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Physical Properties of Compounds Used in Vitamin Synthesis

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Some physical properties, namely vapor pressure, surface tension, density, heat capacity, and heat conductivity, were measured for 20 organic compounds that are used in the synthesis of A and E vitamins.

Introduction

The development of the synthetic vitamin production leads to the necessity of involving new substances in the technology. Unfortunately, the data on the properties of these substances are often incomplete or even unavailable. Particularly, this is true for the group of compounds shown in Table I. Some data on physical properties for a wide temperature range are known only for 3-pentanone (IX) and 2-butenal (X), while for other substances the information on the data is inconsistent and far from complete. The purity of the substances is not indicated in many papers and admixtures are not identified; therefore, we pay special attention to the purification of all the compounds.

Our measurements involve density, heat capacity, and heat conductivity under normal atmospheric pressure as well as vapor pressure and surface tension along liquid/vapor coexistence curves. The experimental data for all the substances are presented by approximation equations, while for 2-methoxy-1-propene (I), 6-methyl-5-hepten-2-one (IV), 3-pentanone (IX), and 2-butenal (X) the full set of thermodynamic properties at the liquid/vapor equilibria between triple and critical points is calculated by the method using corresponding-states theory.

Experimental Section

Optimal conditions of extraction from initial mixtures of pure components (Table I) have been chosen for individual properties of substances and possible admixtures. The following

Table I. Compound Names and Structures of Substances

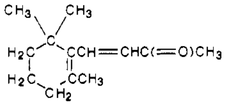
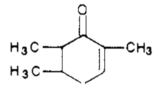
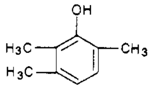
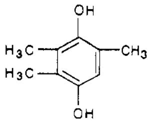
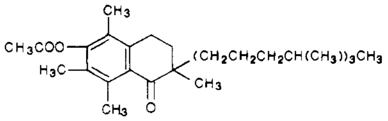
no.	compd	structure	Brutto formula
I	2-methoxy-1-propene	$CH_3C(OCH_3){=}CH_2$	C_4H_8O
II	2,2-dimethoxypropane	$(CH_3)_2C(OCH_3)_2$	$C_5H_{12}O_2$
III	2-methyl-3-buten-2-ol	$CH_3C(CH_3)(OH)CH{=}CH_2$	$C_5H_{10}O$
IV	6-methyl-5-hepten-2-one	$CH_3C(CH_3){=}CHCH_2CH_2C({=}O)CH_3$	$C_8H_{14}O$
V	3,7-dimethyl-6-octen-1-yn-3-ol (dehydrolynalol)	$CH_3C(CH_3){=}CHCH_2CH_2C(CH_3)(OH)C{\equiv}CH$	$C_{10}H_{16}O$
VI	6,10-dimethyl-4,5,9-undecatrien-2-one	$CH_3C(CH_3){=}CHCH_2CH_2C(CH_3){=}C{=}CHCH_2C({=}O)CH_3$	$C_{13}H_{20}O$
VII	6,10-dimethyl-3,5,9-undecatrien-2-one (pseudoionone)	$CH_3C(CH_3){=}CHCH_2CH_2C(CH_3){=}CHCH{=}CHC({=}O)CH_3$	$C_{13}H_{20}O$
VIII	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone)		$C_{13}H_{20}O$
IX	3-pentanone	$CH_3CH_2C({=}O)CH_2CH_3$	$C_5H_{10}O$
X	2-butenal (crotonaldehyde)	$CH_3CH{=}CHCHO$	C_4H_6O
XI	2,5,6-trimethyl-2-cyclohexen-1-one		$C_9H_{14}O$
XII	2,5,6-trimethylphenol		$C_9H_{12}O$
XIII	trimethylhydroquinone		$C_9H_{12}O_2$
XIV	6,10-dimethyl-2-undecanone (hexahydropseudoionone)	$CH_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3C({=}O)CH_3$	$C_{13}H_{26}O$
XV	3,7,11-trimethyl-1-dodecyn-3-ol	$CH_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3C(CH_3)(OH)C{\equiv}CH$	$C_{15}H_{28}O$
XVI	6,10,14-trimethyl-3,5-pentadecadien-2-one	$CH_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3C(CH_3){=}CHCH{=}CHC({=}O)CH_3$	$C_{18}H_{32}O$
XVII	6,10,14-trimethyl-2-pentadecanone (phytone)	$CH_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3C({=}O)CH_3$	$C_{18}H_{36}O$
XVIII	3,7,11,15-tetramethyl-1-hexadecyn-3-ol	$CH_3(CH(CH_3)CH_2CH_2CH_2)_3C(CH_3)(OH)C{\equiv}CH$	$C_{20}H_{38}O$
XIX	3,7,11,15-tetramethyl-1-hexadecen-3-ol (isophytol)	$CH_3(CH(CH_3)CH_2CH_2CH_2)_3C(CH_3)(OH)CH{=}CH_2$	$C_{20}H_{40}O$
XX	α-tocopherol acetate		$C_{31}H_{52}O_3$

