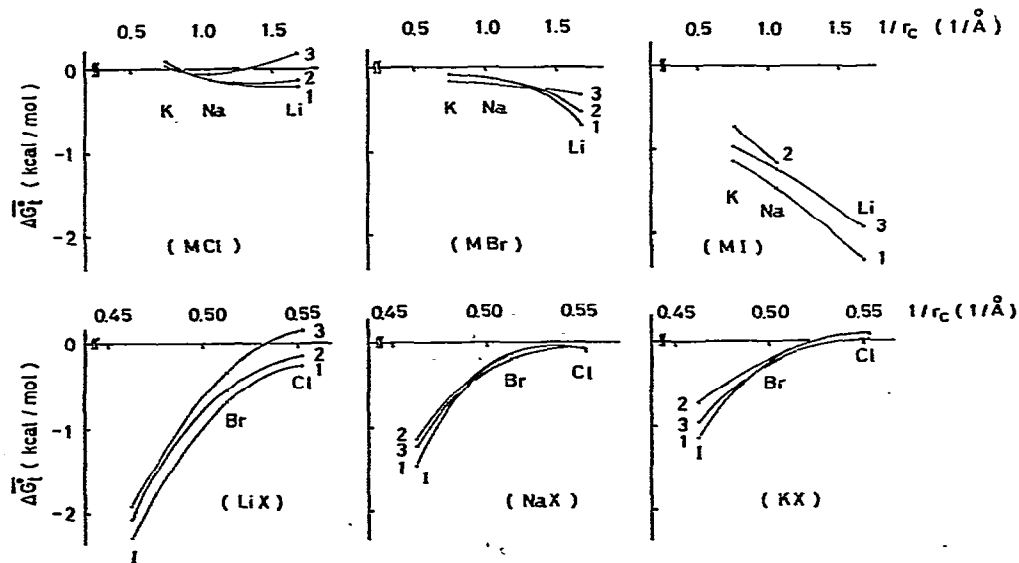


Fig. 4. Relationship between ΔG_i^0 of amides and ionic radii of alkali halides at 165°. 1 = AA; 2 = MAA; 3 = DAA.

and of anion for a series of alkali-metal halides having a common ion. It can be seen that the negative value of ΔG_i° increases with increase in anionic radius and with decrease in cationic radius, and that the change in ΔG_i° is more affected by the size of the anion than that of the cation. It is noteworthy that this trend almost coincides with the order of solubility of the alkali-metal halides in water or ethanol, although there is no experimental evidence for ionic dissociation of these halides in the PEG 20M stationary phase at the column temperatures used. Thus, we postulate that the solubility of alkali-metal halides in the stationary phase parallels that in water, and that the more soluble salt interacts more strongly with the amide molecules to give a salting-in effect. It would perhaps be of interest further to investigate the behaviour of alkali-metal halides in a PEG 20M column, but we have not done so, as our purpose was to establish a suitable salt-containing stationary phase for the separation of amide mixtures. For example, the partition coefficient of BA is similar to (slightly larger than) that of DAA on PEG 20M, so that it would be difficult to separate them using PEG 20M alone; however, the addition of LiCl produces a salting-in effect on BA and a salting-out effect on DAA, so that these compounds would be eluted from such a column in the reverse order to that in which they would leave a salt-free PEG 20M column. Fig. 5 demonstrates this situation and clearly shows that a 20% LiCl-PEG 20M stationary phase leads to complete separation of BA and DAA.

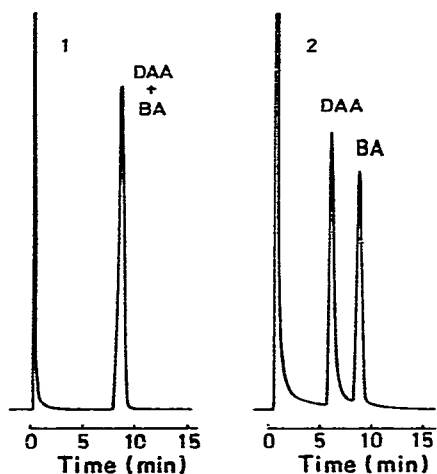


Fig. 5. Separation profile of a mixture of DAA and BA. Conditions: 20% of PEG 20M (1) or 20% of LiCl + 20% of PEG 20M (2) coated on Chromosorb W (60–80 mesh; AW; DMCS-treated) in a column (160 cm \times 3 mm I.D.) of glass tubing; column temp., 185°; injector temp., 220°; carrier gas, helium (40 ml/min); detector, flame ionisation.

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