Thermodynamic Study of Phase Transitions in 2-Methylpropan-2-ol

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The results of an accurate thermal analysis on highly purified samples of 2-methylpropan-2-ol supply evidence for the supposition of the existence of three crystalline phases, which we indicate as crystal I (mp 25.62 °C), crystal II (mp 25.00 °C), and crystal III (mp 21.66 °C). A two-side transition: crystal I $\rightleftarrows$ II has been observed at 14.1 °C. Crystal III, by cooling, undergoes a sluggish transition into crystal II at 9 °C. Cryoscopic behavior of solutions of carbon tetrachloride, *n*-heptane, and sulfolane is consistent with the above results. Metastable equilibria may be detected owing to the fact that the freezing points of the three crystalline phases fall within a narrow temperature range. The cryoscopic constants of the three solid phases have been calculated and fusion entalpies derived. Negative conclusions are drawn concerning the use of 2-methylpropan-2-ol as a reliable solvent in cryoscopy. From thermodynamic data only crystal II is suspected, possessing some globular character.

1. Introduction

A prerequisite for a meaningful discussion of the liquid–solid phase diagram[1] of sulfolane and 2-methylpropan-2-ol was the assumption of the existence of three crystalline forms of 2-methylpropan-2-ol. This statement was consistent with thermodynamic studies of Oetting[2] on pure substance, who reported evidence of two crystalline forms, crystal II being the more stable form from 0 to 12.98 °C, and crystal I becoming the more stable up to the melting point, at 25.81 °C. Oetting postulated too, with a "tongue in cheek" attitude, the existence of an hypothetical crystal III, whose thermochemical data might not be reproduced at will, and whose stability range should lie presumably within 8.38 and 21.31 °C.

2-Methylpropan-2-ol was classed by Timmermans[3] as a "globular" molecule which is consistent with the existence of more than one crystalline form; furthermore the fusion entropy of 5.36 cal/(mol K) drawn from thermochemical data reported by Oetting is very close to the upper limit fixed by Timmermans for "globular" molecules, even if a small entropy of fusion may be thought to originate in the ordering of liquid through hydrogen bonds as well as from a high degree of freedom in the solid. Attention must be called to the fact that literature data[4] on cryoscopic constants range within 6.75 and 12.80, and 2-methylpropan-2-ol has been, by turns, recommended or rejected as a reliable solvent in cryoscopy.

In order to try to solve the question whether the 2-methylpropan-2-ol is a "globular" substance or not and to afford more evidence for the supposition of the existence of the third crystalline form, this work was undertaken.

2. Experimental Section

BDH 2-methylpropan-2-ol was distilled and dried on soda pellets, at reflux, for 2 days. The middle fraction of a further distillation was cut for use.

Reagent grade Carlo Erba carbon tetrachloride was purified by distillation in a 100-cm^3 vacuum jacketed distillation column, packed with glass helices. Only the center third cut of distillate was used.

Sulfolane kindly supplied by Shell Italia was distilled, at reduced pressure, through a 1.3-m Podbielniak column, packed with glass helices; the middle fraction was retained for the experimental measurements. Its melting point checked well with a previously[5] reported value (28.45 ± 0.02 °C).

BDH *n*-heptane, after a preliminary drying with anhydrous magnesium sulfate, was distilled twice and the middle fraction retained for use.

Solutions were prepared by weight (reduced to mass) in a drybox.

The apparatus and procedure adopted in measuring liquid–solid equilibrium temperatures were described elsewhere.[5] Temperatures were measured by a Leeds & Northrup Müller bridge G2 coupled with a NBS-certified platinum resistance thermometer.

3. Results and Discussion

Pure Substances. Figure 1 records the freezing behavior of pure 2-methylpropan-2-ol observed in three sets of experiments in which the cooling rate and the starting temperatures were nearly the same.

Three melting points at 21.66, 25.00, and 25.62 °C and two solid transitions at 9 and 14.1 °C have been observed.