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Table II. Identification of Liquids at 293.15 K

	experimental data			literature data			
compd	density, kg·m^{-3}	refr index	purity, mol %	density, kg·m^{-3}	refr index	purity, mol %	ref
I	763.9	1.3839	99.84	770	1.3824		*1*
II	849.5	1.3781	99.50	844.8	1.3778		*2, 3*
III	823.4	1.4170	99.0	823.0	1.4165		*4*
IV	850.8	1.4404	99.0	850.6	1.4408		*5*
V	878.6	1.4645	99.0	878.8	1.4632		*6*
VI	883.0	1.4880	98.24		1.4860		*7*
VII	895.1	1.5313	98.50	895.4	1.5300	95	*8*
VIII	944.7	1.5210	99.0	947.7	1.5200	99.8	*9*
IX	814.2	1.3924	99.85	814.4	1.3924	99.6	*10*
X	859.2	1.4370	99.0	848.3	1.4361		*11*
XI	933.5	1.4751	99.0	930.6	1.4734		*8*
XIV	830.8	1.4358	99.09	831.5	1.4359		*12*
XV	851.9	1.4511	99.92	850.8	1.4492	96.0	*6, 13*
XVI	866.7	1.4976	99.6	868.4	1.4971		*14*
XVII	836.6	1.4456	99.5	834.8	1.4459		*15*
XVIII	851.7	1.4563	99.92	851.7	1.4562		*14*
XIX	845.4	1.4562	98.74	843.5	1.4570		*16*
XX	958.0	1.4978	98.90	977.3	1.5021		*6, 14*

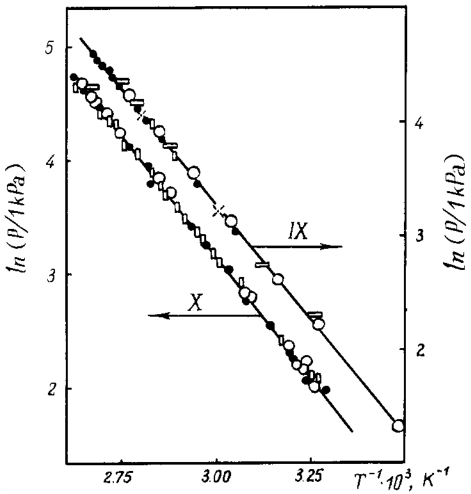

Figure 1. Comparison of the vapor pressure data for 3-pentanone (IX): ▭(*10*), ● (*33*), □ (*34*), × (*35*); ○, our measurements; and for 2-butenal (X): ▯ (*11*), ● (*36*), □ (*37*); ○, our measurements.

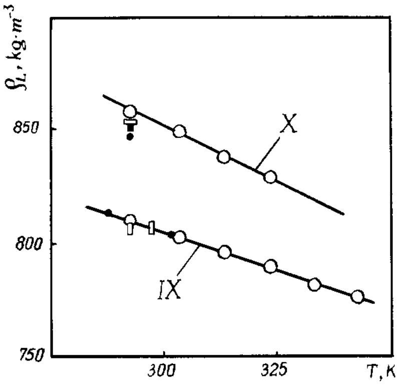

Figure 2. Comparison of the density data for 3-pentanone (IX): ▯ (*10*), ● (*38*); ○, our measurements; and for 2-butenal (X): ■ (*11*), ▭(*39*), ● (*40*); ○, our measurements.

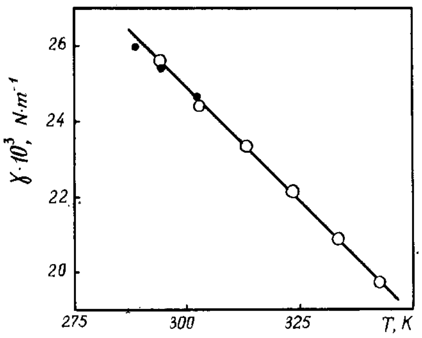

Figure 3. Comparison of the surface tension data for 3-pentanone: ● (*38*); ○, our measurements.

Table III. Identification of Solids by Melting Points

	exptl data		lit. data		
compd	temp, K	purity, mol %	temp, K	purity, mol %	ref
XII	354.65	99.0	355.15		*17*
XIII	443.15	99.0	442.15	96.6	*18*

Table IV. Apparatus Calibration Data

			lit. data			
property	substance	T, K	values	ref	this work	diff, %
density, g·cm^{-3}	acetone	293.15	0.7908	*29*	0.7903	−0.06
	methanol	293.15	0.7925	*30*	0.7928	0.04
	water	333.15	0.9857	*23*	0.9857	0.00
surface tension, N·m^{-1}	*n*-octane	293.15	21.76		21.80	0.2
		303.15	20.79		20.79	0.0
		313.15	19.78	*30*	19.82	0.2
		323.15	18.79		18.70	−0.4
	toluene	293.15	28.53	*30*	28.58	0.05
	water	293.15	72.75	*30*	72.74	−0.01
heat capacity, kJ·kg^{-1}·K^{-1}	water	298.15	4.183	*28*	4.18	−0.1
		343.15	4.187	*28*	4.19	0.1
heat conductivity, W·m^{-1}·K^{-1}	toluene	298.15	0.1336	*28*	0.1338	0.15

methods of purification and analysis were used: drying over $NaSO_4$, $MgSO_4$, K_2CO_3, and $CaCl_2$; rectification through columns with efficiency equal to 50 theoretical column trays; fractional distillation under atmospheric pressure and vacuum conditions; crystallization from mixtures of aromatic hydrocarbons; sublimation; and an analytical gas–liquid chromatography as a method of purity control.

Multistage fractional distillation under the atmospheric pressure (for I, III, IX–XI) and at residual pressures varying from 6.7 to 67 Pa (for II, IV–VIII, XIV–XX) is the basis of most of the purification processes. The purification of the solids (XII and XIII) was carried out by alternate sublimation and crystallization of mixtures.

The output content of the product of interest was determined by the method of area normalization of gas–liquid chromatography curves. Density, refractive index, and purity values of the liquid components at 298.15 K are given in Table II. Melting temperatures for two solids are presented in Table III.

