Table VII. Viscosity of Ternary System Heptane(1)-Iso-octane(2)-Toluene(3)

	Composition		Exptl viscosity, cS
	x_1	x_2	t, 25°C
	0.1780	0.0508	0.616
	0.2999	0.0856	0.599
	0.4721	0.1347	0.596
	0.0702	0.0681	0.622
	0.1982	0.1923	0.600
	0.3622	0.3514	0.613
	0.0411	0.0567	0.621
	0.2031	0.2819	0.590
	0.2174	0.3018	0.586
	0.0822	0.1977	0.603
	0.2668	0.6423	0.652
	0.0296	0.0071	0.648
	0.5717	0.3040	0.639
	0.4787	0.2584	0.599
	0.0809	0.0429	0.633
		Ternary parameter	RMSD
McAllister's method		0.450	10.210^{-3}
Heric's method		−0.089	10.710^{-3}

mined by a least-squares method applied to the difference of the experimental value and the value of the sum of all terms except the term containing the ternary parameter.

The method of Heric can also be extended to ternary systems:

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_3 \ln \nu_3 + x_1 \ln M_1 + x_2 \ln M_2 + x_3 \ln M_3 - \ln (x_1M_1 + x_2M_2 + x_3M_3) + \delta_{123} \quad (8)$$

where:

$$\delta_{123} = x_1x_2[\beta_{12}' + \beta_{12}''(x_1 - x_2)] + x_1x_3[\beta_{13}' + \beta_{13}'' (x_1 - x_3)] + x_2x_3[\beta_{23}' + \beta_{23}'' (x_2 - x_3)] + \alpha_{123}x_1x_2x_3 \quad (9)$$

The ternary parameter α_{123} was computed by means of the same method as used for the computation of the ternary parameter of the equation of Kallidas and Laddha, but in this method by awarding a weight to the data points that was inversely proportional to the square of the probable error of the product $x_1x_2x_3$.

The ternary parameters and the root-mean-square deviation of the computed and experimental data are inserted in Table VII. The root-mean-square deviation of both methods is almost equal. The prediction by means of both methods was within 1-2%.

Acknowledgment

The authors are grateful to G. Goethals, director of the Laboratory of Industrial Organic Chemistry and Chemical Engineering, for his interest in this work.

Nomenclature

M_i = molecular weight of component i
r_i = molecular radius of component i
x_i = mole fractions of component i
α_{ij}, α_{ijk} = binary, ternary interaction parameter
β_{ij}', β_{ij}'' = binary parameters correlating the interaction parameter to the composition
δ_{ij}, δ_{ijk} = deviation from noninteraction in a mixture
μ = viscosity, cp
ν_i = kinematic viscosity of component i, cS
ν_{ij}, ν_{ijk} = binary, ternary parameter of the equation of McAllister

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Received for review February 12, 1974. Accepted August 22, 1974.

Solubility and Solvate Formation of Lithium Perchlorate in Lower Nitriles

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Solubility data for $LiClO_4$ in acetonitrile and propionitrile are determined by use of cooling curve methods adapted for nonaqueous solvents. Partial phase diagrams for these systems are presented. A distinct dystectic corresponding to the compound $LiClO_4 \cdot 4MeCN$ is obtained in the acetonitrile system with a less pronounced dystectic appearing in the propionitrile system. Results are discussed in terms of ion-solvent interactions.

The stoichiometry of solid adducts between electrolytes and solvents in which they are readily soluble can often be used as a guide to likely coordination patterns of the ions in solution. These patterns can then be used in formulating models of electrolyte solutions (*1*), although caution is necessary in exercising such analogies.

In this paper, phase diagrams are presented showing the stoichiometry and thermodynamics of the systems $LiClO_4$-MeCN and $LiClO_4$-EtCN in the nitrile-rich composition range.

Experimental

The purification procedures for lithium perchlorate, acetonitrile, and propionitrile have been described elsewhere (*2*).

Phase diagrams were recorded by use of the cooling method. The system $LiClO_4$-MeCN was examined with an apparatus which consists essentially of a Pyrex test tube with a ₸ 24/40 ground joint as container, and a ½-in. Teflon-coated magnetic stirring bar. Several indentations

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were made in the walls to improve mixing by breaking up the cylindrical flow pattern, which tended to promote nonuniform cooling. A mercury-in-glass thermometer graduated in 0.1° intervals and calibrated against the available standards was used for temperature measurement, and the whole unit was placed in a 250-ml Erlenmeyer flask which acted as both support and air jacket: cooling with laboratory air was sufficient over the temperature range studied. Supercooling of 2–5°C was normal in this system and was corrected in the usual manner by back extrapolation.

