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HETEROGENEOUS EQUILIBRIUM BETWEEN THE CONDENSED PHASE AND VAPOR OF APROTONIC SOLVENTS AND ELECTROLYTES BASED ON THEM

II. SOLVENT MIXTURES

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Experimental results for the saturated vapor pressure of mixtures of organic solvents with electrolytes based on them are given, together with thermodynamic characteristics of the vaporization process calculated on this basis.

Earlier, in [1], the factors stimulating the study of the equilibrium between condensed phase and vapor in mixtures of organic solvents and electrolytes based on them were formulated. Using the methods of sample preparation and of experiment described in [1], the saturated vapor pressure was measured for two-component mixtures of tetrahydrofuran (THF) with γ-butyrolactone (γ-BL) and propylene carbonate (PC) of two compositions (by volume) — 1:1 and 3:7 — and also of electrolytes based on them. As before, lithium perchlorate ($LiClO_4$) was used as the ionogenic component of the electrolyte.

As an example, in Fig. 1, values of the saturated vapor pressure of the given solvent mixture and, for comparison, data for the individual solvents of which they are composed are given.

The primary thing to notice is that the experimental data for each mixture, despite the significant difference in boiling point of the components (338.85, 474.45, and 509.35°K [1]

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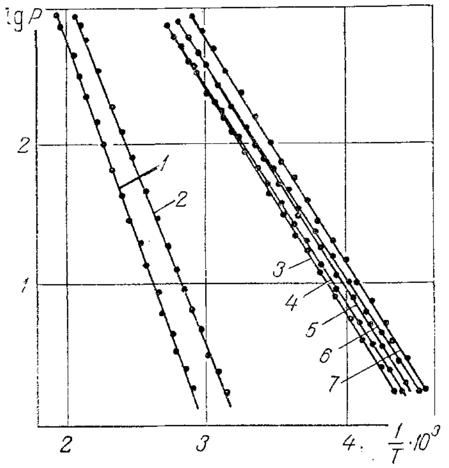

Fig. 1. Temperature dependence of the saturated vapor pressure P of individual solvents and their mixtures: 1) PC; 2) γ-BL; 3) PC:THH (7:3); 4)γ-BL:THH (7:3); 5) PC:THF (1:1); 6) γ-BL:THF (1:1); 7) THF.

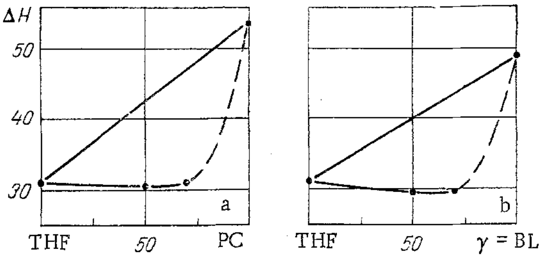

Fig. 2. Total latent heat of vaporization of two-component solvents ΔH, kJ/mole, as a function of their composition: 1) THF—PC; 2) THF—γ-BL.

for THF, γ-BL, and PC, respectively), are well approximated, when represented in the coordinate system log P — 1/T, by linear dependences of the form log P = A — B/T, with the same values of A and B over the whole of the investigated temperature range (but different values for each system, of course). At the same time, as is evident from Fig. 1, the composition of the solvent mixture has relatively little influence on its saturated vapor pressure, which is determined mainly on the low-boiling component (THF). This is evident in the practically complete independence of the total latent heat of vaporization of the system PC:THF and γ-BL: THF on their quantitative composition (up to 70% — by volume — of the first components: Fig. 2). Evidently, in the experimental conditions (i.e., with the given qualitative and quantitative compositions of the mixture), the gas phase is represented mainly by the more volatile component (THF), which also allows the above approximating equation to be used, though it is valid, strictly speaking, for the description of the interphase equilibrium of the individual materials.

Thermodynamic characteristics of the vaporization process of the mixed solvents, calculated on the basis of the experimental results obtained, are given in Table 1, together with the values of A and B. All these quantities are determined with a confidence level of 0.95, using the method of least squares in analyzing the experimental results.

Table 2 gives the thermodynamic characteristics of the vaporization of 1 M solutions of lithium perchlorate in the mixed solvents and values calculated by the above method for the constants A and B in the equations approximating the temperature dependence of their vapor pressure.

Comparison of the thermodynamic characteristics of the vaporization process of electrolytes and the corresponding solvent mixtures shows that they are little different, which is because of the relatively low concentration of lithium perchlorate. The results of comparing data on the saturated vapor pressure are both qualitatively and quantitatively confused.

TABLE 1. Thermodynamic Characteristics of Vaporization Process of Mixed Solvents (two-component systems)

Solvent composition	Temperature range, °C	ΔH_T^0, kJ/mole	ΔS_T^0, J/mole·°K	Bp,* °K	$\lg P = A - \frac{B}{T}$	
					A	B
PC:THF (1:1)	237—355	30,81±0,38	87,46±1,15	353,45	7,43±0,06	1608±20
PC:THF (7:3)	238—367	31,10±0,67	85,32±1,53	366,65	7,31±0,08	1624±35
γ-BL:THF (1:1)	235—355	29,79±0,46	84,07±1,72	354,30	7,27±0,09	1555±24
γ-BL:THF (7:3)	238—370	29,97±0,55	81,35±2,10	369,15	7,12±0,11	1565±29

*At atmospheric pressure.

TABLE 2. Thermodynamic Characteristics of Vaporization Process of 1 M Solutions of $LiClO_4$ in Mixed Solvents (three-component systems)

Solvent composition	Temperature range, °K	ΔH_T^0, kJ/mole	ΔS_T^0, J/mole·°K	Bp,* °K	$\lg P = A - \frac{B}{T}$	
					A	*B*
PC:THF (1:1)	232—358	29,39±0,59	82,43±0,95	357,65	7,17±0,05	1534±31
PC:THF (7:3)	230—377	30,39±0,51	81,14±1,53	375,00	7,11±0,08	1586±27
γ-BL:THF (1:1)	243—358	32,82±0,84	93,11±1,34	352,55	7,74±0,07	1713±44
γ-BL:THF (7.3)	238—370	30,85±0,97	83,86±1,72	368,50	7,25±0,09	1610±51

*At atmospheric pressure.

Thus, whereas for the system PC:THF the difference is in complete agreement with general physicochemical laws (in the electrolyte, the vapor pressure and boiling point are respectively lower and higher than in the solvents), for the systems γ-BL:THF at high temperatures (>330°K) an anomaly is observed, for reasons which remain unclear.

NOTATION

P, saturated vapor pressure, mm Hg; T, temperature, °K; ΔH, latent heat of vaporization, kJ/mole; ΔS, change in entropy, J/mole•°K.

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