Vapor pressure was measured by the static method (*19*) with a glass membrane as a null manometer. Portions of the non-

Table V. Vapor Pressure: Experimental Data

T, K	*P*, kPa
I	
281.80	35.06
282.60	36.38
284.20	39.22
285.05	40.59
285.95	41.83
286.90	42.50
288.70	46.84
289.55	50.19
291.05	51.28
292.75	55.51
292.95	56.28
294.05	58.18
295.80	62.68
296.90	65.17
298.30	68.97
298.95	70.56
300.55	74.85
300.65	75.10
302.15	79.69
302.80	81.43
304.25	86.08
304.75	87.43
306.35	92.76
306.90	94.88
308.15	98.52
309.20	102.59
309.55	103.73
II	
292.65	9.74
293.15	10.33
293.65	10.74
293.75	10.84
296.55	12.14
300.45	14.89
300.65	15.06
301.75	15.80
305.15	18.06
313.75	26.50
318.95	32.40
322.15	36.79
329.25	48.05
338.35	66.26
350.65	98.16
352.85	106.31
353.15	107.05
356.95	120.44
III	
289.82	2.24
289.86	2.31
290.18	2.40
290.83	2.45
292.10	2.63
294.81	3.08
295.82	3.20
295.93	3.28
298.95	3.76
300.53	4.24
300.80	4.45
301.96	4.77
302.02	4.80
302.30	4.83
303.64	5.27
303.86	5.29
307.84	6.56
314.59	9.53
323.11	14.80
327.63	18.37
328.21	19.02
335.33	26.34
341.80	35.86
343.06	37.82
345.96	42.95
346.66	44.23
356.91	66.77
356.96	67.00
368.20	101.84
368.28	102.15
370.03	108.56
372.12	116.49
372.28	117.09
IV	
328.36	1.41
328.39	1.45
342.65	2.93
348.99	3.76
354.71	4.81
356.38	5.19
380.92	14.12
383.14	15.45
384.25	16.44
400.44	28.41
401.11	29.01
416.37	47.33
417.36	48.60
422.23	56.47
426.13	62.76
437.32	85.35
440.01	91.54
444.31	102.47
448.11	112.79
451.52	122.94
V	
369.35	3.08
369.95	3.20
378.25	4.47
379.65	4.76
383.25	5.33
384.95	5.88
386.55	6.24
387.55	6.51
391.05	7.44
391.25	7.64
394.65	8.70
395.55	8.99
397.05	9.52
401.55	11.44
403.75	12.33
404.75	12.89
407.05	13.83
409.75	15.43
412.85	17.56
414.05	18.09
414.55	18.40
416.25	19.62
417.05	19.64
419.55	22.16
422.35	23.44
422.55	23.52
424.85	26.22
425.75	26.98
427.45	28.46
429.45	30.36
430.95	31.92
433.65	34.50
437.95	39.80
439.65	41.48
444.85	49.26
445.05	49.68
VI	
349.05	0.12
363.25	0.21
370.15	0.33
376.65	0.51
382.75	0.64
388.05	0.91
394.35	1.24
399.35	1.65
404.65	2.00
409.75	2.57
415.85	3.21
421.75	4.16
VII	
382.56	0.28
387.95	0.33
389.55	0.36
398.85	0.64
406.95	0.96
407.75	1.04
417.95	1.67
418.35	1.72
428.85	2.63
430.25	2.85
433.65	3.52
435.45	4.20
445.65	5.12
448.85	5.88
452.25	6.62
457.45	8.17
VIII	
373.45	0.68
379.95	0.81
384.95	0.99
388.55	1.11
392.85	1.20
399.15	1.57
404.65	2.03
411.15	2.51
417.75	3.20
426.95	4.53
430.25	5.01
436.35	6.31
442.25	7.71
IX	
289.95	3.42
309.85	9.21
319.95	14.22
330.55	22.33
341.35	33.64
350.35	46.50
361.25	66.60
367.45	82.09
370.95	90.18
371.45	91.82
375.15	102.52
X	
288.14	3.32
288.78	3.48
289.36	3.51
289.85	3.60
290.03	3.61
290.73	4.05
290.98	4.11
291.09	4.15
306.19	7.22
309.42	9.12
309.66	9.18
314.51	11.52
321.92	15.45
323.96	16.00
328.58	29.45
329.21	29.73
346.07	39.40
349.96	44.99
350.05	45.12
361.40	65.65
366.34	79.07
369.91	85.33
370.07	85.75
371.76	89.55
371.77	89.70
375.21	100.88
375.49	102.03
375.64	102.44
375.78	102.65
375.98	102.95
XI	
370.83	4.23
385.20	7.77
403.96	15.58
410.02	19.14
425.46	29.51
441.20	47.19
459.50	77.90
460.67	79.80
470.83	102.65
477.79	119.72
477.81	119.85
478.00	119.86
XII	
358.95	0.83
383.44	2.66
407.10	6.33
419.05	9.90
420.43	10.44
447.91	25.64
462.40	39.98
477.54	60.59
481.65	67.54
496.13	96.32
500.76	107.54
502.94	113.51
XIII	
450.15	4.13
456.85	4.92
461.25	5.45
478.05	8.22
480.10	8.70
483.95	9.52
484.15	9.64
489.25	10.97
491.95	11.76
494.35	12.15
496.95	12.94
500.85	13.85
XIV	
379.15	0.57
380.45	0.63
389.75	1.01
391.05	1.09
398.15	1.52
402.65	1.87
408.55	2.51
412.05	2.84
416.05	3.37
420.25	4.05
423.95	4.68
431.95	6.36
432.25	6.40
441.35	8.88
442.75	9.48
451.35	12.41
452.25	13.13
457.15	15.00
457.35	15.85
462.05	17.32
462.15	17.64
471.15	22.92
472.95	24.30
XV	
401.35	1.20
407.25	1.41
412.65	1.72
418.05	1.95
426.05	2.52
433.95	3.21
437.85	3.48
442.05	3.87
449.35	4.75
453.75	5.16
456.95	5.59
463.15	6.68
465.95	7.11
468.55	7.68
472.05	8.25
476.55	9.04
479.45	9.80
481.45	10.46
485.65	11.04
491.75	12.50
495.15	13.74
497.25	14.65
502.75	15.65
507.35	17.26
507.55	17.84
508.35	18.28
509.95	19.25
513.85	20.32
516.25	21.46
520.25	23.12
523.65	23.92
524.25	24.37
XVI	
404.05	0.80
413.85	1.20
429.25	2.11
443.25	3.04
461.05	4.09
470.05	5.09
477.35	6.04
482.15	7.02
482.35	7.08
492.95	8.60
506.35	11.57
513.25	13.04
516.55	13.94
520.05	15.45
526.35	17.49
531.95	20.42
541.35	23.80
550.55	27.57
556.35	30.24
560.65	33.51
XVII	
402.75	0.27
405.65	0.31
407.15	0.33
409.55	0.35
413.25	0.43
415.85	0.48
418.75	0.53
420.95	0.59
422.65	0.64
426.95	0.76
431.05	0.88
435.35	1.05
438.25	1.19
441.35	1.35
446.85	1.68
447.25	1.91
453.55	2.09
456.65	2.32
459.35	2.60
462.95	2.95
466.85	3.35
470.15	3.80
473.25	4.21
475.65	4.36
480.55	4.96
484.95	6.24
488.45	6.85
492.15	7.84
498.25	8.21
500.05	9.88
XVIII	
403.75	0.32
411.25	0.37
418.05	0.45
429.55	0.61
440.95	0.83
447.55	1.03
453.25	1.24
457.75	1.52
XIX	
439.35	0.73
442.35	0.75
442.45	0.84
446.45	0.95
448.35	1.10
451.05	1.15
454.55	1.31
456.65	1.47
458.35	1.53
459.95	1.65
463.95	1.93
468.75	2.20
XX	
466.15	0.35
475.45	0.45
486.55	0.65
493.65	0.83
512.25	1.33
524.35	1.96