Measurements for the system $LiClO_4$–EtCN were made with a modified apparatus. The melting points are generally about 50° lower, and the 15–20-ml sample was cooled with Dry Ice and methanol. The sample tube was vacuum jacketed and stirred with a propeller via a silicone oil seal (GE SF-1017). Temperature was measured with a chromel–alumel thermocouple immersed in a silicone oil well and a Keithley 147 null detector used as amplifier to drive a Moseley (2D-2A) X-Y recorder. The thermocouple emf was also read on a digital multimeter [Lear Siegler-Cimron Model 6735]. Sample composition could be changed over a small range by adding fresh solvent from a weighed syringe through a serum cap located on the end of a side arm.

Supercooling was more extensive than in the acetonitrile system, especially with the more concentrated solutions, and to obtain meaningful cooling curves, it was necessary to cool until solid formed, then raise the temperature to 3–5° above the crystallization point, and cycle the temperature five or six times over a short range to ensure the presence of nuclei in the solution. This procedure usually reduced supercooling to 1–2°C.

An attempt was made similarly to obtain curves for $LiClO_4$–PrCN, but a glassy state resulted which could not be crystallized, and meaningful cooling curves were not obtained.

Results and Discussion

Solubility data for the $LiClO_4$–MeCN and the $LiClO_4$–EtCN systems are given in Table I.

Phase diagrams (of temperature Celsius, T, vs. salt mole fraction, X) for the range of compositions studied are given for $LiClO_4$–MeCN in Figure 1 and $LiClO_4$–EtCN in Figure 2. A quite distinct dystectic is obtained in the $LiClO_4$–MeCN system, corresponding to a composition of $LiClO_4 \cdot 4MeCN$, melting at 50°C. A sample of this compound was made by warming stoichiometric quantities of anhydrous lithium perchlorate and acetonitrile to 70°C and stirring. On cooling, the solid was deposited as colorless plates. The melting point was confirmed within the melting range of 1°C. At higher salt contents than $X(LiClO_4) = 0.25$, the tendency toward glass formation was stronger, and results were less reproducible. The invariant phase formed needle-like crystals which had a vapor pressure of about 2 mm at 20°C. On pumping off the vapor for 2 hr, this solid decomposed, presumably to a lower solvate. The system $LiClO_4$–EtCN gives a similar but less clearly defined dystectic, also at the composition $X(LiClO_4) = 0.20$, and melting at −1.5°C. The solid obtained is more waxy than its acetonitrile analog.

There is no reason to suppose that the composition $LiClO_4 \cdot 4RCN$ does not represent a true molecular compound, the structure of which is largely determined by a tendency of the inner solvation layer of one or both ions to remain rigid. The low melting points of both compounds are an indication of the small lattice energy relative to pure lithium perchlorate, as is the 2-mm dissociation pressure at room temperature of the acetonitrile compound. This lattice energy lowering is the result of in-

Table I. Solubility of Lithium Perchlorate

m	X_{LiClO_4}	t, °C	n[a]
	Acetonitrile		
1.5419	0.05953	24.20 ± 0.01	3
1.8632	0.07106	29.16 ± 0.2	3
2.1402	0.08076	32.8 ± 0.15	3
2.4615	0.09178	36.33 ± 0.05	3
2.9548	0.10818	40.12 ± 0.05	3
3.2253	0.11693	41.94 ± 0.05	4
3.9402	0.13923	45.67 ± 0.03	4
4.4614	0.15480	48.28 ± 0.05	3
5.2365	0.17694	49.50 ± 0.03	5
6.1452	0.20146	49.41 ± 0.01	4
6.2239	0.2035	50.17 ± 0.30	2
7.1865	0.2278	48.85 ± 0.05	2
7.5868	0.2375	41.21	1
7.7932	0.2424	45.66	1
8.4018	0.2560	45.43	1
10.1554	0.2942	[b]	
	Propionitrile		
1.4148	0.0723	∼−43	1
2.5088	0.12141	−21.3 ± 0.1	4
3.0093	0.14218	−12.1 ± 0.2	4
3.7315	0.17049	−0.5 ± 3.5	4
4.1544	0.1862	−3.9 ± 2.0	3
5.7501	0.2710	>0	1
6.8443	0.27378	+2.1 ± 0.1	2
8.1469	0.3097	12 ± 4	2

[a] No. of runs. [b] Forms glassy phase.

