

The Solubility of Ethyl Acetate in Some Perchlorate and Nitrate Solutions.

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The solubility of ethyl acetate at 25° has been measured in 0.25—1M-aqueous solutions of lithium, silver, and sodium perchlorate and nitrate, and also of potassium nitrate. The perchlorates salt in and the nitrates salt out; the effect of the different cations is much smaller. In mixtures of these perchlorates and nitrates at constant ionic strength the salting-in effect of the perchlorate ion can be described by the association constant ($K = 0.52 \pm 0.02$) of a 1 : 1-ethyl acetate-perchlorate complex.

ALTHOUGH numerous studies of the solubility of ethyl acetate in aqueous electrolyte solutions have been made (for summary see Altshuller and Everson, *J. Amer. Chem. Soc.*, 1953, 75, 4823) and the anomalously small salting-out effect of the iodide ion noted, salting in has only been reported for large cations. It was decided to measure the solubility of ethyl acetate in some perchlorate solutions and to compare this with its solubility in the corresponding nitrates.

EXPERIMENTAL AND RESULTS

Materials.—Ethyl acetate was washed with aqueous potassium carbonate solution and water, dried over anhydrous potassium carbonate, and redistilled. All the salts were either "AnalaR" grade or were recrystallised and dried. The silver solutions were standardised gravimetrically as chloride, and the lithium solutions as sulphate.

Method.—A measured volume of each salt solution was shaken with a slight excess of ethyl acetate and the mixture left in a thermostat at either $25^\circ \pm 0.01^\circ$ or $35^\circ \pm 0.01^\circ$ for 2 hr.; 5 c.c. of the aqueous phase were then removed and the dissolved ethyl acetate determined by titration. With the silver solutions the ester was distilled into excess of sodium hydroxide solution. The densities were determined with a density bottle.

Results.—The results are given in Tables 1 and 2, where M_s = molarity of salt; M_E = molarity of ethyl acetate; S = g. of ethyl acetate per 100 g. of solvent; m = molality; $\gamma = S_0/S$; and S_0 = the solubility of ethyl acetate in water. The densities are those of the salt solutions saturated with ethyl acetate.

TABLE 1.

Temp., 25°.										
Salt	M_s	M_E	Density	S	γ	M_s	M_E	Density	S	γ
—	—	0.8426	0.9957	8.048	—	—	—	—	—	—
NaClO ₄	1	0.9376	1.066	9.583	0.8399	0.5	0.8867	1.031	8.750	0.9198
	0.75	0.9128	1.048	9.173	0.8772	0.25	0.8632	1.013	8.383	0.9601
NaNO ₃	1	0.7058	1.048	6.900	1.166	0.5	0.7740	1.022	7.474	1.076
	0.75	0.7395	1.035	7.201	1.118	0.25	0.8010	1.009	7.685	1.047
KNO ₃	1	0.7078	1.053	7.001	1.149	0.5	0.7761	1.024	7.548	1.066
	0.75	0.7406	1.039	7.257	1.109	0.25	0.8056	1.010	7.757	1.038
AgNO ₃	1	0.7612	1.126	7.536	1.068	0.5	0.7868	1.061	7.635	1.054
	0.75	0.7709	1.094	7.550	1.066	0.25	0.8123	1.028	7.823	1.029
AgClO ₄	1	1.008	1.141	10.49	0.7672	0.5	0.9026	1.069	8.960	0.8917
	0.75	0.9605	1.105	9.777	0.8231	0.25	0.8700	1.033	8.465	0.9510
LiNO ₃	1	0.7722	1.033	7.600	1.059	0.5	0.7905	1.014	7.640	1.053
	0.75	0.7770	1.024	7.575	1.063	0.25	0.8130	1.005	7.810	1.030
LiClO ₄	1	1.094	1.050	11.35	0.7091	0.5	0.9330	1.022	9.242	0.8708
	0.75	1.008	1.036	10.22	0.7875	0.25	0.8775	1.009	8.535	0.9430
Temp., 35°.										
—	—	0.7591	0.9926	7.216	—	—	—	—	—	—
NaNO ₃	1	0.6246	1.043	6.088	1.185	—	—	—	—	—
NaClO ₂	1	0.8468	1.061	8.624	0.8368	—	—	—	—	—

TABLE 2.
Temp., 25°.

