ASSOCIATION OF SOME BENZYLDIALKYLAMINES AND THEIR SALTS IN BENZENE SOLUTIONS

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The degrees of association of benzyldibutylamine, benzyldihexylamine, and benzyldibutylamine nitrate in benzene were calculated from their cryoscopic and osmometric data by using the computer program MOP. The amines examined are present as monomers in the solution, benzyldibutylamine nitrate forms tetramers at the temperatures applied (5·5, 25, and 37°C).

The association degree and association constants of amines, R_3N, or their nitrateds, $R_3N.HNO_3$, were calculated from cryoscopic and osmometric data by means of the computer program MOP (ref.[1]), a modification of the Swedish program Letagrop[2-7] based on the assumption that the ionic pairs, B, associate to give the n-mers:

$$n\,\mathrm{B} \rightleftharpoons (\mathrm{B})_n\,. \tag{A}$$

The equilibrium constant is thus

$$\beta'_n = \{\gamma_{(\mathrm{B})_n}[(\mathrm{B})_n]\}/\{\gamma^n_\mathrm{B}[\mathrm{B}]^n\}\,, \tag{1}$$

where γ's are the activity coefficients and n is the association degree.

The activity coefficient ratios for low concentrations of B are generally assumed to be constant[8]. Therefore, the constant β_n,

$$\beta_n = \beta'_n(\gamma^n_\mathrm{B}/\gamma_{(\mathrm{B})_n})\,, \tag{2}$$

is always dealt with.

The analytical concentration of the substance B is then

$$x = [\mathrm{B}] + 2\beta_2[\mathrm{B}]^2 + 3\beta_3[\mathrm{B}]^3 + \ldots\,, \tag{3}$$

whereas the total concentration representing the sum of concentrations of the various associate species is

$$C = x/\bar{n} = [\mathrm{B}] + \beta_2[\mathrm{B}]^2 + \beta_3[\mathrm{B}]^3 + \ldots\,, \tag{4}$$

where $\bar{n}$ is the mean association degree of the substance.

The quantities dealt with in cryoscopy – change in the freezing point, and in osmometry – change in the thermistor resistance, are colligative properties (y) dependent upon the total molal concentration C (in mol kg^{-1}): $y = f(C)$. In the former case, the function is represented by the theoretical relation $y \equiv \Delta T = K_c C$, where K_c is the cryoscopic constant, in the latter case the calibration dependence is expressed either as $y = \mathrm{R}C$, or as $y = \mathrm{R}_1 C + \mathrm{R}_2 C^2$, where the R's are constants.

In case that the colligative property is directly proportional to the concentration C, $y = kC$, then with the proportionality constant k once determined, the mean

TABLE I

Experimental Cryoscopic and Osmometric Data of Benzyldibutylamine in Benzene and Calculated Values of Association Degrees *n*

Amine concentration mol kg^{-1}	Cryoscopy		Osmometry			
	5·5°C [a]		25°C [a]		37°C [a]	
	Δ*t*, K	*n*	Δ*R*, Ω	*n*	Δ*R*, Ω	*n*
0·00940	0·049	1·02	2·387	0·76	1·4813	1·43
	0·047	1·04	2·387	0·76	1·419	1·00
0·01654	0·092	0·93	4·475	0·72	4·863	0·77
	0·089	0·97	4·500	0·71	4·9198	0·76
0·05190	0·234	1·15	9·138	1·10	9·475	1·23
	0·257	1·05	8·963	1·12	10·363	1·13
0·05995	0·311	1·00	10·875	1·07	12·375	1·09
	0·305	1·02	11·025	1·05	12·800	1·06
0·10025	0·473	1·10	17·775	1·09	20·875	1·09
	0·465	1·12	17·925	1·08	20·925	1·08
0·07940	0·378	1·09	14·125	1·09	15·700	1·14
	0·375	1·10	14·125	1·07	16·10	1·11
0·19073	0·953	1·04	35·00	1·06	41·00	1·05
	0·909	1·09	35·25	1·05	40·25	1·07
0·28147	1·367	1·07	53·70	1·02	62·0	1·03
	1·342	1·09	53·70	1·02	62·0	1·03
0·36053	1·672	1·12	68·0	1·03	—	—
	1·672	1·12	69·5	1·01	—	—

[a] Temperature of the measurement.

association degree can be obtained from the measurements as

$$\bar{n} = kx/y\,. \tag{5}$$

The function $y = f(x)$ was evaluated to obtain the association constants β from cryoscopic and osmometric data in such a manner that the sum of squares of deviations (absolute or relative) be minimum. Since the above function cannot be expressed explicit, common regression methods could not be applied. We employed therefore the optimization method of pit-mapping, worked out for solving problems of simultaneous equilibria of complex formation[2-7,9].