Curve (a) illustrates that after an undercooling zone, liquid freezes at 25.62 °C to a crystalline phase which we call crystal I, for the sake of comparison with previous literature.[2,4] This phase, consisting of needles, whose formation is accompanied by a noticeable volume expansion with respect to the liquid on further cooling, undergoes at 14.1 °C a sharp transition to another solid phase, which we indicate as crystal II, according to Oetting.[2]

The freezing curve (b) refers to another run in which the melt leads crystallization, at 25.00 °C, of another solid phase and an abrupt rise in temperature occurs up to 25.62 °C, where true equilibrium conditions are gained, which imply melting of solid into crystal I.

At this point we recall Oetting's statement that no reliable thermodynamic information on the melting process of crystal II could be obtained owing to an exothermic abrupt transformation, presumably to crystal I, which occurred during the melting of crystal II, superheated above the transition temperature II $\rightleftarrows$ I (14.1 °C).

Therefore we have identified as crystal II the solid phase freezing at 25.00 °C in accordance with Oetting's statement and with previous literature[2,4] which afforded evidence for two solid phases, one melting at 25.60 °C and the other at 25.00 °C.

Furthermore we have observed, by way of deep undercooling, liquid may freeze at 21.66 °C to a new solid phase, reasonably crystal III, which, by further cooling, undergoes a sluggish transition at 9 °C into another solid phase, presumably crystal II, according to Oetting.

These experiments were repeated a number of times but no consistent behavior was found, the initial soldification of crystals I, II, and III seeming to be a matter of chance.

Cryoscopic Measurements. Tables I–III and Figures 2–4 summarize the cryoscopic behavior of binary solutions of carbon tetrachloride, sulfolane, and *n*-heptane in 2-methylpropan-2-ol as solvent.[6]

For each solute, initial freezing points of solutions, if plotted against molality, lie on different curves which start from the three above reported equilibrium temperatures of pure liquid solvent with the three different crystalline phases or may be extrapolated

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Table I. Molal Depressions, θ/m (K kg mol^{-1}), of Freezing Points of 2-Methylpropan-2-ol[a]

m	$(\theta/m)_I$	$(\theta/m)_{II}$	m	$(\theta/m)_I$	$(\theta/m)_{II}$	m	$(\theta/m)_I$	$(\theta/m)_{II}$
0	8.28	11.89						
0.0388	8.48		0.3999	8.08		0.8074	7.61	6.42
0.0777	8.01		0.4391	7.88		0.8482	7.57	6.42
0.1557		8.84	0.4784	7.80		0.8870	7.54	6.44
0.1988	8.01		0.5464	7.81		0.9259	7.50	6.46
0.2380	8.18		0.5945	7.88		1.0850	7.45	6.40
0.2769	8.18		0.6812		6.48	1.2406	7.28	6.47
0.3157	7.99		0.7224	7.78		1.3960	7.30	
0.3611	8.05		0.7616	7.67		1.5521	7.10	

[a] Solute is carbon tetrachloride; $(\theta/m)_I$, solid-phase crystal I; $(\theta/m)_{II}$, solid-phase crystal II.

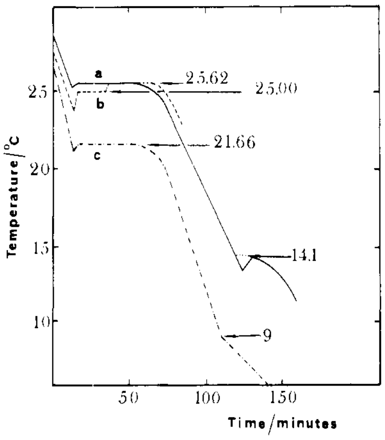

Figure 1. Cooling curves of highly purified samples of 2-methylpropan-2-ol: curve a, solid-phase crystal I; curve b, solid-phase crystal II; curve c, solid-phase crystal III.