volatile compounds were introduced into the membrane camera immediately, while the tensimeter filling in the case of volatile substances was more complicated (*20*). The tensimeter was embedded in oil or in LiCl–water mixture thermostat which allows measurement of the temperature using a mercury thermometer with an error of ±0.1 K. Pressure was measured by a cup mercury manometer with an accuracy of ±13.3 Pa (the results obtained being reduced to normal gravity and to 273.15 K).

The measurements of liquid densities were carried out by using double-capillary pycnometers calibrated with double-distilled degassed water. The method error determined by density

Table VI. Coefficients of Eq 1 and 7 for Representing Vapor Pressure

compd	A	$-B$	T^*, K	P^*, MPa
I	15.653 ± 0.058	3407.4 ± 17.3	605.95	17.634
II	16.077 ± 0.066	4023.4 ± 20.8	709.78	24.099
III	18.723 ± 0.041	5185.2 ± 13.0	843.48	111.164
IV	16.762 ± 0.048	5381.2 ± 18.5	893.46	23.708
V	17.535 ± 0.041	6065.8 ± 16.7	995.81	40.667
VI	19.576 ± 0.445	7644.2 ± 171.4	1148.5	63.815
VII	19.926 ± 0.318	8126.4 ± 133.3	1199.3	66.958
VIII	15.485 ± 0.312	5971.4 ± 126.5	976.56	5.341
IX	16.160 ± 0.064	4319.8 ± 21.8	761.60	25.749
X	15.875 ± 0.175	4218.2 ± 57.4	745.73	20.262
XI	16.254 ± 0.090	5472.6 ± 39.0	943.99	22.367
XII	16.966 ± 0.052	6147.4 ± 22.9	1022.8	28.931
XIII	13.567 ± 0.087	5471.8 ± 41.8	975.43	2.263
XIV	18.321 ± 0.113	7129.0 ± 48.2	1140.4	55.199
XV	13.109 ± 0.036	5193.3 ± 17.2	927.35	1.488
XVI	12.794 ± 0.126	5226.4 ± 61.3	982.79	1.835
XVII	15.738 ± 1.577	6732.4 ± 717.8	1240.3	36.488
XVIII	11.822 ± 0.526	5265.3 ± 227.1	934.44	0.4104
XIX	18.001 ± 0.535	8054.0 ± 241.9	1203.2	12.842
XX	14.426 ± 0.323	7224.9 ± 158.7	1235.1	3.200

measurements of acetone and of methanol was 0.02%.

The liquid–gas surface tension was measured by the capillary method (*20*, *21*). The level of liquid in the capillary was determined by a V-630 type cathetometer with an accuracy ±5 × 10^{-6} m. The relative error of the surface tension experimental data determined from measurements of water, toluene, and *n*-octane was less than 0.5%.

Heat capacity measurements were made at normal atmospheric pressure and in the temperature range 270–340 K by differential adiabatic CDA type calorimeter using the compensation method (*22*). The heat capacity relative error was determined to be ≤2% by comparison of our experimental results for double-distilled water at 298.15 and 343.35 K with the data of ref *23* and for methanol at 273.02 and 294.15 K with the data taken from ref *24*.

Heat conductivity was measured by the stationary hot fine wire method (*25*). The experimental cell contains a platinum capillary which was simultaneously used as the external resistance thermometer, and a 10^{-3} cm diameter thread used as the heater and inner resistance thermometer (*26*, *27*). The result of the heat conductivity control measurement of toluene at 298.15 K differs from the earlier measured (*28*) value by less than 1.2%.