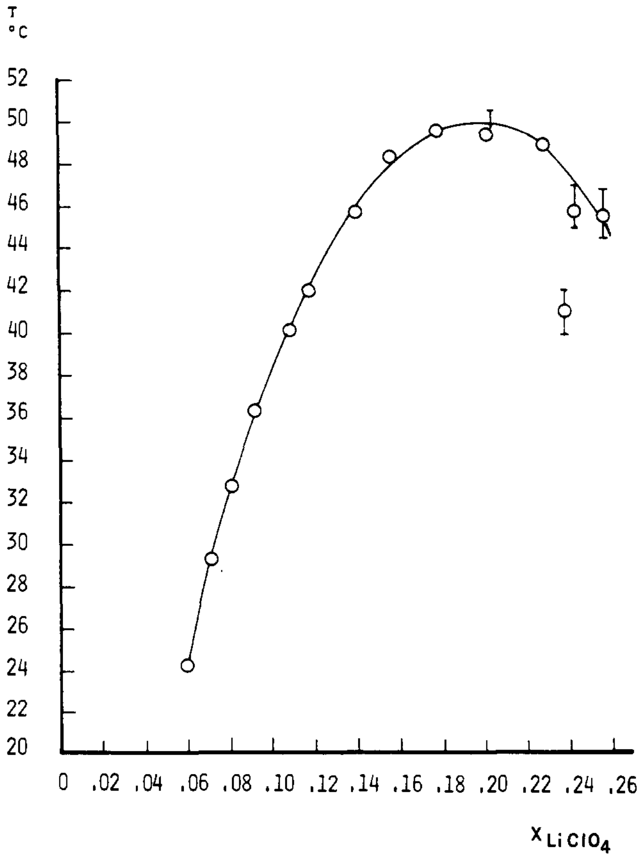

Figure 1. Partial phase diagram for system lithium perchlorate–acetonitrile

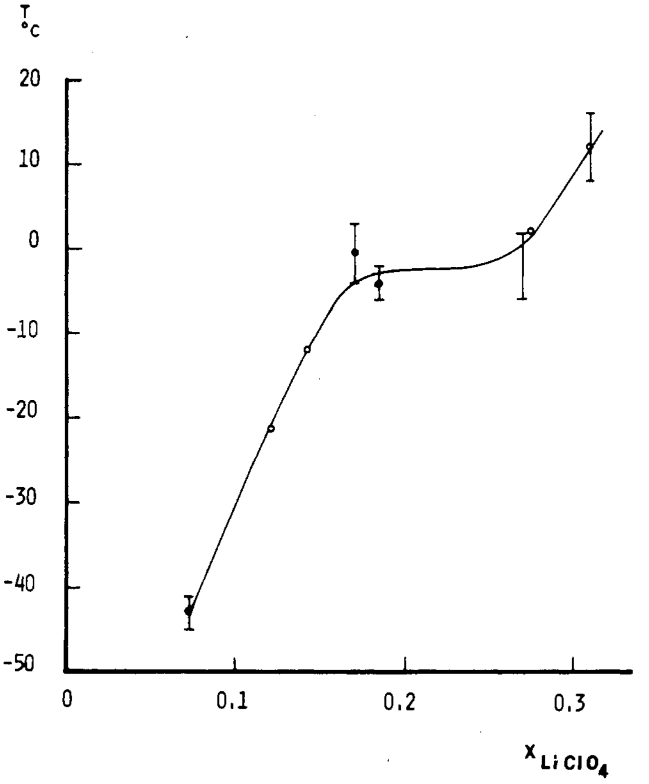

Figure 2. Partial phase diagram for system lithium perchlorate–propionitrile

creasing the mean interionic distance. If so, it would be expected that the acetonitrile compound should have an appreciably higher lattice energy than the propionitrile compound. This is reflected in the 50° difference in their melting points.

The data were analyzed by the method described by Prigogine and Defay (*3*) to obtain approximate heats of fusion of the two solid phases. The equation:

$$\frac{-\Delta H_f^\circ}{R}\left(\frac{1}{T}-\frac{1}{T_c}\right)=\ln\frac{X^l{}_{\mathrm{LiClO_4}}(1-X^l{}_{\mathrm{LiClO_4}})^4}{X^c{}_{\mathrm{LiClO_4}}(1-X^c{}_{\mathrm{LiClO_4}})^4}$$

(where ΔH_f° is the enthalpy of fusion of the solvate, l and c refer to liquid and crystal, respectively, and T is temperature on the Kelvin scale) was solved graphically for ΔH_f° by plotting log $X(\mathrm{LiClO_4})$ $[1 - X(\mathrm{LiClO_4})]^4$ vs. $1/T$. The values were obtained from data on the dilute side of the dystectic only, as data on the other side showed insufficient linearity for analysis, probably due to the intrusion of other dystectics. The enthalpies of fusion are 4.13 kcal·mol^{-1} for $\mathrm{LiClO_4}$–MeCN and 0.95 kcal·mol^{-1} for $\mathrm{LiClO_4}$–EtCN.

It is likely that the expansion of the crystal lattice involved in increasing the chain length of the solvent is largely responsible for the lowering of the heat of fusion, and the butyronitrile analog can therefore be expected to show little stability with respect to glass formation. It seems reasonable to assume from this evidence that the lithium ion in solution is tetrahedrally solvated by nitrile molecules, as no hexa-solvate was found, and that solvation of the perchlorate ion is relatively weak. X-ray crystallographic or spectroscopic evidence is needed to firm up this suggestion. The packing problem evident with the solid lattices does not occur in the liquid, and it would not be expected prima facie that the bond energy between cation and solvating solvent would vary appreciably with solvent chain length.

Acknowledgment

Helpful suggestions by E. E. Schrier (State University of New York at Binghamton) are acknowledged.

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Received for review March 25, 1974. Accepted August 14, 1974.