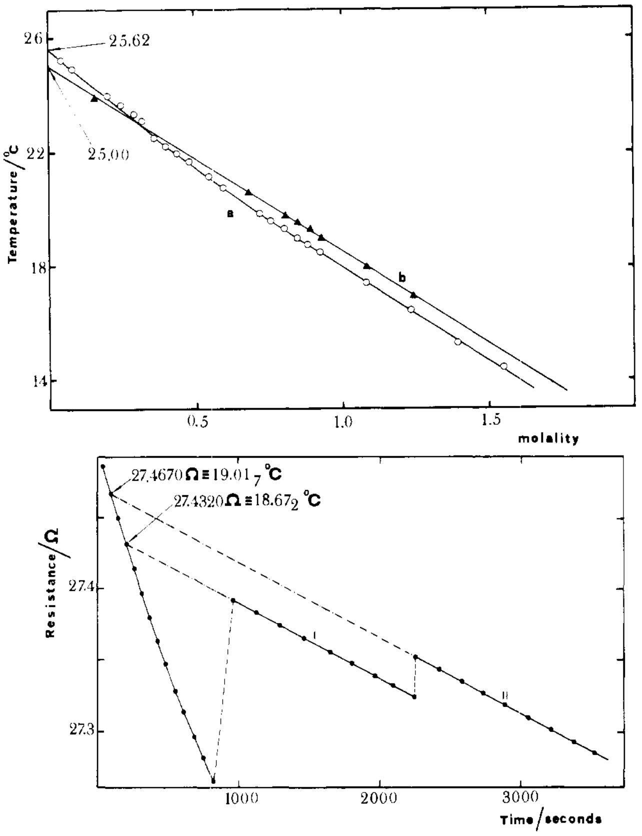

Figure 2. (Top) Equilibrium temperatures of solutions of carbon tetrachloride in 2-methylpropan-2-ol and crystal I (open circles) and crystal II (full triangles) vs. molality m, in the range $0 \leq m \leq 1.6$. (Bottom) Cooling curves of a carbon tetrachloride solution in 2-methylpropan-2-ol at $m = 0.9259$. Initial freezing point of crystal II is 19.01 °C; initial freezing point of crystal I is 18.67$_2$ °C.

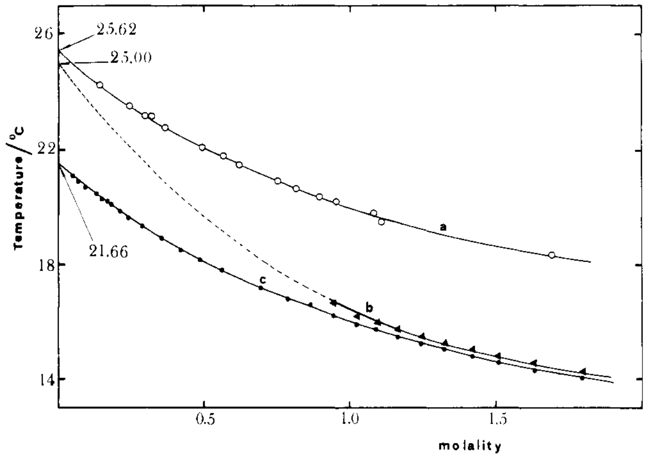

Figure 3. Equilibrium temperatures of solutions of sulfolane in 2-methylpropan-2-ol and crystal I (open circles), crystal II (full triangles), and crystal III (full circles) vs. molality, m, in the range $0 \leq m \leq 1.8$.

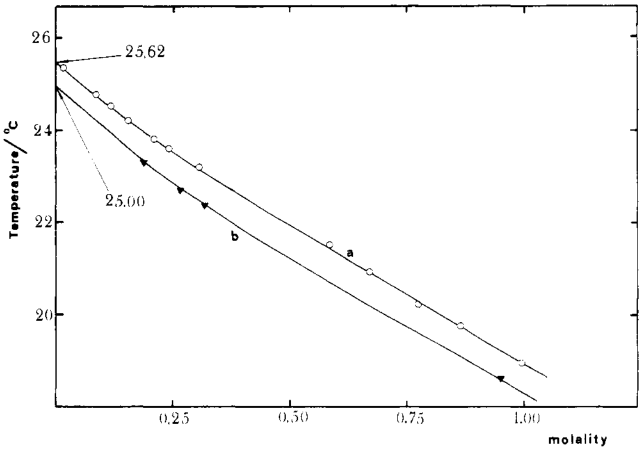

Figure 4. Equilibrium temperatures of solutions of n-heptane in 2-methylpropan-2-ol and crystal I (open circles) and crystal II (full triangles) vs. molality, m, in the range $0 \leq m \leq 1$.

reasonably to these values. Furthermore the slopes of these curves appear to depend on solute.