EXPERIMENTAL

All chemicals used were reagent grade purity. Benzyldibutylamine and benzyldihexylamine were prepared at our laboratory according to[10,11], benzyldibutylamine nitrate was prepared by neutralization of benzyldibutylamine solution in benzene with nitric acid and multiple recrystallization.

The osmometric measurements were carried out on an apparatus Dampfdruck Osmometer (Knauer, FRG), the cryoscopic measurements on a cryoscope set up in our laboratory. The infrared spectra were scanned on a spectrophotometer Perkin-Elmer 325 in the wavelength region 4000—600 cm^{-1} using AgCl cells.

RESULTS AND DISCUSSION

For the determination of the association degree by the cryoscopic and osmometric techniques, the experimental data were related to those of benzil, as this compound has been found not to form polymeric associates in organic solvents[12,13].

From the measurements of benzene solutions of benzil, the cryoscopic constant of benzene was determined to be 5·195 ± 0·081 kg K mol^{-1}, which is in accordance with the tabulated values[14,15]. The calibration constants for osmometry were determined based on the osmometric data of benzil, 195·7 ± 1·1 and 225·7 ± 1·2 kg . . mol^{-1} at 25 and 37°C, respectively. These values were employed for the calculation of the mean association degree $\bar{n}$ of the compound of interest.

In the case of the two amines, benzyldibutylamine (Table I) and benzyldihexylamine (Table II), no association was established over the entire concentration region examined – the substances occur as monomers. This is in accordance with the data obtained for trioctylamine[12]. The infrared spectra also exhibit no changes attributable to association effects (Table III).

It will be possible to investigate the polymerization of benzyldialkylamine salts using the corresponding amines as the calibration substances. For this purpose, the calculated osmometric constants for benzyldibutylamine and benzyldihexylamine are included in Table IV along with those for benzil.

During the extraction of metal salts from acidic nitrate solutions, amine nitrates (generally, $[(R_3N)_{t'}(HNO_3)_{v'}(H_2O)_{x'}]_{y'}$) are formed in addition to the associates of the amines with the metal salts Me^{a+} (generally, $[(R_3N)_t(HMe(NO_3)_{a+1})_u \cdot . (HNO_3)_v(H_2O)_x]_y$). For an evaluation of these complex systems, it is necessary to recognize how the various components of the extraction solutions associate. Solid benzylbutylamine nitrate was therefore prepared, and the association data of this salt in benzene solutions were measured (Table V). The calculated association constants indicate that in benzene solutions this salt occurs as a single associate species – the tetramer, with the log β_4 values 5·70 ± 0·01, 5·58 ± 0·02, and 5·09 ±

TABLE II

Experimental Cryoscopic and Osmometric Data of Benzyldihexylamine in Benzene and Calculated Values of the Association Degree *n*

Amine concentration mol kg^{-1}	Cryoscopy		Osmometry			
	5·5°C [a]		25°C [a]		37°C [a]	
	Δt, K	*n*	ΔR, Ω	*n*	ΔR, Ω	*n*
0·00964	0·050	1·00	2·213	0·88	2·419	0·90
	0·053	0·95	2·031	0·92	2·431	0·90
0·01681	0·089	0·98	4·001	0·81	5·056	0·75
	0·091	0·96	4·003	0·82	5·044	0·75
0·04801	0·254	1·02	9·100	1·02	11·575	0·94
	0·235	1·06	9·350	1·00	11·412	0·95
0·05944	0·300	1·03	11·90	0·97	13·50	1·00
	0·312	0·99	12·125	0·95	13·525	0·99
0·07773	0·412	0·98	14·50	1·04	18·25	0·96
	0·396	1·02	14·825	1·01	18·25	0·96
0·08601	0·418	1·07	18·675	1·00	23·05	0·94
	0·434	1·03	18·925	0·98	22·85	0·95
0·18694	0·899	1·08	32·50	1·12	45·4	0·93
	0·875	1·11	32·5	1·12	45·3	0·93
0·27242	1·374	1·03	55·7	0·96	63·0	0·98
	1·444	0·98	56·0	0·94	—	—

[a] Temperature of the measurement.