The apparatus calibration data are summarized in the Table IV.

Experimental Results

The vapor pressure values have been determined at temperatures limited either by the maximum measured pressure or by the thermal stability of the substances under experiment. They are presented in Table V.

The simplest form of the vapor pressure data presentation is the Clausius–Clapeyron equation

$$\ln P = A + BT^{-1} \tag{1}$$

Equation 1 may be used for approximation of experimental results only within a narrow temperature range as well as for estimations of average enthalpy ΔH and average entropy ΔS of the gas–liquid phase transition. The individual constants of eq 1 are summarized in Table VI.

The liquid density and surface tension values along the coexistence curve have been determined for the temperature range 288.15–343.15 K (Table VII).

Table VII. Density and the Surface Tension Experimental Data

T, K	ρ, g·cm^{-3}	$10^3\gamma$, N·m^{-1}
	I	
288.15	0.7704	19.80
293.15	0.7639	19.14
298.15	0.7561	18.48
	II	
293.15	0.8495	21.44
303.15	0.8387	20.26
313.15	0.8281	19.18
323.15	0.8171	18.08
333.15	0.8058	17.14
343.15	0.7946	
	III	
293.15	0.8234	22.86
303.15	0.8149	22.01
313.15	0.8056	21.08
323.15	0.7950	20.07
333.15	0.7846	19.16
343.15	0.7739	18.23
	IV	
293.15	0.8508	28.47
303.15	0.8436	27.73
313.15	0.8339	26.47
323.15	0.8254	25.49
333.15		24.48
343.15		23.56
	V	
293.15	0.8786	28.23
303.15	0.8695	27.25
313.15	0.8612	26.54
323.15	0.8524	25.57
333.15	0.8438	24.78
343.15	0.8370	24.03
	VI	
293.15	0.8830	31.29
303.15	0.8744	30.26
313.15	0.8668	29.33
323.15	0.8595	28.44
333.15	0.8508	27.52
343.15	0.8420	26.59
	VII	
293.15	0.8951	32.30
303.15	0.8875	31.61
313.15	0.8797	30.72
323.15	0.8721	29.88
333.15	0.8644	28.87
343.15	0.8573	27.95
	VIII	
293.15	0.9447	39.52
303.15	0.9362	38.43
313.15	0.9287	37.24
323.15	0.9206	36.11
333.15	0.9127	34.94
343.15	0.9037	33.77
	IX	
293.15	0.8142	25.54
303.15	0.8045	24.27
313.15	0.7946	23.30
323.15	0.7845	22.22
333.15	0.7720	21.01
343.15	0.7614	19.76
	X	
293.15	0.8592	29.24
303.15	0.8509	28.09
313.15	0.8382	26.77
323.15	0.8285	25.61
333.15		24.45
343.15		23.30
	XI	
293.15	0.9335	31.66
303.15	0.9254	30.67
313.15	0.9172	29.68
323.15	0.9089	29.04
333.15	0.9008	28.61
	XII	
338.15	0.9723	31.02
343.15	0.9678	30.83
	XIV	
293.15	0.8308	26.86
303.15	0.8231	26.33
313.15	0.8156	25.80
323.15	0.8091	25.29
333.15	0.8014	24.59
343.15	0.7942	
	XV	
293.15	0.8519	27.32
303.15	0.8441	26.76
313.15	0.8361	26.09
323.15	0.8288	25.29
333.15	0.8219	24.59
343.15	0.8131	
	XVI	
293.15	0.8667	30.26
303.15	0.8591	29.48
313.15	0.8521	28.68
323.15	0.8446	27.95
333.15	0.8374	27.11
343.15	0.8295	26.30
	XVII	
293.15	0.8366	28.83
303.15	0.8289	28.03
313.15	0.8220	27.24
323.15	0.8148	26.41
333.15	0.8078	25.60
343.15	0.8010	24.87
	XVIII	
293.15	0.8517	28.79
303.15	0.8439	28.15
313.15	0.8368	27.49
323.15	0.8291	26.78
333.15	0.8220	25.97
343.15	0.8155	25.15
	XIX	
293.15	0.8458	28.47
303.15	0.8378	28.04
313.15	0.8305	27.33
323.15	0.8228	26.45
333.15	0.8160	25.56
343.15	0.8076	24.84
	XX	
293.15	0.9578	
303.15	0.9507	
313.15	0.9434	
323.15	0.9369	
333.15	0.9300	
343.15	0.9247	

The surface tension experimental data for all substances have been approximated by the Guggenheim equation

$$\gamma = \gamma_0(1 - T/T_c)^{11/9} \tag{2}$$

the constants γ_0 and T_c being given in Table VIII.

Table VIII. Constants of Eq 2 for Representing Surface Tension

compd	T_c, K	$10^3\gamma_0$, $N{\cdot}m^{-1}$	compd	T_c, K	$10^3\gamma_0$, $N{\cdot}m^{-1}$
I	479.68	60.71	X	601.71	65.77
II	530.63	57.13	XI	787.63	55.60
III	586.45	53.46	XII	1376.3	43.78
IV	645.19	59.70	XIV	877.50	44.21
V	697.18	54.87	XV	774.11	49.01
VI	696.25	60.94	XVI	755.04	55.20
VII	736.52	60.30	XVII	727.87	54.14
VIII	707.48	76.06	XVIII	771.69	51.79
IX	560.95	63.08	XIX	750.24	52.56