In the case of carbon tetrachloride, the equilibrium temperature curves (a) and (b) of crystal I and crystal II with liquid vs. molality (Figure 2) show a steady, almost linear, behavior over the entire explored composition range, crossing at ~23 °C. Therefore the solid phase in equilibrium with the solutions is crystal I in the temperature range 25.62–23 °C, and afterward crystal II becomes the more stable.

Curves (a) and (b) almost overlap in a wide molality range, the deposition temperatures of the two solids differing by less than 0.3 °C; therefore in this region the solidification of one or another crystalline form is only a matter of chance and freezing curves (Figure 2(bottom)) are characterized by an abrupt break, which is indicative that, during solidification, more than one

Table II. Molal Depressions, θ/m (K kg mol^{-1}), of Freezing Points of 2-Methylpropan-2-ol[a]

m	$(\theta/m)_{\rm I}$	$(\theta/m)_{\rm II}$	$(\theta/m)_{\rm III}$	m	$(\theta/m)_{\rm I}$	$(\theta/m)_{\rm II}$	$(\theta/m)_{\rm III}$
0	8.28	11.89	8.65				
0.0490			8.39	0.6221	6.36		
0.0664			8.42	0.7062			6.19
0.0974			8.28	0.7569	5.89		
0.1297			8.12	0.7858			5.96
0.1459	7.86		8.03	0.8223	5.76		
0.1620			8.02	0.8655			5.69
0.1781			7.91	0.8963	5.63		
0.2098			7.85	0.9450		8.73	5.55
0.2420			7.82	0.9481	5.20		
0.2456	7.65			1.0242		8.53	5.41
0.2902			7.58	1.0842	5.21		
0.3007	7.47			1.0876		8.29	5.26
0.3135	7.38			1.1081	5.36		
0.3545			7.35	1.1664		7.74	5.13
0.3720	7.04			1.2452		7.52	4.98
0.4186			7.09	1.3238		7.33	4.84
0.4826			6.89	1.4179		6.88	4.68
0.4957	6.72			1.5120		6.64	4.53
0.5626			6.65	1.6371		6.35	4.36
0.5724	6.27			1.6947	4.18		
				1.7931		5.92	4.14

[a] Solute is sulfolane; $(\theta/m)_{\rm I}$, solid-phase crystal I; $(\theta/m)_{\rm II}$, solid-phase crystal II; $(\theta/m)_{\rm III}$, solid-phase crystal III.

Table III. Molal Depressions, θ/m (K kg mol^{-1}), of Freezing Points of 2-Methylpropan-2-ol[a]

m	$(\theta/m)_{\rm I}$	$(\theta/m)_{\rm II}$	m	$(\theta/m)_{\rm I}$	$(\theta/m)_{\rm II}$	m	$(\theta/m)_{\rm I}$	$(\theta/m)_{\rm II}$
0	8.28	11.89						
0.0158	8.10		0.2115	7.67		0.5852	6.67	
0.0852	8.00		0.2397	7.63		0.6724	6.72	
0.1175	7.91		0.2720		7.75	0.7747	6.71	
0.1543	8.01		0.3050	7.39		0.8642	6.60	
0.1875		9.07	0.3194		7.90	0.9447		6.57
						0.9929	6.54	

[a] Solute is n-heptane; $(\theta/m)_{\rm I}$, solid-phase crystal I; $(\theta/m)_{\rm II}$, solid-phase crystal II.