M_{XNO_3}	M_{XClO_4}	M_{E}	Density	m_{XClO_4}	m_{E}	K
NaNO ₃ -NaClO ₄						
0.75	0.25	0.745	1.052	0.286	0.836	($k_1 = 0.758$) 0.50
0.5	0.5	0.806	1.057	0.560	0.914	0.51
0.25	0.75	0.867	1.062	0.859	0.994	0.50
0	1	0.938	1.066	1.116	1.088	0.52
AgNO ₃ -AgClO ₄						
0.75	0.25	0.795	1.129	0.284	0.904	($k_1 = 0.819$) 0.52
0.5	0.5	0.850	1.133	0.575	0.979	0.52
0.25	0.75	0.919	1.137	0.852	1.072	0.52
0	1	1.008	1.141	1.184	1.194	0.57
LiNO ₃ -LiClO ₄						
0.75	0.25	0.825	1.038	0.282	0.931	($k_1 = 0.844$) 0.53
0.5	0.5	0.903	1.042	0.566	1.020	0.53
0.25	0.75	0.960	1.047	0.866	1.110	0.53
0	1	1.094	1.050	1.180	1.291	0.72
Temp., 35°.						
NaNO ₃ -NaClO ₄						
0.75	0.25	0.661	1.048	0.280	0.738	($k_1 = 0.658$) 0.61
0.5	0.5	0.717	1.053	0.565	0.810	0.56
0.25	0.75	0.783	1.057	0.857	0.894	0.58
0	1	0.847	1.061	1.156	1.001	0.64

DISCUSSION

The chief feature of the results is that the perchlorates increase the solubility of ethyl acetate in water, while the nitrates, like all other anions that have been studied, salt out. The order of the salting out of the cations is $\text{Na} > \text{K} > \text{Ag} > \text{Li}$. Potassium and sodium nitrate and sodium perchlorate obey the Setchenow equation, $\log_{10} \gamma = kM_{\text{salt}}$; k for potassium nitrate agrees with that calculated from Glasstone's results (Glasstone, Dimond, and Jones, *J.*, 1926, 2935), that for sodium nitrate is slightly lower. The effects of the silver and lithium salts are not linear but are approximately so up to an ionic strength of about 0.5. The value of the solubility of ethyl acetate in water at 25° is the same as that given by Altshuller and Everson (*J. Amer. Chem. Soc.*, 1953, **75**, 1727), that at 35° is 2% lower.

The salting in of ethyl acetate by perchlorate ions appears to be directly comparable with the increased solubility of ethyl methyl ketone in perchlorate solutions, described by Duclaux and Durand-Gasselin (*J. Chim. phys.*, 1938, 189), and of γ -butyrolactone in sodium perchlorate solutions (Long, McDevit, and Dunkle, *J. Phys. Colloid Chem.*, 1951, **55**, 814). Table 3, in which values of the Setchenow constant as defined above, at 25°, for γ -butyrolactone are compared with those calculated from recent data for ethyl acetate, shows that this similarity also applies to solutions of alkali halides.

TABLE 3.

Salt	NaCl	NaBr	NaI	NaClO ₄
γ -Butyrolactone	0.067	0.007	-0.088	-0.113
Ethyl acetate	0.189	0.119	0.026	-0.076

It is well known that in order to account for the salting in of non-electrolytes it is necessary to consider short-range forces between the ions, solvent, and non-electrolyte, in addition to the electrostatic effect of the ions (Debye effect) and the volume occupied by the non-electrolyte (McDevit and Long, *J. Amer. Chem. Soc.*, 1952, **74**, 1775; *Chem. Reviews*, 1952, **51**, 119). The reasons for these short-range forces have been much discussed (*e.g.* Bockris, Kitchener, and Bowler-Reed, *Trans. Faraday Soc.*, 1951, **47**, 184; Saylor, Whitten, Claiborne, and Gross, *J. Amer. Chem. Soc.*, 1952, **74**, 1778). The data collected in Table 2 for nitrate-perchlorate mixtures at constant ionic strength of 1 can be used to show that in these solutions this effect can be adequately described by means of the association constant of an ethyl acetate-ClO₄⁻ complex.

The solubility of the ester in the mixed salt solutions can be expressed as $m_E = k_1 + k_2 \cdot m_{\text{XClO}_4}$, where k_1 and k_2 are constants for each cation at 25° [k_2 has the same value (0.276) for the sodium solutions at 25° and 35°]. If it is assumed that the molality of the uncomplexed ethyl acetate is the same at constant temperature in all the solutions containing perchlorate ions and with the same cation at constant ionic strength this equation may be rewritten as $m_E = m_E(\text{free}) + m_{\text{complex}}$.

Values of an association constant K , defined by $K = m_{\text{complex}}/k_1 (m_{\text{XClO}_4} - m_{\text{complex}})$ are included in Table 2.

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