TABLE III

Characteristic Absorption Bands (cm^{-1}) in the IR Spectra of Benzene Solutions of Benzyldibutylamine (BDBuN), Benzyldihexylamine (BDHeN), Benzyldibutylamine Nitrate (BDBuN.HNO_3), and Trioctylamine Nitrate (TON.HNO_3)

Vibration	0·1M-BDBuN	0·1M-BDHeN	0·1M BDBuN.HNO_3	0·1M TON.HNO_3
ν(OH), free	—	—	—	—
ν(OH, H), bonded	—	—	—	—
ν(CH) arom.	2 960 s	2 960 s	2 960 s	—
ν_{as}(CH)	2 930 sh	2 920 s	2 930 s	2 929 vs
ν_s(CH)	2 860 s	2 855 s	2 860 s	2 850 vs
ν(CH), at αC	2 795 m	2 790 w	—	—
$\nu(NH^+)$	—	—	2 670 m, b	2 600 m, b
δ(HOH) in H_2O	—	—	—	—
$\delta(CH_3)$	1 490 sh	1 490 m	1 450 m	1 465 s
$\delta_s(CH_3)$	1 375 m 1 385 m	—	—	1 373 s
$\delta(CH_2)$ (split)	1 462 m 1 450 m	1 470 sh		
$\omega(CH_2)$ (wagging)	1 300 w	1 295 w	—	—
ν(N=O) in HNO_3	—	—	1 630 mb	1 410 s
ν(N=O) in NO_3^-	—	—	1 370 mb	1 285 s
$\nu_s(NO_2)$	—	—	—	—
$\nu(C_{aliph}$—N)	—	—	—	—
ν(CN)	1 000 sh, w	1 090 sh, w	—	1 090 m
$\delta(NO_2)$	—	—	—	1 025 m
δ(OH)	—	—	—	—
$\varrho(CH_2)$ (rocking)	730 m	725 w	—	723 w

TABLE IV

Osmometric Calibration Constants of Benzil and Benzyldialkylamines Defined by Equation (*6*)

Compound	*t*, °C[a]	
	25	37
Benzil	195·7 ± 1·1	225·7 ± 1·2
Benzyldibutylamine	190·7 ± 0·9	215·7 ± 2·2
Benzyldihexylamine	195·3 ± 3·5	233·4 ± 2·2

[a] Temperature of the measurement.

± 0·01 at 5·5, 25, and 37°C, respectively. Lower and higher associate species as well as combinations of pairs of polymerization degrees were considered (Table VI), but the data point to the existence of the tetramer as the single associate.

Comparing the association degree of benzyldibutylamine nitrate with that of trioctylamine nitrate[13] we find a higher polymeric form in the former case; for the latter, the existence of dimers or trimers has been found by means of the program Letagrop[13,16,17] as well as of the program MOP, with the association constants $\log \beta_2 = 1{\cdot}80$, $\log \beta_3 = 2{\cdot}35$ (ref.[17]), $\log \beta_2 = 0{\cdot}90$, $\log \beta_3 = 2{\cdot}48$ (ref.[16]), or $\log \beta_2 = 2{\cdot}22$, $\log \beta_4 = 5{\cdot}52$ (ref.[17]).

The characteristic vibrations in the infrared spectra of the two amine nitrates are given for a comparison in Table III. In the spectrum of benzyldibutylamine nitrate, the NH bands are shifted to higher wavenumbers, which indicates a weaker NH bond in the associate. This complies with the finding[8,12,13] that a weakening of the NH bond in the associate leads to the formation of associates of higher polymerization degrees.

TABLE V

Experimental Cryoscopic and Osmometric Data of Benzyldibutylamine Nitrate in Benzene and Calculated Values of the Association Degree *n*

Analytical concentration of BDBuN.HNO$_3$ mol kg^{-1}	Cryoscopy		Osmometry			
	5·5°C [a]		25°C [a]		37°C [a]	
	Δ*t*, K	*n*	Δ*R*, Ω	*n*	Δ*R*, Ω	*n*
0·0104	0·054	1·00	1·50	1·36	1·53	1·53
0·0202	0·085	1·23	2·57	1·54	2·81	1·60
0·0310	0·091	1·76	3·50	1·73	3·08	1·78
0·0404	0·111	1·89	3·94	1·80	4·63	1·97
0·0498	0·1325	2·12	4·12	2·37	4·90	2·29
0·0612	0·145	2·80	4·41	2·72	5·39	2·56
0·0708	0·128	2·86	5·06	2·74	5·76	2·77
0·0808	0·131	3·20	5·22	3·03	6·56	2·80
0·0909	0·140	3·38	5·41	3·29	6·89	2·89
0·1021	0·141	3·76	5·46	3·66	7·42	3·11

[a] Temperature of the measurement.