Table IX. Heat Capacity Experimental Data

T, K	ρ, $g{\cdot}cm^{-3}$	T, K	ρ, $g{\cdot}cm^{-3}$	T, K	ρ, $g{\cdot}cm^{-3}$
I		VIII		XV	
273.02	2.15	273.20	1.89	272.95	2.23
283.62	2.18	293.80	1.95	293.75	2.43
294.14	2.23	313.60	2.02	313.15	2.56
301.50	2.25	333.75	2.05	343.35	2.69
II		IX		XVI	
273.05	2.01	273.15	2.24	273.35	2.04
298.15	2.09	298.15	2.28	293.95	2.10
313.55	2.12	313.65	2.29	313.65	2.13
334.15	2.24	334.65	2.32	333.55	2.22
III		X		XVII	
273.25	2.58	273.15	2.07	272.95	2.15
298.05	2.80	298.35	2.12	293.85	2.21
313.45	2.90	313.45	2.16	313.60	2.33
333.25	3.06	343.45	2.16	333.65	2.41
343.35	3.12	XI		XVIII	
IV		273.25	1.82	273.35	2.35
273.35	2.08	298.15	1.87	293.85	2.42
298.35	2.13	313.45	1.93	313.85	2.46
313.55	2.18	343.45	2.02	333.55	2.53
343.35	2.20	XII		XIX	
V		273.35	1.44	273.05	2.26
273.35	2.38	298.15	1.65	293.75	2.46
293.85	2.45	313.55	1.95	313.65	2.56
313.55	2.53	333.75	2.05	333.65	2.65
333.65	2.57	338.15	2.06		
		343.55	2.12	XX	
VI				273.05	1.83
272.95	2.01	XIII		293.75	1.90
293.80	2.07	273.35	1.30	313.65	2.00
313.65	2.15	293.95	1.41	333.65	2.05
333.75	2.20	313.65	1.43		
VII		333.55	1.51		
273.25	1.96	XIV			
297.85	1.99	272.95	2.03		
313.55	2.05	293.75	2.09		
343.35	2.10	313.55	2.16		
		343.35	2.29		

The liquid density and heat capacity (Table IX) data under normal atmospheric pressure can be represented by

$$\rho(T) = \sum_{n=0}^{m} a_n T^n \qquad (3)$$

$$C_p(T) = \sum_{n=0}^{m} b_n T^n \qquad (4)$$

where maximum degrees m of polynomials are determined by the Fisher criterion minimum (Table X).

The heat conductivity temperature dependence (Table XI) is described by the Mustafayev linear equation (*31*)

$$\lambda(t) = \lambda_{t=0.55}(1.739 - 1.34t) \qquad (5)$$

where $t = T/T_b$ and T_b is the boiling temperature. The individual constants of the eq 5 are given in Table XII.

Table X. Coefficients of Eq 3 and 4 for Representing Density and Heat Capacity

	equation 3		equation 4	
compd	a_0	-10^3a_1	b_0	10^3b_1
I	1.1816	1.4265	1.177	3.56
II	1.1712	1.0966	0.985	3.71
III	1.1168	0.9973	0.517	7.60
IV	1.1029	0.8582	1.561	1.91
V	1.1243	0.8398	1.483	3.29
VI	1.1201	0.8090	1.131	3.22
VII	1.1178	0.7598	1.373	2.12
VIII	1.1823	0.8104	1.179	2.63
IX	1.1264	1.0619	1.927	1.16
X	1.1668	1.0471	1.722	1.32
XI	1.1736	0.8191	1.052	2.79
XII	1.2766	0.8999	-1.246	9.87
XIII			0.414	3.29
XIV	1.0438	0.7274	1.009	3.71
XV	1.0762	0.7654	0.498	6.47
XVI	1.0833	0.7390	1.262	2.82
XVII	1.0444	0.7101	0.937	4.40
XVIII	1.0644	0.7270	1.592	2.80
XIX	1.0668	0.7547	0.579	6.27
XX	1.1534	0.6690	0.828	3.68

Table XI. Heat Conductivity Experimental Data (T, K; λ, $W{\bullet}m^{-1}{\bullet}K^{-1}$)

compd	λ (294.15 K)	compd	λ (294.15 K)
I	0.150	IX	0.131
II	0.133	XI	0.096
III	0.107	XVI	0.137
IV	0.112	XVII	0.140
V	0.154	XVIII	0.134
VIII	0.128	XX	0.130

VII		XIV		XV		XIX	
T	λ	T	λ	T	λ	T	λ
273.68	0.141	278.38	0.136	278.22	0.138	277.77	0.138
299.20	0.134	298.77	0.130	299.28	0.131	298.24	0.132
314.41	0.130	314.93	0.124	314.65	0.126	315.48	0.127
333.66	0.123	335.33	0.118	333.88	0.120	334.30	0.123
352.80	0.118	351.28	0.114	354.21	0.116	353.77	0.118
371.37	0.113	369.26	0.108	370.95	0.110	371.88	0.112

Table XII. Constants of Eq 5 for Representing Heat Conductivity

compd	T_b, K	$\lambda_{t=0.55}$, $W{\cdot}m^{-1}{\cdot}K^{-1}$
I	307.55	0.328
II	351.45	0.215
III	368.05	0.160
IV	443.85	0.132
V	469.70	0.171
VI	511.56	0.123
VII	555.51	0.132
VIII	534.31	0.128
IX	374.45	0.191
X	375.55	0.272
XI	470.55	0.106
XIV	520.83	0.134
XV	612.35	0.120
XVI	609.65	0.125
XVII	591.85	0.130
XVIII	639.51	0.119
XIX	582.55	0.126
XX	750.60	0.107

The scope of the density, heat capacity, and heat conductivity data has been used for calculating the temperature conductivity

$$k(T) = \lambda/C_p\rho \qquad (6)$$

The results are summarized in Table XIII.