Table IV. Thermodynamic Data on 2-Methylpropan-2-ol Melting Processes[j]

	mp/°C		λ/K kg mol^{-1}		ΔH/cal mol^{-1}		ΔS/cal mol^{-1} K^{-1}	
2-methylpropan-2-ol	this work	lit.	this work	lit.	this work	lit.	this work	lit.
crystal I	25.62	25.50[a]	8.28	(8.45)[c]	1587	1602[d]	5.31	5.42[g]
		25.66[b]		8.37[e]		1622[g]		5.21[c]
		25.43[c]		(8.15)[g]		1555[c]		
		25.81[d]		(8.21)[d]		(1579)[e]		
		25.10[e]		8.25[f]		(1590)[f]		
		25.40[f]						
crystal II	25.00	25.00[b]	11.89	12.8[h]	1101	(1026)[h]	3.69	3.5[h]
		24.80[g]		11.45[h,i]		(1143)[e]		3.8[e]
		24.84[d]						
crystal III	21.66		8.65		1477		5.01	

[a] Reference 4i. [b] Reference 4g. [c] Reference 4a. [d] Reference 2. [e] Reference 4f. [f] Reference 4d. [g] Reference 4c. [h] Reference 4b. [i] Value calculated on extrapolating Atkins cryoscopic data on acetanilide solutions. [j] Values in parentheses are not measured directly.

crystalline phase may originate in the liquid. The extrapolation of the segments of a freezing curve across the undercooling region enables us to evaluate the initial equilibrium temperatures of the solution with crystal I and crystal II, respectively.

Sulfolane seems to stabilize crystal III preferably. Curve (a) (Figure 3) which represents initial freezing points of crystal I vs. molality, is less steep than crystal II–liquid equilibrium curve (b), which, starting from $m = 0.9$, approaches the crystal III–liquid equilibrium curve (c). In the molality range in which these two curves show a quite comparable dependence on composition and almost overlap, cooling curves exibit a sharp break and two initial freezing temperatures obviously can be evaluated, as reported in the case of carbon tetrachloride solutions.

The equilibrium temperatures of crystal I and crystal II in n-heptane solutions (Figure 4) show a quite parallel behavior differing by about 1 °C, at each composition, over the entire explored molality range ($0 \leq m \leq 1$). No indication of crystal III solidification may be drawn from cooling curves in the same region.

Cryoscopic behavior of 2-methylpropan-2-ol as solvent is summarized in Figure 5, where, for each solute, molal depressions, θ/m, calculated from the above reported three equilibrium temperatures of pure liquid solvent with crystal I, II, and III, respectively, are plotted vs. molality. These curves, which in several cases are straight lines, on extrapolation to $m = 0$, give, for each crystalline form, only one value of $(\theta/m)_0$ not depending on solute, which is indicated reasonably, as the cryoscopic constant λ.

The cryoscopic constant $\lambda_{\rm I} = 8.28$ has been obtained on extrapolating to $m = 0$ the three sets of cryoscopic data on solutions of carbon tetrachloride, sulfolane, and n-heptane, respectively. The value of $\lambda_{\rm II} = 11.89$ has been obtained on extrapolation of cryoscopic data of sulfolane solutions; molal depressions of solutions of n-heptane and carbon tetrachloride

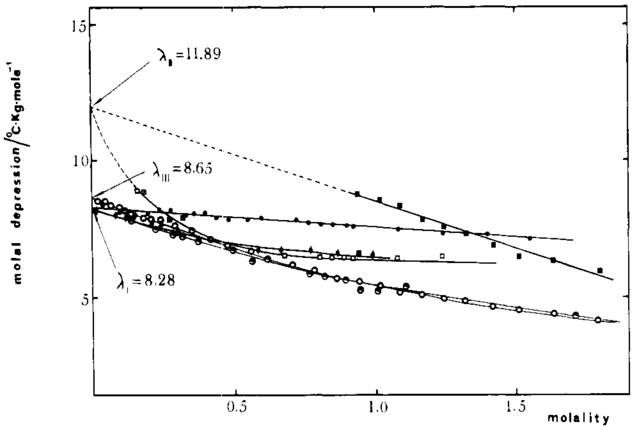

Figure 5. Molal depressions of binary solutions of carbon tetrachloride, sulfolane, and *n*-heptane in 2-methylpropan-2-ol vs. molality: solid phase, crystal I, (●) carbon tetrachloride, (◒) sulfolane (◆) *n*-heptane; solid-phase, crystal II, (□) carbon tetrachloride, (■) sulfolane, (☒) *n*-heptane; solid phase, crystal III, (○) sulfolane.

are consistent with this extrapolated value, even if they may not be extrapolated themselves owing to the lack of low molality data. The cryoscopic constant λ_{III} = 8.65 may be calculated only from data of sulfolane solutions in which this form is stabilized preferably.