TABLE VI

Association Constants of Benzyldibutylamine Nitrate in Benzene

n-mer	log β_n	U_{min}[a]
	5·5°C	
Trimer	4·37 ± 0·17	1·69 . 10^{-2}
Tetramer	5·70 ± 0·01	7·49 . 10^{-4}
Pentamer	7·22 ± 0·15	1·67 . 10^{-2}
Hexamer	8·81 ± 0·38	2·01 . 10^{-2}
Dimer + tetramer	$\beta_2 = 0$	
	$\beta_4 =$ 5·76 ± 0·07	2·32 . 10^{-4}
Tetramer + hexamer	$\beta_4 =$ 4·89 ± 0·43	
	$\beta_6 =$ 6·72 ± 0·23	3·45 . 10^{-1}
	25°C	
Trimer	4·21 ± 0·21	2·41 . 10^{-2}
Tetramer	5·58 ± 0·02	8·26 . 10^{-3}
Pentamer	7·10 ± 0·09	5·79 . 10^{-2}
Hexamer	8·61 ± 0·11	4·34 . 10^{-2}
Octamer	12·10 ± 0·2	4·87 . 10^{-1}
Dimer + tetramer	$\beta_2 = 0$	
	$\beta_4 =$ 5·62 ± 0·05	7·30 . 10^{-4}
Tetramer + hexamer	$\beta_4 =$ 4·48 ± 0·11	
	$\beta_6 =$ 6·42 ± 0·11	3·86 . 10^{-2}
	37°C	
Dimer	30·68 ± 2·8	1·76 . 10^{-2}
Trimer	4·00 ± 0·1	2·88 . 10^{-3}
Tetramer	5·09 ± 0·01	9·43 . 10^{-6}
Pentamer	6·40 ± 0·01	5·42 . 10^{-4}
Hexamer	7·79 ± 0·07	1·58 . 10^{-3}
Heptamer	9·26 ± 0·32	2·53 . 10^{-4}
Octamer	11·92 ± 0·9	1·26
Tetramer + hexamer	β_4 4·52 ± 0·13	
	$\beta_6 =$ 7·10 ± 0·16	8·26 . 10^{-2}

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[a] U_{min} — sum of deviations squares.

REFERENCES

1. Dvořák Z., Jedináková V.: Sb. Vys. Šk. Chem.-Technol. Praze, in press.
2. Sillén L. G.: Acta Chem. Scand. *16*, 159 (1962).
3. Ingri N., Sillén L. G.: Acta Chem. Scand. *16*, 173 (1962).
4. Sillén L. G.: Acta Chem. Scand. *18*, 1085 (1964).
5. Warnqvist B.: Chem. Scripta *1*, 49 (1971).
6. Sillén L. G., Warnqvist B.: Arkiv Kemi *31*, 315 (1969).
7. Ingri N., Sillén L. G.: Arkiv Kemi *23*, 97 (1964).
8. Mamoun A. Muhamed: *Aggregation Equilibria Involving Trilaurylamine, n-Octanol and Hydrochloric Acid in Benzene*, p. 32. Published by KTH, Stockholm 1975.
9. Sillén L. G., Warnqvist B.: Arkiv Kemi *31*, 341 (1969).
10. King H., Work T. S.: J. Chem. Soc. *1942*, 401.
11. Möller F. in the book: *Methoden der Organischen Chemie* (Houben-Weyl) (F. Müller, Ed.), Vol. XI/1, p. 37. Thieme, Stuttgart 1957.
12. Jedináková V., Högfeldt E.: Chem. Scripta *9*, 171 (1976).
13. Jedináková V., Högfeldt E.: Chem. Scripta *9*, 178 (1976).
14. Brdička R., Dvořák J.: *Základy fyzikální chémie*, p. 303. Academia, Prague 1977.
15. Jedináková V., Žilková J.: Proc. IV. Symp. CMEA: Issledovaniya v Oblasti Pererabotki Obluchennogo Topliva, Karlovy Vary, 28. 3.—1.4. 1977, Vol. II, p. 180. Czechosl. Commis. At. Energy, Prague 1978.
16. Markovits G., Kertes A. S. in the book: *Solvent Extraction Chemistry* (J. Dyrssen, O. Liljenzin, J. Rydberg, Eds), p. 390. North-Holland, Amsterdam 1967.
17. Bashol S.: *Thesis*. METU, Ankara 1968.

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