One-Parameter Corresponding States Law

The corresponding-state method makes it possible to extend the data obtained for a limited set of substances to a sufficiently

Table XIII. Values of the Temperature Conductivity (10^8k, $m^2 \bullet s^{-1}$) Calculated from Eq 6

T, K	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XIV	XV	XVI	XVII	XVIII	XIX	XX
293.15	8.92	7.60	4.75	6.23	7.16	6.50	7.63	6.93	7.13	10.4	5.53	7.54	6.38	7.56	7.53	6.53	6.46	7.11
303.15		7.10	4.41	6.00	6.92	6.28	7.43	6.74	6.81	9.91	5.33	7.33	6.12	7.38	7.29	6.39	6.22	6.93
313.15		6.60	4.09	5.80	6.65	6.07	7.26	6.56	6.47	9.46	5.13	7.10	5.90	7.19	7.06	6.25	6.01	6.75
323.15		6.12	3.80	5.59	6.42	5.86	7.05	6.39	6.18	8.96	4.92	6.88	5.71	7.01	6.83	6.12	5.84	6.57
333.15		5.43	3.52		6.18	5.66	6.87	6.23	5.82		4.72	6.65	5.54	6.83	6.59	5.98	5.69	6.40
343.15		5.17	3.25		5.93	5.47	6.69	6.09	5.48			6.43	5.42	6.66	6.36	5.84	5.58	6.22

Table XIV. Initial Data for Calculations of Properties by the Corresponding States Method

compd	T, K	vapor press. P, kPa	ρ, $kg \cdot m^{-3}$	molar mass
I	282.45	36.4		72.10
	293.15		763.9	
	309.20	102.6		
IV	341.05	2.93	809.5	126.19
	443.73	102.5		
IX	298.15		809.53	86.05
	324.39	16.50		
	384.45	133.2		
X	293.15	4.00		70.04
	308.15		842.5	
	375.49	102.0		

Table XV. Thermodynamic Properties of I Calculated by the One-Parameter Corresponding States Method (OCSM)

T, K	P, kPa	$10^{-3}\rho_L$, $kg \cdot m^{-3}$	$10^{-3}\rho_G$, $kg \cdot m^{-3}$	$10^3\gamma$, $N \cdot m^{-1}$	ΔH_{vap}, $kJ \cdot mol^{-1}$	ΔS_{vap}, $kJ \cdot mol^{-1} \cdot K^{-1}$
300	73.5	0.7562	0.00219	18.28	27.52	0.0917
350	355.0	0.6936	0.00966	12.23	24.10	0.0689
400	1121	0.6180	0.0302	6.70	19.75	0.0494
450	2726	0.5076	0.0850	1.95	13.34	0.0296
479.68	4195	0.282	0.282	0.00	0.00	0.0000

Table XVI. Thermodynamic Properties of IV Calculated by the OCSM

T, K	P, kPa	$10^{-3}\rho_L$, $kg \cdot m^{-3}$	$10^{-3}\rho_G$, $kg \cdot m^{-3}$	$10^3\gamma$, $N \cdot m^{-1}$	ΔH_{vap}, $kJ \cdot mol^{-1}$	ΔS_{vap}, $kJ \cdot mol^{-1} \cdot K^{-1}$
350	4.44	0.8031	0.000194	22.94	45.52	0.1301
400	29.54	0.7601	0.00115	18.29	42.39	0.1060
450	120.0	0.714	0.00426	13.85	38.77	0.0862
500	352.6	0.663	0.0120	9.65	34.19	0.0684
550	838.0	0.602	0.0289	5.77	28.63	0.0521
600	1711	0.520	0.0659	2.33	21.34	0.0356
645.19	2965	0.273	0.273	0.00	0.00	0.0000

wider group of substances. In addition, it allows determination of the thermodynamic properties for wide ranges of temperature and pressure values including liquid and gaseous states and the liquid–vapor coexisting line.

According to the Filippov method (*32*), the vapor pressure data can be described by

$$\log (P^*/P) = 3.9726 \log (T^*/T) + \left(\frac{T^*}{T} - 1\right)\left(0.3252 + 0.40529\frac{T^*}{T}\right) \tag{7}$$

which includes two nonuniversal constants: the characteristic temperature T^*

$$T^* = \frac{T_1 T_2}{T_1 + T_2}\left\{0.098805 + \left[0.0097625 + 2.46737 \frac{T_1 + T_2}{T_2 - T_1}\left(\log \frac{P_2}{P_1} - 3.9726 \log \frac{T_2}{T_1}\right)\right]^{1/2}\right\} \tag{8}$$

and the characteristic pressure P^*, which can be determined by two experimental pair of P and T values (Table VI).

Table XVII. Thermodynamic Properties of IX Calculated by the OCSM

T, K	P, kPa	$10^{-3}\rho_L$, $kg \cdot m^{-3}$	$10^{-3}\rho_G$, $kg \cdot m^{-3}$	$10^3\gamma$, $N \cdot m^{-1}$	ΔH_{vap}, $kJ \cdot mol^{-1}$	ΔS_{vap}, $kJ \cdot mol^{-1} \cdot K^{-1}$
300	5.25	0.8081	0.000152	24.75	37.00	0.1225
350	44.65	0.7590	0.00113	19.09	34.40	0.0983
400	203.3	0.7058	0.00463	13.73	30.86	0.0726
450	635.0	0.6441	0.0135	8.73	26.43	0.0587
500	1554	0.5671	0.0324	4.22	20.73	0.0415
560.95	3716	0.275	0.275	0.00	0.00	0.0000