λ_I, λ_{II}, and λ_{III} values are reported in Table IV and melting entalpies, ΔH_I, ΔH_{II}, and ΔH_{III}, and melting entropies, ΔS_I, ΔS_{II}, and ΔS_{III}, are derived and compared with previous literature.

The comparison is satisfactory in spite of the confusion arising from the fact that the existence of the third crystalline phase was ignored hitherto or, at least, regarded with some disbelief. Indeed data more frequently reported by literature refer to crystal I which is the more stable form, whereas, as it concerns crystal II and crystal III, some physical properties of crystal III have been erroneously ascribed to crystal II.

Nevertheless attention must be called on the fact that our value of ΔH_I (=1587 cal/mol) is in good agreement with previous data, ranging within 1555 and 1622 cal/mol, some of them obtained from calorimetric measurements, and also ΔH_{II} (=1100 cal/mol) is consistent with literature data (1026–1143 cal/mol) even if derived from cryoscopic measurements; obviously the comparison is quite lacking in the case of crystal III. Oetting reports indeed a value of 1721 cal/mol, which would be comprehensive of transition entalpy III → I, not measurable directly; furthermore, owing to the difficulty in establishing base curves of heat capacities in the premelting region, the value would be affected by noticeable incertainty.

Melting entalpies exceeding transition entalpies seem to preclude globular properties of 2-methylpropan-2-ol; neverthless if melting entropies are accepted as a valuable criterion of discrimination, the absence of globular character is not quite certain for 2-methylpropan-2-ol crystal II.

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(6) Carbon tetrachloride and sulfolane are "globular" molecules, very similar in size and shape with solvent; the former possesses an approximately central force field whereas the latter exibits a fairly high dipole moment, μ = 4.8 D, of which only the negative part is exposed; *n*-heptane molecules on the other hand differ noticeably in shape and size from the solvent.

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Vapor Pressures of High-Molecular-Weight Hydrocarbons

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A gas-saturation apparatus is used to obtain experimental data at near-ambient temperature; vapor pressures in the range 10^{-1}–10^{-3} torr are presented for the liquids *n*-octadecane, *n*-eicosane, 1-methylnaphthalene, and 2-ethylnaphthalene and the solids naphthalene, anthracene, and phenanthrene. Methods are recommended for extrapolating the data to higher temperature. These vapor-pressure data are useful for dew-point calculations in processing of gases containing heavy hydrocarbons such as those found in coal tars.

Introduction

In recent years, high-molecular-weight hydrocarbons have become increasingly important because of development of energy-related processes: coal liquefaction, oil shale, tar sands, and especially coal gasification. Gasification of coal often produces a byproduct tar which contains hydrocarbons in the boiling range 200–600 °C; to design efficient processes for tar-containing gases, it is essential to predict their vaporization/condensation characteristics.

Hot effluent gases from coal gasifiers, often as high as 1100 °C, are a significant source of sensible heat. Recovery of this energy is accompanied by cooling of the gas with subsequent condensation of the heavy components. To minimize condensate fouling or plugging, design of heat-recovery processes requires knowledge of the thermodynamic properties that govern dew points of gas streams from coal-gasification processes.

A heavy component (i) remains in the gas phase as long as its fugacity f obeys the relation

$$f_i^{v} < f_i^{c} \qquad (1)$$

where superscript v stands for vapor phase and superscript c stands for condensed phase. These fugacities are related to composition by

$$f_i^{v} = y_i \phi_i P \qquad (2)$$

$$f_i^{c} = x_i \gamma_i f_i^{\circ} \qquad (3)$$

where, for component i, y_i and x_i are the mole fractions in the

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