Table XVIII. Thermodynamic Properties of X Calculated by the OCSM

T, K	P, kPa	$10^{-3}\rho_L$, $kg \cdot m^{-3}$	$10^{-3}\rho_G$, $kg \cdot m^{-3}$	$10^3\gamma$, $N \cdot m^{-1}$	ΔH_{vap}, $kJ \cdot mol^{-1}$	ΔS_{vap}, $kJ \cdot mol^{-1} \cdot K^{-1}$
300	5.69	0.8494	0.000162	28.29	36.84	0.1228
400	198.6	0.7574	0.00442	17.30	32.44	0.0811
500	1447	0.642	0.0305	7.50	24.64	0.0493
600	5378	0.310	0.272	0.06	2.35	0.0039
601.71	5475	0.293	0.293	0.00	0.00	0.0000

To determine the temperature dependence of the liquid density along the coexistence curve, the function $z_\rho(\tau, A_F)$ taken from ref *32* was used

$$\rho/\rho_{\tau^{-1}=1.6} = z_\rho(\tau, A_F) \tag{9}$$

where $\tau = T/T_c$ is the reduced temperature, T_c the critical temperature, and $\rho_{\tau^{-1}=1.6}$ the density value at $\tau^{-1} = 1.6$. The similarity criterion

$$A_F = 100P/P_c \qquad \text{at } \tau^{-1} = 1.6 \tag{10}$$

can be calculated by

$$A_F = 23.70 - 7.30 \frac{T^*}{T} - 3.087 \log \left(1 + \frac{9.225MP}{\rho T}\right) \tag{11}$$

where M is molar mass of the substance.

The experimental data used for calculation of thermodynamic properties of I, IV, IX, and X are given in Table XIV. The results for these four substances are presented in Tables XV–XVIII.

Comparisons of the experimental data and the data of other authors with those calculated by the above method are shown in Figures 1–3.

Conclusion

A rational method for the determination of physical properties of a group of important organic liquids is proposed. On the basis of limited experimental data and using the law of corresponding states, it is possible to reduce the necessary amount of data for compilation of the properties of new substances in the liquid–vapor coexistence region.

Registry No. I, 116-11-0; II, 77-76-9; III, 115-18-4; IV, 110-93-0; V, 29171-20-8; VI, 16647-05-5; VII, 141-10-6; VIII, 79-77-6; IX, 96-22-0; X, 4170-30-3; XI, 20030-30-2; XII, 2416-94-6; XIII, 700-13-0; XIV, 1604-34-8; XV, 1604-35-9; XVI, 1604-32-6; XVII, 502-69-2; XVIII, 29171-23-1; XIX, 60046-87-9; XX, 58-95-7; vitamin A, 11103-57-4; vitamin E, 1406-18-4.

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Phase Systems Melamine–H_3PO_4–H_2O and Melamine–NH_3–H_3PO_4–H_2O at 25 °C

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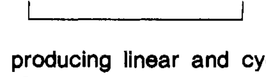
The $C_3H_6N_6$–H_3PO_4–H_2O and $C_3H_6N_6$–NH_3–H_3PO_4–H_2O phase systems were determined from 0 to 50% P_2O_5 at 25 °C. Eleven adducts between melamine and H_3PO_4/$NH_4H_2PO_4$ were isolated, identified, and characterized crystallographically. Below 10% P_2O_5, the solubility of melamine in these systems was less than 0.3%. Above 30% P_2O_5, the solubility of melamine ranged up to about 8%. The results indicate that the precipitation of melamine–phosphoric acid adducts, especially $C_3H_6N_6 \cdot H_3PO_4$, provides a practical process for purifying wet-process phosphoric acid.

Melamine ($C_3H_6N_6$, eq 1) readily forms insoluble adducts with many organic and inorganic acids (*1*, *2*) and has been proposed as a purification and collection agent in many acid reclamation processes (*3*-*7*). Melamine also has been proposed



$$\underbrace{N{=}\overset{\overset{NH_2}{|}}{C}{-}N{=}\overset{\overset{NH_2}{|}}{C}{-}N{=}\overset{\overset{NH_2}{|}}{C}}_{} \qquad (1)$$

as an agent for producing linear and cyclic polyphosphate compounds (*8*). Since the stability of impure wet-process phosphoric acid (WPA) and liquid fertilizers prepared from this acid is limited by dissolved impurities, particularly magnesium [which has a very low saturation composition in fluid fertilizers (*9*)], it seemed feasible that a purification scheme could be developed using melamine.

Thus, a recently developed process (*3*, *4*) has been proposed for this purpose. The process consists of precipitating acidic melamine phosphates from phosphoric acid solutions and subsequently recovering the melamine in aqueous ammonium hydroxide/phosphate solutions. This reclamation process traverses the phase system $C_3H_6N_6$–NH_3–H_3PO_4–H_2O from highly acidic to weakly basic conditions. Phase chemistry data are not available to describe the chemical properties and compositions of the reaction products that will be encountered by the interaction of these materials. A few of the adducts have been encountered, but the characterization data to distinguish them are not available (*10*-*12*).

Experimental Section

To understand the melamine precipitation and regeneration process for the purification of WPA (*3*, *13*), a major research study was conducted to characterize the chemical and physical properties of the equilibrating solids in the systems $C_3H_6N_6$–H_3PO_4–H_2O and $C_3H_6N_6$–NH_3–H_3PO_4–H_2O at 25 °C.

Early in the study it became apparent that numerous unknown materials would be encountered (*1*-*3*). Thus, the initial task was to synthesize and characterize homogeneous samples of each melamine–phosphoric acid adduct. For this phase of the study, a strong reagent-grade H_3PO_4 solution (60% P_2O_5)